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AUTOMATING THE AUTOCLAVE OXIDIZING LEACH PROCESS FOR NICKEL-PYRRHOTITE CONCENTRATES

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The principal controllable parameters affecting the process of nickel-pyrrhotite concentrate autoclave oxidizing leaching [1, 2] are:

the pulp flow rate and level through the autoclave sections;

the partial pressure of oxygen in the steam-gas phase;

the temperature in the autoclave.

The autoclave leaching of nickel-pyrrhotite concentrates has certain perculiarities in control, namely the following.

1. A high rate of heat release in the working range of temperatures, with the result that any excess of temperature due to malfunctioning of the temperature automatic control system causes disruption of the process, sulfur-sulfide buildup on the mixers and heat exchangers, and a sharp drop in autoclave output.

2. The narrow working temperature range and the corrosive and abrasive
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ake it impossible to use
ard automation resources,
pecial development work
quired.
The increased pressure
isk of explosion make it
mportant for monitoring
ontrol systems to be ex-
y reliable.

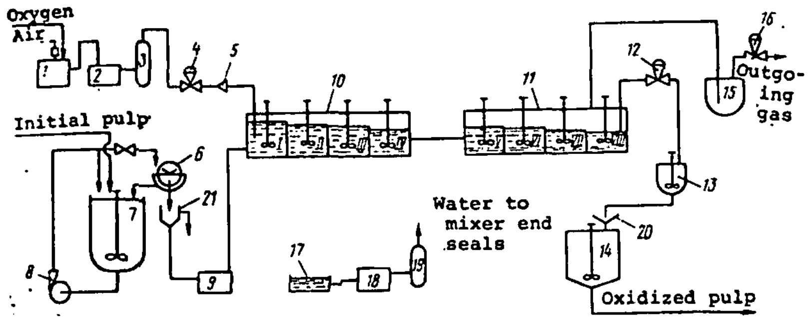

Fig. 1. Routing of apparatus for autoclave oxidizing leaching:
1 - gas mixer unit; 2 - 3GP 13/25 cc
- receivers; 4, 16 - control valves
valves; 6 - pocket feeder; 7 - init
pulp collector; 8 - centrifugal pum
/30 pump; 10, 11 - autoclaves, capa
12 - discharge valve; 13 - intermed
14 - oxidized pulp collector; 15 -
17 - supply tank; 18 - GR 16/40 pum
nels.

AAOL

The experience of the Nickel Industry Research and Design Institute in the adoption of automation on 15 m³ capacity autoclaves at the Yuzhuralnikel' Combine and 1.74 m³ capacity autoclaves at the Madneul Mining and Concentration Combine [3] was utilized in the work, but most of the schemes were perfected in the process of operation.[1]

A diagram of the apparatus routing appears in Fig. 1, and a diagram of the monitoring and measuring instruments and automation system in Fig. 2.

All the systems are

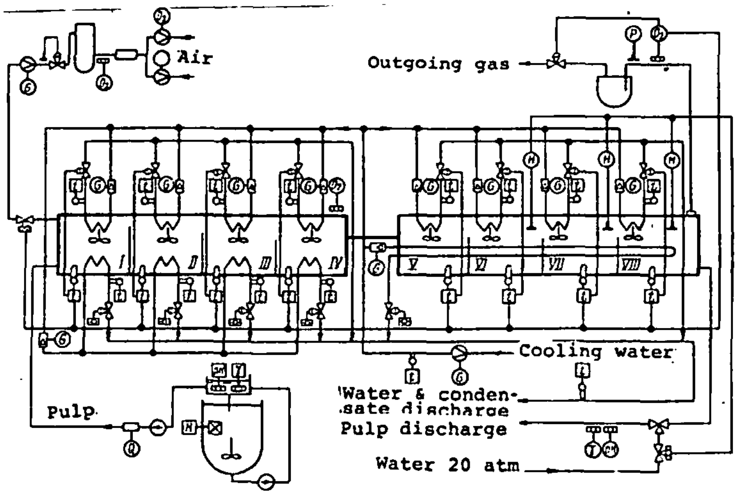

Fig. 2. Diagram of monitoring and measuring instruments and automation system for autoclave oxidizing leaching.

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[1] V. I. Akin'shin, N. I. Burkalenko, N. L. Voloshchuk, G. V. Kosintsev, and M. V. Usupov from the Noril'sk Mining and Metallurgical Combine automation and monitoring and measuring instruments shop and V. I. Keilin from the Nickel Industry Research and Design Institute participated in the work.

essentially standard, but the industry does not manufacture quick-response sensors for measuring the temperature of an aggressive medium or instruments in nonsparking versions to monitor resistances in a narrow range, and does not make up gas analyzers in sets with units to prepare and purify gas at high pressures. The necessary sensors and devices were developed and tested during the operation of the thermal routine control system and the system for purifying the outgoing gas for analysis and for pulp discharge from the autoclave.

Monitoring and Controlling the Temperature in the Autoclave

The nickel-pyrrhotite concentrate leaching reaction is attended by considerable release of heat (∿ 900 kcal/kg). It is advantageous to run the process at higher temperatures, but at 112° C or above the elementary sulfur which forms fuses and prevents the access of oxygen to the sulfides. In addition, the sulfur-sulfide fusion settles on the heat exchanger tubes, causing a sharp deterioration in heat removal and in temperature control. The optimum series of temperatures is in the 108-112° C range. A requirement of control with the minimum dynamic deviation from the setting is therefore imposed on the automatic temperature stabilization system.

The autoclave consists of independent chambers with ideal mixing, the chambers being regarded as subjects of temperature control with lumped values. Independent temperature control circuits are installed. Each circuit consists of the volume of pulp, a temperature sensor, and a secondary instrument with a regulator and a control valve through which cooling water is admitted to the heat exchanger.

The subject of control may obviously be represented as an inertial unit with a positive feedback characterizing the effect of pulp temperature on the reaction rate.

The greatest attention was given to the accuracy and speed of operation of the measuring devices, because the time constant of the subject is commensurate with that of the standard heat sensors.

The measuring elements in the systems had to be perfected. A quick-response chromel-copel calibrating thermocouple with the hot junction welded to the sheath and a platinum resistance thermometer based on the TSP-753 thermometer were tested as the sensitive element. The platinum thermometer can measure temperature with an accuracy of ±0.2° C, whereas the chromel-copel thermocouple has an accuracy of ±1.5° C with approximately the same time lag.

Experience in operating the thermal routine automatic control system shows that it is essential to have not less than two measurement channels in each of the chambers to obtain reliable temperature control. One of the sensors is included in the control system, the other is connected to an indicating instrument. The process can be run by reference to the readings of the latter if there is malfunctioning of the control system. It is also essential to have pulp temperature sensors with a short time lag (not more than 10-15 sec) and a non-standard secondary instrument scale of 80-120° C. Standard instruments (RPD rotameters and PVCh-3E secondary instruments) for monitoring and recording coolant water temperature and flow rate are provided for measuring the heat exchanger heat transfer coefficient. The temperature of the water leaving the coils is monitored by quick-response thermocouples. Recording of thermal characteristics made it possible to organize systematic checks on changes in the heat transfer coefficient and the heat balance according to changes in raw material properties, pressure, pulp feed, mixer speed, and other input values, and to assess changes in the heat transfer coefficient in time.

Adoption of the thermal routine automatic control system ensured reliable and stable operation of the autoclave as a whole. Cases of sulfur-sulfide buildup on the heat exchangers, overflows, and level indicator electrode system became rare and the periods of continuous autoclave operation increased.

To increase the reliability of automatic control system operation, provision should be made in the design for all sensors, converters, and intermediate boxes to be located outside the autoclave working zone. Special premises should be set aside for this purpose, or their locations should be partitioned off.

Monitoring and Controlling the Autoclave Gas Phase Oxygen Content

In the process of leaching, an oxygen-air mixture or bulk oxygen is fed continuously into the first autoclave chamber and the outgoing gas is discharged from the last chamber. The partial pressure of oxygen in the autoclave gas phase can be assessed by reference to its concentration in the discharge. This value both determines the rate of pyrrhotite leaching and substantially affects the passage into solution of the non-ferrous metals which the pyrrhotite concentrate contains. In addition, the degree of oxygen utilization determines whether the process is economic. On the basis of these factors the oxygen concentration of the outgoing gas from the last chamber is maintained at such a level as to obviate the danger of explosion when there are titanium components in the autoclave.

The oxygen concentration is controlled from the monitoring and measuring instrument panel by reference to gas analyzer readings, using a control valve. During final adjustments to the oxygen concentration measurement system, a system of removing pulp inclusions, moisture, aerosols, and harmful impurities from the outgoing gas to be analyzed was developed (Fig. 3). This raised the problem of reducing the delay in instrument readings following installation of additional vessels to the minimum.

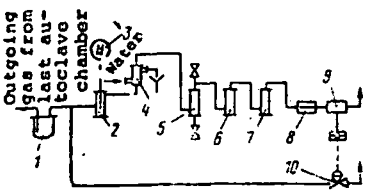

Fig. 3. Purification of outgoing gas for analysis:
1 - droplet trap; 2 - expansion vessel; 3 - electrode type level gauge; 4 - cooler; 5 - labyrinth cleaner unit; 6 - chemical cleaning unit; 7 - drying unit; 8 - air flow regulator; 9 - MN 5130 gas analyzer; 10 - pneumatic valve.

A level gauge was installed in the expansion vessel to indicate filling with pulp or condensate. A part of the gas from the labyrinth cleaning unit is discharged into the atmosphere, to reduce the pressure in front of the gas analyzer and reduce the time lag by increasing the speed of flow through the system. The system is stable in operation and gives reliable gas analyzer protection from the entry of moisture, aerosols, harmful impurities, and particles of pulp.

Stringent requirements are imposed on the valve controlling the outgoing gas oxygen content, which also acts as a seal. The valve is made from acid-- and erosion-resistant material (E1943 stainless steel). An UKN Du6 type valve with redesigned seating and piston is at present in operation.

System for Automatic Maintenance of a Constant Pulp Level in the Autoclave. To stabilize the leaching process, the volumes of pulp in the autoclave sections must be kept constant. This is achieved by cascade overflows on the pulp route on the autoclave and by automatic stabilization of the pulp level in the last autoclave section. The operation of the system for discharging the pulp from the autoclave is described below.

Electrode type pulp level sensors are installed in the seventh and eighth autoclave chambers. Relays based on the IKS-2N type nonsparking relay and developed by the Noril'sk Mining and Metallurgical Combine automation and monitoring and measuring instruments shop are used to monitor the presence of the electrode-pulp circuit. This device makes it possible to monitor the resistance of the circuit in a narrow range and to install the sensor in an atmosphere of bulk oxygen. It is accepted that the pulp reaches its working level only when both electrodes are simultaneously contacted by the pulp for 2-6 sec. This reduces the possibility of the system being triggered by false impulses. The order to discharge comes in through an intermediate relay when the 7th and 8th autoclave sections are filled with pulp. The duration of discharging can be controlled by the operator from the control panel according to the capacity in terms of pulp.

The pilot-plant scale development of systems for the monitoring and automatic control of the autoclave oxidizing leach process for nickel-pyrrhotite concentrates has yielded findings which can be recommended for implementation in an industrial process.

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A Comparison of Evaporite Facies in the Late Paleozoic Amazon and the Middle Cretaceous South Atlantic Salt Basins

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Abstract

Large evaporite basins are characterized by a cyclic alteration of sediments deposited under an arid climate in marine, lagoonal, and subaerial environments, respectively. In the Permo-Carboniferous Amazon Basin, marine calcarenites are abundant, lagoonal sediments consist mostly of coarse halite, and nodular anhydrite was formed below the dry salt flats. In this basin, dominantly marine conditions passed into lagoonal, and ultimately the lagoon broke up into disconnected salt lakes. In contrast, at least in the Sergipe embayment of the Cretaceous South Atlantic salt basin, marine sediments are absent, coarse halite is restricted to "tidal"-type feeding channels, and the marginal lagoons, lakes, and salt flats are characterized by a wide array of carnallite tachyhydrite facies. These differences reflect the greater isolation of the South Atlantic graben from the world ocean.

Introduction

OWING to their great sensitivity to environmental conditions, evaporites are among the best indicators of the facies in which they are deposited. Unfortunately, a lack of continuous coring and no chemical uniformity of the principle evaporite often prevents full use of this trait. It is therefore particularly fortunate that this is not true of the Brazilian Sergipe deposits (South Atlantic) and, to a lesser extent, of those of the Amazon evaporite basin (Fig. 1). These deposits have been extensively explored and abundant core material shows these evaporites are represented by an unusually wide range of evaporite rocks.

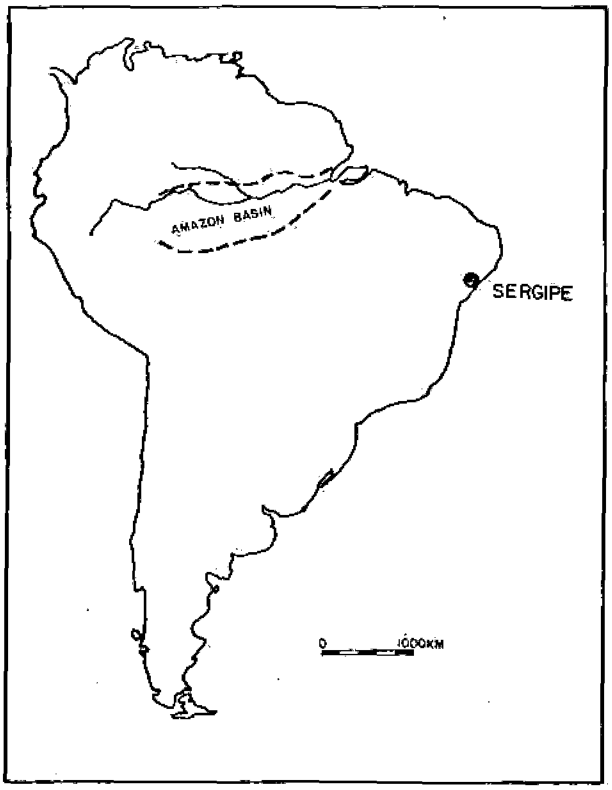


FIG. 1. Location map. Sergipe is only a marginal bay of the large South Atlantic salt basin.

Amazon Basin

The Amazon Basin is a large Paleozoic basin in northern Brazil containing a thick sequence of anhydrite and rock salt. The evaporite sequence itself is of lower Permian age; it is underlain by fusulinid upper Carboniferous (Stephanian) shallow water limestones and sandstones and overlain by upper Permian to Lower Triassic red shales deposited in a continental-lacustrine environment. Thus the evaporite sequence is a regressive one, transitional between an underlying open marine sequence and an overlying continental one. The evaporite-depositing area was subjected to both marine and continental influences. Marine limestone wedged in and intercalated with the evaporites from the open ocean or geosyncline along the western margin of the present South American continent, and fan deltas built up from the Guyanan, Brazilian, and West African cratons that enclosed the basin from the north, south, and east, respectively. Eolic dune sands which derived their material from these fan deltas built up along the margins (Fig. 2).

The texture of the evaporites reflects their exposure to marine and continental influences and shows as well the gradual transition from marine to

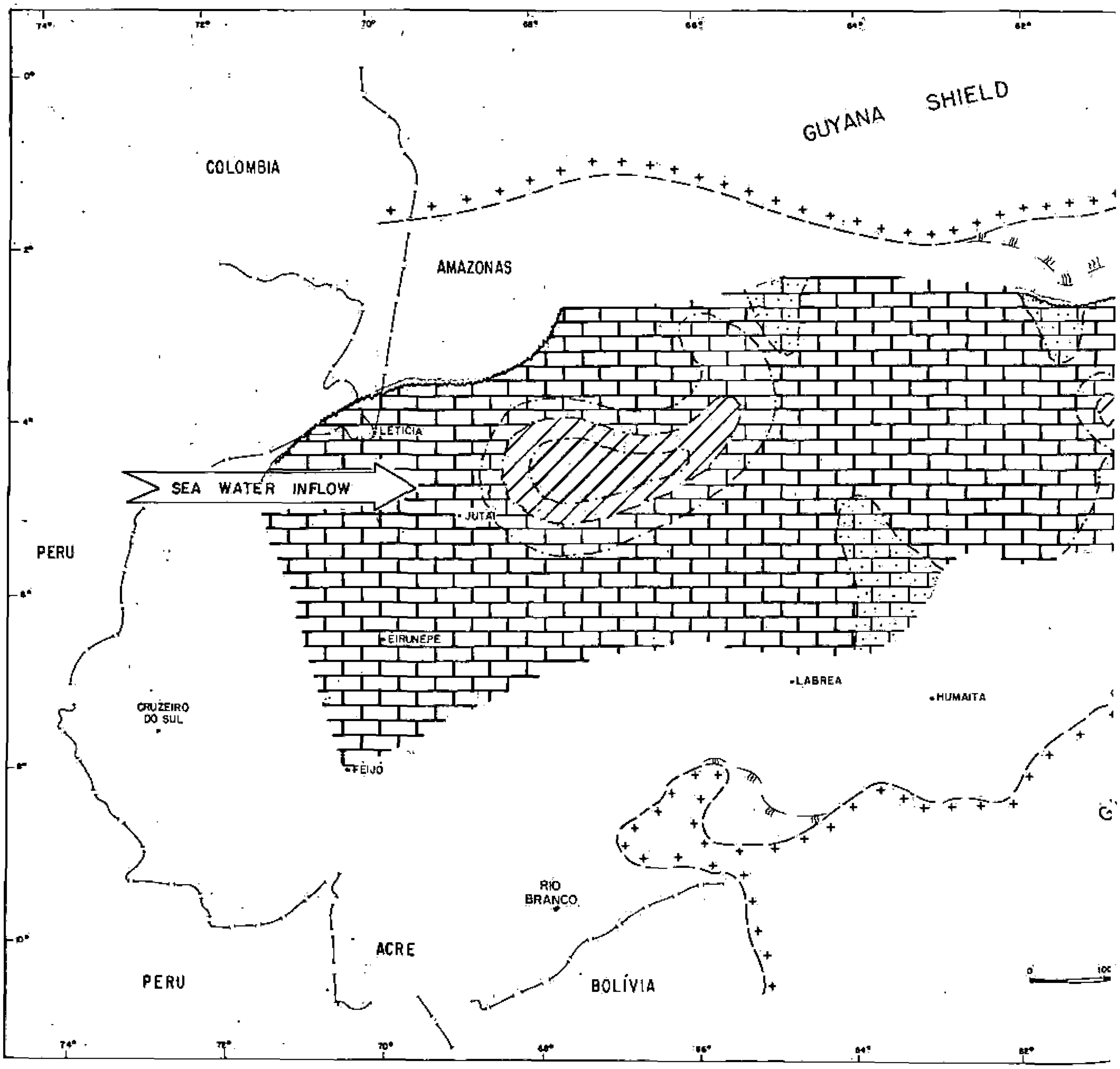
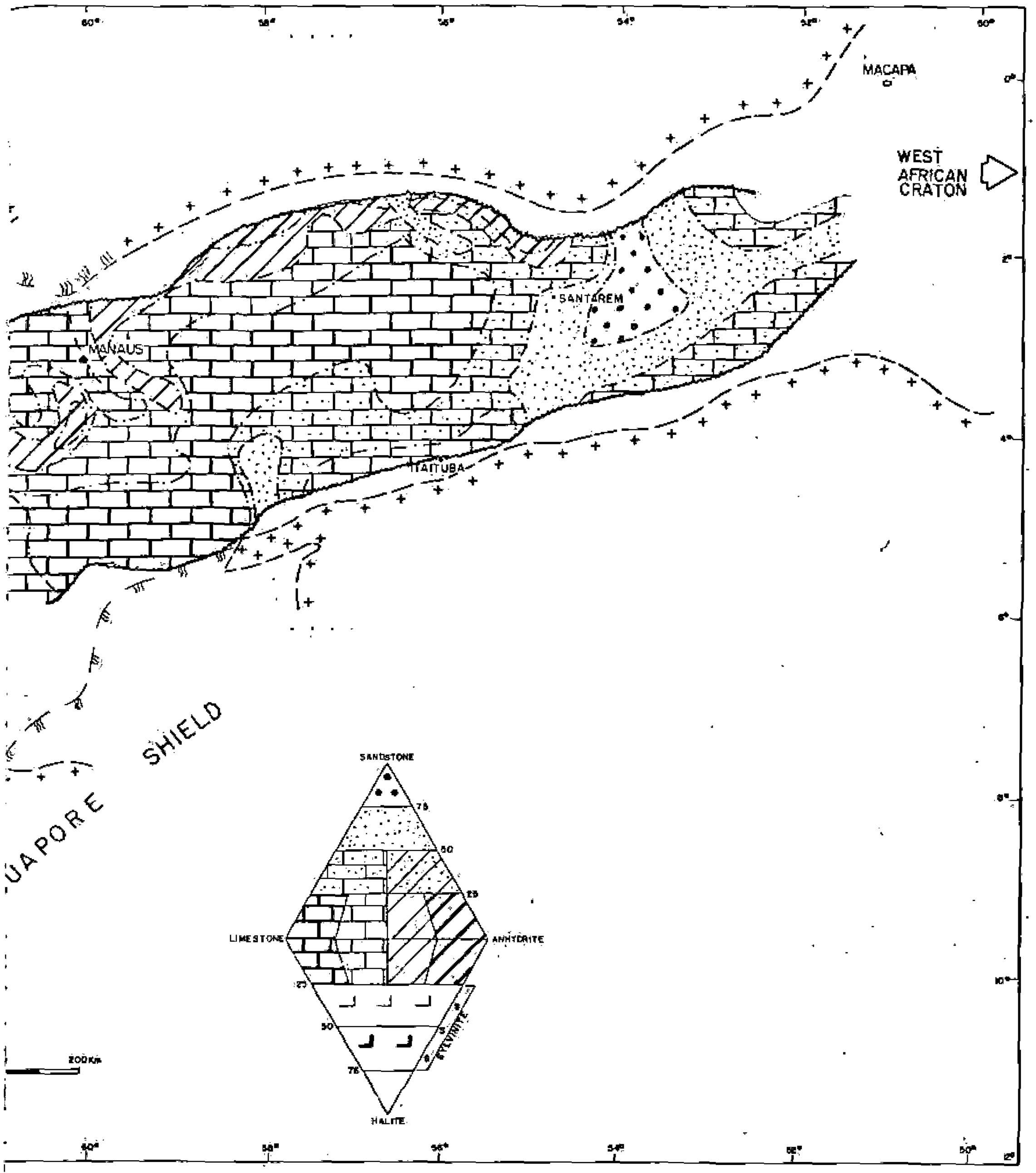


FIG. 2. Amazon Basin, facies map of evaporite cycle II. Fossiliferous normal marine lime-stones don clastics swept in by rivers from the Precambrian shields in the north, south, and particularly the east tion is restricted to small sabkhas.



ninate, deposited in sea water supplied from the Pacific Ocean in the west; the (West African cratons) form deltas and alluvial fans. Large-scale anhydrite deposi-

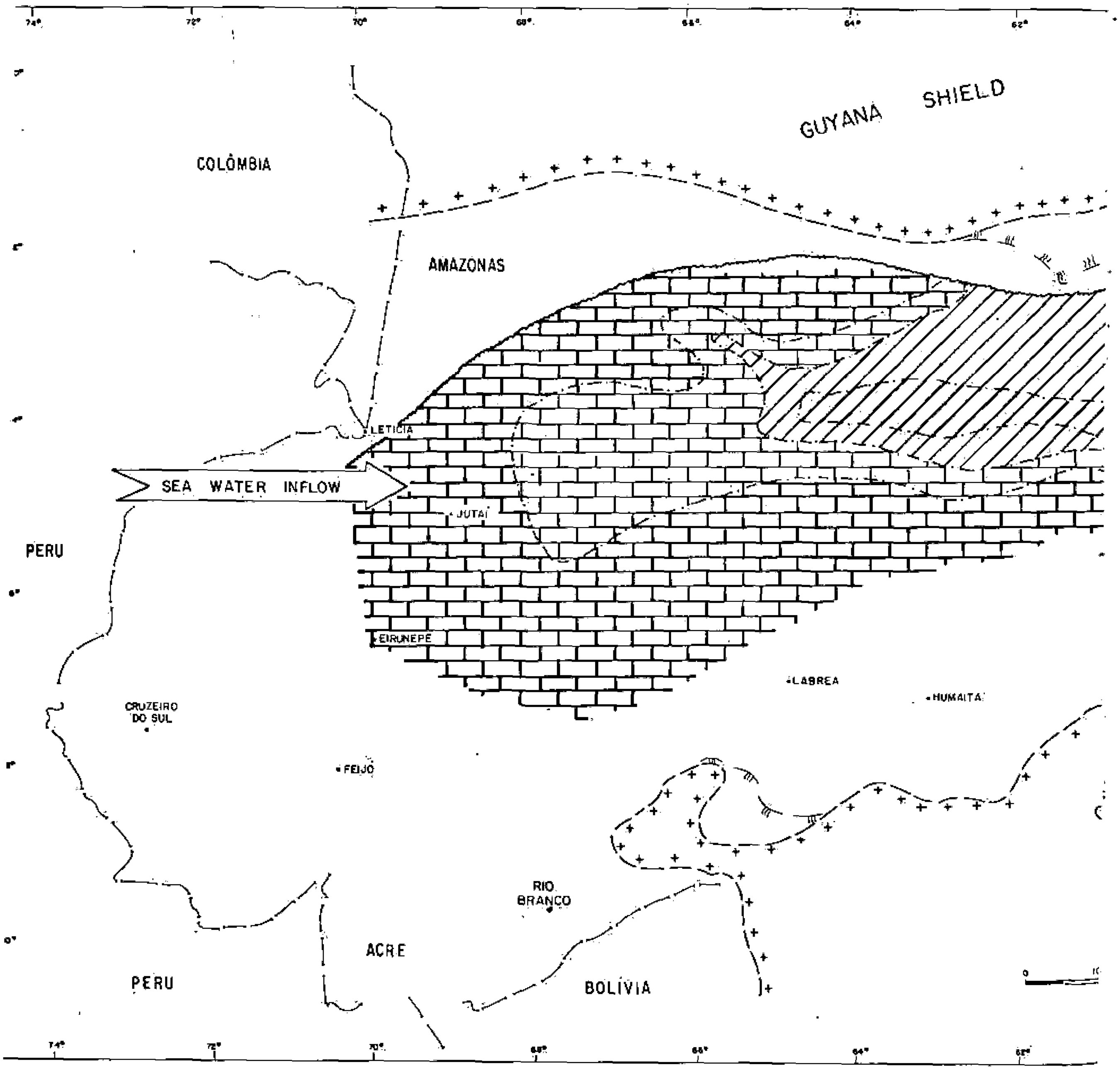
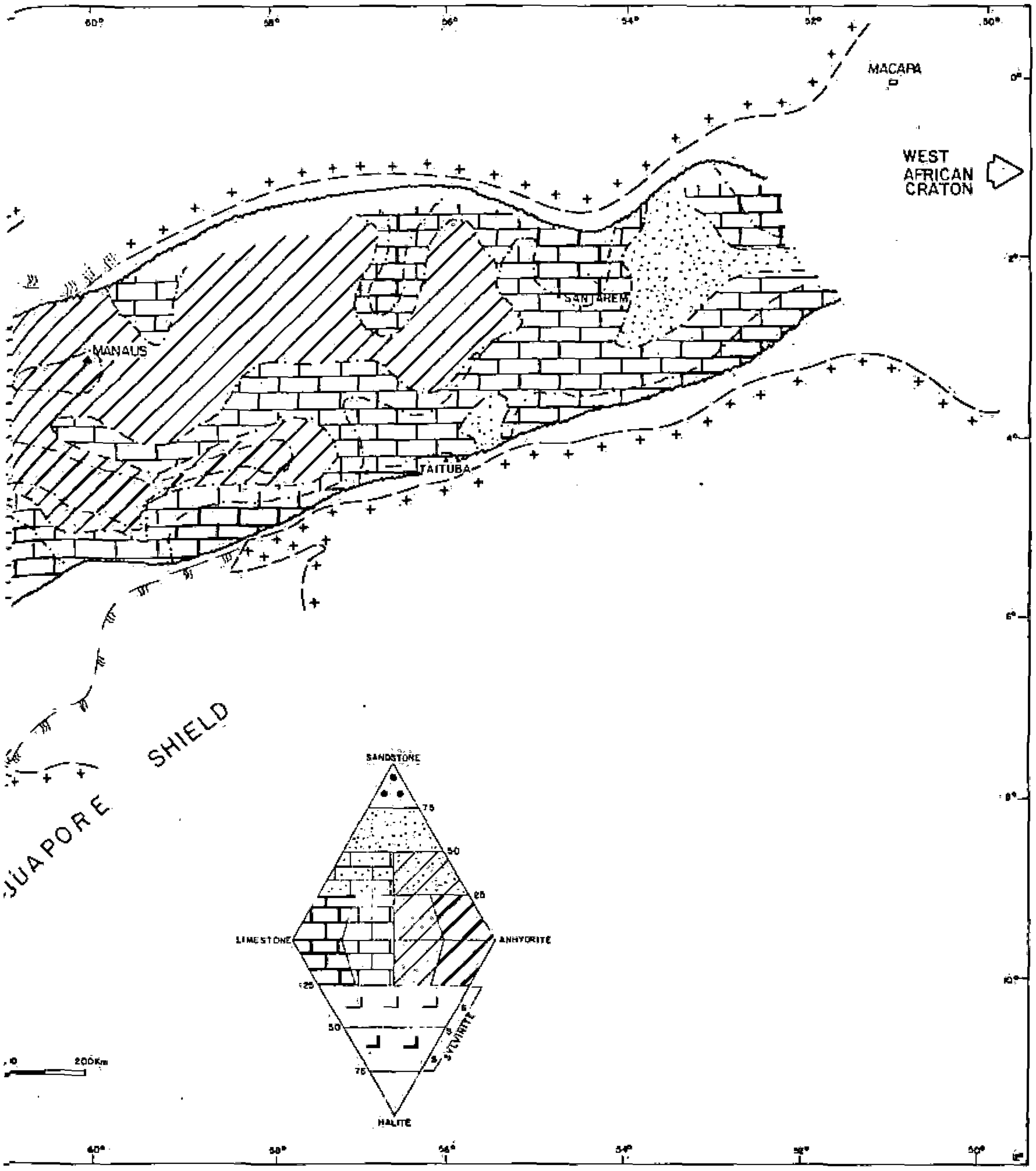


FIG. 3. Amazon Basin, faciès map of evaporite cycle III. Accelerated retreat of the sea leaves large area
tion. In the extreme east, inflowing fresh water lowers salinities, maintaining ps



3 of marine sediments exposed to subaerial evaporation and consequent anhydrite forma-
eudomarine conditions and preserving the calcareous sediments.

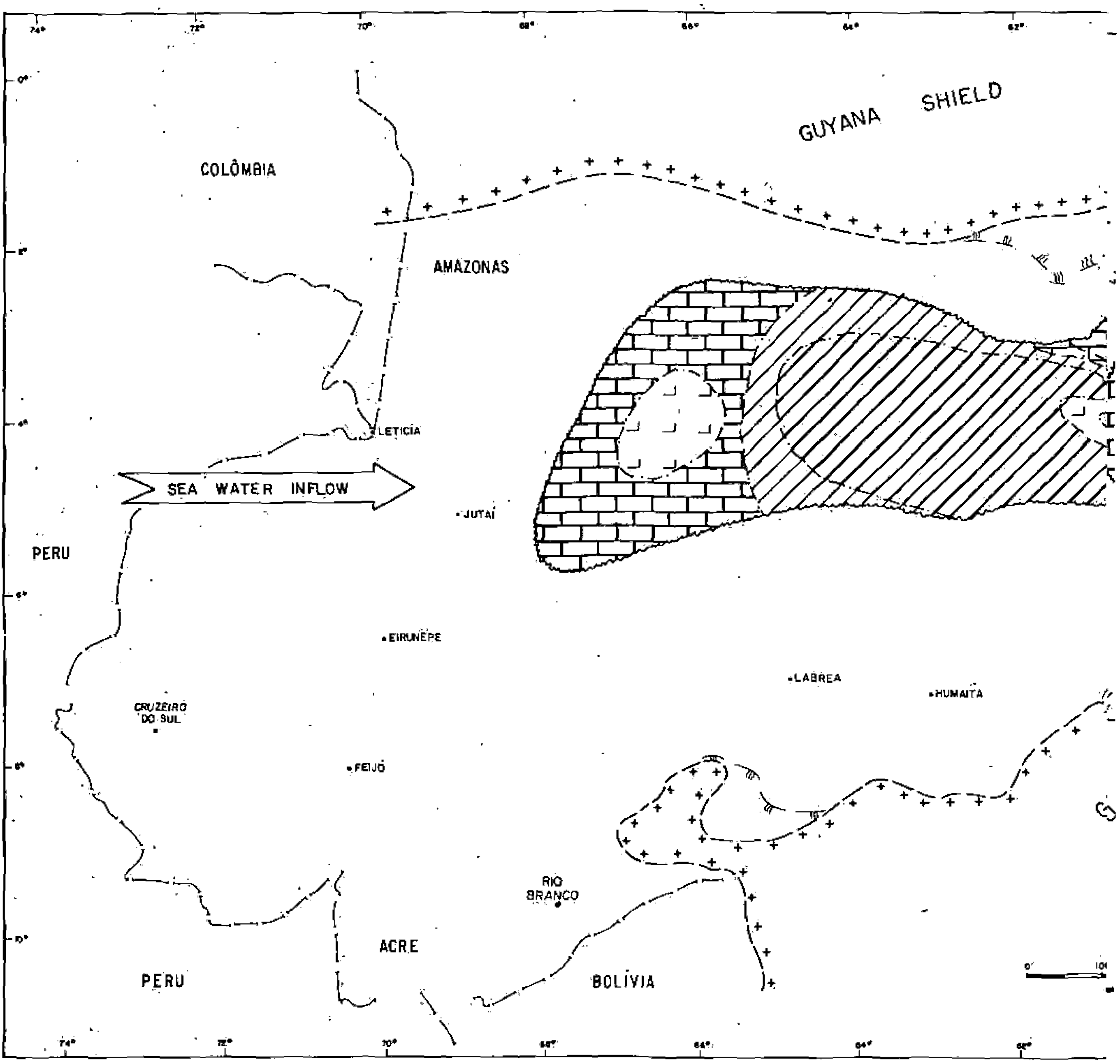
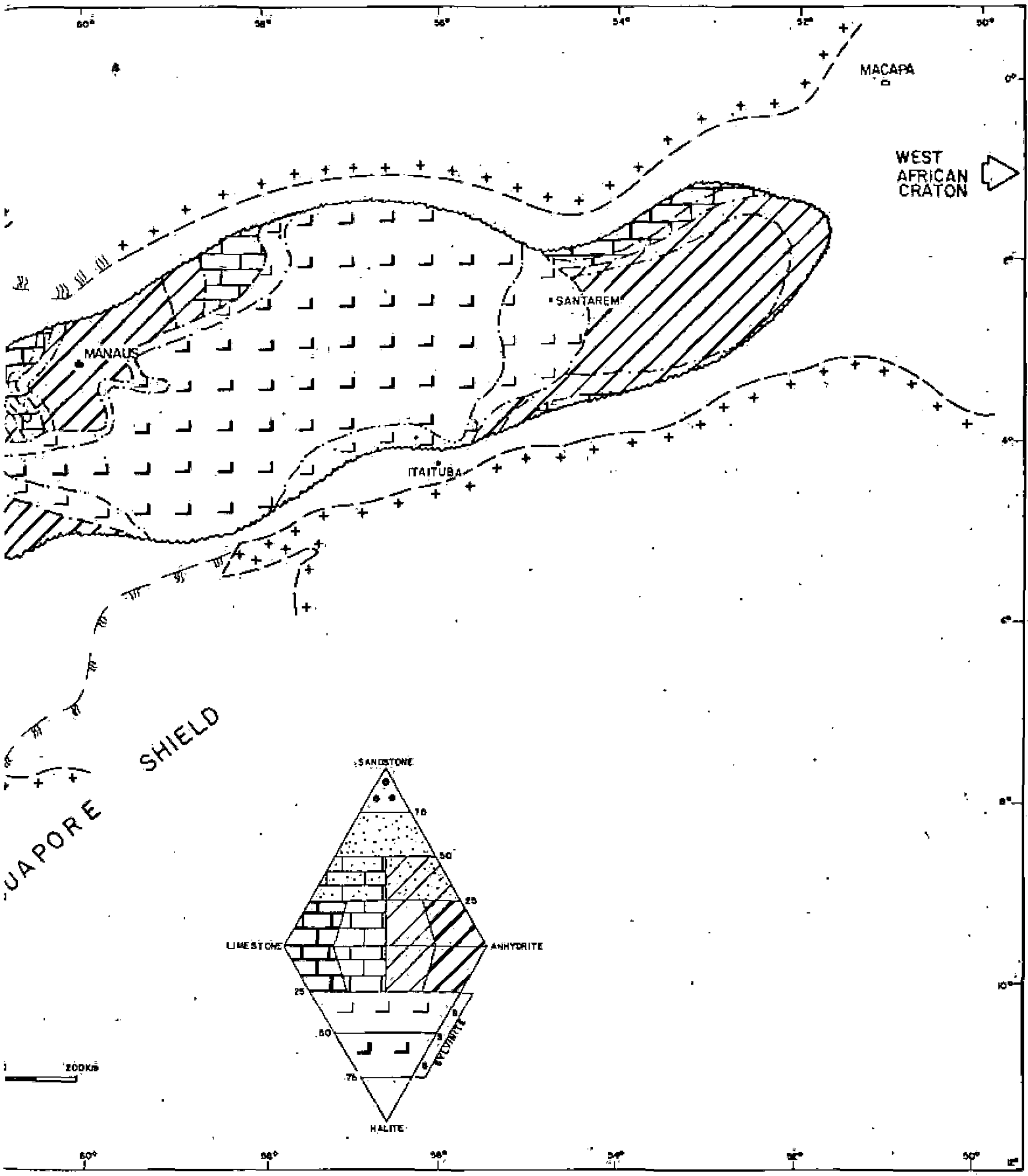


FIG. 5. Amazon Basin, facies map of evaporite cycle V. Much of the basin dur



ing this time was occupied by an extensive salt-depositing lagoon.

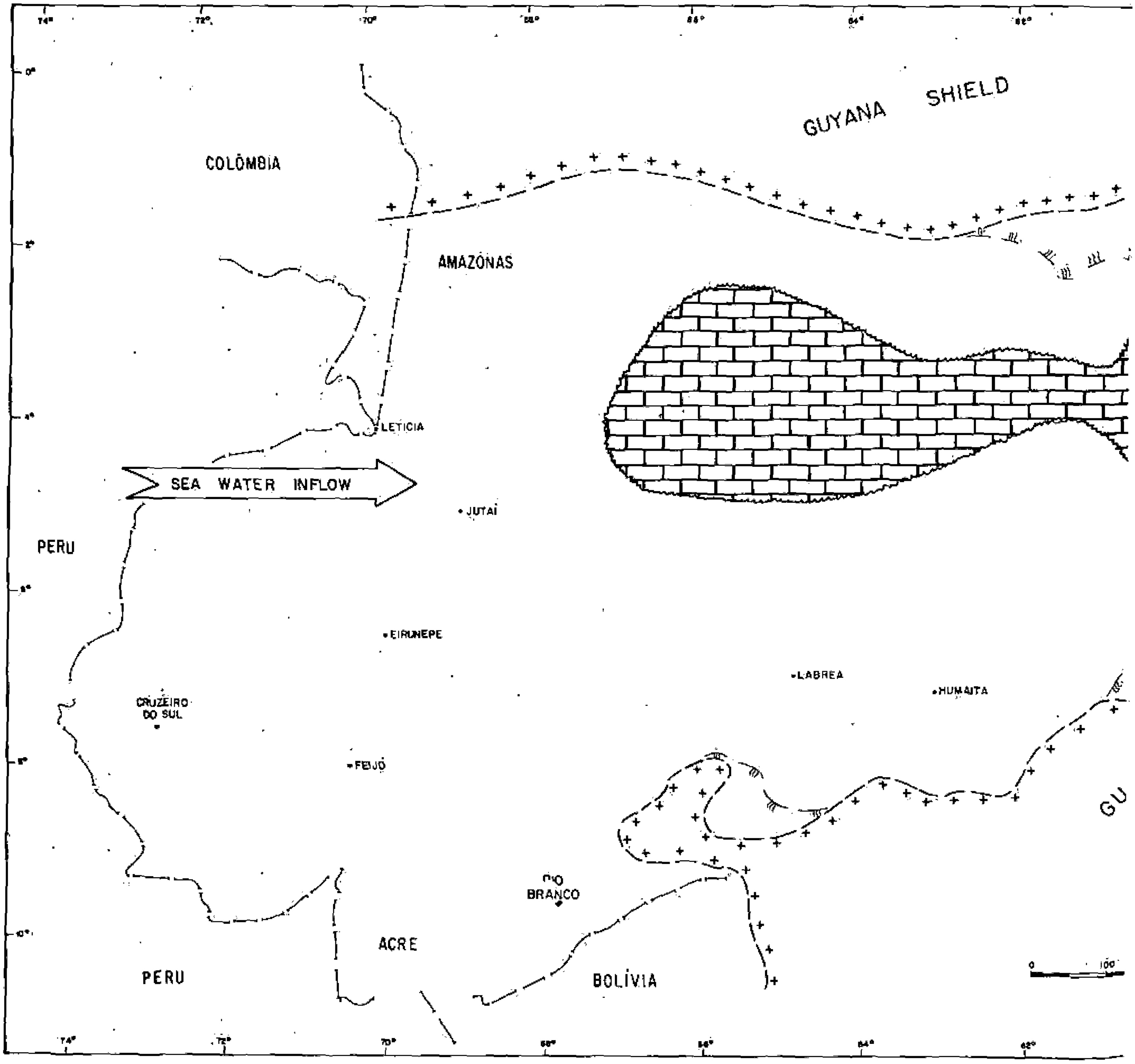
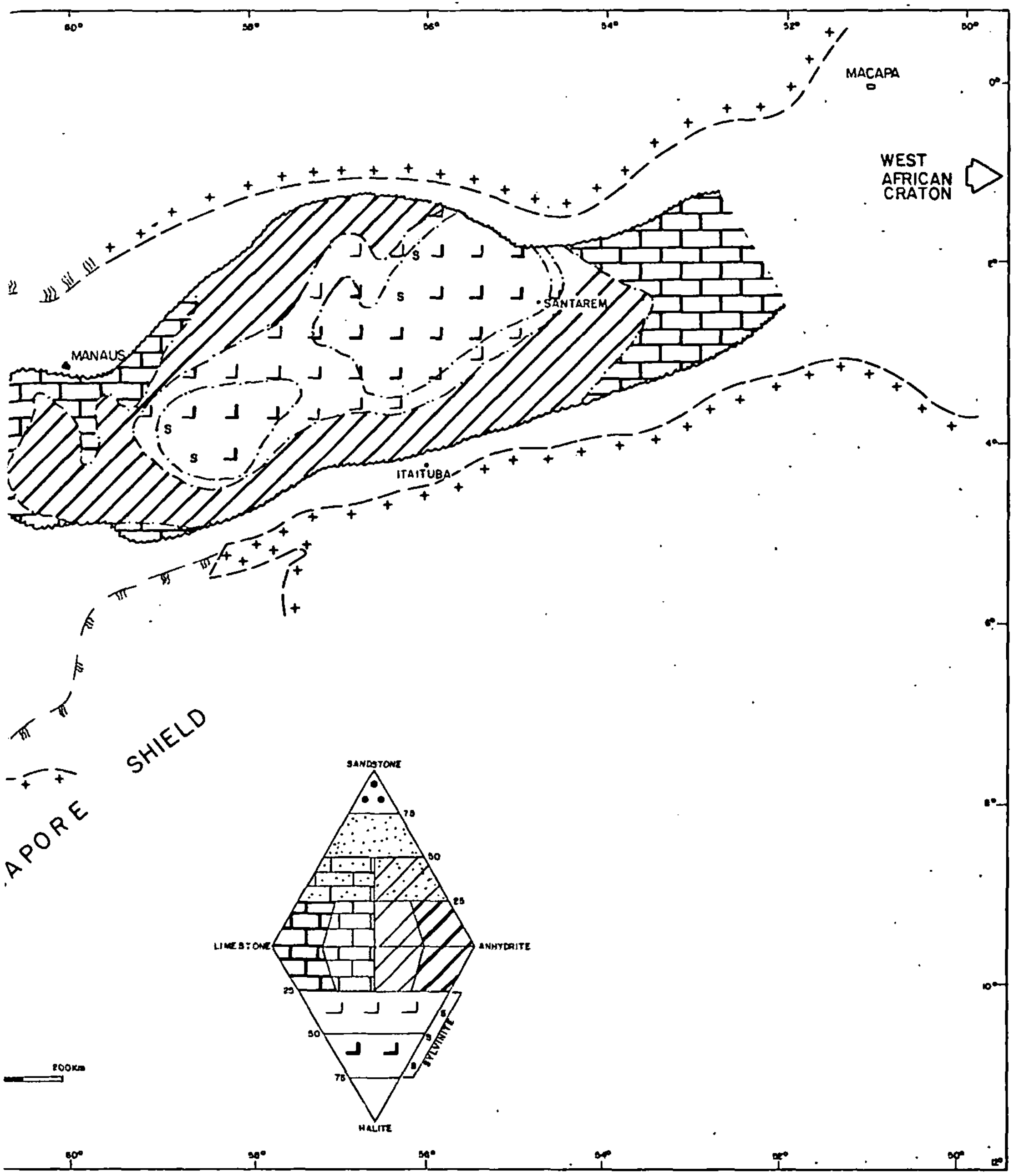


FIG. 7. Amazon Basin, facies map of evaporite cycle VII. During this stage the lagoonal environment grad
The anhydrite margin around the salt is residual, left by the late diageneti



ually broke into isolated salt lakes which deposited first fine halite, then sylvinite.
c dissolution of the halite along the basin margins.

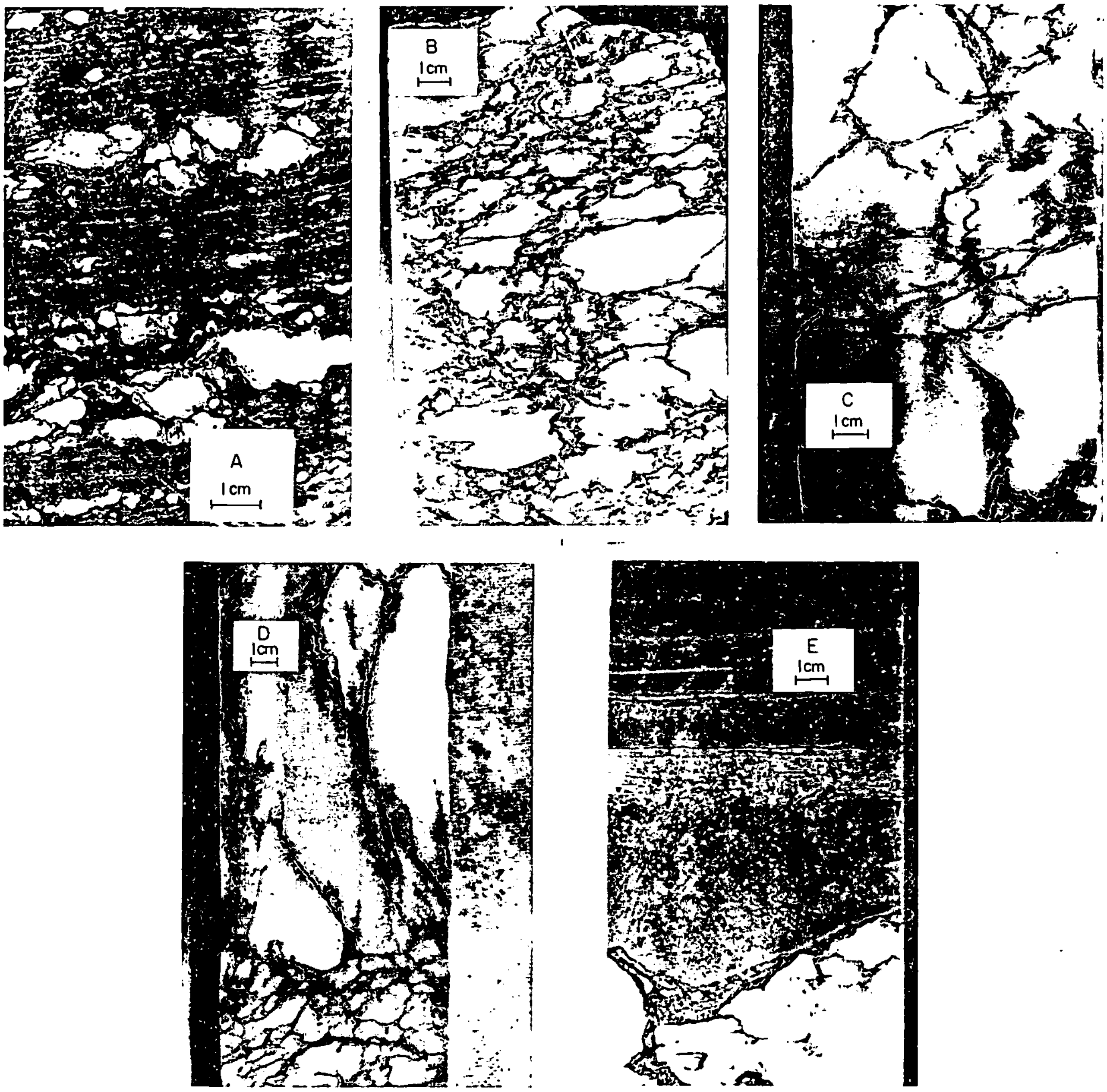


FIG. 4. Polished core slabs from Amazon Basin showing progressive subaerial anhydritization of marine sediments.

A. Small anhydrite nodules appear in the sediments.

B and C. Increasing anhydrite growth constricts the original sediments to a thin interconcretional network.

D and E. When there is no more space left for horizontal growth, the near-surface nodules grow vertically; strongly anhydritized, upheaved terrane is flooded by undisturbed, anhydrite-free marine sediments.

continental conditions. The sequence is cyclic, as most evaporite sequences are, and each succeeding cycle is represented by more continental facies than the previous one. Thus, in the lower cycles (Fig. 3), the dominant evaporites are the product of subaerial transformation of normal marine bioclastic carbonate sediments in a sabkha environment. Nodular anhydrites resulted, with biocalcarenite forming a network between the nodules as well as intercalating in the form of subaerially unaffected layers (Fig. 4).

In the middle part of the sequence, halite is the dominant evaporite rock (Fig. 5). Nodular an-

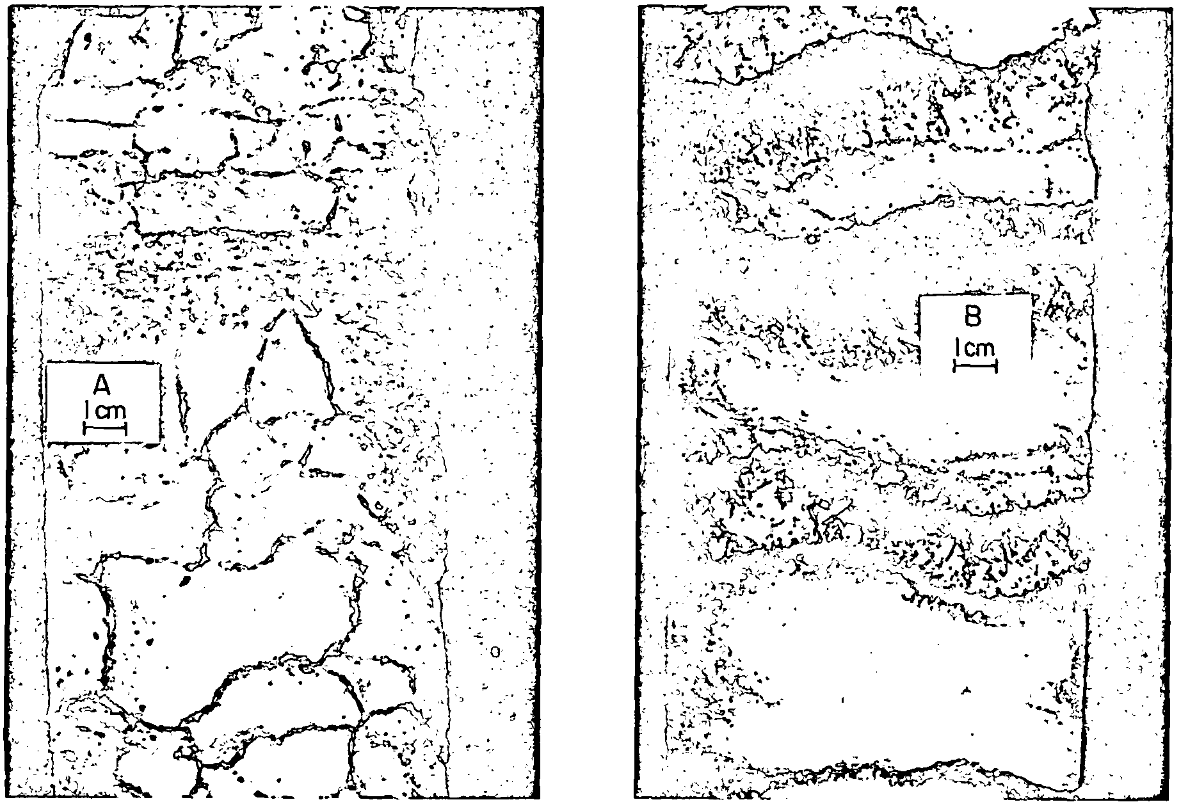


Fig. 6. Cores showing coarse halite formed during the early stages of halite precipitation. The large crystals in A and the irregular bedding in B are both due to repeated dissolution of the salts by undersaturated sea water and their subsequent recrystallization.

hydrite and limestone are restricted to the basal part of each cycle, becoming thinner and thinner in each succeeding one. The halite is typically lagoonal, coarse, and relatively pure; its rather low Br content (about 70 ppm) as well as its large grain size (Fig. 6) indicate that the concentration of the brine did not advance beyond the point of saturation with NaCl. Not until the end of the uppermost lagoonal cycle (VII), as the lagoon disintegrated into isolated lakes, did the basin brine reach a high enough concentration to deposit, first, fine-grained halite with a high Br content and, then, sylvinite (Figs. 7 and 8 A-D).

The uppermost, or continental part of the evaporite sequence, is characterized by essentially lacustrine sediments. In the lakes occupying the basin oxygen-rich (red-green) muds with abundant evidence of periodic desiccation were deposited alternatively with halite, characterized by intense recrystallization as a result of frequently changing salt concentrations and the repeated desiccation of the lakes (Fig. 8 E and F). Most of this halite had been washed into the lakes from subaerially exposed salt beds of earlier cycles. Finally, evaporite sedimentation was reduced to the recurring development of subaerial anhydrite concretions in lacustrine and alluvial muds washed in from the newly formed Hercynian Mountains that had cut off the Amazon Basin from the Pacific.

Sergipe

The colorful hypersaline evaporite sequence of Sergipe is in sharp contrast to the rather unpretentious sequence of the Amazon Basin, characterized by evaporites deposited from relatively low-concentration brines. Sergipe is not the central part of the evaporite basin (that is, under the waters of the South Atlantic Ocean) but is only a marginal bay of the large Red Sea-type South Atlantic evaporite basin that formed during the Middle Cretaceous split of South America from Africa. As in the Amazon Basin, the evaporite sequence is transitional between a continental and a marine group, but in Sergipe the continental sequence is below and the marine sequence above the evaporites, reflecting the gradual invasion of the South Atlantic rift valley by the sea. The evaporite sequence of Sergipe is thus transgressive, in contrast to the regressive sequence of the Amazon Basin.

Although the evaporite sequence in Sergipe is cyclic, its cyclicity is considerably less marked than in the Amazon sequence. This reinforces the idea that the well-defined cyclicity of the late Paleozoic sediments, whether evaporites or coal measures, may be due to eustatic changes resulting from contemporaneous glaciation. No known glaciation occurred during the Cretaceous, and this may explain why the

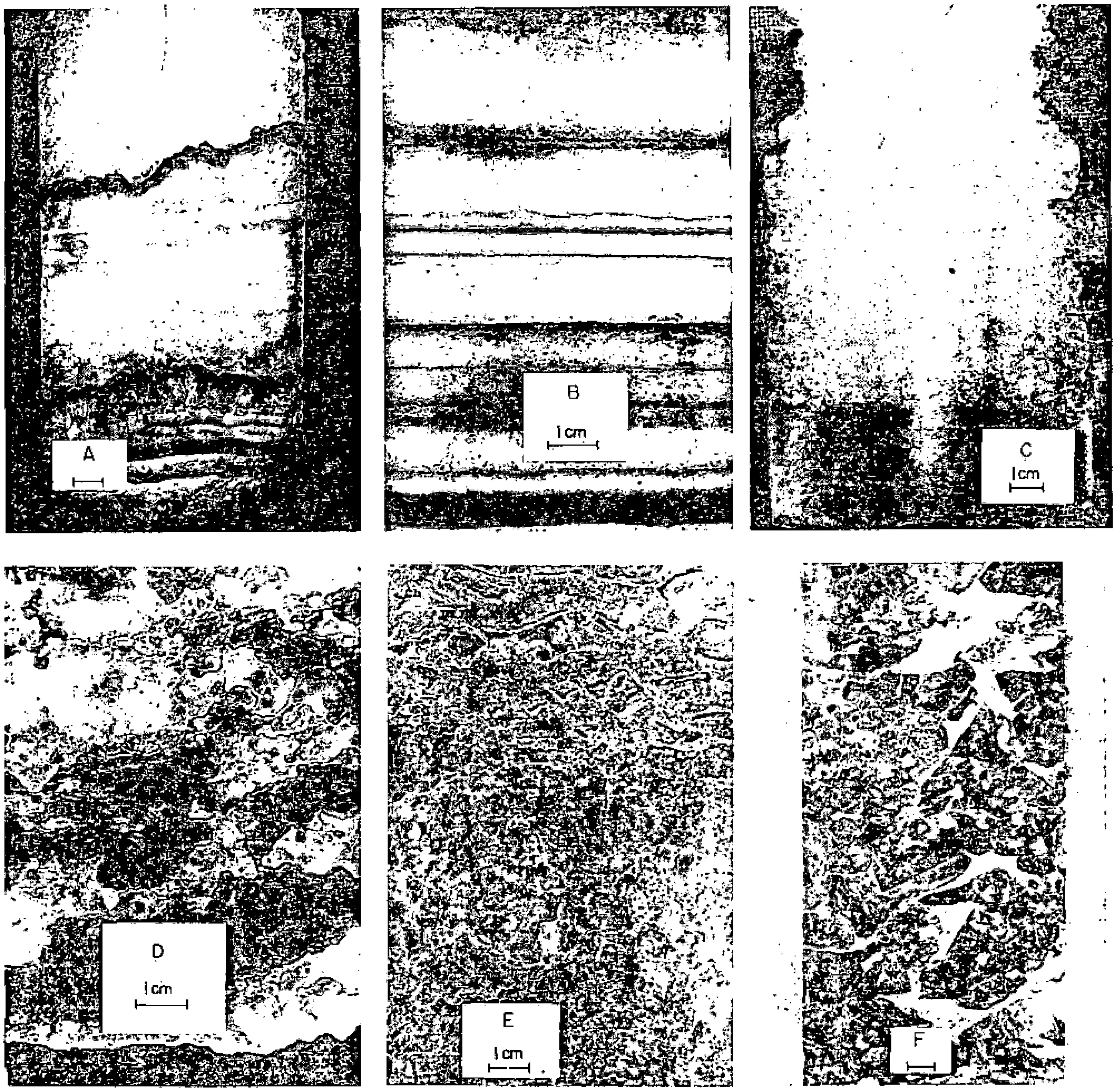


FIG. 8. A. Slabbed core of cycle VII showing bottom growth of coarse halite crystal overlain by fine-grained halite. Massive precipitation of very fine crystals dominated this depositional stage of cycle VII.

B. Slabbed core of cycle VII showing perfect lamination of very fine halite.

C. Slabbed core of white sylvinite from cycle VII. Only selective leaching of the KCl along the core margin betrays any lamination.

D. Slabbed core of basin margin sylvinites. The sylvite crystals are hematite-stained (black in photo) in contrast to the white halite.

E. Slabbed core of halite immediately overlying sylvinite in cycle VII after sylvinite deposition. This material was deposited during periodic flooding of the salt layer by muddy fresh water, causing the recrystallization of salt cubes in the washed-in mud (top).

F. Slabbed core showing continuation of conditions in E except that there is little mud and much halite. Recrystallization after flooding left only a discontinuous mud network (white) between the halite crystals.

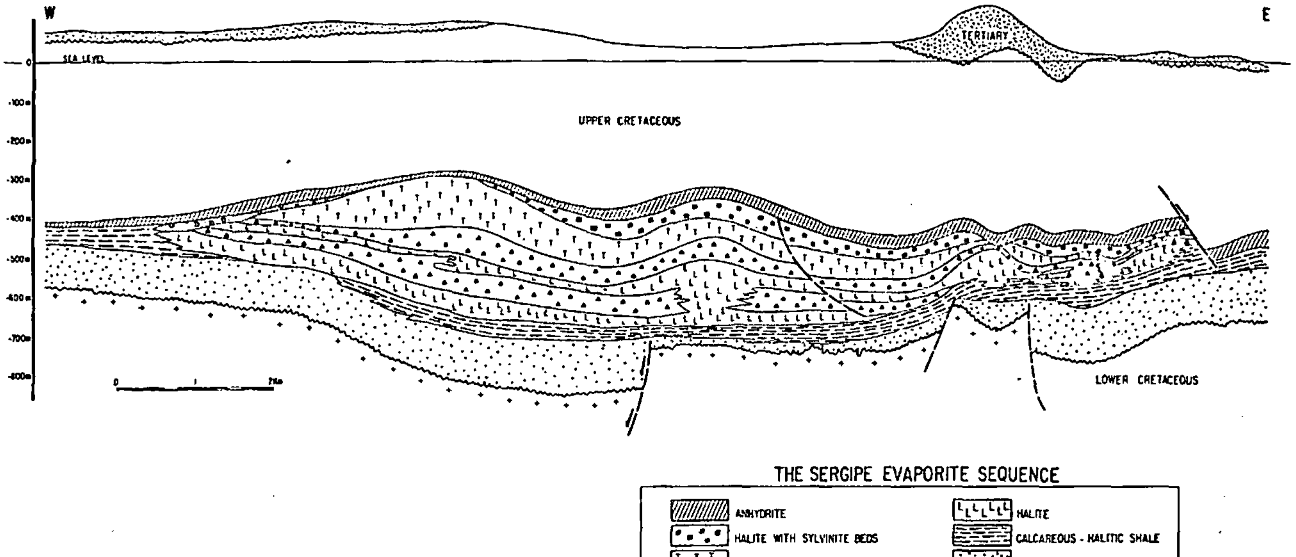


FIG. 9. The transgressive basin-margin evaporite sequence of Sergipe. This consists essentially of a single cycle, passing from halites overlying the basal shales to increasingly soluble carnallites and tachyhydrites, and then back through sylvinite and halite to anhydrite and finally to normal marine sediments.

evaporite sequence of Sergipe consists of only a single large cycle, though it is modulated by several smaller ones (Fig. 9).

FIG. 10. Slabbed core of typical channel evaporite showing coarse halite overlying algal stromatolite in a feeding channel.

The basal part of the evaporite sequence reflects the gradual entry of sea water into the area. It is characterized by calcareous muds and coarse-grained lagoonal halite as well as by algal stromatolites concentrated along tidal channels (Fig. 10).

As the original fresh-water lakes of the South Atlantic graben became replaced by salt-water lagoons of the advancing sea, salt concentrations rose sharply. In Sergipe the lagoonal areas (depressions) became sites of carnallite deposition (Fig. 11), while low-concentration halite continued to form along the tidal channels. In both areas, the halite is markedly different from the relatively low-salinity coarse lagoonal halites of the Amazon Basin. In the channels, it shows a typical skeletal texture, resulting from rapid axial growth in the dense brines. These upward-pointing skeletal halite crystals whose shorter axes point to the sides sometimes grew to a height of several centimeters (Fig. 12A).

In the lagoon areas, new halite-saturated water was brought in only occasionally by the waves and tides. Since the lagoon water was highly concentrated in $MgCl_2$, as shown by the presence of carnallite, the halite precipitated abruptly, with abundant nucleation and consequently very small grain size. This finely crystalline (sucrose) halite is finely laminated and intercalated with the carnallite (Fig. 12 B and C).

The carnallite itself also shows characteristic changes in texture in response to changes in concentration. At first, when the Mg and Ca concentration in the brines was still relatively low, it formed slowly, dissolving and recrystallizing readily, resulting in large nodular crystals (3–7 cm) surrounded by distorted laminae of fine halite (Fig. 12 D). At least part of these crystals formed, like the anhydrite nodules in the Amazon Basin, in subaerially exposed lagoonal sediments, except that in Sergipe the lagoonal sediments consisted of halite and the interstitial brine was close to saturation with carnallite.

With the rise of the Mg concentration in the lagoon, the crystal size of the carnallite diminished as recrystallization became less common. Gradually, nucleation became so abundant that only carnallite of small crystal size (1–3 mm) was deposited, still intercalated with occasional halite laminae deposited from halite-saturated brines carried by the former tidal channels. In the channels themselves, almost no carnallite formed.

Finally, when the inflow through the channels reached its lowest level and carried only hyperconcentrated residual brines, the carnallite gave place to, although occasionally still intercalated with, tachyhydrite. In Sergipe, tachyhydrite forms a monomineralic evaporite rock which is chemically analogous with but considerably more soluble than carnallite. Until its discovery by R. Hite in Thailand, the South Atlantic and primarily Sergipe were the only areas where this mineral was known to form large deposits (in layers up to 100 m thick). With the precipitation of tachyhydrite, the gradual increase in brine concentration came to an end. A renewed increase in the inflow of salt-saturated water to the area, probably related to an improved connection of the South Atlantic with the world ocean, put an end to the deposition of highly soluble evaporites. These inflowing brines, unsaturated in Mg, leached much of the Mg from the carnallite, dissolved tachyhydrite, and precipitated much of the KCl liberated from the former as sylvinite. The resulting sylvinite beds occur in several horizons (Fig. 12E), directly overlying the tachyhydrite as well as farther above it, thus reflecting the gradual transgression of the Mg-unsaturated brines over the terrane. In the lowermost beds, lateral facies changes from carnallite to sylvinite are common. The associated halites show an initially

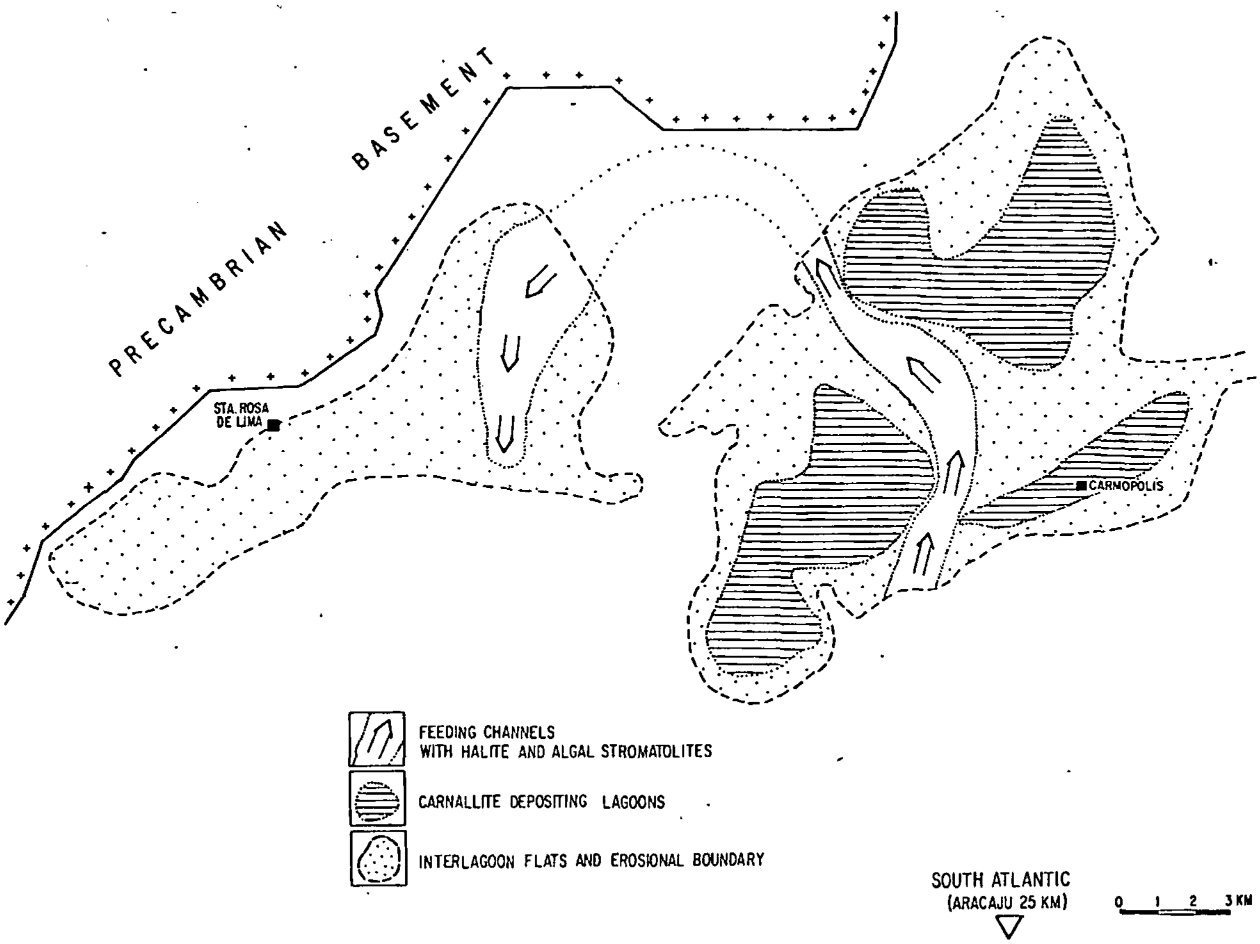


FIG. 11. Paleogeography of the Sergipe evaporites. Feeding channels bring in halite from the salt-saturated South Atlantic graben and deposit skeletal halite as well as, during occasional dilution, algal stromatolites. The lagoons, together wih the frequently emergent inter-lagoon flats fed by the channels, became the sites of, first, carnallite and then tachyhydrite deposition.

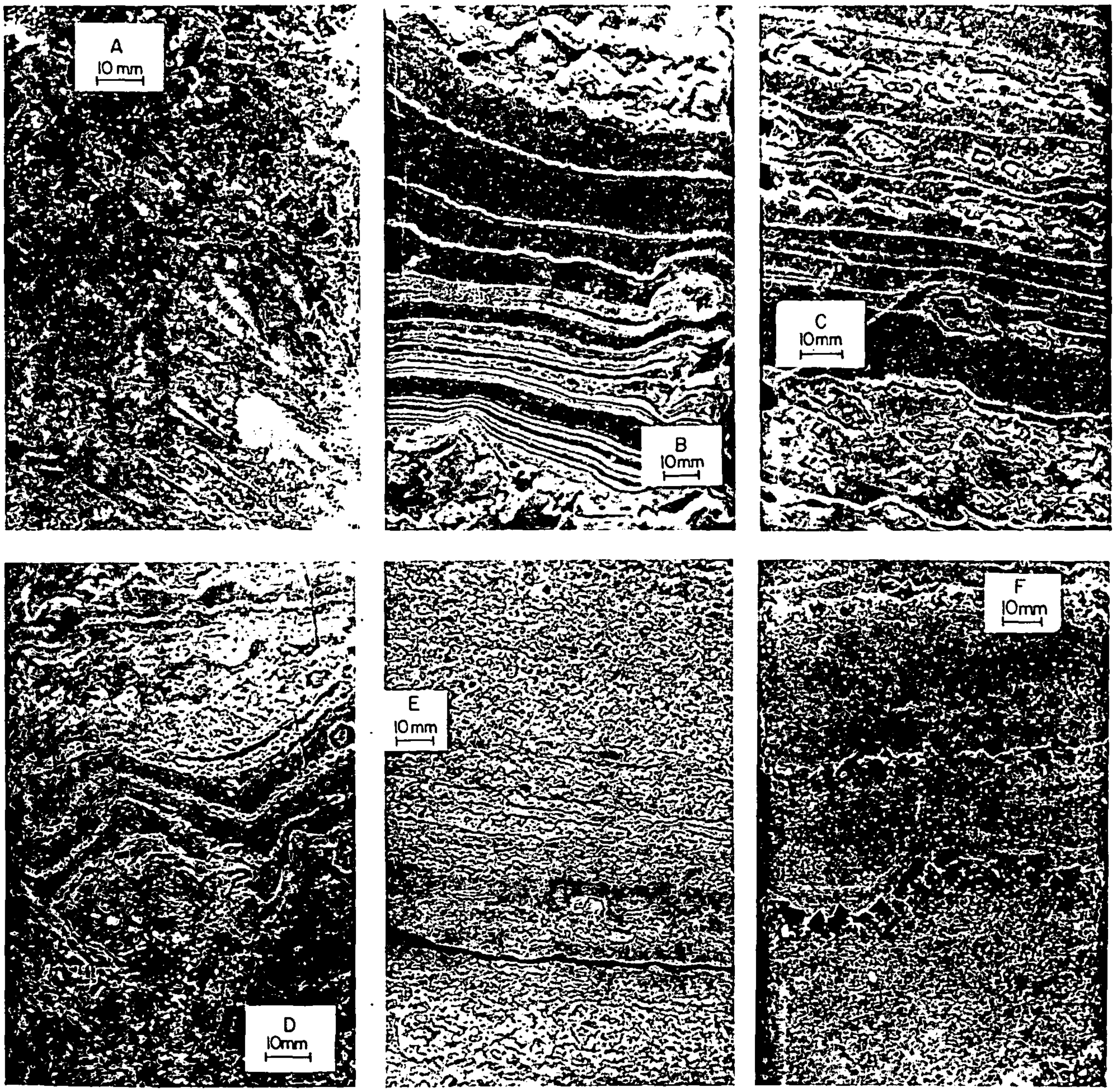


FIG. 12. A. Pennate skeletal halite crystals which grew in very shallow water of a feeding channel.

B. Slabbed core of finely laminated, finely crystalline halite, deposited in a carnallitic lagoon. The growth of a large carnallite crystal (lower left) deflects and ruptures the halite lamination.

C. Slabbed core showing growth of single-crystal carnallite nodules in finely laminated lagoonal halite.

D. Slabbed core containing large carnallite crystals which grew in a fine halite network.

E. Slabbed core from a sylvinite bed showing the intricate, amoebalike intergrowth of halite and sylvite crystals.

F. Slabbed core showing halite crystals grown at the lagoon bottom. This material overlies sylvinite and reflects the falling concentration of lagoon brines after sylvinite deposition and presages the end of evaporite formation as normal sea water flooded the widening South Atlantic ocean.

high, and then gradually decreasing, Br concentration, reflecting the increasing inflow of diluted brines (Fig. 12F). Finally, as normal conditions were stabilized in the widening South Atlantic ocean, massive halite precipitation ceased, giving place to the deposition of shales and limestones in a normal marine environment. In these beds, the only macroscopic evaporite mineral is supratidal anhydrite.

Summary

As this brief analysis demonstrates, the texture, structure, and composition of the evaporites permit a facies interpretation at least as detailed as can be obtained by such a study of the more conventional sediments. Besides the evident advantage the study has for the exploration of potassium and magnesium salt deposits, it can be used as a sensitive indicator of the paleogeographic and tectonic changes taking place not only in the area studied but also in the supplying sea.

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ACTIVATED CARBONS AND GOLD — A LITERATURE SURVEY

SYNOPSIS

The literature on activated carbon is reviewed so as to provide a general background with respect to the effect of source material and activation procedure on carbon properties, the structure and chemical nature of the surface of activated carbon, and the nature of absorption processes on carbon. The various theories on the absorption of gold and silver from cyanide solutions are then reviewed, followed by a discussion of processes for the recovery of gold and silver from cyanide solutions using activated carbon, including a comparison with zinc precipitation.

INTRODUCTION

The current interest in activated carbon for the adsorption of metals from cyanide solutions has prompted us to write a review aimed at familiarizing the reader with the general physical and chemical properties of activated carbons and their application to the recovery of gold and silver from mine solutions and pulps. The first part deals with the properties of carbons, the second with the nature of adsorption processes, and the third with some processes that have been proposed for the extraction of gold from pregnant mine solutions and mine effluent solutions containing small amounts of dissolved gold.

PHYSICAL AND CHEMICAL PROPERTIES OF ACTIVATED CARBON

Source materials

Activated carbons have been made from almost any source of carbonaceous material, including bone, coconut shells, wood, peach pips, peat, bituminous coals, sugar, and even blood. The physical and chemical properties of activated carbon are influenced by both the source material and the conditions of activation, viz, chemical or thermal (gas) activation and the temperature and duration of the process. In Figure 1 are shown photomicrographs of carbons synthesized from different starting materials, which show that the structure of the original organic material, e.g., the cellular structure of the peach-pip and coconut shell products, are still present in the carbon skeleton of the final carbon. Experience has shown that the structure of the carbon skeleton of the product, and hence the quantity and size distribution of the pores developed inside the carbon particle, are strongly dependent on the source material. It is this property that makes carbons from particular sources suitable for specific tasks, e.g., coconut shells for gas-phase adsorption. The adsorptive properties of activated carbon were discovered in the 18th Century, but the first practical application came about in the sugar-beet industry when bone char was introduced as a decolorant in France during the Napoleonic wars. Further application of activated carbon remained fairly static until World War I, when an answer to the use of chlorine gas in warfare was required, and it was found that coconut-shell carbons were most effective as gas adsorbents. These carbons continue to be most important in air purification, while coal-based carbons are most effective in the field of water treatment. This is because the majority of pores in activated carbon originating from coconut shells are small, viz, 20Å in diameter, and thus are suitable for adsorption of small gaseous molecules. Carbons manufactured from bituminous coal have pores whose diameters span the range 20 to 10 000 Å, and these carbons can remove large molecules from liquids, e.g., large molecules responsible for colour.

For adsorption to occur, the molecule must reach the internal surface of the carbon particle by diffusion through the pores. As a result, the pore structure will have a marked influence on the adsorption kinetics, i.e., the rate at which the molecules are adsorbed. Since the pore structure is related to the time and temperature of activation, it also influences the mechanical strength of activated carbon granules.

The structure of the carbon skeleton

The process of charring and activation, described below, produces a material that has a very large surface area, from a few hundred to well over a thousand m^2/g. The structure of activated carbon is essentially graphitic in nature[1], as shown by X-ray-diffraction studies, and is not truly amorphous, but has regions of order that have a graphite-like structure. The same studies[1] have shown that the size of these microcrystalline regions increases with temperature of activation, which might relate to the adsorptive properties of the carbon since these depend strongly on the temperature of activation. In Figure 2 is shown the proposed[2] appearance of the graphitic structure of activated carbon. It can be seen that the layers of carbon atoms are considerably disordered and, also, the separation between the layers is greater than that found in graphite itself.

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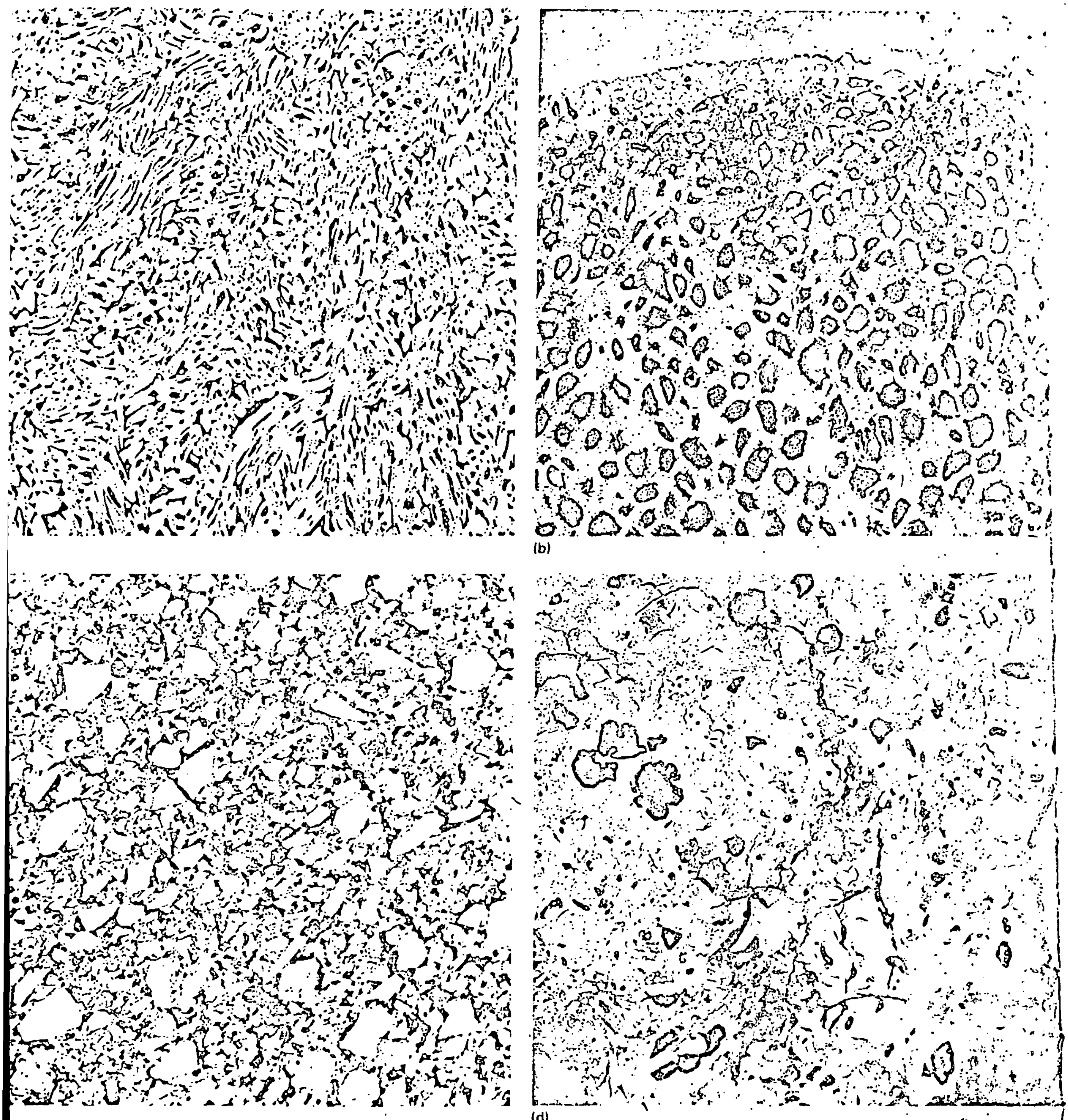


FIGURE 1. Photomicrographs of activated carbons, authors' samples, reflected light, magnification X175. Dark areas are macropores, light areas carbon. (a) coconut shell, (b) peach pip, (c) bituminous coal, and (d) extruded peat based carbon. The dark areas in (a) are channels between the fibres of the coconut shell, and appear to be stripes when cut at right angles, whereas those in (b) are cells in the peach pip, and appear the same whatever the angle of cut.

The pore structure and surface area of carbon are developed during the charring and activation process. The sizes of the pores are important, because they may exert a screening process, which prevents molecules that are too large from being absorbed, or else promote adsorption when the pore diameters are of optimal size for making the maximum number of contacts with the molecule to be adsorbed. For example, the small pores of coconut-shell carbons are ideal for adsorbing small gaseous molecules, which fit more snugly than into the larger pores of other types of carbon. This has led to the use of adsorption of molecules of different sizes by activated carbons as an indication of the distribution of their internal free volume among pores of different sizes. Thus, the small iodine molecule is adsorbed in pores down to 10 Å diameter, so that the 'iodine number' is an indication of the number of pores above this size, while, at the other end of the scale, molasses (a polysaccharide) is adsorbed only in pores above about 30 Å, and the 'molasses number' gives an indication of the number of pores larger than this. A more sophisticated approach is to measure the pressure required to force liquid mercury into the carbon, which indicates the size of the pore into which it is being forced[3]. In Figure 3 is shown a typical-size-distribution diagram obtained by this method. In cross-section the pores in activated carbons may be cylindrical or rectangular, or a variety of irregular shapes, and constrictions may occur. These pores are generally classified in terms of their equivalent diameters, viz,

macropores	500 — 20 000 Å
transitional pores or mesopores	100 — 500 Å
micropores	8 — 100 Å

The chemical nature of the surface

The most important division of carbons is into what Steenberg[5] has called the H- and L-carbons. H-carbons are formed at temperatures in excess of 700 °C (typically around 1 000 °C) and are characterized by taking up acid on immersion in water. L-carbons are activated well below 700 °C, typically around 300 to 400 °C, and are characterized by taking up base on immersion in water. The two types of properties are completely interconvertible. Heating an H-carbon at low temperature will produce an L-carbon, for example. An important aspect of the production of both types is the exposure to oxygen, which is irreversibly adsorbed by the carbon, and only comes off again at high temperatures as CO and CO_2, showing that it is present on the carbon chemically bound to the surface as the all-important 'surface oxides' of the carbon.

Although these surface oxides play an important role in the chemical nature of the carbon, their identity by no means can be regarded as well established. Because the respective temperatures at which the gases are evolved upon outgassing samples of carbon under vacuum correspond with the temperature ranges involved in the production of H- and L- carbons, it has been suggested[6,7] that the surface oxides evolved as CO_2 at lower temperature are responsible for the physico-chemical behaviour of L-carbons, and those evolved as CO at higher temperatures are responsible for H-carbon behaviour. Attempts to identify these surface oxides include acid-base neutralization[8,9] and reaction with specific chemicals to provide information. For example, methylation will give esters with carboxylate groups, which are hydrolysable with base, whereas phenolic groups will give ethers which are not[8,9]. More sophisticated approaches have involved[10]: ESR (Electron Spin Resonance) and NMR (Nuclear Magnetic Resonance), and, more profitably, Internal-reflexion Infrared Spectroscopy (IRS). The last technique, which is discussed in detail by Mattson and Mark[10], has indicated that there are probably carboxylate, phenolate, and quinone-type groups present on the carbon[10] (Figure 4). Unfortunately, IRS suffers from the problem inherent in all infrared techniques of identification, viz, that a large number of groups of different kinds adsorb over similar ranges. The adsorptions have been alternatively interpreted as being due to ether, peroxide, and ester groups in the form of lactones, carboxylic, anhydrides, and cycle peroxides (Figure 4). Because of these uncertainties, it is not our intention to go into the details of

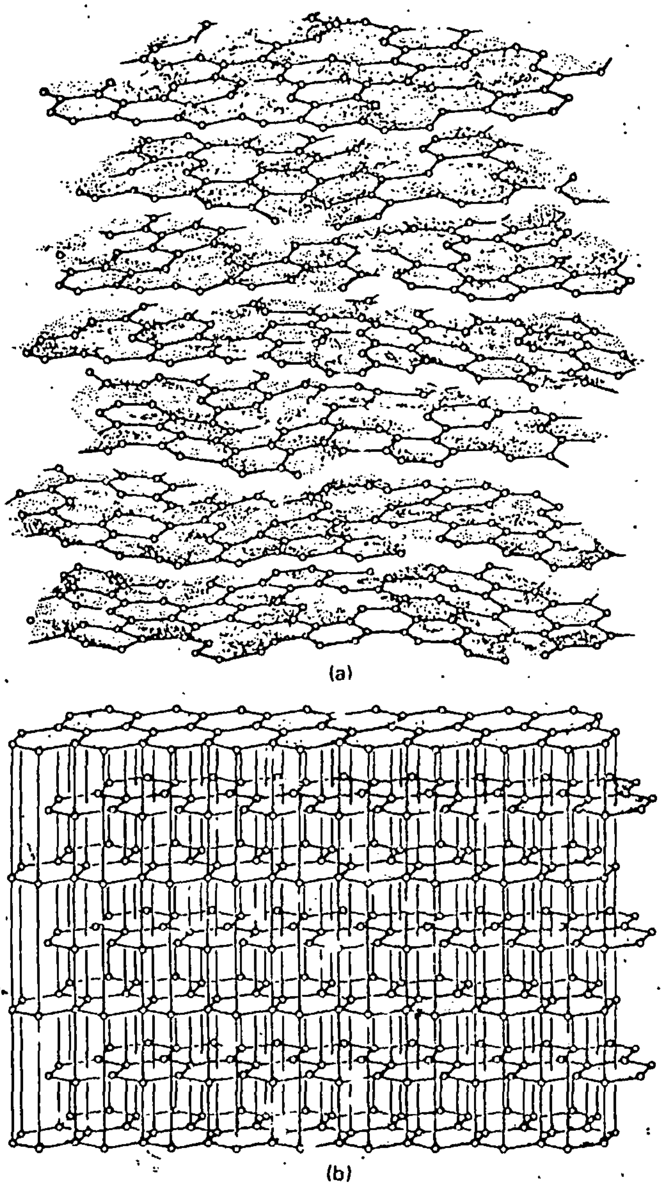


FIGURE 2. Proposed structure of activated carbon (a), with that of graphite (b) for comparison. Adapted from Bokros[2]. The circles denote the positions of carbon atoms, whereas the lines are carbon-to-carbon bonds.

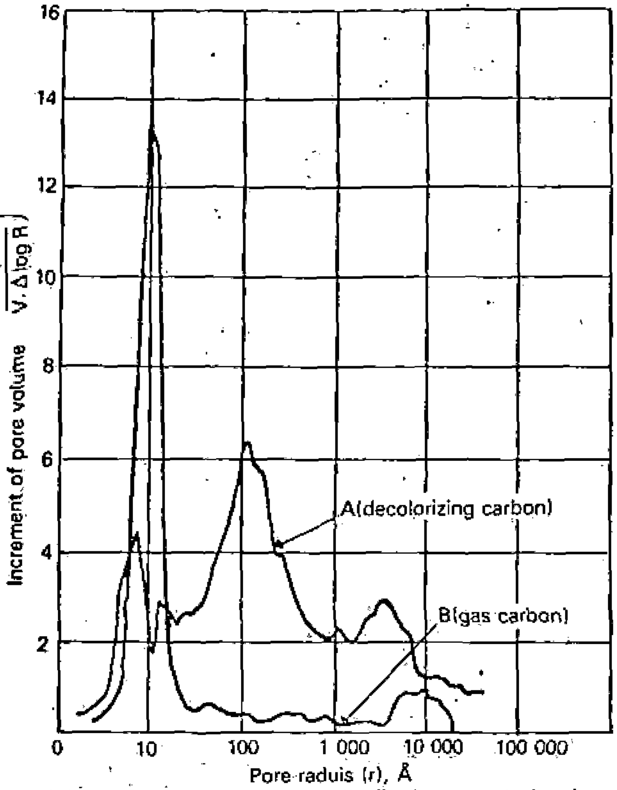


FIGURE 3. The pore-volume distribution of typical activated carbons. A is a coal-based carbon, showing a large number of meso-pores that make it suitable for the adsorption of larger organic molecules. B is a coconut-shell carbon having mainly micropores that make it suitable for the adsorption of small molecules from the gaseous phase. (Adapted from Fornwalt et al[4].)

these oxides further here, but merely to remark that the low-temperature oxides appear to be carboxylate in nature, whereas those formed at higher temperatures appear to be phenolic, or some derivative of this group, such as a lactone. The importance of these groups probably lies in their ability to alter the hydrophobic *versus* hydrophilic properties of the carbon surface, as indicated in the next section.

The activation of carbon usually involves two distinct stages, viz, a preliminary charring step at lower temperatures (300 to 500°C), which drives off the volatile matter of the raw material to leave a hydrophobic carbon skeleton, followed by heating of the char at higher temperatures (700 to 1 000°C) in the presence of air, carbon dioxide, or water vapour (or mixtures of these). This is the activation stage, and the reactive oxygen burns away part of the carbon skeleton as carbon monoxide and carbon dioxide, thereby increasing the internal surface area of the carbon and developing the pore structure. If oxygen is excluded, the resulting carbons have no ability to adsorb acids. ESR experiments have shown that, after heating at high temperatures, a large number of signals from unpaired electrons, indicating ruptured bonds, are present in the carbon. These highly reactive sites react with oxygen when it is admitted, and the signals from the unpaired electrons decrease enormously.

The nature of adsorption processes

Apart from the strong interactions involved in forming chemical bonds between atoms, molecules exert weak attractive and repulsive forces on each other, which differ from those in chemical bonding only in that they are much weaker. These weak van der Waals forces are responsible for the adsorption of non-polar molecules onto surfaces, and are of the utmost importance in the adsorption of organics by activated carbon. In Figure 5 is seen the theoretical curve[10] for the van der Waals interaction of two hydrogen atoms already chemically bound to other atoms, e.g., these might be H atoms bound to C in a hydrocarbon. Apart from the small scale, the curve is similar to the familiar curve of energy *versus* atomic separation for forming chemical bonds. The region where the energy falls below the X-axis, i.e., the sum of the van der Waals radii of the two hydrogen atoms, is energetically favourable for the system, and it is the small attractive forces at these interatomic separations that lead to the adsorption of non-polar molecules onto hydrophobic surfaces. No different in nature is the familiar hydrogen bond, which is involved in attracting more polar molecules like water

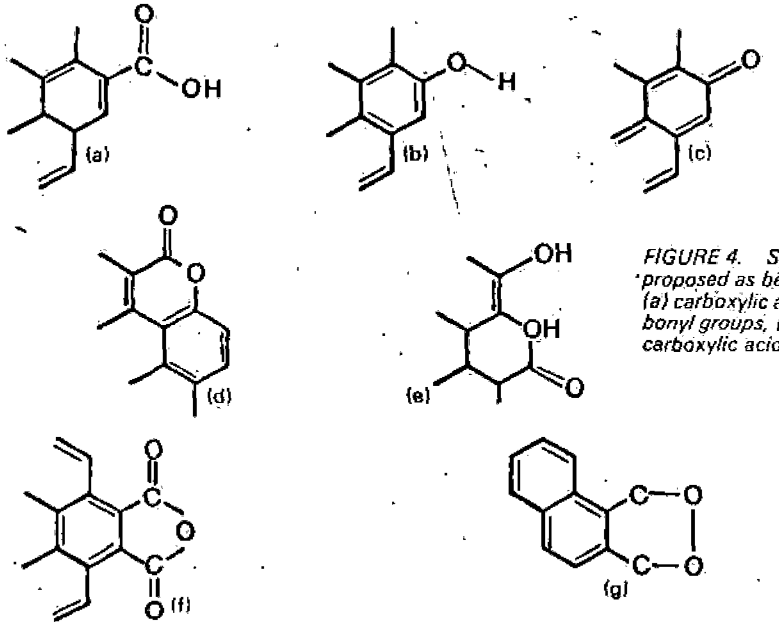
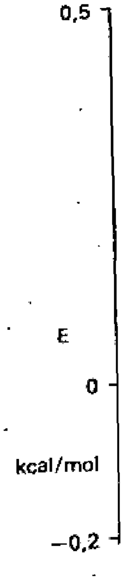


FIGURE 4. Structure of some surface oxides that have been proposed as being present on the surface of activated carbon: (a) carboxylic acid, (b) phenolic hydroxyl, (c) quinone-type carbonyl groups, (d) normal, and (e) fluorescein-type lactones, (f) carboxylic acid anhydrides, and (g) cyclic peroxides.



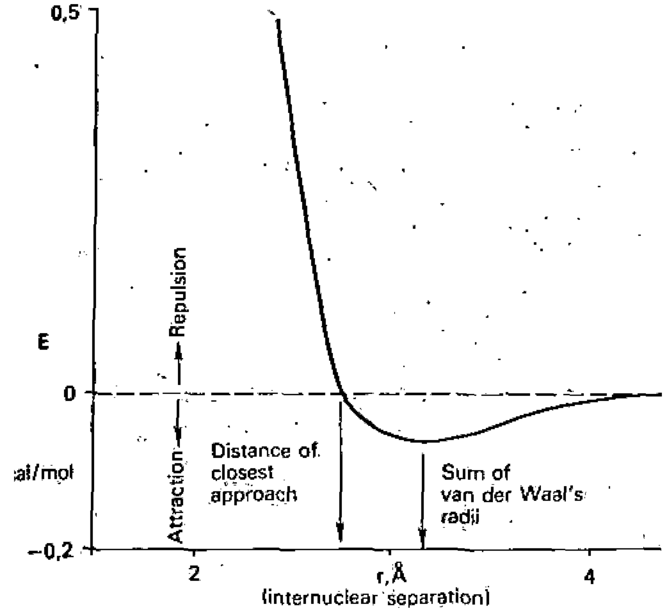


FIGURE 5: The energy of the van der Waals interaction between two hydrogen atoms not chemically bound to each other. Attraction results when the curve falls below zero (dotted line), and it is this type of weak attractive force that is responsible for the physical adsorption of non-polar organic molecules onto hydrophobic surfaces. The curve was calculated by the authors using parameters from Allinger[11].

onto surfaces; so rendering them hydrophilic. These bonds involve attraction between the slightly positively charged hydrogen atom in water and the electron-rich dipoles on other atoms, typically oxygen in water, alcohols, carboxylates, silicates, and so on. Both of these forces are involved in the adsorption of gases onto carbons, as are also other forces variously classified as dipole-dipole forces, dispersion forces, etc., but that are essentially no different in nature from the first two types. Adsorption from aqueous solution may be simply understood as a balance between the much stronger hydrogen-bonding forces and the weaker van der Waals forces. The lattice of liquid water is held together by hydrogen bonds, and non-polar organic molecules generally have only a low solubility in water because the water molecules form strong hydrogen bonds with each other rather than weak van der Waals interactions with the non-polar organic molecule, or a hydrophobic surface incapable of forming hydrogen bonds. It is thus energetically favourable for the organic molecule to escape from the water structure and adsorb onto a hydrophobic surface. However, if the surface is made hydrophilic, the water will adsorb preferentially and the organic molecule will remain in the bulk liquid. Should the organic molecule have a hydrophilic group, e.g., a carboxylate as well as a hydrophobic chain, the best arrangement then will be with the hydrophobic portion attached to the hydrophobic surface, with the hydrophilic end oriented into the bulk aqueous solution, which, of course, is the basis of solubilization of hydrophobic fatty particles in aqueous solution by soaps. The importance of the hydrophobic/hydrophilic balance of the surface is seen in Figure 6, which shows the adsorption of non-polar molecules onto polystyrene matrices as the hydrophilicity increases with the percentage sulphonation of the internal surface, which, unsulphonated, presents a phenyl group at the interface with water[12]. The ion-exchange resin is used to illustrate our point because it represents a well-characterized and well-understood system, which activated carbons do not. As the percentage sulphonation increases from zero, adsorption of the organic increases, because the resin swells better, admitting the aqueous solution. In addition, the sulphonic acid groups form hydrogen bonds with water, and structure it round themselves, rendering it less able to solvate the organic molecules dissolved in it. Therefore, the equilibrium is shifted in the forward direction so that adsorption onto the hydrophobic parts of the internal surface occurs. This is similar to the salting out of organics dissolved in water, where addition of a simple inorganic salt causes the organic to separate out from the aqueous phase. After peaking out, the adsorption of the organic molecules in Figure 6 decreases as more sulphonation takes place, because the surface is now becoming too hydrophilic and water is adsorbed preferentially to non-polar molecules. The small residual affinity for non-polar molecules at even 100 per cent sulphonation accounts for the 'organic fouling' in normal ion-exchange resins.

The above factors lead to a fairly simple behaviour of organic molecules adsorbing onto activated carbons: In an homologous series of organic molecules, e.g., methyl, ethyl, propyl alcohols, the adsorption becomes stronger as more methylene groups are added because the hydrophobic part of the molecule becomes larger, lowering its affinity for the solvent water, and increasing the extent of van der Waals interactions with the hydrophobic surface of the carbon. This gives rise to Traube's rule, which states that the larger homologues in a series will be the most strongly adsorbed. At the same time, because ions are very strongly hydrated (i.e., hydrophilic), activated carbon has, in general, only a small affinity for ions. In Figure 7 is shown the adsorption of acetic acid by activated carbon as a function of pH. Below a pH value of 5 the acetic acid exists as a neutral molecule CH_3COOH, which is reasonably strongly adsorbed by the carbon, but above this pH the proton is lost to give the anion CH_3COO^-, which is

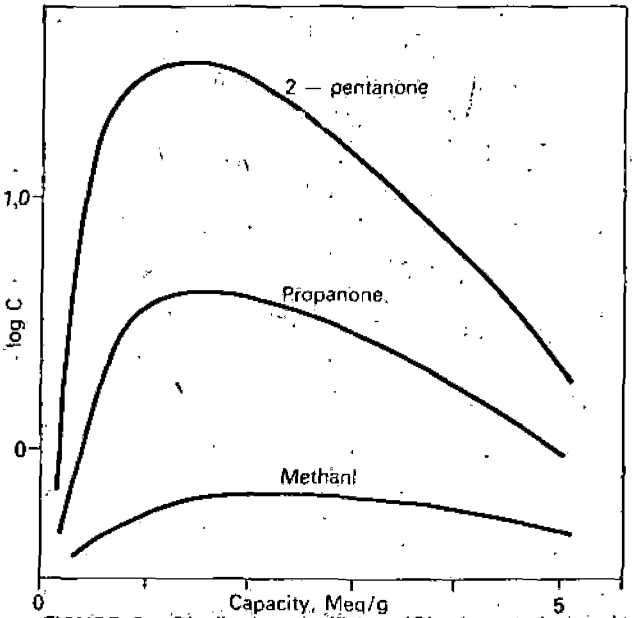


FIGURE 6. Distribution coefficient (C) of neutral organic molecules onto sulphonated polystyrene ion-exchange resins as a function of the degree of sulphonation. This is measured by the capacity of the resin for cations, 5,2 Meq/g representing a substitution of approximately 100 per cent. (Adapted from Rieman[12].)

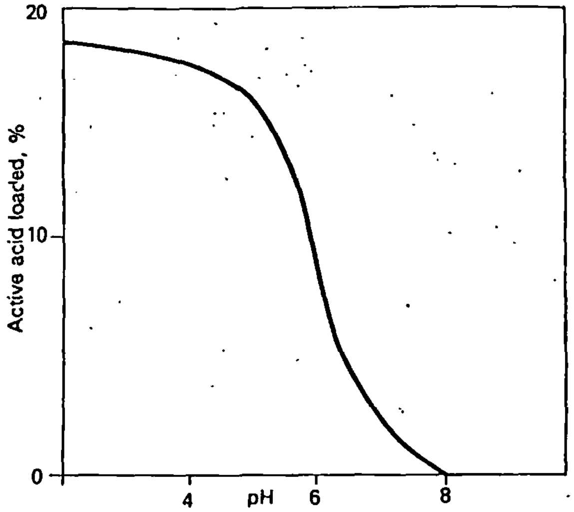


FIGURE 7. Adsorption of acetic acid onto activated carbon as a function of pH. (Semi-diagramatic.)

scarcely adsorbed by the carbon at all. Because of this, it is probable that theories of adsorption of ions such as $[Au(CN)_2^-]$ as ions *per se*, discussed in the next section, can be largely discounted. The key to understanding the properties of activated carbon lies in *solubility* of the adsorbates.

The weak adsorption of acids that does take place is postulated to take place via specific adsorption of anions into the electrical double layer, with non-specific adsorption of cations such as the proton or Na^+ so as to preserve electroneutrality. In Figure 8 is shown a schematic representation of the electrical double layer. Ions are adsorbed onto a surface because of an electrostatic potential on that surface, and form several relatively structured layers extending out into the greater disorder of the solvent. It is postulated[10] that the anions are in the innermost, specifically adsorbed layer, because the adsorption of ionic substances is more sensitive to the nature of the anion than of the cation in these substances.

On the freshly activated carbon, stronger take-up of acid occurs, which is not anion-dependent. Frumkin[13] proposed that oxygen reacts with the freshly activated surface to form surface complexes of the type C_xO, which then react with water according to equation [1]:

$$C_xO + H_2O \rightleftharpoons C_x^{2+} + 2OH^-. \qquad [1]$$

The net effect of this reaction is the removal of protons from the bulk aqueous solution. The formulation C_xO indicates that the exact nature of these groups remains unknown. Garten *et al*[14] proposed that these groups were chromene groups, although it is not apparent how these (Figure 9) could be formed by exposure of carbon to oxygen at room temperature. These would account for the appearance of peroxide ions after reaction with oxygen, and also a very important property of the carbon, namely its reducing ability. Only vague suggestions of the origin of the reducing power of activated carbon are to be found in the literature at present. It is possible that phenolate groups are involved in a quinone-hydroquinone type of redox couple, or that chromene groups may be involved as suggested above. A third possibility is that the graphitic structure of the carbon may act as an 'electron sink' and that electrons are delocalized over this aromatic structure and are available for reducing purposes.

Another important property of carbon is its catalytic ability. This derives from adsorption of the reactants onto the surface, where they react more readily than when in the bulk aqueous solution. This catalytic activity of carbon is caused by a variety of factors. The process of adsorption may activate one of the reactants owing to electronic interaction with the surface, which alters the electron distribution within the molecule, or orients it correctly for reaction. Most important, in practice, is that activated carbon can act as an oxidation catalyst and, for example, can catalyze the oxidation of ferrous ion to ferric by atmospheric oxygen.

ADSORPTION AND ELUTION OF GOLD AND SILVER ON ACTIVATED CARBON

Proposed mechanism of adsorption

Activated carbon was first used as a precipitant for gold in the chlorination process as early as 1880, and for the recovery of gold from cyanide solution in the 1920's at the Yuanmi mine in Australia. In the adsorption of gold from chloride medium, where it is present as the easily reducible $AuCl_4^-$ ion, metallic gold can be usually detected (Figure 10) on the surface of the carbon particles, and so there is no difficulty in deciding on the mechanism of gold absorption from chloride medium. In a cyanide medium, no metallic gold is discernible on the carbon. Theories on the adsorption from cyanide medium can be divided into two types — those that propose that the $[Au(CN)_2]^-$ ion present in cyanide solution is adsorbed as such, and those that propose that it is altered chemically by, for example, reduction to metallic gold or precipitation as the insoluble aurocyanide, AuCN. The earliest theories were of the second type. Green[15] originally proposed reduction to metallic gold by adsorbed carbon monoxide, since heating the carbon to drive off the carbon monoxide destroyed its ability to adsorb gold. Feldtmann[16] pointed out, however, that gold adsorbed from chloride medium was readily

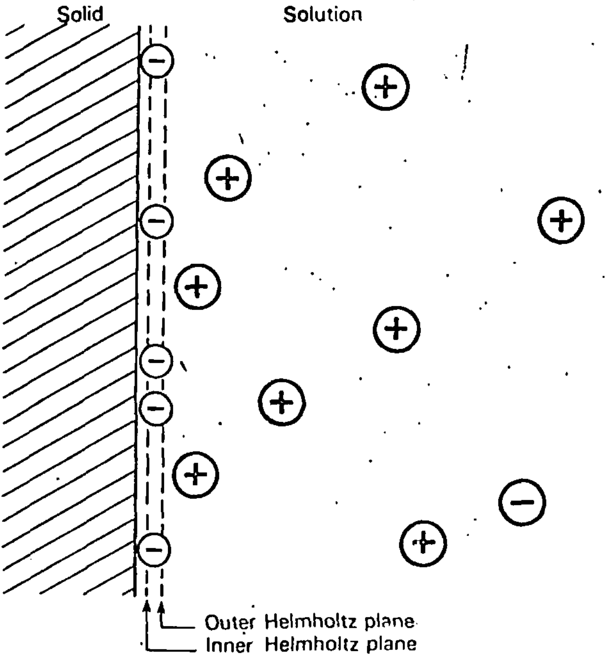


FIGURE 8. Schematic representation of the electrical double layer with specifically adsorbed anions on the surface of the solid and accompanying cations in the diffuse layer. (Adapted from Mattson and Mark[10].)

$Ca^{2+} > Mg^{2+} > H^+ > H^+ > Li^+ > Na^+ > K^+$.

Grabovskii *et al*[21], because of the reducing properties of activated carbon, proposed, on the basis of very little evidence, that the loading of gold from cyanide solutions took place via more or less complete reduction to the metal.

Dixon, Cho, and Pitt[22] proposed that the loading of both $Au(CN)_2^-$ and $Ag(CN)_2^-$ proceeded by an ion-exchange mechanism. Initially[22], it was thought that attraction to positive charges generated in accordance with the ideas of Frumkin[13] occurred. Subsequently[23] in their work on silver cyanide adsorption, it was proposed that specific adsorption into the electrical double layer occurred in accordance with the theory of ionic solvation energy developed by Anderson and Bockris[23] to account for specific adsorption of anions on metal electrodes. According to this model, the more easily dehydrated anions, which are those of largest radius and smallest charge, will be the most strongly adsorbed, since adsorption involves a loss of the hydration sheath. In agreement with this, it was found[23] that the order of strength of adsorption was $[Au(CN)_2] > [Ag(CN)_2^-] > CN^-$, which is the order of decreasing size of the anions. This ignores the fact that such large and weakly hydrated anions as perchlorate are only very weakly adsorbed by the carbon, which, as pointed out by Kuz'minykh *et al*[18], is inconsistent with the loading of the simple anionic complexes by electrostatic effects. The ability of the cyanide ion to depress the loading of $Ag(CN)_2^-$ noted by these authors[23] could just as well be explained through the formation of the more highly charged $[Ag(CN)_3]^{2-}$ anion, which is more weakly loaded.

One can summarize the position with respect to the loading of gold from cyanide solutions onto activated carbon by saying that the theories proposed to account for it fall into three categories:

- those where it is proposed that the gold is still present as the aurocyanide, held by electrostatic or van der Waals type of forces[17,18,21,22],
- those in which it is suggested that it is present as a gold compound other than the aurocyanide ion, e.g., precipitated AuCN[16,17,19], and
- those in which it is proposed that reduction to metallic gold occurs[15,22].

The reader will have gained the impression that there is much confusion and little agreement over the mechanism of gold adsorption. This has derived chiefly from the fact that activated carbon offers little scope for more direct investigations, e.g., X-ray diffraction or infrared spectroscopy, into the nature of the gold species present on the charcoal, and researchers are free to speculate on how the bewildering array of observations on factors affecting gold loading might be explained. Any future meaningful advances will only come about as the result of the successful application of more direct techniques.

PROCESSES FOR THE RECOVERY OF GOLD AND SILVER FROM CYANIDE SOLUTIONS USING ACTIVATED CARBON

Dissolution of gold by cyanidation

In the dissolution of gold by cyanidation, the milled ore is agitated with a dilute alkaline cyanide solution (either sodium or calcium cyanide with lime) in the presence of air. It has been shown[24] that the dissolution proceeds by two reactions, viz, equations [10] and [11]. The relative proportion of the gold that dissolves by either reaction is not always constant, but depends on, for example, the purity of the solution.

$$2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^- \qquad [10]$$

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \qquad [11]$$

Soon after the dissolution of gold and silver by cyanidation had been discovered[25], Johnson[26], in 1894, patented the use of activated carbon as an adsorbent for gold cyanide. In the absence of an efficient elution procedure for the gold-laden carbon, the gold was recovered by burning the carbon to ashes and smelting the gold to bullion, which was an expensive and wasteful procedure. This disadvantage, coupled with the major advances that were made in the technology of gold recovery by cementation with zinc dust at that time, led to a waning of interest in processes utilizing activated carbon for the recovery of gold.

However, in the early 1950's, interest in the metallurgical application of activated carbon was revived when Zadra[27,28] developed a procedure for the elution of gold and silver adsorbed onto carbon granules, which allowed re-use of the carbon. Since then, many other procedures that enable gold and silver to be eluted rapidly and efficiently from carbon have been developed, and these will be briefly dealt with later. Numerous processes for the recovery of gold in which activated carbon was used as an adsorbent for gold cyanide were proposed, and the technical feasibility of some of the processes was demonstrated on a pilot-plant scale. One of the most important properties of the carbon is that, unlike an anion-exchange resin, it retains its gold (and silver) selectivity in the presence of large concentrations of other metal cyanide complexes, e.g., $Cu(CN)_4^{3-}$, $Ni(CN)_4^{2-}$, and $Fe(CN)_6^{3-}$, which are sometimes encountered in pregnant cyanidation liquors. However, as discussed on pages 90-92, the mechanism of the adsorption of gold and silver cyanide on carbon, as yet, is not fully understood.

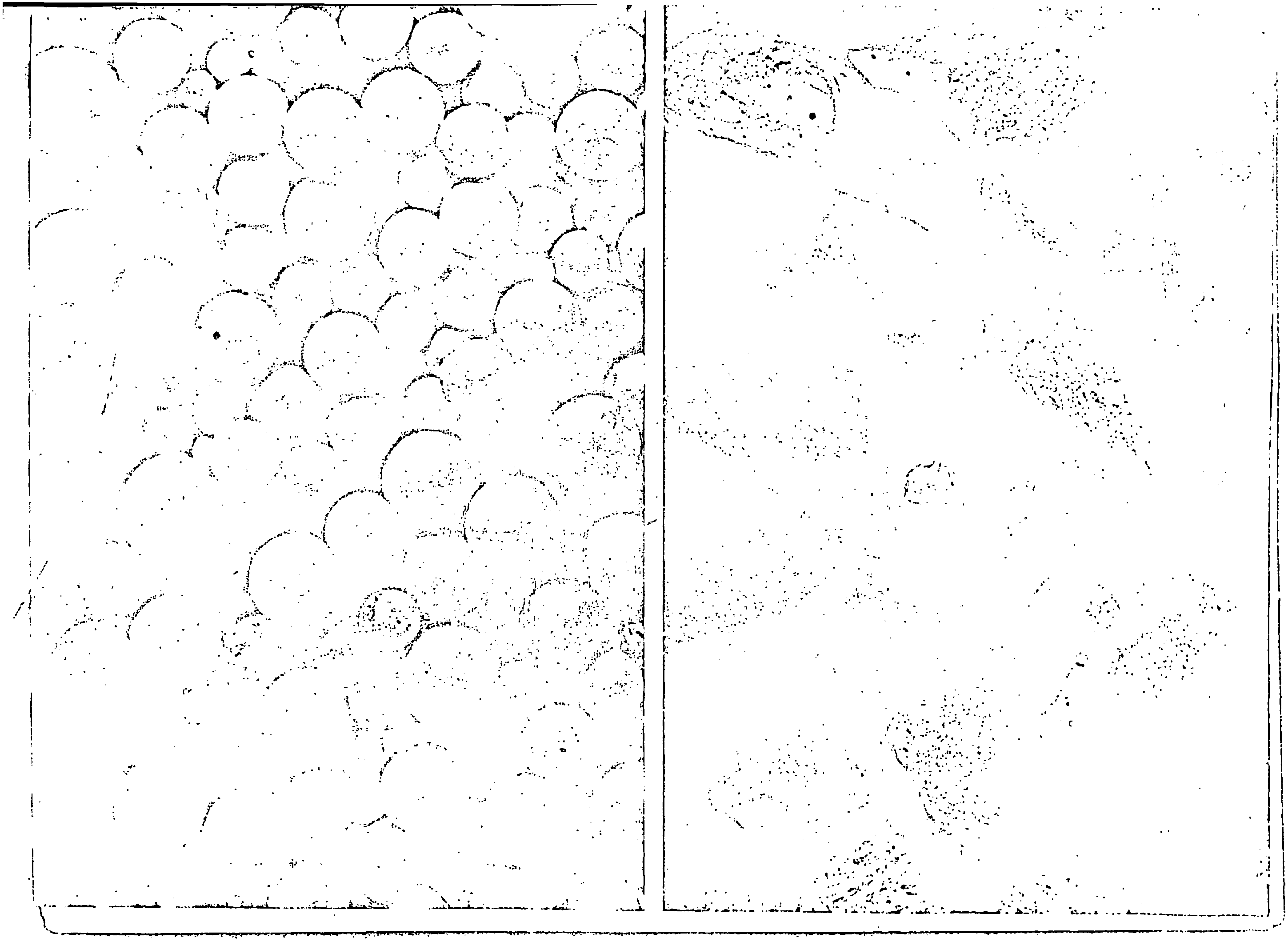
Processes for the recovery of gold and silver from cyanide solutions

Some of the more important processes that have been proposed for the recovery of gold and silver from cyanide solutions and pulps in which activated granular carbon or powder is used as the adsorbent will be outlined in this section. However, owing to the prominence that the carbon-in-pulp (C-I-P) process is enjoying in South Africa at present, a more detailed description of this process, based on the one currently being employed by the Homestake Mining Company[29,30] of South Dakota, will be given.

The carbon-in-pulp process

Zadra and coworkers[27,28] demonstrated the technical feasibility of the carbon-in-pulp process at the United States Bureau of Mines Laboratories. The process incorporated a procedure for the desorption and electrowinning of the adsorbed gold and silver values, and it was

FIGURE 10. Peach pip carbon (top) and a spherical carbon (bottom) derived from polystyrene beads coated with metallic gold after loading from auriferous chloride solutions.



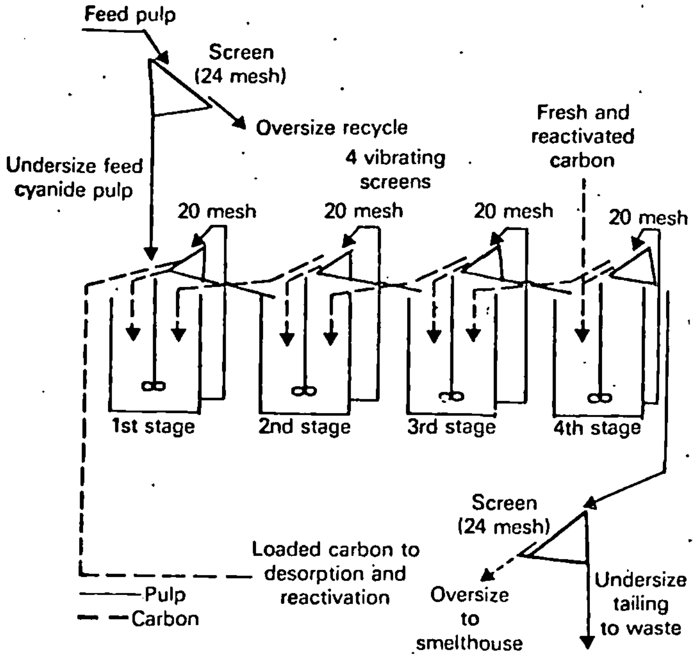


FIGURE 11. Carbon-in-pulp adsorption circuit as used at Homestake. (Adapted from Laxen et al[31].)

this technology that led to the installation of a C-I-P process by the Homestake Mining Company in 1973 when the slime-filtration plant needed to be replaced. This plant has operated successfully from its inception and has demonstrated the viability of the C-I-P process at commercial level. In recent years, the C-I-P process has generated much interest in South Africa, and the excellent results that have been obtained at pilot-plant level at various mines on the Witwatersrand, e.g., Durban Roodepoort Deep and Grootvlei, and Fairview in the Barberton area, have paved the way for the installation of large-scale fully integrated C-I-P plants[31].

In a typical C-I-P gold-recovery process, granular carbon (usually between 6 and 16 mesh) is moved countercurrent to the cyanided pulp in the adsorption contactors. Countercurrent operation is used because the amount of gold that is adsorbed on the carbon is in equilibrium with the residual gold concentration in the solution[32], and therefore low gold tailings in the final stage can be obtained only if the pulp in this stage is contacted with fresh (or reactivated) carbon. The loaded carbon is then eluted by one of the proposed processes, and the gold and silver values in the eluate are recovered by electrowinning.

An important requirement of the C-I-P process is a tough, abrasion-resistant granular carbon, which will minimize the loss of gold in the pulp residue held by fine abraded carbon, which is not recovered by screening at the end of the adsorption circuit. Suitable carbons have been manufactured from coconut shells and certain fruit pips as well as from peat and bituminous coal.

The Homestake Gold Mine

Homestake[29,30] treats about 5 000 tons of ore per day, which, after milling, is split into two fractions, viz, a sand fraction that constitutes 60 per cent of the ore, and the slimes fraction. At present, only the gold in the

cent of the total production. However, owing to the excellent performance of the C-I-P process, it was recently decided to replace the zinc-precipitation circuit used for treating the sand fraction, by a carbon process[33]. Since the filters on this side of the plant are functioning well, a fluidized-bed technique is envisaged in which the clarified liquor will be pumped upflow through columns of granular carbon. About 55 per cent of the gold production comes from the sand fraction, and the remaining 30 per cent is in the gravity concentrate. The concentration of gold in the liquor arising from cyanidation of the sand fraction is about 14 to 15 grams of gold per ton of solution, whereas the gold concentration in the cyanide slimes fraction is about 2 grams of gold per ton of solution.

Adsorption at Homestake. An average of 2 300 tons per day of the slimes fraction, which has been cyanided and from which woodchips and oversize material have been removed by screening at 710 μm, is treated by C-I-P.

Four adsorption stages are employed, and a simplified flowsheet of the adsorption circuit is shown in Figure 11[31]. The pulp is moved from one adsorption stage to the next (a contact time of between 20 and 60 minutes is usually employed) by means of airlifts that are situated on the outside of each adsorption agitator and raise the pulp and carbon granules onto 850 μm vibrating screens. The coarse granular carbon that is retained on the screen is allowed to flow back into the agitator from which it was extracted, while the fine pulp flows through the screen into the next stage. With the movement of pulp through the four stages, the concentration of gold in solution decreases from the first agitator through to the fourth, which is concomitantly accompanied by an increase in the gold content of the carbon as it moves countercurrent to the pulp from stage to stage. The loaded carbon is moved by means of eductors (i.e., water pressure that minimizes losses from carbon abrasion) from the first stage to elution, after the completion of a loading cycle that can be one day, for example. The amount of carbon moved in each cycle depends mainly on the concentration of gold in the influent solution.

To compensate for the removal of the loaded carbon from the circuit, an equivalent amount of carbon is moved up one stage, while fresh (or reactivated) carbon is introduced into the fourth stage. From a head value of about 2 grams of gold per ton of solution, a carbon loading of about 11 kilograms of gold per ton of carbon is achieved, and the tailings, which average 0,015 grams of gold per ton of solution, are discarded.

Elution at Homestake. Elution is conducted in cylindrically shaped vessels (the diameter and height of each vessel is about 116 cm) manufactured from stainless steel and insulated with fibre glass. The vessels, which have conical bottoms, can hold one ton of carbon.

The adsorbed gold and silver values are eluted by a modified Zadra[28] procedure, in which the loaded carbon, after being washed with water to remove residual pulp, is transferred to two elution vessels connected in series. The hot eluant (90 to 93 °C), which is composed of 0,2 per cent NaCN and 1 per cent NaOH, is pumped upflow through the vessels in series at a flowrate of about 1 bed volume per hour. As the eluant containing the desorbed gold and silver values emerges from the barren eluant from the electrowinning stage, after being reheated to 90°C in a heat-exchange unit, is then recycled to the first elution vessel. The eluant has to be fortified regularly by the addition of NaOH and NaCN to maintain the desired concentration of these chemicals.

The gold concentrations in the pregnant and barren eluants are monitored regularly, and it has been found that these values are a good indication of the extent of elution. Generally it has been found that at an eluant flowrate of 1 bed volume per hour, 50 hours are required to elute a carbon with a gold loading of 9,6 kilograms of gold per ton of carbon to less than 160 grams per ton.

Electrowinning at Homestake. The pregnant eluant from the elution circuit is pumped to the electrowinning circuit, which is composed of three electrowinning cells coupled in series. The electrowinning cells, which are of the Zadra type[28], are manufactured from fibre glass and contain anodes of stainless steel and cathodes of steel wool (the strands of the steel wool providing a large surface area for the deposition of gold and silver), the latter being contained in a pervious polypropylene basket. Each week, the cathode in the basket is moved to the adjacent cell, so that each cathode spends 3 weeks in the circuit. After 3 weeks, the cathode in the last cell, which then contains about 30 kg of gold and 6 kg of silver, is removed from the circuit, the gold and silver are smelted to bullion, and a new cathode is placed in the first cell.

Reactivation at Homestake. When the gold content of the carbon goes below 160 grams of gold per ton of carbon, the eluant is drained from the elution vessels and the carbon is given a hot-water wash followed by a cold-water wash to remove any adhering solution. It has been found that the carbon, in addition to adsorbing gold and silver, also adsorbs organic molecules and small quantities of iron sulphide compounds and calcium carbonate, hydroxide, and cyanide, and, since these contaminants are apparently not removed in the desorption cycle, they poison the carbon, which is obvious from the resultant loss of gold activity. Nevertheless, the original activity of the carbon can be restored by suitable reactivation.

At Homestake, reactivation is accomplished by heating of the carbon granules in an externally heated rotary kiln at 600 to 650°C for 30 minutes in the absence of air. After heating, the carbon is allowed to cool in the air, because it has been found that carbon granules become brittle when cooled by quenching in water. After cooling, the carbon granules are wet-screened and the fines are removed. The coarse carbon granules are then ready to be recycled to the adsorption circuit.

In South Africa, difficulties have been experienced on pilot plants owing to the precipitation of calcium carbonate onto the carbon granules[34]. No such problems have been encountered at Homestake, so acid washing to remove the calcium carbonate is not necessary. However, a water-softening reagent, viz, Barochem S35, is added to the cyanided pulp prior to gold adsorption[35].

Advantages of C-I-P over zinc precipitation

The C-I-P process for the recovery of gold has several advantages over the conventional zinc-precipitation process.

It is well known that the cementation reaction is sensitive not only to alkalinity and free cyanide but also to other common constituents of cyanidation liquors, e.g., sulphide salts and the cyanide complexes of copper, nickel, arsenic, and antimony, all of which have the effect of decreasing the gold recoveries. On the other hand, activated carbon retains its excellent ability to scavenge gold and silver even in the presence of large concentrations of the cyanide complexes of the nickel, copper, and iron sometimes encountered in certain South African ores. In the C-I-P process, the activated-carbon granules are added direct to the cyanided pulp, which obviates the expensive filtration and clarification stages that are required for zinc precipitation. Clarification is necessary to eliminate suspended constituents that can coat the zinc particles and retard precipitation of the precious metals. Elimination of dissolved oxygen from the pregnant solution is also essential to prevent the redissolution of the gold. Furthermore, the soluble-gold losses on a conventional plant generally are significantly higher than those encountered in a C-I-P process.

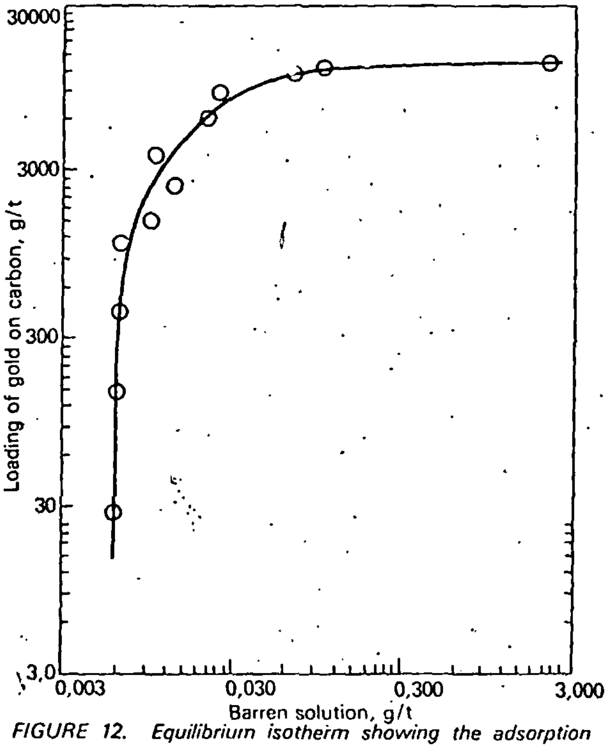


FIGURE 12. Equilibrium isotherm showing the adsorption of gold onto granular activated carbon. (Adapted from Gilmore[32].)

Therefore, it is generally believed that C-I-P offers certain economical advantages over zinc precipitation not only in higher gold recoveries, but also in lower capital and operating costs.

Other applications in gold recovery

In a preliminary laboratory investigation, Gilmore[32] demonstrated the feasibility of using activated carbon for the recovery of small concentrations of soluble gold from flotation-plant waste effluents emanating from base-metal mills. In these plants, sodium cyanide is used as a flotation depressant, and it was shown that carbon was capable of concentrating large amounts of gold from very dilute solutions, and that the gold concentration of the barren solution was in equilibrium with the gold content of the carbon (Figure 12). Thus, in a single-

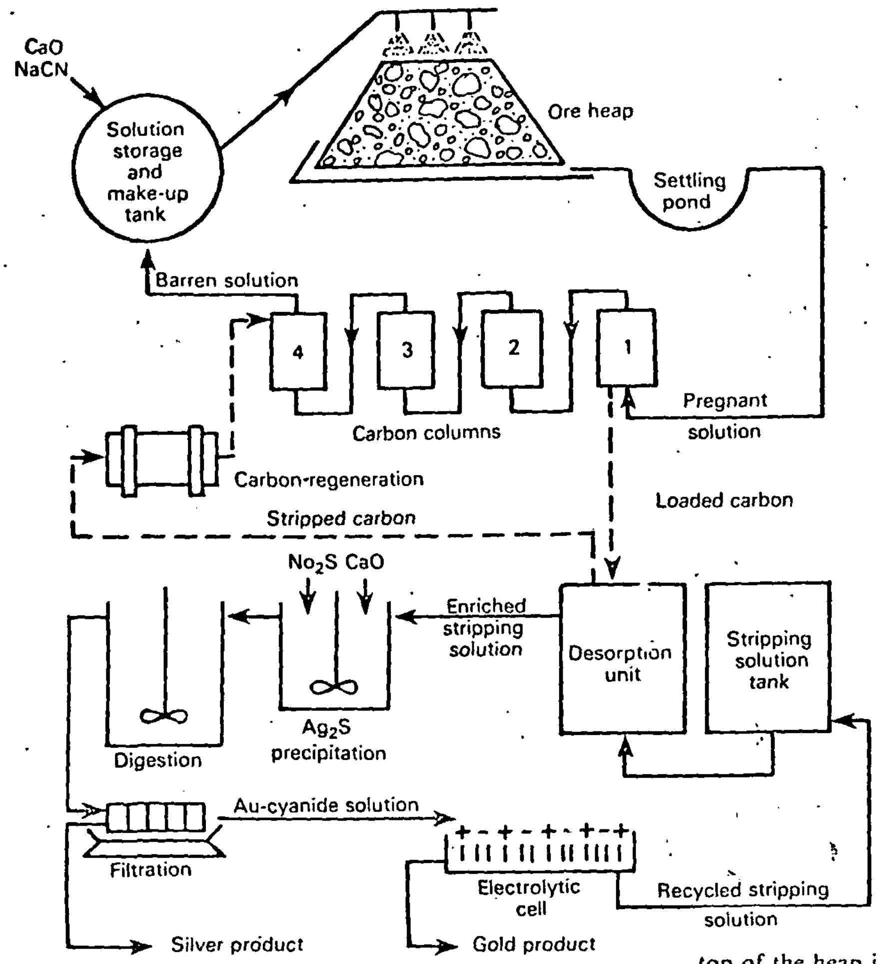


FIGURE 13. Circuit for the heap-leach adsorption of gold onto carbon. (Adapted from Heinen et al[37].)

stage contact of carbon and gold-bearing solution, a barren solution of 0,01 gram of gold per ton of solution was found to be in equilibrium with a gold loading of about 3 kg of gold per ton of carbon.

The excellent scavenging ability of activated carbon for small amounts of dissolved gold in gold-plant effluent streams was demonstrated at pilot-plant level by Nicol[36]. The tests were conducted in an upflow fluidized-bed contactor based on the continuous-ion-exchange (NIMCIX) contactor developed at the National Institute for Metallurgy. Granular coconut-shell carbon, in the size range 1,2 to 2,4 mm in diameter, was used in the tests, and, from a head solution containing about 0,2 gram of dissolved gold per ton of solution, a barren solution containing 0,01 gram of gold per ton could be obtained, provided the carbon in the column was treated with hydrochloric acid at least once a week to remove calcium carbonate that was precipitated onto the carbon granules.

Cyanide heap leaching[37,38] is a comparatively recent hydrometallurgical development for exploiting low-grade gold ores, mine-waste material, or deposits too small to justify the construction of milling facilities, and processes that utilize activated carbon for the recovery of gold have become economically viable owing to the high gold price. Basically, two methods of heap-leach cyanidation are used commercially, viz, short-term leaching of a crushed ore and long-term leaching of run-of-mine material. In the short-term process, the ore is crushed small and stacked on watertight pads, and the top of the heap is sprinkled with a dilute cyanide solution. The cyanide solution percolates through the heap and dissolves the gold and silver values. The leach liquor is subsequently collected on the watertight pad, which is shaped to permit the pregnant solution to flow into storage tanks. On the other hand, long-term leaching is used primarily to extract gold and silver from uncrushed, porous, sub-mill-grade material from open-pit operations[37]. In the absence of mill facilities with a zinc-precipitation circuit, or if the concentration of gold in solution is below a nominal 1,5 grams of gold per ton of solution, adsorption onto activated carbon is the preferred method for recovering the precious metal values.

In a typical carbon-adsorption operation, the pregnant solution is pumped upflow through three to five columns in series, which contain granular coconut-shell carbon, at a velocity sufficient to maintain the bed of carbon in a fluidized state. However, the gold-bearing cyanide solution can also be percolated downward through a fixed bed of activated carbon. The choice of loading technique depends on the amount of undissolved solids in the heap-leach liquor. The most economic method for recovering the precious-metal values from the loaded carbon is by elution and electrowinning, which allows the carbon to be re used. However, many small companies dispatch the loaded carbon to smelters, where the carbon is burnt to recover the gold and silver.

The application of this technology to the treatment of gold ores rich in silver has been found to greatly increase the amount of activated carbon required to effect a high-silver recovery, owing to the fact that the adsorptive capacity of carbon for silver is substantially less than for gold. This problem has been overcome by the development of a processing sequence that consists of recovering the silver selectively, as insoluble silver sulphide (Ag_2S), with sodium sulphide as the precipitant, and, after filtration, recovering the gold from the filtrate with activated carbon. Figure 13 shows the flowsheet proposed by Heinen and coworkers[37] for the heap-leach carbon-adsorption process.

Hussey and coworkers[39] have conducted pilot-plant tests on a C-I-P process for the adsorption of silver from cyanided pulps of a silver ore, and have obtained encouraging results. From a pregnant solution containing an average of 50 grams of silver per ton of solution, a barren solution between 0,60 and 0,40 g/t was obtained. It was also illustrated how data on the rate of silver adsorption as well as equilibrium adsorption curves can be helpful in process design.

As mentioned previously, one of the problems associated with the use of activated carbon for the adsorption of gold and silver from cyanided pulps or clarified solutions originating from Witwatersrand ore bodies is the precipitation of calcium carbonate onto the carbon. It has also been reported[34] that gold cyanide displaces the adsorbed silver. Davidson and coworkers[34] investigated the possibility of overcoming these problems by acidification of plant pregnant solutions prior to the carbon-adsorption stage. Excellent gold and silver adsorption characteristics were obtained at an influent pH value of 5, and no calcium carbonate fouling of the carbon was observed. In the light of this work, it was suggested that significant improvements could be made in the use of activated carbon for the recovery of gold and silver by acidification of cyanided liquors that contain low concentrations of copper.

Testwork at plant scale was recently conducted[31] by the addition of powdered carbon to a repulped cyanidation residue for recovery of dissolved gold values, prior to the recovery of pyrite by flotation. In such a process, the carbon powder is separated from the pulp by flotation, and the gold is recovered by burning the carbon to ashes. The recovery of about 90 per cent of the gold from a head value of 0,16 gram of gold per ton of solution has been reported. A similar process was patented by Chapman[40] in 1939.

Review of elution procedures

Gross and Scott[17] investigated the eluant power of a wide range of inorganic compounds for gold cyanide adsorbed onto carbon. Potassium cyanide and sodium sulphide showed the highest solvent power for the adsorbed gold. This was pursued more recently by Zadra[28] who found that a gold-loaded carbon containing a negligible silver loading could be eluted efficiently with a hot (93 °C) alkaline solution of sodium sulphide. This elution technique is not applicable to carbons carrying silver, since insoluble silver sulphide (Ag_2S) is precipitated in the pores of the carbon and so is retained. However, in the modified Zadra[28] procedure (which was the first practical elution procedure to be developed and is currently being used at Homestake), which utilizes a hot (90 to 93 °C) alkaline cyanide solution (1,0 per cent NaOH + 0,1 per cent NaCN) at atmospheric pressure as the eluant, both gold and silver can be eluted efficiently. In the circuit that was originally proposed, the eluant is pumped upflow through the bed of loaded carbon, and the eluant containing the desorbed gold and silver is then fed to a circular electrowinning cell fitted with a stainless-steel anode and a pervious cathode containing steel wool. As the electrowinning cell and the elution unit form a closed circuit, the eluted gold and silver values are removed from the eluant by electrodeposition as rapidly as they are desorbed from the carbon, and the barren eluant is recycled to the elution circuit. Thus, continuous elution is achieved with the minimum volume of eluant, thereby reducing reagent consumption. The gold and silver values are finally recovered by smelting the wool to bullion. Tests have indicated that 4 litres of solution per kilogram of carbon is sufficient for continuous operation.

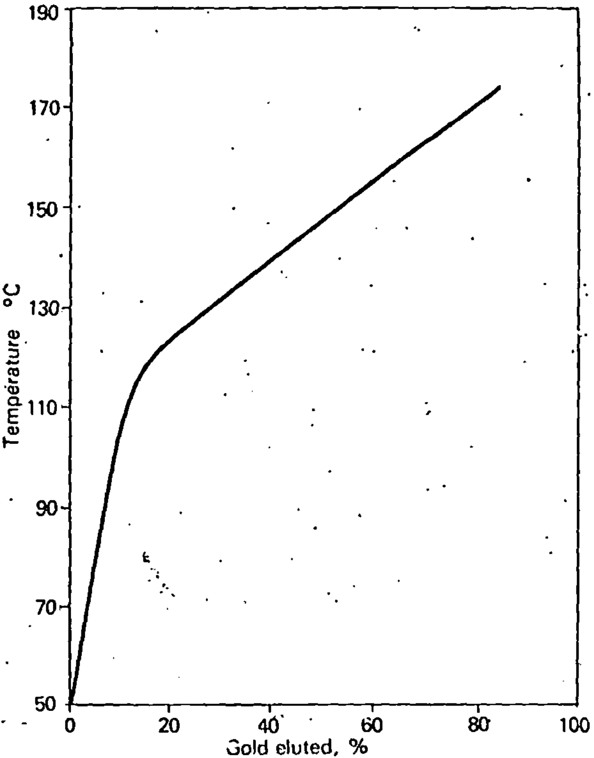


FIGURE 14. Influence of temperature on the elution of gold from activated carbon. (Adapted from Ross et al[42].)

Zadra[28] also reported the efficient elution of gold and silver by a column technique, after preconditioning of the loaded carbon for 30 minutes with a solution composed of 1 per cent NaOH + 0,1 per cent NaCN at 93 °C, followed by draining and elution of the gold and silver values with boiling water. A similar elution technique was developed by Davidson[41] at the Anglo American Research Laboratories. This elution procedure is usually preceded by treatment of the loaded carbon with hydrochloric acid to remove calcium carbonate and nickel cyanide from the carbon.

However, on implementing the modified Zadra elution procedure at the Carlton Mill, Cripple Creek, Colorado, Ross and coworkers[42] found that, contrary to the laboratory elution results of Zadra, from 24 to 48 hours instead of the claimed 6 hours was required in practice to strip a carbon containing between 200 and 400 kilograms of gold per ton down to about 10 kg/t. This prompted them to investigate elution techniques that would strip the gold more rapidly, and led to the development of a pressure method for stripping the gold

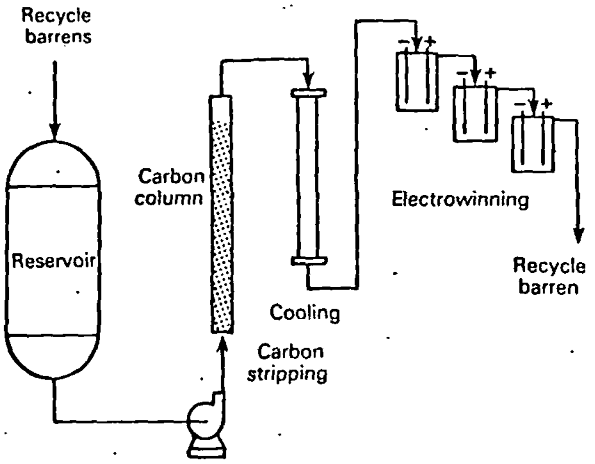


FIGURE 15. Elution circuit for the simultaneous desorption and electrowinning of gold. (Adapted from Heinen et al[37]*.)*

from activated carbon by simultaneous elution and electrolysis in a cyclic process.

It was found that the elution of gold in a pressurized column at high temperatures resulted in a marked improvement in the rate of gold elution compared with that observed at atmospheric pressure. This is apparent from the data in Figure 14, which shows the results of equilibrium elution tests conducted by the mixing of one volume of carbon with five volumes of eluant (composed by 1 per cent NaOH + 0,1 per cent NaCN) at various temperatures up to the boiling point of the eluant at atmospheric pressure, as well as those obtained in a pressurized (360 kPa) elution column at temperatures between 100 and 180°C. The results indicate that, whereas only 8 per cent of the adsorbed gold would be eluted from the carbon at 90°C, more than 90 per cent would be eluted at 180°C, i.e., the rate of elution is about 12 times greater at 180°C. The effect of the composition of the eluant on elution was also investigated, and it was shown that gold could be eluted efficiently with tap water at 150°C, after preconditioning of the loaded carbon with one column volume of 1 per cent NaOH + 0,1 per cent NaCN for 30 minutes. Subsequently, Davidson and coworkers[41] also reported accelerated elution rates with pressure elution.

Nizamutdinova and Chuvasheva[43] reported excellent elution of gold from carbon with anhydrous ammonia under a pressure of about 600 to 1 000 kPa.

Heinen and coworkers[44] found that modification of the alkaline cyanide eluant (1 per cent NaOH + 0,1 per cent NaCN) by the addition of, for example, 20 per cent (by volume) of a water-soluble alcohol (e.g., ethanol or methanol) results in a dramatic improvement in the efficiency of desorption of the gold, so that 99 per cent of the precious-metal values can be eluted in about 6 hours at a temperature of 80°C, as compared with 50 hours without an alcohol additive. Figure 15 shows the proposed[44] elution circuit, which utilizes the Zadra[28] concept of simultaneous elution and electrowinning.

Sodium sulphide was also shown to be effective for selectively precipitating silver from the pregnant eluant, thereby providing a means of producing high-purity gold by subsequent electrolysis.

From this brief review it is apparent that, although efficient elution can be achieved at atmospheric pressure with a hot (90 to 93°C) alkaline cyanide eluant, or after pretreatment of the loaded carbon with a hot alkaline cyanide eluant, followed by elution of the gold and silver values with hot water, the rate of desorption of the precious-metal values can be accelerated markedly on modification of the alkaline cyanide eluant by the addition of a water-soluble alcohol or by conducting the elution at elevated temperature and pressure.

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TMS AIME ANNUAL MEETING

CHICAGO, ILLINOIS, USA
22ND TO 26TH FEBRUARY, 1981

The Committee on 'Process Mineralogy' of the Mineralogical Society invites the submission of abstracts, not to exceed 200 words, of proposed papers for presentation at the 1981 Annual TMS-AIME Meeting in Chicago, Illinois, February 22nd to 26th, 1981.

Topics for sessions on 'Process Mineralogy' should include the applications of mineralogy and petrography to problems in exploration, sampling, mining, and processing of ores, involving the benefication, hydro- and pyrometallurgy of base and precious metals, as well as other metallic and non-metallic ores, including coal and oil shale.

Further information may be obtained from

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Explosives, Annual

APPARENT CONSUMPTION OF INDUSTRIAL EXPLOSIVES AND BLASTING AGENTS IN THE UNITED STATES, 1980

Apparent consumption of explosives and blasting agents in the United States increased 11% to 4.6 billion pounds, according to the Bureau of Mines, U.S. Department of the Interior. Apparent consumption is measured by sales reported by manufacturers.

Ammonium nitrate fuel-mixed blasting agents showed the most significant change in consumption of all classes of explosives and blasting agents in 1980, an increase of 24% over the amount used in 1979.

All principal consuming industries except the coal mining industry used less quantities of explosives and blasting agents in 1980 than in 1979. Over 56% of the total weight was utilized in the mining of coal. Nearly all permissibles and 61% of ammonium nitrate fuel-mixed blasting agents and unprocessed ammonium nitrate were consumed in coal mining. Other high explosives were used primarily in quarrying and nonmetal mining (29%) and construction (26%). The majority of water gels and slurries went into metal mining (41%).

Seven States collectively consumed 60% of all explosives and blasting agents used in the United States in 1980. These were, in order of consumption, Kentucky, Alabama, Pennsylvania, West Virginia, Ohio, Arizona, and Indiana.

Prepared in the Section of Nonmetallic Minerals, July 2, 1981.

Classification of Industrial Explosives and Blasting Agents

"Apparent consumption" of explosives and blasting agents, as used in this report, means sales reported to the Institute of Makers of Explosives (IME) by IME members and provided to the Bureau of Mines on a proprietary basis, plus sales by nonmember manufacturers reported directly to the Bureau on Form 6-1439-A. Classification of explosives and blasting agents by type and use appears as reported by the manufacturers. Sales of explosives and blasting agents imported by nonmanufacturers are not included, but may be locally important. Some quantities are published in such a way as to avoid disclosing company proprietary data.

The principal distinction between explosives and blasting agents is related to their sensitivity to initiation--explosives are cap-sensitive but blasting agents are not, and therefore require a primer. Only "high" explosives are currently reported. "Low" explosives, which burn very rapidly but do not detonate, include principally black powder and propellants. Black powder has not been reported in industrial use since 1971. Both explosives and blasting agents vary widely in composition, although most blasting agents are essentially mixtures of ammonium nitrate plus a fuel.

Water gels and slurries may be either explosives or blasting agents, but for convenience are classified separately in a recognizable category.

The five product classifications used in this report are the same as those adopted by IME. These are:

1. Permissibles.--Grades of high explosives approved by brand name by the U.S. Bureau of Mines or the Mine Safety and Health Administration for use, in a prescribed manner, in underground coal mines, including water gels and slurries approved as permissibles.

2. Other High Explosives.--All high explosives except

   a) permissibles and

   b) any water gels or slurries that would otherwise be classified as high explosives.

Included in the "Other High Explosives" classification are all formulations packaged in metal containers.

3. Packaged and Bulk Water Gels and Slurries.--All water gels and slurries, packaged or in bulk, made by addition of more than 5% water to high explosives or blasting agents, except those approved as permissibles.

4. Ammonium Nitrate Fuel-Mixed Blasting Agents.--Without regard to packaging or container.

5. Unprocessed Ammonium Nitrate.--Prilled or grained ammonium nitrate for use in blasting agents.

Companies covered by this report, including IME members, are:

American Cyanamid Company--Wayne, New Jersey
Apache Powder Company--Benson, Arizona
Atlas Powder Company--Dallas, Texas
Austin Powder Company--Cleveland, Ohio
C-I-L Inc.--Quebec, Canada
Columbia Nitrogen Corp.--Augusta, Georgia
E. I. du Pont de Nemours & Co., Inc.--Wilmington, Delaware
Energy Sciences & Consultants, Inc.--Biwabik, Minnesota
Goex Inc.--Cleburne, Texas
W.R. Grace & Co. ACG--Memphis, Tennessee
Gulf Oil Chemicals Company--Merriam, Kansas
Hawkeye Chemical Company--Clinton, Iowa
Hercules, Inc.--Wilmington, Delaware
Independent Explosives Company of Pennsylvania--Scranton, Pennsylvania
Ireco Chemicals--Salt Lake City, Utah
Kaiser Aluminum & Chemical Corp.--Savannah, Georgia
Monsanto Co.--St. Louis, Missouri
Phillips Chemical Co.--Bartlesville, Oklahoma
Sierra Chemical Company--Reno, Nevada
Southern Explosives Corporation--Glasgow, Kentucky
Trojan Division, IMC Chemical Group, Inc.--Allentown, Pennsylvania
Union Oil Company of California--Los Angeles, California
USS Agri-Chemicals--Atlanta, Georgia

TABLE 1. - Salient statistics of industrial explosives and blasting agents sold for consumption in the United States, 1979-80
(Thousand pounds)

Class	1979	1980
Permissibles	1/47,307	55,461
Other high explosives	1/182,319	175,910
Water gels and slurries	460,913	420,299
Ammonium nitrate fuel-mixed blasting agents	r/1,331,313	1,652,258
Unprocessed ammonium nitrate	r/2/2,068,606	2,248,243
Total	r/4,090,458	4,552,171

r/ Revised.

1/ Some quantities of this class of explosive are included with "Unprocessed ammonium nitrate" to avoid disclosing company proprietary data.

2/ Includes some quantities of permissible explosives and other high explosives.

TABLE 2. - Industrial explosives and blasting agents sold for consumption in the United States by class and use, 1979-80
(Thousand pounds)

Class	Coal mining 1/		Metal mining 1/		Quarrying and nonmetal mining 1/		Construction work 1/		All other purposes 2/		Total	
	1979	1980	1979	1980	1979	1980	1979	1980	1979	1980	1979	1980
Permissibles 3/--	44,891	52,476	281	81	615	716	1,294	973	226	1,215	47,307	55,461
Other high explosives 3/--	25,783	24,912	23,699	25,085	60,734	50,138	52,924	46,185	19,179	29,590	182,319	175,910
Water gels and slurries-------	74,739	94,618	238,738	170,652	107,280	95,196	38,284	35,672	1,872	24,161	460,913	420,299
Ammonium nitrate fuel-mixed blasting agents	r/889,368	1,126,850	65,394	65,637	221,460	187,434	151,669	110,611	3,422	161,726	r/1,331,313	1,652,258
Unprocessed ammonium nitrate 4/-----	r/1,202,612	1,260,286	r/284,708	291,489	r/262,944	242,602	229,951	218,597	r/88,391	235,269	r/2,068,606	2,248,243
Total-------	r/2,237,393	2,559,142	r/612,820	552,944	r/653,033	576,086	474,122	412,038	r/113,090	451,961	r/4,090,458	4,552,171

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r/ Revised.
1/ Some quantities of this use are included with "All other purposes" to avoid disclosing company proprietary data.
2/ Includes some quantities from coal mining, metal mining, quarrying and nonmetal mining, and construction work.
3/ Some quantities of this class of explosive are included with "Unprocessed ammonium nitrate" to avoid disclosing company proprietary data for 1979.
4/ Includes some quantities of permissible explosives and other high explosives for 1979.

TABLE 3. - Industrial explosives and blasting agents sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

State	Use					
	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama	485,646	50	8,277	109,640	60,434	664,047
Alaska	975	2,432	42	7,020	146	10,615
Arizona	29,128	178,010	3,362	2,140	2,000	214,640
Arkansas	3,529	911	6,441	2,290	7,605	20,776
California	1,880	16,525	10,373	7,208	1,662	37,648
Colorado	59,949	23,131	2,327	757	3,581	89,745
Connecticut	---	---	9,938	4,838	361	15,137
Delaware	---	---	193	1,437	165	1,795
District of Columbia 1/	---	---	---	---	---	---
Florida	---	---	28,346	12,758	2,566	43,670
Georgia	162	---	16,174	3,380	6,272	25,988
Hawaii	---	---	312	8	---	320
Idaho	1,375	13,835	11,019	3,139	128	29,496
Illinois	95,268	3	37,375	3,549	6,617	142,812
Indiana	176,971	252	21,971	5,748	3,995	208,937
Iowa	2,536	---	19,282	1,844	7,563	31,225
Kansas	7,200	---	6,264	2,184	10,396	26,044
Kentucky	574,663	6	56,048	27,887	90,580	749,184
Louisiana	8	---	3,242	97	2,596	5,943
Maine	---	---	820	273	5	1,098
Maryland	7,166	---	10,506	3,555	377	21,604
Massachusetts	322	---	3,669	1,653	256	5,900
Michigan	3,251	28,608	25,323	5,386	2,013	64,581
Minnesota	1,660	116,012	4,304	528	3,323	125,827
Mississippi	---	---	443	60	2,145	2,648
Missouri	15,544	5,224	27,884	10,835	6,971	66,458
Montana	38,948	24,635	1,582	1,160	8,623	74,948
Nebraska	3	---	1,756	769	28	2,556
Nevada	---	20,803	1,881	122	389	23,195
New Hampshire	---	---	738	894	62	1,694
New Jersey	---	17	2,894	654	85	3,650
New Mexico	15,115	45,046	5,504	1,105	25,178	91,948
New York	321	392	8,150	5,090	1,913	15,866
North Carolina	3,716	---	18,133	19,086	763	41,698
North Dakota	334	---	---	4	2,176	2,514
Ohio	128,283	488	64,424	9,825	20,994	224,014
Oklahoma	36,126	2,213	7,768	2,294	12,488	60,889
Oregon	83	---	2,758	9,374	604	12,819
Pennsylvania	351,955	1	52,249	14,599	25,634	444,438
Rhode Island	---	---	390	159	---	549
South Carolina	---	---	3,686	2,928	205	6,819
South Dakota	8	542	484	---	3	1,037
Tennessee	50,617	4,830	26,189	30,836	7,191	119,663
Texas	256	2,465	25,942	39,155	9,873	77,691
Utah	1,529	47,418	4,466	1,233	1,889	56,535
Vermont	37	---	851	786	1	1,675
Virginia	109,700	10	13,412	20,087	13,463	156,672
Washington	5,600	5,417	1,560	7,874	692	21,143
West Virginia	210,099	---	4,071	19,248	5,621	239,039
Wisconsin	---	2,464	5,817	6,075	1,463	15,819
Wyoming	139,179	11,204	7,446	467	27,561	185,857
Undistributed	2/	2/	2/	2/	63,305	63,305
Total	2,559,142	552,944	576,086	412,038	451,961	4,552,171

1/ Included with Maryland.

2/ Quantities included with "All other purposes" to avoid disclosing company proprietary data.

TABLE 4. - Industrial explosives and blasting agents sold for consumption in the United States, by State and class, 1980
(Thousand pounds)

	Class					
	Fixed high explosives			Blasting agents		
State	Permissibles	Other high explosives	Water gels and slurries	Ammonium nitrate fuel-mixed blasting agents	Unprocessed ammonium nitrate	Total
Alabama	3,355	2,891	18,443	382,463	256,895	664,047
Alaska	---	2,063	5,031	116	3,405	10,615
Arizona	---	2,420	44,092	12,921	155,207	214,640
Arkansas	---	1,306	2,420	6,678	10,372	20,776
California	---	3,306	6,663	3,842	23,837	37,648
Colorado	331	5,671	22,209	22,296	39,238	89,745
Connecticut	---	1,783	4,306	3,017	6,031	15,137
Delaware	---	2	52	1,741	---	1,795
District of Columbia 1/	---	---	---	---	---	---
Florida	---	11,637	17,585	9,585	4,863	43,670
Georgia	---	2,811	6,650	16,302	225	25,988
Hawaii	---	---	320	---	---	320
Idaho	---	1,746	1,270	708	25,772	29,496
Illinois	536	7,414	7,721	85,969	41,172	142,812
Indiana	408	2,308	7,990	149,659	48,572	208,937
Iowa	143	2,616	5,595	1,558	21,313	31,225
Kansas	4	473	2,191	20,486	2,890	26,044
Kentucky	27,260	9,749	10,378	287,551	414,246	749,184
Louisiana	8	2,666	475	2,794	---	5,943
Maine	---	313	262	523	---	1,098
Maryland	22	3,075	4,101	13,605	801	21,604
Massachusetts	---	2,182	364	2,781	573	5,900
Michigan	10	1,294	20,493	14,287	28,497	64,581
Minnesota	---	517	71,813	38,310	15,187	125,827
Mississippi	---	2,141	450	57	---	2,648
Missouri	12	7,803	5,188	14,740	38,715	66,458
Montana	---	8,135	1,417	1,091	64,305	74,948
Nebraska	1	348	495	1,712	---	2,556
Nevada	---	619	376	6,436	15,764	23,195
New Hampshire	---	1,080	68	478	68	1,694
New Jersey	---	1,350	566	1,690	44	3,650
New Mexico	22	5,762	15,039	30,068	41,057	91,948
New York	7	2,304	2,082	6,320	5,153	15,866
North Carolina	---	2,980	8,811	17,560	12,347	41,698
North Dakota	---	2,177	---	9	328	2,514
Ohio	949	4,953	7,203	75,703	135,206	224,014
Oklahoma	---	3,762	2,932	50,993	3,202	60,889
Oregon	---	3,607	1,258	3,687	4,267	12,819
Pennsylvania	1,349	15,735	41,044	62,919	323,391	444,438
Rhode Island	---	182	---	367	---	549
South Carolina	---	1,124	2,453	3,242	---	6,819
South Dakota	---	9	1,028	---	---	1,037
Tennessee	1,152	7,595	3,856	41,458	65,602	119,663
Texas	---	8,986	4,024	23,462	41,219	77,691
Utah	178	5,078	10,069	937	40,273	56,535
Vermont	1	428	607	639	---	1,675
Virginia	12,123	6,950	9,420	63,064	65,115	156,672
Washington	313	3,387	2,611	335	14,497	21,143
West Virginia	7,093	5,818	3,315	92,867	129,946	239,039
Wisconsin	6	1,356	6,663	6,852	942	15,819
Wyoming	178	3,998	28,900	68,380	84,401	185,857
Undistributed	---	---	---	---	2/63,305	2/63,305
Total	55,461	175,910	420,299	1,652,258	2,248,243	4,552,171

1/ Included with Maryland.
2/ Quantities undistributed to avoid disclosing company proprietary data.

TABLE 5. - Permissible explosives sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

	Use					
State	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama	3,076	---	128	151	---	3,355
Alaska	---	---	---	---	---	---
Arizona	---	---	---	---	---	---
Arkansas	---	---	---	---	---	---
California	---	---	---	---	---	---
Colorado	331	---	---	---	---	331
Connecticut	---	---	---	---	---	---
Delaware	---	---	---	---	---	---
District of Columbia 1/	---	---	---	---	---	---
Florida	---	---	---	---	---	---
Georgia	---	---	---	---	---	---
Hawaii	---	---	---	---	---	---
Idaho	---	---	---	---	---	---
Illinois	457	---	79	---	---	536
Indiana	397	---	11	---	---	408
Iowa	136	---	7	---	---	143
Kansas	---	---	---	4	---	4
Kentucky	26,419	---	36	---	805	27,260
Louisiana	8	---	---	---	---	8
Maine	---	---	---	---	---	---
Maryland	22	---	---	---	---	22
Massachusetts	---	---	---	---	---	---
Michigan	---	---	10	---	---	10
Minnesota	---	---	---	---	---	---
Mississippi	---	---	---	---	---	---
Missouri	1	---	11	---	---	12
Montana	---	---	---	---	---	---
Nebraska	---	---	---	1	---	1
Nevada	---	---	---	---	---	---
New Hampshire	---	---	---	---	---	---
New Jersey	---	---	---	---	---	---
New Mexico	2	---	---	20	---	22
New York	---	---	---	7	---	7
North Carolina	---	---	---	---	---	---
North Dakota	---	---	---	---	---	---
Ohio	665	---	279	5	---	949
Oklahoma	---	---	---	---	---	---
Oregon	---	---	---	---	---	---
Pennsylvania	1,148	---	85	108	8	1,349
Rhode Island	---	---	---	---	---	---
South Carolina	---	---	---	---	---	---
South Dakota	---	---	---	---	---	---
Tennessee	417	---	70	665	---	1,152
Texas	---	---	---	---	---	---
Utah	95	71	---	1	11	178
Vermont	---	---	---	---	1	1
Virginia	12,043	10	---	---	70	12,123
Washington	313	---	---	---	---	313
West Virginia	6,874	---	---	5	214	7,093
Wisconsin	---	---	---	6	---	6
Wyoming	72	---	---	---	106	178
Total	52,476	81	716	973	1,215	55,461

1/ Included with Maryland.

TABLE 6. - Other high explosives sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

State	Use					
	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama	445	---	332	1,045	1,069	2,891
Alaska	---	---	---	1,955	108	2,063
Arizona	---	1,745	221	250	204	2,420
Arkansas	11	6	547	643	99	1,306
California	30	217	472	2,298	289	3,306
Colorado	435	4,902	10	93	231	5,671
Connecticut	---	---	1,118	665	---	1,783
Delaware	---	---	---	---	2	2
District of Columbia 1/	---	---	---	---	---	---
Florida	---	---	4,604	7,033	---	11,637
Georgia	100	---	1,907	789	15	2,811
Hawaii	---	---	---	---	---	---
Idaho	---	791	1	954	---	1,746
Illinois	929	---	5,737	748	---	7,414
Indiana	568	252	1,309	179	---	2,308
Iowa	5	---	2,269	262	80	2,616
Kansas	---	---	98	72	303	473
Kentucky	6,121	---	1,989	815	824	9,749
Louisiana	---	---	209	4	2,453	2,666
Maine	---	---	147	166	---	313
Maryland	119	---	1,740	1,206	10	3,075
Massachusetts	---	---	1,265	764	153	2,182
Michigan	---	372	802	29	91	1,294
Minnesota	10	152	87	268	---	517
Mississippi	---	---	116	59	1,966	2,141
Missouri	359	3,805	2,571	1,068	---	7,803
Montana	476	922	---	776	5,961	8,135
Nebraska	3	---	---	317	28	348
Nevada	---	527	---	26	66	619
New Hampshire	---	---	410	621	49	1,080
New Jersey	---	---	1,185	153	12	1,350
New Mexico	22	4,827	75	804	34	5,762
New York	---	194	857	902	351	2,304
North Carolina	---	---	805	2,165	10	2,980
North Dakota	2	---	---	---	2,175	2,177
Ohio	1,394	463	2,433	561	102	4,953
Oklahoma	21	---	432	575	2,734	3,762
Oregon	1	---	477	2,822	307	3,607
Pennsylvania	5,371	1	6,920	3,170	273	15,735
Rhode Island	---	---	121	61	---	182
South Carolina	---	---	19	1,105	---	1,124
South Dakota	6	---	---	---	3	9
Tennessee	1,008	1,640	2,830	2,117	---	7,595
Texas	12	265	630	2,741	5,338	8,986
Utah	258	2,685	106	839	1,190	5,078
Vermont	10	---	143	275	---	428
Virginia	1,536	---	4,663	640	111	6,950
Washington	37	1,174	32	2,108	36	3,387
West Virginia	4,607	---	223	673	315	5,818
Wisconsin	---	---	114	1,242	---	1,356
Wyoming	1,016	145	112	127	2,598	3,998
Total	24,912	25,085	50,138	46,185	29,590	175,910

1/ Included with Maryland.

TABLE 7. - Packaged and bulk water gels and slurries sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

State	Use					
	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama-------------	11,407	50	1,561	1,291	4,134	18,443
Alaska--------------	2	---	42	4,982	5	5,031
Arizona-------------	---	43,396	46	41	609	44,092
Arkansas------------	19	55	1,717	480	149	2,420
California----------	---	301	4,035	2,196	131	6,663
Colorado------------	5,392	14,854	612	499	852	22,209
Connecticut---------	---	---	1,354	2,868	84	4,306
Delaware------------	---	---	---	---	52	52
District of Columbia 1/	---	---	---	---	---	---
Florida-------------	---	---	14,332	2,457	796	17,585
Georgia-------------	62	---	3,752	739	2,097	6,650
Hawaii--------------	---	---	312	8	---	320
Idaho---------------	---	787	237	158	88	1,270
Illinois------------	2,602	---	3,039	1,125	955	7,721
Indiana-------------	5,115	---	2,614	258	3	7,990
Iowa----------------	90	---	5,142	359	4	5,595
Kansas--------------	205	---	1,108	179	699	2,191
Kentucky------------	7,734	6	1,819	412	407	10,378
Louisiana-----------	---	---	239	93	143	475
Maine---------------	---	---	229	28	5	262
Maryland------------	272	---	2,866	963	---	4,101
Massachusetts-------	---	---	188	130	46	364
Michigan------------	---	18,833	1,652	8	---	20,493
Minnesota-----------	---	70,722	1,036	55	---	71,813
Mississippi---------	---	---	270	1	179	450
Missouri------------	238	310	3,501	982	157	5,188
Montana-------------	784	75	---	364	194	1,417
Nebraska------------	---	---	368	127	---	495
Nevada--------------	---	20	340	14	2	376
New Hampshire-------	---	---	37	29	2	68
New Jersey----------	---	17	479	69	1	566
New Mexico----------	8,935	4,624	347	265	868	15,039
New York------------	42	148	617	1,057	218	2,082
North Carolina------	---	---	5,449	2,996	366	8,811
North Dakota--------	---	---	---	---	---	---
Ohio----------------	752	25	5,369	849	208	7,203
Oklahoma------------	770	11	1,139	424	588	2,932
Oregon--------------	---	---	83	1,170	5	1,258
Pennsylvania--------	24,318	---	14,086	1,011	1,629	41,044
Rhode Island--------	---	---	---	---	---	---
South Carolina------	---	---	1,422	827	204	2,453
South Dakota--------	2	542	484	---	---	1,028
Tennessee-----------	99	727	2,293	692	45	3,856
Texas---------------	---	13	2,308	1,379	324	4,024
Utah----------------	176	8,870	66	393	564	10,069
Vermont-------------	---	---	520	87	---	607
Virginia------------	856	---	3,421	357	4,786	9,420
Washington----------	---	1,033	65	1,314	199	2,611
West Virginia-------	1,306	---	466	1,196	347	3,315
Wisconsin-----------	---	2,464	3,349	672	178	6,663
Wyoming-------------	23,440	2,769	785	68	1,838	28,900
Total----------	94,618	170,652	95,196	35,672	24,161	420,299

1/ Included with Maryland.

TABLE 8. - Ammonium nitrate fuel-mixed blasting agents sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

	Use					
State	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama	326,782	---	437	83	55,161	382,463
Alaska	---	---	---	83	33	116
Arizona	939	6,296	3,095	1,653	938	12,921
Arkansas	3,499	1	2,266	871	41	6,678
California	---	39	1,586	975	1,242	3,842
Colorado	19,764	---	1,705	165	662	22,296
Connecticut	---	---	2,289	728	---	3,017
Delaware	---	---	193	1,437	111	1,741
District of Columbia 1/	---	---	---	---	---	---
Florida	---	---	4,547	3,268	1,770	9,585
Georgia	---	---	10,290	1,852	4,160	16,302
Hawaii	---	---	---	---	---	---
Idaho	---	30	638	---	40	708
Illinois	73,575	3	6,865	1,676	3,850	85,969
Indiana	126,244	---	18,024	5,311	80	149,659
Iowa	6	---	1,403	149	---	1,558
Kansas	6,817	---	3,705	1,929	8,035	20,486
Kentucky	240,025	---	14,711	17,778	15,037	287,551
Louisiana	---	---	2,794	---	---	2,794
Maine	---	---	444	79	---	523
Maryland	6,133	---	5,763	1,342	367	13,605
Massachusetts	---	---	2,115	609	57	2,781
Michigan	386	3,373	10,404	124	---	14,287
Minnesota	---	38,241	29	40	---	38,310
Mississippi	---	---	57	---	---	57
Missouri	4,034	1,109	5,289	4,207	101	14,740
Montana	892	165	---	20	14	1,091
Nebraska	---	---	1,388	324	---	1,712
Nevada	---	5,820	213	82	321	6,436
New Hampshire	---	---	223	244	11	478
New Jersey	---	---	1,226	432	32	1,690
New Mexico	556	138	5,082	16	24,276	30,068
New York	279	---	2,672	2,025	1,344	6,320
North Carolina	---	---	11,879	5,294	387	17,560
North Dakota	4	---	---	4	1	9
Ohio	50,184	---	13,285	6,324	5,910	75,703
Oklahoma	35,243	2,202	4,447	1,203	7,898	50,993
Oregon	82	---	928	2,385	292	3,687
Pennsylvania	43,851	---	13,000	3,808	2,260	62,919
Rhode Island	---	---	269	98	---	367
South Carolina	---	---	2,245	996	1	3,242
South Dakota	---	---	---	---	---	---
Tennessee	28,110	---	5,101	6,906	1,341	41,458
Texas	---	2,187	15,145	4,913	1,217	23,462
Utah	---	846	50	---	41	937
Vermont	27	---	188	424	---	639
Virginia	40,803	---	4,713	14,306	3,242	63,064
Washington	---	---	4	70	261	335
West Virginia	75,563	---	2,448	11,951	2,905	92,867
Wisconsin	---	---	2,354	4,155	343	6,852
Wyoming	43,052	5,187	1,925	272	17,944	68,380
Total	1,126,850	65,637	187,434	110,611	161,726	1,652,258

1/ Included with Maryland.

TABLE 9. - Unprocessed ammonium nitrate sold for consumption in the United States, by State and use, 1980
(Thousand pounds)

State	Use					
	Coal mining	Metal mining	Quarrying and nonmetal mining	Construction work	All other purposes	Total
Alabama	143,936	---	5,819	107,070	70	256,895
Alaska	973	2,432	---	---	---	3,405
Arizona	28,189	126,573	---	196	249	155,207
Arkansas	---	849	1,911	296	7,316	10,372
California	1,850	15,968	4,280	1,739	---	23,837
Colorado	34,027	3,375	---	---	1,836	39,238
Connecticut	---	---	5,177	577	277	6,031
Delaware	---	---	---	---	---	---
District of Columbia 1/	---	---	---	---	---	---
Florida	---	---	4,863	---	---	4,863
Georgia	---	---	225	---	---	225
Hawaii	---	---	---	---	---	---
Idaho	1,375	12,227	10,143	2,027	---	25,772
Illinois	17,705	---	21,655	---	1,812	41,172
Indiana	44,647	---	13	---	3,912	48,572
Iowa	2,299	---	10,461	1,074	7,479	21,313
Kansas	178	---	1,353	---	1,359	2,890
Kentucky	294,364	---	37,493	8,882	73,507	414,246
Louisiana	---	---	---	---	---	---
Maine	---	---	---	---	---	---
Maryland	620	---	137	44	---	801
Massachusetts	322	---	101	150	---	573
Michigan	2,865	6,030	12,455	5,225	1,922	28,497
Minnesota	1,650	6,897	3,152	165	3,323	15,187
Mississippi	---	---	---	---	---	---
Missouri	10,912	---	16,512	4,578	6,713	38,715
Montana	36,796	23,473	1,582	---	2,454	64,305
Nebraska	---	---	---	---	---	---
Nevada	---	14,436	1,328	---	---	15,764
New Hampshire	---	---	68	---	---	68
New Jersey	---	---	4	---	40	44
New Mexico	5,600	35,457	---	---	---	41,057
New York	---	50	4,004	1,099	---	5,153
North Carolina	3,716	---	---	8,631	---	12,347
North Dakota	328	---	---	---	---	328
Ohio	75,288	---	43,058	2,086	14,774	135,206
Oklahoma	92	---	1,750	92	1,268	3,202
Oregon	---	---	1,270	2,997	---	4,267
Pennsylvania	277,267	---	18,158	6,502	21,464	323,391
Rhode Island	---	---	---	---	---	---
South Carolina	---	---	---	---	---	---
South Dakota	---	---	---	---	---	---
Tennessee	20,983	2,463	15,895	20,456	5,805	65,602
Texas	244	---	7,859	30,122	2,994	41,219
Utah	1,000	34,946	4,244	---	83	40,273
Vermont	---	---	---	---	---	---
Virginia	54,462	---	615	4,784	5,254	65,115
Washington	5,250	3,210	1,459	4,382	196	14,497
West Virginia	121,749	---	934	5,423	1,840	129,946
Wisconsin	---	---	---	---	942	942
Wyoming	71,599	3,103	4,624	---	5,075	84,401
Undistributed 2/	3/	3/	3/	3/	63,305	63,305
Total	1,260,286	291,489	242,602	218,597	235,269	2,248,243

1/ Included with Maryland.
2/ Quantities undistributed to avoid disclosing company proprietary data.
3/ Undistributed quantity for this use is included with undistributed "All other purposes."

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ACOUSTIC CORE LOGGING IN BLAST-DAMAGED ROCK

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ABSTRACT

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The Bureau of Mines, in cooperation with the Duval Corp., conducted a blast-fragmentation experiment to determine the feasibility of preparing a porphyry copper-molybdenum deposit for in-situ leaching. The blast was designed with ten 9-inch-diameter blastholes to depths of 110 feet in an equilateral triangle configuration; spacings between blastholes were 15, 20, and 25 ft. One of the major problems in the experiment was in assessing blast damage. Acoustic core-logging equipment and methods were devised and used as one approach in solving this problem. Ultrasonic pulse travel-times were determined in four diametral directions at 2-ft intervals of depth to a final depth of 120 ft in three preblast and six postblast drill cores at the Duval test site. The acoustic logging program provided compressional wave travel-time at 0°, 45°, 90°, and 135° around the core circumference, maximum travel-time difference, mean compressional-wave velocity, and an anisotropy factor. Other acoustic parameters introduced in the analyses were stiffness modulus, seismic quality designation (SQD), and a compensated velocity to account for portions of the core that were nonrecoverable or too highly fractured to permit diametral travel-time measurements.

The acoustic parameters all indicated the deterioration in structural quality from the preblast condition, in which the rock already was badly fractured and weathered, to the more highly fractured postblast condition. Because of the highly fragmented, poor structural condition of the rock after blasting, the rock was indicated to be suitable for in-situ leaching, at least at the 20- and 15-ft blasthole spacings, and even in some zones in the rock at the 25-ft blasthole spacing.

INTRODUCTION

In 1973 the Bureau of Mines conducted a fragmentation experiment in cooperation with the Duval Corp. to determine the feasibility of breaking up, in place, a porphyry copper—molybdenum deposit in preparation for in-situ leaching (D'Andrea et al., 1974). The deposit is located near the Sierrita pit south of Tucson, Ariz. Ten blastholes were drilled to a depth of 110 ft in an equilateral triangle configuration at three different blasthole spacings of 25, 20, and 15 ft (Fig.1). The lower 50 ft of each blasthole was loaded with aluminized slurry blasting agent and the upper 60 ft with stemming.

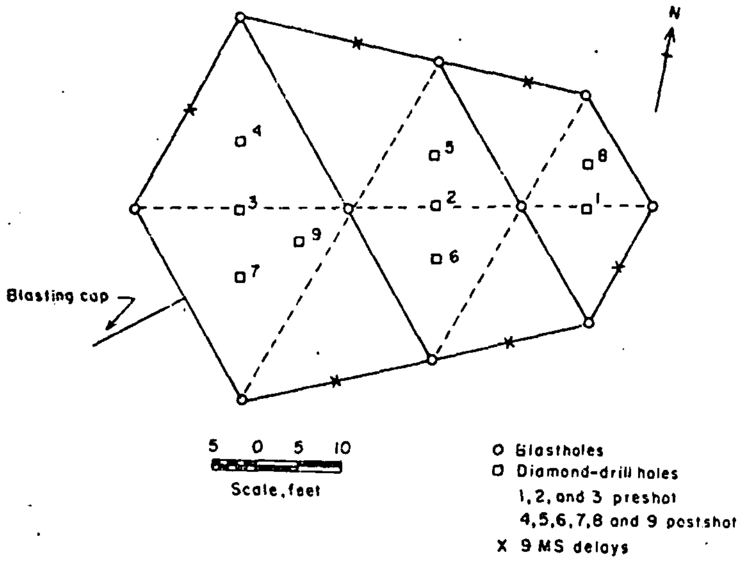
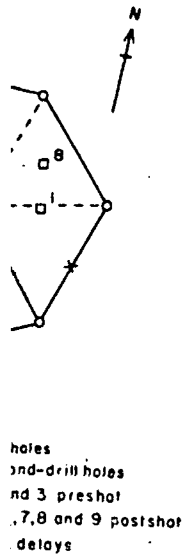


Fig.1. Test blast design.

Diamond-drill cores were taken before and after blasting from the different blasthole spacing zones as indicated in Fig.1. One of the important objectives of the experiment was to find qualitative or quantitative methods of describing the structural condition of the rock before and after blasting, thereby indicating location and magnitude of blast damage. Other methods used to evaluate blast damage in this experiment are described by Steckley et al. (1975).

The degree of fissuration or size of fragments required for successful in-situ leaching is not well known and depends on the physical and structural properties of the host rock as well as on the type and distribution of mineralization. Blast design for in-situ leaching operations at the Old Reliable mine in the Galiuro Mountains of Arizona required shattering the ore body to 11-inch fragments or less, and results from the 4-million-pound ammonium nitrate blast detonated in 1972 produced fragments measuring 9 inches or less (Engineering and Mining Journal, 1972).

This report describes results from acoustic logging methods used on the drill cores to assess the structural integrity of the rock and compare rock condition before and after blasting. In earlier Bureau research, pulse velocities were used to indicate the extent of blast damage from small-charge blasting in a granite (Olson et al., 1973) and shale (Siskind et al., 1973) and from production bench blasting in a granite gneiss (Siskind and Fumanti, 1974). Subsequent improvements in the logging apparatus, technique, and data analyses permit increased information on structural quality of the rock and help reduce ambiguity in interpreting blast damage. The acoustic core-logging apparatus comprises a modification of the acoustic bench (Thill et al., 1968), and interfacing equipment which inputs travel-time readings directly



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into a programmable calculator for computation and immediate printout of results.

Acoustic-wave propagation methods to assess blast damage are based on the fact that cracks impede the progress of acoustic energy propagated in the rock and cause reduction in velocity and amplitude of the wave. The amount of reduction depends on the size, orientation, and density of cracks; on wave type and wave length of the propagating wave; and on the mismatch in acoustic impedance between the rock and the crack-filling medium. Since the acoustic impedance mismatch is substantially larger between rock and air than between rock and fluids or drill muds, the greatest velocity reduction from the effects of cracks, and correspondingly, maximum sensitivity in detecting fragmentation damage will be obtained in dry rock with air-filled cracks. Because the acoustic core logging technique makes comparisons before and after fragmentation in the rock at the same locality and under identical environmental conditions, other causes that might affect the propagation of wave energy in the rock are held nearly constant, and reduction in wave velocity after blasting therefore can be assumed to result from increased fracturing in the rock.

Core logging is presented as an alternative or supplement to the more conventional downhole logging. In acoustic downhole logging, cracks may be filled with water or drill mud, and little, if any, control can be had of the moisture environment. In acoustic core logging, however, the recovery core can be air-dried, thereby increasing the sensitivity of the logging method in detecting fragmentation damage. Other advantages of acoustic core logging over downhole logging are that the equipment can be stationary, less complex, and comparatively inexpensive considering costs of comparable field instrumentation. Moreover, problems peculiar to downhole logging such as those caused by hole size variation and caving in the hole are circumvented. Acoustic core logging is not without its problems, however, some of which are: (1) Measurements are made usually in small intact rock specimens and, therefore, large-scale joints and fractures are not sampled; (2) continuous logs with depth are sometimes difficult to obtain because intervals of core may be missing and depth often is not precisely known; (3) obtaining representative samples at regular intervals may be difficult; and (4) measurements are made in core often disturbed by the drilling and recovery processes. Our sampling and data analyses techniques attempt to minimize some of these problems.

PHYSICAL PROPERTIES

Preliminary rock property determinations made to characterize the rock from the Duval test site included pulse and resonance velocities, dynamic elastic moduli, density, porosity, and permeability. For the resonance tests, several long pieces of core with length/diameter ratios of 4/1 or greater were selected from each of the three preblast cores (Thill and Peng, 1974; Thill et al., 1974). Most of the pieces with sufficient length came from the uppermost

50 ft of drill core. Velocities, density, and dynamic moduli were statistically tabulated and combined for all the preblast holes (Table I). The properties exhibited considerable range because the competency of the rock varied from sample to sample.

TABLE I

Rock properties of Duval test site rock

Property	Mean	N^1	S^2	C^3
Density (g/cm^3)	2.50	16	0.086	3.4
Longitudinal pulse velocity (km/sec)	4.21	16	0.604	14.3
Longitudinal bar velocity (km/sec)	3.65	16	0.647	17.7
Torsional (shear) velocity (km/sec)	1.98	16	0.515	26.0
Dynamic Young's modulus (GN/m^2)	34.4	16	12.19	35.5
Dynamic shear modulus (GN/m^2)	10.5	16	5.29	50.6
Poisson's ratio[4]	0.29	16	0.051	17.5

[1] N = number of specimens.

[2] S = standard deviation = $\frac{(\Sigma x^2 - \bar{x}\Sigma x)^{0.5}}{N-1}$, where x = sample variable and $\bar{x}$ = sample mean.

[3] C = coefficient of variation in % = 100S/mean.

[4] Poisson's ratio is derived from the ratio of longitudinal pulse velocity, V_p, to longitudinal bar velocity, V_o, in the equation:

$\nu = 0.25\ \{[(1-R^2)(9-R^2)]^{0.5} - (1-R^2)\}$, where $R^2 = (V_o/V_p)^2$.

TABLE II

Porosity and permeability of Duval test site rock — preblast

Sample number	Borehole	Porosity (%)	Permeability (10^{-5} darcys)
6071	1	5.0	<0.10
6072	1	4.5	7.27
6073	1	5.3	4.13
6033	2	5.6	0.77
6034	2	4.7	7.39
6035	2	4.5	1.80
6037	2	3.5	<0.10
6038	2	4.0	<0.10
6039	2	4.3	<0.10
6040	2	5.7	<0.10
6041	2	10.4	6.32
6036	2	5.9	0.98
6032	2	6.8	0.55
6044	2	6.7	5.37
6047	2	5.8	2.48
6048	2	5.9	0.47
6043	2	5.9	4.70
Mean Value	—	5.6	2.51

ynamic moduli were statistically
holes (Table I). The properties
npetency of the rock varied

N[1]	S[2]	C[3]
16	0.086	3.4
16	0.604	14.3
16	0.647	17.7
16	0.515	26.0
16	12.19	35.5
16	5.29	50.6
16	0.051	17.5

sample variable and $\bar{x}$ = sample mean.

nal pulse velocity, V_p, to longitudinal

$R^2 = (V_o/V_p)^2$.

eblast

rosity	Permeability (10^-5 darcys)
0	<0.10
5	7.27
3	4.13
6	0.77
7	7.39
5	1.80
5	<0.10
	<0.10
	<0.10
	<0.10
	6.32
	0.98
	0.55
	5.37
	2.48
	0.47
	4.70
	2.51

Porosity and permeability determinations were made on 1-inch-diameter by 1-inch-long solid cylindrical specimens taken from the three preblast cores (Table II). Most of the samples tested were from borehole 2, since many of the specimens selected from holes 1 and 3 did not remain intact during sample preparation. The mean porosity and permeability values probably represent minimal values of these properties, since they are determined in small intact specimens. The in-situ rock includes fractured and weathered zones that should result in higher values of both porosity and permeability for the rock system.

ACOUSTIC CORE LOGGING

The core-logging apparatus measures the transit time of a mechanical impulse transmited across the core diameter and consists of a pulsing unit, sample-holding device, signal-detection unit, display and timing units, and data processing equipment (Fig.2). Cores are placed between the transducer heads in a core holder tray specially designed to accommodate long length of core (Fig.3). The acoustic logging apparatus is a modification of the ultrasonic pulse measurement system and acoustic bench described earlier (Thill et al., 1968; Thill and Peng, 1974). The timing circuitry is interfaced directly into an on-line Hewlett Packard* HP 9810A programmable calculator wherein computations are made and output printed on the typewriter. The flow diagram (Fig.4) outlines the program steps. Program output gives the diametral travel-time at 45° intervals from 0° to 135° around the circumference of the core, maximum travel-time difference, average travel-time and velocity, and the anisotropy factor. Only compressional (P-wave) velocity was used in these determinations. Anisotropy factor was calculated from the maximum travel-time difference divided by the mean travel-time expressed in percent. These acoustic parameters were determined on an intact piece of core within each 2-ft-depth interval along the entire length of each core.

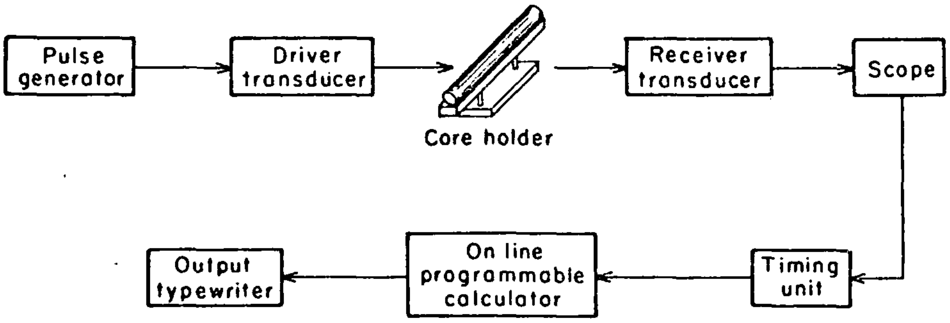

Fig.2. Core-logging apparatus.

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*Trade names are used for identification purposes only and do not imply endorsement by the Bureau of Mines.

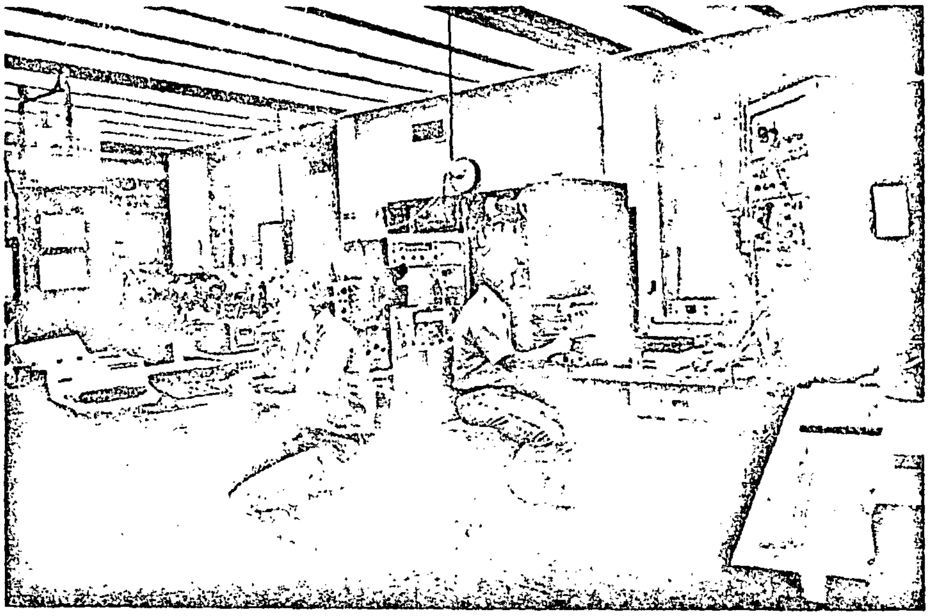


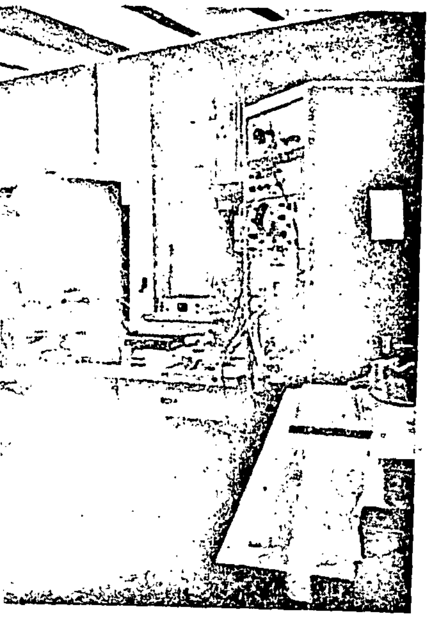
Fig.3. Acoustic core-logging system in operation.

Other parameters determined to indicate structural integrity were the seismic quality designation, SQD; stiffness modulus, Y; and compensated velocity. Rock quality designation, RQD, defined as the total length of all pieces greater than or equal to 4 inches divided by the total length of core run, was used here for comparison with the acoustic data and also in calculating compensated velocity to weigh velocities for fractions of fractured rock.

The three preblast and six postblast cores were air-dried for a minimum period of two weeks before testing. To compensate for any anisotropy caused by preferred orientation of cracks or mineral constituents, travel-times were taken at four positions at 45° intervals around the circumference of the core, and then averaged to provide a mean velocity for each 2-ft interval. The zero position was arbitrary since the drill cores were not oriented. Accuracy in each velocity determination was within 1% (Thill et al., 1968).

Seismic quality designation

SQD compares the determined wave velocity, V (including effects from discontinuities and fractures), to that of an ideal material of the same mineralogical composition. SQD is analogous to RQD in the sense that RQD compares the fractured rock to an unfractured solid run of core with 100% recovery. The idealized velocity is calculated from the volume fraction of each mineral component and the Voigt-Reuss-Hill (VRH) aggregate average of each mineral phase using the relationship:



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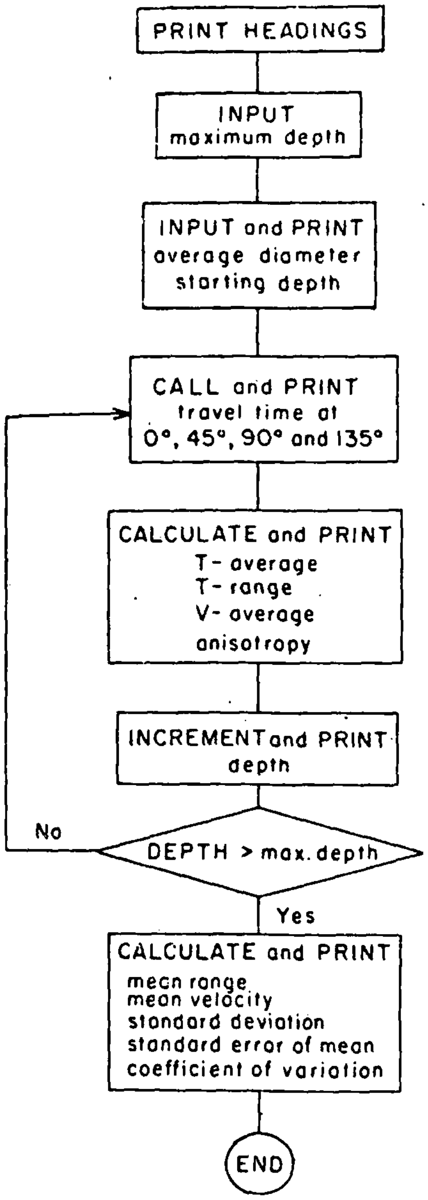

Fig. 4. Flow diagram for core-logging program.

$$1/V_{VRH} = \sum_{1}^{i} f_i/V_i = f_1/V_1 + f_2/V_2 + f_3/V_3 \ldots f_i/V_i \qquad (1)$$

where: V_{VRH} = the nonporous aggregate average velocity,
f_i = the fraction of the total volume occupied by each mineral constituent where $\Sigma f_i = 1$, and
V_i = the single crystal VRH velocity.

Thus SQD is simply the ratio V/V_{VRH}. SQD therefore reflects the rock's structural integrity since velocity changes due to mineralogical differences are compensated for in the V_{VRH} calculation and comparison. For example, when the SQD ratio approaches 1.0, the rock is fresh and intact and has few pores or cracks; conversely, lower ratios indicate poorer structural quality with different amounts of crack or void porosity.

SQD was related to rock quality in a way analogous to the way Deere et al. (1969) relate RQD to rock quality. An SQD base value of 35% was assumed for highly fractured rock, four divisions of rock quality were made in the region from 35 to 95%, and the uppermost five percentile was designated excellent quality as shown in the following tabulation:

SQD(%)	RQD(%)	Rock quality
< 50	0– 25	very poor
50– 65	25– 50	poor
65– 80	50– 75	fair
80– 95	75– 90	good
95–100	90–100	excellent

Stiffness modulus

The stiffness modulus is calculated from density and compressional (P-wave) velocity by the formula:

$$Y = \rho V_p^2 \qquad (2)$$

where: Y = stiffness modulus,
ρ = bulk density, and
V_p = compressional wave velocity.

The stiffness modulus is a quantity similar to Young's modulus, E, and is related to the latter by the relationship:

$$Y = \frac{E(1-\nu)}{(1+\nu)(1-2\nu)} \qquad (3)$$

where ν is Poisson's ratio. Thus, for constant ν, Y varies as does E, and indicates the dynamic stress-strain characteristics of the rock.

Increase in fracture porosity normally is accompanied by decreases in both V_p and Y; hence, structural integrity can be interpreted from changes in V_p and Y. The change in Y is a sensitive indicator of structural changes since Y is a function of V^2.

Compensated velocity

Compensated velocity, V_c, was calculated to estimate a weighted velocity when compensation was made for highly broken or nonrecoverable core over a particular core interval. The RQD was used to weight the velocity by the averaging formula:

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$$V_c^{-1} = \mathrm{RQD}/V_\mathrm{I} + (1 - \mathrm{RQD})/V_\mathrm{F} \qquad (4)$$

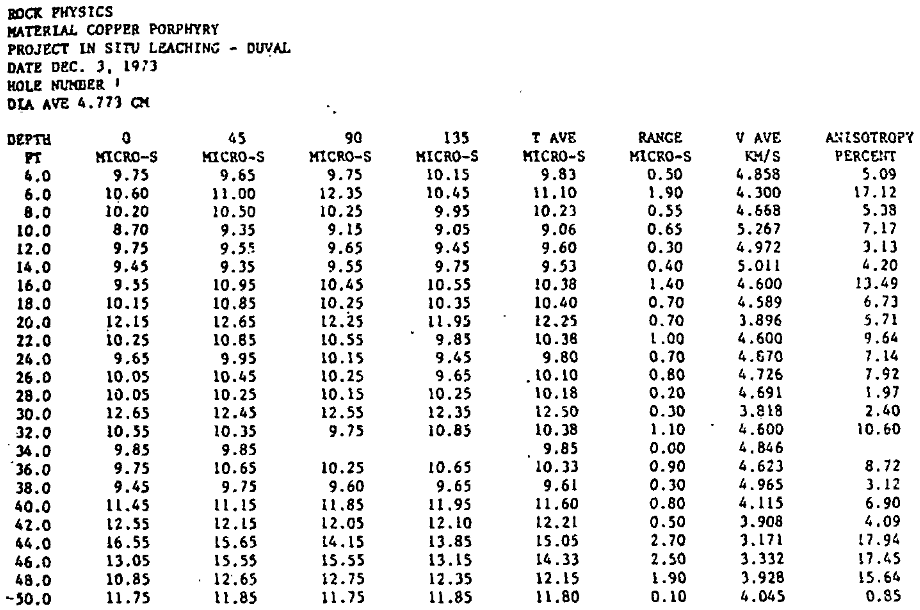
where V_c = compensated mean velocity,
V_I = mean velocity for intact rock,
V_F = velocity for highly fractured rock estimated at 2 km/sec, and
RQD = *fractional* RQD.

As RQD gives the fraction of pieces 4 inches or greater in length in a core run, the assumption is made in eq. 4 that all pieces of core 4 inches or greater in length would have the mean velocity of the intact rock over that particular depth interval or core run, and that the remaining highly fractured or missing core would have an appropriate low velocity. The composite velocity for the preblast or postblast cores was used for the value, V_I, at each depth interval. A value of 2 km/sec was arrived at for V_F from the following considerations: an absolute lower velocity limit, in the absence of any higher velocity materials, would be that for air at 1 atm, that is, 0.33 km/sec. Rock, of course, is a higher velocity material, and even sand and gravel range between 0.6 and 2.5 km/sec, depending upon the degree of consolidation. Previous measurements of velocity in rock fractured in uniaxial compression gave a velocity of about 2 km/sec for highly fractured rock in the "postfailure" region of the stress-strain curve (Thill, 1973). Deere and Miller (1966) also found a lower limiting velocity near 2 km/sec, estimated statistically from a group of 28 rocks comprising 13 different geological rock types. The value of 2 km/sec, therefore, seems to provide a reasonable estimate for highly broken rock. Thus, for 100% recovery of solid core, compensated velocity becomes the mean intact velocity. At the other extreme, when there is no core recovery, or core consists of broken pieces less than 4 inches long in a particular interval, the compensated velocity becomes that for highly fractured rock; that is, 2 km/sec.

ACOUSTIC LOG RESULTS

Online core logging was accomplished by feeding the travel-time data directly into the programmable calculator with simultaneous printed output (Fig.5). Graphs plotted from pulse velocity data at 2-ft-depth intervals show considerable fluctuation with depth for both the preshot and postshot cores (Figs.6 and 7). The in-out fluctuations in the logs correspond to the frequent change in structural character of these rock cores. In perfectly uniform intact rock such fluctuations would be absent.

Averaging velocity over 10-ft intervals reduced fluctuation considerably (Figs.6 and 7, dashed lines), making it easier to interpret overall trends. A trend toward decreasing velocity with depth is shown in the zone from about 25—80 ft in the preblast cores. This trend is opposite that normally anticipated and results from a more deteriorated condition of the rock with depth. The trend reverses at depths of 80—90 ft when velocity begins to increase moderately. Deterioration in the quality of the rock with depth also was evident from visual observations of the preblast core in the core boxes,



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ROCK PHYSICS
MATERIAL COPPER PORPHYRY
PROJECT IN SITU LEACHING - DUVAL
DATE DEC. 3, 1973
HOLE NUMBER 1
DIA AVE 4.773 CM

DEPTH      0         45         90        135       T AVE      RANGE     V AVE    ANISOTROPY
  FT    MICRO-S    MICRO-S    MICRO-S    MICRO-S    MICRO-S    MICRO-S    KM/S     PERCENT
  4.0     9.75       9.65       9.75      10.15       9.83       0.50     4.858       5.09
  6.0    10.60      11.00      12.35      10.45      11.10       1.90     4.300      17.12
  8.0    10.20      10.50      10.25       9.95      10.23       0.55     4.668       5.38
 10.0     8.70       9.35       9.15       9.05       9.06       0.65     5.267       7.17
 12.0     9.75       9.55       9.65       9.45       9.60       0.30     4.972       3.13
 14.0     9.45       9.35       9.55       9.75       9.53       0.40     5.011       4.20
 16.0     9.55      10.95      10.45      10.55      10.38       1.40     4.600      13.49
 18.0    10.15      10.85      10.25      10.35      10.40       0.70     4.589       6.73
 20.0    12.15      12.65      12.25      11.95      12.25       0.70     3.896       5.71
 22.0    10.25      10.85      10.55       9.85      10.38       1.00     4.600       9.64
 24.0     9.65       9.95      10.15       9.45       9.80       0.70     4.670       7.14
 26.0    10.05      10.45      10.25       9.65      10.10       0.80     4.726       7.92
 28.0    10.05      10.25      10.15      10.25      10.18       0.20     4.691       1.97
 30.0    12.65      12.45      12.55      12.35      12.50       0.30     3.818       2.40
 32.0    10.55      10.35       9.75      10.85      10.38       1.10     4.600      10.60
 34.0     9.85       9.85                             9.85       0.00     4.846
 36.0     9.75      10.65      10.25      10.65      10.33       0.90     4.623       8.72
 38.0     9.45       9.75       9.60       9.65       9.61       0.30     4.965       3.12
 40.0    11.45      11.15      11.85      11.95      11.60       0.80     4.115       6.90
 42.0    12.55      12.15      12.05      12.10      12.21       0.50     3.908       4.09
 44.0    16.55      15.65      14.15      13.85      15.05       2.70     3.171      17.94
 46.0    13.05      15.55      15.55      13.15      14.33       2.50     3.332      17.45
 48.0    10.85      12.65      12.75      12.35      12.15       1.90     3.928      15.64
 50.0    11.75      11.85      11.75      11.85      11.80       0.10     4.045       0.85
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Fig.5. Sample data sheet from acoustic logging program.

although such observations could not place a numerical value on the structural condition.

In the postblast cores, the trends in velocity include effects of blast damage superposed over effects from initial discontinuities in the rock. Since these graphs are more complex, they are best interpreted by direct comparison with the preblast condition.

BLAST DAMAGE COMPARISONS

Pulse velocity

Comparisons of the blast-damaged cores with the preblast cores were complicated by the already weathered and fractured condition of the preblast cores. It was observed, in fact, that the mean velocity for postblast hole 4 actually was higher than that of any of the preblast cores (Table III). This could have occurred because intact pieces of core selected in the postblast cores may represent the more durable, intact, higher velocity pieces. Weaker, more friable pieces sampled in the preblast core may have subsequently been broken up by the blast. Averaging all the preblast core data and all the postblast core data over 10-ft-depth intervals in composites gives a better basis for comparison and removes most of the minor discrepancies that occur when comparing one hole with another. Table IV compares averages for all of the preblast (BH 1—3) and postblast (BH 4—9) holes for pulse velocity, RQD, SQD, Y, and compensated velocity.

RANGE MICRO-S	V AVE KM/S	ANISOTROPY PERCENT
0.50	4.858	5.09
1.90	4.300	17.12
0.55	4.668	5.38
0.65	5.267	7.17
0.30	4.972	3.13
0.40	5.011	4.20
1.40	4.600	13.49
0.70	4.589	6.73
0.70	3.896	5.71
1.00	4.600	9.64
0.70	4.870	7.14
0.80	4.726	7.92
0.20	4.691	1.97
0.30	3.818	2.40
1.10	4.600	10.60
0.00	4.846	
0.90	4.623	8.72
0.30	4.965	3.12
0.80	4.115	6.90
0.50	3.908	4.09
2.70	3.171	17.94
2.50	3.332	17.45
1.90	3.928	15.64
0.10	4.045	0.85

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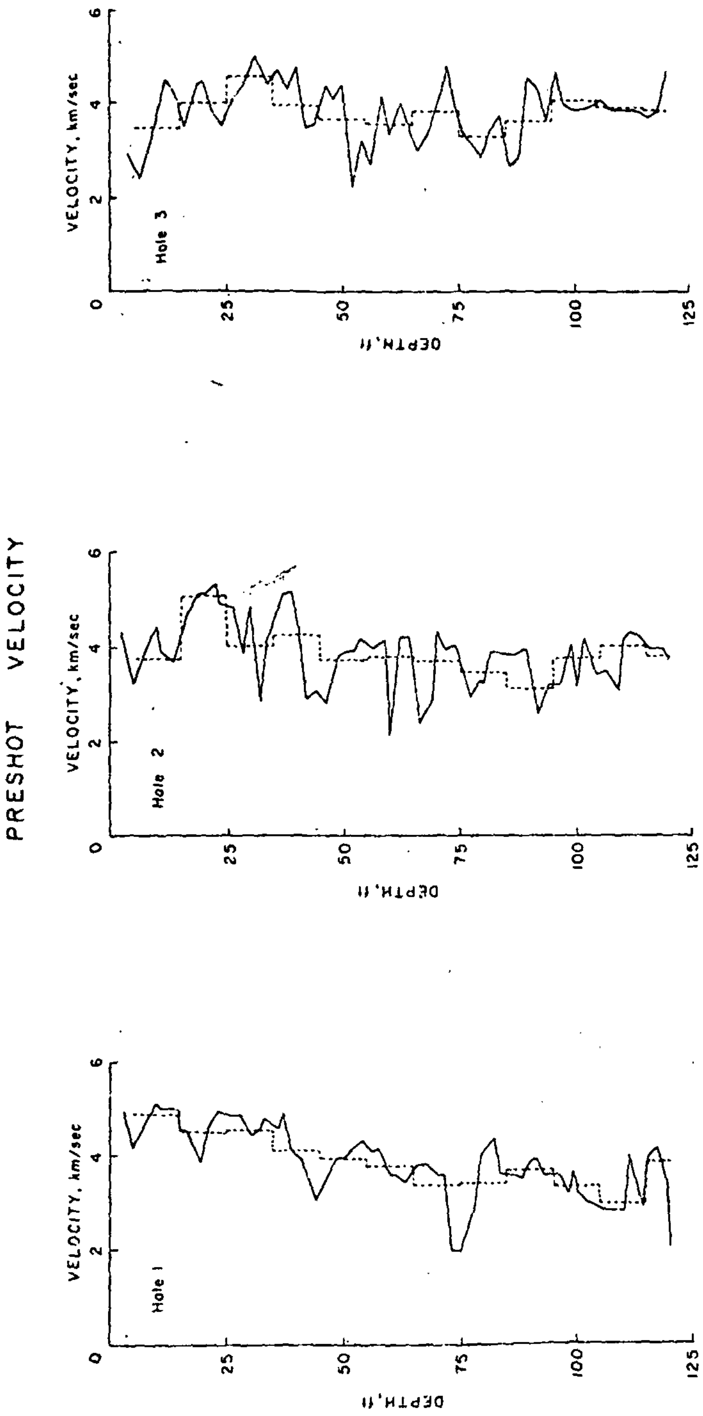

Fig.6. Pulse velocity logs — preshot cores.

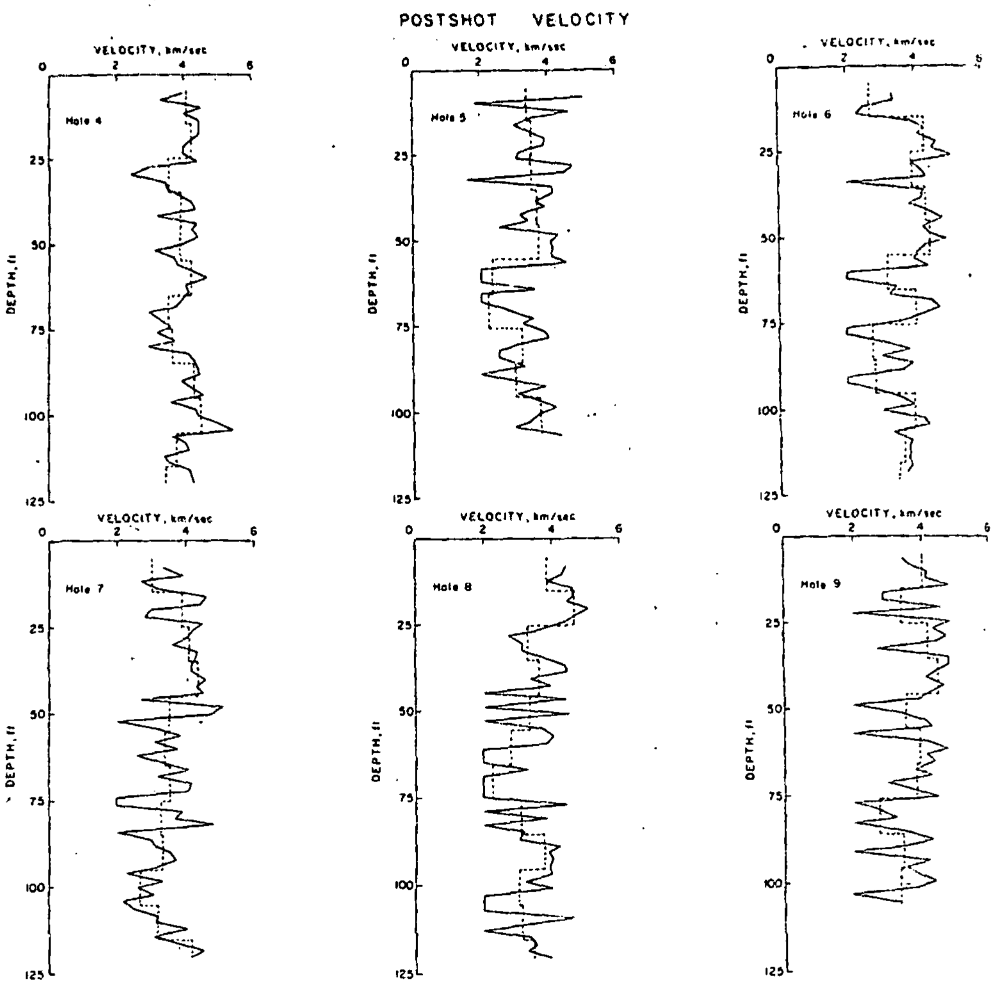

Fig.7. Pulse velocity logs —postshot cores.

The overall averages for velocity show a reduction of 7.5% from the preblast to postblast condition (Table V). Decrease in velocity is calculated from the difference between preblast and postblast velocities divided by postblast velocity. Because of the nonhomogeneity of the rock from location to location indicated by the velocity variation at different depths between the preblast cores, we place little statistical significance on mean velocity reductions of less than a few percent. We note, however, that postblast velocity is always less than the preblast velocity (Fig.8). As indicated earlier, preblast velocity decreases with depth to roughly 80—90 ft and gradually increases below that depth. Velocities are between 4.0 and 4.5 km/sec down to about 40—50 ft and between 3 and 4 km/sec at greater depths with a mean of 3.86 km/sec for the entire length of core.

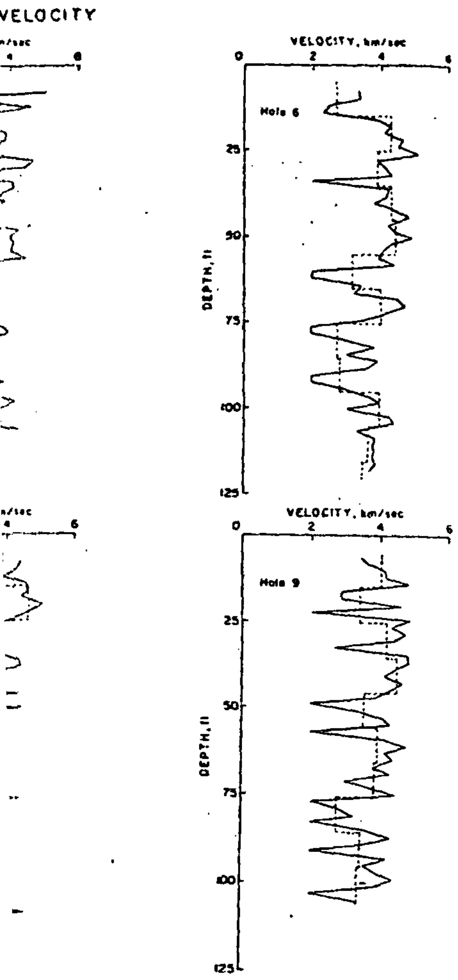

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TABLE III

Summarized velocity for each borehole at 10-ft intervals of depth

Depth (ft)	Pulse velocity (km/sec)								
	BH 1	BH 2	BH 3	BH 4	BH 5	BH 6	BH 7	BH 8	BH 9
5— 15	4.88	3.74	3.46	4.03	3.37	2.70	3.02	3.87	4.03
15— 25	4.51	5.17	4.02	4.25	3.50	4.29	3.88	4.68	3.41
25— 35	4.54	3.99	4.60	3.57	3.49	3.91	4.12	3.31	4.19
35— 45	4.16	4.22	3.97	3.93	3.65	4.30	4.37	3.64	4.48
45— 55	3.98	3.67	3.70	3.90	3.70	4.41	3.53	3.34	3.56
55— 65	3.82	3.78	3.58	4.22	2.83	3.17	3.40	2.80	3.92
65— 75	3.41	3.69	3.86	3.55	2.73	4.00	3.55	2.26	3.85
75— 85	3.43	3.41	3.35	3.65	3.20	2.75	3.30	3.11	2.76
85— 95	3.74	3.07	3.67	4.31	3.03	2.81	3.36	3.79	3.42
95—105	3.38	3.71	4.11	4.49	3.72	3.96	2.72	3.04	3.39
105—115	3.00	3.96	3.98	3.75	—	3.65	3.27	3.13	—
115—120	3.89	3.75	3.92	3.44	—	3.49	4.22	3.94	—
Mean velocity	3.89	3.85	3.85	3.93	3.32	3.62	3.56	3.41	3.70

Blast damage was indicated in the overall reduction in velocity from 3.86 km/sec in the preblast cores to 3.59 km/sec after the blast. Greatest effects from blast damage were expected in the 60- to 110-ft region of the powder column. The lowest recorded velocities did, in fact, occur in that region in the postblast cores, indicating that the rock here was the most broken and in poorest structural condition. Greatest change in velocity between preblast and postblast condition, however, occurred in the stemming region (Fig.9). The stemming zone was a region of higher velocity and more intact rock (based on RQD results) in the preshot core, and the greater change in velocity in the stemming region is interpreted to mean that the rock underwent greatest structural change here. The likely cause of the structural change in the stemming region was the lifting and doming effect of the blast. The comparatively small change in velocity at depth below 115 ft suggests that blast damage extended only a small distance below the powder column.

Anisotropy factor

The anisotropy factor calculated from the range in travel-time at each depth increment fluctuated irregularly with depth (Fig.5). In an isotropic, homogeneous rock, the anisotropy factor would be zero. In a uniform anisotropic rock, the anisotropy factor would be a constant. Thus, the large fluctuations in anisotropy factor in the rock from the Duval site indicated that this rock is nonuniformly anisotropic. Velocity anisotropy in this case was caused mainly by preferred orientation of partially welded or open fractures. In the preshot core, such fractures could be seen cutting across

TABLE IV

Comparison of velocity, RQD, SQD, Y, and compensated velocity in the preblast and postblast drill core

Depth (ft)	Preblast*[1]					Postblast*[2]				
	velocity (km/sec)	RQD (%)	SQD (%)	Y (GN/m^2)	compensated velocity (km/sec)	velocity (km/sec)	RQD (%)	SQD (%)	Y (GN/m^2)	compensated velocity (km/sec)
5— 15	4.03	47	66	40.6	2.62	3.51	28	57	30.8	2.27
15— 25	4.56	59	74	52.0	2.99	4.00	20	65	40.0	2.22
25— 35	4.37	47	71	47.7	2.68	3.76	19	19	35.3	2.20
35— 45	4.12	43	67	42.4	2.57	4.06	21	66	41.2	2.24
45— 55	3.78	37	62	35.7	2.42	3.74	14	61	35.0	2.14
55— 65	3.73	28	61	34.8	2.30	3.39	8	55	28.7	2.07
65— 75	3.65	21	60	33.3	2.21	3.32	11	54	27.6	2.09
75— 85	3.40	23	55	28.9	2.21	3.13	12	51	24.5	2.09
85— 95	3.49	35	57	30.4	2.35	3.45	14	56	29.8	2.12
95—105	3.73	36	61	34.8	2.40	3.55	12	58	31.5	2.11
105—115	3.65	31	60	33.3	2.33	3.45	21	56	29.8	2.19
115—120	3.85	40	63	37.0	2.48	3.77	38	62	35.5	2.43
Mean values	3.86	37	63	37.6	2.46	3.59	18	58	32.5	2.18

*[1] Averaged from boreholes 1—3.

*[2] Averaged from boreholes 4—9.

TABLE V

Comparison of preblast and postblast velocities

Depth (ft)	Preblast BH 1–3 (km/sec)	Postblast BH 4–9 (km/sec)	Difference	Percent decrease
5– 15	4.03	3.51	−0.52	14.8
15– 25	4.56	4.00	−0.56	14.0
25– 35	4.37	3.76	−0.61	16.2
35– 45	4.12	4.06	−0.06	1.5
45– 55	3.78	3.74	−0.04	1.1
55– 65	3.73	3.39	−0.34	10.0
65– 75	3.65	3.32	−0.33	9.9
75– 85	3.40	3.13	−0.27	8.6
85– 95	3.49	3.45	−0.04	1.2
95–105	3.73	3.55	−0.18	5.1
105–115	3.65	3.45	−0.25	7.2
115–120	3.85	3.77	−0.08	2.1
Mean	3.86	3.59	−0.27	7.5

the core at low angles (< 45°) with the core axis. Therefore, propagation velocity normally is low in a path perpendicular to the crack and high in the plane of the crack. The anisotropy was found to be erratic and often large in both the preblast and postblast cores. Postblast results tended to be more erratic than the preblast ones, however, indicating induced blast damage. Because the rock at the Duval test site was initially very fractured, changes in anisotropy factor are not as distinct and indicative of blast damage as they might be for initially uniform, intact rock.

Seismic quality designation

Seismic quality designation was calculated using a modal analysis (Table VI) for the Duval test-site rock and an estimated aggregate average for the rock based on the mineral Voigt-Reuss-Hill (VRH) averages as given in the tables of Simmons (1965). Since aggregate average velocities for chlorite and sericite are unlisted, they were assigned the value 5.78 km/sec given for muscovite. Sericite is mineralogically similar to muscovite, and chlorite comprises only 0.2% of the rock by volume; thus error introduced into the calculation of the aggregate average velocity for the rock should not be great. Using eq. 1, the VRH aggregate average velocity is calculated to be 6.13 km/sec. This velocity considerably exceeded even the highest velocities recorded in the Duval test site core. Although only one modal analysis was available from the rock core for the calculation of the aggregate average velocity, the comparatively high velocities of the mineral constituents (Table VI) indicate that aggregate average velocity would not change much for minor changes in modal

values 3.86 37 63 37.6 2.46 3.59 18 58 32.5 2.18

*1 Averaged from boreholes 1–3.
*2 Averaged from boreholes 4–9.

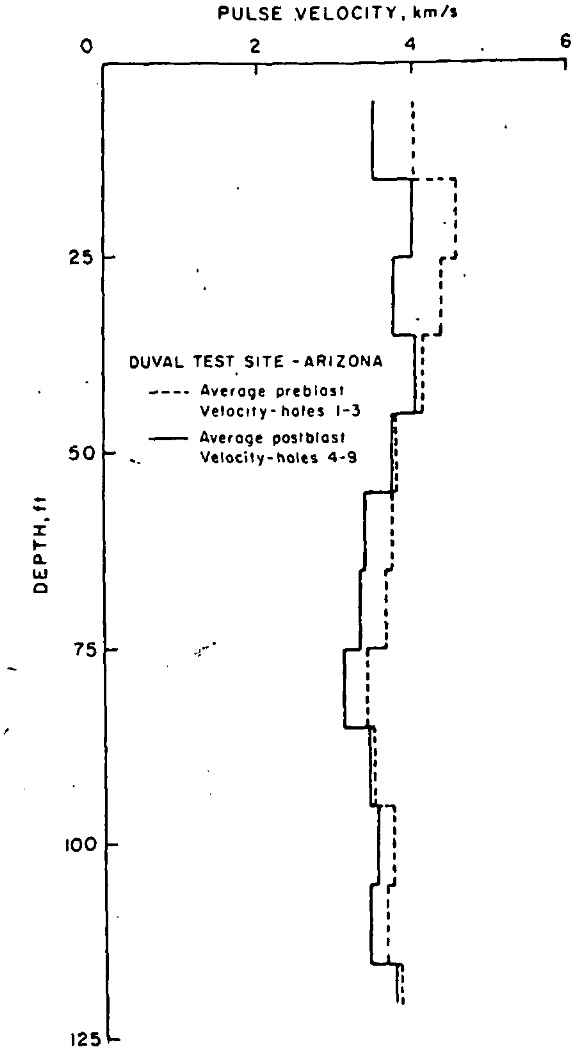

Fig. 8. Pulse velocity log comparing preshot to postshot velocities.

composition. Thus, minor changes in modal analysis would not extensively alter the SQD results.

SQD results for the preblast and postblast core follow trends and indicate fragmentation damage in much the same way as the pulsed velocity results. The main difference is that the SQD value is normalized to the velocity in an ideal unfractured rock of the same composition; hence, results can be interpreted in terms of rock quality. Deterioration in rock quality following blasting is shown in the reductions in mean SQD from 63 to 58% and in RQD from 37 to 18% (Table IV). Based on the earlier breakdown comparing SQD t velocities.

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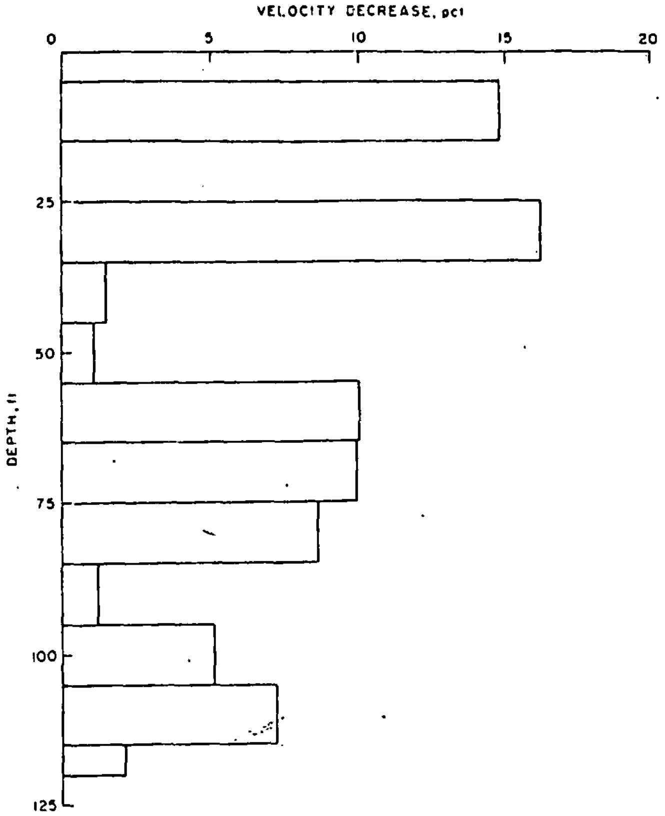


Fig. 9. Percent decrease in pulse velocity with depth after blasting.

TABLE VI

Mineral aggregate average velocities

Mineral	Percent by volume	VRH velocity (km/sec)
Plagioclase	66.6	6.22
Orthoclase/microcline	14.0	6.01
Quartz	11.2	6.31
Biotite	5.0	5.26
Sericite (muscovite)	3.2	5.78
Chlorite	0.2	—

and RQD to rock quality, SQD results ranged from fair to poor, and RQD results from fair to very poor for the quality of the preblast rock. In the postblast rock, rock quality was classified as poor at all depth intervals for SQD, with only one borderline exception, and quality ranged from poor to very poor for RQD. The greater change in RQD than in SQD following blasting was interpreted to mean that comparatively greater damage was

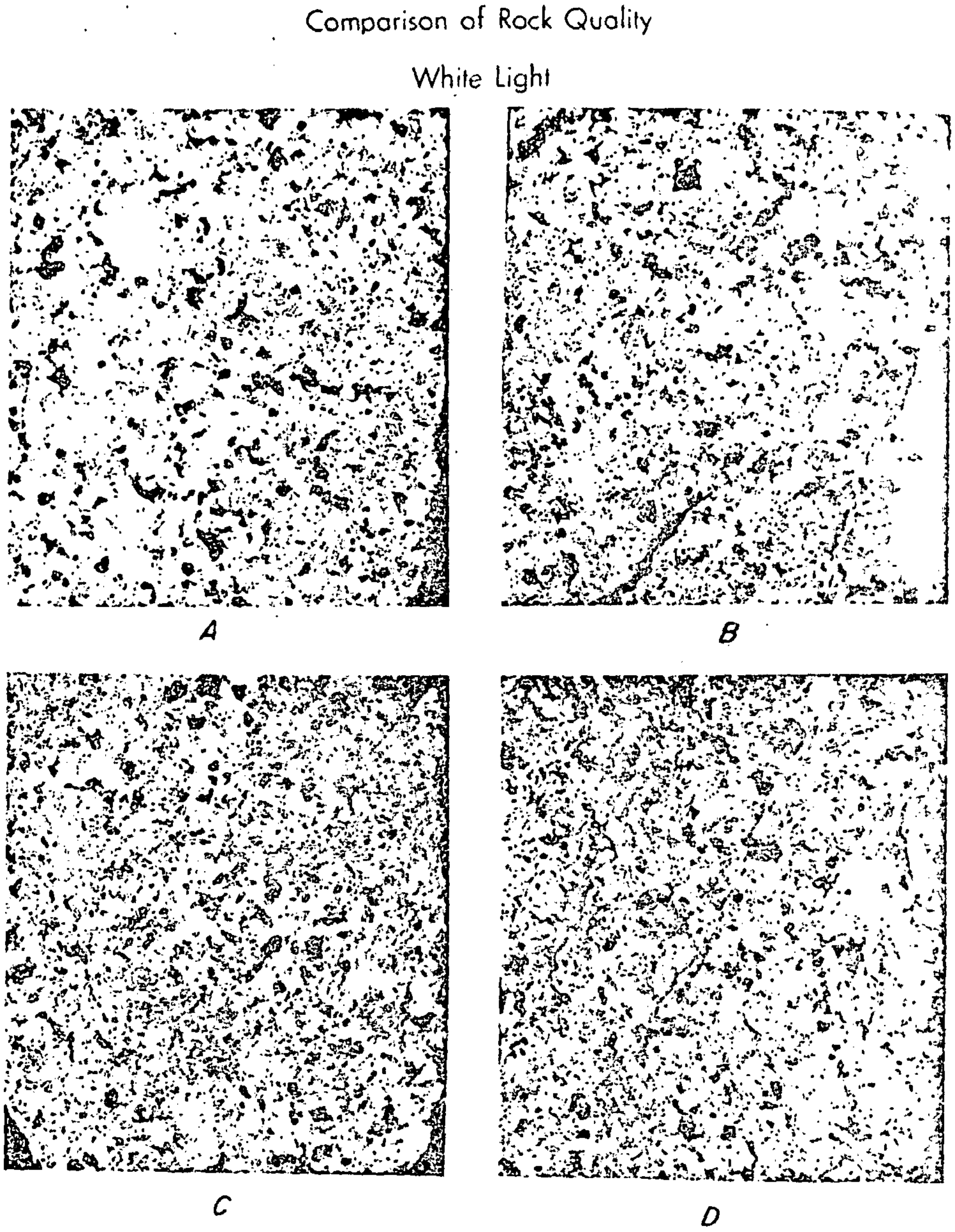
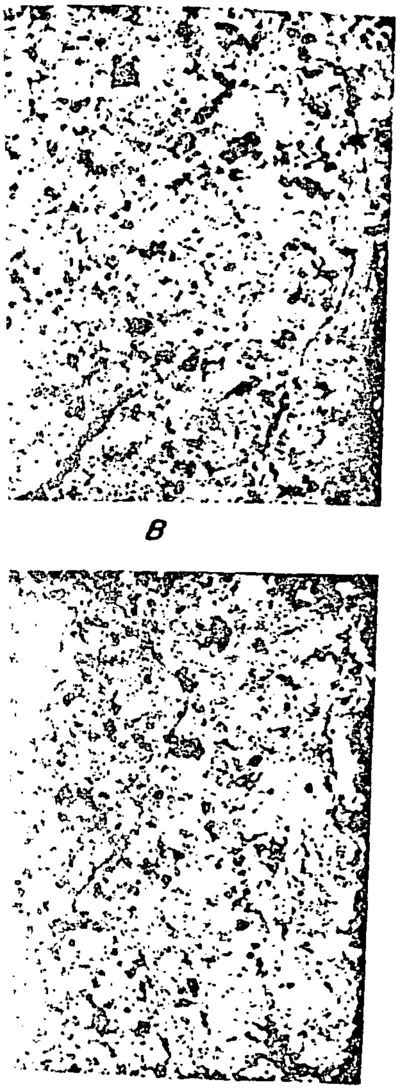


Fig.10. Comparison of rock quality in normal light for SQD of *A*, 77%; *B*, 66%; *C*, 56%; and *D*, 36%.

induced at the macrofracture than at the microfracture scale. That is, RQD sensed comparatively larger fractures that completely severed the core into smaller segments, whereas the SQD determined in small intact specimens sensed mainly microcracks. Both macrofracture and microfracture damage could be important in the leaching process since the larger interconnected



QD of *A*, 77%; *B*, 66%; *C*, 56%;

acture scale. That is, RQD
tely severed the core into
small intact specimens
nd microfracture damage
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fractures permit easy percolation of the acid solutions through the rock from injection to recovery wells along zones of mineralization associated with macro-structures, and the microcracks permit entry of the acid solutions into zones of disseminated mineralization in competent areas of the rock, resulting in more rapid dissolution in the rock.

Samples were taken from the recovery core to examine the rock structure at different values of SQD. The highest value of SQD for the core was 77%, representing fair rock quality. Since no samples characterizing the good or excellent rock quality categories could be obtained from any of the core, samples were obtained at SQD values of 77, 66, 56, and 36%, representing rock qualities respectively in the upper-fair, lower-fair, poor, and very poor categories. Core at these localities was sectioned in half parallel to the core axis and then surface ground to remove saw marks. One half was photographed in ordinary white light (Fig.10), and the other half was treated with a dye penetrant and photographed under black (ultraviolet) light (Fig.11). Specimens were photographed using the same exposure times and lens openings. The dye penetrant was absorbed into fractures, pores, and altered zones in the specimens, sometimes making entire zones glow under the black light. Wave paths corresponding to the velocities used for computing SQD cross the specimen diameter at its midheight. Figs.10 and 11 show that along the wave path, there is a progression from a more fresh, less altered, less fractured rock in *A* to a badly decomposed, highly altered and fractured rock in *D*. Although specimen *A* appears more fresh and less altered than the other samples, it has some alteration, a few minor cracks, and a fair amount of small pores, some of which could have been caused by plucking out material from altered zones during specimen preparation. Therefore, its designation of rock quality based on SQD of "upper-fair" appears appropriate, since its visible quality would not seem to warrant classification in a good or excellent category. Likewise, the designated rock quality from SQD appears appropriate for specimens *B*, *C*, and *D* based on the cursory physical or petrographic examination. The visible fractures and interconnected pores in specimens *C* and *D*, and possibly even *B*, suggest that the rock might respond well to in-situ leaching. Further work may establish that SQD indices of less than, say, 60—65% might indicate rock sufficiently fractured for successful in-situ leaching, assuming the fractures create adequate permeability for leach liquid percolation.

SQD could be determined also in downhole or other seismic surveys and could have an important advantage over RQD in such cases since core recovery would not be required.

Stiffness modulus

Stiffness modulus calculated by eq. 2 is a sensitive indicator of changes in structural condition of the rock since it changes as a function of the velocity squared (Table 4). Furthermore, the stiffness modulus indicates dynamic stress-strain behavior in much the same way as Young's modulus, this being apparent from eq. 3. Stiffness modulus is calculated here using the average

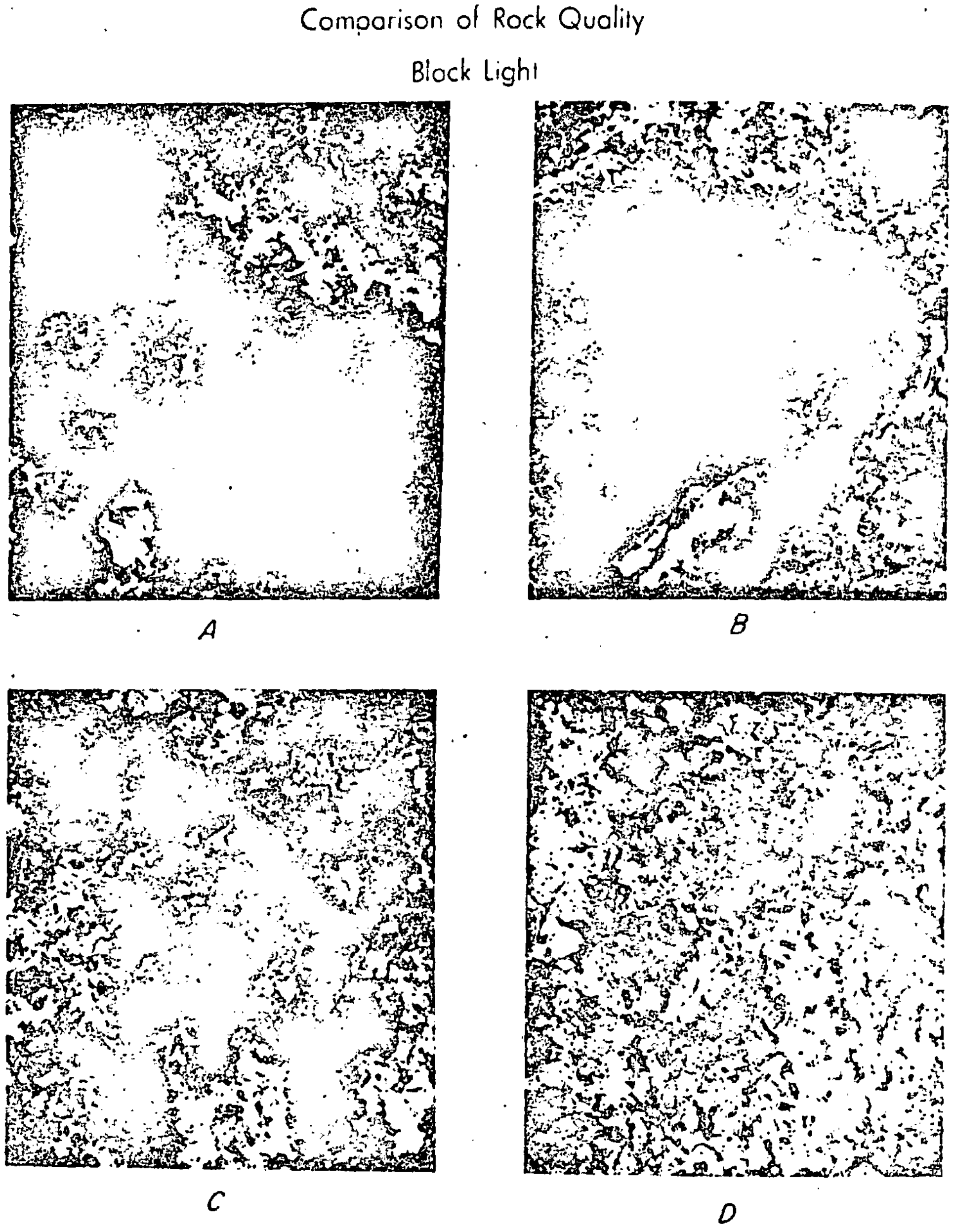

Fig.11. Comparison of rock quality in black light for SQD of *A*, 77%; *B*, 66%; *C*, 56%; and *D*, 36%.

density value of 2.50 gm/cm^3. A more accurate assessment of Y with depth could be obtained by determining density with depth at the same increments as velocity, either by measurements on the rock core or in-situ with density logging surveys.

On the basis of statistical correlation, stiffness modulus can be used to

Quality

QD of *A*, 77%; *B*, 66%; *C*, 56%; and

assessment of *Y* with depth
depth at the same increments
core or in-situ with density

s modulus can be used to

infer static Young's modulus (Deere and Miller, 1966, p.127), and even compressive strength (Judd and Huber, p.636). These relationships implied that the rock at the Duval test site on the average would have low static Young's modulus, less than roughly 30 GN/m^2 ($\simeq 4.0 \cdot 10^6$ psi), and low compressive strength, less than about 69 MN/m^2 ($1 \cdot 10^4$ psi).

Compensated velocity

Compensated velocity calculated by eq. 4 takes into account the fraction of pieces of intact core exceeding 4 inches against the remaining fraction of broken material and is calculated at 10-ft intervals. Both macrofracturing and microfracturing effects were taken into account in the compensated velocity. Velocities fell considerably below those determined on the intact pieces (Table IV). Trends were similar, however, in comparing preblast and postblast values; that is, velocities were lower in the postblast core with greatest change occurring in the top 40–50 ft. Again velocities were lowest in the powder column region, suggesting that most severe blast damage occurred in that zone.

In-situ velocity logs probably would have velocities between that of compensated velocity and that for the intact pieces, depending on the in-situ contact between pieces, and on the moisture condition. Alternatively, compensated velocity might have been calculated from the fraction of recovered core over a particular interval with slightly different results.

Effects of blasthole spacing

Comparing pulse velocity in the preblast cores with the postblast cores in the same vicinity at different blasthole spacings (Table VII), mean velocity was found to decrease only 3% for the 25-ft spacings as opposed to a 12- and 14-% decrease for the 20- and 15-ft spacing, respectively. Mean pulse velocity for postblast core BH 4 actually was slightly higher than for preblast core BH 3 (Table III). The other postblast cores, BH 7 and BH 9, showed only moderate reduction in mean velocity over the preblast condition, notwithstanding that BH 9 was drilled closer to one of the blastholes than any other recovery core (Fig.1). These results suggested that the rock blasted at the 25-ft blasthole spacing was not as effectively broken up as the 20- and 15-ft spacings. The reduction in mean velocity of nearly the same magnitude for both the 20- and 15-ft spacings, on the other hand, indicated that the rock underwent roughly the same degree of blast damage, at least in terms of microstructural damage, at both of these blasthole spacings.

CONCLUSIONS

The determinations of longitudinal pulse velocity, anisotropy factor, RQD, seismic quality designation (SQD), stiffness modulus, and compensated velocity for core recovered before and after blasting at the Duval test site all

TABLE VII

Comparison of pulse velocity in pre- (BH 1—3) and postblast (BH 4—9) cores at different blasthole spacings

Depth (ft)	25-ft spacing				20-ft spacing				15-ft spacing			
	BH 3 (km/sec)	BH 4, 7, 9 (km/sec)	Difference	Percent decrease*[1]	BH 2 (km/sec)	BH 5, 6 (km/sec)	Difference	Percent decrease	BH 1 (km/sec)	BH 8 (km/sec)	Difference	Percent decrease
5— 15	3.46	3.71	—0.25	+7	3.74	3.04	0.70	23	4.88	3.87	1.01	26
15— 25	4.02	3.85	0.17	4	5.17	3.90	1.27	33	4.51	4.68	—0.17	+4
25— 35	4.60	3.96	0.64	16	3.99	3.70	0.29	8	4.54	3.31	1.23	37
35— 45	3.97	4.26	—0.29	+7	4.22	3.98	0.24	6	4.16	3.64	0.52	14
45— 55	3.70	3.66	0.04	1	3.67	4.06	—0.39	+10	3.98	3.34	0.64	19
55— 65	3.58	3.85	—0.27	+7	3.78	3.00	0.78	26	3.82	2.80	1.02	36
65— 75	3.86	3.65	0.21	6	3.69	3.37	0.32	9	3.41	2.26	1.15	51
75— 85	3.35	3.24	0.11	3	3.41	2.98	0.43	14	3.43	3.11	0.32	10
85— 95	3.67	3.70	—0.03	+1	3.07	2.92	0.15	5	3.74	3.79	—0.05	+1
95—105	4.11	3.53	0.58	16	3.71	3.34	0.37	11	3.38	3.04	0.34	11
105—115	3.98	3.51	0.47	13	3.96	3.65	0.31	8	3.01	3.13	—0.12	+4
115—120	3.92	3.83	0.09	2	2.75	3.49	0.26	7	3.89	3.94	—0.05	+1
Mean values	3.85	3.73	0.12	3	3.85	3.45	0.40	12	3.89	3.41	0.48	14

*[1] Percent decrease = $\frac{\overline{V}_{pre}-\overline{V}_{post}}{\overline{V}_{post}}$ 100; increase is indicated by + sign.

Mean values	3.85	3.73	0.12	3	3.85	3.45	0.40	12	3.89	3.41	0.48	14

*' Percent decrease = $\frac{\overline{V}_{pre}-\overline{V}_{post}}{\overline{V}_{post}}$ 100; increase is indicated by + sign.

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showed the effects of blast damage in different ways and with different sensitivity. The acoustic core logging data gave information beneficial in interpreting blast damage and structural quality of the rock. Velocity changes in recovery core indicated the overall structural deterioration caused by blast damage mainly at the microstructural damage level. The compensated velocity provided an overall estimate of mean velocity over a core run taking into account the fraction of a badly fractured, crushed, or nonrecoverable core. Anisotropy factor indicated preferred orientation in fracturing and changes in uniformity with depth. The SQD gave an index useful for indicating change in structural quality of the rock with baseline reference to an ideal, unfractured material of the same composition. Stiffness modulus showed a high degree of sensitivity to changes in structural condition and provided information on stress-strain and even strength behavior.

The data showed that the rock at this site initially was badly weathered and broken with structural quality designated as fair to poor, compared with hypothesized fresh, unfractured rock of the same composition. Reduction in pulse velocity, RQD, SQD, stiffness modulus, and compensated velocity showed that the structural condition of the rock was poorest after blasting in the powder column region (60—110 ft). Rock in the stemming region (0—60 ft) underwent greater change from the blast; however, initially the rock here was in better condition than in the powder column region. The effects of blasting diminished rapidly at depths below the base of the powder column, becoming small at depth of 115—120 ft. RQD showed greater reduction (37—18) than SQD (63—58) suggesting comparatively greater damage was induced at the macrofracture scale sensed by RQD than at the microfracture scale sensed by SQD. Closer correspondence might have been observed between RQD and SQD either if (1) RQD had been measured at a smaller scale, say, considering the length of all pieces ⩾ 1 inch, or (2) velocities had been determined in larger diameter core containing macrofractures.

Comparison of data at the different blasthole spacings indicated that the rock blasted at the 25-ft blasthole spacing was not as effectively broken up as at the 20- and 15-ft spacings. Because of the highly fragmented, poor structural condition of the rock after blasting, the rock was indicated to be suitable for in-situ leaching, at least at the 20- and 15-ft blasthole spacings, and even in some zones in the rock at the 25-ft blasthole spacing.

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THE ADVANTAGES OF CONDITIONING AN OREBODY WITH A CHLORIDE SOLUTION BEFORE IN SITU URANIUM LEACHING WITH A CARBONATE SOLUTION

by Daryl R. Tweeton, U.S. Bureau of Mines; Terry R. Guilinger,
W. Michael Breland, and Robert Schechter, U. of Texas

This paper was presented at the 55th Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, held in Dallas, Texas, September 21-24, 1980. The material is subject to correction by the author. Permission to copy is restricted to an abstract of not more than 300 words. Write: 6200 N. Central Expwy., Dallas, Texas 75206.

ABSTRACT

Laboratory experiments conducted by the University of Texas at Austin as part of a research contract funded by the U.S. Bureau of Mines indicate that conditioning an orebody with a chloride solution prior to carbonate leaching offers two advantages. First, the permeability loss occurring upon the injection of the carbonate solution is reduced. This effect is tentatively attributed to a reduction in precipitation of calcium carbonate. Calcium chloride is soluble, so calcium can be flushed out of the orebody. Second, the great difficulty of complying with current regulations concerning restoration of groundwater quality after leaching with ammonium carbonate may be avoided because the substitution of potassium carbonate for ammonium carbonate may be made economically feasible. Flushing the orebody with potassium chloride before leaching satisfies cation exchange sites with potassium from relatively cheap potassium chloride, thereby reducing the consumption of the more expensive potassium carbonate. Field tests are planned.

INTRODUCTION

The Bureau of Mines Twin Cities (Minnesota) Research Center is conducting research on various aspects of in situ uranium leaching. Discussions with leaching companies have shown that meeting environmental regulations involving restoration of groundwater quality following leaching is a concern. The primary question currently revolves around restoration following leaching with ammonium carbonate. The permissable concentration of ammonium ions in the postleach groundwater is very low. In Wyoming, the limit is 0.5 ppm for water for domestic use. In Texas, the limit is the preleach concentration which is generally less than 0.1 ppm. Restoration to meet these standards has not been demonstrated. The Bureau of Mines has funded research to determine whether substituting leach solutions that present less restoration problems than ammonium carbonate is technically and economically feasible.

The research to be described was conducted at the University of Texas at Austin, funded through a Bureau of Mines contract. The principal investigator is Prof. Robert Schechter. The investigators primarily responsible for developing the chloride preflush are Mr. Terry Guilinger and Dr. Michael Breland.

Past studies have reported on the extent of ammonium ion retention (1) and on methods for hastening the release of ammonium ions with a flushing fluid of a high ionic strength (2). The current report takes an approach different from trying to find a way of making ammonium carbonate acceptable. It suggests that using potassium carbonate, which is now considered too expensive, could be made economically feasible by flushing the formation with potassium chloride before leaching.

The cost is reduced because much of the consumption of leach solution is by cation exchange, so satisfying cation exchange sites with potassium from relatively cheap potassium chloride before leaching would substantially reduce the consumption of expensive potassium carbonate during leaching.

An additional benefit is that clogging tentatively attributed to calcium carbonate precipitation is reduced. Calcium chloride is much more soluble than calcium carbonate, so much of the calcium can be flushed out of the formation before leaching begins.

ALTERNATE LIXIVIANTS

Ammonium carbonate-bicarbonate is currently the most widely used lixiviant. This fact suggests that alternatives have disadvantages or limitations. The suggestion is correct, and they will be discussed below. Oxidizers such as hydrogen peroxide or oxygen must be used with all of these lixiviants.

Sulfuric acid can be used only where the concentration of acid-consumers such as carbonates is not so great as to consume too much acid or generate too much gas. However, where it can be used, it will generally extract more uranium than carbonate lixiviants. An additional

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References and illustrations at end of paper.

advantage is that hydrogen peroxide does not decompose as quickly in acids as in bases.

Carbon dioxide has been considered by many companies and tried by a few. It forms carbonic acid, which will combine with oxidized uranium to form anionic complexes, just as other carbonate lixiviants do. Little published data is available, but discussions with those who have tried it suggest it does not leach as effectively as ammonium, potassium, or sodium carbonate-bicarbonate.

Sodium carbonate-bicarbonate tends to swell clays. Swelling can be so severe that the fluid flow is essentially blocked. It can be used in some deposits where the natural sodium content is high or where the concentration of swelling clay is very low. Some operators have stated that swelling can be minimized by keeping the pH near neutral.

Potassium carbonate-bicarbonate has several technical advantages. It is normally in preleach groundwater in significant concentrations, and is not considered harmful. Therefore, one would expect that restoration requirements would not be as stringent as those for ammonium carbonate-bicarbonate. It does not swell clays as sodium carbonate-bicarbonate does, and it does not generate gas when it contacts carbonates, as acid does. The disadvantage is its high cost, about five times as high for potassium bicarbonate as for ammonium bicarbonate on a molar basis. Operators have considered it too expensive to use. The chloride preflush may make it economically feasible.

THE CHLORIDE PREFLUSH

To be useful, the chloride preflush must provide the claimed advantages without reducing the uranium recovery. Accordingly, column leaching tests were conducted to measure the effect of the preflush on uranium leaching, permeability, and carbonate consumption.

Experimental Procedure

Three different ores were used, designated A, B, and C. All were poorly consolidated sandstone ores. Ore A was from Wyoming and had a cation exchange capacity (CEC) of 12.2 meq/100g. Its carbonate content was quite low, less than 0.1 pct. Ores B and C were from Texas and had CEC's of 11.3 and 9.8 meq/100g, respectively. Each ore was sifted through a sieve with 0.59 mm openings to remove large particles and then blended until uniform.

The leach column was a Hassler cell. Ore was held in a rubber sleeve. With ore A, the column was 1.75 cm in diameter and 30 cm long, and the confining pressure was 2070 kPa (300 psi). With ores B and C, the column was 2.5 cm in diameter and 10 cm long, and the confining pressure was 690 kPa (100 psi).

After the ore was packed, the column was evacuated. With ore A, groundwater from the site containing about 300 ppm sodium and 60 ppm calcium was then pumped through the column. With ores B and C, simulated groundwater containing 200 ppm sodium chloride and 150 ppm calcium chloride was used. The pressure drop across the column was continuously monitored by transducers connected to chart recorders. After the permeability stabilized, the column was again evacuated, and the chloride or carbonate solution pumped through. All pumping was done with a piston-cyclinder pump that provided 1000 ml/stroke so no pulsing occured.

The concentrations of chloride preflush were about 0.1 molar. With ore A, the carbonate concentrations of the leach solutions were 2.0 g/l, and the initial pH values were all about 10.2. The solutions initially contained 0.2 g/l hydrogen peroxide. With ores B and C, the carbonate solutions were 0.1 molar, which is 13.8 g/l for potassium carbonate and 9.6 g/l for ammonium carbonate. The initial pH values were about 11.3 for potassium carbonate and 8.6 for ammonium carbonate. No hydrogen peroxide was added. The effluent was collected and the solutions were analyzed for various cations, anions, and pH.

Uranium Recovery

The percentage of uranium leached out of the cores with and without the chloride preflush was determined for ore A, and the results are shown in table 1. The initial uranium content was calculated by fluorometric analysis of the blended ore. The amount of uranium removed was calculated by fluorometric analysis of the leached core and also from the measured volume and uranium concentration of the effluent solution.

The data show that the chloride preflush did not reduce the uranium recovery. The ammonium carbonate data suggest that the chloride preflush increased recovery. However, more data would be required before a claim that the chloride preflush often increases recovery would be justified.

Permeability

Permeability data for all three ores are presented in table 2. The table lists the ratios of final permeability obtained near the end of each test, after the permeability had stabilized, to the stabilized permeability during the groundwater flow near the start of each test. Results separated by commas are replications. With ore A, the tests involved 6 to 10 pore volumes of groundwater, followed by 3 pore volumes of chloride solution (if used), and then a final permeability measured after 30 pore volumes of carbonate solution. For ores B and C, the tests involved about 18 pore volumes of simulated groundwater, 22 pore volumes of chloride solution (if used), and then a final permeability measured after 20 to 30 pore volumes of carbonate solution.

The data show that the chloride preflush significantly decreased the most serious permeability losses. For both ammonium and potassium carbonate solutions, the permeability loss was less following the chloride preflush than without it. The effect is the largest where it is most needed, that is, where the permeability ratio without the preflush is lowest.

The reduction in permeability loss is attributed to a reduction in calcium carbonate precipitation. Ammonium or potassium tends to drive calcium off clays by ion exchange. The calcium may be transported some distance in a supersaturated condition, but causes clogging when calcium carbonate does precipitate. The clogging can be especially troublesome near production wells. As the leach solution approaches a production well the pressure decreases and some carbon dioxide may go out of the solution, causing calcite to precipitate as the pH rises.

The data suggest that ammonium carbonate is often less damaging than potassium carbonate, but the variability in the ratios and differences in pH do not allow a firm conclusion. The key facts are that whichever of the two leach solutions is chosen, the chloride preflush helps prevent permeability loss, and that permeability is at least as good for potassium carbonate following a preflush as for ammonium carbonate without a preflush.

Carbonate Consumption And Costs

The effectiveness of the chloride preflush in reducing the consumption of potassium carbonate was calculated for ore A. It was calculated from the measured concentrations of potassium and carbonate in the known volumes of effluent of carbonate solution with and without a chloride preflush. When potassium carbonate followed a potassium chloride preflush, the potassium concentration in the effluent carbonate solution stayed at or above the concentration in the feed. Thus, no potassium was being consumed during the carbonate leaching. However, the carbonate concentration in the effluent was lower than in the feed, so some carbonate was being consumed. The carbonate consumption without the preflush was 14.0 meq/100g ore, and was 2.4 meq/100g ore following the preflush. Thus, for this ore, the consumption of potassium carbonate could be reduced 83 pct by using a potassium chloride preflush.

Now consider the reduction in cost of leach solution. The material costs for potassium, ammonium and sodium carbonate, bicarbonate, and chloride are shown in table 3. They were determined from published prices (3) and by contacting vendors. The costs of ammonium carbonate and bicarbonate were calculated assuming that they were made by combining anhydrous ammonia and carbon dioxide. These costs do not include freight, labor, or equipment for handling the chemicals. Assume that potassium bicarbonate is being considered, that a chloride preflush reduces the potassium bicarbonate consumption by 83 pct, and that the reduced consumption of the potassium bicarbonate must be made up by the consumption of potassium chloride on a molar equivalent basis. Then the effective cost of the potassium bicarbonate is (.83) ($3.29/kg-mole) plus (.17) ($30.65/kg-mole) equals $7.94/kg-mole. This is still 1.4 times as expensive as ammonium bicarbonate, so savings in restoration costs would have to be realized to offset the extra leach solution cost. Under the current regulations governing restoration, such savings appear probable.

The cost data also suggest that using a sodium chloride preflush before leaching with sodium bicarbonate could reduce expenses, and should be considered where the formation is amenable to sodium. An ammonium chloride preflush before leaching with ammonium bicarbonate would increase costs because ammonium chloride is more expensive than ammonium bicarbonate. A thorough site specific economic comparison should include not only material costs of the chemicals, but also factors such as freight, labor and equipment for handling the chemicals, including the handling the calcium-rich solutions produced during the preflush, and the possible effects of chloride on the loading ability of resins.

Restoration Flushing

It should be pointed out that potassium ions, like ammonium, are held tightly by clays. The number of pore volumes of groundwater required to lower the concentration by a given amount is not necessarily any smaller for potassium than for ammonium ions. The advantage of using potassium stems from the very low concentrations of ammonium ions allowed in the groundwater after restoration, not from fundamental geochemical differences.

The calcium-rich solution produced during the chloride preflush may be useful during restoration. Depending on the post-restoraton limits set for potassium, it may be advisable to inject a solution of high ionic strength during part of the restoration flushing to facilitate removal of potassium by ion exchange. To avoid creating new restoration problems, the primary cation in the high ionic strength solution should be harmless and found in fairly high levels in natural groundwater. Thus, the calcium-rich solution produced during the chloride preflush appears ideal for that purpose.

CONCLUSIONS

Laboratory experiments have shown that flushing ore with a chloride solution prior to leaching with a carbonate solution reduces permeability losses, and does not reduce the uranium recovery. Experiments showed that if potassium chloride preceeds potassium carbonate, the consumption of expensive potassium carbonate is greatly reduced. Therefore, the substitution of potassium carbonate-bicarbonate for ammonium carbonate-bicarbonate may be economically feasible, thereby avoiding the restoration problems associated with ammonium carbonate-bicarbonate.

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Table 1 Pct of Uranium Recovery, With and Without Chloride Preflush

		Pct uranium recovered	
		With preflush	Without preflush
Ammonium carbonate	From uranium left in ore	85	61
	From effluent concentrations	82	64
Potassium carbonate	From uranium left in ore	83	82
	From effluent concentrations	87	83

Table 2 Ratios of Final Permeability to Initial Permeability, With and Without Chloride Preflush

		Final permeability/initial permeability	
		With preflush	Without preflush
Ammonium carbonate	Ore A	0.89	0.43
	Ore B	0.78, .76, .84	0.42, .37, .53, .25
	Ore C	0.77, .67	0.76, .87
Potassium carbonate	Ore A	0.74	0.65
	Ore B	0.58, .68	0.21, .26, .36
	Ore C	0.68, .80	0.45, .46

Table 3 Prices of Chemicals for Carbonate and Bicarbonate Lixiviants and Chloride Preflushes

	Dollars/kg-mole	Dollars/lb-mole
Potassium carbonate	60.86	27.60
Ammonium carbonate	9.00	4.08
Sodium carbonate	8.95	4.06
Potassium bicarbonate	30.65	13.90
Ammonium bicarbonate	5.60	2.54
Sodium bicarbonate	20.56	9.32
Potassium chloride	3.29	1.49
Ammonium chloride	32.88	14.92
Sodium chloride	2.01	0.91

Ammonium Carbonate Pressure Leaching of Uranium Ores

By B. G. Langston, R. D. Macdonald, and F. M. Stephens, Jr.

WITH the development of uranium ores that contain substantial amounts of acid-consuming compounds, the alkaline leach has become an attractive method for extraction. Considerable work has been done on both atmospheric and pressure-leaching with aqueous solutions of sodium carbonate and sodium bicarbonate as the lixiviants.[1,2,3] For the treatment of uranium-bearing limestones and other high-lime (CaO) ores, the sodium carbonate leach has proven attractive because it avoids the high reagent consumption incurred by the reaction of sulfuric acid with lime. In addition, the corrosion problems with sodium carbonate are negligible as compared with those encountered in the acid-leach system. The sodium carbonate leach, however, does not yield as high an extraction of the uranium as the acid leach and is not attractive for economic reasons when treating ores that are high in sulfates or sulfides.

Although in the sodium carbonate leach process the bulk of the sodium carbonate can be reclaimed and returned to the system, some reagent is consumed by contact with gypsum, pyrite, and silica. Ammonium carbonate would have no advantage over sodium carbonate with respect to the consumption resulting from the presence of gypsum or pyrite in the ores, but consumption resulting from the reaction of sodium carbonate with silica would be eliminated. It was believed that steam stripping of the ammonium carbonate leach solutions to precipitate the uranium and recover the ammonia would give the process an advantage over the sodium carbonate leach, where sodium hydroxide must be supplied to precipitate the uranium.

Chemistry of the Process

If it is assumed that dissolution of uranium in the ore by an ammonium carbonate solution forms ammonium uranyl carbonate, the following equations express the chemistry of the process:

$$9(NH_4)_2CO_3 + U_3O_8 + 1/2O_2 + 9H_2O \rightarrow 3[(NH_4)_4 \cdot UO_2(CO_3)_3 \cdot 2H_2O] + 6NH_4(OH) \quad [1]$$

$$NH_4(OH) + NH_4HCO_3 \rightarrow (NH_4)_2CO_3 + H_2O \quad [2]$$

$$(NH_4)_4UO_2(CO_3)_3 + \text{heat} \rightarrow 4NH_3(\text{gas}) + 3CO_2(\text{gas}) + UO_3 \cdot 2H_2O(\text{ppt}) \quad [3]$$

Because, at atmospheric pressure, ammonium uranyl carbonate decomposes at 212°F, pressure is utilized in the leaching step to minimize the loss of ammonia and carbon dioxide. In addition, to obtain maximum extraction of the uranium from many of the ores, which contain both quadrivalent and hexavalent uranium, pressure facilitates oxidation to the readily soluble hexavalent state in the presence of free oxygen. Although potassium permanganate is an effective oxidizing agent in the ammonium carbonate pressure leach, air is equally effective and much less expensive.

Equation 2 is of interest because ammonium bicarbonate is not required in an ammonium carbonate leach, as is sodium bicarbonate in a sodium carbonate leach. The formation of free ammonium hydroxide within the concentrations obtained in this study had no adverse effect on the dissolution of uranium.

The precipitation of the uranium from the pregnant solution, Equation 3, involves passing steam through the solution, heating it to approximately 212°F, and serving as a sweeping gas to aid in the removal of ammonia and carbon dioxide. Air can be employed as a substitute for steam as a sweeping gas.

The Integrated Plant

A series of five pressure-leaching towers 10 ft high with an inside diameter of 4 in. were fabricated for study of the process variables. Fig. 1 is a photograph of the towers and the countercurrent washing and precipitation tower that was added later to give an integrated plant for evaluation of the unit processes required for both the extraction and recovery of uranium.

Fig. 2 is a flowsheet of the process as visualized for a pilot-plant operating at a feed rate of 12 tons per hour. Although other modifications of the flowsheet might be employed, for the purpose of demonstrating an integrated system, one utilizing a dry grind is shown.

Development of the Leaching Conditions

To determine the amenability of high-lime ores to an ammonium carbonate pressure leach for the extraction of uranium, temperature, pressure, strength of solution, and the amount of oxidation required to convert the quadrivalent uranium to the hexavalent state were considered.

Nine different ores were studied either by small-scale testing or by operation of the pressure leaching towers, but the major emphasis was placed on three of the ores that contained varying amounts of lime (CaO). Table I gives the chemical analysis of these three ores.

Because over 85 pct of the uranium was present in the −200-mesh fractions when the ore was

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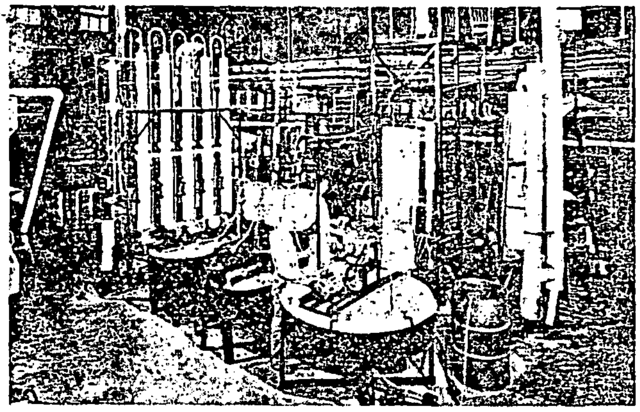


Fig. 1—Integrated plant for the extraction and recovery of uranium by the ammonium carbonate pressure-leach process.

ground to pass a 100-mesh screen, it was believed that grinding to a finer particle size would not materially affect the leaching characteristics of the ore. For most ores a slurry with a 50 pct pulp density was sufficient to prevent classification in the towers.

Temperature: A series of tests was run in the towers at temperatures of 185, 225, and 250°F. A pressure of 90 psig and a solution containing 98 g $(NH_4)_2CO_3$ and 54 g NH_4HCO_3 per liter were chosen arbitrarily, based on preliminary test runs in a batch autoclave. In addition, to provide for oxidation of any quadrivalent uranium in the ore, 1500 cu cm of air per min were passed through the towers. This was the smallest flow rate that could be maintained without plugging the air line with slurry. Fig. 3 shows the effect of temperature and time on the extraction of uranium by the ammonium carbonate leach. The primary effect of temperature was the rate of dissolution of the uranium. The leach temperature had little effect, if any, on the maximum extraction of uranium from the ore; in each case about 93 pct was extracted. However, as the temperature was increased from 185 to 250°F the time required for maximum extraction decreased from 375 to 150 min.

Pressure: A series of tests was run varying the pressure from 80 to 115 psig. A temperature of 225°F was chosen to obtain comparative data as to the effect of pressure on the dissolution of uranium, since at 250°F, approximately 92 pct of the uranium was extracted in Tower 1, representing a retention time of 75 min. Fig. 4 gives the data obtained and shows that, although pressure had little effect on the extraction, when extended retention periods were employed, pressure does affect the rate of dissolution of the uranium.

Although the data in Figs. 3 and 4 are believed to be typical of the relation between temperature, pressure, and the extraction of uranium, it is known that the position of the curves varies with each ore, depending probably on the mineralogical state of the uranium-bearing mineral. Fig. 5 shows a comparison of the performance of three ores run through the pressure leaching towers.

Oxidation with air and oxygen enriched air: Tests were run to determine the amount of air required to convert uranium to the hexavalent form. A temperature of 225°F, a pressure of 90 psig, and a solution containing 98 g $(NH_4)_2CO_3$ and 54 g NH_4HCO_3 per liter were employed and the air flow varied from 1500 to 6000 cu cm per min. Within this range, the amount of air passed through the towers had no effect either on the rate of dissolution of the uranium or the final extraction.

An analysis of the exhaust gases from the towers showed that they contained 17 pct O_2 even at the lowest flow rate studied. Thus, it was concluded that a flow rate of 1500 cu cm per min was sufficient for oxidation of any quadrivalent uranium in the ore. However, because the partial pressure of oxygen in the system might affect the rate of oxidation, a test was run with oxygen enriched air. Oxygen

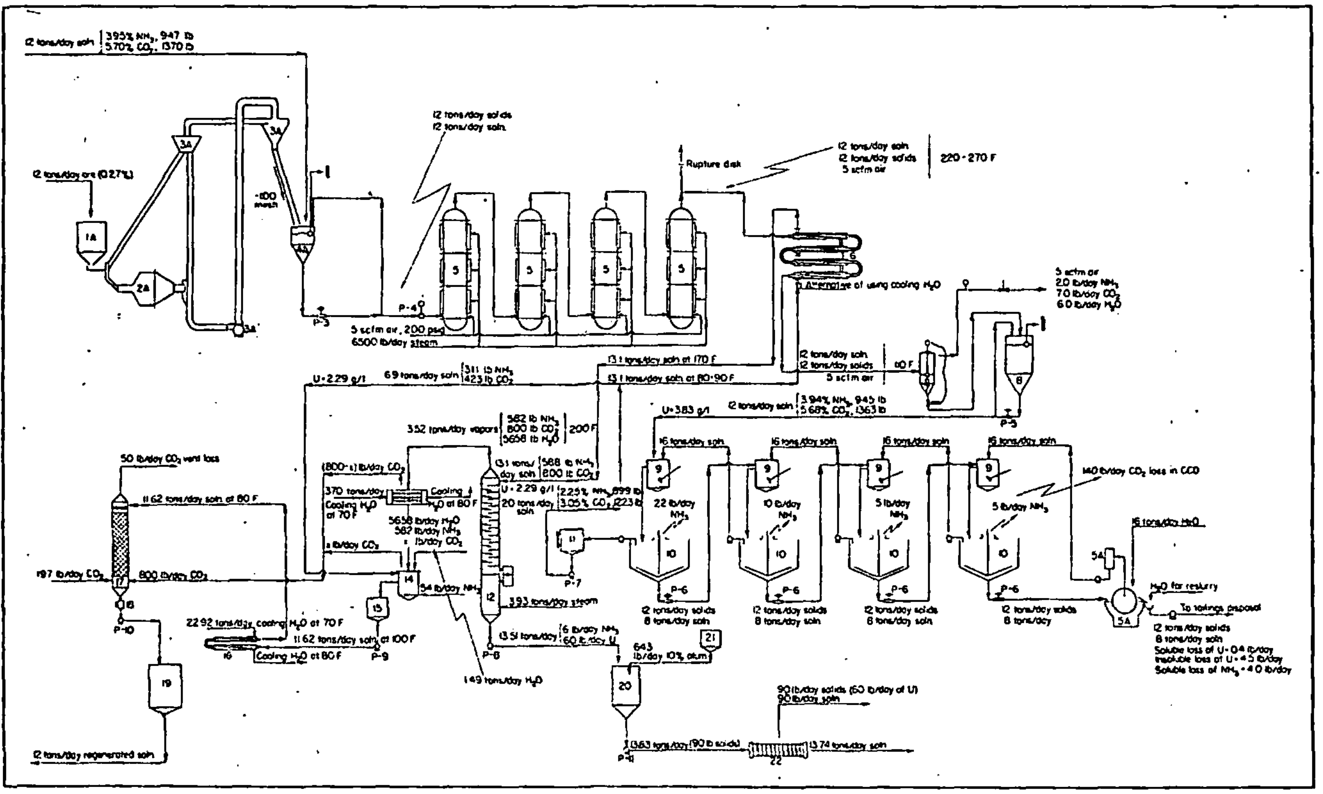
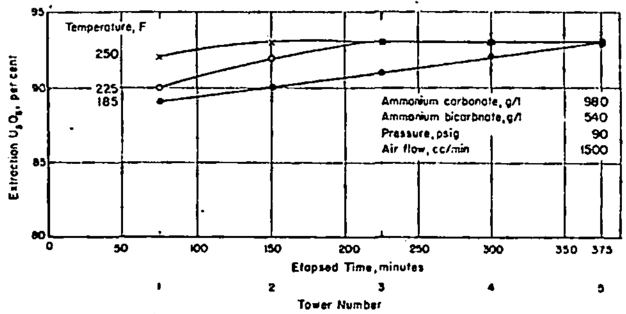
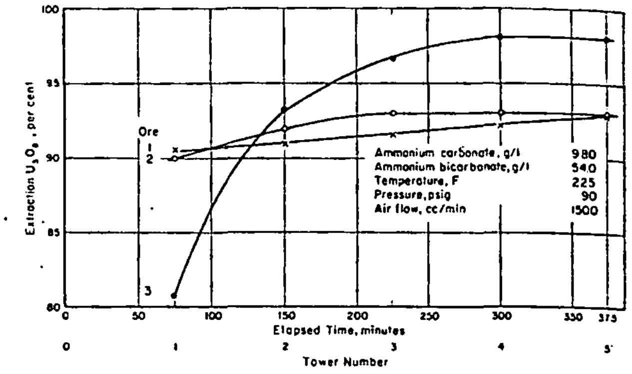


Fig. 2. Process flowsheet for ammonium carbonate leach pilot plant.





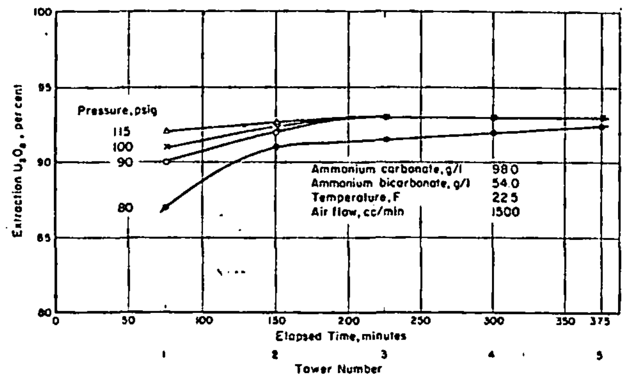


Fig. 3—(upper left) The effect of temperature and time on the extraction of uranium.

Fig. 4—(above) The effect of pressure and time on the extraction of uranium.

Fig. 5—(left) A comparison of the performance of three ores tested in the ammonium carbonate pressure leaching towers.

content of the air was enriched to 30 pct, but addition of this amount of oxygen did not improve either the rate or final extraction of uranium. Although pressures greater than 90 psig or a gas with greater than 30 pct O_2 might have improved the uranium extractions to as much as the 95 pct commonly obtained with a chemical oxidizing agent, further study of oxidation did not appear to be warranted.

Concentration of Ammonium Carbonate and Ammonium Bicarbonate: To evaluate the effect of the concentration of ammonium carbonate and ammonium bicarbonate on the dissolution of uranium, chemical analyses were run on periodic samples of the leach solution from each of the towers. In addition, because the commercial grade ammonium carbonate employed for this work was what is referred to in the literature as *ammonium carbonate of commerce* ($NH_3NH_2CO_2 \cdot NH_4HCO_3$) which decomposes in water to give variable amounts of ammonium carbonate and ammonium bicarbonate, it became necessary to run chemical analyses on the solutions prior to their addition to the repulping tank rather than relying on weighed amounts of the compounds. Fig. 6 shows the data obtained from a series of tests employing varying amounts of ammonium carbonate and ammonium bicarbonate in the leach solution.

Since only small quantities of ammonia and carbonate ions are required for combination with the uranium, then in evaluating the data two factors warrant discussion: 1) total ammonia in the solution contributing to the partial pressure of ammonia in the system and 2) the amount of bicarbonate required to prevent the build up of hydroxyl ions. As shown by Fig. 6, total ammonia content of the solution had a marked effect on the rate of dissolution of the uranium and the maximum extraction. For example, extraction increased from 73.5 to 90 pct in 75 min when concentration of ammonia was increased from 16.3 to 46.2 g per liter. The same change boosted extraction from 86 to 93 pct after the slurry had passed through all the towers.

These data, however, do not indicate any definite effect of the ammonium bicarbonate concentration on the dissolution of uranium. In both tests, represented by Curves A and B, analyses showed that after Tower 1 the solutions contained no ammonium bicarbonate.

To determine whether stabilization of ammonium bicarbonate in solution would improve the dissolution of uranium, the test represented by Curve B was repeated with the addition of 475 cu cm CO_2 per min. Figs. 7 and 8 show that despite addition of carbon dioxide to the system, the rate of dissolution was only improved slightly and maximum extraction was only equal to that obtained in Curve A. These data show that the use of carbon dioxide would permit the use of weaker solutions, but the system appears to have no advantage where the ammonia is recovered by steam stripping.

Precipitation of Uranium From the Ammonium Carbonate Leach Solutions

Uranium can be precipitated merely by heating the solution. This decomposes the ammonium uranyl

Table I. Chemical Analysis of the Ores

Ore	Assay, Pct										
	U_3O_8	V	CaO	Al_2O_3	MgO	C	CO_2	SiO_2	Fe_2O_3	S	L.O.I.
1	0.32	0.02	49.9	1.19	0.62	10.4	37.4	9.13	0.64	0.13	38.9
2	0.12	0.03	5.56	10.0	3.98	0.43	1.41	66.3	2.74	0.20	9.3
3	0.61	0.08	10.8	7.1	2.7	2.6	8.0	61.6	2.56	0.16	12.3

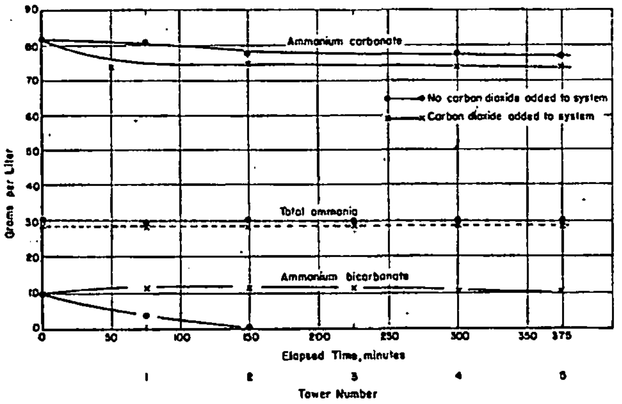


Fig. 6—The effect of concentration of ammonium carbonate and ammonium bicarbonate in the leach solution on the extraction of uranium.

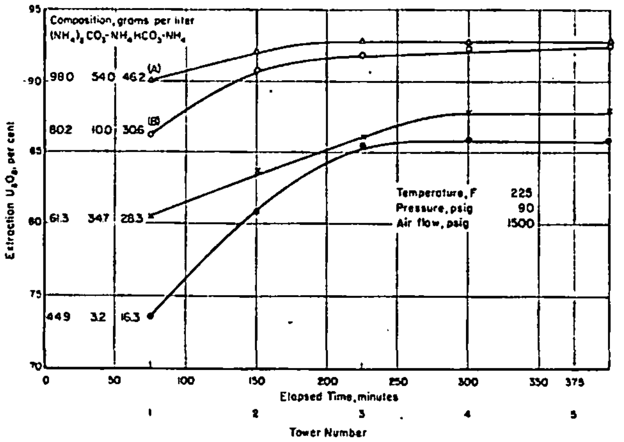


Fig. 7—Concentrations of ammonium compounds in solution with and without carbon dioxide added to the system.

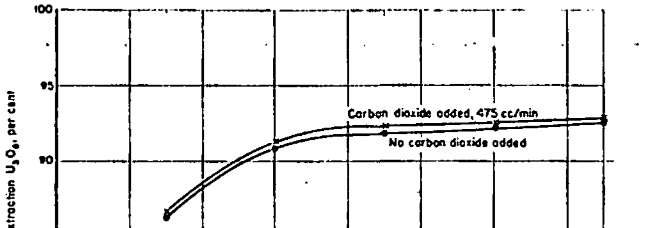


Fig. 8—The effect of the addition of carbon dioxide to the system on the extraction of uranium.

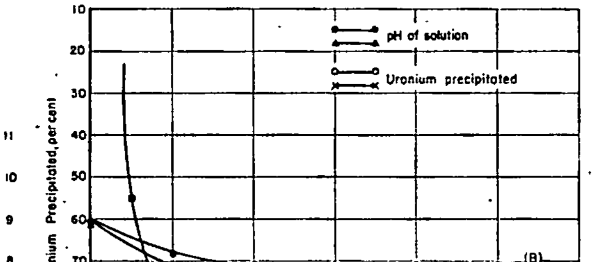


Fig. 9—The effect of time and pH of the solution on the precipitation of uranium by steam stripping.

carbonate and ammonium carbonate-bicarbonate, and expels the ammonia and carbon dioxide, which are then recovered by absorption in a solution brought to a concentration satisfactory for return to the leaching system. The following equations express the chemical reactions involved:

$$(NH_4)_2CO_3(\text{aq}) + \text{heat} \rightarrow 2NH_3(\text{g}) + CO_2(\text{g}) + H_2O(\text{l}) \quad [4]$$

$$NH_4HCO_3(\text{aq}) + \text{heat} \rightarrow NH_3(\text{g}) + CO_2(\text{g}) + H_2O(\text{l}) \quad [5]$$

$$(NH_4)_4UO_2(CO_3)_3(\text{aq}) + \text{heat} \rightarrow 4NH_3(\text{g}) + CO_2(\text{g}) + UO_3 \cdot 2H_2O(\text{s}) \quad [6]$$

$$2NH_3(\text{g}) + CO_2(\text{g}) + H_2O(\text{l}) \rightarrow (NH_4)_2CO_3 \quad [7]$$

In the experimental work, steam was used to heat the solutions and to serve as a sweeping gas. In the operation of the integrated plant, air was substituted for part of the steam. Fig. 9 shows the relation between pH of the solution, time, and the amount of uranium precipitated.

The pH of the pregnant solutions varied from 9.0 to 9.2, depending on the variation in pulp density. In the test represented by the curves A and A′, the pH of the solution was not controlled by the addition of fresh solution. As the ammonia was stripped from the solution, the pH dropped, and almost complete precipitation occurred within 60 min at a pH of 7.3. As the pH dropped to below 7, the precipitate began to redissolve. At the time of maximum precipitation, the stripped solution contained 0.005 g U per liter compared with 2.0 g per liter in the pregnant solution.

To determine whether pH of the solution could be employed for operational control when the pre-

Table II. Chemical and Spectrographic Analysis of Precipitate

	Chemical Assay, Pct				Spectrographic Assay, Pct				
	H_2O (250°F)	L.O.I. (1742°F)	U	V	Fe	Ca	Mg	Al	SiO_2
Ore 1									
Air Dried	23.4	—	44.7	0.40	<0.01	0.05	0.01	1.3	1.3
Ignited 1742°F	—	33.2	67.3	0.50	<0.01	0.08	0.02	2.0	2.0
Ore 2									
Air Dried	6.0	—	49.7	0.25	<0.01	0.34	0.5	0.4	3.1
Ignited 1742°F	—	15.0	59.3	0.21	<0.01	0.40	0.7	0.5	3.7
Ore 3									
Air Dried	7.3	—	59.0	0.40	<0.01	0.12	0.04	1.6	1.3
Ignited 1742°F	—	17.0	72.5	0.44	<0.01	0.16	0.05	2.0	1.8

Table III. Typical Uranium and Ammonia Balance

Uranium Balance			
Basis:			
Ore assay uranium, pct		0.52	
Feed rate, kg per hr		13.63	
Extraction uranium, pct		98.0	
Pregnant liquor assay uranium, g per liter		3.36	
Soluble uranium to CCD system, g		816	
Soluble uranium removed as samples, g		14	
Net soluble uranium to CCD system, g		802	
Distribution of Uranium in CCD System:	**Grams**		**Dist. Pct**
Thickener No. 1 overflow:			
45.4 liter per hr x 1.5 g per liter x 12 hr	789.6		98.4
Soluble loss:			
9.5 liter per hr x 0.11 g per liter x 12 hr	12.6		1.6
Total	802.2		
Distribution of Uranium in Precipitator:			
Loss in barren solution:			
50 liter per hr x 0.006 g per liter x 12 hr	3.6		0.7
Over-all uranium loss:			
Soluble loss + loss in barren solution	16.2		2.3
Ammonia Balance			
Basis:			
Discharge from leaching unit, liter per hr		20.2	
Assay of pregnant liquor, NH_3, g per liter		30.0	
Total NH_3 to CCD system, g		7272	
NH_3 removed by sampling, g		143	
Net NH_3 to CCD system		7129	
Distribution of NH_3 in CCD System:	**Grams**		**Dist. Pct**
Thickener No. 1 overflow:			
45.4 liter per hr x 12.8 g per liter x 12 hr	6973.2		98.0
Soluble loss:			
9.5 liter per hr x 1.2 g per liter x 12 hr	137		
Total	7110.2		
Distribution of Ammonia in Precipitator:			
Ammonia recovery:			
35.2 liter per hr x 15.7 g per liter x 12 hr	6631.7		95.0
Loss in barren solution:			
50.0 liter per hr x 0.30 g per liter x 12 hr	180		2.6
Unaccounted loss	161.5		2.3
Total	6973.2		
Over-all loss:			
Soluble loss + loss in barren solution + unaccounted loss	478.5		6.9

cipitation tower is operated on a continuous basis, a test was run maintaining the solution in the precipitation tower at pH 8 by continuously feeding the pregnant solution to the tower. The curves B and B′ show that by maintaining pH 8, the precipitation tower could be operated on a continuous basis and accomplish almost complete precipitation of the uranium. Although a pH of 7.5 appears to be a critical point with respect to redissolution of the precipitate, it is believed that the critical pH varies with each ore, depending on the salts remaining in the solution after stripping the ammonia.

At the time maximum precipitation of the uranium occurred, more than 99 pct of the ammonia and carbon dioxide had been stripped from the solution.

Composition of the Precipitate: Precipitates were produced from operation of the integrated plant on three ores. Table II gives the data obtained from chemical and spectrographic analysis of these precipitates. These data show that when the precipitates are air dried, uranium content varies from 44.7 to 59 pct. When the precipitates are ignited at 1742°F the uranium content varies from 59.3 to 72.5 pct. As shown by the spectrographic analysis, the variation is caused primarily by solids carry-over from the countercurrent washing circuit. This contamination could have been reduced by employing a clarification filter between the thickener overflow and the precipitation tower. The uranium compound in the air-dried precipitates was identified as $UO_3 \cdot 2H_2O$ by X-ray diffraction. The ignited precipitate was identified as U_3O_8.

Operation of the Integrated Plant for the Extraction and Recovery of Uranium

Because one of the attractive features of the ammonium carbonate pressure leach is the recovery of the ammonia for return to the leaching circuit, a countercurrent decantation washing circuit and a precipitation tower were added to the system. The objective of the program was to demonstrate the uranium and ammonia recovery that could be accomplished in an integrated plant. Although it was not within the scope of this program to actually return the ammonia to the leaching circuit, absorption towers were employed to recover the ammonia from the precipitation tower. Table III gives the uranium and ammonia balance obtained from operation of the integrated plant on Ore 3.

These data show that the soluble loss of uranium from the countercurrent decantation system was 1.6 pct of the uranium in the pregnant liquor and that an additional loss of 0.7 pct was incurred by the barren solution discharged from the precipitation tower. On this basis, the recovery of uranium from Ore 3 was 95.5 pct of the uranium in the feed to the leaching system. In the case of Ores 1 and 2, where approximately 93 pct of the uranium was extracted in the leaching towers, the over-all recovery of uranium was approximately 91 pct of the feed to the integrated plant.

With respect to the ammonia recovery system, the data show that the ammonia lost with the discharge from the countercurrent decantation washing system was equivalent to 1.67 lb NH_3 per ton of dry feed, and that the total loss of ammonia from the system including the loss with the barren solution and the unaccountable loss was equivalent to 5.85 lb per ton of dry feed to the integrated plant.

Conclusions

The data obtained from this study have demonstrated that the ammonium carbonate pressure leach is a technically attractive method for extraction of uranium from high-lime ores.

As in the case of other processes developed for the extraction of uranium from domestic ores, the process does not appear applicable to high gypsum or high vanadium ores. On the other hand, with its low reagent cost for precipitation and the recovery of substantially all of the ammonia, the process appears to have advantage over other alkaline leach processes. In addition, because of these same factors, it is probably competitive with an acid leach of medium-lime ores. At the same time, because an acid leach usually will extract about 98 pct of the uranium from low-lime ores, the acid leach still appears to maintain its advantage. The advantages and disadvantages of the several methods available for extracting uranium from low-grade ores are such that a careful economic comparison should be made for each ore being considered.

References

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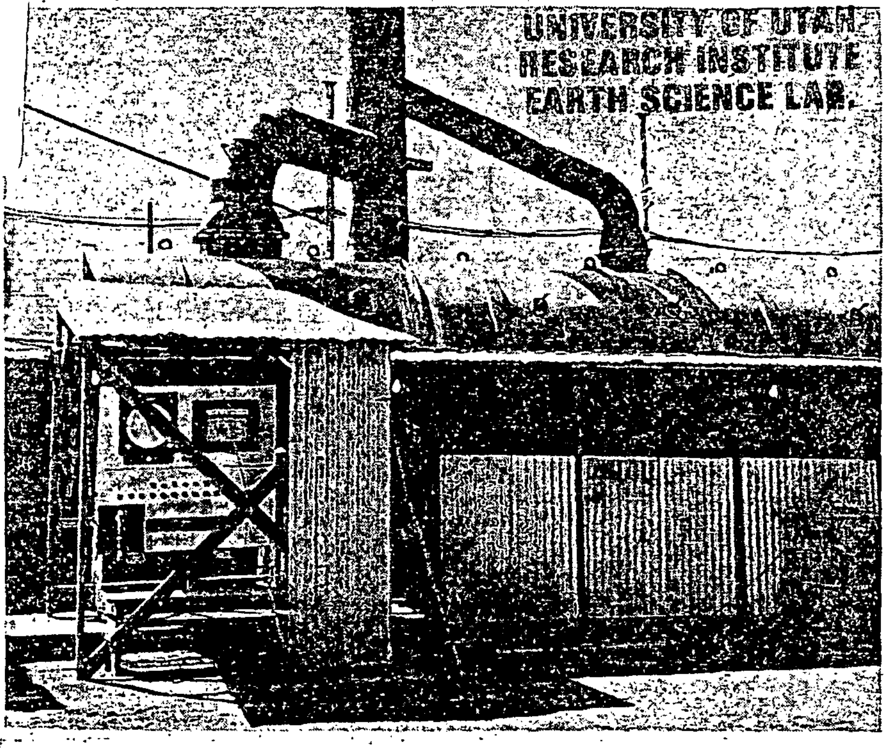
[2] F. A. Forward and J. Halpern: *Developments in the Carbonate Processing of Uranium Ores*, AIME Trans., 1954, vol. 200, p. 1408; JOURNAL OF METALS, December 1954.

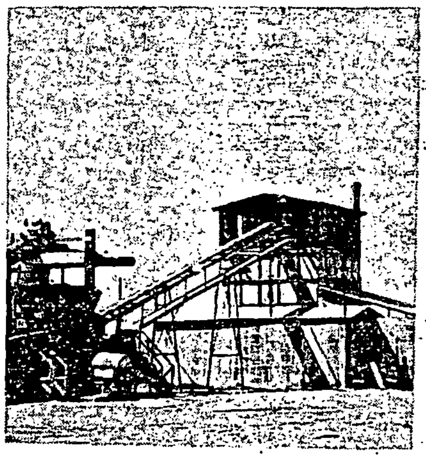
[3] R. W. Mancantelli and J. R. Woodward: *The Beaverlodge Hydrometallurgical Plant*, AIME Annual Meeting, Chicago, February 1955.



HEART OF THE PROCESS is the 54-in. x 42-ft rotary calciner. Fourteen gas-fired burners keep combustion zone temperatures in 1,400-1,500°F range.

Arizona Copper Silicates Respond to Segregation

GEORGE A. FREEMAN is manager of operations; has office in Casa Grande.



GENERAL VIEW of segregation plant. Shed holds fine-ore, coke and salt bins.

THE FIRST COMMERCIAL PLANT in the United States using the segregation process for treating silicate and mixed silicate-sulphide copper ores was recently placed in operation at Transarizona Resources' property south of Casa Grande, Ariz.

The company mines a copper silicate (chrysocolla) ore, averaging 2% copper, from an open pit developed on their mineral holdings — three patented claims in the Lake Shore group, a section of ground adjoining the Papago Indian Reservation, and 22 additional claims known as the Drake group.

Transarizona, controlled by Transcontinental Resources Ltd., a Canadian exploration and development company, is 28 miles south of Casa Grande, the nearest supply and rail center. Both electric power and natural gas for calcining the crushed, screened, and mixed plant feed are available at the plant site. Mining operation in the shallow pit follows standard practice: primary blastholes are drilled with a Gardner-Denver wagon drill and drill rods are fitted with detachable 3½-in. T-C bits.

Broken ore is loaded into 8-ton trucks by a Michigan loader with a 2-yd scoop for subsequent transfer to the processing plant. Blastholes for ammonium nitrate and Primacord are drilled on 6-ft centers to a depth that will give a 12-ft bench. The trucks dump their load onto the elevated stockpile area near the rail grizzly covering a 45-ton ore storage hopper.

Process Not New

In the processing plant, minus 10-mesh ore is heated at 1400°F to 1500°F with sodium chloride and coke (or other carbonaceous materials). This segregation process produces fine metallic copper, which can be recovered by conventional flotation methods.

The USBM and Transarizona Resources ran extensive bench and pilot plant tests but the segregation process is not new. It was developed and patented in the '20s by Mineral Separations Ltd., who, at that time, tried it in Africa. The company built a plant in Southern Rhodesia and Union Miniere du Haut Katanga built one in the Congo. The plants were successful, producing copper concentrates with better than 85% recovery. They were closed after short runs due to a variety of reasons (mechanical problems, economies), but mainly to the low copper price in the depression period.

Transarizona's processing plant is made up of a crushing and screening plant to reduce pit ore to 10-mesh calciner feed; fine-ore storage and mixing units; calcining and cooling unit; ball mill-classifier circuit to reduce cooled calcines to 65 mesh; xanthate flotation; and filter unit.

Pit ore is fed onto the rail grizzly, spaced 12 in. at a rate of 15 to 20 tph. Reduction to 10-mesh calciner feed is done in three stages, the equipment available for this operation consisting of a primary jaw crusher, set 2 in.; vibrating screen with ½-in. openings; secondary cone crusher, set 3/8 in.; 10-mesh vibrating screen; and a 36-in. rolls unit, taking the 10-mesh vibrating screen oversize and operating in closed circuit with the secondary cone crusher.

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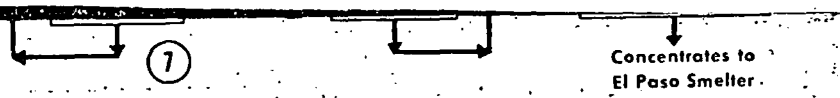
in an 8-cell rougher flotation machine. Froth produced by the first two cells goes to an 8-cell cleaner machine, and the tails are pumped to the tailing pond. Concentrates produced by the first two cells of the cleaner machine are pumped to a 6-ft, 3-leaf disc filter. Cake produced by the filter falls by gravity onto a concrete storage and loading floor below.

Reagent setup is relatively simple. Lime is used for pH control; xanthates for collector; and alcohol for frother. Final concentrates assay from 45% to 50% metallic copper. They are trucked to Casa Grande for shipment to the Asarco smelter at El Paso, Texas.



LEGEND

1. Rail grizzly, spaced 12 in.
2. 45-ton hopper
3. 24x18-in. jaw crusher set 2 in.
4. Vibrating screen with ½-in. openings
5. 3-ft Symons cone crushers set ⅜ in.
6. A-C vibrating screen with 10-mesh deck—5x10 ft
7. 36-in. rolls
8. 400-ton fine-ore bin
9. 3-ton coke bin
10. 3-ton salt bin
11. Weightometer
12. Bucket elevator
13. 12-ton surge bin
14. 15-in. by 42-ft Standard Steel Co. rotary calciner
15. 4x44-ft Baker type rotary cooler
16. 6x12-ft ball mill
17. Rake classifier
18. 5x6-ft conditioner
19. Rougher flotation machine made up of 8 Denver 48-in. cells
20. Cleaner flotation machine made up of 8 Denver 36-in. cells
21. Eimco 6-ft, 6-leaf disc filter
22. Concrete storage and loading floor

ADOPTION OF A CARBON SORPTION SCHEME FOR GOLD EXTRACTION AT THE BELOUSOV PLANT[1]

UDC 669.213

N. I. Taskin, A. G. Romanenko, N. S. Chekanov, K. G. Egorov, and Z. M. Burenko

Practical experience and research show that sorption using carbon agents is the most effective method of extracting precious metals from cyanide solutions of complex chemical composition at polymetallic concentration plants.

Pulverized activated carbons (ground KAD and activated flotation carbon UAF) are now mainly used as carbon sorbents; they have good sorption and kinetic properties, but their use involves difficulties of separation from solutions and pulps.

The present work was carried out to find a highly efficient technology and equipment for extraction of gold with UAF carbon from the copper concentrate thickener overflow at the Belousov Concentration Plant. The thickener overflow precious metals and impurities content (in mg/liter) fluctuates widely:

0.8-2.0 Au
0.5-1.5 Ag
1500-2100 CN_{total}
300-460 Cu
20-30 Zn
30-30 Ca

10-15 Mg
30-40 sulfates
150-270 Cl
1500-2000 carbonates
3-5 xanthates

Research [1,2] has established that a two-stage counterflow sorption scheme is the most promising.

Gold extraction reaches 96% and carbon saturation with gold is 1.0 kg/ton at a UAF carbon consumption of 1.0 kg per m³ of overflow.

It was established during tests on the scheme that a proportion of the gold (10-15%) was being lost with microdispersed particles of gold-bearing carbon and slimes, which were being carried out with the waste overflow from sorption stage II. Various coagulants (ferric chloride, ferrous, copper, and zinc sulfates, and aluminum sulfate) were tested with a view to creating

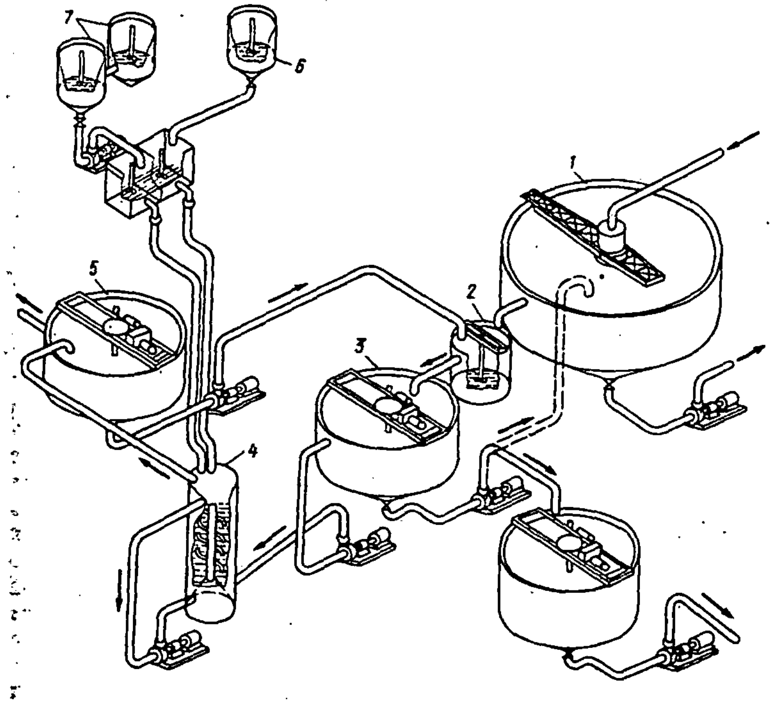


Fig. 1. Scheme for extraction of dissolved gold from copper concentrate thickener overflow: 1 - copper concentrate thickener; 2 - sorption stage I mechanical mixer; 3 - sorption stage I carbon thickener; 4 - sorption stage II hydraulic mixer; 5 - sorption stage II carbon thickener; 6 - solution tank for preparation of carbon suspension; 7 - solution tanks for preparation of aluminum sulfate solution.

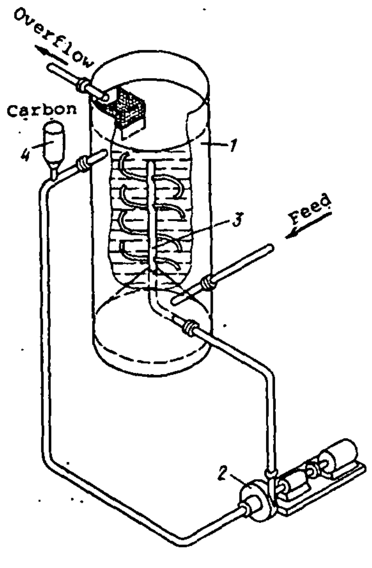


Fig. 2. Hydraulic mixer: 1 - tank; 2 - circulation pump; 3 - central pipe; 4 - receiver channel.

conditions for rapid precipitation of the gold-bearing carbon and to prevent losses. The speed of carbon precipitation in the presence of the various coagulants is approximately the same, amounting to 2-2.5 m/hr.

The sorption capacity of the carbon is reduced by more than 50% in the presence of copper sulfate, by 30% in the presence of zinc sulfate, and by 20-25% in the presence of ferrous sulfate and ferric choride; this makes the sorption process ineffective, and it cannot be used on an industrial scale.

Satisfactory results in terms of gold sorption and carbon coagulation were obtained in the presence of aluminum sulfate. At an aluminum sulfate consumption rate of 1.0 kg/m^3 of overflow, the suspended matter content is reduced from 300-500 to 30-50 g/m^3.

The flow chart for carbon sorption extraction of gold from overflow using a coagulant is shown in Fig. 1.

The prepared 5% water-carbon suspension and 10% aluminum sulfate solution are fed to sorption stage II (4), where they make contact with the overflow from stage I (3), which has been stripped of gold. Carbon from stage II, which is partly saturated with gold, passes continuously to sorption stage I for final saturation from the initial (gold-rich) overflow. The thickened carbon from sorption stage I is a commercial-grade gold-carbon product, which is used to make up a charge with lead concentrate, and the degolded overflow from stage II is sent for neutralization.

A hydraulic mixer designed and manufactured at the Kazmekhanobr Institute has been tested and adopted to intensify the sorption process (Fig. 2).

The hydraulic mixer operates on the following principle: the initial overflow is fed through a tangential pipe to the lower opening in tank 1, which has a conical bottom; as a result the overflow "uncoils" and the tank fills. The overflow, together with the carbon, flows by gravity from the upper opening to circulation pump 2, which pumps the overflow back upon itself through central pipe 3 and radial sprayers, thus producing supplementary intensive mixing.

This efficient mixing reduces external diffusion resistances, maintains good contact between the solution and the carbon, and improves sorption kinetics. A hydraulic mixer of this type does not take up a large floor area and is highly efficient and reliable in operation.

The two-stage scheme for gold sorption with coagulated carbon has passed its industrial tests and was adopted at the Belousov Plant in 1975.

Adoption of the scheme has made it possible to increase gold extraction by 2.9%, yielding savings of 110,000 rubles per year, due to reduced losses of gold with the liquid and solid phases of the copper concentrate thickener waste overflow.

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2. K. B. Lebedev and N. I. Taskin, Tsvetnye Metally, 1973, No. 8, 71-73.

adapt its limestone kiln technology and hardware to the related problem of retorting oil shale. A 30-month demonstration program calculated to cost some $7.5 million, with Development Engineering Inc. (DEI) of Denver as the operator, is planned.

"Private industry, particularly petroleum, natural gas, and electric generating companies, are invited to become participants by individual commitments of $500,000 toward the cost of the program, payable as moneys are expended over the life of the project," John B. Jones, DEI president, said.

The program calls for a semi-works size kiln to be built at the Federally owned Anvil Points oil shale research facility. Under terms of a recent lease agreement between DEI and the government, the Anvil Points works will be available for use in Paraho's experimental work, including a mine, crushing equipment, retorting and related plant, laboratories, and certain on-site housing and office space. The Cleveland-Cliffs Iron Co. has offered to handle the mining for DEI at Anvil Points.

The low per-company cost in the project was made possible by the number of participating companies, and through the use of the mine and supporting equipment at the government facility. According to Harry Pforzheimer, vice president of Sohio Petroleum Co., "A broad spectrum of industry is expected to support the program. It would be desirable for at least 15 companies to participate."

Companies investing in the project on a "participant" basis will receive a favorable license to use the process and hardware on oil shale, the advantages of a pioneer's position in the proprietary technology, the data and information developed, and an opportunity to advise and observe the progress of the program. ☐

AEC and KCC will jointly study potential of nuclear blasting to mine copper

A CONTRACT TO UNDERTAKE JOINTLY a program of investigation, study, and evaluation of in-place copper leaching technology that could be applied in an orebody fractured by a nuclear detonation has been signed by the US Atomic Energy Commission (AEC) and Kennecott Copper Corp. (KCC). The AEC portion of the study will be conducted as part of the commission's Plowshare Program to develop peaceful uses for nuclear explosives.

The process to be studied would involve the possibility of fracturing a deeply buried low grade copper bearing deposit with a nuclear explosive, and then percolating an oxidizing leach fluid through the fractured rock. The leach fluid would then be pumped to the surface, where the copper would be extracted.

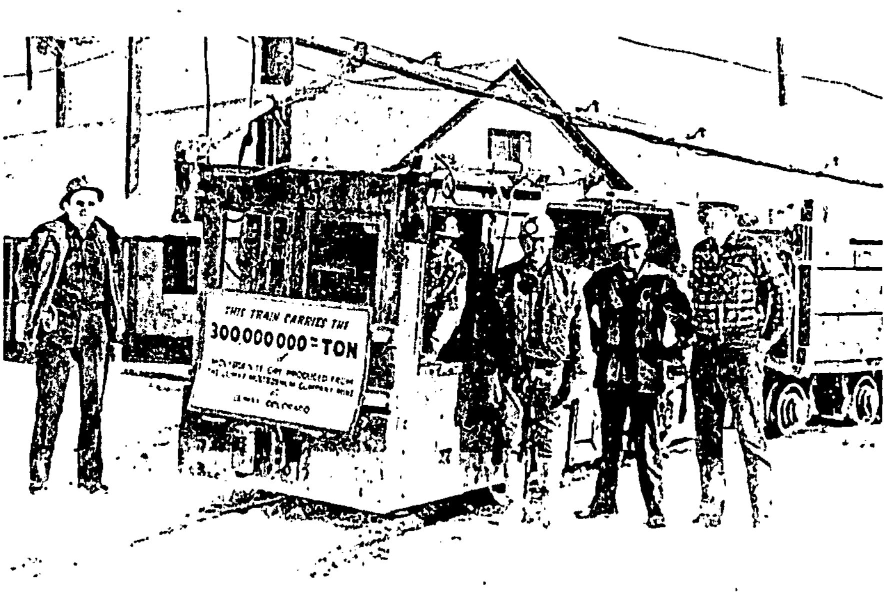
The study will help determine the feasibility of recovering copper from low grade orebodies, many of which are deep underground and are not economically recoverable using conventional mining techniques. The study, designed to investigate the requirements for nuclear fracturing and leaching of a representative orebody, will incorporate data on several orebodies. The results will enable the parties to decide whether an actual leaching experiment should be conducted. No actual field work is contemplated, but a concept will be developed for a surface extraction plant and other facilities needed for processing copper leach solutions.

Preliminary engineering and technical studies will be carried out by Kennecott's Ledgemont Laboratory in Lexington, Mass., and by the AEC's Lawrence Livermore Laboratory in California. Environmental effects will be considered in the study by the AEC's Nevada Operations Office in Las Vegas. The US Bureau of Mines (USBM) will provide advice and assistance in assessing the potential benefits and disadvantages of nuclear in-place copper leaching, as compared with alternative mining practices. The study is expected to be completed late this year.

A KCC scientist who is working on the project, Dr. Robert Hard, told E/MJ that this investigation program does not represent a revival of the old Sloop project considered in 1967 by KCC, the AEC, and USBM. As Hard put it, "This project incorporates newer concepts that were evolved at the AEC's Lawrence Livermore Laboratory. One of the major differences is the fact that the orebodies that will be considered in this new project are primary sulphide orebodies located under the water table, as opposed to primary oxide orebodies located over the water table in the Sloop project."

As the Sloop project was conceived back in 1967, a 20- to 30-kiloton device would be planted at a depth of 1,200 ft in the mineralized zone. After the explosion would come a solution test. Attack wells would flood the rock chimney and establish communication with recovery wells, so that pregnant liquor could be pumped to the surface. At the time of the Sloop project, the problem of radioactive contamination of the copper ore had received attention, and the general conclusion was that it was manageable. The AEC had indicated that the concentration of radioactive isotopes in the leach solution would be sufficiently low so that special shielding against exposure would not be needed.

As conceived at the time of the Sloop project, a nuclear blast for copper leaching would fortunately lock the relatively nonvolatile radionuclides in a congealed "puddle glass" at the bottom of the rock cavity, and only a small percentage would enter the leach solution. Subsequent metallurgical processing by the then newly developed solvent extraction process was being considered to remove virtually all radioactive contaminants from the finished copper. The Sloop project was eventually shelved. ☐



The 300 millionth ton of molybdenite ore produced by the Climax Molybdenum Co. mine at Climax, Colo., was hauled from the Phillipson level recently. The Climax mine, which has produced more ore than any other underground mine in North America, continues to produce nearly 14 million tpy of raw ore, according to the company.

After more than 40 years as a producing area supplying a major portion of the mine's total output, the Phillipson level is nearing exhaustion. Continued operations from the main producing level, the Storke, and from the new 600 level will maintain production at its 43,000 tpd capacity. The mine has been one of the world's leading producers of molybdenum since it began operations in 1918. ☐

(Continued on p 30)

E/MJ THIS MONTH IN MINING

Asarco and Dow Chemical to leach deep copper orebody in situ in Arizona

A PATTERN FOR COPPER MINING in the future may be set by a joint project of American Smelting and Refining Co. (Asarco) and the Dowell Div. of Dow Chemical Co., which plans to use sulphuric acid to leach out copper in situ, then recover the copper by plating anodes in an electrowinning plant.

In the 50-50 joint venture operation, Dowell will use techniques developed in oilfield work to help Asarco exploit a copper oxide body near Florence, Ariz. It is estimated that there are about 300-400 million lb of copper about 1,100 ft underground at the 90-acre Asarco site. The depth of the orebody is too great for an open-pit mine, and the grade—less than 1%—is not high enough to merit sinking shafts. Leaching in situ, it is believed, offers an economic alternative. Dowell says it will be the first time this process has been used for leaching at such a depth.

Dowell has started drilling five holes at the site. Four will be used for injection of a weak acid solution, and one will be a producing well. Drilling will take six weeks to two months, then water will be pumped in under pressure to fracture the orebody. The pressure used will be around 1,000-1,500 psi at the surface, which is relatively low in comparison with the 3,000-10,000 psi used in oilfields. The flow will be about 1 to 1.5 bbl per minute. Sometime this fall, depending on how long it takes to saturate the orebody and establish a flow pattern, Dowell will start metering concentrated acid into the water, forming a 3% acid solution in water to leach out the copper. It is expected that sufficient results will be available for an evaluation of the process by early 1973.

According to Dowell, this system could make smelters obsolete within 15 years because it is a cleaner process. On the other hand, it is likely that the Environmental Protection Agency will be monitoring the project to determine the possibility of the water table being polluted by the acid. Dowell says there is little likelihood of such pollution because stainless steel pipes will be used to carry the solution down to the orebody, and after that, the already weak solution will be neutralized by reaction with the ore.

Initially, Dowell will use oilfield service triplex pumps—three-cylinder pumps made of carbon steel—but expects that eventually these, too, will have to be of stainless steel to avoid corrosion.

The solution obtained from the producing well will be shipped by tank trucks to Asarco's San Xavier plant, south of Tucson (about 75 mi away), where the copper will be recovered by electrowinning. A plant will be built at Florence as soon as the mine proves successful.

Currently, the electrowinning operation at San Xavier is used to recover copper leached from copper oxide, which is obtained along with sulphide copper from Asarco's adjacent open-pit Mission mine.

Leaching operations are very inefficient, according to Dowell. But the company expects its experience in dealing with fluids underground will enable it to recover at least 60% of the copper at Florence over a period of 20-25 years. The process will be more than economical with only 30% recovery, according to Dowell.

A pilot plant using a similar process has been operated by Kennecott Copper Corp. for about two years at Ruth, Nev. However, that orebody is only about 300 ft deep, as against 1,100 ft for the Dowell-Asarco project. Dowell did the initial hydraulic fracturing of the body. The Kennecott plant is small scale, pumping about 30-40 gal of solution per min. About 10-15 lb of copper results from every 1,000 gal. Kennecott is operating its plant intermittently to obtain data. So far, results have been very encouraging, according to Kennecott's Research Center in Salt Lake City, and the company is planning to expand the pilot plant and put it into continuous production.

In another recent development, Ranchers Exploration and Development Co. is planning to leach copper from its Old Reliable mine in Arizona, a deposit of oxidized and secondarily enriched copper (E/MJ, April 1972, pp 98-100). In this case, the orebody was first shattered by 2,000 tons of explosive, placed according to a plan devised by E.I. Du Pont de Nemours & Co., which is providing explosive and technical assistance. Also, since the Old Reliable deposit is located in a hillside, Ranchers Exploration plans leach percolation. The area above the deposit will be terraced, perforated pipes will be laid on the terraces for irrigation of the orebody, and the leaching solutions will be drawn off by gravity at the base of the mine.

Amax chief sees marketing challenge for copper

THE COPPER INDUSTRY WILL BE CHALLENGED over the next 10 years to develop a more aggressive marketing approach, it was suggested recently by Ian MacGregor, chairman and chief executive officer of American Metal Climax Inc. (Amax).

MacGregor told the spring meeting of the Copper Development Association that "Free World copper production will remain somewhat in excess of demand through the rest of the 1970s, and possibly not until 1982 might demand overtake supply. At that time, it is estimated that Free World primary and secondary supply will have increased to close to 11 million tpy, while demand, including exports to the Eastern Bloc nations, may slightly exceed the 11 million-tpy figure."

This 10-year outlook, MacGregor declared, "indicates to me that we, as an industry, have a marketing opportunity ahead. We must do some re-thinking about the capabilities of our industry, and how all of us—whether miner, custom smelter, or fabricator—can work together to achieve the common goal of increasing copper usage."

MacGregor cited the success of CDA in developing such new uses for copper as the Decade 70 House of New Concepts, the *Copper Mariner* shrimp boat, copper solvent plumbing, the Exemplar automobile, and the life safety sprinkler system. "I heartily endorse CDA's approach to market development, which emphasizes the creation of whole systems using copper," MacGregor said, "and the impressive job of creating these copper systems and seeing them through the prototype stage to commercial reality. However, our industry—which supports CDA—is not following through forcefully and exploiting the lead-time advantage. We must pick up where CDA's initial goals are achieved."

MacGregor stated that the copper industry has primarily been "concerned with sales—that is, moving metal at a profit—but when it comes to marketing, the finding of new applications that will serve as future outlets for our production, we are not attuned to the total effort required."

"There is great danger," he told the meeting, "that the industry has not developed the marketing expertise of familiarity with today's sophisticated technology and the systems selling approach and techniques necessary for the expansion of the market base for copper. We should be selling plumbing systems rather than copper tubing, roofing systems rather than sheet . . . To think in terms of systems and market, rather than merely sell copper, requires a versatile sales force that can talk to research groups, design engineers, production people, and general managers of companies—on their own terms."

MacGregor called on the industry to "fully understand the implications of new markets, have the required alloys readily available, and be willing to offer technical service to support new high-technology applications."

(This Month continued on p. 20)

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(This Month continued on p 20)

AN EXAMINATION INTO THE CONDITIONS FOR EXTRACTING NICKEL FROM SERPENTINITE ORE WITH AMMONIA SOLUTIONS

UDC 669.243(729.1)

Guillermo Samaleya and N. A. Filin

The ammonia method of treating oxidized nickel ores, applied to ochreous ores, has been developed in detail and is being used worldwide. However, none of the attempts made to use it to treat serpentinite ores have yet yielded positive results [1,2]. Despite roasting at high temperature (1000-1100° C) for 3 hours and more, nickel extraction to solution did not exceed 70-80%. It is considered [3] that nickel will combine in magnesium silicate and this hinders its extraction. Only Caron [4] has been able to achieve high nickel extraction (89%) from ores, containing 1.47% Ni, 8.7% Fe, and 27.9% MgO. He confirms the conclusion that any increase of the magnesium content or reduction of the iron content in ore will lead to a drop in nickel recovery.

Today, for the first time, we have data on work done to treat high-magnesial serpentinite ore by the ammonia method. The composition of the examined ore is 1.41-1.68% Ni, 0.013-0.026% Co, 4.09-6.49% Fe_2O_3, 31.51-32.5% MgO, and 40.45-42.9% SiO_2.

It was established by petrographic analysis that serpophyte is the principal mineral as a nickel-carrier.

Differential-thermal analysis showed that at 670° C, an endothermic effect exists which, according to the literature, is caused by the decomposition of the magnesium silicate and the transfer of the serpentinite to an amorphous state.

At 790-800° C, an intensive endothermic effect emerges which, according to the literature, is caused by crystallization of the olivine.

As the ore reducing agent, use was made of charcoal, cane-sugar extracts, and two varieties of Cuban bitumen:

Form of bitumen	C, %	H, %	Ash content, %	Yield of volatiles, %
No. 1	78.16	7.42	1.6	63.8
No. 2	44.19	9.62	39.4	33.9

By compressing the extract in an atmosphere of argon and air, it was possible to determine their carbon and ash content to be 10% and 1%, respectively.

Reduction was performed in a boat, placed inside a 23-mm diameter quartz tube. A detached resistance furnace was used to heat the charge. The heating rate was 10 deg/min.

The rapidly cooled cinder was leached in a glass, cone-shaped vessel 37 cm high. A ceramic filter was placed at the bottom of the vessel to disperse the air. The rate of air feed was 1 lit/min and it was first passed through a solution with a concentration of ammonia and carbonic acid capable of lowering their losses from the leached pulp.

Under constant leaching conditions (100 g/l NH_3 and 50 g/l CO_2, a l:s ratio of 10:1, $\tau = 180$ min, and $t = 20°$ C), a study was made of the effect which the following factors had on nickel passage to solution: the reduction temperature; the duration; the ore and coal size; the amount of coal; and the duration of the period used to cool the cinders.

The effect of the coal-reduction temperature on nickel extraction to solution (held for 120 minutes) was:

t, ° C	600	700	900	950	1000	1050
Ni extraction to solution	34.3	58.3	59.6	78.1	85.8	84.3

The effect of the reduction time on nickel extraction to solution was (in %):

	τ, min			
t, ° C	30	60	120	210
950	80.5	--	78.1	20.7
1050	85.8	--	84.3	71.6

Increasing the ore size to above 0.105 mm, with the coal size kept at a constant value (0.105 mm) leads to a drop in the degree of nickel extraction. For example, where reduction is performed at 950° C for two hours there will be a 78.1% extraction from ore 0.105 mm in size; for ores, 0.315 and 3.2 mm in size, the extraction would be 70.2% and 37.7%, respectively.

It was found that to attain the maximum nickel extraction it would be sufficient to add coal in an amount 6-7% of the ore weight. At the same time, the cinder should be cooled rapidly in order to avoid any drop in extraction indices.

With a 2-hour reduction with bitumen (10% of the weight of ore, 0.105 mm in size), the following data were obtained:

The effect of the reduction temperature, using bitumen, on nickel extraction is as follows (in %):

	t, ° C				
Form of bitumen	500	600	700	900	1000
No. 1	20	58	87	90	89
No. 2	--	45	81.2	88	87
No. 1 with additions 1% of the charge weight	--	82*	87	83.5	78

*Temperature of 650° C

The effect of the reduction period, when using bitumen No. 1, on nickel extraction to solution is as follows (in %):

	τ, min			
t, ° C	30	90	120	210
700	85	87	87	84
900	94.1	92.8	90	90.7

If reduction is conducted for 2 hours at 900° C, then it would be possible to reduce ores up to sizes of 0.85 mm with the use of bitumen. It is difficult to reduce ores of larger sizes and nickel extraction is dropped to 82.6% for 3.2-mm ores.

It was established that in order to achieve a maximum nickel extraction, it would be adequate to add bitumen No. 1 (in an amount no greater than 4% of the ore weight) to ore.

Reduction using cane-sugar extracts will provide worse results because of its low reduction capacity. The extracts used contained a total of about 10% carbon.

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half of 1976. Total cost of the first phase of the project is estimated at upwards of $135 million. The company has ore reserves considered sufficient for producing more than 100 million lb of product annually.

Shimura Kako Co., Sumitomo Metal Mining Co. and Tokyo Nickel Co. have agreed to purchase the output of the plant for 15 years. Project participation agreements have been signed with these companies and with Mitsui and Co., Nissho-Iwai Co. and Sumitomo Shoji Kaisha, Ltd.

An experimental in-place leaching test will be undertaken in Arizona by American Smelting and Refining Co. Asarco has reached an agreement in principle with Dow Chemical Co. to conduct a test on a deposit containing perhaps 100 million tons of oxide ore, which may assay in excess of 0.4 percent copper.

The plan is to leach the deposit with sulfuric acid solutions which would then be recovered through wells. The copper would in turn be recovered from the solutions. It was pointed out that the project would provide an additional outlet for sulfuric acid from the company's Hayden, Ariz. smelter.

A copper facility is planned at the lead smelter of Bunker Hill Co. at Kellogg, Idaho. The new plant will process by-products from Bunker Hill's lead and zinc smelters by pressure leaching, solvent extraction and electrowinning to produce high grade cathode copper at the rate of approximately 10 tpd. Scheduled completion for the project is the end of the first quarter of 1974. Engineering and construction management of the facility has been contracted to Holmes & Narver, Inc.

Use of coal rather than natural gas for the generation of electrical power has been recommended in a report released by the Alberta Energy Resources Conservation Board. The report suggests that coal probably would provide additional electrical energy at lower cost than gas over the next 30 years.

The province currently produces more than 1.8 trillion cu ft of gas annually for shipment outside the province. If the Board's recommendations were adopted, an additional 10 to 12 trillion cu ft might be released as surplus to the province's needs over the next 30 years.

Researchers at Pennsylvania State University believe that a plant called eleocharis acicularis may be one answer to establishing plant life in acid streams. The plant is described as a bright green reed that is a relative of the Biblical papyrus. It has been observed in acid streams in mats as large as a putting green and colonies of eleocharis have been termed underwater oases by Richard Wagner, assistant professor of botany at Penn State. He believes it might be used as a starter crop in which micro-organisms, algae and insects could take hold.

The reason the plant grows in acid streams is unknown, but it has to date been found only in quiet pools or where there is a slight downhill grade in the stream bed. The plant is said to lend itself to transplantation.

The Cornwall iron ore mining operations of Bethlehem Steel Corp. at Cornwall, Pa. are being shut down after more than 230 years of continuous operation. Bethlehem had been planning an orderly closure of the mines for some years, but last year hurricane Agnes accelerated those plans because of inundation of underground workings at Cornwall. It is estimated that some 110 million tons of ore have been mined from two deposits at Cornwall—one of which outcropped and was mined by surface mining methods and one of which occurred 150 ft below surface.

Anaconda Co. has entered into a $110.8-million lease covering all of the equipment at the company's new 120,000-tpy primary aluminum reduction plant at Sebree, Ky. This is believed to be the largest equipment lease ever arranged for a single facility. It extends for 20 years and allows for renewal or purchase of the equipment at fair market value.

Seven equity investors provided $38.8 million in the form of ownership participations in an equipment trust and three insurance companies made loans totaling $72 million, secured by the equipment. United States Leasing International, Inc. negotiated equity for the transaction and First Boston Corp. placed the debt.

The Sebree plant is located near Henderson, Ky. It is to begin production during the second quarter. It is Anaconda's second reduction plant and increases the company's annual output capacity to about 300,000 tons of primary aluminum.

May, 1973

1976 v17 N8

THE ANTICIPATED EFFICIENCY LEVEL IN HYDROMETALLURGICAL PROCESSING OF MADNEUL' CONCENTRATES

UDC 669.334.012.7

T. P. Geleishvili, I. A. Terent'ev, and R. N. Dundua

The Madneul' Mining and Concentration Combine came into operation in 1974 in the Bolnisi region in the Georgian SSR, mining and processing copper pyrite ore from the Madneul' copper-barite-polymetallic deposit. In accordance with the scheme, the basic product from the Combine (copper concentrate) is shipped for further processing to the Alaverdi Copper and Chemical Combine, where spare capacity is available in both the roasting and the copper-smelting shops. Very little capital investment will therefore be required (only for expansion of the refining process) and additional copper, sulfur, and by-products will be obtained with the minimum outlay.

However, having regard to the increased demand in the national economy for a number of higher-grade products and to the necessity for gradually phasing out pyrometallurgical processes generating large amounts of dust and gas, the Institute of Physical and Organic Chemistry of the Academy of Sciences of the Georgian SSR, the Institute of Inorganic Chemistry and Electrochemistry of the Academy of Sciences of the Georgian SSR, and the Caucasus Institute of Mineral Raw Materials have collaborated with the Nickel Industry Research and Design Institute, the Urals Copper Industry Research and Design Institute, and the Madneul' Combine in developing an essentially different (autoclave-hydrometallurgical) scheme for integrated processing of Madneul' copper ore mixed with Chiatura low-grade manganese ore.

The scheme provides for the following:

autoclave oxidizing leaching of copper concentrate;

hydrogen reduction of copper powder and the production of various copper rolled stock sections by powder metallurgy methods;

leaching the manganese carbonate ore with the residual solution from hydrogen reduction of copper;

electrolysis of the manganese sulfate solution to produce active electrolytic manganese dioxide, a valuable and scarce product for the electrical engineering industry;

extraction of copper, gold, and silver from the autoclave mud;

processing the production waste.

The autoclave-hydrometallurgical scheme for processing copper and manganese material was acknowledged to be the most efficient of the series of process schemes and versions examined (provision was made in all cases of copper powder production for processing to obtain copper strip). By comparison with the other versions, in this version commodity output increases by 30% and the profit is doubled, capital investment being approximately the same as in the other versions; the lowest adjusted expenditure per ruble of commodity output is therefore assured.

In 1973-1974 the pilot autoclave installation at the Madneul' Combine was used to complete the experimental work on integrated autoclave-hydrometallurgical processing of copper and manganese raw material, obtaining and delivering the necessary data for final technical and economic justification of the construction of a hydrometallurgical plant.

The Nickel Industry and Design Institute enlisted the aid of the Leningrad Research Institute of the State Chemical Industry Plant Design Institute and the State Research and Design Institute for Alloys and Non-Ferrous Metalworking in working out the technical and economic justification with various ways of using the autoclave copper powder (see Table).

The calculations showed that processing copper concentrate from the Madneul' Combine with Chiatura low-grade manganese ore at a hydrometallurgical plant gave better technical and economic results than copper concentrate processing at the Alaverdi Copper and Chemical Combine, the annual saving being 10.7 million rubles.

Principal Technical and Economic Results of Hydrometallurgical Processing of Copper Concentrate

Indices	Copper product versions	
	copper powder	copper strip & copper briquets
Capital expenditures, millions of rubles....	94,0	101,8
Circul.capital, mil. r.	6,0	6,0
Productive capital, millions of rubles....	100,0	107,8
Capital expenditure per ruble of commodity output, rubles........	1,44	1,47
Return on capital, r/r.	0,69	0,68
Prime cost of commodity output. mil. of rubles	40,1	40,7
Expenditure per ruble of commodity output k.	57,7	58,6
Profit, mil. of rubles.	29,4	28,7
Profitability, % of productive capital....	29,4	26,6
Amortization period of capital investment yr.	3,2	3,5

The economic efficiency level of the hydrometallurgical scheme is governed by the following:

a) the use of processes for the treatment of copper concentrate and the production of copper powder which ensure full utilization and a high degree of extraction of minerals without producing harmful gases, dust, and effluents;

b) the intake into production of low-grade manganese material for which there is no industrial demand at present;

c) the utilization of the industrial effluent in various branches of the national economy.

The principal technical and economic results of the process scheme are given in the Table.

Note: in publishing this paper the Editorial Board view is that the problem touched upon requires additional study, taking account of the solution of the problem of economic efficiency in the tenth five-year plan.

AUTOCLAVE EXTRACTION OF PLATINUM METALS FROM ACID SULFATE SOLUTIONS USING THIOUREA

UDC 669.21/23:66.046.8

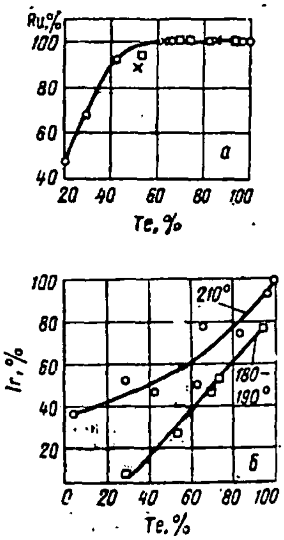
V. Sh Barkan

An extremely effective method of precipitating platinum metals using thiourea is widely used in analytical practice. This method is unsuitable for industrial use because of the need for evaporating large volumes of acid solutions to a sulfuric acid concentration of about 80% (to achieve a temperature of 200-220°C). The possibility of precipitating platinum metals using thiourea with solution heating in an autoclave was therefore studied.

Autoclave Extraction of Precious Metals with Thiourea

Indices	Rb	Ru	Ir	Ag	Se	Te	As	H_2SO_4	Cu	Ni
Content: in initial solution, mg/l.....	86	32	13	28	—	140	80*	220*	30*	25*
in discharged solution, mg/l..	Undet.	Undet.	3,7	Undet.	—	75	780*	220*	—	—
in solid residue %...............	1,0	0,35	0,10	1,65	0,3	1,3	0,3	—	50	4
Extraction from solution, %.....	100	100	71	100	—	64	—	—	—	—

* Content in g/l



Relationship of Ru extraction (a) and Ir extraction (b) from the solution to the tellurium extraction at temperatures of:
X - 160°C; - 180-190°C
O - 210°C.

Solutions of the following composition (in g/liter) were used: 150-250 H_2SO_4, 4-30 Ni, 20-30 Cu, 1-3 Me, and 0.8-1.5 As; in mg/liter: 80-200 Rh, 30-80 Ru, 10--30 Ir, 0-40 Ag, 30-80 Se, and 150-700 Te; Pd and Pt were absent. Thiourea was added to the test solution, which was then heated to the prescribed temperature, and cooled and filtered after holding for 10-20 min. Autoclaves were used without mixing, because the process being studied consists of the formation of soluble thiourea complexes and their subsequent thermal breakdown to form metal sulfides, i.e., the initial system is homogeneous. The thiourea consumption varied from 1.2 to 25 g/liter, and the temperature from 160 to 220°C.

The experiments showed that rhodium was completely precipitated in all the routines tested. For complete extraction of all the platinum metals, including iridium, a temperature of 210-220°C is required and a thiourea consumption permitting complete precipitation of tellurium (see Fig.). Precipitation of Se and Ag in the entire range of temperatures studied (160-220°C) preceded precipitation of Ru and Ir and was complete; there was practically no precipitation of As.

The precious metals content of the residue is determined first by the thiourea consumption, because the entire excess of thiourea goes to precipitate copper; second, it is determined by the relative Se and Te content of the solution. Under optimum conditions, the residues contain (in %): 1.2-2.7 total platinum metals; 3-4 Te, 0.3--0.4 Se, and 1.2-1.3 As, with the remainder copper sulfide.

Calcining at 600°C followed by leaching with sulfuric acid solution (100 g/liter) were used to concentrate this primary product. Under these circumstances a concentrate containing 13% total platinum metals and 13% Ag was produced from a residue containing 1.3% total platinum metals, 1.3% Ag, and 1% Te.

No more than 1-2% platinum metals passed into solution during leaching; in view of its small amount this solution is returned to autoclave precipitation with the initial solution. Industrial tests were made in a continuous column-type titanium autoclave with a 300-mm column diameter. Thiourea (5 kg/m³) was added beforehand to the initial solution, from which Pd, Pt, and Au were absent, and it was fed into the autoclave (pressure in last column 10-11 gauge atmosphere). Heating was by live steam to an average temperature of 180°C, and holding time was 1 hr. Under these conditions, Rh, Ru, and Ag were entirely precipitated, and precipitation of Ir and Te was 17% and 64%, in complete accordance with the laboratory tests (see Table). Live steam should not be used because it dilutes the solution; external heating maintaining a solution temperature of 210-220°C is the most effective.

AN ASSESSMENT OF ENERGY REQUIREMENTS IN PROVEN AND NEW COPPER PROCESSES

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December 31, 1980
Final Report

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16. Abstract

Energy requirements are presented for thirteen pyrometallurgical and eight hydrometallurgical processes for the production of copper. Front end processing, mining, mineral processing, gas cleaning and acid plant as well as mass balances are included. Conventional reverberatory smelting is used as a basis for comparison. Recommendations for needed process research in copper production are presented.

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PREFACE

This study, An Assessment of Energy Requirements in Proven and New Copper Processes, was performed by subcontractors operating in cooperation with an advisory committee made up of faculty members of the Department of Metallurgy and Metallurgical Engineering and the Department of Mining Engineering of the University of Utah. This arrangement was requested by the Department of Energy to provide a management function by the University of Utah in staging and coordinating the work.

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*Specific tasks are listed in Table A-1.

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Data and process description for the AMAX Dead Roast Process were provided by Eric L. Frueh of AMAX Base Metals, Research and Development, Inc., and the process description for the Electroslurry ™ process was provided by Frank Baczek, Project Manager, Envirotech, Corporation.

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EXECUTIVE SUMMARY

A. OBJECTIVES AND SCOPE

At the request of the Department of Energy, the University of Utah, Arthur D. Little, Inc., Mountain States Research, Inc., and Ford, Bacon and Davis Utah Inc. have undertaken an assessment of energy expenditures in various copper producing processes. Objectives may be listed as follows:

- Determine energy expenditures in existing and recently developed copper technology;
- Aid government and industry in screening and developing processes which are least energy intensive;
- Provide information that will direct research toward constructive areas for energy conservation; and
- Compile and disseminate energy analyses for selected new technology areas to industry and government.

The processes selected for study along with the companies primarily concerned with analyzing each process are listed in Table A-1. The University of Utah acted as prime contractor for the project with Arthur D. Little, Mountain States Research and Ford, Bacon and Davis Utah, acting as principal sub-contractors. In most cases the University of Utah personnel acted as advisors and coordinators on each process.

It must be strongly emphasized that the analysis undertaken in this report is strictly on an energy basis and does not directly address economic considerations or, in some cases, the technological feasibility of the processes considered. These areas would have to be evaluated carefully before an overall decision could be made to adopt a given process. Likewise a complete evaluation would have to include the consideration of the nature of the ore, its composition and plant location and capacity in determination of process feasibility.

B. APPROACH

Several recent efforts for the estimation of copper processing energy requirements are evident in the literature. Articles by Kellogg (1974, 1977) and Kellogg and Henderson (1976) consider energy consumption for producing copper from nine pyrometallurgical processes. A study by Arthur D. Little (1976) delineates energy requirements in relation to pollution control requirements in some of the newer processes. Fairly complete assessments of energy use in conventional copper production have been attempted by Battelle Columbus Laboratories (1975) and by Gordian Associates (1975). A thorough and detailed analysis, however, of energy expenditures for the complete range of copper processing is not presently available.

1. Criteria for Process Selection

Ores of copper are classified as sulfide, native copper or oxide. Of these, sulfide porphyry deposits account for about 90% of the U. S. production, most of the world output, and most of the estimated commercial copper reserves of the world. Therefore, this study focuses on processes

TABLE A-1

COPPER PROCESSES EVALUATED/COMPANIES ASSIGNED FOR EVALUATION

Process	Section	Company
Mining Operations	1.2	Ford, Bacon and Davis Utah, Inc. and University of Utah
Mineral Processing Operations	1.3	Mountain States Research and Development and University of Utah
Gas Cleaning	1.4	Arthur D. Little, Inc.
Acid Plant	1.5	Arthur D. Little, Inc.
Refining	1.6	Arthur D. Little, Inc.
In Situ Solution Mining	1.7	Mountain States Research and Development and University of Utah
Copper Cementation	1.8	Arthur D. Little, Inc.
Conventional Smelting	2.3	Arthur D. Little, Inc.
Impurity Control	2.4	Arthur D. Little, Inc.
Electric Furnace Smelting	2.5	Mountain States Research and Development
Outokumpu Flash Smelting	2.6	Arthur D. Little, Inc.
INCO Flash Smelting	2.7	Arthur D. Little, Inc.
Top Blown Rotary Converter Smelting	2.8	Arthur D. Little, Inc.
Noranda Continuous Smelting	2.9	Ford, Bacon and Davis Utah, Inc.
Mitsubishi Continuous Smelting	2.10	Arthur D. Little, Inc.
Queneau-Schuhmann Continuous Smelting	2.11	Arthur D. Little, Inc.
AMAX Dead Roast Blast Furnace Smelting	2.12	AMAX
Segregation Process	2.13	Ford, Bacon and Davis Utah, Inc.
Thermo Electron Chlorination Process	2.14	Mountain States Research and Development
Oxy-Fuel Reverberatory Smelting	2.15	University of Utah
Oxygen Sprinkle Smelting	2.16	Arthur D. Little, Inc.
Arbiter Ammonia Leach Process	3.2	Arthur D. Little, Inc.
Roast Leach Electrowin Process	3.3	Mountain States Research and Development
Cymet-Ferric Chloride Process	3.4	Arthur D. Little, Inc.
Sherritt-Cominco Process	3.5	Arthur D. Little, Inc.
Nitric-Sulfuric Acid Leach Process	3.6	Ford, Bacon and Davis Utah, Inc.
University of Utah — Martin Marietta Process	3.7	Arthur D. Little, Inc.
Electroslurry-Envirotech Process	3.7A	Envirotech Corporation
Roast/Sulfite Reduction Process	3.8	Ford, Bacon and Davis Utah, Inc.

that extract copper from sulfide ores. Sulfide ores, after mining, are primarily treated by crushing, grinding and froth flotation to produce a concentrate of sulfide minerals. In contrast, many oxide ores are not amenable to concentration and are treated with dilute sulfuric acid to dissolve the copper.

The extraction of copper from sulfide ores is conveniently divided into four segments:

- mining — ore containing 0.4 to 2% copper is blasted and excavated;
- beneficiation — copper minerals are crushed, ground and separated from the gangue materials to produce a concentrate containing about 25% to 30% copper;
- smelting — concentrates are smelted and reacted to produce anode copper containing 98% to 99% copper; and
- electrorefining — the anode copper is refined to produce over 99.9% pure cathode copper.

This report evaluates a wide range of processes covering the spectrum from those that have been in operation on a full scale to those on which data are still being gathered on a laboratory scale. These processes cover the treatment steps necessary for the production of cathode quality copper from sulfide resources.

The front-end processes for the production of concentrates (i.e., mining and beneficiation) are analyzed separately to define the important parameters that affect overall energy consumption in the production of copper. For the remainder of the analysis, a fixed concentrate input composition is assumed. Plants of conventional size (i.e., 100,000 tons/year of copper) for pyrometallurgical and hydrometallurgical processes are considered. The process criteria are:

Mill Feed Grade (Dry Basis)	**Mill Concentrate Grade (Dry Basis)**	**Annual Plant Capacity**
• 0.55% Copper	• 25% Copper • 28% Iron • 31% Sulfur	100,000 Tons Cathode Copper
Cut-Off Grade	**Mill Recovery**	**Base for Comparison**
• 0.29% Copper	• 87.5%	Conventional Reverberatory Smelting: 98.7% Recovery

The subject matter in the text is organized into three general groupings: Front-end Operations, Pyrometallurgy and Hydrometallurgy. Within each section, individual processes are presented in an essentially random sequence, reflecting the order in which the information was received and developed and the inclusion of additional processes during the course of this study. Summary information, however, is organized under the headings: Older Proven, Newer Proven and New Unproven for pyrometallurgical processes and Commercial Processes and New Unproven Processes for hydrometallurgical processes.

Table B-1 lists the processes analyzed to be compared to the conventional processes they replace. Production steps from mining through refining or reduction are indicated.

TABLE B-1

PROCESS STEPS AND CLASSIFICATION USED IN THIS STUDY COMPARISON IS MADE TO CONVENTIONAL SMELTING

	Mining	Beneficiation	Smelting	Refining
Conventional Processes	Open Pit Mining	Grinding and Froth Flotation	Reverberatory	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	Outokumpu Flash	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	INCO Flash	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	Electric Furnace	Electrorefining
Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Noranda Continuous	Electrorefining
Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Mitsubishi Continuous	Electrorefining
Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Oxy-Fuel Reverberatory	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Top Blown Rotary Converter	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Queneau-Schuhmann Continuous	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Oxygen Sprinkle Reverberatory	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	AMAX Dead Roast Blast Furnace	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Segregation	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Thermo Electron Chlorination	Electrorefining

TABLE B-1 (Continued)

	Mining	Beneficiation	Leaching	Reduction
Commercial Hydrometallurgical Processes	Open Pit Mining	Grinding and Froth Flotation	Arbiter Ammonia	Electrowinning
Commercial Hydrometallurgical Processes	Open Pit Mining	Grinding and Froth Flotation	Roast-Leach	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Sherritt/Cominco	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Nitric-Sulfuric	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Acid Ferric Sulfate	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Electroslurry-Ferric Sulfate	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Cymet Ferric Chloride	Hydrogen Reduction
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Roast/Sulfite	Ammonium Bisulfite
In Situ Solution Mining	Partial Underground Mining	None	Leaching in Place	Solvent Extraction – Electrowinning

2. Method of Analysis

The analysis involved the calculation/estimation of material balances for each process based on available data. It should be noted that, when available, actual operating data for unit operations have been used. In addition, several general processes, such as gas cleaning, sulfuric acid production, and electrorefining common to most processes were considered. Next, a Level 1 analysis was performed which calculated the fossil fuel equivalent of all forms of purchased energy consumed in the process, and credited for byproduct heat recovery only in those cases where such heat recovery was carried out in plant practice. In addition, a Level 2 analysis was performed where the fossil energy equivalent of the major materials consumed in each process was evaluated separately. Table B-2 lists the energy values for various energy sources and commodities utilized in this study. This analysis of individual processes was supplemented by a theoretical analysis of energy requirements to go from a pre-defined initial state (e.g., sulfide concentrates) to a pre-defined final state (e.g., blister copper at 1200°C, slag at 1200°C, and off-gases at 400°C), in order to estimate the minimum energy requirements. Since impurity behavior is a major impediment to the widespread adoption of some of the newer pyrometallurgical technology, it has been investigated separately.

TABLE B-2

ENERGY VALUES FOR FUELS, OTHER ENERGY SOURCES AND COMMODITIES

Commodities	Unit	Million Btu per Unit
Metallurgical Coke	Net Ton	31.5
Distillate Fuel Oil	Gallons	0.139
Natural Gas	Cubic Foot	0.001
Electrical Energy	Kilowatt-hour	0.0105
Steam	Pound	0.0014
Carbon Electrode	Net Ton	82.0
Graphite Electrode	do	160.0
Limestone	do	0.104
Nitric Acid	do	14.2
Refractory	do	26.6
Sand (silica sand)	do	0.042
Oxygen	do	4.41
Lime	Pound	0.0027
Sulfuric Acid	Net Ton	0.83
Ammonia	Net Ton	41.73
Hydrogen	Net Ton	234.0
Scrap Iron	Net Ton	18.0
Nitric Acid	Net Ton	14.2
Ammonium Nitrate Blasting Agent	Net Ton	30.0

Source: U.S. Department of the Interior, Bureau of Mines Information Circular, IC 8781, 1978.

It is important to note that all pyrometallurgical processes are strictly comparable (i.e., the iron in the concentrate ends up as a silicate slag and the sulfur in the concentrate ends up as sulfuric acid). In the hydrometallurgical processes, the iron ends up as a variety of jarosites or iron oxides while the sulfur either remains in the elemental state or is converted to throwaway gypsum and/or jarosites. The byproduct sulfur has not been allowed any credit in energy balances. If such credit were allowed (on the basis of comparing this sulfur against Frasch sulfur), the energy per ton of cathode copper would decrease by about 6% but a similar credit would have to be given those processes producing sulfuric acid or liquid SO_2.

Similarly, refractory consumption data for a wide variety of pyrometallurgical processes were not generally available and therefore refractory consumption was excluded from Level 2 analysis in many instances. However, such consumption appears to fall in the range of 20-50 lb of refractory per ton of cathode copper which is equivalent to less than 1% of the total energy consumed in cathode copper production. Similarly, no credit has been allowed for by-product metals.

In this energy analysis, actual operating data have been used for the various unit operations, when such data were available. This accounts for differences among similar unit operations. For these, no attempt has been made to rationalize these variations. For Level 2 values, broad variations are to be expected since consumables are process specific.

C. ASSESSMENT OF ENERGY CONSUMPTION

1. Mining and Concentration

Today open pit mining is extended to depths of as much as 1,500 feet below the rim. The energy use and dollar cost of hauling rock from such depths become limiting factors in determining the life of the surface mining operation. Energy use and dollar cost optimization represent separate analysis strategies. There is an increasing bias relative to energy optimization as its availability is constrained, as its unit cost goes up, as mining proceeds to ores of lower grade, and as environmental protection regulations increase. The cutoff grade significantly affects the tonnage of the ore going to the mill and the tonnage going to dump leaching. Using an average mill feed grade of 0.55% copper and a cutoff grade of 0.29% copper, the energy use in mining (Level 1 plus Level 2) is listed in Table C-1. The analysis is presented in terms of energy per ton of cathode copper produced and is based upon a copper recovery of 87.5% in concentrating and 98.7% by conventional smelting. From a sensitivity analysis which varies the cutoff grade, it can be shown that the energy per normalized ton of cathode copper charged to mining decreases, while that charged to milling increases. The resulting counter-active changes produce a small net energy difference in the overall energy requirement; although a minimum is indicated at a cutoff value of 0.4% copper.

The increased recovery of copper from dump leaching as the cutoff grade increases does not markedly decrease the average energy use per ton of cathode copper produced. This insensitivity results from the high energy use in current dump leaching practice. Conversely, the energy use per net ton of cathode copper produced is very sensitive to stripping ratio and pit depth.

Energy use in milling is very sensitive to mining cutoff grade when normalized in terms of cathode copper produced. The approximate energy use per net ton of ore milled (Level 1 plus

TABLE C-1

ENERGY USE IN MINING FOR A STRIPPING RATIO OF 1.25

Unit	Million Btu's per Ton Cathode Copper	% Total Mining Energy*
Drilling	0.612	3.0
Blasting	3.895	19.4
Loading	1.849	9.2
Hauling	13.137	65.2
Ancillary	0.638	3.2
Total	20.131	100.0

*Level 1 plus Level 2.

Level 2) is 0.156 million Btu of which 60% is in the grinding step. Assuming an average recovery of 87.5% in concentration and 98.7% in conventional smelting, milling energy is 42.57 million Btu per net ton cathode copper when produced from a mill head ore grade of 0.55% Cu.

It appears that major improvement in energy use in milling will require optimized energy use in grinding. This conceivably may be achieved by the application of stabilizing control strategies in the grinding operation itself and in related operations such as flotation and classification. This analysis points to potential energy savings in the use of autogenous and semi-autogenous mills for certain copper sulfide ores. Also pebble mills may be an attractive option for grinding when viewed in terms of energy optimization.

The tonnage of ore mined and beneficiated depends upon the final recovery inherent in the pyrometallurgical or hydrometallurgical process used. The results of a sensitivity analysis are presented in Table C-2. Clearly the energy of mining and beneficiation is relatively insensitive to recovery for the range of 97.0 to 99.5 percent recovery.

TABLE C-2

ENERGY FOR MINING AND BENEFICIATION

End Process Recovery	Million Btu/Ton Cathode Copper		
%	Mining	Concentration	Total
97.0	20.48	43.32	63.80
97.5	20.38	43.09	63.47
98.0	20.27	42.87	63.15
98.5	20.17	42.66	62.83
98.7*	20.13	42.57	62.70
99.0	20.07	42.44	62.51
99.5	19.97	42.23	62.20

*Base Case is 98.7% recovery for conventional smelting and refining.

2. Pyrometallurgical Technology

Table C-3 lists the energy use evaluated for several older and newer commercial and proposed pyrometallurgical processes. Included in the table are Level 1 plus Level 2 values for each process. The range of values for each category are also listed. The mining and milling values may be adjusted relative to conventional smelting with a recovery of 98.7% according to Table C-2.

TABLE C-3

ENERGY USE IN COPPER PYROMETALLURGY TECHNOLOGY FOR SMELTING AND REFINING
(Million Btu/Ton Cathode Copper)

Category	Process	Total Level 1 plus Level 2	Range
OLDER PROVEN PROCESSES	Conventional Smelting (Green Charge)	35.16	30-44
	Conventional Smelting (Calcine Charge)	30.92	
	Electric Furnace Smelting	42.97	
	Outokumpu Flash Smelting	18.92	19-21
	INCO Flash Smelting	21.25	
NEWER PROVEN PROCESS	Noranda Continuous Smelting	24.00	20-29
	Mitsubishi Continuous Smelting and Converting	19.76	
	Oxy-Fuel Reverberatory Smelting	28.62	
NEW UNPROVEN PROCESSES	Top Blown Rotary Converter Smelting	23.56	20-24
	Queneau-Schuhmann Continuous Smelting	22.63	
	Oxygen Sprinkle Smelting	22.43	
	AMAX Dead Roast Blast Furnace Smelting	19.58+1.5*	
	Segregation Process	21.03	
	Thermo-Electron Chlorination Process	20.20	

To obtain the total energy required for producing a ton of cathode copper the energy for mining and concentrator operations must be added. For a 98.7% recovery in the smelting operation the estimated mining energy is 20.13 and concentrator energy is 42.57 million Btu/ton cathode copper.

*Value reported by AMAX for electro-refining is approximately 1.5 million Btu less than value used for other processes in this study; also, energy requirement for fugitive emissions control is not included.

It is important to note that the energy-based comparison amongst processes can be significantly different from an economic comparison between same processes since the labor and fixed capital requirements for the processes may vary considerably. Similarly, the processes produce different types of environmental intrusions (fugitive emissions, waste water, slag and sludge) and the costs or future potential cost of dealing with these streams may vary from process to process. What is presented here is a comparative discussion of the processes based on energy consumption alone.

Table C-3 shows that conventional smelting is energy intensive. It uses large quantities of hydrocarbon fuels, deriving little energy from the combustion of the sulfides. Hot calcine smelting (roast-reverberatory) practice is less energy intensive than green charge practice by approximately 4 million Btu, mainly resulting from lower fuel and air requirements and the resultant decrease in the volume of offgas which must be handled. The Oxy-Fuel process at about 29 million Btu shows considerable improvement over conventional smelting. More important, while sulfur recovery as acid in conventional smelting is below 70%, sulfur recovery in Caletones Oxy-Fuel smelting would be over 90%.

Electric Furnace Smelting is the most energy intensive of all of the pyrometallurgical processes analyzed in this study. The addition of fluid bed roasting could reduce the fuel requirements by approximately 3 million Btu's per ton of cathode copper.

It is evident (see Table C-3) that two of the older proven processes based on matte smelting, Outokumpu Flash Smelting and INCO Flash Smelting, fall in the lowest range of energy consumption (19-21 million Btu per net ton cathode copper produced). This is a significant improvement over conventional smelting and illustrates the important conclusion that with the many technological improvements incorporated in these processes over the last 30 years, there has been a significant improvement in energy efficiency. Newer proven processes (based on matte smelting) fall in the mid-range of energy consumption (19-29 million Btu/net ton cathode copper produced). These are the Mitsubishi, Noranda and Oxy-Fuel Processes. Of these the Mitsubishi and Noranda Processes are at the lower end of the range and are close in energy consumption to the flash smelting processes.It should be noted that improved reactor design in general also makes these processes more environmentally acceptable. This is particularly true for developments which reduce converter aisle-type operations in a process, reducing fugitive emissions.

Six processes are newer, unproven processes and fall into two categories. Three of these processes are based upon matte smelting. They are TBRC, Q-S, and oxygen sprinkle smelting. These three processes fall in the same energy range (20-24 million Btu/net ton cathode copper produced) as other newer processes based on matte smelting. Three processes, not based on matte smelting, are the AMAX Dead Roast Blast Furnace, Segregation and Thermo Electron processes. These processes similarly show relatively low energy usage. However, the energy values for the Amax Dead Roast Blast Furnace process would have to increase for controlling fugitive emissions.

The AMAX Dead Roast Blast Furnace process and the Segregation process, have been tested only on a pilot plant basis, but not on a commercial scale. The Segregation process has been tested on a commercial scale for refractory silicate ores but not on roasted calcines. It is difficult to analyze the Thermo Electron Corp. process comparatively, since background data are incomplete and are based on bench scale tests only.

As stated earlier, when available, actual operating numbers for the various unit operations have been used. This accounts for the variation in values presented for similar steps in Level 1 analyses. Some differences such as smelting energy and surplus steam generation are expected for the various pyrometallurgical processes. Also, although process units perform similar functions in different processes, operating conditions such as matte grade, degree of oxygen enrichment in smelting and converting, air preheat etc. vary considerably leading to differences in energy requirements. Other process steps should be similar. For these, no attempt has been made to rationalize the variations although subtle differences may, in fact, exist for the separate processes. Where the deviation is large, special note is made of the differences. Broad variations are expected for Level 2 values since consumables are process specific. Table C-4 lists the Level 1 plus Level 2 values for unit operations within each process illustrating the degree of variation. Some of the major variations are:

- The energy requirements for electric smelting are highest reflecting to a large extent the inefficiency of power generation based on fossil fuels.

- The fugitive emissions control energy use for the Mitsubishi Process is approximately 25% of that attributed to other processes reflecting the transfer of molten matte through launders. For the Q-S Process no energy has been assigned for fugitive control, since all the processing will be done in a single reactor. For electric smelting, energy for fugitive emission is not listed separately but is included under cold gas cleaning. The energy for fugitives emission control is likely to be similar for the Segregation process and the Amax Dead Roast Blast Furnace process because they both involve handling of dusty calcines. Although Table C-4 shows 3.57 million Btu/ton for fugitive emission control in the Segregation process, the actual requirements need to be established for both processes.

The values shown in Table C-3 may be compared to the values reported by Kellogg and Henderson (1976) for several pyrometallurgical processes. This comparison is shown in Table C-5 where the Kellogg & Henderson values have been adjusted to the same basis as Table C-3 by adding an average value of 3.57 million Btu/ton copper for fugitive emission control and 4.69 million Btu/ton for electrorefining.

Evolutionary development of pyrometallurgical processes employing matte smelting chemistry may be viewed in terms of two major developments beyond conventional reverberatory smelting; namely, flash smelting and continuous processing. In the future, energy saving features, improved environmental acceptability, minimal loss of copper in the slag, large capacity, fugitive emission control and design features minimizing heat loss must receive special attention. The conventional reverberatory-Pierce Smith process is clearly obsolete. Flash furnace technology, now over 30 years old, and well proven, may be viewed as modern transitional-proven technology, while Mitsubishi and Noranda are modern continuous-proven processes. It is difficult to assess whether or not these latter two are transitional. Mitsubishi uses three smelting steps and, while it is effective in conserving on fugitive emission energy requirements, it deviates from a single reactor concept. The Noranda process is too new to assess from this point of view. It is continuous, but slag cleaning appears to be a problem. Oxygen sprinkle smelting by these citeria may be viewed as transitional, unproven, representing a potentially significant linking between older and newer technologies. The TBRC is difficult to analyze in the same framework as the other processes mentioned, except it must be considered at this point as somewhat unproven for large scale smelting of copper. It is limited in size, operates best on high grade mattes and has the added capability of fire refining. The Q-S process as designed is capable of going from copper feed to blister copper and falls in the category of modern and continuous-unproven processes. A similar version, the QSL (Queneau-Schuhmann-Lurgi) process for lead is now at the demonstration stage in Germany by Bundes Minesterium Súr Forsching und Technologie. The demonstration plant (250 tpd galena) is funded at a level of $25 million U.S., one-half by German industry and one-half by the German government with tests to be completed by the end of 1982.

TABLE C-4

ENERGY (MILLION BTU/NET TON COPPER) COMPARING SIMILAR STEPS IN PYROMETALLURGICAL PROCESSES

Section	2.5	2.3a	2.3b	2.15	2.10	2.9	2.11	2.16	2.7	2.8	2.6	2.12
Process Designation	Electric Furnace Copper Smelting	Conventional Smelting, Wet Charge	Conventional Smelting, Dry Charge	Oxy-Fuel Reverberatory Smelting	Mitsubishi Continuous Smelting & Converting	Noranda Continuous Smelting	Queneau-Schuhmann Oxygen Process	Oxygen Sprinkle Smelting	INCO Flash Smelting	Top Blown Rotary Converter	Outokumpu Flash Smelting	AMAX Dead Roast – Blast Furnace
LEVEL 1												
Materials Handling:		.73	.73	.73	.66	.79	.66	.73	.73	.73	.57	
Dry or Roast:	2.67		.66	1.35	1.29	.80	1.47	1.72	1.86	1.86	1.23	1.58
Heat Recovery												-4.73
SMELTING												
Fuel		25.01	14.50	9.27	6.46	3.72		1.38		.40	.80	10.88
kWh	19.03	.64	.64	.64	1.58	1.26		.64	.05	1.16		1.27
Surplus Steam		-10.00	-4.35	-3.71	-8.00	-1.82		-1.09			3.43	- .50
CONVERTING												
kWh	2.92	1.63	1.26	1.63	1.42	.37		1.26	0.94		.64	
Fuel	3.58	.54	.32	.50	.25	.09		.23				
Slag Cleaning					1.35	1.31					1.49	
GAS CLEANING												
Hot Gas	.78	4.03	2.83	1.27	.86	.69	.13	.64	.59	.51	0.42	
Cold Gas	2.21	.25	.40	.48	.32		.05	.24	.31	.34	0.21	.84
Fugitive Emissions		3.57	3.57	3.57	.89	3.57		3.57	3.57	3.57	3.57	
Acid Plant	4.74	2.27	3.87	4.51	4.08	3.10	4.30	3.91	3.19	4.09	3.86	4.18
Water		.10	.10	.10	.10		.10	.10	.10	.10	.10	
Anode Furnace Electrorefining	5.10	5.82	5.82	5.82	5.82	5.82	5.82	5.82	5.82	5.82	5.82	6.03
TOTAL LEVEL 1	41.03	34.59	30.35	26.16	17.08	19.70	12.53	19.15	17.16	18.58	15.28	19.55
LEVEL 2												
Misc. Materials					.63	.65	2.80			0.13	.04	
Oxygen				1.88	1.29	3.17	6.70	2.71	3.53	4.74	3.04	
Electrodes	.86				0.16							
Fluxes	.12	.04	.03	.04	.06	.02	.05	.03	.02	.02	.01	.03
Water		.08	.08	.08	.08		.08	.08	.08	.08	.08	
Anode Furnace Electrorefining	.51	.47	.47	.47	.47	.47	.47	.47	.47	.02	.47	.01
TOTAL LEVEL 2	1.49	.59	.58	2.47	2.69	4.31	10.10	3.29	4.10	4.99	3.64	.04
GRAND TOTAL	42.52	35.18	30.93	28.63	19.77	24.01	22.63	22.44	21.26	23.57	20.87	19.59

TABLE C–5

COMPARISON OF TOTAL ENERGY (LEVEL 1 PLUS LEVEL 2) WITH VALUES FROM KELLOGG AND HENDERSON (1976) FOR SEVERAL PYROMETALLURGICAL PROCESSES

Process	Total Energy Consumption Level 1 plus Level 2 (Million Btu/Net Ton Cathode Copper) This Study	Kellogg and Henderson (1976)[a]
Conventional Smelting: Green Charge[b]	35.16	26.73
Conventional Smelting: Calorie Charge[c]	30.92	23.84
Electric Furnace Smelting[d]	42.97	32.55
Outokumpu Flash Smelting[e]	18.92	20.51, 23.69
INCO Flash Smelting[f]	21.25	18.20
Noranda Continuous Smelting[g]	24.00	20.53, 29.41
Mitsubishi Continuous Smelting[h]	19.76	22.21

a. Add to Kellogg values, 3.57 million Btu/ton cathode copper for fugitive emissions and 4.69 million Btu/ton cathode copper for electrorefining.
b. This study: no air preheat; Matte Grade – 42.0%.
Kellogg and Henderson: 72% preheated to 220°C, Matte Grade – 35%.
c. This study: no air preheat; Matte Grade – 50.0%.
Kellogg and Henderson: 72% preheated to 220°C, Matte Grade – 43.5%.
d. This study: no air preheat; Matte Grade – 41%.
Kellogg and Henderson: no air preheat, Matte Grade – 35%.
e. This study: enriched air 36.5 wt % oxygen, preheated to 200°C, Matte Grade – 65%.
Kellogg and Henderson: (1) air preheat at 77% to 1000°C, low oxygen enrichment Matte Grade – 59%.
(2) air preheat 80% to 200°C, higher oxygen enrichment Matte Grade – 61.4%.
f. This study: oxygen, Matte Grade – 50.45%.
Kellogg and Henderson: pure oxygen, Matte Grade – 54.3%.
g. This study: oxygen enrichment, Matte Grade – 70% Cu.
Kellogg and Henderson: (1) Blister copper, no air preheat.
(2) Oxygen enrichment, Matte Grade – 75% Cu.
h. This study: Oxygen enrichment (40.9%), no preheat, Matte Grade – 65%.
Kellogg and Henderson: air preheat 25% to 275°C.
moderate oxygen use, Matte Grade – 64.5%.

Following the above logic and using the data of this study, it appears that the reactor of the future, with a production capacity of 100,000 tons per year, most likely will be a single continuous reactor capable of minimizing convective and radiative heat loss, fugitive emissions, and effective in removal of impurities. Such a single reactor should meet the following conditions:

- Produce blister copper low in impurities;
- Produce a clean slag;
- Increase SO_2 concentration and minimize gas volume;
- Fully ultilize the fuel energy in the copper-iron sulfide feed; and
- Provide close control over emissions.

For smaller operations, e.g., 25,000 tons per year, other options appear likely, e.g., the TBRC may be well suited to plants of this size as may be several hydrometallurgical processes.

3. Hydrometallurgical Technology

Table C-6 lists the Level 1 plus Level 2 energy requirements for the eight hydrometallurgical processes considered in this study. Energy usage for in situ solution mining is also included, and is discussed in Section C.4. The hydrometallurgical processes are grouped according to three ranges of energy (Level 1 plus Level 2) required. The total energy values, including mining plus beneficiation, are also listed in Table C-6. The table clearly shows that hydrometallurgical processes in general are more energy intensive than smelting. This comes mainly from high Level 2 components and ineffective use of the heat of reaction. The processes having lowest Level 2 components, viz., Roast-Leach-Electrowin, Cymet Ferric Chloride Leach, Electroslurry and Sulfite Reduction, are notably less energy intensive and, in terms of energy, are comparable with Conventional or Electric Furnace Smelting.

TABLE C-6

ENERGY USE IN COPPER HYDROMETALLURGICAL TECHNOLOGY
(Million Btu/Ton Cathode Copper)

Process	Concentrate to Refined Copper Total Level 1 Plus Level 2	Range	Range (Mining to Refined Copper)
Roast Leach Electrowin*	30.45		
Cymet Ferric Chloride Leach	30.92	24-31	87-94
Roast/Sulfite Reduction	23.64		
Electroslurry—Envirotech	39.61		
U of U/MM Ferric Sulfate Acid Leach	49.45	40-50	103-113
Sherritt Cominco	48.13		
Arbiter Ammonia Leach*	62.05	60-75	123-138
Nitric-Sulfuric Acid Leach	74.45		
In Situ Solution Mining	–	–	approx. 80

*Processes which have been used commercially. To obtain the total energy required for producing a ton of cathode copper the energy for mining and concentrator operations must be added. For 98.7 percent recovery in the smelting operation the estimated mining energy is 20.13 and the concentrator energy is 42.57 million Btu/Ton of cathode copper.

All of these processes, with the exception of the Cymet Ferric Chloride Leach and the Sulfite Reduction process, employ electrowinning for metal reduction. Improvement in electrowinning thus presents an area for reduction in the overall energy use in these processes. Chemical reductants, used in the Cymet and Sulfite Reduction processes are clearly less enegy intensive than conventional electrowinning. The Envirotech Electroslurry cell appears to be operable with approximately 25 to 30 percent less energy than conventional electrowinning.

Combination processes, using both pyrometallurgical and hydrometallurgical steps, are generally less energy intensive than all-hydrometallurgical processes. The combination processes are Roast-Leach-Electrowin, Cymet Ferric Chloride, Sherritt-Cominco, and Sulfite Reduction.

The all-hydrometallurgical processes in general are the most energy intensive. These are the Arbiter Ammonia Leach, the Nitric-Sulfuric Acid Leach and the Ferric Sulfate Leach. The Electroslurry modification of the Ferric Sulfate Leach is less energy intensive than the University of Utah/Martin Marietta version based on electrowinning because of the lower cell voltage of the electroslurry electrowinning step. The Arbiter Ammonia Leach is less energy intensive than the Nitric-Sulfuric Acid Process, resulting principally from the high heat of reaction since sulfide sulfur is oxidized all the way to sulfate. Improvements in the Nitric-Sulfuric Acid and Arbiter processes require a more effective recovery of waste heat.

In general, the high energy requirement for hydrometallurgical processes results from electrowinning, inefficient use of reaction heat, high process steam requirements, and large Level 2 components. It does appear that significant improvements can be made in energy usage by more effective waste heat recovery, new electrowinning technology, and the combination of alternate lower energy unit processes.

The Smelting-Electrorefining processes recover byproducts such as precious metals, selenium, and tellurium in the form of anode slimes. This stream of slimes is small, about 5 to 25 lb per ton of cathode. The slimes are treated by a combination of processes to recover these byproducts. Technology for the recovery of such byproducts from the hydrometallurgical processes is not as well developed. Furthermore, it will involve the handling and treatment of much higher volumes of solids residues (iron oxides and/or jarosites), about 3 to 6 tons per ton of cathode. This treatment is likely to entail more energy consumption than anode slimes treatment. An exception to this is the Sherritt-Cominco Process which produces only 0.7 tons of solid residue per ton of cathode copper, thus enhancing precious metals recovery. In addition this process can recover the associated metal values such as molybdenum and zinc.

One of the major apparent benefits of hydrometallurgical processing is the absence of significant emissions to the air from process units. In pyrometallurgical processing, on the other hand, the control of emissions is expensive in both energy and economic terms. This has to be weighed against the increased potential for water pollution. In this analysis, we have allowed for a significant amount of energy for the control of fugitive emissions in pyrometallurgy (about 4 million Btu per ton of cathode). In spite of this, there is a significant difference in energy consumption between the two types of processes generally in favor or pyrometallurgy.

Of all the processes proposed, Roast/Sulfite Reduction has the greatest potential for competing with smelting processes in terms of energy usage. However, the process is unproven. Also, effective recovery of heat from the roasting step by an auxiliary heat exchange system seems capable of reducing the reported values appreciably for both the Roast Leach and Sulfite Reduction.

The construction of hydrometallurgical process plants capable of producing 100,000 tons of copper per year seems unlikely, at least in the next decade. Application to smaller tonnages is more likely, i.e., less than 25,000 tons per year of finished copper. The hydrometallurgical process most likely to succeed in the future will have to be designed to recover process heat in a useful form and will require vastly improved electrowinning technology or use chemical reductants.

processing in the molten state, the procedure requires conditions which will maximize the reduction and separation of the copper. It should be noted that the Q-S process best addresses these questions conceptually.

- Continuous one-step smelting processes are energy efficient as compared to two-step processes because of better utilization of heats of reaction. In addition, a hot-matte transport step and the attendant heat loss and fugitive emissions are eliminated. Several of the new generation of pyrometallurgical processes can be operated in continuous one-step fashion. However, the potential for transfer of arsenic, antimony and bismuth to the metallic copper phase in such processes requires special design criteria. Current electrorefining technology is generally inadequate for handling significant levels of these impurities in anode copper. Therefore, research on unit operations which would remove these impurities from blister copper prior to electrorefining in a single continuous reactor would be very desirable. The successful implementation of this research would lead to true one-step smelting of copper concentrates and may result in a saving of 10-20% of the energy used in smelting. Potential approaches would include slagging and/or vaporization of the impurities. Future research for a large capacity copper smelting process for optimizing energy usage, environmental control and minimizing metal loss should be centered around the development of a single continuous reactor.
- The flue dusts collected in pyrometallurgical processing are rich in volatile impurities such as arsenic, zinc, and lead. Because of the high copper content (over 5%), these dusts are generally recycled. However, when impurity concentrations reach such levels that this recycling has a deleterious effect on copper quality, the dusts have to be stockpiled or discarded. This reduces copper recovery and represents a significant energy loss. Appropriate processes for flue dust treatment would prevent this loss and also recover valuable byproducts.
- Steam recovered from waste heat in smelters is used to generate electric power to drive the blowers in the acid plant and for converter air. If the smelter had an adjoining electrolytic refinery, the low level steam, after a topping steam turbine cycle, could be used for electrolyte heating. A detailed assessment of utility requirements in a smelter/refinery complex is necessary to quantify the potential for energy saving using this approach.

4. Hydrometallurgy

While hydrometallurgical processes show a higher level of energy consumption than pyrometallurgical processes, they are at an early state of development and, therefore, offer considerable potential for improvement. The areas for research and evaluation are:

- Research to decrease energy consumption in electrowinning is important since electrowinning consumes 21-24 million Btu's per ton of cathode copper or almost 20% of the total. This energy could be reduced by a direct approach to increase the efficiency of electrowinning by lowering overpotentials and by investigating alternative anode reactions. Another approach would be to avoid the use of electric energy for reduction (which incorporates the inefficiencies in electric power generation) and use, instead, other reductants such as hydrogen, sulfur dioxide, and other reducing gases or coal.

- Research is desirable to optimize the transfer of heat from the exothermic leaching reactions to the reactants more effectively. This would involve major modifications in reactor design.
- Research in hydrometallurgy process development most likely should move towards processes which pretreats the chalcopyrite feed to provide a more suitable feed material and either avoids electrowinning by using chemical reductants or uses some totally new, low energy electrowinning step.
- It may be possible to generate electrical energy while recovering copper by treating copper concentrates in a slurry electrode/fuel cell configuration. Research in this area has potential for energy savings in the future.

5. In Situ Solution Mining

While all of the research ideas discussed earlier increase conventional reserves by reducing energy requirements and costs, in situ solution mining is unique in that it adds low grade deep-seated deposits (which cannot be exploited economically by conventional technology) to the reserves of available copper.

A multi-faceted R & D program is desirable for optimizing the overall extraction of copper by in situ leaching techniques including a demonstration phase under field operating conditions to improve the technique to obtain higher recoveries than the 50% recovery assumed in this study. Specifically, such a program would include work on:

- actual oxygen or air consumption related to the type and extent of mineralization;
- application of recent developments in blasting stressed rock with flooded joints;
- weathering and leaching characteristics of copper porphyry ores under extended period of ore-solution contact;
- quantification of reactions with host rock potentially capable of complexing copper and consuming lixiviant; and
- modeling and simulation for optimization.

E. ENERGY SAVINGS POTENTIAL

The energy savings potential of the research ideas presented in Secton D is not uniform. Table E-1 shows estimates of this energy savings potential in terms of million Btu's per ton of cathode copper in the first numerical column. Since the U.S. produces about 2 million tons of copper from primary sources, the total potential for energy savings in the U.S. would be approximately 2 million times these numbers if we assume that each technique was successfully adapted to primary copper production. The actual savings that could be realized would vary considerably. For example, improvements in mining and milling would be applicable to the production of other ores and minerals or mineral products, such as cement. On the other hand, some of the techniques (e.g., flue dust treatment) are probably necessary only for a fraction of the concentrates used in primary copper production.

The second column shows the estimated probability of success in each area. The probabilities are designated "very high" and "high" if the approach has already been demonstrated in some fashion and requires technology transfer. The probability is designated "medium" if the direction of research and development is reasonably well defined but requires further work. Finally, the probability is designated "low" if the direction of research is not fully defined.

TABLE E-1

CHARACTERIZATION OF RESEARCH IDEAS

	Potential Energy Savings MMBtu/Ton	Probability of Success[2]	R&D Cost Implication[3]	Range of Applicability	Type of Research[5]
Mining					
Haulage vs. trucks	4	VH*	1	R	S,D
Blasting vs. crushing/grinding	Trade-off	H	1-2	R	S,D
Concentration vs. dump leaching	20-25	H	1	R	S,D
Fundamentals of dump leaching					
Increase aeration and copper extraction	10-20	M	2-3	R,G	L.P,D
Grinding					
Pebble mill autogeneous	4	M	2	R	S,L
Stabilizing control					
Optimal energy control	13	M	2-3	?	S,L
New classification techniques					
Other milling devices	NA[1]	L	1-2	G	L,P
Pyrometallurgy					
Waste heat for drying	0.7	H	1	R,G	S
Pyrometallurgical slag cleaning	2	M	3	R,G	S,L,P,D
Impurity removal from blister	2	M	3	R,G	S,L,P,D
Flue dust treatment	1	L	2-3	R	S,L,P,D
Waste heat steam/cogeneration	4-5	VH*	1	R	S
Single continuous reactor technology	4-7	H	3-4	G	P,D
Hydrometallurgy					
Electrowinning	8	L	3	G	S,L,P,D
Use of alternate reduction schemes	15	H	3	G	S,L,P,D
Reactor design for optimum heat transfer	3	H	1-2	G	S,D
In Situ Mining	2D	M	4	R,G	S,L,D

*Where applicable.

1. NA – Not available for "blue sky" type of ideas.
2. VH – Very high – approach has been demonstrated successfully elsewhere in the industry.
   H – High – approach based on technology transfer but not demonstrated.
   M – Medium – direction of research is known; needs further work.
   L – Low – direction of research not fully defined.
3. $0.1 Million = 1; $1 Million = 2; $10 Million = 3; $100 Million = 4.
4. R = Retrofit; G = Grassroots.
5. L = Laboratory; P = Pilot plant; D = Demonstration; S = Study.

The third column shows our assessment of the R&D cost implications. The fourth column characterizes each idea in terms of its potential for retrofit into existing plants versus its applicability to new, grassroots plants. This is an indication of the rate at which these ideas may be adopted, if successful. The last column shows the type of research necessary before the techniques will be adopted by industry.

Finally, it is important to address concepts not included in the specific recommendations as stated, or listed in Table E-1. Any process should be considered from the origin of the ore (mining) to the finished product as a total system. In this context significant energy conservation may result by matching individual steps to optimized energy conservation. Matching ore chemical and physical characteristics, minor and major impurities, and potential for by-product recovery with the process steps selected may have significant energy conservation implications.

Examples are:

- trade off between explosives and primary crushing in the open pit;
- bulk flotation followed by grinding and selective flotation;
- concentrate pretreatment before smelting or hydrometallurgical processing; and
- merging of hydrometallurgical and pyrometallurgical steps.

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1.0 FRONT-END OPERATIONS

1.1 INTRODUCTION

The various processes contributing to the production of a refined cathode copper product fall into two clearly defined categories, first the front-end processes of mining, concentration, and dump leaching, and second the subsequent processes of extraction and refining the copper concentrate product or the reduction of the copper in the dump leaching solution.

For the purpose of this analysis, the concentrate feed to the extraction and refining processes is assumed to conform to standard specification. We can thus consider these extraction and refining operations on an independent basis, conversion taking place from a standard feed to a standard product.

By contrast the front-end processes are open-ended on both sides; the mining operations being tied to the physical characteristics of the orebody and to the configuration of the mine, and the production requirements of both mining and concentrating depending on the conversion efficiency (percent recovery of contained copper) of the extraction and refining processes.

1.2 MINING OPERATIONS

1.2.1 Introduction

Some 90% of all copper ore mined in the U.S. comes from openpit operations (Engineering & Mining Journal, June 1977). While the balance must ultimately swing towards the mining of deep-seated deposits by underground or remote mining methods as the near-surface deposits become exhausted, the dominant role of openpit mining may be expected to continue or even increase in the nearer term of, say, the remainder of this century. In view of the complexities and variations of underground mining methods, and their relatively small contribution, this study is restricted to an examination of energy demand for surface mining operations only.

Two significant parameters affect energy demand in openpit mines, the physical dimensions of the excavation and the grade of ore sent to the mill. The operation of hauling broken ore and waste rock accounts for a major portion of the energy consumption; thus energy consumption is dependent on the vertical and horizontal dimensions of the excavation. As the pit becomes deeper, the energy for moving broken rock will increase, firstly because of the increased lift and haul distance to be travelled, and secondly because the ratio of waste to ore may increase with depth. The planning of openpit mines is today extended to depths of as much as 1,500 feet below the pit rim. The energy and dollar cost of hauling rock from such depth may dictate the economic life of surface mining.

The average mill-head grade of copper ore mined in the U.S. has shown a continuously decreasing trend since the start of this century, despite the fact that the real price of copper metal has not increased. Technological improvements in mining and processing methods have reduced unit costs, while concurrently, the richer ores have become exhausted and replaced by lower grade ore. Consequently, more ore must now be mined and treated to produce a given amount of copper metal. While we may expect technological innovation to continue at least at the same tempo as in the past, it must be remembered that the incentive in the past was to replace expensive manpower by cheap energy. Increased mechanization usually results in higher energy consumption per unit of production. As the cost of energy increases, the conflict between energy optimization and dollar optimization is likely to resolve itself, that is, as energy becomes more costly the profit motive of private enterprise will focus more attention on energy conservation, and technological innovation and economic policy decisions will be directed toward this objective.

A further consideration of growing significance in the past decade has been the increasing emphasis on environmental protection through government regulation. Compliance with the requirements of these regulations will undoubtedly add to the energy and dollar cost of the mining and extraction operations, reflecting on mining policy in terms of higher cut-off grade and curtailment of the economic life of the mine. In view of the above factors, the trend of falling average mill head grade may well be reduced, or even reversed.

1.2.2 Method of Analysis

The principal objective of this investigation is to determine the order of magnitude of energy consumption for each of the sequential processes required to produce a final cathode copper product. Two main subdivisions are recognizable — the front-end operations of mining and treating the ore to produce a copper sulfide concentrate, and the subsequent operation of extraction and refining to produce a cathode copper product. While the extraction and refining processes are independent of the front-end operations (assuming a standard concentrate composition) the converse is not necessarily true; loss of metal during refining affects the tonnage of ore to be mined, crushed, milled and concentrated by flotation (per ton of cathode copper produced). The total energy attributable to a particular extraction and refining process must therefore take account of its metal recovery factor as reflected in the front-end energy requirement.

The energy assessment for the mining operations is contingent on the physical characteristics of the ore body and the pit conformation. An initial attempt was made to obtain actual energy consumption data for operating openpit mines in the U.S.A. However, the mining companies were unwilling to divulge such information, although it is known that the relevant data is submitted in the form of routine reports to the Department of Energy. Consequently, it was decided to revert to an analytical type of assessment based on hypothetical mineralization and mining models. It is believed that this approach gives estimates of acceptable definition, and has the added advantage that the model parameters can be varied at will to ascertain their sensitivity to change. These models are described below.

1.2.2.1 The Mineralization Model

Mineral values are not evenly distributed throughout an ore body. Values ranging from high to low tenor usually follow a law of probability such that the occurrence of some values is more common than that of other values. This probability density distribution will vary from deposit to deposit.

In an openpit mine it is usually necessary to mine the low grade ground in order to gain access to the payable high grade ore. Only rock above a predetermined cut-off value is sent to the plant for treatment. The low grade rock below this value goes to the waste dump or to surface leach dumps for recovery of some of the copper content by acid leaching.

The mineralization model used in this simulation is typical of a porphyry copper deposit although it does not necessarily correspond to any particular deposit. It is assumed that the average copper value of blocks of ore of minable size is log-normally distributed within the ore body such that the mean value of the ore body is 0.45% Cu, and the logarithmic variance of values is 0.2(%) Cu (U.S. House of Representatives, June 1976). This probability density distribution is shown graphically in Figure 1.2-1. (a)

It follows that as the cut-off grade is increased the tonnage available for mining is reduced, while the average value of the tons mined is increased. Mathematically this relationship may be expressed as follows:

$$\text{Fraction of total tons above cut-off grade} = \int_{gc}^{\infty} f(x) \cdot dx$$

$$\text{Average grade of tons above cut-off grade} = \frac{\int_{gc}^{\infty} x \cdot f(x) \cdot dx}{\int_{gc}^{\infty} f(x) \cdot dx}$$

The grade/tonnage relationship is shown graphically in Figure 1.2-1 (b), and is tabulated in Table 1.2.1. A cut-off grade of 0.29% Cu is chosen as a base for this analysis, that is, 70% of the tonnage mined from the ore body will go to the mill at an average value of 0.55% Cu, and 30% of the tonnage mined from the ore body will go to surface leach dumps at an average grade of 0.22% Cu.

1.2.2.2 The Mine Model

Figure 1.2.2 is a cross section through a typical openpit mine exploiting a roughly cylindrical ore body extending vertically in depth. The model is based on the following assumptions:

Vertical depth below rim (H) = 750′
Dynamic slope angle of sidewalls (θ) = 30°
Ave. slope of haul roads in pit = 6%
Surface haul to dumps = 2500 ft. @ 6% grade
Surface haul to primary crushes = 2500 ft. level
Overburden/ore body stripping ratio $\left(\frac{AC}{CB}\right)$ = 1.25
Mill head value of ore = 0.55% Cu
Value of flotation concentrate = 25% Cu
Value of flotation tails = .069% Cu
  i.e., recovery factor ore to concentrate = 87.455%
Recovery factor concentrate to cathode copper = 98.67%
  i.e., recovery factor ore to cathode = 86.29%
Primary cathode copper produced per year = 100,000 tons

Tonnage Notation: (Refer to Figure 1.2.2)
TO = Tons ore sent to mill (DB)
TM = Tons mined from ore body (CB)

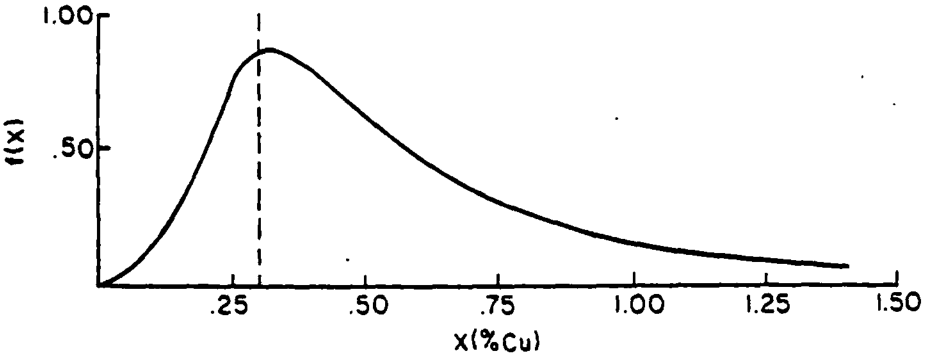

FIGURE 1.2–1 (a) LOG–NORMAL DISTRIBUTION OF Cu GRADES

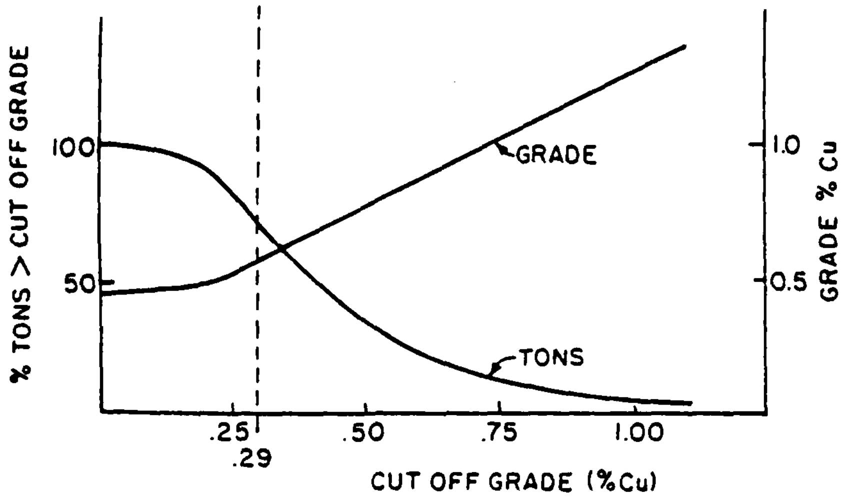

FIGURE 1.2–1 (b) GRADE/TONNAGE RELATIONSHIP

TABLE 1.2-1

GRADE/TONNAGE RELATIONSHIP

Cut off Value (% Cu)	Tons > COV* (%)	Average Grade (% Cu)	
		Tons > COV	Tons < COV
0	100	.45	––
.22	85	.50	.17
.29	70	.55	.22
.34	58	.60	.24
.40	48	.65	.27
.45	39	.70	.29
.50	32	.75	.31
.55	26	.80	.32

* COV = Cut off value

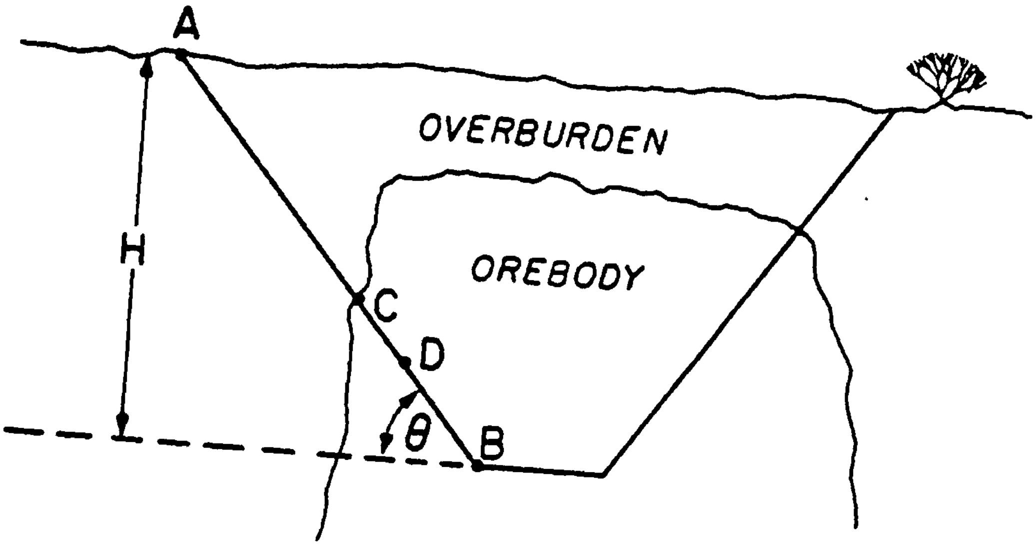

FIGURE 1.2-2 THE MINE MODEL

TD = Tons ore sent to dump leach (CD)
TS = Tons overburden stripped (AC)
TW = Total tons mined from ore body not sent to mill (AD)
TT = Total tons mined (AB)

Stripping Ratio Notation (Refer to Figure 1.2.2)

RSM = Ratio of tons of overburden stripped to tons mined from ore body
RDO = Ratio of tons ore sent to dump leach to tons of ore sent to mill
RSO = Ratio of tons of overburden stripped to tons of ore sent to mill
RWO = Ratio of total tons mined from ore body not sent to mill to tons of ore sent to mill
RSM = TS/TM = AC/CB
RDO = TD/TO = CD/DB - - - - CD = DB • RDO
RSO = TS/TO = AC/DB - - - - AC = DB • RSO
RWO = TW/TO – AD/DB - - - - AD = DB • RWO
RSM = TS/TM = AC/CB - - - - CB = AC • RSM

Examples of calculations:

0.55% = ore grade
.8629 = fractional recovery from ore to cathode copper.
100,000 = tons of cathode copper/yr.

$$\text{Tons to mill (TO)} = \frac{100{,}000 \times 2{,}000}{.55 \times 20 \times .8629} = 21.0706 \times 10^6 \text{ tons/year}$$

RSM = 1.25
RDO = 30/70 = .4286
$TD = TO \times RDO = 21.0706 \times 10^6 \times .4286 = 9.0309 \times 10^6$
$TM = TO + TD = (21.0706 + 9.0309) \times 10^6 = 30.1015 \times 10^6$
$TS = TM \times RSM = 30.1015 \times 10^6 \times 1.25 = 37.6268 \times 10^6$
$TW = TS + TD = (37.6268 + 9.0309) \times 10^6 = 46.6577 \times 10^6$
$TT = TW + TD = (46.6577 + 21.0706) \times 10^6 = 67.7283 \times 10^6$
$RWO = TW/TO = 46.6577 \times 10^6/21.0706 \times 10^6 = 2.2144$
$RSO = TS/TO = 37.6286 \times 10^6/21.0706 \times 10^6 = 1.7857$

1.2.3 Analysis of Energy Demand in an Openpit Mine

Energy utilization in an openpit mine is analyzed in the context of the above models and in relation to the headings below, using typical values extracted from published literature and operating mine data. The energy consumption attributable to each operation is shown diagramatically in Figure 1.2.3 in terms of Btu per short ton of refined cathode copper produced. For the particular model used in this analysis, the overall energy attributable to the mining operation is 27.999 million Btu per ton of refined cathode copper produced.

1.2.3.1 Drilling

The estimate of the energy utilization for drilling operations is based on published data of drilling equipment, and tonnage duties for 4 large copper mines in the State of Arizona. The calculated average energy consumption amounts to 904 Btu per short ton of broken rock produced. In terms of our model, this converts to 0.612×10^6 Btu per ton of cathode copper produced (see Appendix 1.2.3.1).

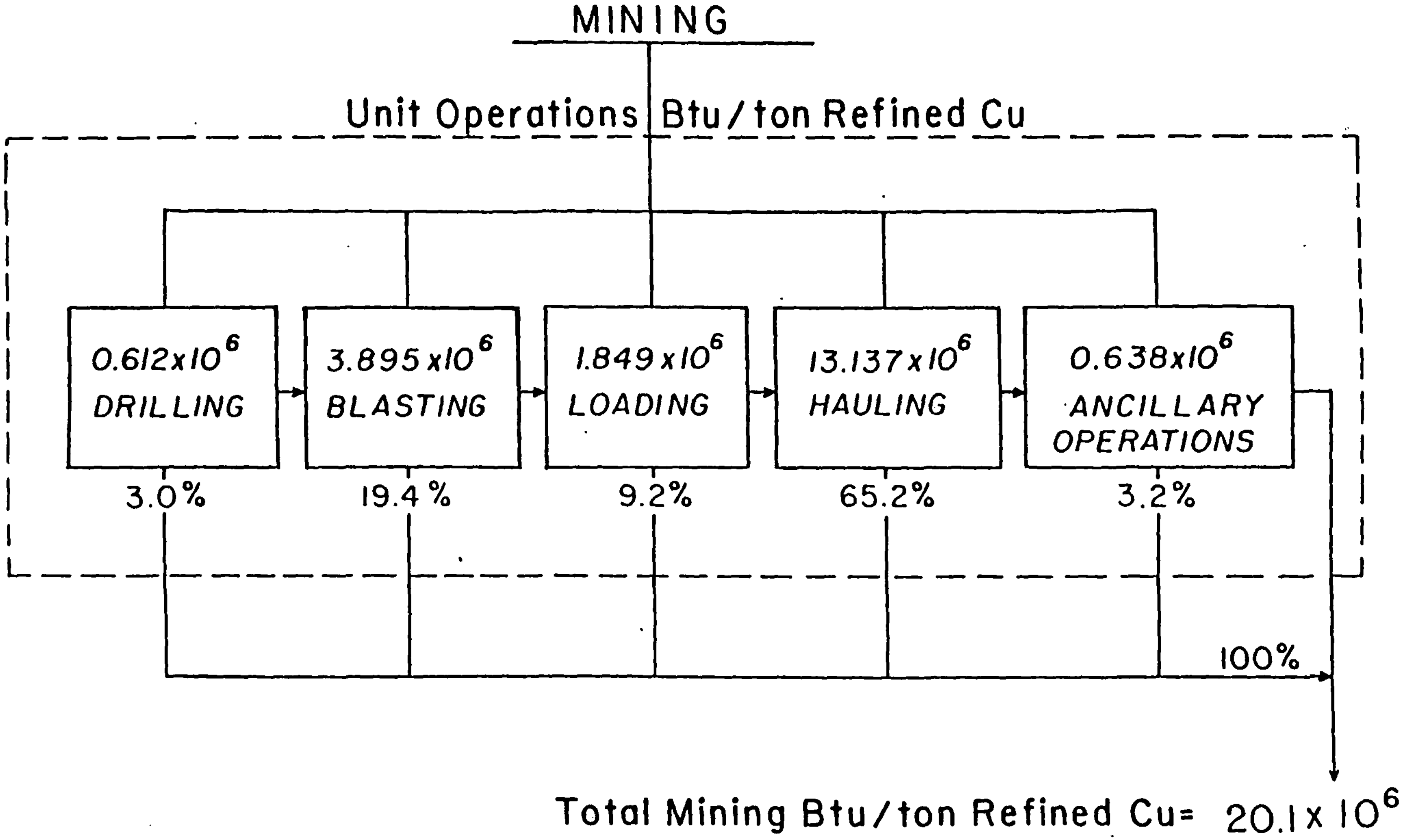

FIGURE 1.2-3 ENERGY REQUIREMENTS FOR EACH OPERATION IN MINING

Drilling is a relatively small user of energy, accounting for some 3.0% of the total energy consumed in the mining operation. (See Fig. 1.2.3.) No significant energy saving developments in drilling technology are anticipated in the foreseeable future.

1.2.3.2 Blasting

It is considered that explosives are a primary source of energy and that the operation of rock fragmentation is an energy function. It is therefore necessary to convert explosive energy into coal equivalent in the same way as has been done for electric power and diesel fuel.

The explosive agent used in openpit mines is primarily ANFO, ideally a mixture of 94.5% ammonium nitrate plus 5.5% fuel oil. The energy value of ammonium nitrate is estimated as 30.0 million Btu per ton (this value will vary depending on the production process used to produce ammonia whether from primarily natural gas feedstock or as a by-product from steel plant coking ovens.) A weighted average blasting agent factor of 0.27 lbs of explosives per ton of rock blasted is derived in Appendix 1.2.3.2. We can calculate the energy value of 1 lb of blasting agent (ANFO) in terms of its equivalent coal energy as follows:

$$\begin{aligned}
&.945 \text{ lb. Ammonium Nitrate} &&= 0.945 \times 30 \times 10^6/2000 \\
& &&= 14175 \text{ Btu} \\
&.055 \text{ lb. Fuel Oil} &&= .055 \times 138690 \\
& &&= 7268 \text{ Btu} \\
&1 \text{ lb. Blasting Agent} &&= 21443 \text{ Btu Coal Energy}
\end{aligned}$$

Neglecting fuses, detonators and primers to initiate the explosion, we calculate the blasting energy consumption for our model as follows:

$$\begin{aligned}
\text{Blasting Energy} &= .27 \times 21443 \text{ Btu/ton Rock} \\
&= 5790 \times 67.7283 \times 10^6 \text{ Btu (total)} \\
&= 3.895 \times 10^6 \text{ Btu/ton Cathode Copper}
\end{aligned}$$

In terms of this model, blasting accounts for 19.4% of the total energy used in mining (Table 1.2.3). It is clear that any increase in the cost of energy will be reflected as a substantial rise in the cost of explosives. It may be anticipated that this rise in cost will stimulate research into more efficient use of explosives and could substantially modify present philosophies regarding the optimization of explosive utilization in relation to the other mining activities such as loading and hauling.

1.2.3.3 Loading

We assume an average power utilization factor for loading equipment of 0.6 kWh per bank cubic yard (BCY) of copper ore of density 4500 lbs./BCY. (Pfleider, Surface Mining, p. 439).

$$\frac{.6 \times 2000 \times 10239}{4500} = 2730 \text{ Btu/ton rock.}$$

$$\frac{2730 \times 67.7283 \times 10^6}{100{,}000} = 1.849 \times 10^6 \text{ Btu/ton cathode copper}$$

The energy used for loading operations will vary relative to the conditions of loading, the equipment used, and the nature of the shot rock. The indicated energy utilization of 1.849 x 10^6 Btu/ton of cathode copper represents only some 9.2% of the total energy used in mining, compared with 19.4% for explosives (Fig. 1.2.3).

Mine operators continuously seek to optimize fragmentation with respect to the overall economics of drilling, blasting, loading, hauling and primary crushing. Under conditions of relatively cheap abundant energy, preference is given to production equipment utilization, that is, the blasting operation is designed to produce a fragmentation size grading with minimum representation of large rocks which may adversely affect the loading operation; consequently, the fine end of the spectrum is unnecessarily over-represented. As energy becomes less plentiful and more costly, it can be expected that the bias of attention will swing toward more effective use of explosive energy.

1.2.3.4 Hauling

The traditional method of hauling rock in openpit mines is by means of a fleet of rear dump trucks which may range in size from 30 tons to 250 tons carrying capacity. The weight of the empty truck is some 75% of the live load. This nonproductive weight must be moved twice the distance of the live load, up the incline carrying the load, and return empty. A significant part of the total energy consumption is used in moving the carrier. Such inefficient use of energy invites examination of alternative forms of transportation of broken rock.

Two large openpit copper mines in the State of Arizona have introduced continuous conveyor belt systems as a partial replacement of truck haulage. Broken ore and waste is hauled by truck from the active benches to primary crushers located at a central point within the pit. The crushed rock is moved by conveyor belt to surface, either to the waste dump or to the mill. These systems are described respectively by J. J. Coille and F. W. Sweitzer. Operating statistics covering a significant continuous period of truck hauling and conveyor transportation have been confidentially provided by one of these mines. The analyzed results are summarized in Appendix 1.2.3.3 in relation to a synthetic unit of performance representing the product of tons moved by effective level feet traveled (TELF).

Consider the effective work performed in hauling rock up an incline by dump truck, neglecting the nonproductive work of moving the carrier up and down the slope:

Effective work per ton = Slope distance x (Rolling resistance + Gravity resistance)
Rolling resistance = 40 lb./ton for a normal mine haulage road
Gravity resistance = (20 x % grade) lb./ton
Effective work per ton = SD (40 + 20 x % grade)

The product SD(2 + % grade) is a proportional measure of the effective work accomplished, equivalent to moving one ton of rock through an equivalent level distance (ELF) of SD(2+% grade).

Total Effective Work = Tons x SD (2 + % grade) TELF.

An estimate of the energy consumed for transporting broken rock can now be made in respect to the mine model previously discussed. (See Fig. 1.2-4.) Assume conventional rock hauling by rear dump truck operating at an average energy utilization factor of 0.2963 Btu/TELF as derived in Appendix 1.2.3.4.

In Figure 1.2.4 we have:

H = Depth of pit
HT = Average lift for overall tonnage
HS = Average lift for overburden stripping
HM = Average lift for tons mined from ore body

$$\frac{AC}{AB} = \frac{TS}{TT} = \frac{37.6268}{67.7283} = .5556$$

AB = 750/sin 30° = 1550
AC = 1500 x .5556 = 833'
CB = 1500 – 833 = 667'
HT = 750/2 = 375'
HS = 1/2 AC sin 30° = 208'
HM = 2 HS + 1/2 CB sin 30° = 583'
Stripping duty = TS x Slope Dist x (2 + % grade)

$$= 37.6268 \times 10^6 \times 208 \times \frac{100}{6} \times (2 + 6)$$

$$= 1.0435 \times 10^{12} \text{ TELF}$$

Add duty for surface transportation of ore and waste to primary crushers and dumps respectively:

To Dumps = TW x Slope Dist (2 + % grade)
= $46.6577 \times 10^6 \times 2500 \times 8$
= 933154×10^6 TELF
To Primary Crushers = TO x Slope Dist (2 + % grade)
= $21.07 \times 10^6 \times 2500 \times 2$
= 1.05×10^{11} TELF
Mining Duty = TM x Slope Dist (2 + % grade)

$$= 30.10 \times 10^6 \times 583 \times \frac{100}{6} \times 8$$

= 2.40×10^{12} TELF
Total Hauling Duty = 4.42×10^{12} TELF
Energy/ton Cathode Copper = $4.42 \times 10^6 / 100{,}000$
= (13.137×10^6 Btu, by computer)

Referring to Figure 1.2.3 it can be seen that the hauling operation accounts for 65.2% of the total energy, consumed by openpit mining under the assumed conditions of the model.

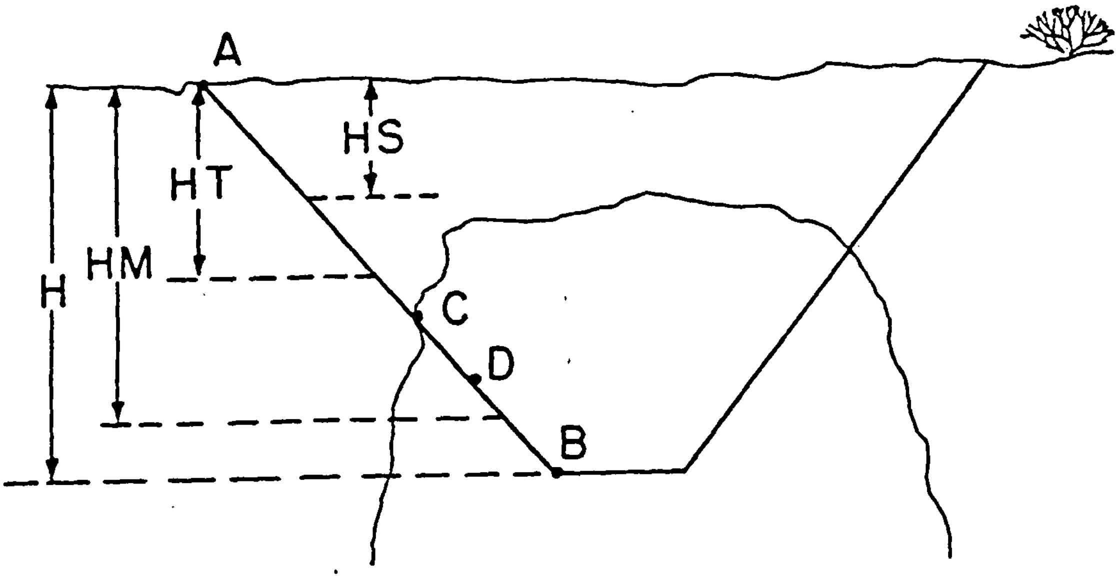

FIGURE 1.2-4 AVERAGE HAUL LIFT DUTY

In Appendix 1.2.3.3 it is shown that at the mine concerned the installation of a conveyor belt system to partially replace truck haulage resulted in a saving of some 30% in energy consumption. While the use of belt conveyors would not be feasible for all openpit mine configurations, it is clear that rock transportation is one area where very thorough research and development will pay big dividends in terms of savings in energy and dollar costs, especially as openpit mines grow in depth and extent in the future.

1.2.3.5 Ancillary Operations:

The ancillary operations associated with openpit mining are extremely diverse and their energy consumption is difficult to estimate. However, the total energy consumed by these operations is relatively small so that an error in estimation will have little if any effect on the overall outcome of this investigation. The following estimates are made (See Appendix 1.2.3.4):

Auxiliary mobile equipment = 0.399×10^6 Btu/ton Cu
Dewatering = 0.016×10^6 Btu/ton Cu
Reclamation equipment = 0.021×10^6 Btu/ton Cu
Revegetation = 0.202×10^6 Btu/ton Cu

Total 0.638×10^6 Btu/ton Cu

It is shown in Figure 1.2.3 that ancillary operations account for some 3.2% of the total energy consumption for mining operations.

1.2.4 Sensitivity Analysis

Three basic parameters may substantially affect the energy consumption of the front-end operations of mining and/or copper sulfide concentration. These are the average grade of the ore treated, the overburden to orebody stripping ratio (RSM), and the pit depth below the surface rim. The sensitivity of the model to changes in these parameters is tested by computer in relation to conventional extraction practice of sulfide concentration, reverberatory smelting, fire converting and electro-refining.

1.2.4.1 Sensitivity to Changes in Cut-off Grade

The grade/tonnage relationship given in Table 1.2.1 will apply, provided the mineralization model does not change. However, it must be remembered that some of the contained copper in the reject tonnage below cut-off grade may subsequently be recovered by means of dump leaching (see section 1.2.5). Provisionally neglecting this possible recovery of additional copper, the sensitivity of the model to change in cut-off grade is shown in Table 1.2.2.

TABLE 1.2.2

EFFECT OF VARYING CUT-OFF GRADE

Cut Off Grade (% Cu)	Millhead Grade (% Cu)	Tons Milled x 10^6	Btu x 10^6/ton Cath. Copper Produced			
			Mining	Conc.	Refining	Total
0	.45	26.6005	17.4	53.7	35.2	106.3
.22	.50	23.515	18.3	47.5	35.2	101.0
.29	.55	21.070	20.1	42.6	35.2	97.9*
.34	.60	19.086	22.2	38.6	35.2	95.9
.40	.65	17.444	24.7	35.2	35.2	95.1
.45	.70	16.061	28.1	32.4	35.2	95.8

*Standard Reference

It can be seen in the above tabulation that the effect of lowering the cut-off grade will be to decrease the energy per ton of cathode copper produced for the mining operation, while increasing that for the concentrating operation. For this model the counter-active changes result in a very small net change in overall energy requirement, although a minimum is indicated at a cut-off value of .34% Cu.

Let us now consider the effect of recovering some of the copper content of the reject ore below the cut-off grade by dump leaching (Sect. 1.2.5). Reference to Table 1.2.3 shows that the tonnage of reject ore will increase as the cut-off grade is increased, and its average grade will also increase; in other words the potential recovery of copper by dump leaching will be substantially increased. The energy cost of this additional copper is estimated in Sect. 1.2.5 at 93.74 million Btu/ton. The average effect of a change in cut-off grade is tabulated below.

TABLE 1.2.3

OVERALL EFFECT OF VARYING CUT-OFF GRADE

Cut-off Grade (% Cu)	0	.22	.29	.34	.40	.45
Tons Milled (x 10^6)	26.60	23.52	21.07	19.09	17.44	16.06
Mill-head Grade (% Cu)	.45	.50	.55	.60	.65	.70
Copper Produced (Tons)	100,000	100,000	100,000	100,000	100,000	100,000
Btu/ton Copper (x 10^6)	106.3	101.0	97.9	95.9	95.1	95.7
Tons Leached (x 10^6)	0	4.15	9.03	13.82	18.90	25.12
Dump Grade (% Cu)	0	.17	.22	.24	.27	.29
Copper Produced (Tons)	0	2,351	6,622	11,056	17,007	24,284
Btu/ton Copper (x 10^6)	0	93.7	93.7	93.7	93.7	93.7
Total Tons Treated (x 10^6)	26.60	27.67	30.10	32.91	36.34	41.18
Total Cu Produced (Tons)	100,000	102,351	106,622	111,056	117,007	124,284
Ave. Btu/ton Cu (x 10^6)	106.3	100.8	97.6	95.7	94.9	95.3
% Resource Recovery	.835	.822	.787	.750	.715	.671

The above estimates are based on broad assumptions regarding mineralization characteristics, pit conformation and plant layout. Nevertheless it is apparent that an interesting scope for optimization studies exists in this area — that is, in the trade-off of energy conservation versus resource recovery. Changes in technology or design could well result in material changes in the selection of cut-off grade for a particular mine.

1.2.4.2 Sensitivity to Changes in Stripping Ratio

Table 1.2.4 indicates the way the energy consumed in mining varies with the overburden to orebody stripping ratio (RSM).

TABLE 1.2.4

EFFECT OF VARYING STRIPPING RATIO

Stripping Ratio (RSM)	Btu x 10^6/ton Cathode Copper Produced			
	Mining	Conc.	Refining	Total
1.00	17.79	42.57	35.17	95.53
1.25	20.13	42.57	35.17	97.87*
1.50	22.47	42.57	35.17	100.21
1.75	24.81	42.57	35.17	102.55
2.00	27.15	42.57	35.17	104.89
2.50	31.84	42.54	35.17	109.57

*Standard Reference.

1.2.4.3 Sensitivity to Changes in Depth

The energy expended in transporting broken rock is a function of the lift and horizontal distance moved. (Refer to Section 1.2.3.4.) This relationship is reflected in the total energy for mining as shown in Table 1.2.5.

TABLE 1.2.5

EFFECT OF VARYING DEPTH OF PIT

Depth of Pit (Feet)	Btu x 10^6/ton Cathode Copper Produced			
	Mining	Conc.	Refining	Total
500	24.67	42.57	35.17	102.95
750	28.00	42.57	35.17	106.28*
1000	31.36	42.57	35.17	109.64
1250	34.71	42.57	35.17	112.99
1500	38.05	42.57	35.17	116.33

*Standard Reference.

1.2.5 Dump Leaching

Dump leaching accounts for some 30% of the primary copper produced in the United States. While much of this comes from the treatment of old existing low grade copper dumps, it is clear that the recovery of some of the copper content of currently mined low grade ore should be taken into consideration in the overall assessment of the energy content of domestic copper production.

For the purpose of this analysis it is assumed that all the low grade ore below the cut-off value will be systematically placed in finger dumps suitable for current acid leaching. (Refer to the mineralization model section 1.2.2.1, and Table 1.2.1.) The base condition for this analysis calls for a cut-off grade of .29% Cu, giving 30% of mineralized ore below cut-off grade sent to the leach dumps at an average value of .22% Cu.

The energy for dump leaching is predominantly required for the circulation of the leacheate solutions; this in turn is essentially a function of the lift and horizontal distance from the cementation plant to the top of the leach dumps. The following specifications are assumed:

Finger Dumps: 150′ Vert x 400′ flat top x 800 base.
Lift from plant to top of dump 450′
Hor. Dist. from plant to dump 5000′
Tons leached per year (TD in sect. 1.2.2.1) = 9.0309 x 10^6 tons @ .22% Cu
  9.0309 x 10^6 x .22 x 20 = 39.7360 x 10^6 lbs Cu/year
  @ 33% recovery = 6622.667 tons/year
  @ 360 days per year = 36,792 lbs/day
  Leacheate concentration .5 gr/litre = 4.2 lbs/1000 U.S. gal.
  Daily Circulation = 8.7600 x 10^6 gal./day
  = 6083 gal./min.

From Ingersoll Rand Hydraulic Data Tables for 14" I.D. pipe we get:

Q = 3077 gpm
V = 6.42 ft/sec
H_V = .64 ft
H_F = 1.58 ft/100′

Pumped Flow of barren solution
  Gravity Head = 450 ft
  Spray Head = 50 ft
  Velocity Head = 1 ft
  Friction Head = 79 ft
  Fittings = 40 ft
  620 ft

Q = 6083 x .13369
= 813 ft^3/min

Return flow of pregnant solution
  Minm. Head for free flow = (5000 x .0158) + 1 = 80 ft.
  Therefore gravity head of 300 ft will effect return flow.

$$\text{Water Horsepower} = \frac{H \times Q \times 62.4}{33{,}000}$$

$$= \frac{620 \times 813 \times 62.4}{33{,}000}$$

= 953 H.P.

Pump H.P. @ 70% efficiency = 1362 H.P.

Energy per day = $1362 \times .745 \times 24$

= 24,346 KW hr/day

x 10,239 Btu/kWhr = 249.28×10^6 Btu/day

$$\text{Specific Energy} = \frac{249.28 \times 10^6 \times 2000}{36{,}792}$$

= 13.551×10^6 Btu/ton Cu.

On the basis of the above assumed conditions we have 6622 tons per year of copper extracted by dump leaching low grade ore (below cut-off grade) at a front-end energy cost of 13.551×10^6 Btu per ton of contained copper. The gross energy cost per ton of cathode copper produced must take account of the subsequent refining processes. Assume that dump leach ore does not carry any cost of mining, and that the cement copper is introduced into the reverberatory smelting furnace with the copper sulfide concentrate feed. The gross energy cost will then be:

Energy for circulating solutions = 13.55×10^6 Btu/ton Cu

Energy for cementation (Sect. 1.8) = 45.05×10^6 Btu/ton Cu

Energy for refining (Sect. 2.3) = 35.14×10^6 Btu/ton Cu

Total Energy = 93.74×10^6 Btu/ton Cu

1.2.6 Conclusion

The energy attributable to mining is to a large extent dependent on the physical parameters of the individual mine concerned, in particular on the nature of mineralization, the cut-off grade demarcating 'ore to mill' from 'low grade ore to dumps,' the overburden to ore stripping ratio, and the depth and dimensions of the pit. Reference to Section 1.2.4 indicates the extremely wide range of possible variation in energy requirement.

In addition to the sensitivity to internal mining parameters, the energy required by the mining operation per ton of cathode copper produced is a function of the recovery factor in the succeeding processes of copper sulfide concentration and refining. The lower the recovery in these processes the more ore must be provided by the mining operation to produce the final target of 100,000 tons of refined cathode copper. This reflected additional energy demand in the front-end processes should be taken into account in the assessment of alternative processes.

This report highlights certain areas where further research may be fruitful in the context of energy conservation. These are:

Rock hauling
Explosive utilization
Optimization of cut-off grade taking account the trade off between conventional concentration and dump leaching.

With the rapidly rising cost of energy it is considered that normal economic motives will tend to stimulate accelerated research in the above areas in the future.

1.2.7 References

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APPENDIX 1.2.3.1

Energy Consumption: Blasthole Drilling

The calculation of direct energy consumption for blasthole drilling is based on published equipment provision for four large open pit copper mines (Engineering and Mining Journal, June 1977) and the manufacturer's estimates of unit energy consumption for the relevant equipment.

Mine A

Operating Data: 5-45R Rotary Drills
190,000 tons mined per day
5 drills/shift x 3 shifts/day x 7.25 hr/day = 108.75 hr/day

Diesel Fuel

108.75 hr/day x 12.86 gal/hr = 1,399 gal/day
1399 gal/hr x 138,690 Btu/gal = 194,027,310 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 21 gal/day
21 gal/day x 148,690 Btu/gal = 3,122,490 Btu/day
Total Direct Energy = 197,149,800 Btu/day

Mine B

Operating Data: 5-40R Rotary Drills
2-60R Rotary Drills
135,000 tons mined per day
7 drill shifts per day
7 drill shifts/day x 7.25 hr/shift = 50.75 hr/day
Assume use of drills is proportional to number of drills.

40R 50.75 hr/day x 5/7 = 36.25 hr/day
60R 50.75 hr/day x 5/7 = 14.5 hr/day

Diesel Fuel

40R 36.25 hr/day x 10.71 gal/hr = 388 gal/day
60R 14.5 hr/day x 19.29 gal/hr = 280 gal/day
688 gal/day x 138,690 Btu/gal = 95,418,720 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 10 gal/day
10 gal/day x 148,690 Btu/gal = 1,496,900 Btu/day
Total Direct Energy = 96,915,620 Btu/day

Mine C

Operating Data: 4-45R Rotary Drills
4-60R Rotary Drills
256,000 tons mined per day
5 drills per shift 3 shifts per day
15 drill shifts/day x 7.25 hr/shift = 108.8 hr/day
Assume use of drills is proportional to number of drills

45R 108.8 hr/day x 4/8 = 54.4 hr/day
60R 108.8 hr/day x 4/8 = 54.4 hr/day

Diesel Fuel

40R 54.4 hr/day x 12.86 gal/hr = 699.6 gal/day
60R 54.4 hr/day x 19.29 gal/hr = 1,049.4 gal/day
Total = 1,749.0 gal/day
1,749.0 gal/day x 138,690 Btu/gal = 242,658,810 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 26 gal/day
26 gal/day x 148,690 Btu/gal = 3,865,940 Btu/day
Total Direct Energy = 246,434,750 Btu/day

Mine D

Operating Data: 4-60R Rotary Drills
107,400 Tons mined per day
4 drill shifts per day 1 shift per day
7.5 hr/shift
4 drills/shift x 7.5 hr/shift = 30.0 hr/day

Diesel Fuel

60R 30 hr/day x 19.29 gal/hr = 579 gal/day
579 gal/hr x 138,690 Btu/gal = 80,301,510 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 9 gal/day
9 gal/day x 148,690 Btu/gal = 1,338,210 Btu/day
Total Direct Energy = 81,639,720 Btu/day

Mine	Tons Mined Per Day	Energy Equivalent Btu/day
A	190,000	197,149,800
B	135,000	96,915,620
C	256,000	246,434,750
D	107,400	81,639,720
Total	688,400	622,139,890

Average Energy = 622,139,890 Btu/day
688,400 tons mined/day
= 904 Btu/ton mined

APPENDIX 1.2.3.2

Energy Consumption: Explosives Utilization

Derivation of the powder factor used in calculation of blasting energy use is accomplished in the following manner:

Mine	Tons Mined per Year^2		Powder Factor lb/ton		lb Blasting Agent Used per Year
1	39,514,000	x	0.20	=	7,902,800
2	27,108,000	x	0.27	=	7,319,160
3	36,583,486	x	0.43	=	15,380,898
4	57,046,000	x	0.25	=	14,261,500
5	18,672,100	x	0.62	=	11,576,702
6	145,264,340	x	0.224	=	32,510,159
Total	324,187,926	x	(0.27)	=	88,951,219

$$\frac{88{,}951{,}219 \text{ lb ANFO/yr}}{324{,}187{,}926 \text{ T/yr}} = 0.27 \frac{\text{lb ANFO}}{\text{T}}$$

The tonnage-weighted-average blasting agent use for six large open pit copper mines is 0.27 lb/T.

APPENDIX 1.2.3.3

Energy Consumption: Rock Hauling

The following tabulation is a summary of actual operating statistics covering the transportation of broken rock by dump truck and conveyor belts for a continuous period of nine months, as provided confidentially by a large openpit copper mine in the State of Arizona.

TRUCK HAULING (Waste and Ore)

Ore and Waste Rock hauled = 3.898×10^{8} short tons
Average slope distance = 5730 feet
Average Vertical Lift = 221.5 feet
Average gradient = 3.87%
Total Effective work units = 1.311×10^{12} TELF
Diesel fuel consumed = 2,759,279 gallons
*Coal energy equivalent = 3.827×10^{7} Btu
Lube oil consumed = 39,361 gallons
*Coal energy equivalent = 5.89×10^{9} Btu
Total Energy Consumption = 3.886×10^{11} Btu
Unit Energy consumed = 0.2963 Btu/TELF

WASTE ROCK CONVEYING

Waste rock transported = 2.064×10^{7} short tons
Slope length of conveyor system = 7,079 feet
Vertical lift = 414 feet
Average gradient = 5.86%
Total effective work units = 1.149×10^{12} TELF
Electric power consumed = 2.0924×10^{7} kWhr
*Coal energy equivalent = 2.142×10^{7} Btu
Unit energy consumed = 0.1865 Btu/TELF

WASTE ROCK CRUSHING

Waste rock crushed = 2.064×10^{7} short tons
Electric power consumed = 4.581×10^{6} kWhr
Coal energy equivalent = 4.69×10^{10} Btu
Unit Energy consumed = 2,272 Btu/ton

ORE CONVEYING

Ore transported = 2.214×10^{7} short tons
Slope length of conveyor system = 18,216 feet
Vertical lift = 457 feet
Average gradient = 2.51%
Total effective work units = 1.819×10^{12} TELF
*Coal energy equivalent = 3.533×10^{7} kWhr
Unit energy consumed (ore) = 0.1989 Btu/TELF
Mean unit energy (ore and waste) = 0.1941 Btu/TELF

*Coal energy equivalents
1 gal. diesel fuel = 138,690 Btu
1 gal. Lube oil = 149,690 Btu
1 kWhr = 10,239 Btu

Significant unit energy consumption figures extracted from the above tabulation are:

Truck Hauling = 0.2963 Btu/TELF
Conveyor Transportation = 0.1941 Btu/TELF
Waste Rock Crushing = 2272 Btu/ton

Considering only the existing conveyor system we have:

Energy Consumed – Waste crushing = 4.69 x 10^{10} Btu
– Waste conveying = 2.142 x 10^{10} Btu
– Ore conveying = 3.617 x 10^{11} Btu
– Total = 6.229 x 10^{7} Btu
Haul Duty – Waste conveying = 1.149 x 10^{12} TELF
– Ore conveying = 1.819 x 10^{12} TELF
– Total = 2.968 x 10^{12} TELF

If the above hauling duty were to be performed by dump trucks operating at an average unit energy factor of 0.2963 Btu/TELF, the total energy consumption would amount to 879, 338 x 10^6 Btu. The energy saved by the conveyor installation is therefore 256,461 x 10^6 Btu, or some 30% of the equivalent all truck system. On a 12 month basis the saving would amount to 341,948 x 10^6 Btu, or the coal equivalent energy of 2.5 million gallons of diesel fuel per year. In areas where electric power is generated from coal the conversion to conveyor belt system would have the added attraction of reducing the demand for scarce diesel fuel by some 6.3 million gallons per year.

APPENDIX 1.2.3.4

Energy Consumption: Ancillary Operations

The following broad estimates are made of energy consumed by operations in an open pit mine:

	Btu/ton Copper
1. Auxiliary Mining Equipment	0.399 x 10^6
2. Pit Dewatering	0.016 x 10^6
3. Reclamation Equipment	0.021 x 10^6
4. Revegetation	0.202 x 10^6
Total	0.638 x 10^6

1. **Auxiliary Mining Equipment**

	No. of Units	X	Fuel Consumption gal/hr	X	Shifts/ Day	X	Days/ Year	X	Utilization 70%	=	Gallons per Year
Track Dozers	12		14		3		312		0.7		110,000
Rubber Tired Dozers	4		11		3		312		0.7		28,800
F.E. Loaders	3		18		3		312		0.7		35,400
Graders	5		7		3		312		0.7		23,000
Water Trucks	2		9		3		312		0.7		12,000
ANFO Trucks	2		6		1		312		0.7		2,600
Pickups (Gasoline)	60		2		3		312		0.7		78,600

Total Diesel = 211,800 gal/yr
Total Gasoline = 78,600 gal/yr

Diesel Fuel and Gasoline

$$211{,}800 \text{ gal/yr} \times 138{,}600 \text{ Btu/gal} = 2.9355 \times 10^{10} \text{ Btu/yr}$$
$$78{,}600 \text{ gal/yr} \times 125{,}800 \text{ Btu/gal} = 0.9888 \times 10^{10} \text{ Btu/yr}$$

Lube Oil

@ 1.5% of fuel use = 4356 gal/yr
$$4356 \text{ gal/yr} \times 148{,}690 \text{ Btu/gal} = \underline{0.0647 \times 10^{10} \text{ Btu/yr}}$$
$$\text{Total Energy Use} = 3.989 \times 10^{10} \text{ Btu/yr}$$

$$\frac{3.989 \times 10^{10} \text{ Btu/yr}}{100{,}000 \text{ T Cu/yr}} = 0.399 \times 10^{6} \text{ Btu/ton Cu}$$

2. **Pit Dewatering**

Assumed Data: Precipitation – 10 inches/year
Pit Diameter – 3,000 ft
Pit Depth – 750 ft.
Length of pipe for pumping 2000 ft
No evaporation or precipitation

$$\text{Pit area} = \pi r^2 = 3.14 \times (1500)^2 = 7.068 \times 10^6 \text{ ft}^2$$

$$\text{Volume of precipitation} = 7.08 \times 10^6 \text{ ft}^2 \times \frac{10 \text{ in.}}{\text{yr}} \times \frac{\text{ft}}{12 \text{ in.}} = 5.89 \times 10^6 \frac{\text{ft}^3}{\text{yr}}$$

$$\frac{5.89 \times 10^6 \frac{\text{ft}^3}{\text{yr}} \times 7.48 \frac{\text{gal}}{\text{ft}^3}}{525{,}960 \frac{\text{min}}{\text{yr}}} = 83.8 \frac{\text{gal}}{\text{min}} \quad \text{pumping duty}$$

Assume evaporation rate equals the ground water infiltration rate to the pit; therefore total pumping duty for pit dewatering is 84 gal/min.

Pumping	4" CI pipe, 84 gal/min velocity = 2.14 ft/sec friction loss = 0.83 ft/100 ft
Gravity Head	750 ft
Friction Head	17 ft
Velocity Head	—
Fittings @ 50% H_f	8 ft
Total Head	775 ft

$Q = 84$ gal/min x 0.13369 ft^3/gal = 11.23 ft^3/min

$$\text{Water Hp} = \frac{\text{HQ x } 62.4}{33{,}000} = \frac{775 \text{ x } 11.23 \text{ x } 62.4}{33{,}000} = 16.5 \text{ Hp}$$

$$\text{Pumping Efficiency @ } 70\% \ \frac{16.5 \text{ Hp}}{0.7} = 23.5 \text{ Hp}$$

Energy Requirement

$$23.5 \text{ Hp x } 0.754 \frac{\text{kWh}}{\text{Hp}} \text{ x } 24 \frac{\text{hr}}{\text{day}} = 420 \frac{\text{kWh}}{\text{day}}$$

$$420 \frac{\text{kWh}}{\text{day}} \text{ x } 10239 \frac{\text{Btu}}{\text{kWh}} = 4.3 \text{ x } 10^6 \frac{\text{Btu}}{\text{day}}$$

$$\frac{4.3 \text{ x } 10^6 \frac{\text{Btu}}{\text{day}} \text{ x } 365.25 \frac{\text{day}}{\text{yr}}}{100{,}000 \frac{\text{T Cu}}{\text{yr}}} = 0.016 \text{ x } 10^6 \frac{\text{Btu}}{\text{Ton Cu}}$$

3. Reclamation Equipment

Assume that reclamation proceeds at the same rate as the dumps are built with suitable delay in time to allow leaching of the dumps to proceed to completion.

From previous calculations, the finger dumps will hold 6000 tons per foot of dump.

$$\frac{47.1991 \text{ x } 10^6 \text{ T/yr}}{6000 \text{ T/ft}} = 7{,}866 \text{ ft of dump/year}$$

Area to be reclaimed is the top and the outward end of the dump. The sides of the dump will only be reclaimed at the completion of mining.

Top Area of Dump

400 ft wide x 7,866 ft long = 3,146,400 ft^2

End Area of Dump

400 ft wide at top, 800 ft wide at bottom, 249 ft slope

$$\frac{400\text{ ft} + 800\text{ ft}}{2} \times 249\text{ ft} = 149{,}400\text{ ft}^2$$

Total dump area reclaimed each year = 3,259,800 ft^2

The dump will be covered with 0.5 ft of topsoil

$$\frac{3{,}259{,}800\text{ ft}^2 \times 0.5\text{ ft}}{27\text{ ft}^3/\text{yd}^3} = 60{,}367\text{ yd}^3/\text{yr}$$

Assume scraper production rate of 125 yd^3/hr, at an approximate 3000 ft haul distance.

$$\frac{60{,}367\text{ yd}^3/\text{yr}}{125\text{ yd}^3/\text{hr}} = 483\text{ hr/yr}$$

Also assume for this job that a dozer and a grader are required for the same length of time as the scraper.

		Fuel Consumption		
Scraper	483	hr/yr x 15.8 gal/hr	=	7,631 gal/yr
Dozer	483	hr/yr x 10.0 gal/hr	=	4,830 gal/yr
Grader	483	hr/yr x 5.8 gal/hr	=	2,801 gal/yr
Total Diesel Fuel			=	15,262 gal/yr

Energy Consumption

Diesel fuel 15,262 gal/yr x 138,600 Btu/gal = 2.115 x 10^7 Btu/yr

Lube Oil

@ 1.5% of Diesel Fuel = 229 gal/yr

229 gal/yr x 148,690 Btu/gal = 3.405 x 10^7 Btu/yr

Total 2.149 x 10^7 Btu/yr

$$\frac{2.149 \times 10^9\text{ Btu/yr}}{100{,}000\text{ T Cu/yr}} = 2.1 \times 10^4\text{ Btu/ton Cu}$$

4. Revegetation

The sprinkling system is calculated for a finger dump 1522 ft long. For reclamation of the total waste, a dump with a total length of 7866 ft is required per year. Several wells will be required to obtain the amount of water required for reclamation purposes.

Assume sprinkling duty required is three hours per day, 270 days/year.

For a 1522 ft long dump with spray nozzles on 100 ft centers, 60 nozzles are required at 25 gal/min each at 35 lb/in^2.

60 x 25 gal/min = 1500 gal/min
3 hr/day x 270 day/yr = 810 hr/yr sprinkling required

Assume for pumping duty:

Wells average 800 ft deep at 2000 ft from dump
Dumps 150 ft high
Gravity head = 950 ft

For each section, the distribution line is a 10 inch line 3750 ft long. Laterals are 6 inch line with 2250 ft required.

Main Distribution Line

10 inch 3750 ft long carrying 1500 gal/min.
Velocity head = 0.6 ft
Friction head = 1.25 ft/100 ft (Cast Iron Pipe)
3750 ft x 1.25 ft/100 ft = 47 ft

Laterals

3-6 inch lines total length of pipe 2250 ft carrying 500 gal/min
Velocity head = 0.5 ft
Friction head = 2.02 ft/100 ft (Cast Iron Pipe)
2250 ft x 2.02 ft/100 ft = 45 ft

Gravity Head	=	950 ft
Pressure Head	=	81 ft
Friction Head	=	92 ft
Fittings @ 50% H_f	=	46 ft
Velocity Head	=	1 ft
Total Head		1170 ft

Q = 1500 gal/min x 0.13369 ft^3/gal = 200 ft^3/min

$$\text{Water Hp} = \frac{HQ \times 62.4}{33{,}000} = \frac{1170 \times 200 \times 62.4}{33{,}000} = 442 \text{ Hp}$$

@ 70% efficiency $\frac{442}{0.7}$ Hp = 631 Hp required for one 1522 ft section.

$$\frac{7866 \text{ ft of dump/yr}}{1522 \text{ ft}} = 5.17$$

631 Hp x 5.17 = 3262 Hp required for total dump

$$3262 \text{ Hp} \times 0.745 \frac{\text{kWh}}{\text{Hp}} \times 810 \text{ hr/yr} = 1.968 \times 10^6 \text{ kWh/yr}$$

1.968 x 10^6 kWh/yr x 10,239 Btu/kWh = 2.0155 x 10^{10} Btu/yr

$$\frac{2.015 \times 10^{10} \text{ Btu/yr}}{100{,}000 \text{ T Cu/yr}} = .202 \times 10^6 \text{ Btu/ton Cu}$$

1.3 MINERAL PROCESSING OPERATIONS

Beneficiation of copper sulfide ores is accomplished by size reduction and froth flotation. Several tons of ore must be handled to produce one ton of copper. The finer the grind for liberation the higher the energy requirements per pound of copper. Also, the harder the ore the greater the energy requirement for any specific grind.

Figure 1.3-1 illustrates a typical flowsheet for a copper concentrator. For purposes of this study crushing is done in three stages to minus ⅜-inch size and grinding in a single stage ball mill in closed circuit with cyclones to 15 to 20 percent on 65-mesh. The coarse rougher concentrate is reground for final mineral liberation. This flowsheet was chosen because it represents a fair percentage of operating mills.

1.3.1 Material Balance

For the material and energy requirements of a copper concentrator without molybdenum recovery, a porphyry ore containing 0.55 percent copper was selected. The porphyry type ore was considered typical since approximately 88 percent of copper ores in the United States are from porphyry ore deposits in the western states. The 0.55 percent copper is the weighted average of all ore grades from producing porphyry copper mines in the United States as published by the USBM Minerals Commodities Profile (1977).

Froth flotation has been known and widely practiced for over fifty years. This method is employed for all copper sulfide ores from porphyry deposits. Information on froth flotation theory and practice is available in a two volume compilation (Fuerstenau, 1976).

The recovery of copper from ore to concentrate is assumed to be 87.5 percent. The concentrate grade is set at 25 percent copper, 28 percent iron, and 31 percent sulfur. These assumptions are used to calculate the copper material balance shown in Table 1.3-1.

1.3.2 Energy Balance

Tabulation of the energy requirements is shown in Table 1.3-2 and Table 1.3-3. It is evident from Table 1.3-2 that the major electrical energy consuming step in the process is the primary grinding step (process step 2). The actual percentage of level 1 energy input is 72%. The crushing and flotation steps (process steps 1 and 3) also require sizable amounts of electrical energy, while regrinding, filtering, and pumping of new and recycled water each requires a relatively small amount of electrical energy. Table 1.3-3 also shows that steel liners and cast balls represent a sizable energy expenditure as consumed items. Most steel consumption is in crushing and grinding, constituting 65% of the level 2 energy requirement. Flotation reagent production requires very little energy.

Energy used to produce grinding balls, ball mill liners, and crusher liners has been variously stated. In some cases scrap steel is the basic raw material while in other cases new steel is the basic raw material. Two and a half tons of scrap represents the same energy as one ton of new steel (Kellogg, 1977). Production energy of new steel slabs is given as 22 x 10^6 Btu per ton. The same article shows the production energy for steel slabs, grey iron, and steel castings as 24.9 x 10^6 Btu per ton. The same author (Kellogg, 1976) shows the energy requirements for steel balls and liners as 36 x 10^6 Btu per ton. Another author (Makhjani, 1972) gives the production energy for high grade steel alloys as 202 x 10^6 Btu per ton. This figure does not seem to apply but it has been

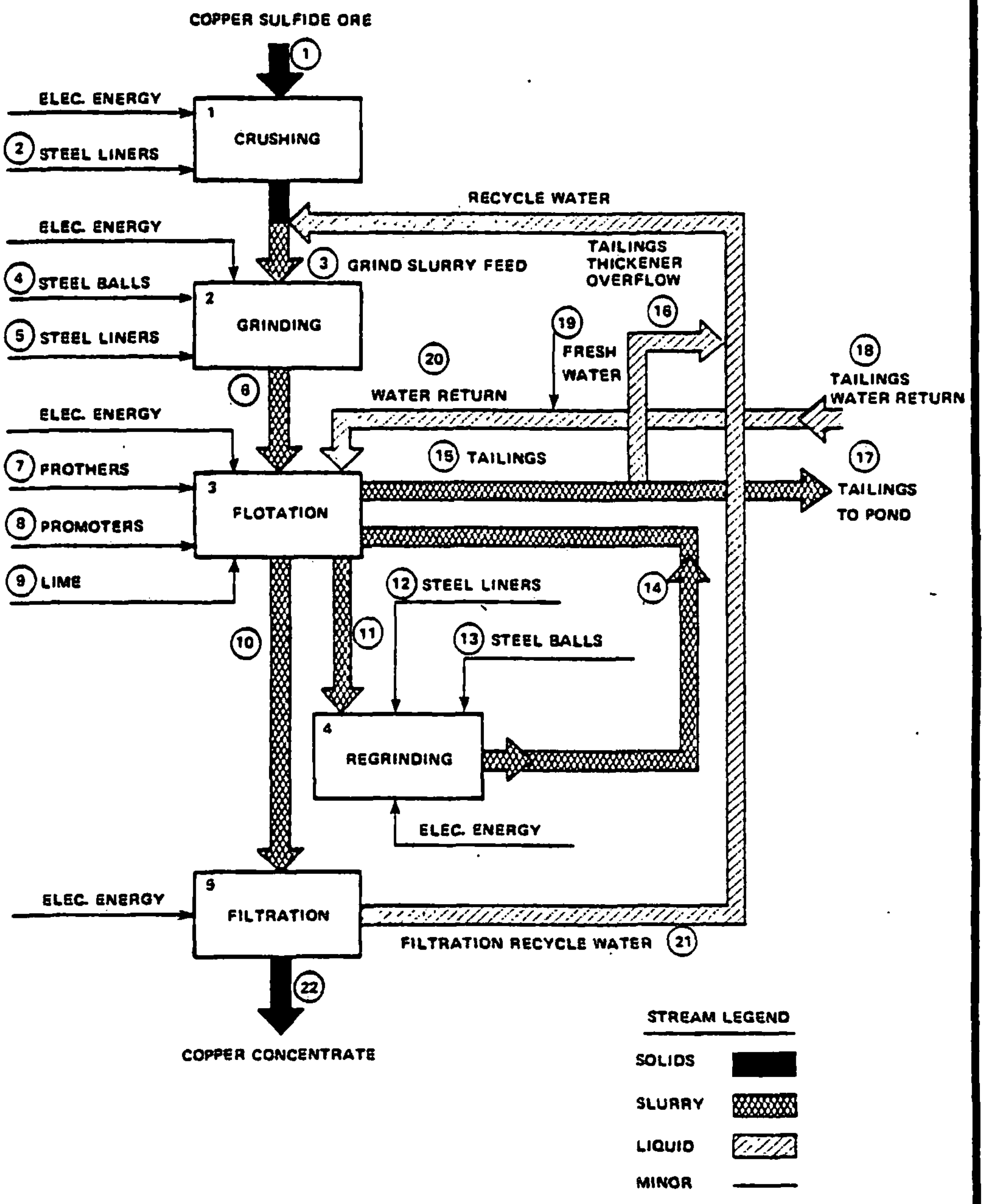

FIGURE 1.3-1 COPPER SULFIDE CONCENTRATOR

TABLE 1.3-1 MATERIAL BALANCE COPPER SULFIDE CONCENTRATOR

BASIS: 1 Ton Concentrate (25% Cu, 28% Fe, 31% S)
0.55% Ore Grade - 87.5% Recovery
0.07% Tailings Grade

Stream No.	Description	Solids (Tons)	Water (Tons)	Other (Lbs)
1	Ore Feed	51.95		
2	Steel Liners			0.061
3	Crushed Ore Slurry (70%)	51.95	22.26	
4	Steel Balls			1.5
5	Steel Liners			0.1
6	Flotation Feed Slurry (30%)	51.95	121.22	
7	Frothers			0.07
8	Promotors			0.08
9	Lime			3.0
10	Concentrate Slurry (75%)	1.00	3.00	
11	Regrind Slurry (20%)	1.90	7.60	
12	Steel Liners			0.004
13	Steel Balls			0.04
14	Regrind Recycle (20%)	1.90	7.60	
15	Tailings to Thickener	50.95	118.33	
16	Tailings Overflow		19.37	
17	Tailings Underflow (34%)	50.95	98.96	
18	Tailings Return		62.60	
19	Fresh Water Makeup		36.36	
20	Water Return		98.96	
21	Filtration Recycle Water		2.89	
22	Copper Concentrate	1.00	0.11	

TABLE 1.3-2 **ENERGY REQUIREMENTS** Level 1

FOR COPPER SULFIDE CONCENTRATOR

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON OF ORE	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON OF ORE
1	Crushing	KWH	1.85	0.0105	0.019425
2	Grinding	KWH	8.89	0.0105	0.093345
3	Flotation	KWH	1.16	0.0105	0.012180
5	Filtration	KWH	0.19	0.0105	0.002520
*	Regrinding	KWH	0.24	0.0105	0.001995
*	New Water	KWH	1.63	0.0105	0.009555
*	Recycle Water	KWH	0.91	0.0105	0.017115
				TOTAL	0.156135

*Not Shown on Flowshee

TABLE 1.3-3

ENERGY REQUIREMENTS

Level 2

FOR COPPER SULFIDE CONCENTRATOR

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON OF ORE	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON OF ORE
1	Crushing				
	A) Liners	LB	.06	0.018	0.00108
2	Grinding				
	A) Balls	LB	1.50	0.018	0.027
	B) Liners	LB	0.10	0.018	0.0018
3	Flotation				
	A) Frothers	LB	3.00	0.0041	0.0123
	B) Promotors	LB	0.08	0.02	0.0016
	C) Lime	LB	0.07	0.02	0.0014
*	Regrinding				
	A) Liners	LB	0.04	0.018	0.00072
	B) Balls	LB	0.004	0.02	0.00008
				TOTAL	0.04598

*Not shown on flowshee

used by others. The energy requirements for high carbon ferro-chromium is given as 61 x 10^6 Btu per ton (Battelle, 1975). Most of the liners in use today are chromium-molybdenum type while the grinding balls are low alloy steel. In this calculation the value of 18,000 Btu per pound given by H.H. Kellogg for liners and grinding balls is used since it seems to more nearly represent the use of scrap iron, new iron, and alloys. The electrical energy conversion factor is taken from the same article. The energy use, per ton of ore milled, was obtained from private communication with one of the latest copper plants built. Direct kWh meter readings are taken from each step of the process. These total kWh readings are converted to kWh per ton by dividing by the tons processed. The kWh or Btu per pound of copper is directly dependent upon the recoverable copper content of the ore.

1.3.3 Impact of Autogenous Grinding

The significant contribution of iron, and steel consumption to the total energy requirement for conventional grinding is of particular interest in view of the development of autogenous grinding technology in the mineral processing industry. The consumption of iron and steel can be reduced considerably when the ore is self grinding. Many operations in Europe now practice either autogenous or semi-autogenous grinding and the state of the art for this technology was discussed at a recent autogenous grinding conference in Trondheim, Norway, June, 1979. Based on the analysis of this data (Digre, 1979) and the use of standard relationships which have been developed for conventional grinding (Mular and Bhappu, 1978) the energy effectiveness of conventional grinding can be compared to that of autogenous grinding. Figure 1.3-2 presents this comparison for a typical copper ore with a work index WI of 13.1 kWh/ton and abrasion index AI of .095. Here the total energy required for grinding by various methods is plotted versus an autogenous grinding factor. The autogenous grinding factor, β, gives a measure of the energy inefficiency of self-breakage for the ore and is defined as the ratio of the operating work index for autogenous grinding to a standard laboratory ball mill work index as established by a Bond grindability test or the equivalent thereof. The overall energy requirement for each alternative has been calculated as:

$$
\begin{aligned}
&\text{TOTAL ENERGY REQUIRED FOR COMMINUTION} = \\
&\quad (\text{NET CRUSHING ENERGY}/\epsilon_C) \\
&\quad + \beta\,(\text{NET BALL MILL ENERGY}/\epsilon_B) \\
&\quad + \left(\frac{\text{STEEL CONSUMED AS MEDIA \& LINERS}}{\text{ENERGY “CONTENT” OF STEEL}}\right) \\
&\quad + \text{ENERGY FOR COMMINUTION CIRCUIT AUXILIARIES}
\end{aligned}
$$

Of course, the energy consumption for conventional grinding and pebble grinding is independent of the autogenous grinding factor, whereas the energy consumption in autogenous grinding will reflect the extent to which self-breakage contributes to the energy economy. Available data indicates that the autogenous grinding factor for copper ores is generally between 1.35 and 1.6 with occasional values as low as 0.75. When β is small the energy required for autogenous grinding is less than that required for conventional grinding, since the inefficiency of autogenous breakage is more than offset by the elimination of media requirements, however, when the inefficiency exceeds 45-50% (β = 1.45-1.50) the advantage of no media expense disappears. The comparisons shown in the figure are not indisputable, but are based on the best available data. These data do indicate that for copper ores which are very amenable to autogenous grinding, a reduction in

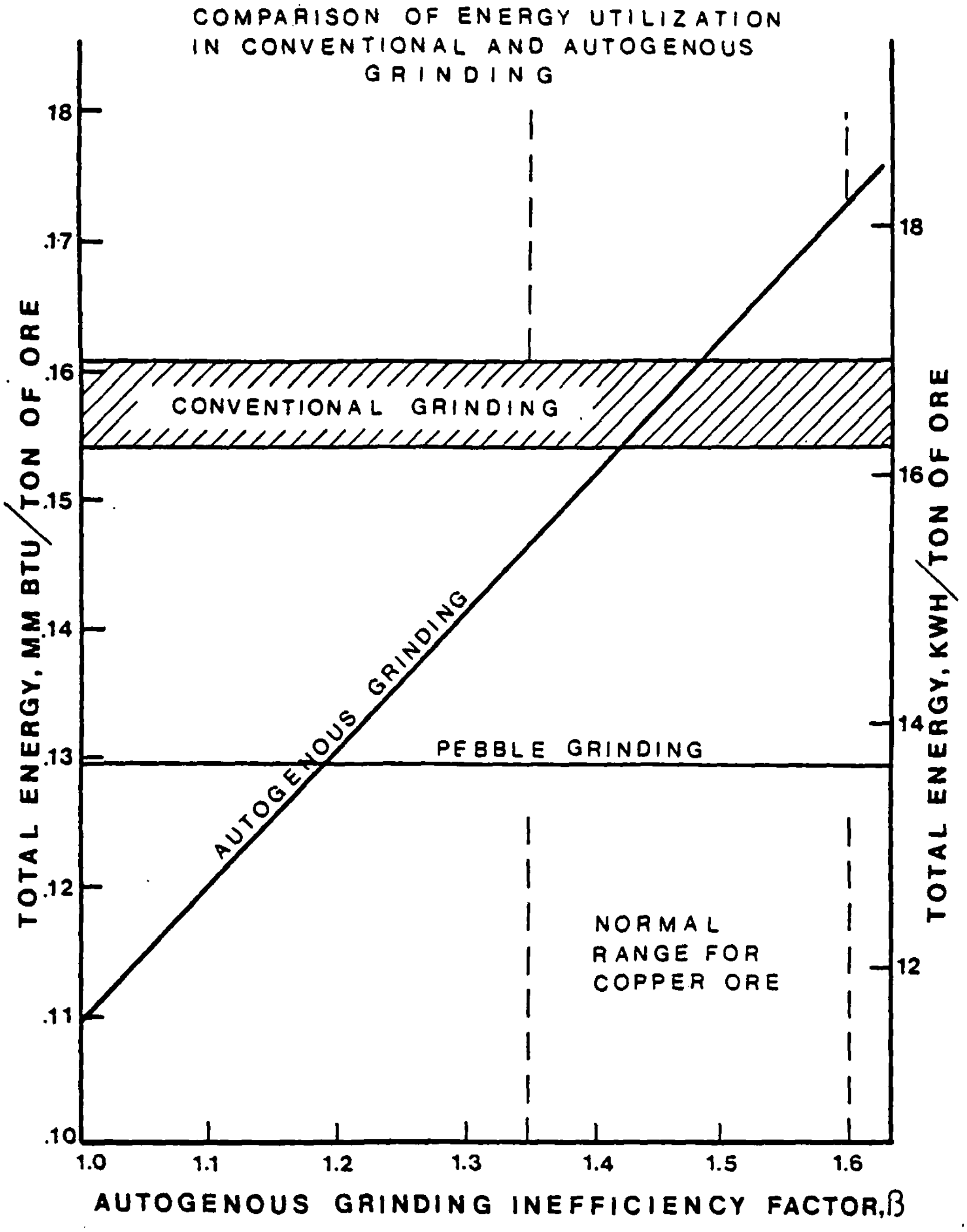

FIGURE 1.3-2 COMPARISON OF ENERGY REQUIRED FOR CONVENTIONAL, AUTOGENOUS, AND PEBBLE GRINDING OF TYPICAL COPPER ORES

energy requirements of up to 10% may be possible. Further reductions may be possible through the use of pebble milling although the energy cost associated with the production of pebbles must be taken into consideration.

1.3.4 Improvements in Operating Efficiency

One method of reducing the energy requirement (Btu/Ton) for an existing mineral processing plant involves improving the operating efficiency by increasing the production rate at a fixed power input. A major source of operating inefficiency is often uncontrolled fluctuations in the quality of the ore coming into the plant. During the last decade significant advances have been made in the development of on-line instrumentation for mineral processing systems including: particle size analyzers, mass flow measurement systems, solid phase and liquid phase composition analyzers. In addition, inexpensive and reliable computers for process control have become available. In many instances stabilizing control strategies have been developed for grinding (Herbst and Rajamani, 1979) and flotation circuits (Cooper and Paakinen, 1979); typical improvements in throughput (or equivalently energy efficiency) have been on the order of 5-10%. Optimizing control strategies (Herbst and Rajamani, 1979a) promise even greater improvements but to date none have been implemented in U.S. copper concentrators.

Similarly another important factor in determining the capacity of a closed grinding circuit is the efficiency of size separation. Size separation (classification) is typically accomplished with mechanical classifiers or hydrocyclones, the latter being preferred in the design of new plants. It is intuitively evident that if misplaced fine material of the desired size range is being returned along with coarse material to size reduction, the mill capacity will be reduced correspondingly. Under these circumstances, the mill will be regrinding material which is already of a suitable size. If, on the other hand, the fine material is not misplaced in the coarse material stream, the mill will have a greater capacity and the fresh feed rate can be increased.

The effect of classifier efficiency on the grinding circuit capacity is revealed in at least two computer simulation studies (Herbst; Grandy and Fuerstenau 1973), (Luckie and Austin 1975). In one analysis, examination of the results reveals that the grinding circuit capacity could be increased by as much as 50 percent by improved classifier efficiency. The results from another simulation suggest the grinding circuit capacity could be increased by as much as 64 percent if perfect size separation could be achieved. In view of the fact that the efficiency (as measured by the coefficient of separation which represents the fraction of feed material separated ideally) of most hydrocyclones, even under the best of circumstances, is only 50 percent and that the efficiency of mechanical classifiers is even lower, considerable improvement in grinding circuit capacity could be achieved by improved classifier efficiency.

Considerable potential exists for the optimization of entire plant (and mine) performance. Traditional ideas concerning the "best" size for run of mine ore, primary crusher product, secondary crusher product, primary grinding product and secondary grinding product may change if the energy economy of the *overall* size reduction process is taken into account. In addition integrated grinding and flotation circuit performance may be improved from an energy efficiency point of view by reducing the extent of size reduction (and therefore liberation) in the primary grinding circuit. In this emerging process strategy, locked particles in the small mass rougher concentrate are reground to achieve the final high degree of liberation required for the production of the specified grade of cleaner products. The solution of these and other integrated optimization problems promises to improve significantly the overall energy economy of existing mineral processing plants.

1.3.5 Effect of Declining Head Grades

Declining head grades will result in higher costs and energy requirements for copper extraction in the future. The overall effect of ore grade on energy consumption for various ore types has been estimated (Kellogg, 1979) and is depicted in Figure 1.3-3.

In terms of energy accounting for mineral processing operations, the head grade will have a direct effect on the total energy requirement of the process for two reasons. First, more ore must be processed to recover the same amount of copper from a lower head grade ore and second, as the head grade drops the ore will probably have to be ground finer to achieve the same recovery. If the energy input per ton ore is maintained constant, the recovery must drop; it appears to be a reasonable assumption, based on plant observations, that the copper content of the flotation tailing will remain approximately constant. The significance of this effect is presented in Table 1.3-4. As a result of the constant tail assay assumption, it is seen that the recovery decreases from 90.3% to 76.9% as the head assay decreases from 0.7% Cu to 0.3% Cu. The energy per ton of ore remains constant at 202,115 Btu. However, the energy per ton of concentrate more than doubles when the head assay drops from 0.7% Cu to 0.3% Cu. This increase corresponds to an increase in energy per ton of copper contained in the concentrate from 32 million Btu to 88 million Btu.

Some questions may be raised regarding the change of liberation size with a decrease in head assay and the increased energy that may be required to achieve the desired level of liberation. Neither good enough data nor accurate enough mathematical models are available to evaluate the effect in a rigorous manner, however, this effect was evaluated using simple liberation models (Gaudin, 1939; Weigel and Li, 1967) and it was found to be insignificant for low grade materials such as the copper porphyry ores under consideration.

1.3.6 Conclusions and Recommendations

1.3.6.1 Conclusions

Concentrators include standard and well-established unit operations. No major developments requiring less energy have been introduced in concentration in the last few decades. However, several minor modifications in process strategy which may be considered to be fine tuning of the circuit, offer promise for modest energy savings. Crushing and grinding are the major energy consuming steps in the process and any improvement in these steps would have the largest impact as far as energy input is concerned. The use of large flotation cells has improved process efficiency and lessened energy usage.

1.3.6.2 Recommendations

Improved energy conservation in mineral processing operations can be effected by efforts to implement existing technology and by the development of a concerted research program to establish new technologies for energy conservation.

1.3.6.2.1 Implementation of Existing Technology

1) Application of existing stabilizing control strategies for grinding and flotation
2) Careful evaluation of the potential of autogenous or pebble grinding versus conventional grinding on an ore by ore basis
3) Optimal allocation of energy between blasting, crushing, grinding and regrinding.

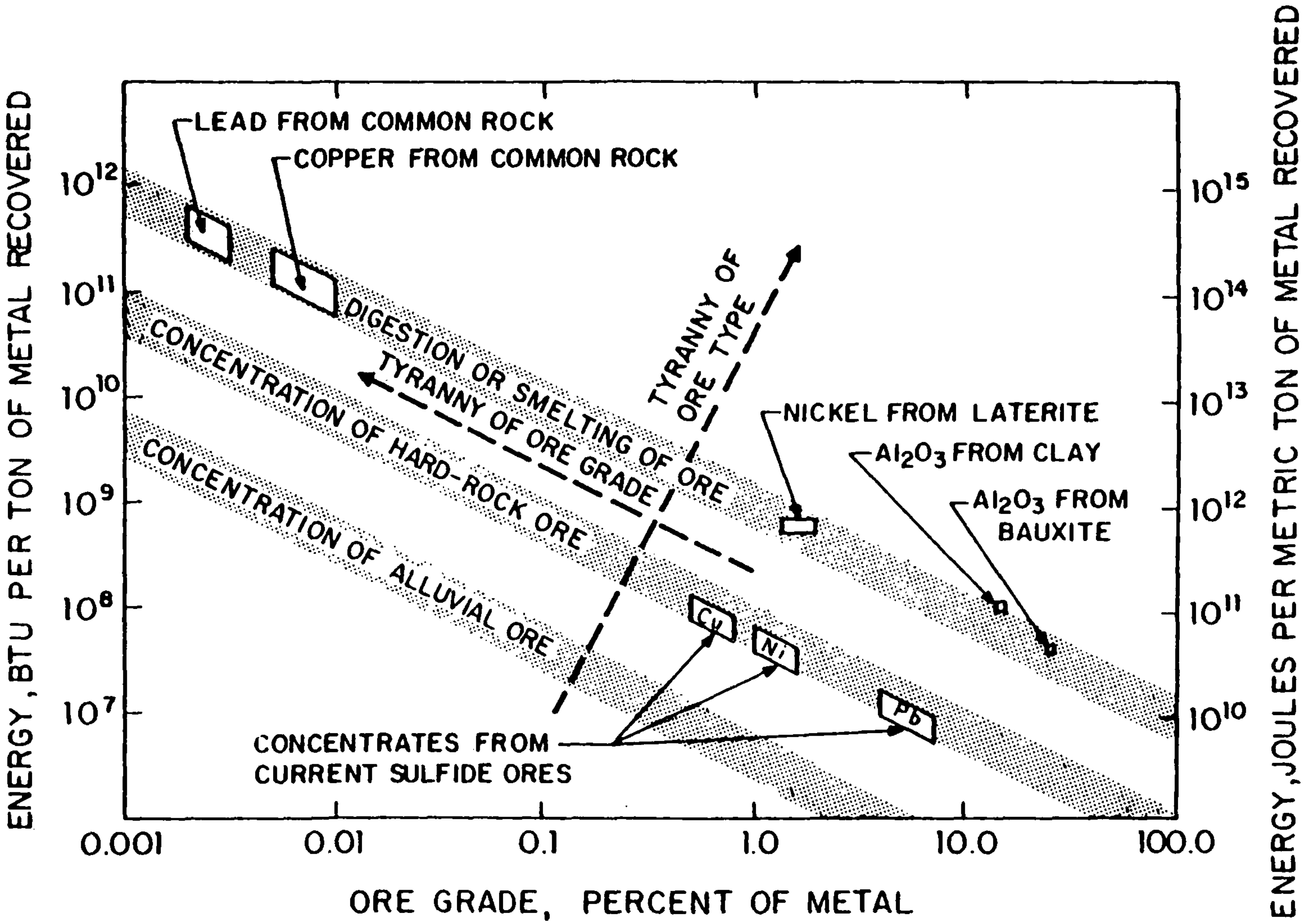

FIGURE 1.3-3 ENERGY-ORE GRADE RELATIONSHIPS FOR VARIOUS SOURCE MATERIALS, Kellogg (1978)

TABLE 1.3-4 EFFECT OF HEAD GRADE ON TOTAL ENERGY CONSUMPTION

Head Assay	Tail Assay	Recovery Percent	Tons Ore per Ton Concentrate	BTU per Ton Ore	MM BTU per Ton Concentrate	MM BTU per Ton of Cu in Concentrate
0.30	0.07	76.9	108.4	202,115	21.91	87.64
0.35	0.07	80.2	89.0	202,115	18.00	72.00
0.40	0.07	82.7	75.5	202,115	15.27	61.08
0.45	0.07	84.7	65.6	202,115	13.26	53.04
0.50	0.07	86.2	58.0	202,115	11.72	46.88
0.55	0.07	87.5	51.9	202,115	10.50	42.00
0.60	0.07	88.6	47.0	202,115	9.51	38.04
0.65	0.07	89.5	43.0	202,115	8.69	34.76
0.70	0.07	90.3	39.6	202,115	8.00	32.00

1.3.6.2.2 New Research

1) Development of more efficient classification devices for closed circuit grinding
2) Development of optimizing (as opposed to stabilizing) control strategies for grinding and flotation
3) Identify and develop more efficient reduction devices for copper ores.

1.3.6.3 References

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1.4 GAS CLEANING

1.4.1 Introduction

All unit operations, i.e., roasting, smelting and converting in copper smelting produce an off gas containing sulfur dioxide and particulates. Gas cleaning comprises the removal of particulates from all gas streams while still hot in electrostatic precipitators. Those gas streams with sulfur dioxide concentrations high enough to require sulfur dioxide removal in an acid plant are further cleaned to ensure efficient acid plant operation. These strong sulfur dioxide gas streams are cooled and the remaining dust removed in spray towers (or venturi scrubbers). Electrostatic precipitators remove acid mist from the gas and makes it ready for treatment in a contact acid plant.

1.4.2 Process Description

A flowsheet depicting gas cleaning in a conventional smelter (roast/smelt/convert) is presented in Figure 1.4-1.

1.4.2.1 Hot Gas Cleaning

Hot gas cleaning is normally done separately on the roaster, smelting furnace, and converter with recycle of the recovered dust back into the smelting furnace. The principal purpose is to recover copper contained in the dust.

The off-gas stream typically contains sulfur dioxide, some sulfur trioxide, water vapor, and other volatiles (metal oxides, sulfides, etc.). If the temperature of the gas drops below the acid dew point (about 400°F), acid mist can condense as sulfuric acid (H_2SO_4) presenting severe corrosion problems. Cyclones, bag filters, and settling flues have been used to remove the dust, but current practice generally is to use electrostatic precipitators.

The physical properties of the off-gas are such that maximum efficiency in the electrostatic precipitators is attained at about 700°F and around 100°F (i.e., minimum resistivity). Since the gas cannot be cooled below about 400°F because of the acid mist problem, the higher temperature operation is normally preferred (about 400-600°F).

The off-gas leaving the smelting furnace is cooled in a waste heat boiler to the range of 400-600°F before passing into the hot electrostatic precipitator. The off-gas leaving the converter passes through flues where a significant portion of the dust is removed. Also the gas is cooled with water sprays, with radiating flues, by dilution, or with waste heat boilers to about 400-600°F before entering the hot electrostatic precipitator. In practice, normally, the temperature at which hot electrostatic precipitators operate ranges from about 400-600°F. ASARCO operates hot electrostatic precipitators at 240-300°F in order to control the volatiles, principally arsenic. The resistivity of the dust is controlled by acid conditioning, i.e., spraying acid or injecting sulfur trioxide from the acid plant and by monitoring the acidity of the dust. Enough acid is added so as to provide conditioning but not to cause excessive corrosion.

Depending upon the discharge temperature, the off-gas from the roaster may or may not be cooled before passing into a dust removal device (separate electrostatic precipitators or cyclone, or blending with off-gas from smelting furnace/converter).

1.4.2.2 Cold Gas Cleaning

Following hot gas cleaning, the separate off-gas streams to be treated for sulfur dioxide recovery are usually combined before being fed into cold gas cleaning. Whereas the purpose of the hot gas cleaning is to remove dust to recover its copper value, the purpose of cold gas cleaning is to remove dust to prevent fouling of the acid plant. This is usually accomplished in a spray tower, although some installations have used venturi scrubbers or both.

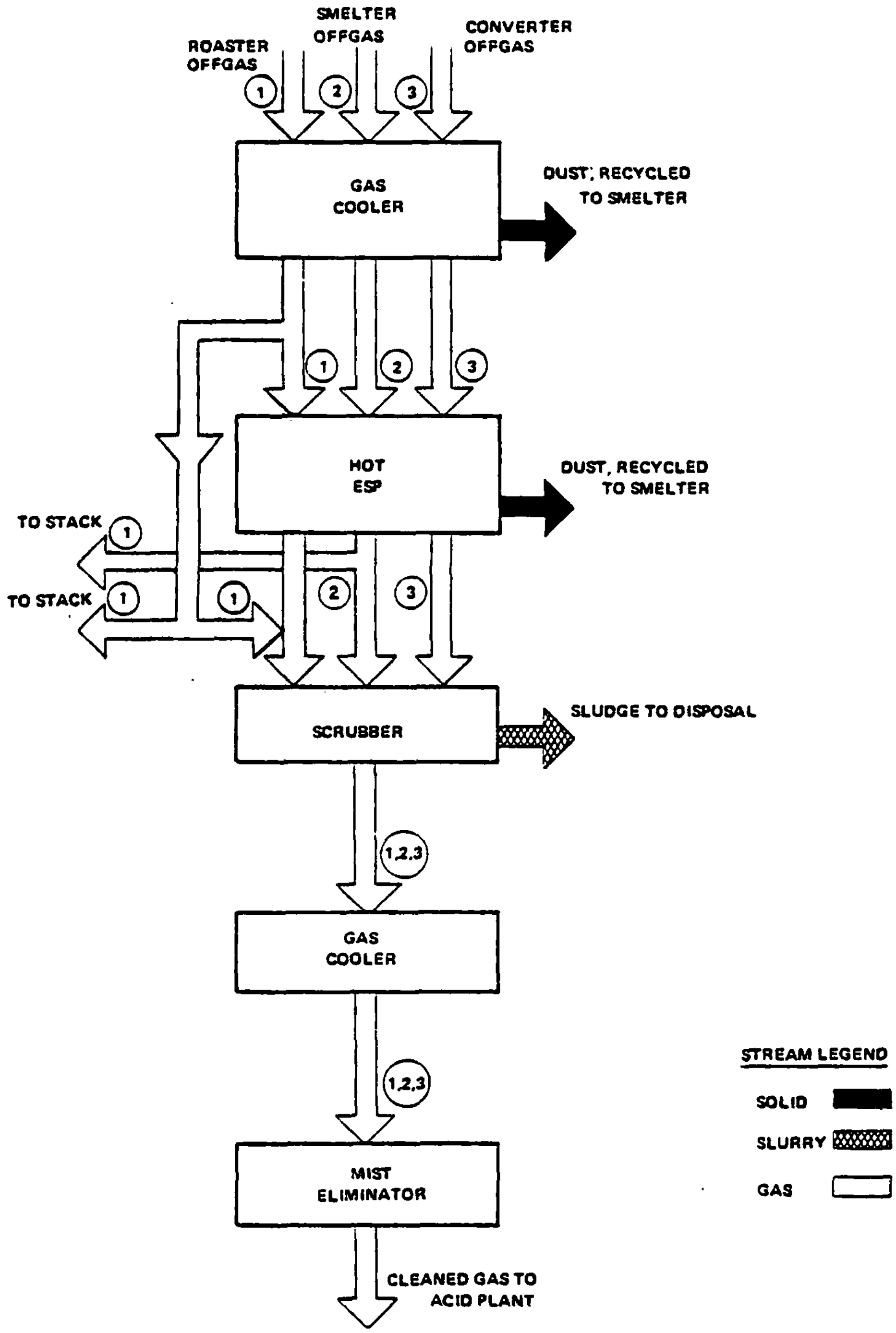

FIGURE 1.4-1 GAS CLEANING IN COPPER SMELTING

In the spray towers the off-gas is scrubbed with weak sulfuric acid removing most of the remaining dust. At the same time, the gases are cooled allowing any acid mist to condense. The gases may be further cooled in an indirect cooling tower before entering a mist precipitator (usually an electrostatic precipitator) which removes the last traces of dust and reduces the amount of water vapor contained in the gas stream. Cooling and mist elimination are important factors in controlling the overall water balance in the acid plant.

1.4.3 Key Variables

The economics of gas cleaning/acid plants are determined by several key variables, the gas volume, sulfur dioxide concentration, water vapor concentration and free oxygen.

1.4.3.1 Design

In general, copper smelters produce several off-gas streams from the roasting, smelting, and converting operations. The roasting off-gas tends to be high in sulfur dioxide, relatively low in volume and relatively constant (especially fluid-bed units, to a lesser degree in multi-hearth units). The smelting off-gas ranges from very high volume-low sulfur dioxide (less than 2% sulfur dioxide) on conventional reverberatory furnaces to low volume-high sulfur dioxide (more than 50% sulfur dioxide on some of the newer technologies) and is usually relatively constant. Converter off-gas tends to be high sulfur dioxide (average 5% sulfur dioxide) but the volume fluctuates drastically during the blow: the sulfur dioxide also tends to vary, being higher on the finish blow than on the slag blow.

1.4.4 Energy Requirements

The energy requirements for hot and cold gas cleaning are presented in Table 1.4-1

1.4.5 Fugitive Emissions Control

In this section we have estimated the energy requirements associated with fugitive emissions control at a smelter producing 100,000 tons of copper per year. The emission control system is based on building enclosure, especially of the converter aisle and secondary hooding of process equipment. The collected gases would be filtered in a baghouse and exhausted via the main stack. This system roughly corresponds to the type of fugitive emissions control used in some foreign smelters.

The fugitive gas stream is essentially at ambient temperature and is much larger than the other streams from the process units which are also ultimately exhausted via the main smelter stack. As a consequence, the stack gas will require reheating to increase buoyancy and achieve the proper degree of dispersion necessary to meet NAAQS (National Ambient Air Quality Standards). The energy requirements for fugitive emissions control is estimated to be 340 kWh per ton copper or 3.57 million Btu per ton of copper. It is assumed that heat necessary to provide buoyancy is provided by waste heat.

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TABLE 1.4-1 **ENERGY REQUIREMENTS** Level 1

GAS CLEANING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Hot gas cleaning	Thous. SCF		0.00336	
2	Cold gas cleaning	Thous. SCF		0.00126	

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1.5 ACID PLANT

1.5.1 Introduction

All unit operations in copper smelting, i.e., roasting, smelting, and converting produce an off-gas containing sulfur dioxide and particulates. Environmental control regulations require the removal of sulfur dioxide from rich gas streams (above 4-5% sulfur dioxide); weak streams may be vented after particulate removal. Current practice in the United States for sulfur dioxide recovery involves the treatment of gas streams from roasting, new smelting furnaces and converting in contact plants which fix the sulfur dioxide as sulfuric acid; reverberatory furnace gases are vented after particulate removal.

1.5.2 Process Description

Figure 1.5-1 shows a flowsheet for an acid plant treating gas from cold gas cleaning as described in section 1.4. In a contact process acid plant, the gas entering the plant from cold gas cleaning is first dried in scrubbing towers using moderate (78%) and/or strong (94/96%) sulfuric acid to remove any water vapor. Downstream of the driers a blower is used to move the gas through the remaining equipment.

The incoming gas, containing sulfur dioxide and oxygen is passed over a vanadium pentoxide catalyst where it reacts to form sulfur trioxide

$$SO_{2(g)} + 1/2\ O_{2(g)} \longrightarrow SO_{3(g)} \qquad \Delta H_f^o = -23.49 \text{ kcal/g-mole} \qquad (1.5.1)$$

The gas stream is then passed through an absorption tower where the sulfur trioxide is absorbed in sulfuric acid forming more concentrated acid. ASARCO reports using a 98 percent acid with the strength of acid controlled within close limits to ensure good absorption.

$$SO_{3(g)} + H_2O_{(\ell)} \longrightarrow H_2SO_{4(\ell)} \qquad \Delta H_f^o = -31.14 \text{ kcal/g-mole} \qquad (1.5.2)$$

Reaction 1.5.1 is an equilibrium reaction. The conversion ratio is a function of temperature and concentration. To maximize conversion to sulfur trioxide (and hence sulfur dioxide removal) and to meet pollution control requirements, most modern plants use a double contact/double absorption (DC/DA) scheme where the gas passes through a catalyst (converter) bed, is cooled, and passes through a second (and possibly third) converter bed followed by an absorber (for sulfur trioxide removal). The gas then passes through a third and fourth converter bed (with interstage cooling) followed by a pass through a second absorber. Off-gas from the final absorber is vented to the atmosphere and typically contains less than 500 ppm sulfur dioxide.

In the older single contact/single absorption (SC/SA) plants, the gas would pass through several beds of the converter and into the absorption tower only once resulting in a lower conversion efficiency (about 95%). A DC/DA plant operates at a higher conversion efficiency (about 99.5 percent conversion) than an SC/SA plant and complies with current U.S. environmental regulations.

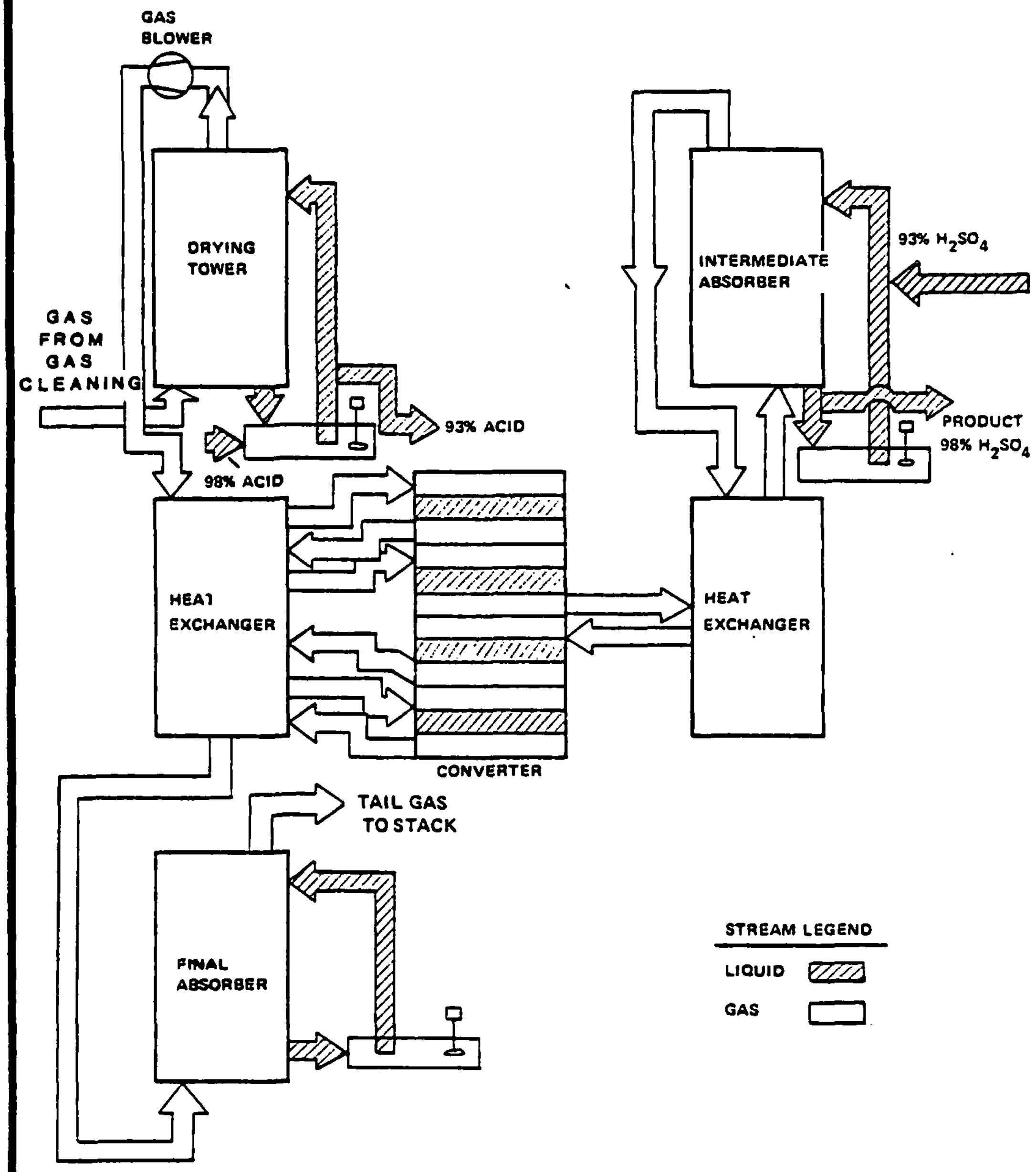

FIGURE 1.5-1 DC/DA ACID PLANT

The conventional DC/DA process can be used on feed gas containing up to 8.5-9.0 percent sulfur dioxide. In maintaining an autothermal operation, the loss of heat as sensible energy to the incoming gas and product acid is balanced against the heat released by conversion of sulfur dioxide to sulfur trioxide and absorption of the sulfur trioxide. For gas streams containing about 5-9 percent sulfur dioxide, this balance can be maintained by adjusting the heat transfer surface and the cooling water rate. Increasing sulfur dioxide concentrations result in temperature rises in the converter beds leading to greater duties on the heat exchangers.

Beyond 8.5-9.0 percent sulfur dioxide, additional heat transfer surface would be required to remove the excess heat generated in the unit and to avoid overheating in the converter beds. Lurgi has proposed the use of a split gas stream along with an economizer/evaporator to remove the excess heat and allow processing of 16 percent sulfur dioxide with no loss in efficiency. In principle, it should be possible to treat even stronger sulfur dioxide streams and export low pressure steam to other process units. To the best of our knowledge, no one is currently operating an acid plant on gas over 9 percent sulfur dioxide.

In some instances where the market is available, liquid SO_2 or elemental sulfur can be produced.

1.5.4 Energy Balance

Energy requirements for DC/DA acid plants are presented as a function of gas volume and sulfur dioxide concentration in Table 1.5-1. As noted earlier, acid plant energy consumption is related to sulfur dioxide concentration and volume. At sulfur dioxide concentrations of less than 5 percent, thermal energy is needed to preheat the incoming gas and forms a significant part of the total energy use. Above 5 percent sulfur dioxide, preheating is not required and energy is only consumed in the pumps and blowers. It is assumed that concentrated sulfur dioxide streams (more than 9 percent volume sulfur dioxide) would be diluted with air to 9 percent sulfur dioxide before being processed in the acid plant.

1.5.5 References

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TABLE 1.5-1 **ENERGY REQUIREMENTS** Level 1

DC/DA ACID PLANT

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	SO_2 concentration of gas to acid plant				
	A) 4-5% SO_2*	Thous. SCF		$(-1.1098 \times \% SO_2) + 5.5592$	
	B) 5-9% SO_2	Thous. SCF		$(6 \times 10^{-4} \times \% SO_2) + 7.2 \times 10^{-3}$	
	C) 9% and above Volume of gas is diluted to 9% SO_2	Thous. SCF		0.0126	

*Assume acid plant wil shut dow below 4% SO_2

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TABLE 1.6-4 **ENERGY REQUIREMENTS** **Level 1**

MELTING ANODE SCRAP IN REVERBERATORY FURNACE

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	FIRE REFINING				
	A) Distillate fuel oi	Gal.	35	0.139	4.87
	B) Natural gas, polin	SCF	560	0.001	0.56
	C) Metallurgical coke	NET TON	0.008	31.5	0.25
2	ELECTRO REFINING				
	A) Electrical energy	KWH	20	0.0105	0.21
	B) Steam (waste heat credit)	LBS	-1060	0.0014	-1.48
				TOTAL	4.41

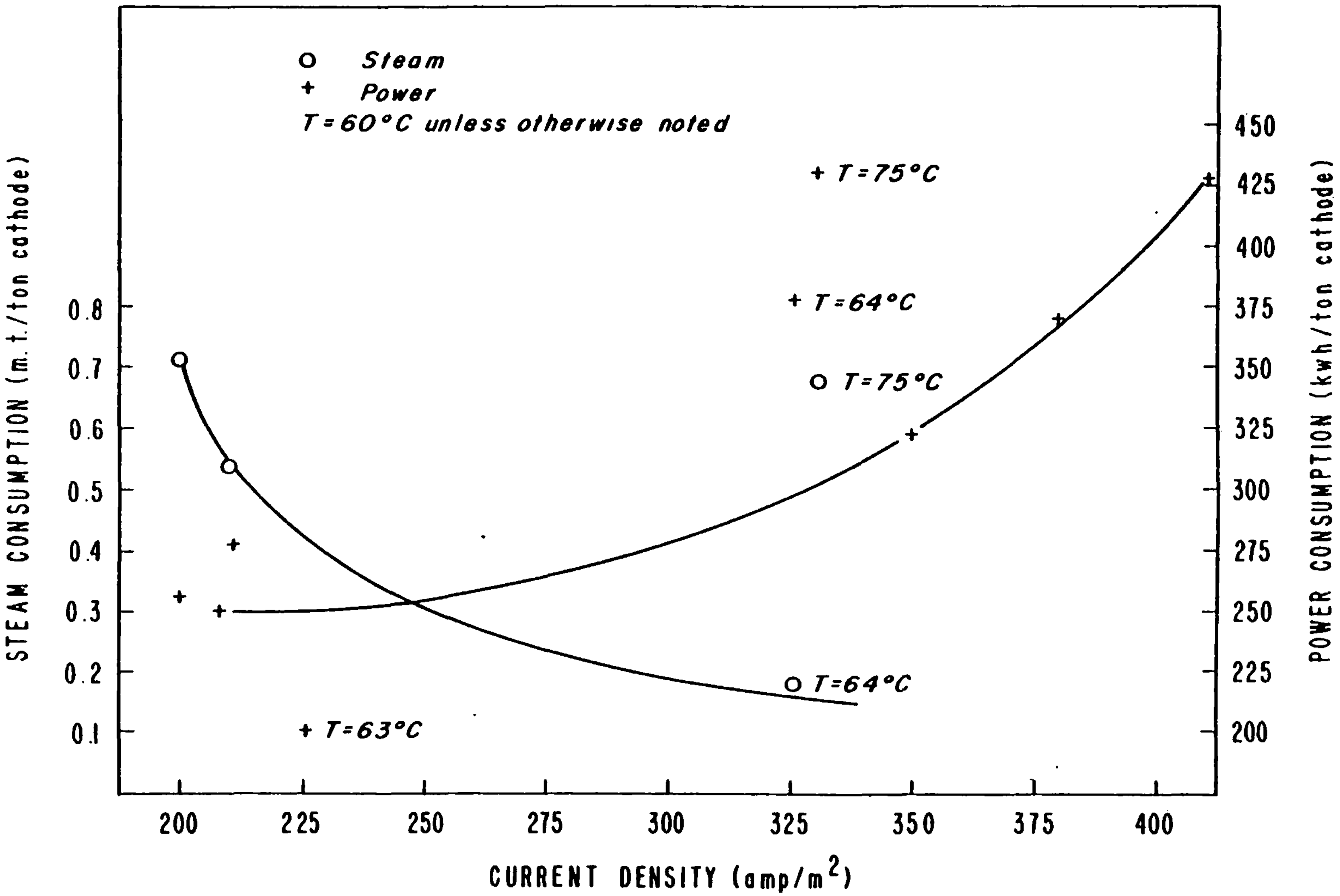

FIGURE 1.6-3 TRENDS FOR STEAM AND POWER CONSUMPTION VERSUS CURRENT DENSITY IN ELECTROREFINING

This trend towards higher current density will reduce the overall cost of electrorefining although the energy consumption will increase. For a new electrorefinery, the breakdown in operating costs is approximately as follows (Arthur D. Little, 1976):

Electricity	2.3%
Other utilities	1.8
Chemicals and materials	7.9
Labor	19.9
Fixed Costs (including return on capital)	68.1
TOTAL	100.0%

This breakdown shows that incentives for cost savings and technological change in electrorefining will be to decrease the fixed cost component (by increasing the rate at which copper is refined) and through automation. For example, if current density is increased from 200 amps/m^2 to 350, the copper production would increase by approximately 70-75 percent while energy consumption would increase only by 30 percent per ton of product. The overall cost reduction resulting from this would be about 35-40 percent.

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1.7 IN-SITU EXTRACTION OF DEEP SEATED COPPER DEPOSITS

1.7.1 Introduction

In situ mining is the in-place extraction of metals from their ores located within the confines of a mine. The material to be leached may include fractured or unfractured ore, stope fill, caved material, and ores in permeable zones. Alternately, it may be ore dumps, heaps, slag piles, and tailing ponds. These materials represent an enormous, untapped potential source of all types of metals.

The field of in situ mining encompasses the following steps:

(1) The preparation of ore for subsequent in-place leaching,

(2) The flow of solutions and ionic species through rock masses and within rock pores,

(3) The leaching of minerals with inexpensive and possibly regenerable leaching reagents under conditions prevailing in-place,

(4) The generation and regeneration of such solution, and

(5) The recovery of metals or their compounds from the metal-bearing solutions.

Accordingly, the overall scope of this potential mining method embraces interdisciplinary science and technology requiring application of principles of basic sciences, mineral technology, hydrology and economics. A flow diagram of the in situ extraction of copper is depicted in Figure 1.7-3.

1.7.2 Model Design

To assess the energy impact of in situ extraction of copper, a specific model must be designed which builds upon data available for a typical copper porphyry ore. Laboratory results obtained by researchers at Lawrence Livermore Laboratory (LLL) (Braun, et al., 1974) were used as a basis for calculation. The LLL laboratory study involved the leaching of a run-of-mine copper porphyry ore from the San Manuel Mine (Magma Copper Company, Arizona). In the test, 5.8 x 10^3 kg (6.38 tons) were leached in 1.42 cubic meters of solution for 717 days at 90 degrees centigrade and 400 psia oxygen over pressure. The copper curve of Figure 1.7-1 illustrates the experimental results obtained, where the fraction of the copper extracted is plotted against the number of days. The San Manuel ore was observed to weather appreciably, accelerating the rate of extraction.

An initial analysis suggests that hydrofracturing for access to a porphyry type deposit with highly disseminated copper and iron sulfides is least likely to be successful. This was, in fact, the result of the Safford field study carried out recently by Kennecott Copper Corporation. At the other end of the spectrum is complete rubblization such as could result by block caving mining or by nuclear rubblization as suggested by the Lawrence Livermore Laboratory experiment (Braun, et al., 1974). Block caving or nuclear rubblization results in an inter-particle porosity of approximately 30 to 40 percent. While a nuclear device is capable of generating an approximate 35 percent porosity without ore withdrawal, conventional explosives appear unlikely to be usable without some ore withdrawal. Also, any caving technique will produce upwards of 40 percent porosity if freely falling fragments pack randomly. As the space becomes more confined, lower and lower porosities occur in an ascending chimney of rock.

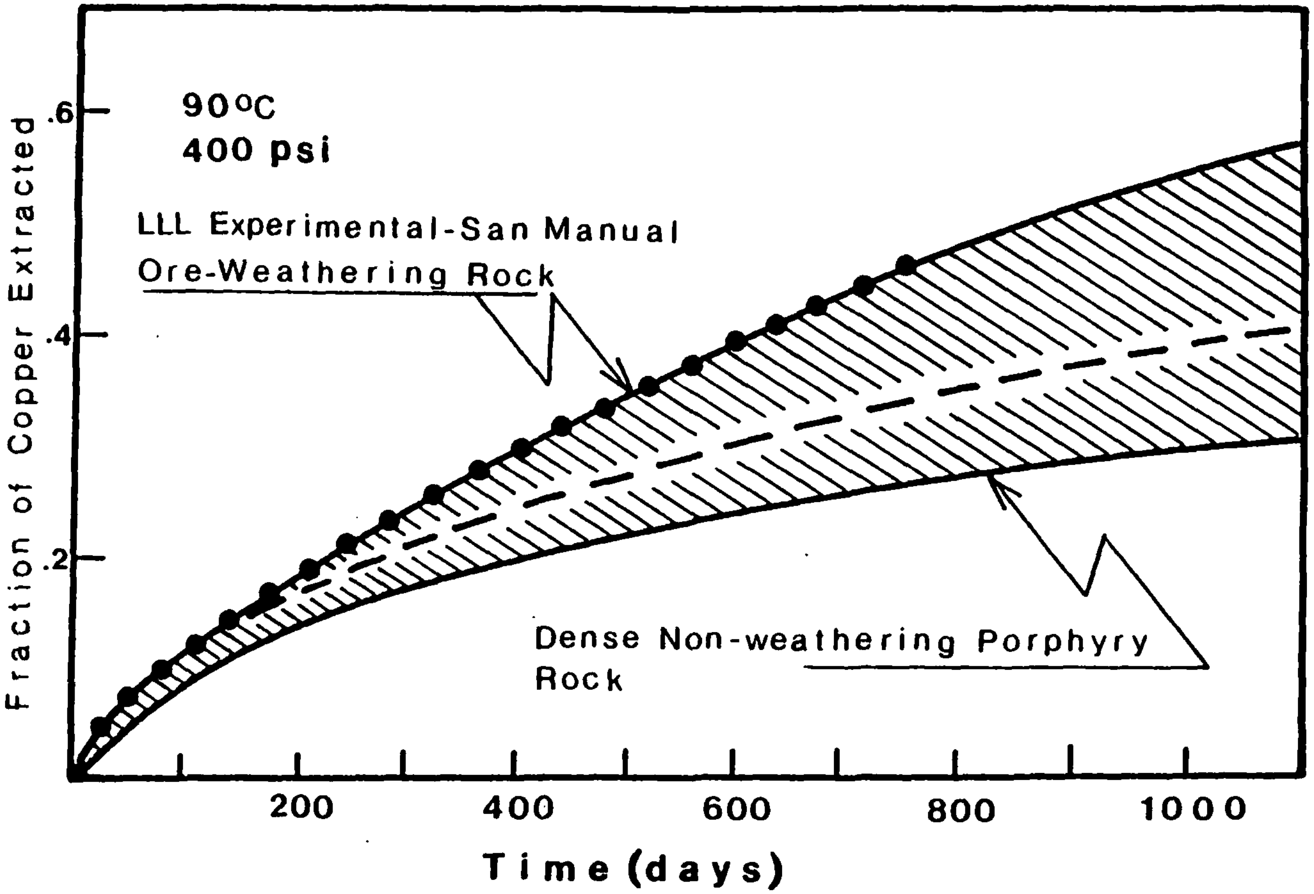

FIGURE 1.7-1 COMPARISON OF WEATHERING AND NON-WEATHERING ORE. DASHED LINE USED FOR DESIGN CALCULATIONS. UPPER CURVE IS FOR LLL EXP-1 USING SAN MANUEL ORE AT 90°C AND 400 PSIA OXYGEN

If conventional explosives, followed by block caving, were employed to simulate the LLL experiment, a void for the explosive would amount to approximately 15 percent of the total volume. Clearly, simulation of the LLL design with conventional explosives is not warranted. This has led us to a design which we refer to as "uniform rubblization" and is an approach employing explosives to shatter the ore into a pattern of free space generated through the joint efforts of Mountain States Engineering and the departments of Mining Engineering and Metallurgical Engineering at the University of Utah.

The design for field application is based upon an ore unit consisting of a cubic block 1,000 feet on a side. Four to possibly eight such blocks may be accessed by one shaft in one 1,000-foot layer. Multiple layers in depth may also be accessed by the shaft providing rubblization proceeds from the bottom of the deposit upward. Considering one unit only, the design incorporates the generation of a minimum of 8 percent porosity by mining lamellae 10 feet in height every 100 feet of depth. Pillars 10 feet on a side would be generated with 20-foot spacing between pillars. Ten such lamellae would be developed in each 1,000-foot ore unit. The 8 percent minimal porosity was arrived at on the basis of explosive rubblization producing a mean rock fragment diameter of 10 centimeters with average crack openings of approximately 3 millimeters. Uniformity is achieved by phased rubblization using conventional explosives. The explosive would be loaded into bore holes produced by drilling from each room and pillar section. Delayed detonation would be employed to attenuate the explosive shock-wave.

For purposes of calculation leading to laboratory experimental design, a typical copper porphyry ore containing 0.7 percent copper and a pyrite to chalcopyrite ratio of 2.0 to 1 will be considered. The bulk ore density is taken as 150 pounds per cubic foot. One unit block would contain 75 x 10^6 tons of ore. Using an average grade of 0.7 percent copper, a unit would contain approximately one billion pounds of copper. Successful exploitation would depend upon a recovery of approximately 50 percent of the copper in a 5-year period. Rubblization of ore in-place against a free surface requires 0.25 (open pit) to 1.0 pound of explosive per ton of ore depending upon the degree of rubblization required. Using a value of 0.5 pound of explosive per ton of ore, a unit block would require 37.5 million pounds of ANFO explosive. By detonating the blast into free space produced by mining, minimal random packing should occur resulting in a fairly uniform distribution of fracturing throughout the ore body. The permeability is estimated to be approximately ten to one hundred fold greater than the surrounding unbroken rock.

Leaching would be carried out using modified bore-hole mining technology with a pattern of down pumping, outpumping, and oxygen injection holes. In operation, continuous oxidation would proceed by oxygen injection into the ore body while a slow, continuous flow of solution is injected and removed. Oxygen would be introduced as needed, probably resulting in two-phase flow. The solution flow rate used in the following analysis is based upon a typical flow rate used in dump leaching of 0.25 gallon per square foot per hour. If the free flowing solution volume of the rubblized deposit is 8 percent of the total volume, the free liquid or pore volume would be 8 x 10^7 cubic feet or 2.7 x 10^9 liters. At the above flow rate, approximately 100 days would be required for one pore volume of liquid to pass through the rubblized deposit. For purposes of calculation, the depletion of contained copper during each pore volume transfer will be considered small compared to the total. Approximately 20 pore volumes will be considered in the calculation.

1.7.2.1 Oxygen Consumption and the Acid Balance

For an ore having a pyrite to chalcopyrite molar ratio of 2 to 1, 11.75 moles of oxygen are required for each mole of copper produced assuming the iron is oxidized to the plus three valence state and all sulfur is oxidized to sulfate. The overall reactions are:

$$CuFeS_2 + H_2O + \frac{17}{4} O_2 = CuSO_4 + H_2SO_4 + \frac{1}{2} Fe_2O_3$$

$$2FeS_2 + 4H_2O + \frac{15}{2} O_2 = Fe_2O_3 + 4H_2SO_4$$

The iron would precipitate as hydrated oxides and as jarosite salts depending upon the solution chemistry. The five moles of acid generated induce accelerated weathering of gangue constituents. Dynamic buffering of the system in steady-state represents a balance between the acid producing reactions involving the sulfide minerals and the acid consuming reactions involving the sulfide and the gangue minerals. The gangue mineral reactions will vary greatly depending upon the mineral make-up of the ore. Typically important gangue reactions would be those involving calcite and feldspar. Potassium feldspar reacts in the sequence:

$$\text{K feldspar} \longrightarrow \text{K-mica} \longrightarrow \text{Kaolinite} \longrightarrow Al^{3+} + 6H_4SiO_4$$

The overall reactions would be:

$$2KAlSi_3O_8 + 4H_2SO_4 + 8H_2O = Al_2(SO_4)_3 + K_2SO_4 + 6H_2SiO_4$$

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$

The previous work carried out at LLL indicated that enhanced leaching occurred as a result of the weathering of the host rock.

1.7.2.2 Calculated Copper Extraction

In Figure 1.7-1 the upper curve, as mentioned, illustrates the laboratory results for the LLL experiment in which relatively extensive weathering occurred. The bottom curve represents the calculated extraction for a dense non-weathering ore which is limited by diffusion through pores. It is assumed the 50 percent passing diameter is 10 centimeters and the ore size distribution follows the log normal relationship. The dashed curve of Figure 1.7-1 represents a modestly weathering ore. The dashed curve is represented by the equation:

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = 1.86 \times 10^5 \ t$$

where α is fraction of copper extracted and t = days. The above equation is considered conservative for a typical porphyry type mineralization. Based on the working curve, the copper released expressed as grams per liter, total cumulative tonnage, and tons per day were calculated. Also, using an oxygen efficiency of 0.85 the oxygen requirement was evaluated. The calculated results are summarized in Table 1.7-1.

TABLE 1.7-1

CALCULATED PRODUCTION DATA FOR IN SITU EXTRACTION FROM ONE BLOCK:

ONE PORE VOLUME (PV) = 2.27×10^9 ℓ
RETENTION TIME = 100 days

Pore Volume	Time (days)	Fraction Reacted	$[Cu^{2+}]$ gpe	Total Cu Produced (Million Tons)	Daily Avg. Cu Production tons/day	Oxygen Requirement tons/day	Oxygen Requirement Cumulative Total (tons)
1	100	.110	21.3	0.053	531	3,690	3,690
2	200	.170	11.6	0.082	290	2,016	5,706
3	300	.210	7.74	0.101	193	1,341	7.047
4	400	.240	5.80	0.116	145	1,008	8,055
5	500	.270	5.80	0.130	145	1,008	9,063
6	600	.290	3.90	0.140	97	674	9,737
7	700	.310	3.90	0.150	97	674	10,410
8	800	.330	3.90	0.160	97	674	11,090
9	900	.350	3.90	0.169	97	674	11,760
10	1000	.370	3.90	0.179	97	674	12,430
11	1100	.385	2.90	0.186	73	507	12,940
12	1200	.400	2.90	0.193	73	507	13,450
13	1300	.415	2.90	0.200	73	507	13,960
14	1400	.430	2.90	0.208	73	507	14,460
15	1500	.445	2.90	0.215	73	507	14,970
16	1600	.460	2.90	0.222	73	507	15,480
17	1700	.470	1.90	0.227	48	334	15,810
18	1800	.480	1.90	0.232	48	334	16,140
19	1900	.490	1.90	0.237	48	334	16,480
20	2000	.500	1.90	0.242	48	334	16,810

Figure 1.7-2 illustrates the calculated results. There is a marked fall-off in solution concentration with time, beginning with very high initial solution concentrations. The horizontal upper (dashed) line of Figure 1.7-2 represents a theoretical continuous production level capable of producing 100,000 tons of copper per year (270 tons per day). Clearly there would be great difficulty in designing an extraction plant to handle the effluent from one unit block. Field production would require initial control of copper extraction either by limiting flow to progressively greater portions of the unit block or by limiting the oxygen flow rate. Phasing in additional rubblized blocks would be required after approximately 200 days to provide a continuous level of production at 270 tons per day.

The solid curves of Figure 1.7-2 refer to maximum production at oxygen saturation. If five years is taken as the effective time for 50 percent removal, we note from Figure 1.7-2 that the 435,000 tons (actually 49 percent of the copper) could be produced from a single unit block in five years by operating at a continuous rate of 130 tons per day or 47,500 tons per year as indicated by the lower dashed line. Beyond five years the rate of production would fall off since the rate of extraction would shift from rate of solution withdrawal to rate of oxygen diffusion into the ore fragments.

1.7.3 The Mining Plan

The mining plan is based upon a 1,000-foot cube of porphyry copper containing 0.70 percent copper with a pyrite to chalcopyrite ratio of 2 to 1. The cube extends from 500 feet to 1500 feet below the permanent water table. The cube contains 7.5×10^7 metric tons of the above mineralization in a major zone of barren porphyry. It is to be leached in-place by a procedure to be described which outlines the preparation of the cube for leaching. Leaching will be over a 5-year period and copper recovery is expected to be 50 percent.

The energy required to prepare and leach the cube is estimated to be 4,921,000 million Btu's, expended over a period estimated at approximately 10 years.

The development program entails the establishment of an underground mine, the extraction of 8 percent of the ore body to create voids, the installation of solution seals surrounding the ore body (if required), and all other procedures that would enhance leaching and recovery following the shattering of the ore cube.

The development program will be carried out on a work schedule of 24 hours per day, 340 days per year.

1.7.3.1 Site Selection

Choose the shaft site most favorable to surface plant topography and to skirt 200 feet away from the exact mid-point of one side of the ore cube. Bear in mind the surface plant will include all the normal buildings and facilities to support a medium sized underground mining operation including dump space for 8.0×10^9 kg of waste and space to install a pad to heap leach more than 5.0×10^9 kg of ore.

1.7.3.2 Shaft Installation

Drill a pilot PQ wireline core hole at the shaft site to 2,600 feet in depth for detailed data on lithology and water to be encountered in sinking.

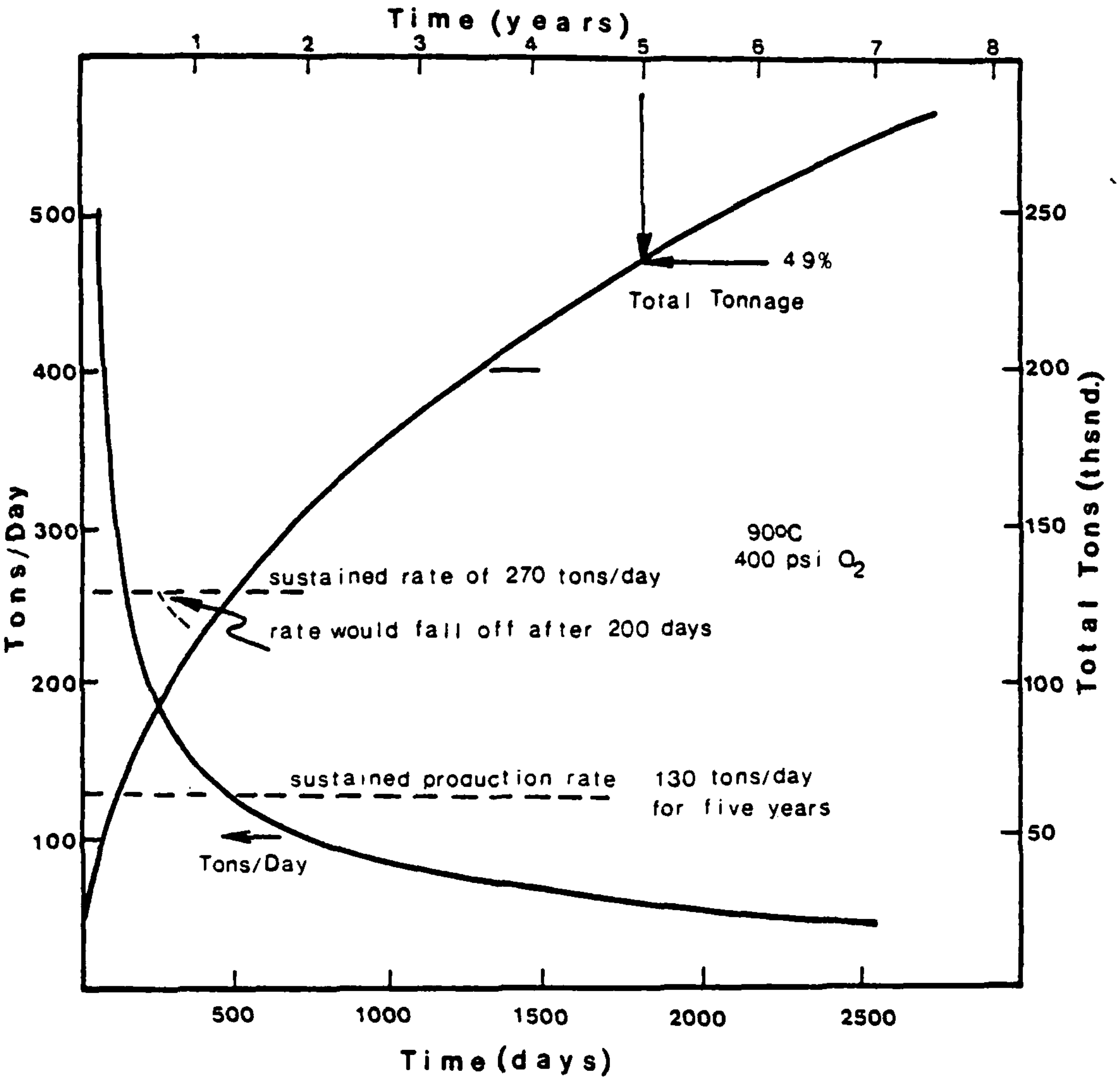

FIGURE 1.7-2 CALCULATED RECOVERY RATE (tons/day) AND TOTAL TONNAGE PRODUCED FROM A UNIT BLOCK OF COPPER PORPHYRY ORE

By truck mounted equipment, excavate the first 50 to 100 feet of shaft and concrete from collar to competent ground. As this is being accomplished the headframe, hoist, compressor, building, and other surface ancillaries can be in the process of installation.

When the shaft achieves 1,460 feet depth, cut a station to serve the injection well field platform. At the 1,600 foot level and each 100 feet below the 2,510 level, cut an appropriate station.

Sink to 2,600 feet below collar and install between the 2,510 and bottom levels the 800 MT capacity pocket, skip loading device, and station. The 2,510 level station will be much larger than others to accommodate the first aid station, minor repairs shop, and emergency supplies.

1.7.3.3 Ore Pass Raise

This system of 6-foot by 6-foot raises will be designed on a 70 degree slope reversed between each level (1,460-2,510 levels) to act as retarders against free-fall velocity. The ore pass system will be in the pillar between shaft and ore body and will be connected with each level by a separate, short 5-foot by 5-foot raise at 70 degrees from a level grizzly with 24-inch openings. The 2,510 level will serve as the main grizzly location with a retarder-feeder admitting the muck from the ore pass to the grizzly with bars at 12-inch spacings immediately above the pocket.

1.7.3.4 Ventilation and Shaft

The four-compartment shaft will utilize the two center compartments for counter-balance hoisting, one compartment for service lines and manway, while the other will be smooth-lined for ventilation air downcast from surface blower. The other compartment will serve as upcast air until the second opening has been installed.

1.7.3.5 The Emergency Escapeway

Upon achieving the 2,510 level, a drift will be started toward the opposite side of the ore block on that level. It will extend 200 feet beyond the ore block into the wall rock directly opposite the shaft, at which point an up-reamed, 6-foot diameter shaft will be bored, using 13¾-inch pilot hole from surface. This second connection with surface will be concrete lined to 5-feet inside diameter and will serve as a ventilation exhaust conduit and an emergency man escapeway.

1.7.3.6 Mining for Voids

To create the needed 8 percent voids to blast to in the ore block, 10-foot horizontal, room-and-pillar slices will be mined at 100-foot intervals in the ore block and one such slice will be made immediately under the block. The number of these slices will depend on the time frame chosen to complete the overall development program. If a 3,000 tons per day shaft facility is installed, the overall development program is estimated to consume 9 years. With a 9,000 ton per day shaft, that period could be 6 years. If leaching is started on the lower one-third of the ore body, production of copper could begin at one-third to one-half of the above time frame. There will be approximately 7,000,000 tons of ore and development waste removed from the shaft and the capital cost for excavating and transporting the materials will be approximately double for the 9,000 over the 3,000 ton per day capacity.

1.7.3.7 Preparation for the Rubblization of the Ore Block

As a slice is nearing completion, special drilling equipment can be moved in to drill 4-inch diameter holes in preparation for the rubblization blast.

1.7.3.8 Placement of the Leach Reagent Injection Platform

Forty feet above the top of the ore block, 8,300 feet of 6-foot by 7-foot drift will be driven to serve 81 injection holes on 100-foot centers. The drift from a shaft station 1,460 feet below collar will carry the oxygen and leach solution headers to the grid of 8-inch holes drilled into the top of the broken ore after rubblization.

1.7.4 Energy Consumption in Mining and Fracturing

1.7.4.1 Electric Power

The mine surface and underground plants will ultimately have 3,050 connected horsepower with an average over the first 1½ years of 20 percent (610 HP) connected, and 100 percent connected the remaining 6½ years of the 8-year mine development period.

Energy expended: 1,605,000 million Btu = 6.76 x 10^6 Btu/ton copper

1.7.4.2 Diesel Power

Principal consumption is by load-haul-dump units underground (assuming public electric power is delivered to the site in place of diesel generator).

114,000 million Btu = 0.07 x 10^6 Btu/ton copper

1.7.4.3 Other Petroleum

17,000 million Btu = 0.07 x 10^6 Btu/ton copper.

1.7.4.4 Explosives

Using a 0.5 pound of explosive per ton of material broken including detonators, boosters, etc., for total blasted metric tons = 75,806,384,568,000 million Btu = 2.14 x 10^6 Btu/ton copper.

1.7.4.5 Bore Escape Shaft (Electric)

This 6-foot diameter shaft will be upreamed through a 13¾-inch pilot hole from surface and the following energy use could be combined with "Electric Power."

8,000 million Btu = 0.03 x 10^6 Btu/ton copper.

1.7.4.6 Underground Drilling of Blast Holes

The approximate 4,600 holes on 10-foot centers, 50-feet deep can be drilled by special lowhead drills capable of vertical up and down drilling 4-inch to 6-inch diameter holes. Power can be either electric or diesel.

1,324,000 million Btu = 5.57 x 10^6 Btu/ton copper.

1.7.4.7 Total Energy Expended in Mining

5,353,000 million Btu = 22.54 x 10^6 Btu/ton copper (47,500 tons per year copper for 5 years)

1.7.5 Energy Consumption in Copper In-Situ Extraction

In this in-situ leaching process, the oxidation of chalcopyrite and pyrite is carried out by pumping oxygen in the fractured ore. About 13,160 pounds of oxygen are required to obtain one ton of copper assuming 85 percent oxygen efficiency. This oxygen requirement represents an energy consumption of 23.7 million Btu's per ton of copper produced as shown under Energy Use Level 2 (Table 1.7-3). Moreover, the oxidation of sulfides underground produces sufficient sulfuric acid for leaching of the copper values.

On the other hand, the reaction of oxygen with sulfides is an exothermic one producing about 57.3 million Btu's of energy per ton of copper oxidized, nearly half of which is consumed in heating the leach solution and the ore in-place up to 90 degrees centigrade. Mountain States Research and Development's (MSRD) calculations indicate that about 29.6 million Btu's are required for heating the leach solution and the fractured ore in-place. This results in the surplus of about 27.7 million Btu's energy. However, MSRD believes that this surplus energy is not in a usable form and no credit is allowed in the energy balance.

The copper values from the leach solution will be recovered using the solvent extraction-electrowinning (SX-EW) process to obtain directly salable cathode copper as shown in the flowsheet (Figure 1.7-3). In the proposed flowsheet, 3,000 gallons per minute of leach solution averaging 8.0 grams per liter copper will be processed in an appropriate SX-EW plant to produce 130 tons per day of cathode copper at an efficiency of 90 percent.

The energy requirement for the SX-EW process as calculated by MSRD amounts to about 24 million Btu's per ton cathode copper produced. Additional energy requirements in the overall process include 1.4 million Btu's for pumping of the leach solution (3,000 gallons per minute) and 29.6 million Btu's for heating the solution and ore in-place to 90 degrees centigrade. It should be noted that much of the heat, once generated, will be retained in the fractured ore underground and the above energy requirement represents additional energy needed to make up the heat losses sustained during leaching and processing.

The energy uses in the proposed in-situ leaching process under level 1 and Level 2 are summarized in Table 1.7-2 and Table 1.7-3 respectively.

As can be seen, the total energy required for producing one ton of cathode copper by in-situ extraction including both Levels 1 and 2, amounts to 80.6 million Btu's. This quantity is in line with the energy required by other hydrometallurgical and pyrometallurgical processes including mining and concentration. One would expect that the in-situ extraction would be less energy intensive than other conventional mining and surface processing methods. In reality, the process is less energy consuming per unit of copper, but the recovery is about 50 percent as compared to about 85 to 90 percent for conventional mining and surface processing methods. This observation clearly pinpoints the need for research and development resulting in higher recoveries than 50 percent.

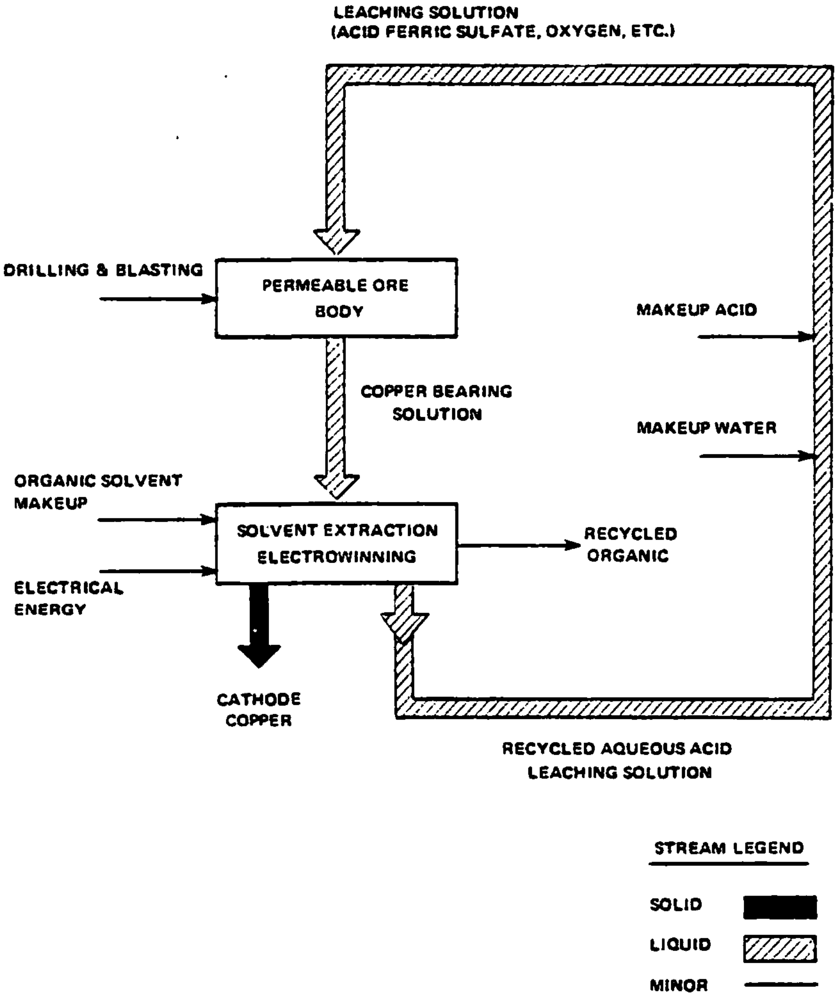

FIGURE 1.7-3 COPPER IN SITU LEACHING

TABLE 1.7-2 **ENERGY REQUIREMENTS** Level 1

INSITU LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Mining and Fracturing				22.5
	Leaching				
	A) Pumping Solution				1.4
	B) Heating Solution and ore in place				29.6
	Solvent Extraction Electrowinning				24.0
	Energy Produced in the Process* (oxidation of sulfides)				-29.6
				TOTAL	47.9

*Energy produced in the oxidation of sulfides is actually 57.3 x 10^6 Btu, but we are accounting for only heat required for heating the solution and the broken ore.

TABLE 1.7-3 **ENERGY REQUIREMENTS** Level 2

INSITU LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Mining and Fracturing Explosives	LBS	143	.060125	8.6
	Leaching Oxygen	LBS	13,160	.0018	23.7
	SC-EW Reagents	LBS	24.92	.0172	0.4
				TOTAL	32.7

1.7.6 Conclusions

The in-situ extraction of copper from a deep seated sulfide copper deposit should be an attractive process from the view of energy consumption, since Mountain States Research and Development's study indicates that about 75 million Btu's are required to produce one ton of cathode copper. This consumption is in line with energy consumption by other hydrometallurgical methods. The major shortcoming of the process is the assumption that only 50 percent of the copper is recoverable in this process. If higher recoveries than 50 percent are achievable then the in-situ process would be truly an attractive approach. If the comparison is made with conventional mining and concentration of ore from a deep-seated deposit the in-situ method appears even more attractive.

1.7.7 Recommendations

Since the overall recovery of 50 percent makes the in-situ process little better than other hydrometallurgical processes in energy use, research efforts should concentrate on methods to increase the overall recovery of copper. Accordingly, an in-depth R&D program is necessary for improving the overall extraction of copper. This study should include a demonstration phase to determine the effectiveness of the process under operating conditions in-situ. Also the use of air instead of oxygen should be considered for certain conditions of ore depth and mineralization. An appreciable energy saving could be made using air and conditions permitting its use should be determined. Comparable tests in bench scale and large pilot scale research is needed to assess the following:

1) Actual oxygen consumption related to the type and extent of mineralization needs to be evaluated quantitatively.

2) Use of air compared to oxygen to determine the effect of oxygen partial pressure.

3) Recent developments (Coursen, 1979) in blasting stressed rock with flooded joints indicates the amount of explosive needed may be as low as that for open pit mining. This would reduce the total Level 2 energy by 4.8×10^6 Btu/ton copper. Explosive technology which will reduce the amount of explosive needed for uniform rubblization should be tested under conditions approximately the specific in-situ mining plan.

4) In connection with 3) above, field tests on rubblization should include up-flow flushing to remove fines produced by sliding joints during blasting. It appears such flushing can remove fines effectively, resulting in permeabilities of 2 or 3 Darcys.

5) The fanning or spreading effect of gases through open joints in a blasted ore body should be determined under conditions of two-phase flow.

6) Weathering and leaching characteristics of copper porphyry should be determined for extended periods of ore-solution contact time to improve model predictability.

7) Comparison of small scale and large scale tests should be correlated by a detailed model to test and improve scale up precision.

8) Solution chemistry capable of recovering precious metals concurrently or sequentially should be considered.

9) Reactions with host rock potentially capable of precipitating copper and consuming lixiviant should be quantified.

1.7.8 References

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1.8 COPPER CEMENTATION

1.8.1 Introduction

The recovery of copper from dilute leaching solutions by precipitation with iron, i.e., cementation, represents a significant source of recoverable copper representing approximately 10% of domestic mine output. The solutions obtained from in-situ, dump and heap leaching are dilute (15 kg/m^3 copper). Cementation offers a simple and efficient means of recovering copper from such dilute solutions. The product of precipitate or cement copper is impure and requires further pyrometallurgical upgrading.

1.8.2 Process Description (Biswas and Davenport, 1976)

The cementation of copper from solution is described by the reaction

$$Fe^{0} + Cu^{++} \rightarrow Cu^{0} = Fe^{++} \qquad (1.8.1)$$

Other metals such as aluminum and zinc can be used. However, steel scrap is an economic cementation agent of choice. The pregnant leach solution is made to flow through a pile of scrap steel at which time the copper precipitates on the iron surfaces and is removed under the influence of solution flow as flake or powder. The copper is usually contaminated with iron (typical analysis 85-90% Cu, 0.2-2% Fe, 0.5% SiO_2 + Al_2O_3, remainder oxygen). Stoichiometrically, about 0.88 ton of iron is required to cement one ton of copper. In industrial practice the iron consumption is 1.5-2.5 tons per ton of copper cemented out due mainly to the following side reactions:

$$Fe^{0} + 2Fe^{+++} = 3Fe^{++} \qquad (1.8.2)$$

$$Fe^{0} + 2H^{+} = Fe^{++} + H_{2(g)} \qquad (1.8.3)$$

Atmospheric oxygen contributes to excess iron consumption oxidizing the iron or producing ferric ions that consume metallic iron. Some of the copper may also oxidize and redissolve requiring reprecipitation.

Thermodynamics indicate that the equilibrium ionic ratio $A_{Fe2}+/A_{Cu2}+$ is about 10^{25} at 25°C. This extremely large ratio indicates that reaction 1.8.1 can proceed until virtually all the copper ions are precipitated from solution. In industrial practice more than 90% of the copper is removed from the pregnant liquors before they are recycled to the leaching circuit. The kinetics of cementation have been studied extensively, and it is generally agreed that the rate controlling step is the diffusion of copper ions to the steel surface. Thus, the rate of copper precipitation

(Nadkarni and Wadsworth, 1968) is proportional to the concentration of copper, in solution, the exposed iron area and the specific rate constant 'k'

$$dC_{Cu_2}+/dt = -\,kA\,C_{Cu}+_2 \qquad (1.8.4)$$

The specific rate constant and hence the cementation rate increases with increasing temperature and degee of agitation. In addition, minimizing the concentration of Fe^{+3} ions and atmospheric oxygen lowers the effect of side reactions 1.8.2 and 1.8.3 leading to more efficient iron utilization. It has been shown that iron consumption approaches stoichiometric requirement when carried out in a nitrogen atmosphere (Biswas and Reid, 1972).

The flow sheet for the recovery of copper from dilute solutions by cementation is shown in Figure 1.8-1. The simplest and most common cementation system is the open launder in which the pregnant leach solutions flow by gravity down a wooden or concrete trough or series of troughs filled with steel scrap. The launders vary in dimensions and form — straight line or zigzag. Table 1.8-1 summarizes the operating parameters for launder precipitation plants. In more recent launder designs the scrap steel is held on wooden grids positioned above the launder bottom. This permits the cement copper to fall to the bottom of the launder where it can be recovered from the steel scrap. Open launder operations involve higher scrap steel usage with up to three times the stiochiometric requirement actually being used. It also requires considerable labor to handle steel scrap additions and to recover cement copper.

Several compact and dynamic cementation systems have been developed and used industrially (Spedden et al., 1966). The most successful is the Kennecott Cone precipitator in which the pregnant leach solution is forced upwards in a swirling motion through shredded steel scrap.

The Kennecott Cone system consists of a cylindrical tank, 6-7 m high, 4-6 m diameter, in which a 4-m high stainless-steel cone is fixed (apex down). The upper third of the cone is constructed of stainless-steel screen. The pregnant leach solution is swirled into the cone via two rings attached to the inside of the cone (one-third and half-way up) through laterally directed openings on the rings. The solution swirls upwards through the shredded steel scrap and the copper precipitates as contact is made.

The swirling action washes the copper from the iron surfaces and the particles become suspended in the solution. The copper particles are carried upward to near the top of the cone where, as the velocity decreases due to the widening of the cone, they sink through the screen part into the collection area at the bottom of the tank.

The Kennecott Cone is a high capacity unit (10 m^3min^{-1} of solution in a 7 m high, 4 m diameter vessel; Malouf, 1973). The system is flexible and two or more cones can be placed in a series (or series with a launder) to maximize copper recoveries and throughput or to handle solutions with high copper concentrations. In addition to the high throughput rate, the cone has the advantage of a low iron consumption, in the order of 1.6 times the stoichiometric requirement compared with 2.3 for equivalent launder techniques (Spedden et al., 1966). The Kennecott Cone has proven to be very efficient and it is now used extensively in association with large heap-leach operations.

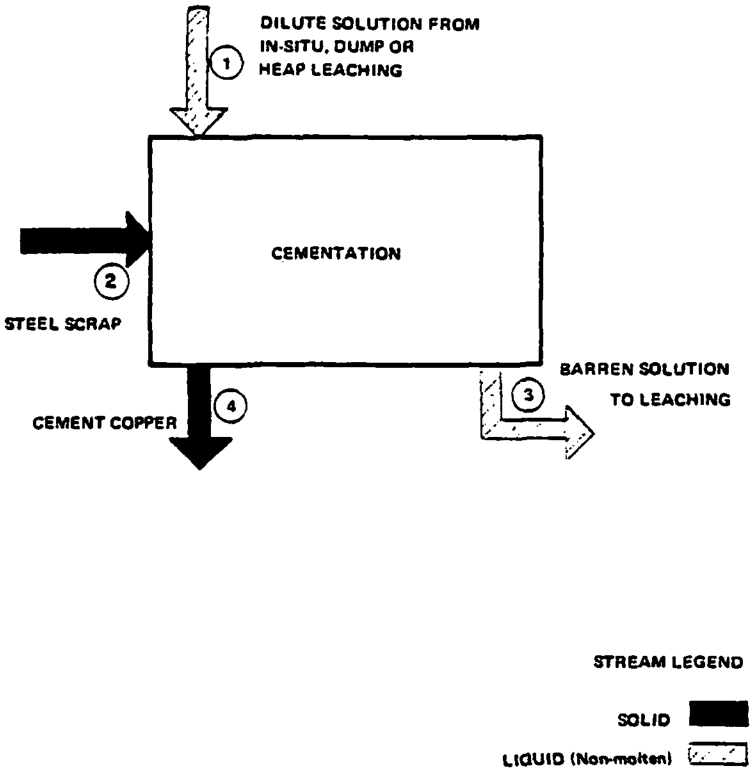

FIGURE 1.8-1 COPPER CEMENTATION

TABLE 1.8-1 COMPARISON OF LAUNDER PRECIPITATION PLANTS (JACOBI, 1964)

	Inspiration copper	Ohio Cu, (Bingham Canyon)	Anaconda (Butte)	Andes Copper	Cananea
Launder system	Zigzag	Straight line	Straight line	Zigzag	Zigzag
Daily production (tonnes)	11	9	8	8	22
Leach solution flow ($m^3 min^{-1}$)	9.5	3.2	19.0	2.2	5.1
Copper concentrations (kg m^{-1})					
Pregnant leach	0.85	2.04	0.31	2.41	3.30
Post cementation	0.02	0.06	0.02	0.07	0.36
Recovery of launders (%)	97	97	95	97	89
Number of launder units	32	200	20	18	40
Dimensions of launder units					
Length (m)	12	5	30	19	12
Width	0.5	0.8	3	3	1.5
Depth	1.5	0.8	0.9	1.8	0.9
Total launder volume (m^3)	290	640	1620	1850	650
Velocity of leach solution (m min^{-1})	2.0	9.8	2.0	0.4	0.1
Contact time (min)	19.2	50	78	875	88
Ratio: $\frac{\text{Daily copper production}}{\text{Total launder volume}}$ (tonnes day m^{-3}')	0.04	0.014	0.005	0.004	0.03

Other dynamic precipitation techniques such as the tumbling of scrap in submerged drums have been tried but much of the copper precipitate produced was colloidal in size and difficult to recover.

1.8.3 Materials Balance

The principal material consumption is iron as scrap. Depending on the type of operation, the scrap iron consumption can range from 1.5 to 4 tons per ton of cement copper (Woodcock, 1967) and 1.5 to 2.5 tons (Biswas and Davenport, 1976)

1.8.4 Energy Requirements

Level 1 energy requirements in cementation consist principally of electrical energy in pumping solutions in precipitation cones and launders. The energy use is small and is estimated at 5 kWh per ton of cement copper or 0.05 million Btu per ton of cement copper.

The only materials consumption is the iron scrap used in cementation. Based on an iron use of 2.5 tons per ton of copper and an energy value of steel scrap of 18 million Btu per ton (Battelle, 1975), this results in an energy use of 45 million Btu per ton cement copper. Thus, the level 2 energy usage is 45.05 million Btu per net ton cement copper.

1.8.5 Utilization of Cement Copper

The most common method of treatment of cement copper is by melting it in smelting furnaces or converters. An alternate but rarely used method is to dissolve the cement copper in a basic aqueous solution followed by hydrogen reduction to yield copper powder (<150 μm) of 99.9% purity (EMJ, 1967). A German patent (Reid, 1972) according to which copper at 99.8% purity is produced by carrying out the cementation reaction under nitrogen followed by a sulfuric acid washing and a nitrogen atmosphere drying. This process will, if successful, produce a material suitable for powder metallurgy applications.

1.8.5.1 Disposition of Copper Precipitates

Table 1.8-2 shows the disposition of cement copper (precipitates) at U.S. copper smelters. It is seen that most of the precipitates used at smelters (88.5%) are added to the reverb or roaster. It should also be noted that precipitates represented about 3.9% of the tonnage of copper concentrates charged at U.S. smelters.

1.8.5.2 Energy Requirements

Many smelting furnaces use precipitates as a portion of the charge. The energy requirements presented in subsequent sections represent actual operation energy use, i.e., for a mix of concentrates and cement copper. Based on the enthalpies of copper and iron sulfides and cement copper at their melting points, it is estimated that melting copper precipitates requires 15 percent of the energy used to melt on a per ton contained copper basis. If precipitates are charged to a converter, the excess heat can be used to melt the precipitates. However, this is rarely practiced because the moisture in the precipitates can cause hazards in converter operations and dust handling problems increase.

Table 1.8-2

DISPOSITION OF PRECIPITATES AT U.S. SMELTERS
(1971-73)

Smelter	Approximate Annual Tonnage: Concentrates	Approximate Annual Tonnage: Precipitates, Reverbs, Roasters	Approximate Annual Tonnage: Converters	Precipitate Use (%): Reverb Roasters	Precipitate Use (%): Converters
Asarco, El Paso	295,600	3,000	9,000	25	75
Hayden	529,812	1,743	2,614	40	60
Tacoma	273,603	0	3,995	0	100
Phelps Dodge, Douglas	680,509	10,500	6,500	62	38
Morenci	810,000	16,000	1,200	93	7
New Cornelia	206,471	1,640	2,445	40	60
Kennecott, Garfield	780,542	52,650	2,211	96	4
Hayden	296,282	13,215	43	100	0
Hurley	265,442	36,700	405	99	1
McGill	283,196	16,435	0	100	0
Inspiration	282,200	28,500	0	100	0
Magma, San Manuel	798,500	0	0	0	0
Anaconda, Anaconda	647,870	37,840	0	100	0
Copper Range, White Pine	247,100	0	0	0	0
TOTAL	6,397,127	218,223	28,413	88.5	11.5

Source: Economic Impact of New Source Performance Standards on the Primary Copper Industry, Arthur D. Little, Inc., October 1974.

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2.0 PYROMETALLURGY

2.1 INTRODUCTION

This section deals with copper extraction processes that involve high temperature processing to produce a final blister copper product which is subsequently fire refined and electrorefined to the pure cathode product. Section 2.2 presents an analysis of the theoretical energies involved in the conversion of the standard concentrate to blister copper. The process is exothermic when pure oxygen is used to convert the concentrate to copper and produces surplus heat. If a mixture of air and oxygen is used, as the nitrogen in the gases increases, its heat content rapidly changes the surplus heat to a deficit. With pure air 4.2 million Btu per ton of cathode copper is necessary to overcome the energy deficit. It is evident from this analysis that oxygen enrichment of air blowing processes is energy efficient. If the heat liberated by the oxidation of sulfides in the charge can be recuperated or used efficiently in a given process, a low overall energy cost will result for the process.

The conventional roast, reverberatory matte smelting, converting process was treated in section 2.3 to provide a "yardstick" by which the other pyro-processes could be measured. The other processes chosen for study range from those that have had considerable commercial utilization such as the electric furnace (2.5), Oxy Fuel Reverb (2.15), the flash smelting processes (2.6, 2.7) and the Noranda process (2.9) to the Q-S process (2.11) presently under development by Dravo and the Thermo Electron Process (2.14) which has not been at the present time completely tested on a laboratory scale.

The Top Blown Rotary Converter Process (2.8) is an example of a process successful in the steel industry which has been adapted to nickel and copper sulfide smelting. It has only recently been used commercially in British Columbia for the first time on a copper ore concentrate. The Mitsubishi Process (2.10) is an example of a modern continuous smelting and converting process with a unique design. The AMAX Dead Roast Process (2.12) which utilizes a small blast furnace for final reduction of the copper oxide. The Segregation Process (2.13) is a novel process involving a combination chloridizing roast and coal reduction step which appears to be energy efficient.

Finally a section is included on impurity control in pyrometallurgical processes (2.4) since impurity elements play an important role in the nature of the subsequent smelting operations. Some elements may be valuable by-products while others are detrimental to the quality of the final cathode copper and are difficult and costly to remove. It is concluded that the single step smelting processes may retain more of the impurity elements in the final blister copper than the conventional smelting process and hence the continuous processes may have to either use more pure ores or be modified to include a separate converting or impurity removal step.

2.2 THE THEORETICAL ENERGY FOR SMELTING COPPER CONCENTRATES TO UNREFINED BLISTER COPPER

2.2.1 Introduction

As a base line for comparing real processes, an idealized theoretical energy for smelting is desired. Smelting is defined as the unit process of metallurgy in which the desired product, metal or matte, is separated from an undesired one, slag, by a gravity separation amongst the two liquid, condensed phases. Normally, a gas will also be present. A narrow interpretation of the definition would lead to the conclusion that no real copper smelting process meets these criteria, because the so-called slag phase is not liquid, it is itself a two-phase system of liquid slag and solid magnetite (Fe_3O_4) which can amount to as much as 30 percent of the slag weight. Magnetite causes bottom build-up in relatively quiescent furnaces, and is blamed for poor settling of matte out of slags, and therefore high slag losses. Consequently, the first step in making a material balance from which theoretical energy may be calculated is selection of a slag which should prevent magnetite formation by using available thermodynamic and activity data.

2.2.2 Selection of Slag Composition

Magnetite cannot form when conditions do not allow the following reaction, Eqn. 2.2.1, to proceed.

$$3FeO(\text{in slag}) + 1/2\ O_2\ (\text{in surroundings}) = Fe_3O_4(S) \qquad (2.2.1)$$

Thus the formation of magnetite requires the existence of FeO and a sufficient pressure of oxygen in the surroundings. FeO exists in the slag phase because FeS has been oxidized into it and into SO_2 in the gas phase. Thus the raw material for magnetite formation being present, what is the pressure of oxygen? The highest oxygen pressure encountered when going from concentrates to copper is where the oxidation of white metal, Cu_2S, occurs. The highest oxygen pressure will then result from the reaction of Eqn. 2.2.2.

$$Cu_2S + O_2 = 2Cu(\text{liquid}) + SO_2(\text{gas}) \qquad (2.2.2)$$

This would correspond to an 80% Cu matte grade. Actual matte grades are generally lower, and those encountered in modern processes may be around 70% Cu. In this case, the oxygen pressure would be fixed by Eqn. 2.2.3.

$$FeS + 1.5\ O_2 = FeO + SO_2 \qquad (2.2.3)$$

The equilibrium constant of this reaction is readily calculated from thermodynamic data, and has the form shown in Eqn. 2.2.4.

$$K_3 = (\text{activity FeO x pressure } SO_2)/[\text{activity FeS x (pressure } O_2)^{1.5}] \qquad (2.2.4)$$

Activity of FeO can be controlled by selecting a suitable slag, adding for example proper amounts of SiO_2 and CaO, known as "fluxes." Since the reaction uses up oxygen almost quantitatively, the pressure of SO_2 depends on oxygen content of the oxidant. If pure oxygen is used, then SO_2

pressure is approximately equal to atmospheric. If air is used, it will be about 15% as shown by equation 2.2.5 (based on 79% N_2 21% O_2 in air):

$$FeS + 1.5\ O_2 + 5.64\ N_2 = FeO + SO_2 + 5.64\ N_2 \qquad (2.2.5)$$

For the more general case, one gets the result of Eqn. 2.2.6:

$$\text{pressure of } SO_2\ (\text{atm}) = \%\ O_2\text{, blast } (150 - 0.5 \times \%\ O_2\text{, blast}) \qquad (2.2.6)$$

Since activity of FeS in matte is nearly equal to its molar fraction, one can estimate it from percent Cu in matte by Eqn. 2.2.7:

$$\text{activity FeS} = (1 - 0.006918 \times \%\text{Cu,matte})/(1 - 0.005605 \times \%\text{Cu,matte}) \qquad (2.2.7)$$

It appears that if activity of FeO is at about 0.35, then magnetite cannot form in the temperature range 1200-1300°C for oxygen contents in the blast up to 100%. Also, equilibrium copper in slag will be below 0.5%. (Yazawa, 1974).

By extrapolating activity data in the system CaO-FeO-SiO_2 (Timucin, 1970) down to 1300°C, it was found that a silica-saturated slag containing 10% CaO, and 45% each of FeO and SiO_2 had the desired activity. According to the work of Rontgen its viscosity was about 5 poises, and according to Henderson its density is 3.3, so that with a matte density of about 5, separation should be satisfactory.

In the slag, Al_2O_3 is considered chemically equivalent to SiO_2 on a weight basis in correcting the ideal slag composition to one made from gangue in the concentrates and fluxes. The fluxes are regarded as being pure SiO_2 and pure $CaCO_3$. The oxygen used is treated as pure O_2.

With these assumptions, the material balance is as shown in Table 2.2-1 and the energy balance as in Table 2.2-2. Thus the oxidation of green concentrates to blister copper is exothermic, with surplus energy of 1.9 million Btu per net ton of contained copper. Were one to use a lower SiO_2 slag, as is the common practice, the calculated energy surplus would be greater for two reasons, one being the formation of Fe_3O_4, with its higher heat of formation than FeO, and the other a decrease in the weight of slag. It is however felt that the actual energy surplus in this case would be decreased rather than increased because of the operating problems brought about by magnetite.

2.2.3 Effect of Air-Oxygen Mixtures

The effect of using a mixture of air and oxygen rather than pure oxygen is to add nitrogen gas and thereby increase the heat content of the gases, soon changing the heat surplus into a deficit. The heat content of nitrogen at 1250°C is 9.39 kcal/gm mol. Therefore the 528 kcal surplus would be consumed by the addition of 56.23 mols of N_2. Since the oxygen supplied is 1535 grams or 47.97 gm mols, it is seen that a blast containing less than 46% oxygen will change the surplus into a deficit. If air is used, heat in nitrogen will rise to 1695 kcal/kg Cu or 6.10 million Btu/ton Cu, changing the surplus to a deficit of 4.2 million Btu.

TABLE 2.2-1

Material Balance for the Production of Unrefined Blister Copper from the Standard Concentrate under Idealized Conditions

Basis: 1000 net tons Cu in Blister

INPUT	tons	OUTPUT		tons
Green Concentrates	4500	Blister Copper		1020
Silica Flux	970	Slag		
Lime Flux	366	SiO_2	1319	
		Al_2O_3	140	
Oxygen	1535	FeO	1459	
		CaO	289	
		MgO	25	
		Cu	13	
		S	16	
		Other	12	3283
		Gas		
		H_2O	450	
		CO_2	161	
		SO_2	2457	3068
TOTAL INPUT	7371	TOTAL OUTPUT		7371

Table 2.2-2

Energy Balance for Production of Blister Copper from Standard Concentrates

Basis 1000 gm Cu or One Net Ton Cu in Unrefined Blister

Input		kcal/kg Cu	Million Btu/net ton Copper
Oxidation of sulfur		2743	9.88
Oxidation of iron		1215	4.37
Formation of slag		208	.75
Formation of alloy		5	.02
Total energy input		4171	15.02
Output			
Sensible heat at 1250°C			
Blister copper		188	.68
Slag		1255	4.41
Gas-SO_2	591		
CO_2	55		
H_2O	296	942	3.39
Decomposition			
sulfides	824		
$CaCO_3$	156	980	3.53
Evaporation of water		308	1.11
Total accounted for		3643	13.12
Surplus, by difference		528	1.90
Total energy output		4171	15.02

2.2.4 References

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2.3 CONVENTIONAL SMELTING

2.3.1 Introduction

Conventional pyrometallurgical practice for recovery of copper from its sulfide concentrates (reverberatory smelting) is fairly uniform from smelter to smelter and is adapted to treating fine grained sulfide concentrates consisting mainly of copper and iron sulfides and gangue.

Copper's strong affinity for sulfur and its weak affinity for oxygen as compared with that of iron and other base metals form the basis for the three major steps in producing copper metal from sulfide concentrates; roasting, smelting and converting. There are approximately 100 reverberatory furnaces in use worldwide (Biswas and Davenport, 1976).

2.3.2 Process Description

The process flowsheet is shown in Figure 2.3-1.

2.3.2.1 Raw Materials

Flotation concentrates containing from 15-30% copper constitute the bulk of the feed to the smelters. In addition, smelters will charge cement copper (produced by precipitation of copper in solution with iron) containing 70-85% copper.

2.3.2.2 Drying

The flotation concentrates can contain 10-15% moisture. Cement copper can contain as much as 30% moisture. The charge to a reverberatory furnace can be dried so that its overall moisture content is 4-8% without unduly increasing dusting problems in the reverb. The removal of moisture in drying reduces the fuel requirements in the reverb. Also the drier acts as a blender for homogenizing the charge. Rotary or multiple hearth driers are used for drying the feed materials.

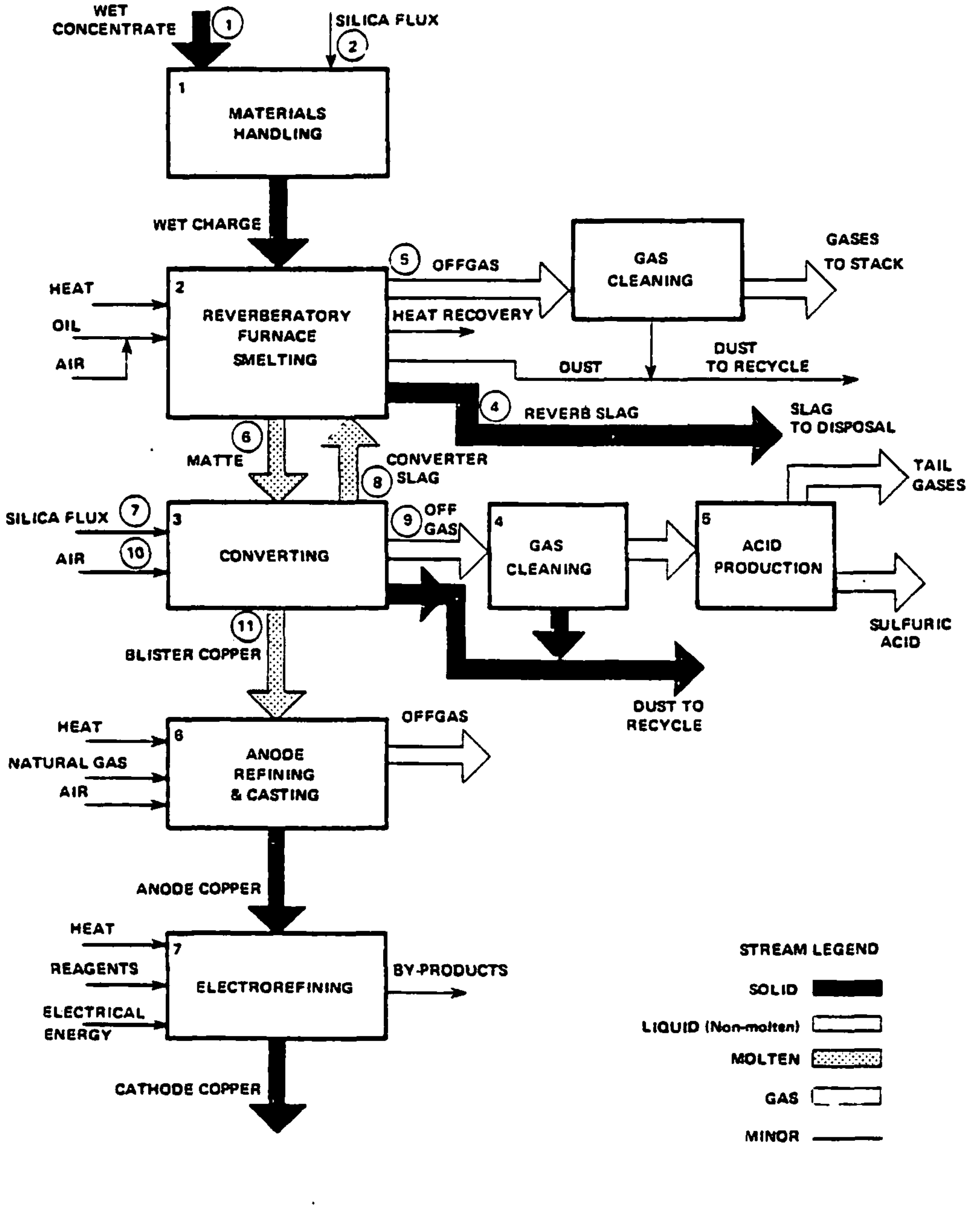

FIGURE 2.3-1 REVERBERATORY SMELTING PROCESS

2.3.2.3 Roasting

About half the copper smelters in the U.S. roast their charge prior to smelting in the reverberatory furnace. The older smelters use multiple hearth roasters for this purpose while the new smelters use fluidized bed roasters.

The object of roasting is to regulate the amount of sulfur in the charge and to remove certain volatile impurities such as arsenic, antimony, and bismuth. In the case of custom or toll smelters, the composition of feed materials can vary widely. Hence, roasting in addition blends and homogenizes the charge. Smelters with access to high-grade, low-impurity concentrates eliminate roasting and smelt the concentrates directly.

Elimination of some of the sulfur in roasting results in a higher grade matte in the reverberatory furnace and hence decreases the oxidizing load on the converters. Sulfide roasting can be autogenous and additional fuel is not required. The charging of hot roasted calcines into the reverberatory furnace can decrease its fuel consumption per ton of charge by about 40% and consequently increase a reverb's unit capacity. The lower fuel requirement per ton of charge when using calcine smelting also reduces the volume of reverb off-gases. In addition, roasting also reduces the emissions of sulfur dioxide from the reverb by removing the loosely held or "labile" sulfur in the concentrates which would otherwise evolve in the reverb upon melting of the minerals.

$$2CuFeS_2 = Cu_2S + 2FeS + S \quad (2.3.1)$$
$$FeS_2 = FeS + S \quad (2.3.2)$$
$$S + O_2 = SO_2 \quad (2.3.3)$$

Both types of roasters (multiple hearth and fluidized bed) usually operate around 1200°F. Sulfur dioxide concentration in the wet off-gas is usually 5-10% with new multiple hearth roasters and lower for old multiple hearth roasters (2-5% sulfur dioxide). With fluid bed roasters the wet off-gases can run 10-12% sulfur dioxide. Both types of roasters, therefore, can produce a steady stream of relatively rich off-gases suitable for sulfuric acid manufacture. Both types of roasters involve the handling and collecting of large quantities of hot abrasive dust which can lead to high maintenance costs.

2.3.2.4 Reverberatory Furnace Smelting

Roasted and unroasted materials, after mixing with suitable fluxes, are smelted in reverberatory furnaces. Liquid converter slag is also charged into the reverberatory furnace to recover its copper content. Heating of the charge is accomplished by burning fuel in the furnace cavity, the heat being transmitted to the charge primarily by radiation from the roof, walls and flame.

A reverb can use natural gas, fuel oil or pulverized coal as fuel. Most U.S. smelters have gas/oil capability and many are planning a switch to coal.

The maximum smelting capacity of a reverb is limited by the amount of fuel that can be burned (a function of reverb shape and size) and the quantity of heat required by a unit weight of charge. Reverb throughput can be increased by drying the charge, preheating the charge by roasting, and preheating and/or oxygen enrichment of the combustion air.

These other techniques rely on scrubbing of the reverb gases to absorb sulfur dioxide and then treating the scrubber liquor to either strip the sulfur dioxide (to produce a more concentrated stream suitable for acid manufacture) or to produce a disposable solid.

At the Ajo smelter in Arizona, Phelps Dodge installed an experimental system for absorbing sulfur dioxide in reverb and converter gases in dimethylaniline (DMA) and stripping the DMA to produce a more concentrated stream of sulfur dioxide. The system was operated intermittently by Phelps Dodge and is no longer in use. Other absorption-concentration systems have also been tried at other U.S. smelters, e.g., the citrate system at Magma Copper in Arizona and at Bunker Hill in Idaho. These systems are also no longer in operation. The DMA scrubbing system at Asarco's Tacoma, Washington smelter is the only absorption-concentration system in operation at a copper smelter in the U. S. This installation scrubs converter gas and not reverb gas. Asarco used the DMA system at their Selby, California lead smelter for many years.

The Smelter Control Research Association has studied several strategies for controlling reverb emissions and selected a dual-alkali scrubbing process as the most cost effective. In this process, the reverb gas is scrubbed with an ammonium hydroxide liquor and the absorbed sulfur oxides are precipitated as a calcium sulfite/sulfate sludge with lime (SCRA, 1977).

At the Onahama smelter in Japan, the reverb gases were ducted directly to an acid plant temporarily while the plant was being converted from conventional green charge smelting to the Mitsubishi process. The acid plant did not achieve autogenous operation (E&MJ, 1972).

2.3.2.5 Converting

Matte produced in the reverberatory furnace is transferred in ladles to the converters using overhead cranes. The converters used in copper smelting are of the cylindrical Peirce-Smith type, the most common size being 13' x 30'. Air is blown from the side through a series of openings called tuyeres. During the initial blowing period (the slag blow) iron sulfide in the matte is preferentially oxidized to iron oxide and magnetite and sulfur is removed with the off-gases as sulfur dioxide. Flux is added to the converter to combine with iron oxide and form a fluid iron silicate slag. When all the iron is oxidized, the slag is skimmed from the furnace leaving behind "white metal" or molten cuprous sulfide. Fresh matte is charged into the converter at this stage and the slag blowing continued until a sufficient quantity of white metal has accumulated. When this happens, the white metal is oxidized with air to blister copper during the "copper blow." The blister copper is removed from the converter and cast or subjected to additional fire refining prior to casting. Converter blowing rates can vary between 12,000 to 30,000 scfm of air. Also, the sulfur dioxide content of the off-gases is lower during the "slag blow" than during "copper blow."

Cooling of the hot converter gases is necessary in order to prevent thermal damage to the dry gas cleaning equipment. When this cooling is accomplished by adding dilution air, sulfur dioxide concentrations in the converter off-gases can vary from 1-7% and this gas is considered too dilute for sulfuric acid manufacture. When air dilution is prevented with close fitting hoods or with Hoboken converters, the off-gases average 5-10% sulfur dioxide. However, when dilution air is not used, cooling devices such as waste heat boilers, air/gas heat exchangers or water sprays are necessary to protect the dry gas cleaning equipment.

The converter gases pass via a balloon flue or individual high velocity flues to dry gas cleaning equipment such as cyclones and electrostatic precipitators. Thus, with proper hooding, the converter off-gas is sufficiently high in sulfur dioxide so as to be suitable for sulfuric acid manufacture, but converting by its very nature is a batch operation and the off-gas flow rates vary widely. In the smaller copper smelters which use two or three converters, the scheduling of converter blows in order to obtain relatively steady flows to the acid plant is a difficult problem.

2.3.3 Material Balance

Table 2.3-1 shows the material balance for green charge smelting.

2.3.4 Energy Requirements

Table 2.3-2 presents the Level I energy requirements for green charge smelting, in million Btu per ton of blister copper.

The energy used in materials handling and general utility (material transport, blending and bedding of concentrate and flux, slag granulation and disposal, operation of control systems and plant lighting) is estimated at 15.5 kwh/ton concentrate smelted, or 147,000 Btu fuel equivalent.

Table 2.3-3 presents the Level II energy requirements for green charge smelting.

Tables 2.3-4 and 2.3-5 present the Level I and Level II energy requirements for calcine charge smelting. A multiple hearth roaster has been assumed for concentrate roasting. The sulfur distribution is as follows: roaster 50%, reverb 15%, converter 30% and fugitives 5%.

2.3.5 Conclusions

Conventional smelting (green charge reverb smelting or roast-reverb smelting) is characterized by the use of large quantities of hydrocarbon fuels because the process makes little use of the energy available from oxidation of the sulfide charge. The limited degree of oxidation in the reverb as well as the dilution of the resultant sulfur dioxide by combustion gases and leakage air results in a gas stream that cannot be economically treated for sulfur recovery.

The smelting of hot calcines requires less smelting fuel than that for wet charge smelting because the heat of oxidation of the sulfides is utilized in drying and preheating the charge. In many cases, the roasting can be carried out without an external source of fuel. The lower smelting fuel requirement also results in lower combustion air requirements and a smaller off-gas volume thereby requiring lesser energy for gas cleaning. The matte produced in the reverb has a higher matte grade resulting in further decrease in the energy requirements for converting and converter gas cleaning. Also, the recovery of sulfur as acid is also higher.

The recovery of sensible heat from reverberatory furnace off-gas through the use of waste heat boilers has been standard practice for many years. The recovery of waste heat from roaster gases is not practiced mainly because of lower off-gas temperatures and the high dust load has made the small amount of recoverable energy uneconomic. The temperature of operation of a fluid bed roaster is around 1500°F and there is a potential for waste-heat recovery by immersing heat transfer surfaces inside the fluidized bed. In a Dorr-Oliver slurry feeding type of design, the roaster is operated adiabatically so that excess heat is used to evaporate the water used in producing the slurry. In the Lurgi-type design waste heat is recovered via heat transfer surfaces immersed in the bed itself. To our knowledge, none of the fluid bed roasters at smelters in the United States recover waste heat. Spray cooling and dilution is used to cool the gas to a temperature suitable for feed to the acid plant.

In the reverberatory furnace, copper and sulfur form the stable copper sulfide. Excess sulfur unites with iron to form a stable ferrous sulfide. The combination of the two sulfides, known as matte, collects in the lower area of the furnace and is removed. Such mattes may contain from 15 to 65% copper, with a 40 to 45% copper content being most common. The matte also contains impurities such as antimony, arsenic, iron, and precious metals.

The remainder of the molten mass containing most of the other impurities known as slag, being of lower specific gravity, floats on top of the matte and is drawn off and discarded. Slags in copper smelting are ideally represented by fayalite, but contain alumina from the various charge materials and calcium oxide which is added for fluidity. Since reverb slags are discarded, the copper contained in the reverb slag is a major cause of copper loss in pyrometallurgical practice. The concentration of copper in the slag increases with increasing matte grade.

When using a reverb for green charge smelting, 20% to almost 45% of the sulfur in the feed is oxidized and is removed from the furnace with the off-gases. The wet off-gases can contain 1.5-3% sulfur dioxide. When using calcine smelting, sulfur dioxide evolution is lower and about 10-15% of the sulfur in the unroasted feed material is contained in the reverb off-gases. Sulfur dioxide concentration in the wet off-gases in this case can vary between 0.5 to 1%.

The hot gases from the reverb are cooled in waste heat boilers which extract a portion of the sensible heat in the gases. A considerable amount of dust is removed in the waste heat boiler and the gases are further cleaned in electrostatic precipitators before venting to the atmosphere.

Reverberatory furnaces can vary in width from about 22 feet to 38 feet and in length from about 100 feet to 132 feet. The roofs of the older reverberatory furnaces are sprung arch silica roofs, while almost all the newer furnaces have suspended roofs of basic refractory. Over the years, two types of reverberatory furnaces have evolved, each with its specific charging methods. The first and older is the deep bath reverberatory furnace which contains a large quantity of (in excess of 100 tons) molten slag and matte at all times. In modern deep bath reverberatory furnaces, the molten material is held in a refractory crucible with cooling water jackets along the sides which greatly diminishes the danger of a breakout of the liquid material. In deep bath smelting, several methods exist for charging. Wet concentrates can be charged using slinger belts (high speed conveyors) that spread the concentrates on the surface of the molten bath. Dry concentrates or calcines from the roaster can be charged through the roof or via a Wagstaff gun (an inclined tube). Roof charging (side charging) is rarely practiced in conjunction with deep bath smelting because of potential dusting problems with fine dry calcine and explosion problems with green charge.

The second type of reverberatory furnace is the dry hearth type in which a pool of matte exists mainly at the tapping end. The dry hearth type furnaces are charged with wet or partially dried concentrates (green feed smelting), or with calcines through the roof. In the latter case the dusting problem can be quite severe for fine concentrates.

As noted earlier, reverb gases are too dilute in sulfur dioxide to be suitable for autogeneous sulfuric acid manufacture. Several attempts have been made to control emissions from the reverb by other techniques but these have not been practiced for long on a commercial basis.

TABLE 2.3-1 REVERB SMELTING: GREEN CHARGE

[TONS PER TON BLISTER COPPER]

STREAM NO.	(1)		(2)		(4)		(5)		(6)	
STREAM NAME	HET CONCENTRATE		SILICA FLUX		REVERB SLAG		REVERB OFF GAS		MATTE	
COMPOSITION	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.9932	25.0			0.0132	0.44			1.0416	42.0
Fe	1.112	28.0	0.0072	1.40	01.124	37.33			.7648	30.82
S	1.2316	31.0			0.0292	0.97			.6192	24.97
O_{Fe}*	0.0188	0.47	0.0032	0.60	0.3192	10.60			.0552	2.21
S_iO_2	0.3428	8.63	0.456	90.0	1.1844	39.34				
AL_2O_3	0.1342	3.45	0.0208	4.0	0.1752	5.82				
CaO + MgO	0.1164	2.93	0.010	2.0	0.1348	4.48				
Others	0.0208	0.52	0.010	2.0	0.0308	1.02				
H_2O	0.39728						1.06211			
SO_2							1.2392			
O_2										
CO										
CO_2							2.3656			
N_2							7.8110			
TOTAL	4.37008	100.00	.5072	100.00	3.0108	100.00	11.2387		2.4808	100.00
TEMP. (°F)		60		60	2250		2350		2150	
STATE		S		S		L		G		L

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.3-1 (cont.) REVERB SMELTING: GREEN CHARGE

[TONS PER TON BLISTER COPPER]

STREAM NO.	(7)		(8)		(9)		(10)		(11)	
STREAM NAME	CONVERTER FLUX		CONVERTER SLAG		CONVERTER OFF GAS		CONVERTER AIR		BLISTER Cu	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu			.0616	4.08					.980	98.0
Fe	.006	1.40	.7696	50.93					.001	0.1
S			.0364	2.41					.009	0.9
O_{Fe}*	.0024	0.60	.2324	15.38					.0015.	0.15
SiO_2	.3856	90.00	.3856	25.50						
Al_2O_3	.0172	4.00	.0172	1.14						
CaO + MgO	.0084	2.00	.0840	0.56						
Others	.0085	2.00							.0085	0.85
H_2O										
SO_2					1.148	31.36				
O_2							.7504	23		
CO										
CO_2										
N_2					2.51221	68.64	2.51221	77		
TOTAL	.4281	100.00	1.5112	100.00	3.66021	100.00	3.26261	100.00	1.0	100.0
TEMP. (°F)	60		2250		2300		60		2200	
STATE		S		L		G		G		L

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.3-2 **ENERGY REQUIREMENTS** Level 1

CONVENTIONAL SMELTING: GREEN CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling and General Utility				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Reverb. Smelting				
	A) Fuel: Fuel Oil	GAL	179.9	0.139	25.006
	B) Electrical Energy	KWH	60.8	0.0105	0.638
	C) Waste Heat Recovery: Steam	LBS	7140	0.0014	-10.000
3	Converting				
	A) Electrical Energy	KWH	155	0.0105	1.628
	B) Fuel: Fuel Oil	GAL	3.9	0.139	0.542
4	Gas Cleaning				
	A) Hot Gas Cleaning				
	1- Reverb (1.5% SO_2)	Thous. SCF	1000.9	0.00336	3.363
	2- Converters (7.0% SO_2)	Thous: SCF	198.7	0.00336	0.668
	B) Cold Gas Cleaning				
	1- Converters (7.0% SO_2)	Thous. SCF	198.7	0.00126	0.250
	2- Fugitive Emissions Control	KWH	340	0.0105	3.570
5	Acid Plant				
	A) Converter Gas (7% SO_2)	Thous. SCF	198.7	0.0114	2.265
*	Water Pollution Control				
	A) Electrical	KWH	9.0	0.0105	0.095
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	34.575

TABLE 2.3-3

ENERGY REQUIREMENTS

Level 2

CONVENTIONAL SMELTING: GREEN CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb. Smelting A) Silica Flux	TONS	0.518	0.042	0.022
3	Converting A) Silica Flux	TONS	0.437	0.042	0.018
*	Water Pollution Control A) Lime	LBS	30.0	0.0027	0.081
6,7	Anode Casting and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	0.589

*Not shown on flowsheet

TABLE 2.3-4 **ENERGY REQUIREMENTS** Level 1

CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
*	Roaster				
	A) Electrical Energy	KWH	62.7	0.0105	0.658
2	Reverb. Smelting				
	A) Fuel: Fuel Oil	GAL	104.3	0.139	14.498
	B) Electrical Energy	KWH	60.8	0.0105	0.638
	C) Waste Heat Recovery: Steam	LBS	3107	0.0014	-4.350
3	Converting				
	A) Electrical Energy	KWH	120	0.0105	1.260
	B) Fuel: Fuel Oil	GAL	2.3	0.139	0.320
4	Gas Cleaning				
	A) Hot Gas Cleaning				
	1- Roaster (10% SO_2)	Thous. SCF	149.2	0.00336	0.501
	2- Reverb (0.85% SO_2)	Thous. SCF	525.	0.00336	1.764
	3- Converters (7% SO_2)	Thous. SCF	167.3	0.00336	0.562
	B) Cold Gas Cleaning				
	1- Roaster (10% SO_2)	Thous. SCF	149.2	0.00126	0.188
	2- Converter (7% SO_2)	Thous. SCF	167.3	0.00126	0.211
	3- Fugitive Emissions Control	KWH	340.0	0.0105	3.570
5	Acid Plant				
	A) Roaster & Converter Gas (8.4% SO_2)	Thous. SCF	316.5	0.01224	3.874
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095

TABLE 2.3-4 (Cont.) **ENERGY REQUIREMENTS** Level 1

CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	30.339

*Not shown on flowsheet.

TABLE 2.3-5 Level 2

ENERGY REQUIREMENTS

CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	<u>Reverb. Smelting</u> <u>A) Silica Flux</u>	TON	0.375	0.042	0.016
3	<u>Converting</u> <u>A) Silica</u> Flux	TON	0.290	0.042	0.012
*	<u>Water Pollution Control</u> <u>A) Lime</u>	LBS	30.0	0.0027	0.081
6,7	<u>Anode Furnace and Electrorefining</u>	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	0.577

*Not shown on flowsheet

Only three or four smelters in the United States are recovering heat from converter off-gases by using water-walled uptake hoods, the others use some form of dissipative cooling (dilution radiation or convection to reduce the temperature of the off-gas). The companies that have attempted to recover heat from the converter off-gases have had mixed success. To overcome acid condensation on the heat transfer surface, its temperature must be maintained above 400°F even when there is no off-gas from the converter. Thus, when a converter is not in operation, the working fluid (steam or water) heats the air leaking into the converter hood. Fuel must be burnt for keeping the working fluid warm. In some instances, this energy consumption can exceed the amount of waste heat recovered.

Little attempt has been made to recover waste heat from the anode furnaces and cathode melting furnaces. An exception is the Outokompu Harjavalta plant where anode furnace off gas is used to dry concentrates, reportedly decreasing fuel requirements for drying by aproximately 25%. The anode furnaces only operate intermittently and are operated primarily as a holding furnace. Because of the low gas volume, the waste heat potential is limited. If anode refining is carried out along with scrap melting, as practiced in the secondary copper industry, the off-gas volume and the waste heat recovery potential would be higher. The ASARCO shaft furnace has the cathodes moving counter-current to the gas stream and is therefore an efficient heat exchanger by itself. Consequently, there is little additional potential for waste heat recovery in cathode melting in the ASARCO shaft furnace.

The principal developments with respect to decreasing energy requirements has been the oxygen enrichment of combustion air in the reverberatory furnace. The principal effect is decreasing the amount of nitrogen per unit of combusted fuel. This results in:

- An increased flame temperature and hence an increased rate of heat transfer to the charge.
- An increased residence time of the combustion gases (due to the lower volume per unit of fuel) and hence more complete transfer of their heat to the charge.
- A decreased carry off of sensible heat in the effluent gas.

These lead to increased smelting rates and decreased fuel consumption (Biswas and Davenport, 1976). Experiments on an INCO reverberatory furnace (Saddington, et al., 1967) indicates that oxygen enrichment of combustion air to 27% oxgyen reduces fuel consumption by about 20%. Alternatively, if the fuel rate is kept constant production rate can be increased about 35% at a level of oxygen enrichment of 26% oxygen. Similar results have been obtained with Russian reverberatory furnaces (Kupriakov and Artemeiv, 1974). Oxygen enrichment to a level of 30% is used on a regular basis in five or six reverberatory furnace operations (Niimura, et al., 1973) (Kupriakov and Artemeiv, 1974). Enrichment above this level leads to excessively high temperatures and excessive refractory wear at the burner end. Industrial tests, as part of a program to increase enrichment to 40-50% oxygen, at the Almalyk smelter (Kupriakov and Artemeiv, 1974) demonstrate that this problem might be overcome by supplying the fuel with a shortage of oxygen and by supplying the remainder of the oxygen via vertical roof pipes spaced regularly down the length of the furnace.

At the Caletones smelter in Chile, oxy-fuel burners were tried in reverbs over a period of several years, finally getting to complete elimination of air-oil burners. A 50% decrease in fuel usage and doubling of daily production rate are predicted based on an energy balance evaluation of air-oil versus an air fuel reverb. Although the refractory usage increased considerably with oxygen-fuel burners, as production was doubled the retractory usage per ton of copper produced did not increase as a result of switching from air-fuel to oxygen-fuel burners (Schwarze, 1977).

The converting of matte using air (low-to-medium matte grades) is autogenous. In fact, coolants such as scrap or cement copper must be added in most cases to prevent the converter from overheating. The enrichment of converter air lowers the quantity of nitrogen and thus permits the charging of larger quantities of coolant. An alternate coolant is copper concentrate which in addition to cooling the system melts to form matte and slag. Extensive tests in the United States and Japan have showed that with oxygen enrichment (30-40%), a significant proportion of the concentrates entering a smelter can be smelted in the converter (Tsuromoto, 1961; Messner and Kinneberg, 1969). Principal problems in the process are the high rate of refractory wear in the tuyere region due to overheating caused by the oxygen enriched blast, and excessive fugitive dust.

2.3.6 References

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2.4 IMPURITY CONTROL IN PYROMETALLURGICAL COPPER PROCESSES

2.4.1 Introduction

Copper sulfide concentrates are normally associated with a number of elements. These include: Au, Ag (noble metals); =Co, Ni, Pt, Pd (Group VIII); Zn, Cd Hg (Group II-B); Sn, Pb (Group IV-A); Mo (Group VI-B); Bi, Sb, As (Group V-A); Se, Te (chalcogens) and Cl (halogen), in addition to gangue. Of the elements listed above, some of the elements such as Mo and Zn are removed in the concentration process or occur in small enough quantities that they need not be removed. The principal elements of interest are (1) Au, Ag, Se, Te, representing valuable byproducts and (2) Zn, Pb, Sn, Bi, Sb, representing principal impurities. The following is a discussion of the impurity elimination characteristics of various processes, pyrometallurgical processes which produce blister copper and the further purification of blister copper to anode grade copper. Finally, impurity distributions in electrorefining are discussed. It should be emphasized that data on impurity distribution presented in this section although based on operating data are meant as a guide and are not to be considered typical of specific processes, operating on a specific concentrate.

2.4.2 Reverberatory Smelting and Converting

2.4.2.1 Reverberatory Smelting

Over many decades reverberatory smelting processes have been highly perfected with respect to minor element control. Reverberatory smelting provides a high recovery of valuable byproducts such as Au, Ag, Se, Te to copper while assuring an excellent elimination of detrimental elements such as Zn, Pb, Sn, Bi, Sb, and As. The two mechanisms for impurity removal are (1) oxidation and slagging, and (2) volatilization.

The elements removed by slagging are those whose oxides have a high negative free energy of formation. Besides iron, the elements removed to some degree by oxidation and slagging include Co, Ni, Zn, As, Sb, Bi, Ca, Mg *, Al*, Ba*, Na*, K*, Mn*, Li*, Ti*, V*, and Sn. At the same time some of the highly deleterious impurities — As, Sb, Bi, Se, and Te — are removed either by volatilization either as sulfides or oxides or in the elemental form. About 99 percent of the Pb, 54 percent of the Bi, 50 percent of the Sb, 21 percent of the As, and 60 percent of the Se and Te are eliminated in the reverberatory furnace (Keller, 1902). The behavior of metals other than copper and iron in reverberatory smelting is estimated in Table 2.4-1.

These data serve only as a guide and the precise distribution of minor elements depends upon the smelting conditions and the type of process. The most important points are:

- Gold, silver, the platinum metals, cobalt and nickel enter the matte almost completely. These metals are carried forward to the converting operation and they are finally recovered as byproducts during the electrorefining of anode copper.

- Significant quantities of impurities harmful to copper also enter the matte; specifically antimony, arsenic, bismuth, lead, selenium and tellurium. Some of these are also recovered as byproducts during subsequent converting and refining operations.

- Much of the zinc reports in the slag from which it can be recovered by "slag fuming" (reduction) if it is present in sufficient quantities.

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* Removal of these elements is complete in the smelting and subsequent converting operations.

TABLE 2.4-1

ESTIMATED DISTRIBUTION OF ELEMENTS DURING MATTE SMELTING

Metal	Distribution Matte	 Slag	 Volatized*
Alkali and alkaline earth metals aluminum, titanium		100	
Ag, Au, platinum metals	99	1	
Antimony	30	55	15
Arsenic	35	55	10
Bismuth	10	10	80
Cadmium	60	10	30
Cobalt	95	5	
Lead	30	10	60
Nickel	98	2	
Selenium	40		60
Tellurium	40		60
Tin	10	50	40
Zinc	40	50	10

*Not including solids blown from the furnace (dust losses).

Source: Ruddle, 1953, Yazawa and Azakami, 1969, Mackey, et al., 1975, published in Biswas and Davenport, 1976.

2.4.2.2 Converting

In the converter, due to the more strongly oxidizing conditions, and to the rapid passage of air, a great deal of impurity elimination takes place. Here the last traces of the less harmful impurities (Ca, Mg, Al, etc.) are removed and further amounts of the more tenaciously held impurities (As, Sb, Bi, Se, and Te) are eliminated. Converting may be expected to eliminate from ordinary mattes (low grade ~40 percent), 70 percent of Sb, 80 percent of the arsenic, 50 percent of the Se and Te, and 95 percent of the bismuth (Peters, 1907). Another source reports that 95-98 percent of the lead, 94-96 percent of the bismuth, 71-73 percent of antimony, 81-84 percent of arsenic, 19-52 percent of selenium and tellurium is removed during converting (Keller, 1899). Later experimental work indicates that little Se and Te is removed during converting (Baker and Hallowes, 1950).

Table 2.4-2 summarizes the distribution of elements between blister copper, slag, and gas phase. Table 2.4-3 presents the composition of dusts from electrostatic precipitators operating on converter gases.

It is seen from Table 2.4-2 that As, Bi, Cd, Ge, Hg, Pb, Sb, and Sn are extensively removed as vapors during converting while most of the zinc is removed along with iron in the slag. Precious metals, and to a lesser degree, nickel and cobalt, proceed forward with the blister copper from which they are recovered during electrorefining.

There is also considerable entrainment of matte and slag droplets in the high-velocity converter waste gases. The solidified droplets are caught in the flue system (mostly in "ballon flues" but also in electrostatic precipitators) and are generally recycled within the smelter. The droplets have the approximate composition of the liquids at the time of ejection.

The dusts and vapors from converters contain sufficient copper for them to be recycled to the smelting furnace or to the converter itself. However, this procedure returns all of the impurities to the circuit and hence some smelters treat the dusts for impurity removal before they are recycled or these dusts are stockpiled. Bismuth in particular is recovered from converter dusts because: (a) it causes brittleness in the final copper anodes and (b) it is a valuable byproduct.

2.4.3 Flash Smelting

2.4.3.1 Outokumpu Flash Smelting (Harkki and Juusela, 1974)

The feed at the Harjavalta smelter usually contains only limited amounts of deleterious impurities such as As, Sb, Bi, Zn, etc. (Table 2.4-4) and hence no special treatment is needed. The flash smelting technique is flexible, i.e., copper content of the matte may vary from 40 to 80 percent, the flue dusts, or some part of them, may be taken out of circulation if they are enriched in some components. On account of this flexibility, different types of concentrates can be smelted. The distribution of elements can be affected even in the furnace by changing the process variables. The distribution of elements in the settler, flue dust, and gas phase, can be controlled and desired products from flash smelting achieved.

In the flash smelting furnace the impurity elements are distributed between slag, matte and flue dust. As the flue dust is normally circulating, the final distribution is between matte and slag. A small amount of the elements or compounds with a relatively high vapor pressure may be

TABLE 2.4-2

DISTRIBUTION (ESTIMATED) OF IMPURITY ELEMENTS DURING CONVERTING

	Blister Copper	Gas[1]	Slag[2]
Ag	90	0	10
Au	90	0	10
Pt metals	90	0	10
As	15	75	10
Bi	5	95	0
Cd	0	80	20
Co	80	0	20
Fe	0	0	100
Ge	0	100	0
Hg	10	90	0
Ni	75	0	25
Pb	5	85	10
Sb	20	60	20
Se	60	10	30
Sn	10	65	25
Te	60	10	30
Zn	0	30	70

[1] Not including ejected droplets of matte and slag.

[2] Including entrained matte.

Source: Ruddle, 1953; Yazawa and Azakami, 1969; published in Biswas and Davenport, 1976.

TABLE 2.4-3

COMPOSITE CONVERTER COTTRELL DUST ANALYSES FOR THE GASPE AND NORANDA SMELTERS

	Analysis (%)										
Smelter	Cu	Pb	Zn	Cd	Bi	Sb	S	SiO	Ag	Au	In
Gaspe	10.2	27.9	7.5	0.31	1.95	0.80	9.3	NR	NR	NR	NR
Noranda	11.0	22.1	13.9	0.82	--	0.18	10.2	6.5	0.04	0.0005	0.12

Source: Stanley, et al., 1972, published in Biswas and Davenport, 1976.

TABLE 2.4-4

COMPOSITION OF CONCENTRATE AT HARJAVALTA

Cu	Fe	S	Zn	Co	Ni	Pb	As	Sb	Bi	Se	Au	Ag
(percent)											(grams/10^3 kg)	
22.7	32.1	34.3	4.0	0.2	0.1	0.5	0.3	0.02	0.003	0.003	3.4	102

Source: Harkki and Juusela, 1974.

carried over to the gas phase through the electrostatic precipitator further to the sulfuric acid plant or the elemental sulfur producing units. If impurities are concentrated into the dusts, the dust circulation can be interrupted to prevent their accumulation in slag or matte from which their elimination may be difficult.

The distribution of elements between matte and slag is mainly controlled by the oxygen potential of the slag, which is characterized by the Fe^{2+}/Fe^{3+} ratio. When the oxygen potential increases, the slagging of components also increases. There seems to be a correlation between the Fe^{2+}/Fe^{3+} ratio in slag and the copper content of matte. Figure 2.4-1 shows shows the mass distributions (i.e., the amount of the component in the slag divided by its amount in the slag and matte). Some of the lines are shown dashed because the results are strongly affected by factors other than matte grade such as content in feed, reaction shaft temperature, etc. The data in Figure 2.4-2 are based on the test runs carried out at the Harjavalta Smelter and in the pilot plant of Outokumpu Metallurgical Research Center in Pori.

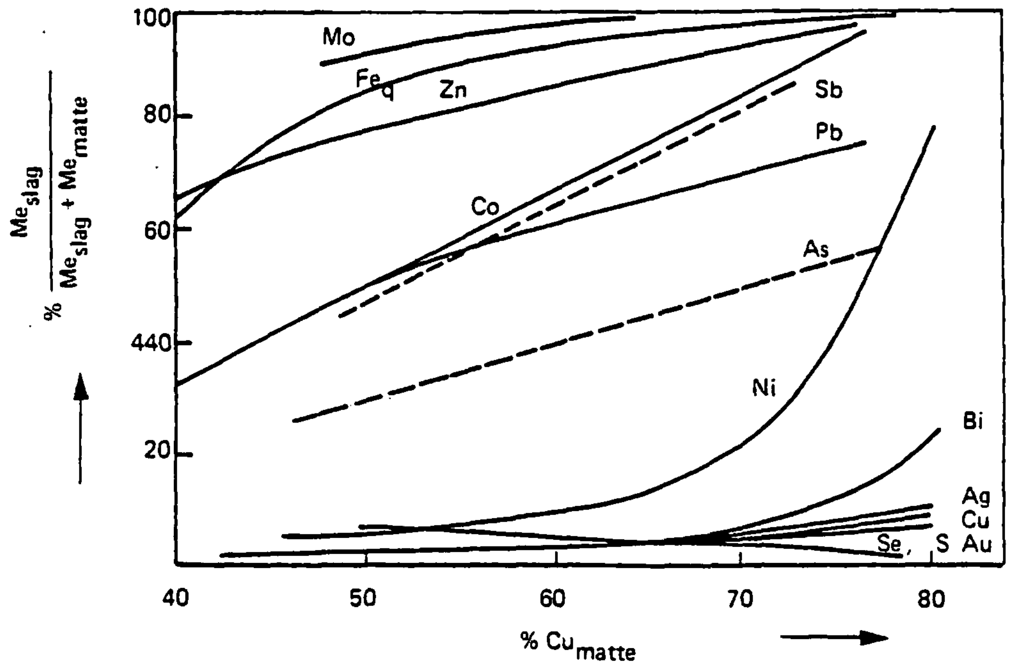
The flue dust is formed from the components following the gas phase to the uptake shaft and further to the waste heat boiler and electrostatic precipitator, where the temperature decreases to about 300°'C. At this lower temperature many of the volatile components can be collected as dust.

The amount of the so-called mechanical dust depends mainly on the concentrate, the formation of suspension in the reaction shaft, the shape of the furnace, the flow pattern in the furnace and on other physical factors. The amount of volatile components is controlled by the above mentioned factors as well as by the degree of oxidation and the reaction shaft temperature. The composition of the flue dust is affected by the gas composition in the boiler and electrostatic precipitator, which can be sulphidizing or oxidizing.

When the flue dust distributions are presented in the same way as the settler distributions, it is noted that some components are mainly in the mechanical dust (Cu, Ni, Co, Fe, and Au), other components being strongly affected by the degree of oxidation or by the reaction shaft temperature (Figures 2.4-2 and 2.4-3). The scatter in some flue dust distributions (dashed lines) is often due to the matte grade not being the only parameter affecting the results. The amount of feed, the percentage of elements in the feed, the reaction shaft temperature, gas volume and many other factors have their specific effects. The amount of the material going through the electrostatic precipitators is not calculated in these distributions.

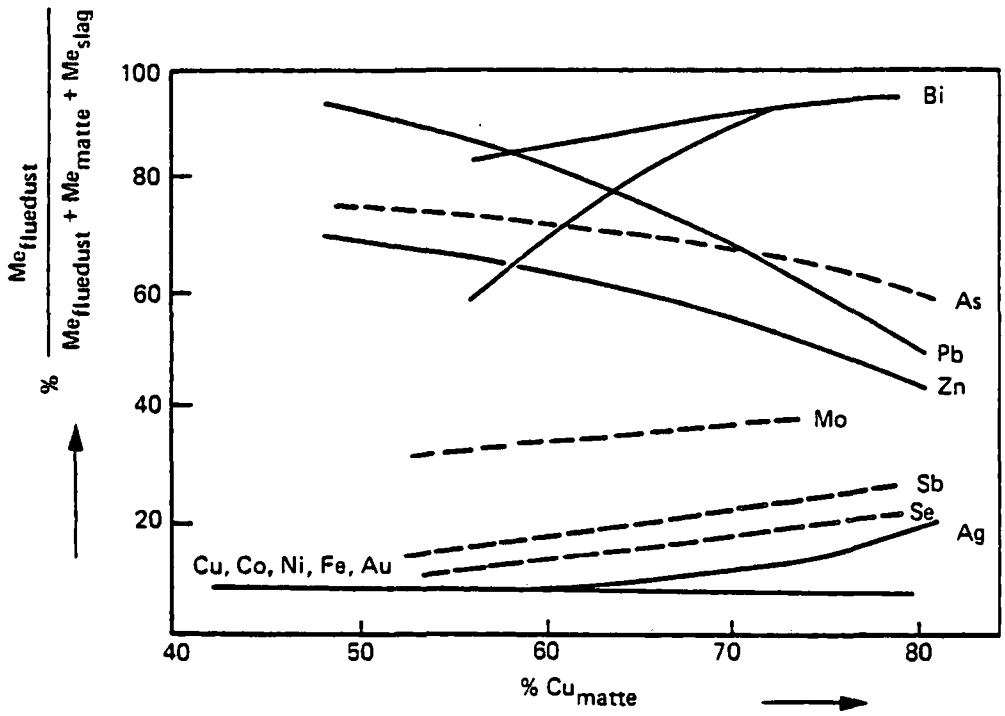
The process parameters may be controlled to optimize the elimination of volatile components, e.g., Pb, Zn, Bi, As, and remove them from the circuit with part or all of the flue dust fraction. The removal of Bi is carried out by this method in the flash smelter of Peko-Wallsend Metals Limited in Tennant Creek, where the Bi content in the concentrate is about 0.7 percent. The pilot plant tests gave a Bi recovery in flue dust of over 90 percent. The Dowa Mining Company, Ltd. at their Kosaka Smelter in Japan reduces the circulating amount of Pb, Zn, As, Bi, and Cd by special treatment of flue dusts.

The distribution in gas phase is calculated from the amount of components collected after the electrostatic precipitators. Depending on the vapor pressure and temperature, some of the compounds (e.g., As, Hg, Se, Te) pass with the gas phase through the conventional dust separation, after which they can be recovered selectively (e.g. concentrated sulfuric acid scrubbing for Hg removal).



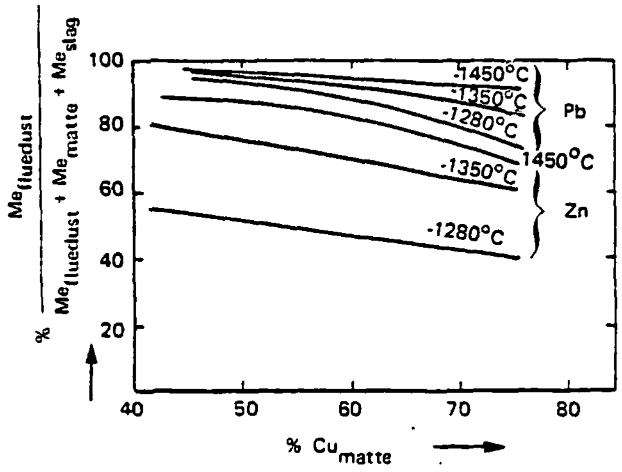
Source: Harkki and Juusela, 1974.

FIGURE 2.4-1 SLAG-MATTE DISTRIBUTION IN COPPER FLASH SMELTING



Source: Harkki and Juusela, 1974

FIGURE 2.4-2 FLUE DUST DISTRIBUTION IN COPPER FLASH SMELTING



Source: Harkki and Juusela, 1974.

FIGURE 2.4-3 EFFECT OF REACTION SHAFT TEMPERATURE ON FLUE DUST DISTRIBUTION OF Pb AND Zn

2.4.3.2 INCO Flash Smelting

The Copper Cliff concentrates are relatively free of impurities. The copper concentrates generally average less than 0.01 percent Bi + As + Se and less than 0.1 percent Pb. The off-gases from the flash furnace amount to 4300 scfm at an output of about 1200 tons per day of concentrates. The off-gases contain less than 3 percent of the feed as dust and between 5 to 70 percent of the bismuth, 20 to 50 percent of the lead and arsenic, and 5 to 15% of the selenium in the concentrates smelted depending on the type of concentrate and the oxygen potential. (Solar et al., March 1979).

There is also data on impurity distributions during oxygen flash smelting in a converter (Bell. et al., 1978). When flash smelting to about white metal composition with Cottrell dust additions to the feed, 13-16 percent of the input arsenic and bismuth reported to the matte with 15-30 percent reporting to the slag. On flotation of the slowly cooled slag about 90 percent of the lead and zinc are eliminated to the tailings, so that recycle of zinc and lead by the flotation concentrate is small.

2.4.4 Mitsubishi Continuous Copper Smelting and Converting Process

Table 2.4-5 shows the distribution ratios of impurities. Column "A" gives the values calculated by Yazawa. The values in column "B" are calculated from the analyses of matte and slag in the Mitsubishi Process smelting furnace. Column "C" shows the values calculated from the anlayses of white metal and converter slag at the end point of a converter slag-making stage in conventional processes. Although the matte grade is 65 percent in case "B" and 76 percent in "C," there is a considerable difference in the distribution ratios of impurities. Such difference seems to indicate that the distribution ratios are affected by slag compositions.

In the Mitsubishi process, the sulfur content in blister is below 0.5 percent which is lower than that in blister which is in equilibrium with white metal. Further, there is no indication that a white metal layer exists as a separate phase in the converting furnace (Suzuki, 1973 and Suzuki and Nagano 1972). Such non-existence of a white metal layer seems to give the Mitsubishi process more favorable conditions for removal of impurities with slag. The favorable conditions in the Mitsubishi process are also pointed out by (Yazawa, 1967). The distribution ratios calculated from the analyses of converting furnace slag and blister copper in the Mitsubishi process are given in column "F."

The levels of antimony, arsenic and bismuth in Mitsubishi blister copper have been published but they have not been discussed in terms of the proportions retained from the original feed to the smelter. However, retention of Sb, As, and Bi in Mitsubishi blister copper is likely to be high because of the continuous contact between matte and metal in the converting furnace. For this reason some extra care will have to be taken with the electrorefining of Mitsubishi copper. The Mitsubishi process may produce impure blister when treating high impurity concentrates.

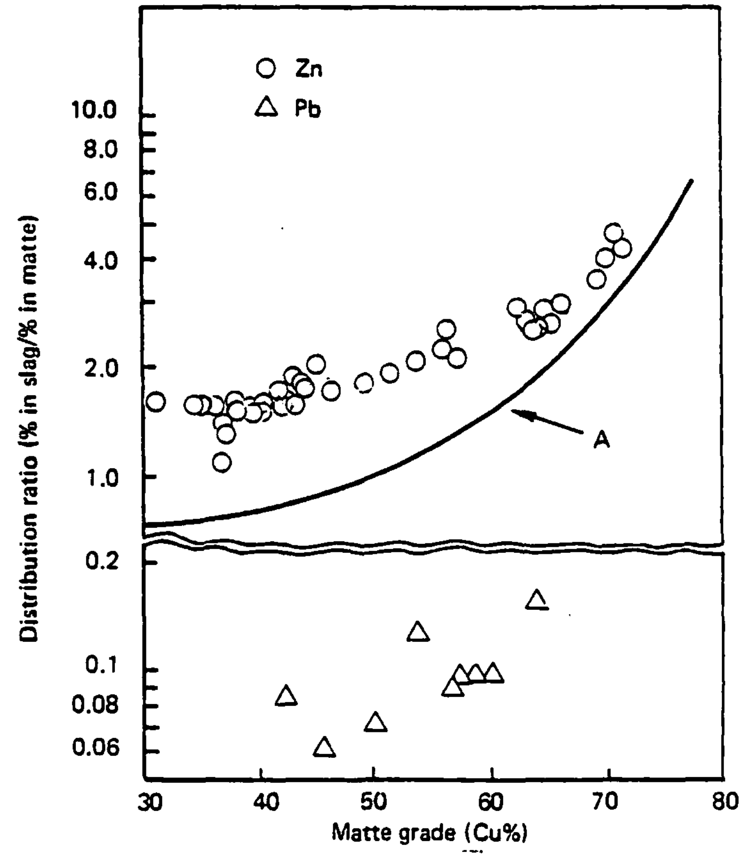
The distribution ratio of zinc (shown as ratio of weight percent) in the smelting furnace of the Mitsubishi process is plotted against matte grade in Figure 2.4-4. The line "A" in the figure represents data reported by (Okunev and Aglitskii, 1954). The normal matte grade in the Mitsubishi process is in the range of 60-65 percent and the distribution ratio under such

TABLE 2.4-5

DISTRIBUTION RATIOS OF IMPURITIES

Element	A aMO/aMS	B cM/cS	C cWM/cS	D cB/cWM	E cB/cS	F cB/cS
Pb	1.5×10^{-2}	1.6-5.0	0.9	15	13.5	2-6
Sb	37	0.25	1.0	13.6	13.6	0.1-0.3
As	--	2.1	1.0	9	9	6
Bi	0.68	--	--	8.1	--	--

Note: a: activity c: weight % MO: oxide MS: sulfide
WM: white metal S: slag B: blister



Source: Suzuki and Shibasaki, 1975

FIGURE 2.4-4 DISTRIBUTION OF LEAD AND ZINC BETWEEN MATTE AND SLAG conditions is approximately, 2.5. If the slag fall (defined as weight of slag to weight of concentrate) is 80 percent and the matte fall is 40 percent (defined as weight of matte to weight of concentrate), the distribution of zinc into slag would be 85 percent. Tbe ZnS content in matte is then oxidized in the converting furnace and distributed into slag. Since the converting furnace slag is returned to the smelting furnace, almost all zinc is distributed into the smelting furnace slag (discard slag) and removed from the system. This is also true of conventional practice where almost all the zinc is distributed in the slag and removed from the system.

The distribution of lead and zinc in the Mitsubishi process smelting furnace is shown in Figure 2.4-4. The major portion goes to the matte phase. PbS in matte is then partially oxidized to PbO in the converting furnace and distributed into slag. The distribution ratio of lead (% Pb in slag/%Pb in blister) is between 3 and 5. The average distribution ratio was experimentally determined to be 1.2 at the end point of a converter slag-making stage. A considerable amount of lead goes into blister copper. The separation of lead by the removal of flue dusts from the system therefore would become necessary when concentrate high in lead is treated.

Figure 2.4-5 gives the volatilization ratios of lead and zinc in the Mitsubishi process versus the lead and zinc contents in concentrate. When concentrate high in lead and zinc is treated, the volatilization ratio for zinc is in the range of 20-30 percent and that of lead is 60 percent.

The total carryover of mechanical dusts represents only 2-3 percent of the charged concentrate in the Mitsubishi process, comparable to that in the reverberatory furnace. Approximately one half of the dust is collected in the waste heat boiler and the other half in a precipitator. The volatile elements are concentrated into the flue dusts and can be removed out of the system.

2.4.5 TBRC Smelting

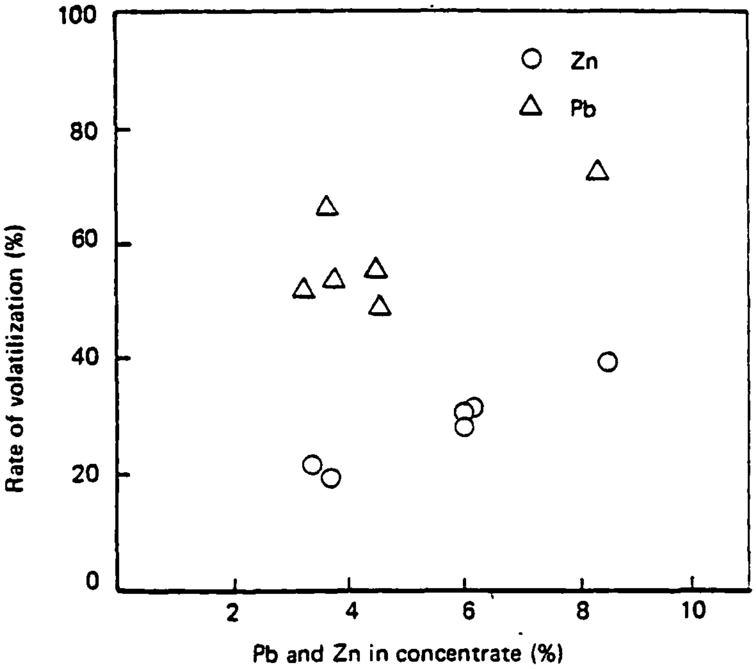
Full scale tests have demonstrated that 91.3% of the arsenic, 91.0% of lead, 89.7% of bismuth and 88.7% of selenium is eliminated in TBRC Smelting (Daniele, Jacquay, 1974).

2.4.6 Summary

The blister copper produced by single-step smelting processes such as the Noranda process will tend to contain more of the antimony, arsenic and bismuth from the original smelter charge than the blister copper produced by conventional smelting/converting operations (Mackey et al., 1975).

In conventional smelting/converting operations, these impurities are removed to a large extent by volatilization of their sulfides (Yazawa and Azakami, 1969) during the slag-forming stage of converting, i.e., before metallic copper is formed. In the case of single-step smelting, however, metallic copper is always present and a considerable fraction of the As, Bi and Sb dissolves in the copper before volatilization can occur. Once dissolved in the copper, these metals are difficult to remove pyrometallurgically because of their low chemical activities (Yazawa and Azakami, 1969).

Thus, the anodes prepared from single-step process blister copper tend to have a higher level of As, Bi and Sb than standard anodes. This necessitates more careful electrorefining, more extensive electrolyte purification, and it may, in fact, restrict the adoption of single-step smelting processes to the smelting of low impurity concentrates.



Source: Suzuki and Shibasaki, 1975.

FIGURE 2.4-5 RELATION BETWEEN RATES OF VOLATILIZATION AND CONTENTS IN CONCENTRATE

The other alternative is to break the continuous process, to include a converting option as has been done with the Noranda process by Kennecott in Utah. Another option would be to refine the crude copper obtained by the continuous process.

2.4.7 Fire Refining of Blister Copper to Anodes

Although the fire refining step can remove impurities such as As, Sb, Bi and Fe to some extent, these impurities are difficult to remove by oxidation from liquid copper (Yazawa and Azakami, 1969). Some operations, e.g., Tsumeb in S.W. Africa, have used sodium carbonate slags to reduce the As, Sb and Bi content of crude blister to acceptable levels.

2.4.8 Electrorefining

The purpose of electrorefining is to remove impurities and recover valuable byproducts. The principal impurities in copper anodes are As, Bi, Fe, Ni, Pb, Sb, Se and Te. These must be refined from the copper. In addition, Ag and Au are usually present in quantities large enough to be worth recovering. The behavior patterns of these impurities during electrorefining are as follows (Biswas and Davenport, 1976):

- Ag, Au and Platinum Metals — Gold and platinum metals do not dissolve in the electrolyte. Silver dissolves from the anode to a certain extent but it is precipitated from the electrolyte as AgCl by dissolving a small amount of NaCl or HCl in the electrolyte. Any appearance of these metals in the cathode is due to the mechanical entrapment of small quantities of anode slimes.

- S, Se and Te — Sulfur, selenium and tellurium are present in the anodes as compounds with copper or silver, i.e., Ag_2Se, Cu_2Se, Ag_2Te, or Cu_2S. These compounds mainly enter the anode residues (slimes) in a manner similar to the noble metals (Table 2.4-6).

- Pb and Sn — Lead and tin both form sulfates which are insoluble in the electrolyte [$PbSO_4$ and Sn $(OH)_2SO_4$] and hence they do not enter the electrolyte to any appreciable extent.

- As, Bi, Co, Fe, Ni and Sb — All of these metals tend to dissolve electrochemically from the anode along with (and even preferentially to) the copper of the anode. They tend, therefore, to build up in the electrolyte during electrorefining. These impurities must be removed from the electrolyte or they will eventually contaminate the cathode copper, mainly by occlusion of impure electrolyte in the growing cathode deposits. Removal of As and Ni is accomplished in a bleed stream in a purification section of the refinery. The composition limits of these impurities in refinery electrolyte is given in Table 2.4-6.

- Table 2.4-7 shows the distribution of impurities between the anode residues and electrolyte and it indicates that significant quantities of As and Sb report in the anode residues, most likely as the result of compound formation with copper in the anode. Bismuth behaves similarly. In addition, it is believed that to some extent As, Bi and Sb combine to form arsenate precipitates which also enter the anode residues.

TABLE 2.4-6

COMPOSITION RANGES OF ELECTROLYTES IN MODERN COPPER REFINERIES

Metal	Proportion into Anode Residues (%)	Proportion into Electrolyte (%)
Au	99	<1
Ag	98	2
Se and Te	98	2
Pb	98	2
Sb	60	40
As	25	75
Ni	5	95
Fe		≈100

Source: Eichrodt and Schloen, 1954, published in Biswas and Davenport, 1976.

TABLE 2.4-7

PROPORTIONS OF ANODE IMPURITIES ENTERING RESIDUES AND ELECTROLYTE AS ESTIMATED BY EICHRODT AND SCHLOEN (1954)

Component	Concentration (kg m^{-3})
Cu	40-50
H_2SO_4 (free)	170-200
	Upper Limits
Ni	20 (Inco)
As	10
Fe	2
Sb	0.5
Cl	0.03
Specific gravity	1.25±0.03
Temperature	60-65°C

Source: Eichrodt and Schloen, 1954, published in Biswas and Davenport, 1976.

2.4.8 References

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2.5 ELECTRIC FURNACE SMELTING

2.5.1 Introduction

This report includes material and energy requirements for copper smelting process using an electric furnace. Electrical furnace smelting is described in detail by (Biswas and Davenport, 1976).

The process described in this model is a modification of the Inspiration Consolidated Copper Company electric smelter at Miami, Arizona. The major modification is on the front end by adding a fluid bed roaster and deleting a rotary dryer. These modifications reduce power requirements and heat losses in the furnace by lowering the required operating temperature to produce 40 percent matte. The fluid bed roaster alone reduces the furnace fuel requirements by 3.03 million Btu's per ton cathode copper (Kellogg and Henderson, 1967).

The use of fluid bed roasting or rotary drying is highly dependent on the makeup of concentrates fed to the plant. High proportions of cement copper and chalcocite, as at Inspiration, would reduce the amount of sulfur in the feed to make it insufficient for the fluid bed roasting. In this model, one of the basic assumptions is the availability of concentrates bearing 31% S (dry basis), which is sufficient sulfur to justify the addition of a fluid bed roaster.

The first successful tests on smelting of sulfide ores in an electric furnace were made in Norway at the Sulitjelma Mine in 1911-1913. The first commercial furnace was completed in 1929 at this mine with a proven annual capacity of 5,000 tons of blister copper. The conversion to electric furnace smelting was very slow, restricted to areas where hydroelectrical energy competed favorably with fossil fuels. By 1970 there were only 25 electric copper furnaces operating, with a total capacity of 6 million tons of copper concentrate per year, and none of these were in the United States.

Due to increased environmental constraints on emissions from copper smelters, three electric furnaces have been constructed and have been operating in the United States since 1970. All three of these operations recover the sulfur dioxide from the electric furnace for sulfuric acid manufacturing.

The high equivalent fuel requirement of the electric furnace smelter is largely the result of low thermal efficiency in the production of electric power.

2.5.2 Process Description

2.5.2.1 Roasting and Furnace Charging

Copper sulfide concentrates containing 10 to 12 percent moisture are partially roasted in a fluid bed roaster and the bone-dry hot calcines are fed to the electric furnace as shown in the process flowsheet (see Figure 2.5-1). The amount of sulfur burned in the roaster is sufficient to produce a 40 percent copper matte. In a variation of this process, the copper concentrate is dried to 3 to 4 percent moisture before being fed to the electric furnace. This method, however, is practical only in cases of low sulfur content in the feed, and thus, will not be considered for a copper sulfide concentrate containing 31 percent sulfur. Heated calcine requires less fuel and so increases the furnace efficiency. Dry calcines are combined with dust collected from roaster, cyclones, and electrostatic precipitators and recycled converter slag to form the furnace feed. The feed is conditioned with limestone and silica flux to enhance proper slag formation. Furnace electrodes dip in the molten slag and the heat required to smelt the solid calcines is generated by the resistance of the slag to the high amperage electrical current. Solid furnace slag is a poor electrical conductor, but as the slag melts it dissociates into ionic form in the liquid state and becomes a relatively good electrolyte (Rosenkranz, 1976).

2.5.2.2 Electric Furnace Operation

Air is introduced under control to oxidize iron sulfides to iron oxides and sulfur dioxide. Molten slag, less than 0.5 percent copper, is continuously tapped and discarded. Matte is conveyed to converters for further processing and the gas from the electric furnace containing furnace dust, nitrogen, oxygen, carbon dioxide, sulfur dioxide, and a small amount of sulfur trioxide goes to gas cleaning.

Matte at a temperature of 2100 degrees Fahrenheit is blown with air or oxygen in the converter to produce blister copper. Air is injected under pressure to complete the oxidation of copper sulfide and any remaining iron sulfides to blister copper, iron oxide, and sulfur dioxide. Off-gas also goes to gas cleaning. Silica flux is added to aid formation of converter slag, which is recycled to the electric furnace. Blister copper is then treated in the anode furnace by first flowing with air to remove sulfur and then poled with reformed gas to remove oxygen. The slag which is skimmed from the anode furnace is returned to the converter. Anodes are cast and refined to electrolytic copper.

2.5.2.3 Acid Plant Operation

A double adsorption contact acid plant is incorporated in the process. The gases from roaster, furnace, and converter are combined and sent to final cleaning before entering the sulfuric acid plant. In the oxidation of sulfur dioxide to sulfur trioxide, the heat of the reaction is recovered to provide steam and to cool the sulfur dioxide gas.

2.5.3 Material and Energy Requirements

The material and energy requirements for electric furnace copper smelting are shown in Tables 2.5-1, 2.5-2 and 2.5-3. Table 2.5-2 includes Level 1 direct energy inputs. Table 2.5-3 contains Level 2 materials and their energy equivalents. Energy equivalent for electrical power and energy consumption values for fluid bed roating, dust handling, converting, are taken from (Kellogg and Henderson, 1967).

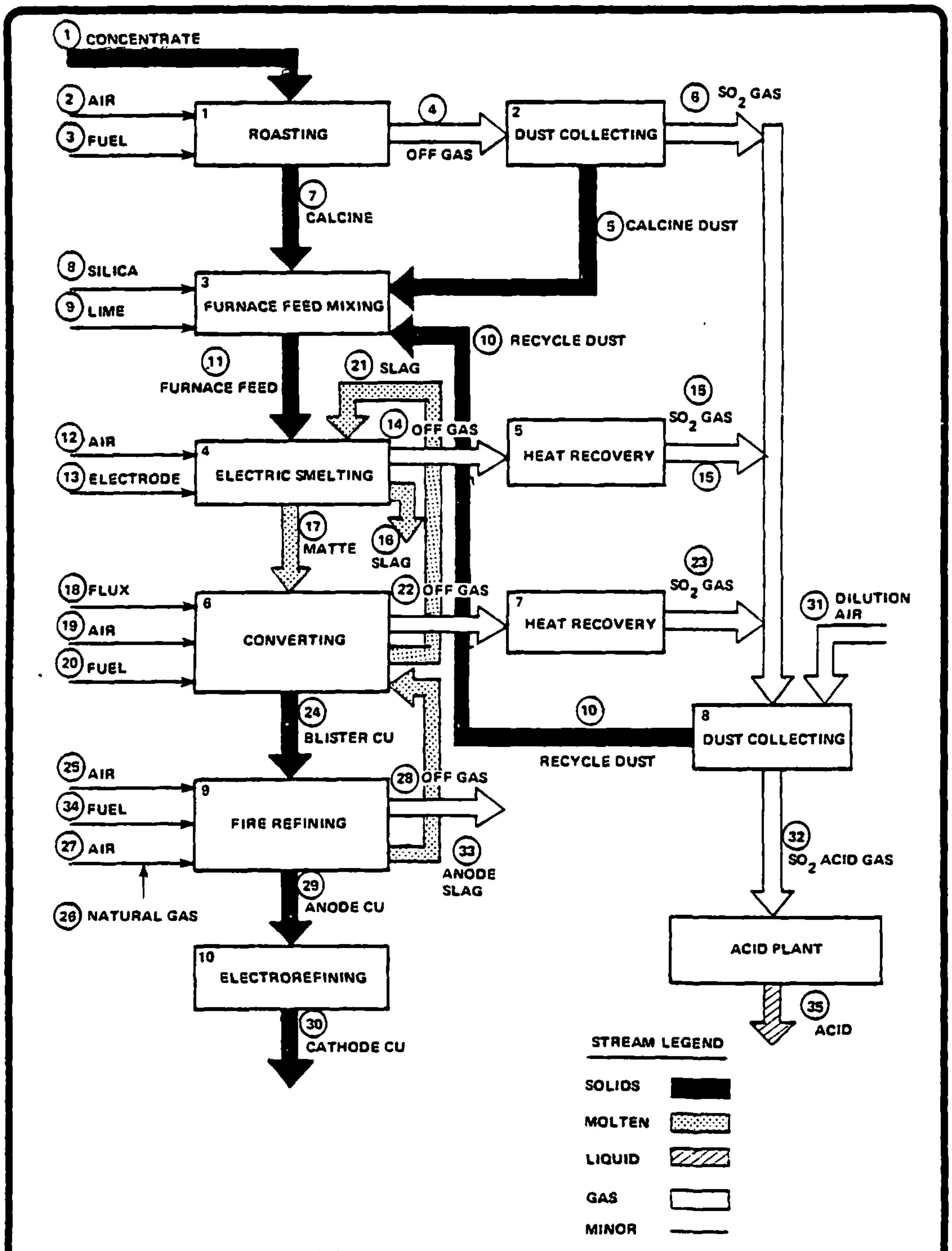

FIGURE 2.5-1 ELECTRIC FURNACE

TABLE 2.5-1 ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		ROASTER AIR		ROASTER FUEL		ROASTER OFF GAS		CALCINE DUST	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.016	25.001					.762	10.257	.648	28.053
Fe	1.087	26.738					.652	8.776	.554	24.002
S	1.260	30.997					.567	7.626	.482	20.855
FeO	.028	.690					.231	3.106	.196	8.493
Fe_2O_3	.042	1.040					.032	.427	.027	1.167
SiO_2	.351	8.630					.263	3.541	.224	9.684
AL_2O_3	.140	3.450					.105	1.415	.089	3.871
$CaCO_3$	.048	1.183					.036	.485	.031	1.327
CaO	.092	2.271					.069	.932	.059	2.548
H_2O	.554						.606	8.159		
Fuel					.056	100.000				
O_2			.842	23.000			.101	1.354		
N_2			2.819	77.000			2.819	37.943		
SO_2							1.011	13.611		
CO_2							.176	2.369		
TOTAL	4.064	100.000	3.661	100.000	.056	100.000	7.429	100.000	2.309	100.000
TEMP. (F)	60		60		60		1200		1000	
STATE	S		G		L		G		S	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	ROASTER SO_2 GAS		CALCINE		SILICA FLUX		LIME FLUX		RECYCLE DUST	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	.114	2.232	.254	28.053					.178	22.837
Fe	.098	1.910	.217	24.002					.106	13.674
S	.085	1.660	.189	20.855					.093	11.897
FeO	.035	.676	.077	8.493					.035	4.449
Fe_2O_3	.005	.093	.011	1.167	.003	2.000	.000	1.000	.008	1.088
SiO_2	.039	.771	.088	9.684	.124	90.000	.001	2.000	.132	17.003
AL_2O_3	.016	.308	.035	3.871	.006	4.000			.016	2.028
$CaCO_3$	.005	.106	.012	1.327			.037	96.000	.005	.695
CaO	.010	.203	.023	2.548	.006	4.000	.000	1.000	.010	1.335
H_2O	.606	11.838								
O_2	.101	1.965								
N_2	2.819	55.054								
SO_2	1.011	19.749								
CO_2	.176	3.437								
Cu_2O									.001	.103
Fe_2SiO_4									.158	20.331
Fe_3O_4									.013	1.655
AL_2SiO_5									.010	1.262
$CaSiO_3$									.013	1.645
TOTAL	5.120	100.000	.905	100.000	.138	100.000	.038	100.000	.778	100.000
TEMP (F)	1100		1200		60		60		100	
STATE	G		S		S		S		S	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	FURNACE FEED		FURNACE AIR		ELECTRODE		FURNACE OFF GAS		FURNACE SO_2 GAS	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.079	25.895					.011	2.857	.011	2.857
Fe	.878	21.061					.009	2.248	.009	2.248
S	.763	18.303					.008	1.969	.008	1.969
FeO	.308	7.380								
Fe_2O_3	.049	1.178					.001	.176	.001	.176
SiO_2	.568	13.631					.006	1.454	.006	1.454
AL_2O_3	.146	3.496								
$CaCO_3$	.085	2.035								
CaO	.098	2.356								
Carbon					.010	100.000				
O_2			.062	23.000			.015	3.870	.015	3.870
N_2			.206	77.000			.206	54.018	.206	54.018
SO_2							.019	4.990	.019	4.990
SO_3							.006	1.559	.006	1.559
CO_2							.075	19.793	.075	19.793
Cu_2O	.001	.019					.000	.002	.000	.002
Fe_2SiO_4	.158	3.794					.019	4.930	.019	4.930
Fe_3O_4	.013	.309					.001	.308	.001	.308
AL_2SiO_5	.010	.236					.003	.793	.003	.793
$CaSiO_3$	.013	.307					.004	1.033	.004	1.033
TOTAL	4.168	100.000	.268	100.000	.010	100.000	.381	100.000	.381	100.000
TEMP. (F)	811		350		60		1300		1100	
STATE	S		G		S		G		G	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	FURNACE SLAG		FURNACE MATTE		CONVERTER FLUX		CONVERTER AIR		CONVERTER FUEL	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	.016	.491	1.161	40.966						
Fe	.013	.386	.836	29.500						
S	.011	.338	.809	28.546						
Fe_2O_3	.066	2.000	.001	.038	.021	2.000				
SiO_2	.544	16.517	.004	.154	.924	90.000				
AL_2O_3					.041	4.000				
CaO					.041	4.000				
Fuel									.087	100.000
O_2							1.787	23.000		
N_2							5.981	77.000		
Cu_2O	.000	.000	.001	.038						
Fe_2SiO_4	1.846	56.020	.015	.564						
Fe_3O_4	.116	3.504	.001	.038						
AL_2SiO_5	.297	9.006	.002	.075						
$CaSiO_3$	.387	11.737	.003	.113						
TOTAL	3.296	100.000	2.834	100.000	1.026	100.000	7.768	100.000	.087	100.000
TEMP. (F)	2250		2100		60		60		60	
STATE	L		L		S		G		L	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	CONVERTER SLAG		CONVERTER OFFGAS		CONVERTER SO_2 GAS		BLISTER COPPER		OXIDIZING AIR	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.109	5.280	.052	.607	.052	.607	1.000	97.561		
S	0.077	3.729	.000	.001	.000	.001	.001	.117		
Fe_2O_3	0.018	.873	.003	.035	.003	.035	.000	.009		
SiO_2	0.368	17.820	.087	1.009	.087	1.009	.002	.183		
H_2O			.082	.944	.082	.944				
O_2			.458	5.300	.458	5.300			.014	23.000
N_2			5.981	69.167	5.981	69.167			.048	77.000
SO_2			1.173	13.563	1.173	13.563				
SO_3			.366	4.238	.366	4.238				
CO_2			.277	3.200	.277	3.200				
Cu_2O	0.000	.007	.001	.009	.001	.009	.015	1.469		
Fe_2SiO_4	1.088	60.025	.139	1.611	.139	1.611	.005	.540		
Fe_3O_4	0.105	5.072	.012	.135	.012	.135	.001	.052		
AL_2SiO_5	0.061	2.946	.007	.079	.007	.079	.0005	.030		
$CaSiO_3$	0.079	3.840	.009	.102	.009	.102	.0005	.039		
TOTAL	2.065	100.000	8.648	100.000	8.648	100.000	1.025	100.000	.062	100.000
TEMP. (F)	2250		2200		1100		2100		60	
STATE	L		G		G		L		G	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)		(27)		(28)		(29)		(30)	
STREAM NAME	ANODE FUEL		REDUCING AIR		ANODE OFF GAS		ANODE COPPER		CATHODE COPPER	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu							1.176	100.000	1.000	100.000
H_2O					.009	10.895				
Fuel	.000	100.000								
O_2			.004	23.000	.002	2.270				
N_2			.014	77.000	.062	70.731				
SO_2					.002	2.725				
CO_2					.012	13.379				
TOTAL	.000	100.000	.018	100.000	.087	100.000	1.176	100.000	1.000	100.000
TEMP. (F)	60		60		1800		1800		60	
STATE	L		G		G		L		S	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

STREAM NO.	(31)		(32)		(33)		(34)		(35)	
STREAM NAME	DILUTION AIR		SO_2 ACID GAS		ANODE SLAG		MAKEUP WATER		SULFURIC ACID	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Fe_2O_3					.000	.959				
SiO_2					.002	19.585				
H_2O			.688	4.391			.299	100.000	.287	7.000
H_2SO_4									3.812	93.000
O_2	.527	23.000	1.100	7.026						
N_2	1.763	77.000	10.770	68.765						
SO_2			2.203	14.067						
SO_3			.372	2.378						
CO_2			.528	3.372						
Fe_2SiO_4					.006	66.422				
Fe_3O_4					.001	5.575				
AL_2SiO_5					.000	3.238				
$CaSiO_3$					.000	4.221				
TOTAL	2.290	100.000	15.661	100.000	.009	100.000	.299	100.000	4.099	100.000
TEMP. (F)	60		550		1800		60		100	
STATE	G		G		L		L		L	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(36)					
STREAM NAME	SO_2 TAIL GAS					
COMPOSITION	wt.	wt.%				
O_2	.553	4.662				
N_2	10.770	90.793				
SO_2	.011	.093				
CO_2	.528	4.453				
TOTAL	11.862	100.000				
TEMP. (F)	100					
STATE	G					

TABLE 2.5-2 **ENERGY REQUIREMENTS** Level 1

ELECTRIC SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Flued Bed Roasting				
	A) Compressed Air	MILLION SCF	91.046	0.0042	.382
	B) Misc. Elec. Power	KWH	0.772	0.0105	.008
	C) Fuel	GAL	15.484	0.1474	2.282
					2.672
2	Hot Gas Handling	MILLION SCF	112.864	0.00252	0.284
4	Electric Furnace				
	A) Direct Power	KWH	1381.1	0.0105	14.502
	B) Misc. Elec. Power	KWH	430.97	0.0105	4.525
	C) Hot Gas Handling	MILLION SCF	7.105	0.00252	0.018
					19.045
6	Converters				
	A) Compressed Air	MILLION SCF	193.253	0.0147	2.841
	B) Hot Gas Handling	MILLION SCF	187.715	0.00252	.473
	C) Matl. Handling Elec.	KWH	6.86	0.0105	.075
	D) Fuel	GAL	24.28	0.1474	3.579
					6.965
8	Dust Collecting				
	A) Misc. Elec. Power	KWH	210	0.0105	2.205/Ton Anode
9	Anode Refining and Casting				
	A) Fuel	GAL	0.01175	.1474	0.002/Ton Anode
	B) Natural Gas	MILLION SCF	0.000188	1000	0.188/Ton Anode
	C) Misc. Elec. Power	KWH	13.94	0.0105	0.146/Ton Anode
	D) Hot Gas Handling	MILLION SCF	2.215	0.00252	0.006/Ton Anode
					0.342
10	Electrorefining				
	A) Direct Elec.	KWH	448	0.0105	4.704
	B) Misc. Elec. Power	KWH	5.0	0.0105	0.053
					4.757

TABLE 2.5-2 (Continued) **ENERGY REQUIREMENTS** Level 1

ELECTRIC SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Acid Plant				
	A) Elec. Power - Cold Gas	MILLION SCF	362.67	0.00132	0.479
	Elec. Power - Acid Plant	MILLION SCF	362.67	0.01176	4.265 4.744
				TOTAL	41.014

TABLE 2.5-3 **ENERGY REQUIREMENTS** Level 2

ELECTRIC SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Furnace Feed				
	A) Silica Flux	LBS	275.3	0.00005	0.014
	B) Limestone	LBS	76.61	0.00005	0.004
	C) Electrodes	LBS	20.85	0.041000	0.855
6	Converters				
	A) Silica Flux	TON	1.026	0.100	0.103
	Utilities				
	A) Electric Energy	KWH	48.73	.0105	0.512
9	Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
				TOTAL	1.956

2.5.4 Conclusions

Electric smelting is not as efficient in energy requirements as the conventional reverberatory smelting. The addition of fluid bed roasting, however, reduces the furnace fuel requirement by about three million Btu's per ton cathode copper. Gross energy requirement in electric smelting is 43.0 million Btu's per ton cathode copper versus 31.0 million Btu's per ton for conventional reverberatory smelting.

2.5.5 Recommendations

A roasting step should be incorporated into the electric smelting process, since this results in reducing the overall consumption of energy. Since electric smelting indicates the highest energy consumption of all the pyrometallurgical processes considered, further research and development efforts in electric smelting may not be justified.

2.5.6 References

Biswas, A.K. and W.G. Davenport, Extractive Metallurgy of Copper, Pergamon International Library, New York, 1976.

Kellogg, H.H. and J.M. Henderson, Extractive Metallurgy of Copper, Vol. 1, Ch. 19, American Institute of Mining, Metallurgical and Petroleum Engineers, Baltimore, Maryland 1967.

Rosenkranz, R.D., "Energy Consumption on Domestic Primary Copper Production," U.S. Bureau of Mines, IC8698, 1976.

2.6 OUTOKUMPU FLASH SMELTING

2.6.1 Introduction

The Outokumpu Flash Smelting Process was developed in the years 1946-49. The first commercial Plant went into service in 1949 at Harjavalta Works, Finland.

There are currently 30 licensees of the Outokumpu process, with 23 plants in actual operation.

As an example, the process as used at Harjavalta is described, and variations are then described.

2.6.2 Process Description

The Outokumpu Flash Smelting Process is a pyrometallurgical process for the extraction of copper from sulfide ore concentrates. This process utilizes the heat generated by the exothermic oxidation reactions of iron and sulfur in the concentrate. The conventional operations of roasting, smelting, and partial converting are combined into a single unit operation of flash smelting. The major advantages of this method are a reduction in energy consumption and the production of a stream of gas high in sulfur dioxide which is suitable for sulfuric acid manufacture or the production of elemental sulfur.

Figure 2.6-1 is a flowsheet of the process at Harjavalta. After drying in a direct oil-fired kiln, the charge, consisting of concentrates and silica sand, is transported by means of a pneumatic conveying system to the flash furnace. The flash furnace is divided into three parts: the reaction shaft, the settler, and the uptake.

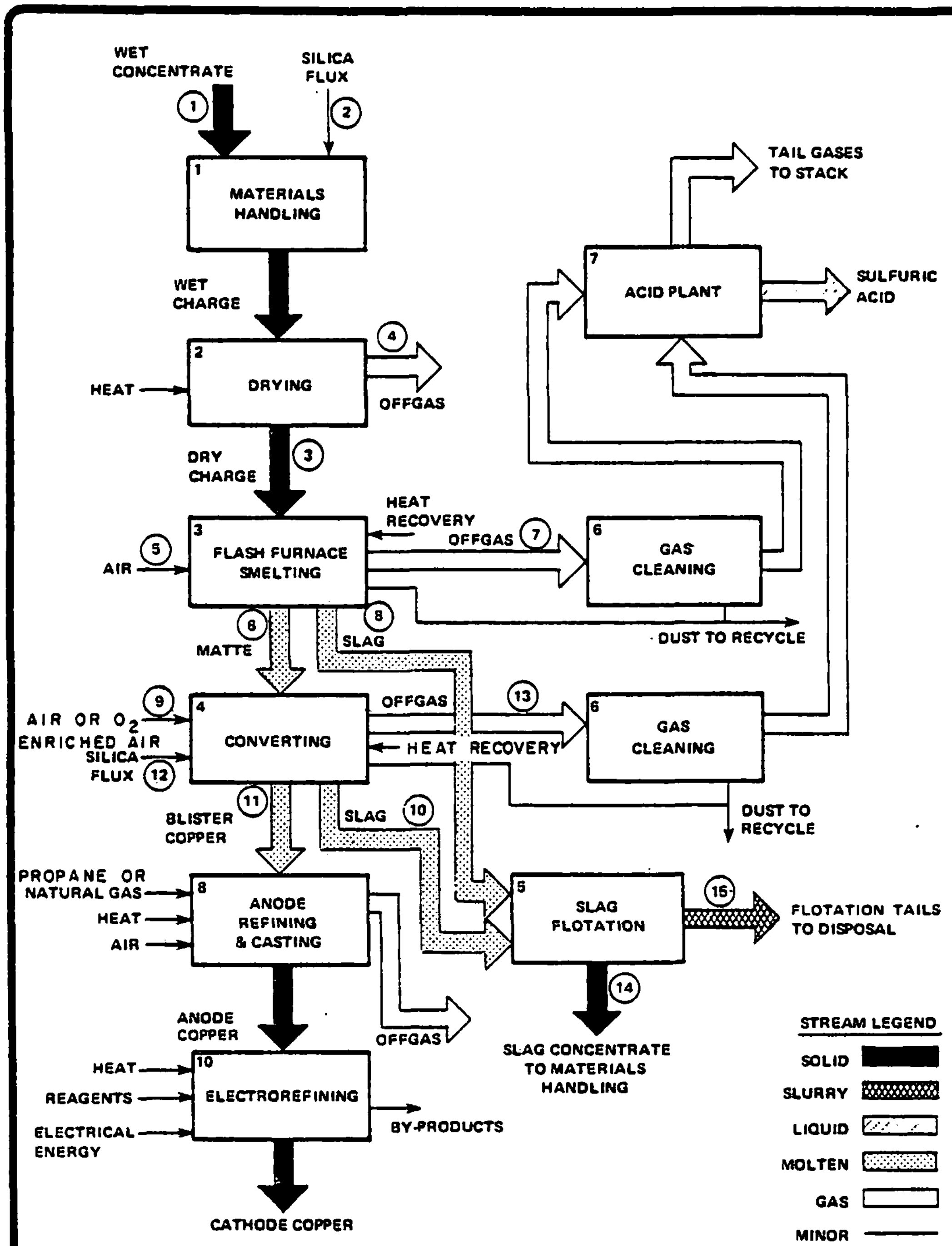

FIGURE 2.6-1 OUTOKUMPU FLASH SMELTING PROCESS

The concentrates together with the flux are smelted in the reaction shaft in suspension, which offers the most favorable conditions for rapid heat and mass transfer. The heat requirements for smelting are supplied almost entirely by the iron and sulfur oxidation. To balance heat requirements, additional fuel, preheated air and/or oxygen-enriched air can be used. Since 1971, preheated, oxygen-enriched air (200°C, 30-75% oxygen) has been used by Outokumpu. Under these conditions the reaction proceeds without additional fuel.

Molten particles are separated from the gas stream in the settler. Matte drops through the slag to the bottom of the settler. Matte grade is a function of the total oxygen/concentrate ratio and can be varied from 45-80%. One process in operation in Poland produces blister copper directly.

Because of high matte grade and incomplete settling action of matte particles, the slag has a relatively high copper content (0.8-2.5% copper), and slag cleaning is necessary. Slag cleaned at Harjavalta by froth flotation, which recovers the copper, mainly as sulfides from the slag. This concentrate is recycled back through the smelter. After cleaning, the slag copper concentration is about 0.4-0.6%, and this slag is sent for disposal.

To recover heat and dust, the smelter gases pass through the uptake to a waste heat boiler. Gases are then sent to an electrostatic precipitator. Flue dust is recycled to the smelter and the rich, clean sulfur dioxide gases are used for the production of sulfuric acid or elemental sulfur.

Saturated process steam from the waste heat boiler can be used to preheat the oxygen-enriched air that goes to the smelter, to generate power, to produce oxygen, for general heating purposes, and to drive rotating machines (pumps, blowers, etc.).

Matte is treated further in conventional converters to obtain blister copper. Due to the high matte grade and short blowing time, the converter capacity requirements are less than conventional. Converter slag is cleaned together with smelter slag. In considering the total plant complex, energy savings result from the operation of the converters in sequences which provide a steady gas stream to the acid plants. Also higher matte grades result in a lower total gas volume because of less infiltration (1-2%) of outside air in the flash smelting furnace.

Blister copper is transferred to an oil-fired rotating anode furnace, fire-refined, and cast into anodes.

A process for taking chalcocite and digenite concentrates directly to blister copper in one step has been developed at Outokumpu and is currently being used with 23% copper content chalcocite concentrates at a plant in Poland. The heat value of these compounds is low due to the low iron content, and high oxygen enrichment is necessary. Slag is cleaned to remove the relatively high copper content in the slag by electric furnace reduction. Total recovery of copper is up to 99% of the copper in the feed.

2.6.3 Material Balance

The material balance for the production of blister copper is shown in Table 2.6-1.

TABLE 2.6-1 OUTOKUMPU FLASH SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET PRIM. CONCENTRATE		FLASH SILICA FLUX		DRY CHARGE (with slag concentrate)		DRYER OFF GAS		FLASH FURNACE AIR (dry)	
COMPOSITION	wt.	dry wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%
Cu	0.9982	22.50			1.0484	24.34				
Fe	1.1180	25.20	0.0024	1.40	1.1613	26.96				
S	1.2378	27.90			1.2563	29.17				
O_{Fe}*	0.0188	0.423	0.0010	0.60	0.0293	0.68				
S_iO_2	0.3446	7.767	0.1534	90.00	0.5140	11.93				
AL_2O_3	0.1377	3.105	0.0068	4.00	0.1483	3.44				
CaO + MgO	0.1170	2.637	0.0034	2.00	0.1238	2.87				
Others	0.0208	0.468	0.0034	2.00	0.0252	0.59				
H_2O	0.4437	10.00					0.4690		0.0165	0.5
SO_2										
O_2									1.1781	36.5
CO										
CO_2										
N_2									2.0302	63.0
TOTAL	4.4366	100.00	0.1704	100.00	4.3067	100.00			3.2248	100.00
TEMP. (°F)	60		60		150		250		392	
STATE	S		S		S		G		G	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.6-1 (cont.) OUTOKUMPU FLASH SMELTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	FLASH FURNACE MATTE		FLASH FURNACE OFF GAS		FLASH FURNACE SLAG		CONVERTER AIR		CONVERTER SLAG	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wet wt.%	wt.	wt.%	wt.	dry wt.%
Cu	1.0078	65.00			0.0407	1.9			0.0178	4.95
Fe	0.1879	12.12			0.9735	45.45			0.1861	51.90
S	0.3402	21.94			0.0193	0.9			0.0045	1.25
O_{Fe}*	0.0146	0.94			0.2971	13.87			0.0594	16.58
S_iO_2					0.5140	24.00			0.0836	23.3
AL_2O_3					0.1416	6.61			0.0019	0.52
CaO + MgO					0.1238	5.78			0.0019	0.52
Others					0.0306	1.43			0.0035	0.98
H_2O			0.0165							
SO_2			1.8162							
O_2							0.4253	26.00		
CO										
CO_2										
N_2			2.0302				1.2106	74.00		
TOTAL	1.5504	100.00	3.8629		2.1418	100.00	1.6359	100.00	0.3587	100.00
TEMP. (°F)	2200		2400		2300		60		2250	
STATE	L		G		L		G		L	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.6-1 (cont.) OUTOKUMPU FLASH SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	BLISTER CU		SILICA FLUX		CONVERTER OFF GAS		FLOT. CONC.		FLOT. TAILINGS	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wet wt.%	wt.	dry wt.%
Cu	0.990	99.0					0.0502	35.00	0.0082	0.35
Fe	0.003	0.3	0.0013	1.40			0.0409	28.53	1.1187	47.46
S	0.003	0.3					0.0185	12.92	0.0052	0.22
O_{Fe}*	0.0005	0.05	0.0006	0.60			0.0096	6.67	0.3470	14.72
S_iO_2			0.0834	90.00					0.5815	24.67
AL_2O_3			0.0037	4.00					0.1377	5.84
CaO + MgO			0.0019	2.00					0.1223	5.19
Others	0.035	0.035	0.0019	2.00			0.242	16.88	0.03654	1.55
H_2O										
SO_2					0.6708					
O_2										
CO										
CO_2										
N_2					1.2106					
TOTAL	1.0	100.00	0.0927	100.00			0.1434	100.00	2.3571	100.00
TEMP. (°F)	2200		60		2300		60		60	
STATE	L		F		G		S		S	

*Oxygen associated with FeO and Fe_3O_4

2.6.4 Energy Requirements

Table 2.6-2 and Table 2.6-3 present the Level I and Level II energy requirements for Outokumpu flash smelting.

2.6.5 Discussion

The most economical and practical way of flash smelting for a particular plant largely depends on local circumstances such as price of energy, need for scrap melting, treatment of process gases, and prices and recoveries of other metals in the concentrates. The following discussion examines the variables in using the flash smelting method developed by Outokumpu.

2.6.5.1 Matte Grade

Matte grade depends on the oxygen-concentrate feed ratios, the furnace temperature, and the amount of impurities in the concentrate. In R&D work at Outokumpu and in connection with operating industrial plants, the flash smelting furnace product has ranged from low grade matte, containing 35% copper to white metal and further to blister copper. Slags have varied from 0.6-15% depending on oxygen-concentrate feed ratios and furnace temperature. Raising the matte grade decreases the need for additional fuel in flash smelting because of a fairly large portion of the latent heat value of the concentrate itself is used at the smelting stage (Haarki, 1976) but also increases the amount of copper in the slag.

2.6.5.2 Heat Requirements in Smelting

To balance heat requirements not met by the exothermic reactions in smelting, additional fuel, preheated air and/or oxygen-enriched air can be used.

By using oxygen-enriched air (consequently, reduced gas volume), the capacity of the smelter can be considerably increased, and fuel consumption is significantly reduced. Present practice also enables the unit to operate without fuel addition. Preheating of process air reduces the smelting furnace gas volume and offers savings in the capital costs of the equipment on the gas side. Preheating the process air can offer energy savings in reduced fuel consumption in the smelter and by utilizing process steam from a waste heat boiler.

2.6.5.3 Waste Heat

The Outokumpu process uses a waste heat boiler as part of its gas treatment cycle. The steam recovered from the boiler can be used for preheating process air, producing oxygen-enriched air (Juusela, 1974), or generating electric power, although the latter is generally too expensive to be practical.

2.6.5.4 Flue Dust

Flue dust is usually recycled but can also be treated separately to recover valuable metals or to eliminate harmful elements.

2.6.5.5 Treatment of Sulfur Dioxide in Off Gases

In development work, Outokumpu used two methods for handling the sulfur dioxide produced. Originally, the gases from the converter and smelter were combined, and the sulfur dioxide was treated to produce sulfuric acid. This is common practice.

TABLE 2.6-2 **ENERGY REQUIREMENTS** Level 1

OUTOKUMPU FLASH SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	54.4	0.0105	0.571
2	Drying				
	A) Fuel Oil	GAL	7.7	0.139	1.06
	B) Electric Energy	KWH	16.3	0.0105	0.171
3	Flash Smelting				
	A) Electrical Energy	KWH	76.1	0.0105	0.799
	B) Waste Heat Recovery	LBS	-1807	0.0014	-2.529
4	Converting				
	A) Electrical Energy (material handling + blowing)	KWH	60.7	0.0105	0.637
	B) Waste Heat Recovery	LBS	-648	0.0014	-0.907
5	Slag Flotation				
	A) Electrical Energy	KWH	142.3	0.0105	1.494
6	Gas Cleaning				
	A) Hot Gas Cleaning	Thous. SCF	165.2	0.00252	0.416
	B) Cold Gas Cleaning	Thous. SCF	165.2	0.00126	0.208
	C) Fugitive Emission Control	KWH	340	0.0105	3.570
7	Acid Plant				
	A) Smelter and Converter Gas (10% SO_2)	Thous. SCF	306.7	0.0126	3.864
x	Water Pollution Control				
	A) Electric Energy	KWH	9.0	0.0105	0.095
8,9	Anode Furnace and Electrorefining	TONS OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	15.279

TABLE 2.6-3

ENERGY REQUIREMENTS

Level 2

OUTOKUMPU FLASH SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Flash Smelting				
	A) Oxygen	TON	0.593	4.41	2.615
	B) Silica Flux	TON	0.249	0.042	0.010
4	Converting				
	A) Oxygen	TON	0.096	4.41	0.423
	B) Silica Flux	TON	0.101	0.042	0.004
5	Slag Flotation				
	A) Flotation Reagents	LBS	2.0	0.02	0.040
x	Water Pollution Control				
	A) Lime	LBS	30.00	0.0027	0.081
8,9	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	3.641

In 1962, a method for recovering elemental sulfur by high temperature reduction from the gases was developed by Outokumpu. If no market for sulfuric acid exists near the smelter, this can be a favorable alternative. This method involves the reduction of sulfur dioxide in the uptake of the furnace by using pulverized coal, or gaseous or liquid hydrocarbon reductants. The design and operation of the flash furnace is modified to produce a high sulfur dioxide, low oxygen stream suitable for this reduction step. Since various side reactions occur during the reduction, leading to the formation of sulfur compounds such as COS, the gases, after passing through the waste heat boiler and electrostatic precipitator, are catalyzed to convert the sulfur compounds into sulfur vapor. The vapor is condensed to produce elemental sulfur.

2.6.5.6 Slag Cleaning

Since the flash smelting process produces slags containing sufficient amounts of copper to make its recovery feasible, slag cleaning is normally used. Two methods are used with this process: flotation and electric furnace slag cleaning.

Flotation involves slow cooling of the slag to permit precipitation/agglomeration of copper sulfides and metallic copper. The slag is then crushed and ground, and copper is recovered via froth flotation. The concentrate recovered is then fed back to the smelter, usually mixed with the ore concentrate and flue dust.

In electric furnace slag cleaning, a reducing environment is provided which decreases the solubility of copper in the slag. Also, the slag is kept molten and fluid for an extended period of time to allow for entrained matte particles to coalesce, settle, and form a matte pool at the bottom of the furnace. Coke or coal is used as the reducing agent.

The matte phase from this furnace also goes to the converter.

A few smelters utilize both techniques, i.e., flotation for converter slag and electric furnace for flash furnace slag.

2.6.5.7 Blister Copper Production

As noted in the process description for Harjavalta, copper concentrates can be taken directly to blister copper in one stage. This is advantageous especially for concentrates containing less iron than normal. The copper content in the slag is high compared to processes producing matte and the slag must be treated separately.

2.6.6 Conclusions

Flash smelting utilizes the heat evolved from oxidizing part of the sulfide charge to produce much or all of the energy required for smelting. The recovery of waste heat from the flash furnace off-gas is standard practice. The amount of fuel required for smelting can be reduced by increasing the preheat temperature of flash furnace air, oxygen enrichment of flash furnace air and the degree to which the charge is oxidized in the furnace, i.e., the matte grade. The lowered fuel consumption also results in reduced off-gas volume. Present practice enables the flash furnace to operate without fuel addition with oxygen enrichment in the range of 30-75% oxygen and a preheat temperature of 200°C.

Increasing the matte grade decreases the need for additional fuel in flash smelting because a fairly large portion of the fuel value of the concentrate is used at the smelting stage. In addition, production of high grade matte leads to energy savings in converting.

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2.7 INCO FLASH SMELTING

2.7.1 Introduction

The INCO Metals Company (INCO), Copper Cliff, Ontario, Canada, is among the pioneers of the commercial use of oxygen in liquid-phase pyrometallurgy. In the years 1945 to 1949 the company developed a process for direct flash smelting of copper sulfide concentrates with oxygen. In 1952, the first commercial scale oxygen flash smelting furnace was brought into service at Copper Cliff. There are currently two copper processing plants, the other the Almalyk Smelter in the USSR using the oxygen flash smelting method for recovery of copper, and the following is a general description of the process as used at Copper Cliff.

2.7.2 Process Description

The INCO Oxygen Flash Smelting Process is a pyrometallurgical process for the extraction of copper from sulfide concentrates. Characteristic of this process is autogenous flash smelting, utilization of high purity 95-99.5% oxygen, and production of gases with a high content of sulfur dioxide (80%) that can be further processed to produce liquid sulfur dioxide or reduced to elemental sulfur or to sulfuric acid using converter gases, smelter secondary emissions or air as diluent.

Figure 2.7-1 is a general flowsheet for the oxygen flash smelting process. The procedure as shown is followed by INCO with the exception that only 50% of the converter slag is currently returned to the smelting furnace because nickel contained in the feed concentrate (typically about 1%) must be rejected with at least a portion of the copper converter slag. INCO reprocesses the remainder of the converter slag through the nickel reverberatory furnace for recovery of nickel and copper. In this paper, recycle of converter slag through the flash furnace has been considered for purposes of material and energy balances, since the content of copper in the slag is appreciable (4%).

Copper concentrates are received at the dryers in the form of filter cake containing 8% moisture. Each dryer unit consists of a blower, natural gas-fired heater, fluidized bed dryer, and collection baghouse. Since 1971, two fluidized bed dryers have been used at INCO for preparing a proportioned concentrate/sand mixture.

High purity tonnage oxygen is received at the furnace at 23 psig, and a reduction in pressure to 15 psig is made for piping to the burners.

The flash furnace has opposed pairs of burners and a central gas uptake. The proportioned feed mixture is gravity-fed through the burners where it combines with oxygen and then enters the furnace. Ignition is instantaneous, and the smelting temperature is maintained solely by the oxidation of the iron sulfides while the concentrates are in suspension. The iron oxides produced are fluxed by the sand to generate an iron silicate slag. The remaining copper, iron, and sulfur collect as matte below the slag layer.

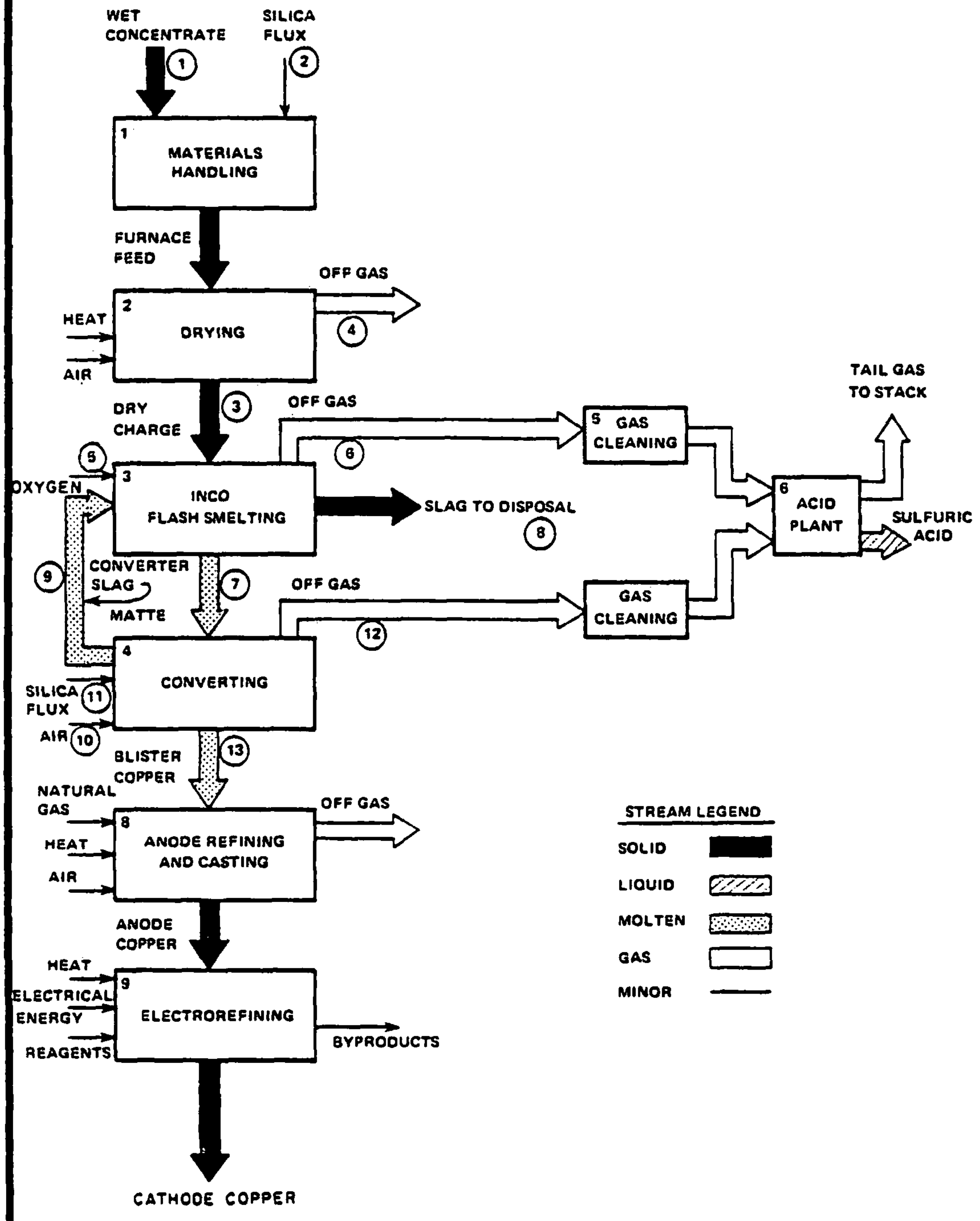

FIGURE 2.7-1 INCO OXYGEN FLASH SMELTING PROCESS

Slag at 2250°F is skimmed manually and then discarded. Prior to 1964, pyrrhotite cleaning of the slag was carried out, but this practice has been discontinued at INCO (Merla, 1972) because overall copper losses were not decreased significantly.

Gases, containing about 80% sulfur dioxide, leave the flash furnace at 2300°F and are led to a settling chamber where particulate solids are removed, and the gases are cooled to 1300°F. Further cooling is achieved with water in a splash tower after which the gases are passed through three venturi scrubbers in series and a Cottrell precipitator. The clean sulfur dioxide gases are then sent for liquefaction, which is done by cooling and compressing. If sulfuric acid were to be produced the settling chamber would be followed by a spray cooler and electrostatic precipitator.

Matte, containing about 47% copper, is removed from the furnace at 2150°F and is transferred to Peirce-Smith converters for processing to blister copper. Operating practice for converting at INCO is standard except that about 50% of the converter slag is recycled through the nickel side of the plant for recovery of nickel and copper and about 50% is returned to the flash furnace. Offgases from the converter contain about 4-5% sulfur dioxide after dilution with cooling air and are exhausted through a stack.

Blister copper from the converter is further processed by anode refining and casting and electrorefining.

As the off-gas volume is typically less than 5,000 SCFM, in most cases a waste heat boiler cannot be justified either from an energy savings, or economic operational integrity standpoint.

2.7.3 Material Balance

Table 2.7-1 presents the material balance for the INCO flash smelting process.

2.7.4 Energy Requirements

Tables 2.7-2 and 2.7-3 present Level I and Level II energy requirements for the INCO flash smelting process.

2.7.5 Conclusions

INCO Flash Smelting under autogenous conditions, using tonnage oxygen (95-99.0% O_2) and a 29-30% Cu 30-31% Fe & 33-34% S feed concentrate, will typically yield matte grades in the 40-45% range, though excursions as low as 35% Cu or as high as 55% Cu have been experienced due to changes in operating conditions. Throughout this range the furnace partition coefficient (%Cu in matte/%Cu in slag) has remained at about 70. Return of molten (or cold) converter slag to the furnace will increase this autogenous matte grade by as much as 5 percentage points of copper, depending on the quantity recycled. It should be understood that for all typical copper concentrates being processed through an INCO type flash furnace at a specific feed rate that there is a specific autogenous matte grade. This autogenous matte grade can however be varied in a number of proven ways. Increasing the furnace feed rate will decrease matte grades while increases in furnace slag silica content by the use of higher furnace flux additions will increase matte grades. Additions of "inert" materials such as smelter dusts, converter slags, limestone or water will also increase the autogenous matte grade. Decreasing additions of these inert materials will of course decrease the matte grade. In certain cases very minor additions (less than 1% of concentrate feed rate) of fuel (i.e., pulverized coal) will decrease the matte grade very substantially (up to 10 percentage points of copper). In almost 30 years of operation no magnetite buildup on the furnace bottom has been experienced and the original bottom installed in the

TABLE 2.7-1 INCO OXYGEN FLASH SMELTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		FLASH SILICA FLUX		DRY FURNACE CHARGE		DRYERS OFF GAS		FLASH FURNACE OXYGEN	
COMPOSITION	wt.	wet wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wet wt.%	wt.	wt.%
Cu	0.9995	22.50			0.9995	23.19				
Fe	1.1194	25.20	0.0044	1.40	1.1238	26.08				
S	1.2383	27.87			1.2383	28.73				
O_{Fe^*}	0.0186	0.42	0.0019	0.60	0.0205	0.48				
S_iO_2	0.3450	7.77	0.2807	90.00	0.6257	14.52				
AL_2O_3	0.1379	3.11	0.0125	4.00	0.1504	3.49				
CaO + MgO	0.1171	2.63	0.0062	2.00	0.1233	2.86				
Others	0.0220	0.50	0.0062	2.00	0.0282	0.65				
H_2O	0.4442	10.00	0.0064		0.0086		0.5213	8.17		
SO_2										
O_2							1.2142	19.03	0.8917	95.60
CO										
CO_2							0.1133	1.78		
N_2							4.5309	71.02	0.0411	4.40
TOTAL WET	4.4420		0.3183		4.3183		6.3796			
TOTAL DRY	3.9978	100.00	0.3119	100.00	4.3097	100.00	5.8583	100.00	0.9328	100.00
TEMP. (°F)	60		60		77		225		77	
STATE	S		S		S		G		G	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.7-1 (cont.) INCO OXYGEN FLASH SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	FLASH FURNACE OFF-GAS		FLASH FURNACE MATTE		FLASH FURNACE SLAG		CONVERTER SLAG		AIR TO CONVERTER	
COMPOSITION	wt.	wet wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu			1.0273	50.45	0.0195	0.72	0.0373	3.96		
Fe			0.4816	23.65	1.1266	41.80	0.4771	50.55		
S			0.4854	23.83	0.0387	1.44	0.0218	2.31		
O_{Fe}*			0.0336	1.65	0.3282	12.18	0.1471	15.59		
S_iO_2					0.8675	32.18	0.2389	25.31		
AL_2O_3					0.1612	5.98	0.0108	1.14		
CaO + MgO					0.1287	4.77	0.0054	0.57		
Others			0.0085	0.42	0.0251	0.93	0.0054	0.57		
H_2O	0.0086	0.52								
SO_2	1.4851	90.16								
O_2									0.5683	23.20
CO										
CO_2										
N_2	0.1535	9.32							1.8814	76.80
TOTAL WET	1.6472									
TOTAL DRY	1.6386	100.00	2.0364	100.00	2.6955	100.00	0.9438	100.00	2.4497	100.00
TEMP. (°F)	2241		2151		2241		2241		60	
STATE	G		L		L		L		G	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.7-1 (cont.) INCO OXYGEN FLASH SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(11)		(12)		(13)			
STREAM NAME	CONVERTER SILICA FLUX		CONVERTER OFF-GAS		BLISTER COPPER			
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%		
Cu					0.9800	98.00		
Fe	0.0038	1.40			0.0010	0.1		
S					0.0090	0.90		
O_{Fe}*	0.0016	0.60			0.0015	0.15		
SiO_2	0.2418	90.00						
Al_2O_3	0.0108	4.00						
CaO + MgO	0.0054	2.00						
Others	0.0054	2.00			0.0085	0.85		
H_2O								
SO_2			0.9047	32.47				
O_2								
CO								
CO_2								
N_2			1.8814	67.53				
TOTAL DRY	0.2688	100.00	2.7861	100.00	1.0000	100.00		
TEMP. (°F)	60		60		2200			
STATE	S		S		L			

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.7-2

LEVEL 1

ENERGY REQUIREMENTS

INCO FLASH SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Drying				
	A) Fuel: Natural Gas	SCF	1750	0.001	1.750
	B) Electrical Energy	KWH	10.0	0.0105	0.105
3	Flash Smelting				
	A) Electrical Energy	KWH	4.5	0.0105	0.047
4	Converting				
	A) Electrical Energy	KWH	89.8	0.0105	0.943
5	Gas Cleaning				
	A) Hot Furnace Gas Cleaning (81% SO_2-Dry Basis)	THOUS. SCF	22.1	0.00336	0.074
	B) Hot Converter Gas Cleaning (7% SO_2-Dry Basis)	THOUS. SCF	153.0	0.00336	0.514
	C) Cold Furnace Gas Cleaning (75% SO_2-Dry Basis)	THOUS. SCF	32.6	0.00126	0.041
	D) Cold Converter Gas Cleaning (5% SO_2-Dry Basis)	THOUS. SCF	213.6	0.00126	0.269
	E) Fugitive Emission Control	KWH	340.0	0.0105	3.570
6	Acid Plant				
	A) Smelter and Converter Gas (11.1% SO_2-Dry Basis)	THOUS.	253.5	0.0126	3.194
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095

*Not Shown on Flowsheet

TABLE 2.7-2 (cont.) **ENERGY REQUIREMENTS** LEVEL 1

INCO FLASH SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
7,8	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	17.152

TABLE 2.7-3 **ENERGY REQUIREMENTS** LEVEL 2

INCO FLASH SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Flash Smelting				
	A) Oxygen	TON	.933	3.78	3.526
	B) Silica Flux	TON	.312	0.042	0.013
4	Converting				
	A) Silica Flux	TON	.269	0.042	0.011
*	Water Pollution Control				
	A) Lime	LBS	30.0	0.0027	0.081
7,8	Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
				TOTAL	4.099

*Not shown on flowsheet

second production furnace which commenced operation in 1953 is still in use. The recycle of converter slag first tested in 1978 has been incorporated as a regular operating practice and is currently being held at a rate of about 50% of total converter slag generated, with the limitation being the nickel content of the feed rather than the furnace operation. This reversion has not decreased the furnace matte/slag partition coefficient. The INCO furnace produces a low off gas volume, typically about 5,000 SCFM with a high sulfur dioxide content (80% SO_2). As a result, dusting rates are low and typically run in the range of 2-3% of the feed rate. Generally it is not considered economic to install a waste heat boiler on the furnace because of the exceptionally low off gas volume. The high SO_2 gas strength is ideally suited to the production of liquid SO_2 or as a sweetener for other smelter gases in the production of sulfuric acid.

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2.8 THE TOP BLOWN ROTARY CONVERTER (TBRC) SMELTING

2.8.1 Introduction

The Kaldo Process was first used commercially in 1957, in Sweden, to produce steel from high phosphorus iron ore. INCO Limited adapted the converter employed in the Kaldo Process to nonferrous smelting in 1959 in a three-ton pilot plant furnace in Sweden for the blowing of nickel sulfide to metallic nickel. In 1965, INCO installed a ten-ton converter of this type in a smelter (naming it TBRC) at its research facilities in Port Colborne, Ontario, to convert nickel sulfide into nickel metal and to convert copper, nickel sulfides and copper sulfides to metal. As a result of successful pilot plant testing, two 14-foot diameter furnaces were installed at INCO's Copper Cliff nickel refinery at Sudbury, Ontario and three in Sovako, Indonesia.

In 1971, INCO gave Dravo a worldwide exclusive license to design, engineer and construct copper smelters using the TBRC process. Through a joint venture by Dravo and INCO, in 1973, the TBRC smelter for nickel conversion was applied to production scale tests of copper smelting at INCO's Copper Cliff refinery. Successful pilot tests were made with an ore concentrate containing 29% copper, 30% iron and 30% sulfur plus silica and trace elements.

The first commercial scale introduction of the TBRC technique to copper metallurgy occurred within the secondary copper industry. La Metallo-Chimique S.A., Belgium (with secondary copper smelters at Beerse, Belgium, and Alton, Illinois) has, since the mid-sixties, developed techniques for TBRC smelting and refining of copper-bearing secondary raw materials including techniques for slag refining and extraction of valuable byproducts. One of the features of the development is a jacketed furnace shell.

At Tennant Creek in Australia, two 25-ton TBRC type top blown, rotary converters were installed by Peko-Wallsend and brought on stream in January 1974 and operated for 14 months. These units were installed at less than a 5° angle. The TBRCs were used for treating high grade mattes (65% Cu) containing 0.2% Bi. With the TBRC's ability to provide heat and control atmosphere, it was possible to eliminate bismuth by volatilization from 0.2% to 0.04% Bi. This was achievable by prolonged converting times, at a high expense in fuel oil and lining life.

The first commercial copper smelter designed and engineered by Dravo using the TBRC smelter technology is operated by Alton Mines Ltd. in Kanloops, British Columbia. The Alton ore body is principally native copper with some bornite, chalcocite and chalcopyrite and is concentrated to a metallic concentrate that averages 82% copper and a flotation concentrate containing 51% copper and 7.1% sulfur.

2.8.2 Process Description

The TBRC vessel is similar to the basic vessel used in the Kaldo process for steel production. Thrust rollers secure the vessel longitudinally, and motor-driven support rollers support the vessel in its frame and rotate it at variable operating speeds from 0-40 RPM. Different speeds are used in different process stages, e.g., low RPM while charging and high RPM at the end of the white metal blow and during the anode refining stage. High RPM increases process reaction rates and efficiencies, but also increases refractory wear. The furnace can be tilted through 360° for filling, blowing, and pouring. The process flow-sheet is shown in Figure 2.8-1.

A movable, tight-fitting hood covers the open end of the converter. This hood carries the process lance, charging chute, and INCO flash burner, all of which are water-cooled. The process lance utilizes oxygen, fuel and air in various combinations to act as either a burner or blowing lance. The hood is closed over the vessel mouth whenever processing takes place. The hood can be swung away from the vessel mouth, the TBRC rotated, and molten material or scrap that is too large for the chute can be added. The vessel is inclined between 15°-20° during operation. The angle is selected to obtain an optimum balance between degree of fill and agitation (Daniele and Jaquay, 1972).

The smelting of copper concentrates is essentially an autogenous operation in the TBRC. The charge consisting of concentrate and flux is prepared and dried. Smelting would be accomplished by the flash smelting technique as demonstrated by INCO in their continuing development efforts (Bell, 1978).

Dravo no longer considers multiple TBRCs to be the best way to go on a new large tonnage smelting facility (Daniele, Jaquay, 1972 and 1974). Today, Dravo's approach is that although multiple TBRCs are a technically feasible approach, it is doubtful that they can compete on a capital cost basis with a large primary smelting unit producing continuous high strength off-gases for use in a sulfuric acid plant. However, the TBRC can be considered as a viable alternative to Peirce-Smith converters where the primary unit produces high grade matte.

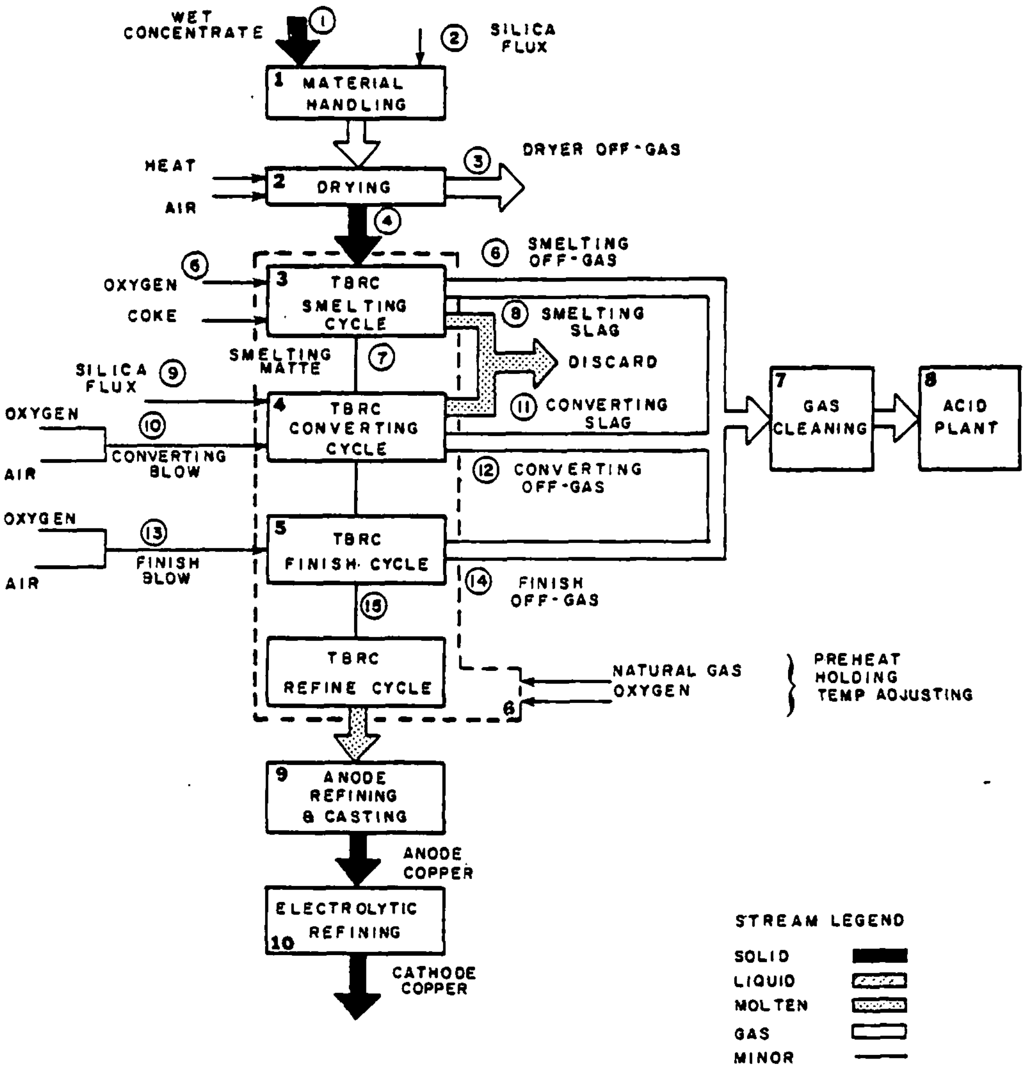

FIGURE 2.8-1 TOP-BLOWN ROTARY CONVERTER™ PROCESS

The TBRC™ Process represents a complete process — smelting, converting, and refining. The overall capital competitveness of the process, however, lies in a range up to 700-800 TPD copper concentrate. As capital cost was not a criterion in these studies, the following energy consumption information is based on a TBRC™ copper smelter producing copper from approximately 1200 TPD chalcopyrite concentrate. Such a smelter would require four (4) operating TBRC vessels.

A typical cycle would include the following process steps:

1. Flash smelting of a pre-fluxed concentrate with oxygen.
2. Cleaning of flash smelting slag.
3. Pouring slag from vessel.
4. Begin converting step by adding silica flux and blowing with oxygen enriched air.
5. Cleaning of converting slag and pouring from vessel.
6. Begin finish blow to produce blister copper.
7. Further de-sulfurize and then de-oxidize to produce anode or fire-refined copper.

In a 1200 TPD smelter each TBRC converter would not perform all seven (7) steps. A typical utilization would be two (2) smelting and slag cleaning, one (1) converting, and one (1) finish blow and refining.

Cycle Descriptions:

The concentrate smelting TBRCs are preheated to operating temperatures. Pre-fluxed and dried (<1% H_2O) concentrate is charged through an INCO flash smelting burner. Temperature control is maintained by adjusting the O_2:Concentrate ratio. This ratio varies with different concentrate grades. Once the available volume is filled, a slag cleaning step is performed, then the slag is poured from the TBRC vessel. The sequence is repeated until an optimum volume of matte has been accumulated for the converting stage. More than 50% of the slag is removed during the smelting cycle stage.

The converting cycle begins when sufficient 55-60% copper matte has been accumulated. This can be accomplished by either building up the matte level in one TBRC or transferring matte from another TBRC to the converting vessel. Should the matte contain impurities, e.g., arsenic, antimony, bismuth, lead, etc., an impurity volatilization step would be performed prior to blowing commencing. Once the converting cycle is begun, silica flux is added via the charging chute. The process lance is set for an oxygen-air mixture, approximately 30% O_2 by volume, and blowing proceeds. Once sufficient slag is produced it is either subjected to a slag cleaning step or transferred to another TBRC for cleaning.

The complexity introduced by matte, slag, and white metal transfers in a large tonnage smelter is the reason that a single primary smelting unit may be preferable. Another choice to minimize transfers is slow cooling and milling of the converting stage slags. This could also enhance overall copper recovery, e.g., Afton Mines Ltd., recycles slag to their concentrator and achieves $99\%^{+}\%$ copper recovery.

Once all the iron is slagged and the slag removed from the TBRC, the finish blow, white metal to copper, begins. Again, blowing utilizes a mixture of oxygen and air. Once oxygen levels of

0.15-0.20% are achieved (0.1% sulfur or less), reduction can begin by adding carbon to the bath. Here one of the advantages of the high speed rotary vessel comes into play. Further desulfurization takes place during de-oxidation due to the forced mixing of copper sulfides and oxides. This permits the TBRC to perform the anode furnace or fire refining furnace function. The copper is removed from the furnace by tilting the TBRC downward and pouring the copper into ladles beneath the furnace.

The exhaust gases from the furnace are collected in the hood which is connected to gas cooling and cleaning equipment. The clearance between the hood and the rotating furnace is held to as little as 2 inches to limit the amount of ambient air entering the exhaust system at this point. The negative pressure in the hood is controlled to the minimum value which will prevent the escape of exhaust gas. Sulfur dioxide concentration in the exhaust gases is generally high enough for economic recovery of the sulfur as sulfuric acid or as elemental sulfur (Jaquay). An exception to this is at the Afton mines smelter where the concentrate has low sulfur content. The sulfur dioxide in the gases at this operation are removed by a Dravo designed dual alkali scrubbing system (Pazour, 1978).

Close control of the furnace atmosphere, the turbulence of the bath, the oxygen/air mixture, and the temperature of the melt is necessary for useful operation of the TBRC. Computer control, utilizing a heat and material balance (Jaquay), can be used to determine the amounts of raw material, flux, oxygen, and air that are required to reach a desired melt condition of temperature, composition, or volume. To supplement this and provide for necessary adjustments, slag and matte samples are sent to a lab for a check on chemical composition and the temperature is measured by an immersion thermocouple or optical pyrometer.

The turbulence in the bath is controlled by varying the rotational speeds. Constant vessel rotation enhances gas/solid/liquid contact and heat distribution. High oxygen efficiency can be maintained by adjustment of the rotational speed and lance angle. Tests done by INCO indicated that oxygen efficiency can be maintained above 90% (Daniele and Jaquay, 1972) (Bell, 1978).

The lance is used to control the smelting atmosphere by the injection of different combinations of fuel, air, and oxygen to obtain neutral, oxidizing, or reducing conditions as required. The temperature of the charge can be raised by injecting oxygen and fuel through the lance which will burn and mix the two gases at the nozzle. Alternatively, temperature can be lowered by adding scrap or low iron concentrates, by introducing water into the converter to use up the excess heat or by a greater air to oxygen ratio (Bell et al., 1978).

2.8.3 Material Balance

Table 2.8-1 shows the material balance for smelting of concentrates by the top blown rotary converter process.

2.8.4 Energy Requirements

Table 2.8-2 presents the Level I energy requirements for TBRC smelting, in million Btu per ton of blister copper.

The energy used in materials handling and general utility is estimated at 15.5 kWh per ton concentrate smelted, or 147,000 Btu fuel equivalent.

Table 2.8-3 presents the Level II energy requirements for TBRC smelting.

TABLE 2.8-1

TBRC^{TM} PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		SMELTING SILICA FLUX		DRYERS OFF GAS		DRY FURNACE CHARGE		SMELTING OXYGEN	
COMPOSITION	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%
Cu	0.9995	22.50					0.9995	23.19		
Fe	1.1194	25.20	0.0044	1.40			1.1238	26.08		
S	1.2383	27.87					1.2383	28.73		
O_{Fe}*	0.0186	0.42	0.0019	0.60			0.0205	0.48		
S_iO_2	0.3450	7.77	0.2807	90.00			0.6257	14.52		
AL_2O_3	0.1379	3.11	0.0125	4.00			0.1504	3.49		
CaO + MgO	0.1171	2.63	0.0062	2.00			0.1233	2.86		
Others	0.0220	0.50	0.0062	2.00			0.0282	0.65		
H_2O	0.4442	10.00	0.0064		0.5213	8.17	0.0086			
SO_2										
O_2					1.2142	19.03			1.000	95.60
CO										
CO_2					0.1133	1.78				
N_2					4.5309	71.02			0.046	4.40
TOTAL WET	4.4420		0.3183		6.3796		4.3183			
TOTAL DRY	3.9978	100.00	0.3119	100.00	5.8583	100.00	4.3097	100.00	1.046	100.00
TEMP. (°F)	60		60		225		77		60	
STATE	S		S		G		S		G	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.8-1 (cont.)

TBRC^{TM} PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	SMELTING OFF-GAS		SMELTING MATTE		SMELTING SLAG		CONVERTING FLUX		CONVERTING BLOW	
COMPOSITION	wt.	wet wt.%	wt.	wet wt.%	wt.	wt.%	wt.	wet wt.%	wt.	wet wt.%
Cu			0.9893	56.83	0.0107	0.60				
Fe			0.2763	15.87	0.8475	47.46	0.0028	1.40		
S			0.4056	23.30						
O_{Fe}*							0.0011	0.60		
SiO_2					0.6257	35.04	0.1781	90.00		
AL_2O_3					0.1504	8.42	0.0079	4.00		
CaO + MgO					0.1233	6.90	0.0040	2.00		
Others			0.0696	4.00	0.0282	1.58	0.0040	2.00		
H_2O	0.0086						0.0040			
SO_2	1.660	44.1								
O_2	0.472	12.6							0.2667	32.86
CO										
CO_2										
N_2	1.626	44.1							0.5449	67.14
TOTAL WET							0.2010			
TOTAL DRY	3.758	100.00	1.7408	100.00	1.7858	100.00	0.1979	100.00	0.8166	100.00
TEMP. (°F)	1800-2000		2250		2300		60		60	
STATE	G		L		L		S		G	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.8-1 (cont.) TBRC™ PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	CONVERTING SLAG		CONVERTING OFF-GAS		FINISH BLOW		FINISH OFF-GAS		BLISTER COPPER	
COMPOSITION	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%	wt.	wet wt.%
Cu	0.0083	1.31							0.98	98
Fe	0.2791	44.03							0.001	0.10
S									0.009	0.90
O_{Fe}*	0.0829	13.08							0.0015	0.15
SiO_2	0.1781	28.10								
Al_2O_3	0.0079	1.24								
CaO + MgO	0.0040	0.63								
Others	0.0736	11.61							0.0085	0.85
H_2O										
SO_2			0.3166	22.49			0.4904	26.08		
O_2			0.1256	8.92	0.3065	32.86	0.1952	10.38		
CO										
CO_2										
N_2			0.9656	68.59	0.6262	67.14	1.1950	63.54		
TOTAL WET										
TOTAL DRY	0.6339	100.00	1.4078	100.00	0.9327	100.00	1.8806	100.00	1.0	100.00
TEMP. (°F)	2300		1800-2000		60		1800-2000		2200	
STATE	L		G		G		G		L	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.8-2

ENERGY REQUIREMENTS

LEVEL 1

TBRC^{TM} PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Drying				
	A) Fuel: Natural Gas	SCF	1750	0.001	1.750
	B) Electrical Energy	KWH	10	0.0105	0.105
3-6	TBRC TOTAL				
	A) Fuel: Natural Gas	SCF	400	0.001	0.400
	B) Electrical Energy	KWH	110.9	0.0105	1.164
7	Gas Cleaning				
	A) Hot Gas Cleaning				
	Smelting	SCF x 10^3	74.9	0.00336	0.252
	Converting	SCF x 10^3	32.9	0.00336	0.110
	Finish	SCF x 10^3	42.8	0.00336	0.144
	B) Cold Gas Cleaning (10.8% SO_2)	SCF x 10^3	270.5	0.00126	0.341
	C) Fugitive Emission Control	KWH	340.0	0.0105	3.570
8	Acid Plant				
	A) All Process Off-Gases (9% SO_2)	SCF x 10^3	324.5	0.0126	4.089
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095
9,10	Anode Furnace & Electrorefining	TON CATHODE	1.0	5.824	5.824
					18.570

*Not on Flowsheet

TABLE 2.8-3 **ENERGY REQUIREMENTS** LEVEL 2

TBRC$^{\text{TM}}$ PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	TBRC - Smelting				
	A) Oxygen	TON	1.000	3.78	3.780
	B) Silica Flux	TON	0.312	0.042	0.013
	C) Coke	TON	0.004	31.50	0.126
4	TBRC - Converting				
	A) Oxygen	TON	0.1026	3.78	0.388
	B) Silica Flux	TON	0.198	0.042	0.008
5	TBRC - Finish				
	A) Oxygen	TON	0.1179	3.78	0.446
6	TBRC - Preheat, Hold & Temp. Adjust				
	A) Oxygen	TON	0.0338	3.78	0.128
*	Water Pollution Control				
	A) Lime	LB	30	0.0027	0.081
9,10	Anode Furnace and Electrorefining	TON OF CATHODE	1.0	0.016	0.016
					4.986

*Not on Flowsheet

2.8.5 Conclusions

TBRC copper smelting process allows for the control of vessel atmosphere, bath temperature and turbulence that result in control of oxidation potential, improved gas/solid/liquid contact and improved thermal efficiency. As pure oxygen is used, the fuel used in smelting is small for heating the converters and adjusting temperature. The principal fuel use is in drying. The off-gas volume is small and rich in sulfur dioxide, maximum 50%.

2.8.6 References

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2.9 NORANDA CONTINUOUS SMELTING

2.9.1 Introduction

The estimated energy requirement of the Noranda continuous smelting process to produce an equivalent 100,000 tons per year of cathode copper is 23.03 x 10^{11} Btu. The process configuration upon which this estimate was based is the new three continuous-smelting vessel operation at Kennecott's Garfield Smelter. This smelter was chosen because it is the only example of the Noranda system in the United States, and it is the only smelter designed from the beginning for the Noranda system. However, due to the newness of this facility, there is not significant operating data available upon which to base an energy evaluation; consequently, the energy calculations were based on data obtained from Noranda Mines Ltd.'s Horne Smelter at Noranda, Quebec. In addition to the calculated primary energy requirements, amounts of consumables (i.e., oxygen, fluxes, etc.) required to produce 100,000 tons of cathode equivalents were compiled, from which energy requirements were calculated.

The development of the Noranda continuous smelting process began in 1964 (Themelis, et al, 1972). The process is based on the thesis that the operating and capital cost of smelting and converting could be reduced by combining the conventional reverberatory smelting furnace and the batch-operated copper converting furnaces into a single vessel, performing both functions in a continuous operation. The heat from converting (oxidation of sulfur and iron) would be used in smelting the copper concentration and producing a high sulfur blister copper that would be "finished" in a converter or an anode furnace fitted with additional tuyeres. Based on this concept and laboratory experiments, a semi-commercial scale pilot plant was constructed in the latter part of 1967 and early 1968. The 35 ft. long x 9½ ft. diameter vessel was designed to smelt 100 tons per day of concentrate. Based upon the successful results of the pilot plant, an 800 tpd continuous smelting vessel, which is 17 ft. in diameter by 70 ft. long, was built at Noranda in 1973. (Hallett, 1976) Figure 2.9-1.

Since the conception of the Noranda continuous smelting process, substantial concern has been expressed as to the impact of SO_2 and particulate emissions from copper smelters upon air quality. These concerns were first formalized in the Clean Air Act and its amendments of 1970, which limit the concentration of sulfur oxides and particulates in the atmosphere and required those industries contributing to the general level of pollution to affect any changes necessary to comply with the newly enacted "Ambient Standards."

Conventional copper reverberatory-converter systems required substantial modification to meet these requirements. In fact, some felt that air quality standards could not be met with a modified reverberatory smelting system due to the substantial volumes of reverberatory gases containing about 1% to 2% SO_2, which were difficult to treat economically. With both the

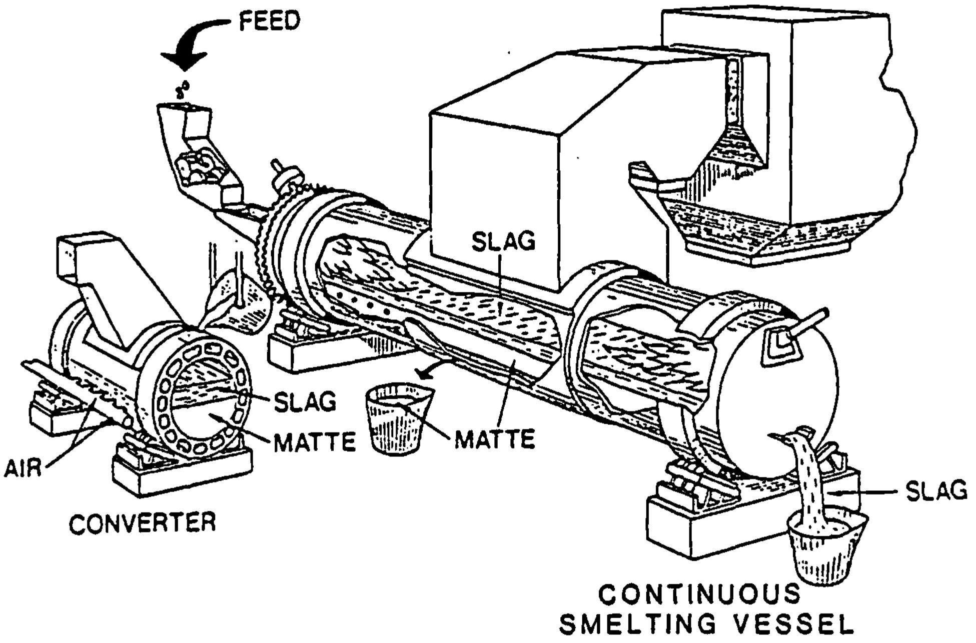

FIGURE 2.9-1 NORANDA CONTINUOUS SMELTING VESSEL WITH CONVERTER

Courtesy Kennecott Copper Corporation

smelting and converting being performed in a single vessel, the Noranda off-gases at the vessel mouth contained 16% to 20% SO_2 that could be readily treated in a single or double contact acid plants.

In 1973, Kennecott committed itself to using the Noranda continuous smelting system. (Dayton, 1979) During subsequent testing by Kennecott and Noranda, the originally conceived process producing blister was modified to produce a high-copper matte. The matte (70%-75% Cu, 5% Fe, 21% S) would then be blown to blister in a finishing converter using oxygen-enriched air to suit Kennecott concentrate. Kennecott chose the matte smelting option due to the fact that impurities in their copper concentrates, i.e., arsenic, antimony and bismuth, would be concentrated in the blister phase if the matte and metal were held in a single vessel.

Metallurgical modeling of the Noranda smelting system and the Kennecott tankhouse provided some interesting considerations. Tankhouse investigations revealed that arsenic, antimony, and bismuth, or their compounds can detrimentally affect electrolyte composition, anode slime fall, and cathode quality. In addition, the total impact of these elements might not be apparent for years since the achievement of a steady-state electrolyte composition and electrorefining operation at a large refinery can take years.

Anode and cathode copper of acceptable quality could not be assured if blister copper were to be produced directly in the smelting vessel, so it was decided to make use of a two-step matte-making and converting process.

2.9.2 Process Description

Kennecott Copper Corporation's smelter at Garfield, Utah, consists of three continuous smelting vessels and four Peirce-Smith converters. Each smelting vessel is a horizontal brick-lined cylinder 70 ft. long by 17 ft. in diameter. Feed materials (concentrates, precipitate and fluxes) are introduced into the smelting vessel through an end wall via a slinger belt onto the molten bath. Oxygen enriched air (up to 35% O_2) is injected into the bath through 63 tuyeres. At higher oxygen enrichment percentages, the heat of reaction of the oxidation of iron and sulfur is almost sufficient to melt the input materials and sustain an autogenous process. The required supplementary heat is supplied at the feed end of the reactor by a gas/oil oxygen-enriched air burner and by an oxyfuel burner at the slag end.

The predetermined matte grade in the smelting vessel is maintained by controlling the ratio of feed material to oxygen input. Control of the reactor is achieved by metering the quantities of materials fed from the bins on belt scales and metering of the oxygen and air flows. The ratio of these inputs (O_2/concentrate) required to obtain the desired matte grade is determined by computer and displayed on a cathode ray tube. The variable speed belts and valves are then set to achieve the calculated ratio and resulting matte grade. Flux is added at a precalculated rate to maintain the desired iron to silica ratio in the slag.

Feeding is continuous resulting in a steady increase in liquid levels within the reactor. As the control of matte and slag levels is an important aspect of reactor control, these levels are periodically determined by "dip stick" measurement. Slag and matte are tapped off periodically to maintain levels within desired limits.

Matte is tapped into 260 cu. ft. ladles positioned on matte carriers. These carriers are moved into the converter aisle by a capstan winch controlled by the smelting vessel operator. The ladles are then transported to the converters by overhead crane.

Slag is tapped into 400 cu. ft. ladles and transported with Kress haulers to a slag cooling area. As reactor slag contains high copper values varying from 3% to 9%, it is slowly cooled and treated by milling and floating to recover the copper. The tailings from the slag flotation operation contain 0.3% to 0.4% copper resulting in an overall smelter recovery of about 99.2%.

Of the four standard 13' x 30' Peirce-Smith converters, only two converters are required for normal operations, with the third on standby and the fourth undergoing routine overhaul. Blast air is controlled on a constant volume basis at about 25,000 CFM which permits high production rates and the stabilization of gas flows to the acid plants. With a matte grade of 70% to 75% copper and the high blowing rates, converter cycle times are on the order of 2-4 hours. Fluxes and secondaries are conveyed to portable hoppers, which are transported by the converter aisle cranes, to pedestals adjacent to each converter. From here, flux is fed via a short conveyor and chute into the mouth of the converter. The converters are equipped with primary and secondary hoods, the latter being used to collect fugitive gases during out-of-stack periods and pouring operations.

A new system of hot metal haulage from the converters to the anode furnaces has been developed to cut energy requirements. Blister was formerly transported some thousand yards in open pots on tractor haulers. In the new system, the molten metal is transported in insulated torpedo cars mounted on rails. Each car has a conning tower structure to admit and empty molten metal, eliminating the shell encountered in the open pots, which required remelting. The blister copper in the anode furnace is fire refined and cast as anodes to be electro-refined at the refinery.

Process gases from continuous smelting vessels are directed via a water-cooled hood to a waste heat boiler where some heat and a portion of the particulates are removed. The stream is further cleaned in hot cyclones before entering dry electrostatic precipitators. The gas effluent of the electrostatic precipitators is sent to the acid plants.

Converter gases are also channeled through water-cooled hoods to particulate dropout chambers. The gases are next passed through three shot coolers (air-to-gas heat exchangers) for further cooling of gases and removal of particulates before reaching the dry electrostatic precipitators. Dust reclaimed upstream from the electrostatic precipitators is recycled into the smelting vessels. The electrostatic precipitator dropout is pelletized and stockpiled on a concrete pad.

Fugitive emissions are captured with secondary hooding systems on the furnaces and at tapping locations. These dilute emissions are drawn into a pair of large flues on top of the smelter building through ducts fitted with large fans. This gas flows into a single downcomer and into the mixing chamber upstream from the stack.

Control of gas flow to the 1,200 ft. stack is complex. If gases are too hot, they will burn the fiberglass liner; if they are too cold, plume buoyancy is reduced. Tailgases from the acid plants, normally less than 0.4% SO_2, are mixed with the fugitive enissions, with waste heat from the three direct-fire boilers at the smelter power plant and the two direct-fired steam superheaters, and with hot air from the shot coolers. The entire system must be balanced to function safely and efficiently.

2.9.3 Material Balance

The estimates for material and energy requirements are based on energy models developed by Noranda Mines Ltd. for the continuous smelting vessel and converters for the matte mode with two levels of oxygen enrichment. A flowsheet for the process is presented in Figure 2.9-2. This flowsheet designates the process steps and material streams, which are summarized as a material balance in Table 2.9-1.

2.9.4 Energy Requirements

The energy requirements (Level 1) for each process step are presented in Table 2.9-2. The level 2 energy requirements based on consumables usage are presented in Table 2.9-3.

2.9.5 Discussion

The energy requirements for Noranda Continuous Smelting can be reduced by raising the oxygen enrichment level in the tuyere and burner air, by raising the matte grade in the bath and by preheating the tuyere and burner air. Perhaps the most practical of these methods of reducing the energy requirements is increasing oxygen enrichment of the tuyere and burner air. Two Noranda Simulations indicate that the fuel requirement for the reactor decreases from 3.96×10^6 Btu for an oxygen enrichment of 30% to 2.65×10^6 Btu per ton of cathode copper for an oxygen enrichment of 36%. Of course, this decrease in fuel results from an increase of oxygen usage of approximately 3100 Scf per ton of copper. Since the extra oxygen required about 5×10^5 Btu to produce, the net energy savings is about 8×10^5 Btu per ton of copper. While some studies have been performed on oxygen enrichment a definitive optimization of oxygen enrichment in the Noranda reactor has not been accomplished.

The possibility of decreasing the fuel requirements by raising the matte grade is limited due to the impurity levels in the copper concentrate as discussed earlier. In the Kennecott flow scheme the matte transferred from the reactor contains 70% copper. This level may be raised to 75% to 78% without significant impurity pick up; however, at the present time, this grade increase reduces operating flexibility without commensurate decreases in operating costs and does not appear justified.

Preheating the tuyere and burner air can reduce the energy requirements of the reactor by about 160,000 to 170,000 Btu per ton of copper produced for every 100°F the air temperature is raised. This method of reducing fuel usage may require changes in the blowers and piping at high preheat temperatures. One of the advantages of this energy saving technique is that it can use waste heat recovered from the reactor off-gas.

Another possible use of recovered waste heat is the drying and preheating of concentrates. However, if this technique is to be used to full advantage, another method of feeding the concentrates into the bath should be developed. Presently, reactor feed is dried to 7-8% moisture and then charged through the end of the vessel on the bath. If the reactor feed were dried and preheated further, the dust loading of the reactor off-gas would be increased. Consequently, if dried and preheated reactor feed is anticipated to reduce energy consumption, a method of impinging the feed into the bath (e.g., lances), or using other methods of feeding to minimize the dust loading in the off-gas must be developed.

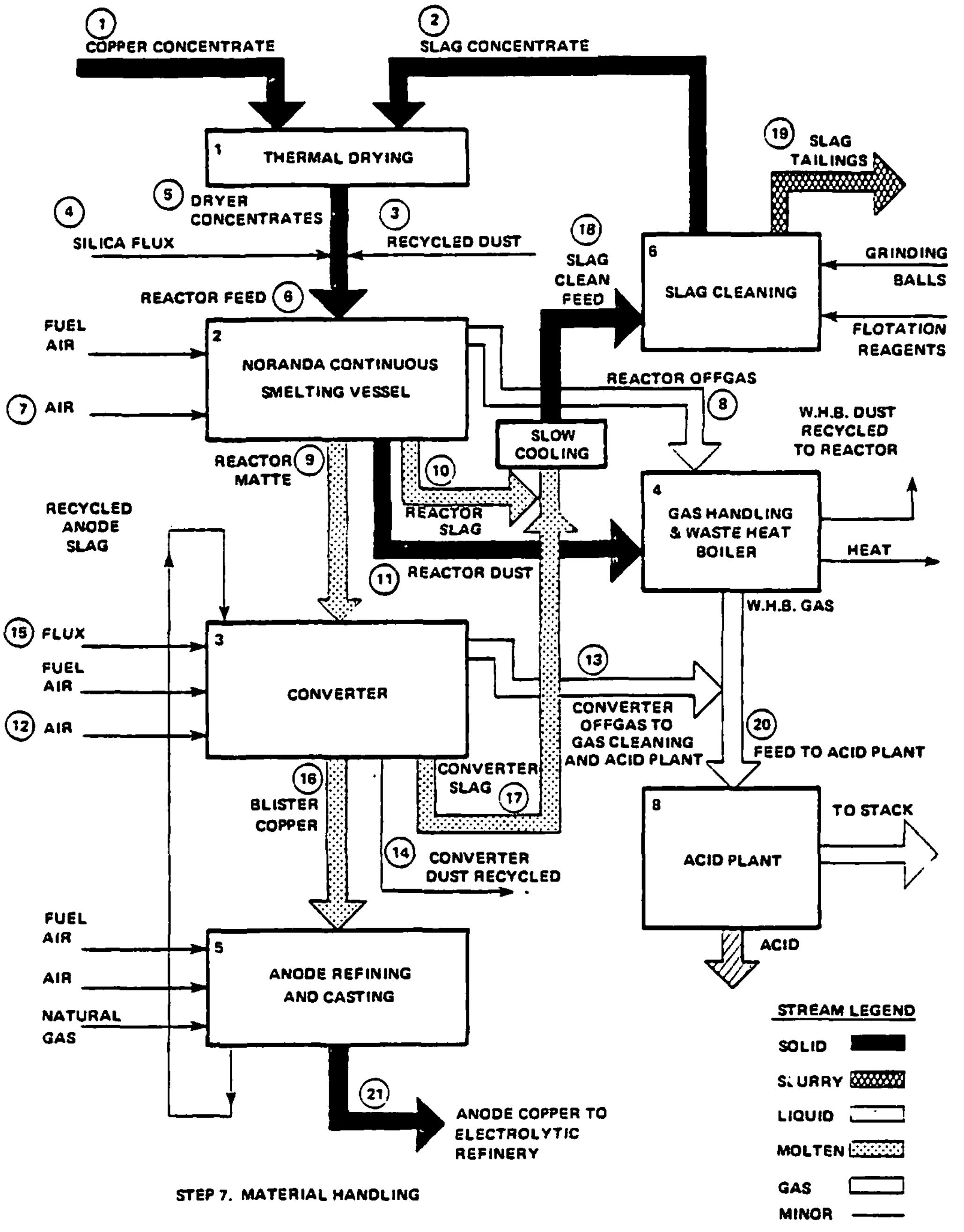

FIGURE 2.9-2 NORANDA CONTINUOUS SMELTING

TABLE 2.9-1 NORANDA CONTINUOUS SMELTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		SLAG CONCENTRATE		RECYCLED DUST		REACTOR FLUX		DRYER CONCENTRATE	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.990	22.49	0.245	32.32	0.049	26.34			1.235	24.73
Fe	1.108	25.18	0.157	20.71	0.011	5.38	0.024	6.38	1.265	25.34
S	1.225	27.83	0.059	7.78	0.029	15.59			1.284	25.72
O_{Fe}*	0.020	0.45	0.049	6.46	0.003	1.61	0.002	2.12	0.069	1.38
S_iO_2	0.343	7.79	0.088	11.61	0.01	5.38	0.286	76.06	0.431	8.63
AL_2O_3										
CaO + MgO										
Others	0.275	6.24	0.081	10.69	0.084	45.16	0.032	8.50	0.356	7.13
H_2O	0.441	10.02	0.079	10.42			0.026	6.91	0.353	7.07
SO_2										
O_2										
CO										
CO_2										
N_2										
TOTAL	4.402	100.00	0.758	100.00	0.186	100.00	0.376	100.00	4.993	100.00
TEMP. (°F)	77°		77°		77°		77°		77°	
STATE	S		S		S		S		S	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.9-1 (cont.) NORANDA CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	REACTOR FEED		REACTOR AIR		REACTOR OFFGAS		REACTOR MATTE		REACTOR SLAG	
COMPOSITION	WT.	WT.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.284	22.82					1.00	69.88	0.245	8.26
Fe	1.299	23.09					0.098	6.85	1.191	40.17
S	1.313	23.34					0.294	20.54	0.059	1.99
O_{Fe}*	0.08	1.42					0.01	0.70	0.397	13.39
SiO_2	0.727	12.92							0.717	24.18
Al_2O_3										
CaO + MgO										
Others	0.472	8.39					0.029	2.03	0.356	12.01
H_2O	0.451	8.02			0.638	10.70				
SO_2					1.860	31.21				
O_2			1.392	32.95	0.111	1.86				
CO										
CO_2					0.228	3.83				
N_2			2.833	67.05	3.123	52.40				
TOTAL	5.626	100.00	4.225	100.00	5.960	100.00	1.431	100.00	2.965	100.00
TEMP. (°F)	77°		77°		2400°		2200°		2200°	
STATE	S		G		G		L		L/S	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.9-1 (cont.) · NORANDA CONTINUOUS SMELTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	REACTOR DUST		CONVERTER AIR		CONVERTER OFFGAS		CONVERTER DUST		CONVERTER FLUX	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.039	23.78					0.010	45.95		
Fe	0.01	6.10					0.001	4.55	0.003	4.0
S	0.026	15.85					0.003	13.64		
O_{Fe}*	0.003	1.83							0.001	1.0
SiO_2	0.01	6.10							0.058	73.0
Al_2O_3										
CaO + MgO										
Others	0.076	46.34					0.008	36.36	0.012	15.0
H_2O									0.005	7.0
SO_2					0.569	43.63				
O_2			0.343	32.70	0.029	2.23				
CO										
CO_2										
N_2			0.706	67.30	0.706	54.14				
TOTAL	0.164	100.00	1.049	100.00	1.304	100.00	0.022	100.00	0.079	100.00
TEMP. (°F)	2200°		·		2300°		2250°		77°	
STATE	L/S				G		L/S		S	

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.9-1 (cont.) NORANDA CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	BLISTER		CONVERTER SLAG		FEED TO SLAG CLEANING		SLAG TAILS		FEED TO ACID**	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.980	98.00	0.010	4.74	0.255	8.02	0.010	0.40		
Fe	0.001	0.10	0.097	45.97	1.288	40.56	1.131	45.29		
S	0.009	0.90	0.001	.47	0.060	1.89	0.001	0.04		
O_{Fe}*	0.002	0.20	0.032	15.17	0.429	13.51	0.380	15.22		
S_iO_2			0.058	27.49	0.775	24.40	0.687	27.51		
AL_2O_3										
CaO + MgO										
Others	0.008	0.80	0.013	6.16	0.369	11.62	0.288	11.54		
H_2O									0.961	4.28
SO_2									3.735	16.62
O_2									2.667	11.87
CO										
CO_2									0.324	1.44
N_2									14.784	65.79
TOTAL	1.000	100.00	0.211	100.00	3.176	100.00	2.497	100.00	22.471	100.00
TEMP. (°F)	2250°		2250°		77°		77°		500°	
STATE	L		L/S		S		S		G	

*Oxygen associated with FeO and Fe_3O_4

**Including dilution air

TABLE 2.9-1 (cont.) NORANDA CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(21)					
STREAM NAME	COPPER ANODES					
COMPOSITION	wt.	wt.%				
Cu	0.980	99.80				
Fe						
S						
O_{Fe}*						
S_iO_2						
AL_2O_3						
CaO + MgO						
Others	0.002	0.02				
H_2O						
SO_2						
O_2						
CO						
CO_2						
N_2						
TOTAL	0.982	100,00				
TEMP. (°F)	77					
STATE	S					

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.9-2

LEVEL 1

ENERGY REQUIREMENTS

NORANDA CONTINUOUS SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Charge Drying				
	A) Natural Gas	SCF	800	0.001	0.800
2	Continuous Smelting				
	A) Fuel (Natural Gas)	SCF	3,717	0.001	3.717
	B) Compress tuyere air	million SCF	0.08555	14.7	1.258
	C) Compress burner air	million SCF	0.009417	0.63	0.006
	D) Steam credit	LBS	1900	0.000955	-1.815
3	Converting				
	A) Fuel (Natural Gas)	SCF	90	0.001	0.09
	B) Compress Tuyere air	million SCF	0.024934	14.7	0.366
4	Gas Handling				
	A) Reactor and converter (75% dilution)	million SCF	0.274	2.520	0.690
	B) Fugitive gas	million SCF	10.5	0.34	3.570
5	Anode Furnace and Electrorefining	KWH	1.00	5.824	5.824
6	Slag Concentrator	KWH	124.2	0.0105	1.307
7	Material Handling	KWH	75	0.0105	0.790
8	Acid Manufacture	KWH	295	0.0105	3.096
				TOTAL	19.699

TABLE 2.9-3 **ENERGY REQUIREMENTS** LEVEL 2

NORANDA CONTINUOUS SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Continuous Smelting				
	A) Silica Flux	LBS	715	0.000021	0.015
	B) Oxygen	Million SCF	0.0166	159.2	2.643
3	Converting				
	A) Silica Flux	LBS	151	0.000021	0.003
	B) Oxygen	Million SCF	0.003276	159.2	0.522
5	Anode Furnace				
	A) Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
6	Slag Concentrator				
	A) Reagents	LBS	1.9	0.0200	0.038
	B) Balls and liners	LBS	34.0	0.0180	0.612
				TOTAL	4.301

Another area that might result in energy savings as well as decreased use of potentially scarce natural gas or fuel oil is the mixing of coal with the reactor feed. This practice has been demonstrated in the Noranda Reactor; however, the use of coal has not been optimized nor has it totally eliminated the use of fuel oil or natural gas. In addition to the reduced use of natural gas and fuel oil, the coal igniting directly on the bath appears to improve the heat transfer characteristics.

Two other areas in which energy conservation may be accomplished are the utilization of the waste heat in the off-gas from the converters and utilizing the heat available in the reactor slags. Presently neither of these heat sources are considered sufficiently practical to be utilized in the present Kennecott operation.

2.9.6 Conclusions and Recommendations

The Noranda process is a proven pyrometallurgical process requiring about 23×10^6 Btu per ton of cathode copper for Level 1 plus Level 2 energy requirements. The energy requirements for Noranda continuous smelting can be reduced by raising the oxygen enrichment level in the tuyere and burner air, by raising the matte grade and by preheating the tuyere and burner air. Computer simulations indicate that the fuel requirement for the reactor can be decreased by about 8×10^6 Btu per ton of cathode copper for an oxygen enrichment of 36 percent. Reducing fuel requirement by raising the matte grade is limited by increased impurity levels in the copper concentrate. Preheating tuyere and burner air may reduce the energy requirements by 1.6×10^6 Btu per ton of cathode copper for every 100°F the air is heated. Waste heat could also be used to dry and preheat the concentrate. Recommendations for areas of useful research are as follows.

- Perform tests to determine the optimum oxygen enrichment to be used in the Noranda Reactor reflecting total operating costs including fuel, labor, refractories, etc.
- Demonstrate the practicality of preheating tuyere and burner air in the Noranda Reactor. Develop methods to charge dried and preheated reactor feed to the Noranda Reactor without increasing the reactor off-gas dust load.
- Perform tests to determine the optimum coal usage and to minimize the use of fuel oil and natural gas.

2.9.7 References

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2.10 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

2.10.1 Introduction

The Mitsubishi Continuous Copper Smelting and Converting Process was developed by the Mitsubishi Metal Corporation with development work starting in 1961. The first commercial plant using this process was put into operation in 1974 at Naoshima smelter. A second plant has been built for Texas Gulf at Timmins, Ontario.

Following is a description of the process as used at Naoshima.

2.10.2 Process Description

The Mitsubishi process is a continuous process for copper smelting and converting. The major advantages of the process are production of a high grade matte (65% copper) with low level copper loss in the discard slag, low fuel requirement for the smelter, and production of relatively high sulfur dioxide strength (14-15%) gases that permits efficient sulfur recovery. All furnaces are of the stationary type, and molten products are transferred by gravity through sealed launders, which prevents spill gases and the sulfur dioxide emissions that normally accompany these transfers.

Figure 2.10-1 is a flowsheet of the process.

Naoshima uses a concentrate bedding system to produce a uniform composition of the concentrates to be smelted. The concentrate mixture is dried in a dryer unit combining a rotary and a flash dryer to a moisture content of less than 1%.

Charge materials consisting of the dry concentrates, silica flux, limestone flux, recycled converter slag, and dusts are fed into the smelter through feeding lances which inject the materials directly into the matte layer. The lances are designed so that the charge materials are provided with enough speed to be caught effectively in the molten bath in the smelter.

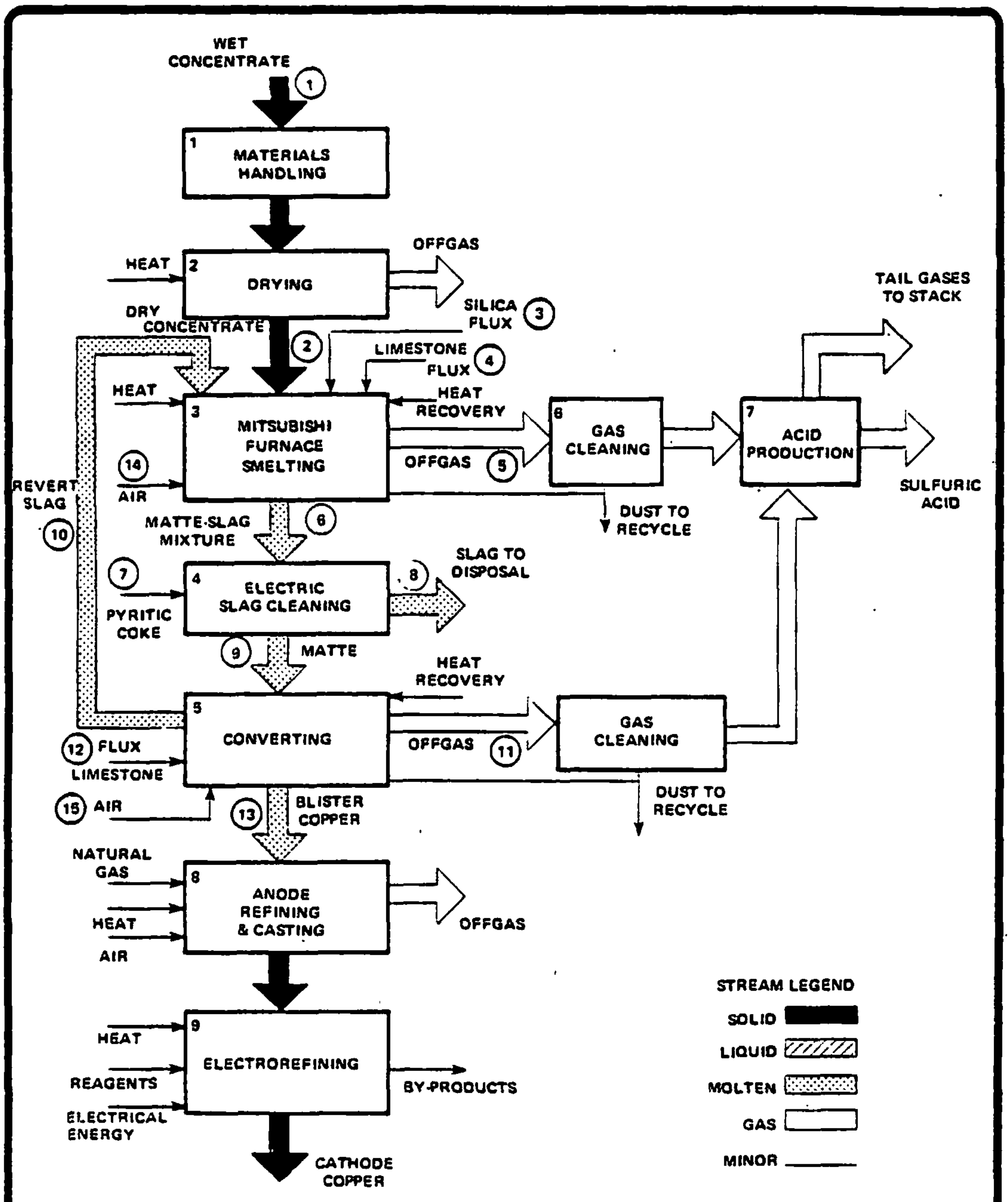

FIGURE 2.10-1 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

In the furnace the charge is smelted to produce matte and slag. The slag layer is extremely thin, and the molten bath consists mostly of matte containing 60-65% copper, thus making possible a high oxygen efficiency, top blowing operation with relatively low pressure blast (Nagano, 1976). Oxygen enrichment of the air to the smelter is about 33%, and the fuel requirement for the smelter is low. Air can also be preheated for further efficiency, although this is not currently done at Naoshima.

The smelted mixture continuously overflows through an outlet hole and is transferred to the slag cleaning furnace, which is an electric furnace that separates the mixture into slag and matte. Small amounts of reducing agents, pyrites, and/or coke breeze are added to reduce further the copper content in the slag. At Naoshima, only coke breeze is added at present in order to minimize the sulfur emissions.

The slag, containing 0.5-0.6% copper, is continuously tapped through a slag overflow hole, granulated with water and discarded.

The matte is gravity-fed to the converting furnace where it is continuously converted into blister copper by blowing oxygen-enriched (23%) air and limestone flux (and cement copper as a cooling material when required), through lances.

Blister copper is siphoned out of the converting furnace, completely separated from the slag, to a holding furnace from which it is then tapped and sent to an anode furnace.

The converter slag, containing 10-20% copper, is tapped from the converter, water-granulated, dried, and then returned to the smelting furnace.

Gases from the smelting and converting furnaces contain 14-15% sulfur dioxide and are cooled to approximately 350°C through respective waste heat boilers. The gases from the boilers are combined, sent to a Cottrell precipitator for removal of dusts, and then sent to an acid plant.

Dusts can be treated in two ways, depending on the amount of impurities in the concentrates. When treating concentrates with a low content of impurities, dusts from the furnaces and precipitator are recycled back to the smelting furnace. When concentrates contain a high amount of impurities, economical recovery of dusts from the system for subsequent recovery of lead and zinc is possible (Suzuki, 1973).

Naoshima uses computer control of the process for sampling and analyzing feed materials, for adjustment of the flux and air ratios as necessary, and for adjustment of the firing rate for temperature control in the furnace.

2.10.3 Material Balance

Table 2.10-1 shows the material balance for the continuous Mitsubishi smelting and converting process.

2.10.4 Energy Requirements

Table 2.10-2 and 2.10-3 show the level I and level II energy requirements for the Mitsubishi continuous smelting and converting process.

TABLE 2.10-1 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		DRY CONCENTRATE		SILICA FLUX		LIMESTONE FLUX		SMELTER GASES	
COMPOSITION	wt.	wet wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.9944	22.5	0.9944	24.9						
Fe	1.1139	25.2	1.1139	27.8	0.0093	1.4	0.000	0.8		
S	1.233	27.9	1.233	30.8						
O_{Fe}*	0.0186	0.4	0.0186	0.5	0.004	0.6	0.0003	0.3		
S_iO_2	0.3433	7.8	0.3433	8.6	0.600	90.0	0.0022	2.1		
Al_2O_3	0.1372	3.1	0.1372	3.4	0.0267	4.0				
CaO + MgO	0.1165	2.6	0.1165	2.9	0.0133	2.0	0.0575	54.9		
Others	0.0207	0.5	0.0207	0.5	0.0133	2.0				
H_2O	0.4419	10.0	0.0221	0.6					0.0736	1.4
SO_2									1.777	33.7
O_2									0.0173	0.3
CO										
CO_2							0.0439	41.9	0.4386	8.3
N_2									2.9648	56.3
TOTAL	4.4195	100.00	3.9997	100.00	0.6666	100.00	0.1047	100.00	5.2713	100.00
TEMP. (°F)	60		190		60		60		2200	
STATE		S		S		S		S		G

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.10-1 (cont.) MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	MATTE-SLAG		COKE		DISPOSAL SLAG		MATTE		REVERT. SLAG	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.0484	23.5			0.0144	0.5	1.034	64.1	0.054	14.2
Fe	1.2705	28.5	0.0014	7.0	1.1256	39.2	0.1463	9.1	0.1466	38.3
S	0.3568	8.0	0.0002	1.0	0.0087	0.3	0.3528	21.9	0.0046	1.2
O_{Fe}*	0.3392	7.6	0.0003	1.5	0.3187	11.1	0.0207	1.3	0.0593	15.6
S_iO_2	0.9483	21.3	0.0008	4.0	0.9490	33.0			0.0029	0.8
AL_2O_3	0.1639	3.7			0.1639	5.7				
CaO + MgO	0.2685	6.0			0.2686	9.3			0.0811	21.3
Others	0.0669	1.5	0.0172	86.5	0.0255	0.9	0.0586	3.6	0.0328	8.6
H_2O										
SO_2										
O_2										
CO										
CO_2										
N_2										
TOTAL	4.4625	100.00	0.0199	100.00	2.8744	100.00	1.6124	100.00	0.2813	100.00
TEMP. (°F)	2200		60		2200		2200		2372/60	
STATE		L		S		L		L		L/S

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.10-1 (cont.) MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	CONV. OFF GAS		LIMESTONE FLUX		BLISTER COPPER		SMELTER AIR		CONVERTER AIR	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu					0.980	98.0				
Fe			0.0011	0.70	0.001	0.1				
S					0.009	0.9				
O_{Fe}*			0.0004	0.30	0.0015	0.2				
S_iO_2			0.0029	2.0	0.0085	0.8				
AL_2O_3										
CaO + MgO			0.812	55.0						
Others										
H_2O										
SO_2	0.6778	29.3								
O_2	0.1279	5.5					0.9306	40.9	0.5523	28.6
CO										
CO_2	0.1255	5.4	0.062	42.0						
N_2	1.3807	59.8					1.3427	51.1	1.3807	71.4
TOTAL	2.3119	100.00	0.1476	100.00	1.000	100.00	2.2733	100.00	1.933	100.00
TEMP. (°F)	2100		60		2372		60		60	
STATE	G		S		L		G		G	

*Oxygen associated with FeO and Fe_3O_4

**Includes carbon from coke

TABLE 2.10-2 **ENERGY REQUIREMENTS** Level 1

MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	63.1	0.0105	0.663
2	Drying				
	A) Fuel Oil	GAL	9.271	0.139	1.289
3	Smelting				
	A) Fuel Oil	GAL	39.9	0.139	5.546
	B) Electrical Energy	KWH	150.0	0.0105	1.575
4	Electric Slag Cleaning				
	A) Electrical Energy	KWH	128.1	0.0105	1.345
5	Converting				
	A) Fuel Oil	GAL	1.8	0.139	0.250
	B) Electrical Energy	KWH	135.0	0.0105	1.418
*	Waste Heat Recovery				
	A) Steam	LB	5713	0.0014	-7.998
*	Heating Launders				
	A) Natural Gas	SCF	918.0	0.001	0.918
6	Gas Cleaning				
	A) Hot Gas Cleaning (11.4% SO_2)	Thous. SCF	256.3	0.00336	0.861
	B) Cold Gas Cleaning (11.4% SO_2)	Thous. SCF	256.3	0.00126	0.323
	C) Fugitive Emissions Control	KWH	85	0.0105	0.893
7	Acid Plant				
	A) Smelter and Converter (9.0% SO_2)	Thous. SCF	323.9	0.0126	4.081
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095
8,9	Anode Furnace and Electrorefining	TONS OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	17.083

* Not shown on flowsheet

TABLE 2.10-3

ENERGY REQUIREMENTS

MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

Level 2

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Smelting				
	A) Silica Flux	TON	0.691	0.042	0.029
	B) Limestone Flux	TON	0.106	0.104	0.011
	C) Oxygen	TON	0.201	3.78	0.760
4	Electric Slag Cleaning				
	A) Coke	TON	0.020	31.5	0.630
	B) Electrodes	TON	0.001	160	0.160
5	Converting				
	A) Oxygen	KWH	0.138	3.78	0.522
	B) Limestone Flux	TON	0.151	0.104	0.016
*	Water Pollution Control				
	A) Lime	LBS	30	0.0027	0.081
	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	2.677

*Not shown on flowsheet

2.10.5 Effect of Oxygen Enrichment on Energy Consumption

Table 2.10-4 shows the effect of oxygen enrichment on energy consumption. Increased utilization of tonnage oxygen in smelting process increases smelting rate, decreases fuel consumption and decreases off gas volume and consequently size of gas treatment facilities. The effect of oxygen enrichment to 50% has been tested (Suzuki, 1979).

2.10.6 Conclusions

The oxidant in the smelting and converting furnaces is oxygen-enriched air (30-36% oxygen in smelting and 25-28% in converting). The fuel requirement could be lowered by increasing the level of oxygen enrichment. Waste heat boilers are used to recover heat from both the smelter and converter off-gas. In the Mitsubishi process, the intermediate products, i.e., matte and slag, are transferred through sealed launders, thus eliminating the fugitive emissions that accompany matte tapping, charging of converter, and slag skimming, which are all inevitable in conventional converter operation. Consequently, the fugitive emissions problem is considerably reduced.

2.10.7 References

Kellogg, H.H. and J.M. Henderson, "Energy Use in Sulfide Smelting," Extractive Metallurgy of Copper, International Symposium on Copper Extraction and Refining, Las Vegas, Nevada, February 22-26, 1976.

"Mitsubishi Develops New Copper Smelting Process," *American Metal Market*, November 16, 1971, pp. 1-5.

"MI Process for Continuous Copper Smelting and Converting," Mitsubishi Metal Corporation publication.

"Mitsubishi Metal Builds New Copper Smelter on Tidewater," *World Mining*, Vol. 16(12), 2963, p. 60.

Nagano, T. and T. Suzuki, "Commercial Operation of Mitsubishi Continuous Copper Smelting and Converting Process," paper presented at the 105th AIME Annual Meeting, Las Vegas, Nevada, February 1976.

Suzuki, T. and T. Nagano, "Development of New Continuous Copper Smelting Process," Joint Meeting MMIJ-AIME, Tokyo, Japan, May 24-27, 1972.

Suzuki, T., "The Mitsubishi Process — Operation of Semi-Commercial Plant," The Latin American Congress of Mining and Extractive Metallurgy, Santiago, Chile, August 26-September 3, 1973.

Suzuki, T., I. Oyama, and T. Shibasaki, "Computer Control in Mitsubishi Continuous Copper Smelting and Converting Process," the 103rd AIME Annual Meeting, Dallas, Texas, February 1974.

Suzuki, T. and M. Goto, "Recent Improvements in Mitsubishi Process Operation," Annual Meeting of Metallurgical Society of AIME, Tucson, Arizona, December, 1979.

TABLE 2.10-4

EFFECT OF OXYGEN ENRICHMENT ON FUEL USE IN MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

	This Study	Mitsubishi
Smelting Furnace		
Matte Grade (%)	64.1	65
Oxygen Enrichment of Lance Blast (wt %)	40.9	58.3
Fuel Requirements (10^6 Btu/Ton Cathode Cu)	5.546	0.866
Tonnage Oxygen (Tons/Ton Cathode Cu)	0.201	0.838
Converting Furnace		
Oxygen Enrichment of Lance Blast (wt %)	28.6	32.9
Fuel Requirements (10^6 Btu/Ton Cathode Cu)	0.25	0.015
Tonnage Oxygen (Tons/Ton Cathode Cu)	0.135	0.193

Sources: Arthur D. Little, Inc., and Mitsubishi Metal Corp.

2.11 QUENEAU-SCHUHMANN CONTINUOUS SMELTING

2.11.1 Introduction

The Queneau-Schuhmann (Q-S) oxygen process was proposed by Dr. Paul E. Queneau and Dr. R. Schuhmann, Jr. Their invention covers a process and apparatus which provide continuous, autogenous conversion of sulfide ore concentrates to metal in a single reactor (Queneau and Schuhmann, 1976). Dravo has the worldwide rights to the process and apparatus for copper, nickel and cobalt concentrates. For the treatment of lead concentrates, this concept is further along the path of commercialization. Its pilot plant development has been completed at the Berzelius Works in Duisburg, Germany by Lurgi as the Q-S-L (Queneau, Schuhmann, Lurgi) process for the direct production of lead (Queneau, 1977). This pilot plant was operated in the batch mode (as countercurrent continuous flow was not possible) and the results obtained are reported to be promising (Journal of Metals, 1978). A decision was made to build a Q-S-L demonstration plant of 50,000 tons per year bullion capacity (Schwartz et al., 1980) and is now under construction.

2.11.2 Process Description

The following description is for a *conceptual* copper plant and is based on the literature and discussions with Dr. Queneau. Figure 2.11-1 is a flowsheet of the process.

The Q-S converter is a long, gently sloped vessel of circular cross section with blister copper discharge at one end and slag and gas discharge at the other. Autogenous converting is carried out by staged bottom blowing with oxygen in one main section of the furnace toward the blister copper discharge end. Slag cleaning is carried out in the other main section towards the slag discharge end by bottom blowing with a coal-sulfur dioxide-oxygen mixture, which the inventors term 'deconverting.' The vessel is mounted for slow oscillation about its horizontal axis and is tiltable for access to and maintenance of the submerged oxygen injectors. Under operating conditions the molten bath layers separate out into matte, slag, and a pool of crude copper. The vessel is sloped and stepped longitudinally for the disposition of matte and metal and to inhibit their back flow towards the slag cleaning region.

The reactor geometry, the feeding arrangement for solids and fluids and the location of the submerged injectors are designed to establish a multi-stage sequence of progressive oxidation along the length of the reactor with the highest oxygen activity at the copper discharge end and the lowest oxygen activity at the slag discharge end. To achieve this lengthwise staging, matte and slag flow countercurrently, low grade matte from the slag cleaning region of the furnace joins fresh matte from incoming feed and the stream is progressively desulfurized to white metal and finally to crude copper, as it flows down slope towards discharge. Copper-rich slag from the metal discharge end with its magnetite load moves in the opposite direction, is progressively reduced and finally cleansed of copper by agitation with a mixture of sulfur dioxide, coal and oxygen followed by settling.

The several oxygen injectors extend through the refractory lining of the vessel and introduce oxygen below the matte-slag interface. Fluid shielding with hydrocarbon fluid analogous to that used in oxygen steelmaking by Eisenwerk Maximillianshuette. In the Q-S process a non-combustible, protective fluid such as nitrogen or sulfur dioxide is used instead of a hydrocarbon fluid. The sulfur dioxide is obtained by recirculating cooled off-gas from the reactor and nitrogen from the oxygen plant tail gas. The use of sulfur dioxide-protected oxygen injection makes

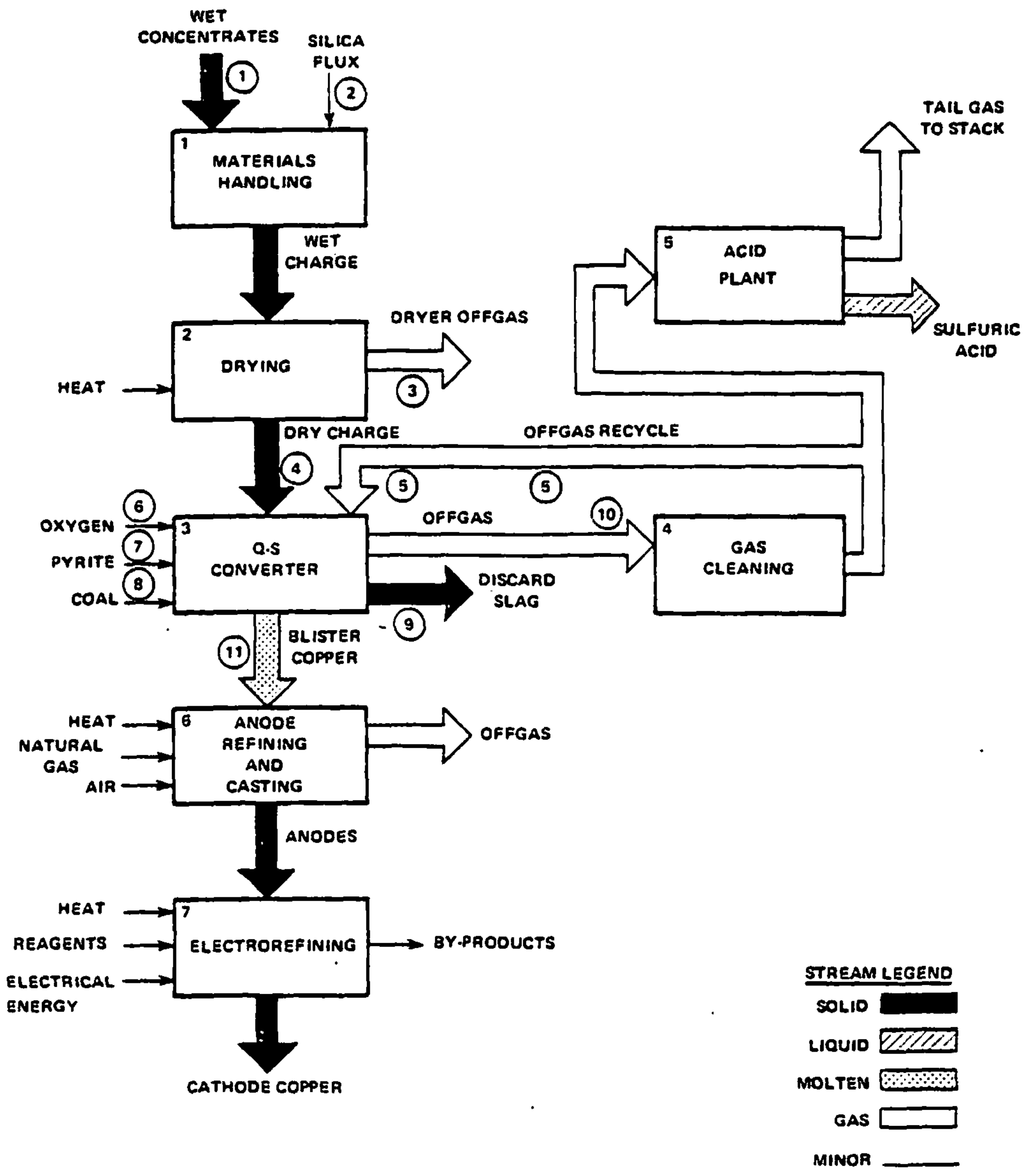

FIGURE 2.11-1 QUENEAU - SCHUHMANN OXYGEN PROCESS

possible the production of an off-gas analyzing up to 90% sulfur dioxide by volume if liquid sulfur dioxide is a marketable product.

Copper concentrates and necessary fluxes that have been dried down to less than 1% or less moisture are introduced over the bath through appropriate feeders. A substantial fraction, usually more than two-thirds, of total oxygen input usually accompanies the concentrates. The addition of concentrates is staged in the converting section, to assist in maintaining the desired chemical gradients along the length of the reactor. A relatively high ratio of oxygen to concentrate is used towards the metal discharge end, in contrast to lower oxygen ratios towards the slag cleaning end. Iron sulfide may be added without oxygen in the slag cleaning region.

Slow oscillation of the reactor increases the effective contact area between the reactants, by distributing incoming solid feed materials over the surface of the bath and by causing injected gases to sweep back and forth through it. Shell displacement is also conducive to increased refractory life in the submerged injector and slag line zones.

Slag cleaning is achieved by a controlled reversal of the converting reaction to achieve slag cleaning (termed deconverting) and is achieved by injecting powdered coal, sulfur dioxide and oxygen. The mixture lowers the ferric/ferrous ratio and the equivalent oxygen potential of the slag substantially and causes formation of low grade matte in situ by deconverting reactions such as

$$\mathrm{FeO\ (slag)} + \mathrm{SO_2} + 3\,\mathrm{CO} \rightarrow \mathrm{FeS\ (matte)} + 3\,\mathrm{CO_2} \tag{2.11.1}$$

$$\mathrm{Cu_2O\ (slag)} + \mathrm{FeS\ (matte)} \rightarrow \mathrm{Cu_2S\ (matte)} + \mathrm{FeO\ (slag)} \tag{2.11.2}$$

It is claimed that a slag containing 0.2% Cu can be obtained which can be discarded.

An optional feature carried out in a separate apparatus utilizes deconverting for off-gas sulfur fixation as FeS. The sulfur dioxide, together with a carbonaceous reducing agent and oxygen, is injected into molten converter slag to produce liquid iron sulfide which is cast into pigs for sale or stockpile. However, in order to fix all the sulfur in this form an additional source of iron is normally needed with most U.S. chalcopyrite concentrates.

The Q-S converter will require relatively sophisticated control instrumentation to permit close approach to steady state operation with optimum chemical and thermal conditions in all sections. Primary stoichiometric control is based on accurately metering, analyzing, and proportioning concentrates, fluxes, carbonaceous reducing agent, and gases to yield the desired products. Short term fluctuations are accommodated by accumulation or depletion of matte and metal in the converter.

A convenient criterion for this purpose is the ratio of ferric iron to total iron in the slag determined by slag sampling and analysis. The ferric iron to total iron is expected to vary from above about 0.2 at the metal discharge end, down to about 0.05 at the slag discharge end (converting copper sulfide concentrates at 1300°C). Other control means include monitoring of product weights, chemical analysis and temperatures. The temperature can be controlled by varying the quantity of recirculated sulfur dioxide, nitrogen content of oxygen, by water injection and in some cases by feeding the concentrate or flux as a slurry.

The excess heat could be more effectively used to melt cement copper or copper scrap. The reactor is designed to operate at a relatively high temperature level, under standard cooling means for refractory protection.

The high operating temperatures, which are characteristic of this process, allow the use of slags high in magnetite and silica during converting and high in silica during deconverting while maintaining the required fluidity needed for rapid reaction and clean phase separation.

A Q-S reactor capable of processing at least 1200 metric tons per day of chalcopyrite concentrate to crude copper is 20 feet in diameter and 150 feet long and has a 1% slope (Queneau, 1977). As most of the oxygen is used for flash oxidation above the bath, the independently regulatable injectors can be spaced six feet or more apart (compared to six inches between Peirce-Smith tuyeres). The gas flow rate through the individual Q-S injector can be half the usual flow rate through a Peirce-Smith tuyere. This results in the formation with minimum splash of an orderly series of moderately turbulent reaction pools separated by calmer settling zones (similar in concept to a mixer-settler configuration). In addition, ample settling basins are provided at both ends of the reactor and between the converting and deconverting operations.

2.11.3 Material Balance

Table 2.11-1 presents the material balance for the Q-S oxygen process. It is based on limited data available in literature and discussions with Dr. Queneau. In comparison to some of the other material balances presented for other pyrometallurgical processes, this material balance is more speculative and would have to be revised, if necessary, when more data become available.

2.11.4 Energy Requirements

Table 2.11-2 and Table 2.11-3 present the Level I and Level II energy requirements for the Q-S process.

2.11.5 Conclusions

The Q-S process for copper smelting is conceptual. However, laboratory scale work on phase separations is underway at United States universities. The Q-S process is perhaps a decade from commercial utilization.

As the smelting is carried out in a single reactor eliminating the need for transfer of molten intermediate products, the fugitive emissions problem is considerably reduced.

2.11.6 References

"Environmentally Clean Lead Bullion Production," *Journal of Metals,* Vol. 12, December 1978, pp. 11-12.

Queneau, P.E. and R. Schuhmann, Jr., "The Q-S Oxygen Process," *Journal of Metals,* Vol. 26(8), August 1974, p. 14.

Queneau, P.E., "Oxygen Technology and Conservation," *Metallurgical Transactions B,* Vol. 8B(3), September 1977, pp. 357-369.

TABLE 2.11-1 QUENEAU-SCHUHMANN CONTINUOUS SMELTING

(TONS PER TON BLISTER COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATES		SILICA FLUX		DRYER OFFGAS		DRY CHARGE		OFFGAS RECYCLE	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	dry wt.%	wt.	wt.%
Cu	0.9899	25.00					0.9899	19.53		
Fe	1.1087	28.00	0.0155	1.4			1.1242	22.18		
S	1.2275	31.00					1.2275	24.22		
O_{Fe}*	0.0186	0.47	0.0067	0.6			0.0253	0.50		
S_iO_2	0.3417	8.63	0.998	90.00			1.3397	26.43		
AL_2O_3	0.1366	3.45	0.0444	4.0			0.181	3.57		
CaO + MgO	0.116	2.93	0.0222	2.0			0.1382	2.73		
Others	0.0206	0.52	0.0222	2.0			0.0428	0.84		
H_2O	0.440				0.4748	44.7	0.0044			
SO_2									0.088	88.0
O_2										
CO										
CO_2					0.1367	12.9			0.0103	10.3
N_2 + Ar					0.4515	42.5			0.0017	1.7
TOTAL	4.3996	100.00	1.1089	100.00	1.063	100.00	5.073	100.00	0.100	100.00
TEMP. (°F)										
STATE										

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.11-1 (cont.) QUENEAU-SCHUHMANN CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	OXYGEN		PYRITE (FeS_2)		COAL		DISCARD SLAG		OFFGAS	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu							0.0099	0.3		
Fe			0.0513	46.6	0.0022	2.0	1.1766	35.0		
S			0.0587	53.4	0.0029	2.6	0.0134	0.4		
O_{Fe}*					0.0107	9.7	0.3639	10.8		
SiO_2					0.004	3.6	1.3437	40.0		
Al_2O_3					0.003	2.7	0.1840	5.5		
CaO + MgO					C 0.0804	73.1	0.1382	4.1		
Others					H 0.0014	1.5	0.0428	1.3		
H_2O					N 0.0053	4.8			0.0521	1.8
SO_2									2.5334	86.9
O_2	1.7018	98.0								
CO										
CO_2									0.2948	10.1
N_2 + Ar	0.0347	2.0							0.0364	1.2
TOTAL	1.7365	100.00	0.110	100.00	0.1102	100.00	3.3591	100.00	2.9167	100.00
TEMP. (°F)										
STATE										

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.11-1 (cont.) QUENEAU-SCHUHMANN CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(11)					
STREAM NAME	BLISTER COPPER					
COMPOSITION	wt.	wt.%				
Cu	0.980	98.00				
Fe	0.001	1.10				
S	0.009	0.90				
O_{Fe}*	0.0015	0.15				
S_iO_2						
Al_2O_3						
CaO + MgO						
Others	0.0085	0.85				
H_2O						
SO_2						
O_2						
CO						
CO_2						
N_2 + Ar						
TOTAL	1.000	100.00				
TEMP. (°F)						
STATE						

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.11-2 **ENERGY REQUIREMENTS** LEVEL I

QUENEAU - SCHUHMANN CONTINUOUS SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
	A) Electrical Energy	KWH	63.1	0.0105	0.662
2	Drying				
	A) Fuel Oil	GAL	10.6	0.139	1.473
4	Gas Cleaning				
	A) Hot Gas Cleaning (78.3% SO_2)	Thous. SCF	39.2	0.00336	0.132
	B) Cold Gas Cleaning	Thous. SCF	39.2	0.00126	0.049
5	Acid Plant				
	A) Smelter Off Gas (9% SO_2)	Thous. SCF	341.0	0.0126	4.297
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	12.532

*Not shown on Flowsheet

TABLE 2.11-3 **ENERGY REQUIREMENTS** LEVEL 2

QUENEAU - SCHUHMANN CONTINUOUS SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Q-S Oxygen Smelting				
	A) Oxygen	TON	1.7719	3.78	6.698
	B) Silica Flux	TON	1.131	0.042	0.048
	C) Coal	TON	0.112	25.00	2.800
*	Water Pollution Control				
	A) Lime	LBS	30.0	0.0027	0.081
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	10.095

Queneau, P.E. and R. Schuhmann, Jr., "Metallurgical Process Using Oxygen," U.S. Patents: 3,941,587, March 2, 1976; 3,988,148, October 26, 1976; 3,988,149, October 26, 1976; 3,990,889, November 9, 1976.

Queneau, P.E. and R. Schuhmann, Jr., "Apparatus for a Metallurgical Process Using Oxygen," U.S. Patent 4,085,923, April 25, 1978.

Schwartz, W.H, P. Fischer, P.E. Queneau, R. Schuhmann, Jr., "QSL — A Continuous Process for Environmentally Clean Lead Production," Lead-Zinc-Tin '80, World Symposium on Metallurgy and Environmental Control, TMS-AIME, Las Vegas, Nevada, February 24-28,1980.

Schuhmann, R., Jr. and P.E. Queneau, "Thermodynamics of the Q-S Process for Coppermaking," International Symposium on Copper Extraction and Refining, Las Vegas, Nevada, February 22-26, 1976.

2.12 AMAX DEAD ROAST-BLAST FURNACE SMELTING

This section is based on analysis provided by AMAX Base Metals Research & Development, Inc.

2.12.1 Summary

The energy requirements of the AMAX Dead Roast-Blast Furnace Process were estimated to be 19.58 million Btu's per ton of cathode copper based on a proposed 30,000 ton per year of cathode copper flow sheet.

2.12.2 Introduction

In the early production of copper using a blast furnace, the smelting of calcine or ores containing both iron and copper was discouraged because a substantial proportion of the iron would tend to be reduced with the copper and a large amount of copper would be lost in the slag. In the AMAX Dead Roast-Blast Furnace Process (Rajcevic, 1977; Opie, 1979), the dead roasting of concentrates is carried out at a temperature high enough to form a calcine containing a preponderance of ferric iron oxide as evidenced by the formation of substantial amounts of copper ferrite. During smelting, the copper oxide is reduced to copper while the iron oxide is reduced only to ferrous oxide due to the short residence time in the low column shaft of the blast furnace. The ferrous oxide reacts with silica and other gangue minerals to form the slag. A good grade blister copper is produced directly and no matte is formed as long as the concentrate is roasted to less than 1.5% sulfur.

The Dead Roast-Blast Furnace Process as shown in Figure 2.12-1 consists of the following steps:

1. The sulfide concentrate is dead-roasted in a fluid bed to remove more than 97% of the sulfur in a continuous operation similar to that employed for roasting pyrite or zinc sulfide concentrates. The SO2 gas produced (10-14%) is consistent in composition and in rate of production.
2. The roasted calcine is briquetted or pelletized with a small flux addition.

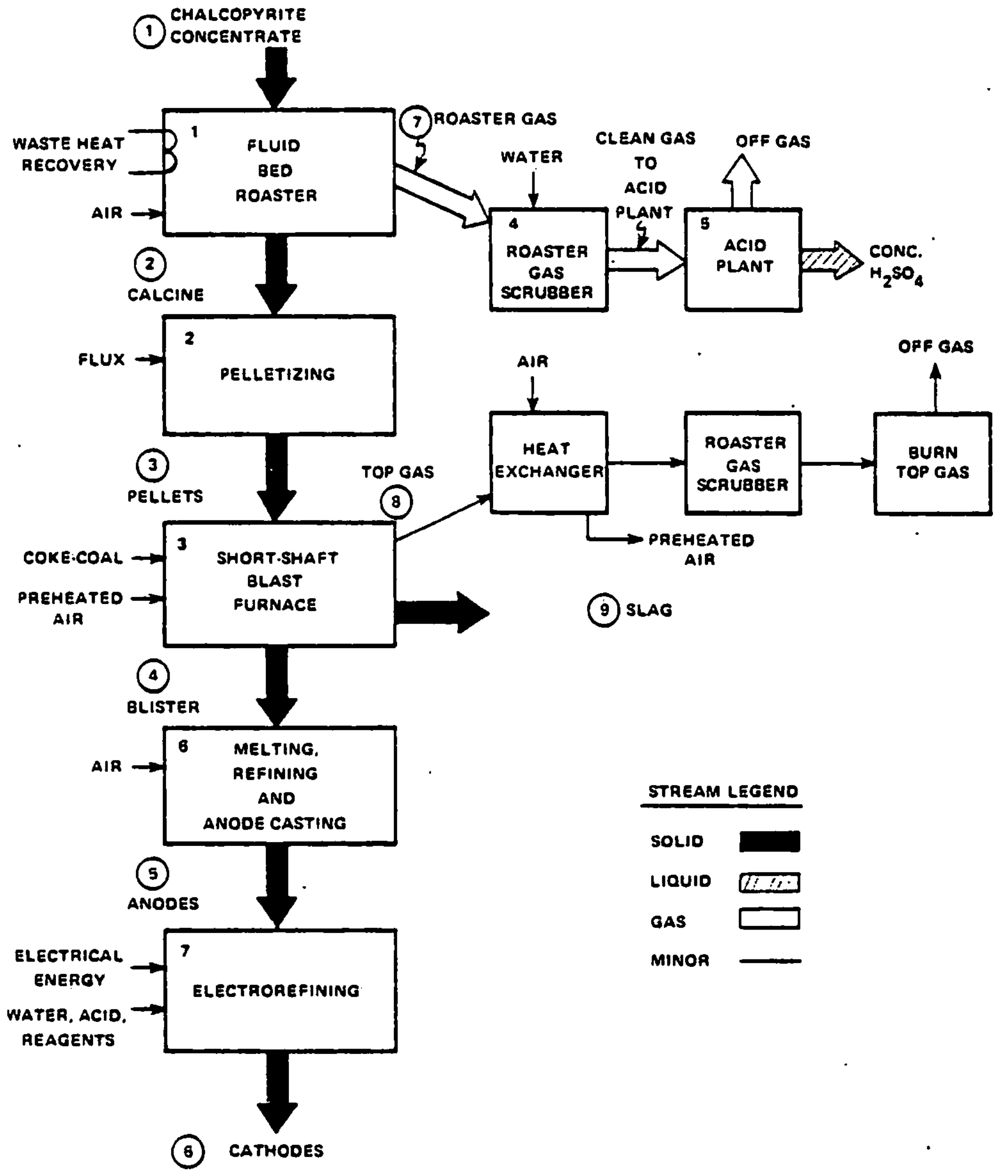

FIGURE 2.12-1 AMAX DEAD ROAST-BLAST FURNACE PROCESS

3. The agglomerates are smelted at a rapid rate in a blast furnace with a very low charge-column to produce a high-grade blister copper and a low-grade copper slag. Copper is selectively reduced from the copper-iron oxide calcine to form blister while substantially all of the iron reports in the slag.

2.12.3 Advantages of the Process

2.12.3.1 Excellent Sulfur Control

About 97% of the sulfur input to the plant is oxidized to a rich SO_2 gas of constant composition which can be converted to sulfuric acid in a relatively low cost acid plant. No matte or converter slag, saturated in SO_2, are formed, thus the fugitive emissions resulting from transfer of these materials need not be contended with. The sulfur in the calcine feed to the blast furnace, amounting to about 3% of the sulfur in the concentrate, distributes between slag, blister and furnace gases. Sulfur can be forced into the furnace gases by enriching the blast with oxygen. However, a major portion of the sulfur in the furnace gases reacts with volatile metal oxides forming sulfates which are collectable as solids in a baghouse resulting in furnace emissions which meet current SO_2 standards.

2.12.3.2 Low Capital Costs

Compared to commercially proven matte smelting processes, capital costs have been estimated to be lower by 20 to 40 percent depending on scale. The smaller the scale, the greater the savings. These lower costs result from:

1. A simplified SO_2 gas collection system.
2. A smaller acid plant because SO_2-containing gases from the roaster are highly concentrated, smaller in volume, and continuously generated.
3. A water-jacketed furnace design requiring no refractories in the shaft. Because of the rapid smelting rate, the furnace is small compared to other smelting furnaces.
4. Simplified plant layout because no conventional crane aisle is needed for ladle transfer. Converters are not required.
5. No need for slag cleaning if a 96% copper recovery is economically acceptable.

2.12.3.3 High Metal Recoveries

Recovery of copper and precious metals in a good grade blister is as high as 96% without slag cleaning. By cleaning the slag in either an electric furnace, or by grinding and flotation, recoveries can exceed 98%. It is believed that a simple two-stag settler with the second stage operating with a reducing gas or carbonaceous cover will result in a throwaway slag with copper losses competitive with those from conventional matte smelters. Table 2.12-1 summarizes materials balance data.

2.12.3.4 Energy Conservation

The fluid-bed roaster with a properly designed waste-heat boiler has the potential of producing enough electricity or steam to supply the major power requirements of the plant (Opie, 1979). Furthermore, because of the low charge column in the blast furnace, low-grade coke or mixtures of coke and other solid carbonaceous fuels can be used. Additional energy if needed could be recovered from the high temperature furnace off-gases. Tables 2.12-2 and 2.12-3 show an energy balance, following the procedure used by H.H. Kellogg (Kellogg, 1976).

TABLE 2.12-1 DEAD ROAST - BLAST FURNACE

(TONS PER TON BLISTER COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		CALCINE		PELLETS		BLISTER		ANODES	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.020		1.020		1.020		0.980	98.00	0.980	100.00
Fe	0.902		0.092		0.902		0.010	1.00		
S	1.078		0.010		0.010		0.010	1.00		
S_1O_2	0.275		0.275		0.422					
AL_2O_3										
CAO + MgO										
Others	0.186		0.823		0.823					
H_2O										
SO_2										
SO_3										
CO_2										
O_2										
N_2										
CO										
R										
TOTAL	3.461		3.030		3.177		1.000	100.00	0.980	100.00
Temp (^oF)	77		1562		77		2552		77	
STATE	S		S		S		L		S	

TABLE 2.12-1 (cont.) DEAD ROAST - BLAST FURNACE

(TONS PER TON BLISTER COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		
STREAM NAME	CATHODES		ROASTER GAS		TOP GAS		SLAG		
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	
Cu	0.980	100.00					0.04		
Fe							0.892		
S									
S_IO_2							0.422		
AL_2O_3									
CAO + MgO									
Others							0.578		
H_2O			1.892	17.69	0.01	0.30			
SO_2			2.039	19.06					
SO_3			0.137	1.28					
CO_2			0.068	0.64	1.265	37.83			
O_2			0.137	1.28					
N_2			6.314	59.04	1.863	55.71			
CO					0.206	6.16			
AR			0.108	1.01					
TOTAL	0.980	100.00	10.695	100.00	3.344	100.00	1.732	100.00	
TEMP (^oF)	77		1562		2552		2552		
STATE	S		G		G		S		

TABLE 2.12-2 **ENERGY REQUIREMENTS** Level 1

AMAX DEAD ROAST - BLAST FURNACE

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roasting				
	A) Air Compressor	Kg	8402	0.000102	0.857
	B) Fuel, Start Up Only	MILLION BTU	0.200	1.00	0.200
	C) Waste Heat Recovery	MILLION BTU	4.728	1.00	4.728
2	Pelletizing	KWH	50	0.0105	0.525
3	Smelting				
	A) Core-Coal Blend	LBS	880	0.01236	10.876
	B) Blast Compressor (Air)	Kg	2186	0.000579	1.266
	C) Top Gas Heat Recovery	Kg	2.14	0.23271	-0.498
4	Gas Handling				
	A) Roasted and Smelter	MILLION SCF	0.3341	2.52	0.842
5	Acid Manufacture	KWH	398.48	0.0105	4.184
6	Anode Casting	TON	1.00	1.346	1.346
7	Electrorefining				
	A) Electrical	KWH	272.38	0.0105	2.86
	B) Process Heating	LBS	1300	0.0014	1.82
				TOTAL	19.54

TABLE 2.12-3 **ENERGY REQUIREMENTS** Level 2

AMAX DEAD ROAST - BLAST FURNACE

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	<u>Smelting</u>				
	A) Flux	TON	0.15	0.10	0.015
6	<u>Melting and Refining</u>				
	A) Flux	TON	0.10	0.10	0.010
7	<u>Electrorefining</u>				
	A) Acid and Reagents	TON	0.0165	0.83	0.014
				TOTAL	0.039

2.12.3.5 Flexibility

Although it is prudent to operate all units of the plant together, if desired the roaster-acid plant and briquetting or pelletizing facility could still be operated when the blast furnace is shut down and vice versa as long as some storage of furnace charge is allowed for. This makes possible the alternative of locating the roaster-acid plant-agglomerating facilities near a mine site where acid could be used for treating oxide ore. The blast furnace, in turn, could be located near a copper refinery or a cheap source of coal. The calcine agglomerates could also serve as feed for a secondary smelter.

2.12.3.6 References

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2.13 SEGREGATION PROCESS

2.13.1 Introduction

This report contains estimates of the material and energy requirements for a copper extraction process. The process is commonly called and is referred to in this report as the "segregation" process. The technique employed for copper extraction is similar to that of the TORCO process used for processing refractory oxide ores (Mackay and Gibson, 1969; Heath, 1970; Pinkney, 1969). These ores are not amenable to conventional froth flotation or to acid leaching. The segregation process considered herein, however, is modified for treatment of chalcopyrite concentrates. A detailed description of such a modified process is given in Opie, Coffin and Cusanelli (1977).

2.13.2 Process Description

The main processing features are (1) a roasting of the concentrates to oxidize the copper and iron sulfide minerals and (2) a segregation step in which the calcine from the roast is reacted with a mixture of coal and salt (NaCl) at 870°C (see Figure 2.13-1). Enough excess heat is produced

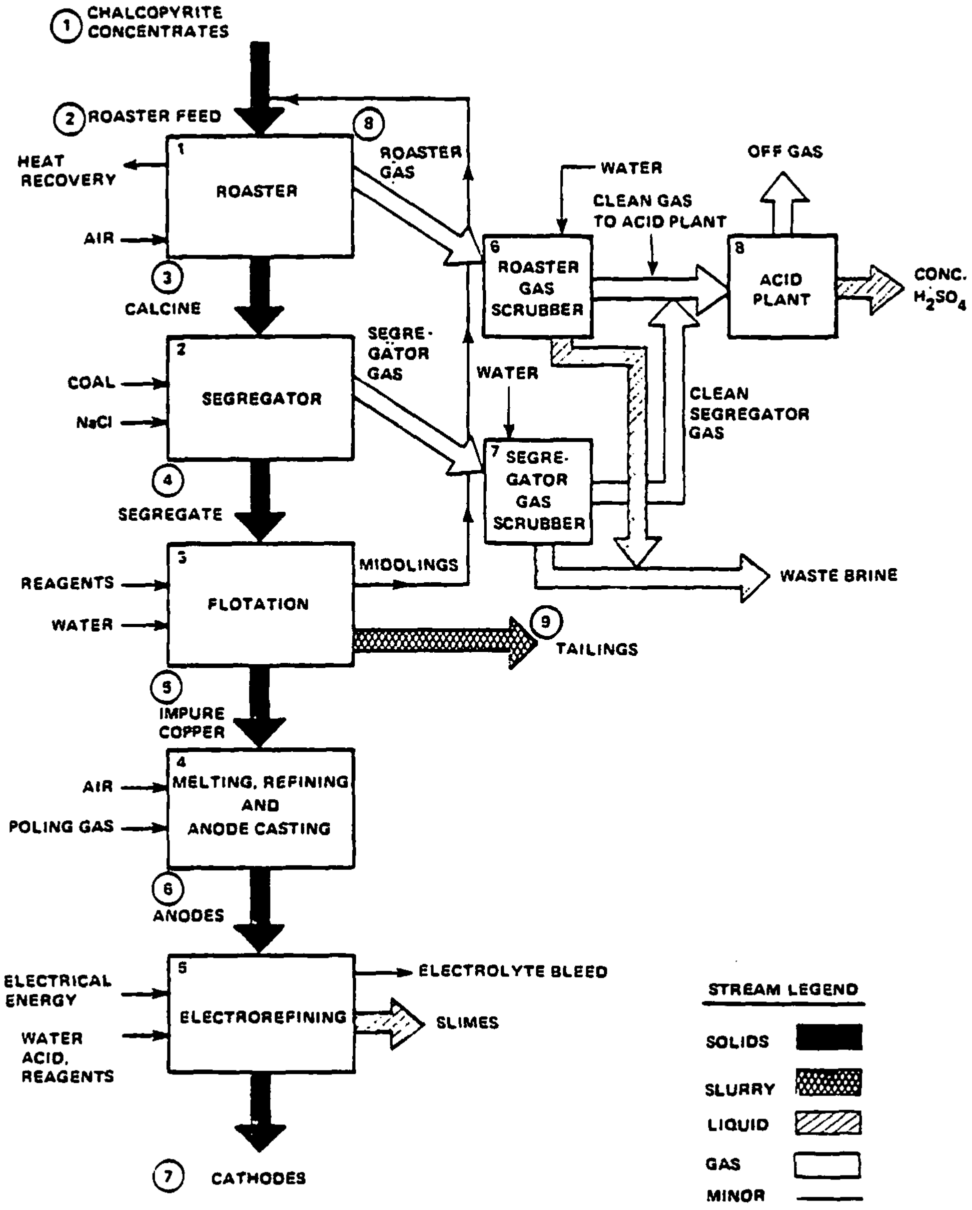

FIGURE 2.13-1 SEGREGATION PROCESS

from the roasting reactions to allow significant waste heat recovery. The roaster and segregator equipment is advantageously designed so that the temperature of the calcine can be maintained during the segregation step by heat loss from the roaster. The product from the segregation step is a carbonous material with the copper in the form of discrete particles of up to 1-mm diameter. This segregate is amenable to froth flotation. Further processing consists of segregate division, a gangue and an impure copper steam, by flotation and of electrorefining the impure copper to a wire-grade or cathode-grade product.

The major stoichiometric relationships for the processing reactions are as follows:

Roaster Operation, Process Step 1

a. Chalcopyrite combustion

$$2CuFeS_2 + 6.5O_2 \rightarrow 2CuO + Fe_2O_3 + 4SO_2 \qquad (2.13.1)$$

b. Pyrite combustion

$$2FeS_2 + 5.5O_2 \rightarrow Fe_2O_3 + 4SO_2 \qquad (2.13.2)$$

Copper Segregation, Process Step 2

Sodium chloride, reacting with water vapor and with the acid constituents of the gangue, produces hydrogen chloride which reacts with the copper minerals. Copper is volatilized as cuprous chloride, diffuses to the surface of the coal, and is immediately reduced by hydrogen produced from the volatile fraction of the coal or by the water-gas reaction. Hydrogen chloride is regenerated, and a new cycle of reaction begins. In this way, a small amount of sodium chloride is used to transfer the copper from the gangue and copper minerals to the surface of the coal particles (Rey, 1967).

Reaction Sequence

$3CuO + 3HCl + 1.5H_2 \rightarrow Cu_3Cl_3 + 2H_2O$	chlorination	(2.13.3)
$1.5C + 3H_2O \rightarrow 1.5CO_2 + 3H_2$	water-gas reaction	(2.13.4)
$Cu_3Cl_3 + 1.5H_2 \rightarrow 3Cu + 3HCl$	copper reduction	(2.13.5)
$3CuO + 1.5C \rightarrow 3Cu + 1.5CO_2$		(2.13.6)

2.13.3 Material Requirements Evaluation

Estimates of material and energy requirements for a modified segregation process appropriate for the treatment of chalcopyrite concentrates are summarized by process step and totaled in Tables 2.13-1, 2.13-2, and 2.13-3. The process considered is based on descriptions provided by (Opie, et al., 1977) and by (Rampacek, et al., 1959). For a modern application of the segregation technique for the extraction of copper from chalcopyrite concentrates, a 98% recovery of copper is feasible (Opie, et al., 1977). Flotation, electrorefining, gas scrubbing, and sulfuric acid recovery steps are added as would constitute a complete process flowsheet. Figure 2.13-1 depicts the process steps with designators for each process element. The summary of calculated material flows is listed in Table 2.13-1.

TABLE 2.13-1 SEGREGATION PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		ROASTER FEED		CALCINE		SEGREGATE		IMPURE COPPER	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.00	25.00	1.176	24.09	1.176	26.77	1.176	27.52	0.980	83.97
Fe	1.118	27.95	1.559	31.93	1.559	35.50	1.559	36.48	0.01	0.86
S	1.245	31.13	1.245	25.50	0.010	0.23	0.010	0.23	0.01	0.86
C			0.020	0.41			0.186	4.35	0.167	14.31
SiO_2										
AL_2O_3										
CaO + MgO										
Others	0.637	15.92	0.882	18.07	1.647	37.50	1.343	31.42		
H_2O										
SO_2										
SO_3										
O_2										
CO										
CO_2										
N_2										
TOTAL	4.00	100.00	4.882	100.00	4.392	100.00	4.274	100.00	1.167	100.00
TEMP. (°F)	70°		70°		1600°		1600°		70°	
STATE	S		S		S		S		S	

TABLE 2.13-1 (cont.) SEGREGATION PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	ANODES		CATHODES		ROASTER GAS		TAILINGS		MIDDLINGS	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%		
Cu	0.980	100.00	0.980	100.00			0.020	0.89	0.176	19.73
Fe							1.118	50.00	0.441	49.44
S										
C									0.02	2.24
S_iO_2										
AL_2O_3										
CaO + MgO										
Others							1.098	49.11	0.255	28.59
H_2O					0.667	21.95				
SO_2					2.412	0.89				
SO_3					0.098	6.07				
O_2					0.225	0.62				
CO										
CO_2					0.069	2.05				
N_2					7.520	68.42				
TOTAL	0.980	100.00	0.980	100.00	10.991	100.00	2.236	100.00	0.892	100.00
TEMP. (°F)	70°		70°		1600°		70°		70°	
STATE	S		S		G		S		S	

TABLE 2.13-2 **ENERGY REQUIREMENTS** Level 1

SEGREGATION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roaster				
	A) Waste Heat Recovery	BTU	-4.58	1.00	-4.58
	B) Fuel (start up only)	BTU	0.2	1.00	0.20
2	Segregator				
	A) Coal	TON	0.33	25.00	8.25
3	Flotation				
	A) Electrical	KWH	22.5	0.0105	0.236
4	Melting, Refining and Anode Casting				
	A) Heating and Melting (Fuel Oil)	GAL	19.5	0.150	2.925
	B) Poling Gas	SCF	225	0.0010	0.225
5	Electrorefining				
	A) Electrical	KWH	272	0.0105	2.856
	B) Process Heating (Steam)	LBS	1300	0.0014	1.820
6,7	Gas Scrubbers				
	A) Electrical	KWH	62	0.0105	0.651
	Ancillary Loads				
	A) Electrical	KWH	50	0.0105	0.525
8	Acid Plant	KWH	398.48	0.0105	4.184
*	Fugitive Emissions Control	KWH	340.00	0.0105	3.570
				TOTAL	20.862

TABLE 2.13-3

Level 2

ENERGY REQUIREMENTS

SEGREGATION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Segregator				
	A) NaCl	TON	0.022	0.49	0.011
3	Flotation				
	A) Reagents	LBS	3.26	0.02	0.065
4	Melting, Refining and Anode Casting				
	A) Flux	TON	0.1	0.76	0.076
5	Electrorefining				
	A) Acid and Reagents	TON	0.0165	0.83	0.014
	B) Glue	TON	0.00003	40.00	0.0012
	C) Thiourea	TON	0.00003	40.00	0.0012
	D) Hydrochloric Acid	TON	0.000002	9.25	0.00002
				TOTAL	0.168

2.13.4 Energy Requirements Evaluation

A summary for the energy requirements for the process is listed in Tables 2.13-2 and 2.13-3. The energy evaluation is based on the material summary presented above. Table 2.13-2 is a listing of "Level-1" requirements. The listing is on a modular basis in sequential processing order. At "Level 1," the chemicals and other consumables in the process are not included except for the fuel used. Table 2.13-3 is a listing of "Level 2" energy requirements — chemicals, fluxes, refractories and other consumables used on a continuous basis in association with the process. Energy equivalent estimates are included in the tables and the equivalent fuel requirements are calculated and summed. This information supports all values given in the tables, but is too extensive for inclusion as footnotes.

The energy requirements presented in Tables 2.13-2 and 2.13-3 are evaluated with the consideration that the process is operated in a conventional manner. The totals are termed "operational" in the above summary table. The operational estimate does not include special processing features for economizing to reduce energy consumption. For an estimate that does consider special features for energy reduction (a "theoretical" estimate), the recovery of coal may be considered. Since less than half of the coal fed to the segregator is consumed in the copper recovery reactions (37%), a significant energy reduction would occur by the recovery and recycle of unreacted coal. The potential for Level-1 energy requirement reduction is 5.43 million Btu/ton product (calculated from energy equivalent values given in Table 2.13-2). The resulting Level-1 theoretical energy requirement is 8.03 million Btu/ton product.

2.13.5 Discussion

Historically, the segregation step was discovered in 1923 during experimental work in which oxide ores of copper were being treated with coal to reduce the copper to the metallic state prior to ammoniacal leaching (Moulden and Tapin, 1928; Rey, 1935 and 1936). By 1931, the technique had been further developed by the construction of two plants in Africa for treating oxide ores. One plant was built at Southern Rhodesia by the Minerals Separation Company (50 tons of ore/day). The other plant was built at Katanga in the Belgian Congo by the Union Miniere de Haut Katanga (350 tons of ore/day). Recovery was reported as about 87% on the Minerals Separation Company plant. No data is available on the Union Miniere de Haut Katanga plant. Both plants closed after a short period of operation because of mechanical and economical difficulties (Rampacek, et al, 1959; Rey, June 1967 and March 1968).

Since the early development of the segregation technique, many investigators have been interested in the perfection of methods and equipment (Rey, 1935, 1936, 1967) evaluated the treatment of low-grade oxide ores and mixed sulfide-oxide ores. Sutulov (1963) has evaluated the factors of time, temperature, and coke and salt percentages. His results show that the segregation process could be an alternative to beneficiation. McKinney and Evans (1963) have demonstrated that it is technically feasible to apply the process to oxide ores in a direct-fired rotary kiln; thus, rendering the method more attractive for commercial application. The effects of different salts and various additions of salts on the volatilization of copper was investigated by McKinney and Waddleton (1962) and Marcuson (1978). Pollard and Pease (September 1960, March 1961) report on a 1-ton/hour pilot plant constructed by the Lampa Mining Co., Ltd. at the Berenguela Mine, Peru. Silver was also extracted, and the plant development was considered as generally suitable for any ore that may be segregated. Pinkney and Plint (1967, 1968), Pinkney (1969), Mackay and Gibson (March 1968, December 1968 and September 1969), and Heath (1970) report on the treatment of refractory ores with the TORCO segregation process developed in South Africa. Freeman (1960, 1961) reports on the processing of silicate ores at the Hecla Mining Co. and El Paso Natural Gas Co., Lakeshore Copper Property, Arizona.

Highly significant aspects in the evaluation of energy requirements for the segregation process are the recovery of waste heat from the roaster, the consumption of coal in the segregator, the melting-refining-anode-casting energies, and the energy for electrorefining. The first two items, heat recovery and coal consumption, are sensitive to chalcopyrite concentrate composition and, to some extent, on process design considerations. The latter two items are mainly dependent on the production rate of cathodes. The sensitivity of the processing energy requirements is such that a concentrate composition change resulting in a 10% reduction of waste heat recovery increased the energy requirements by 6%.

2.13.6 Conclusions and Recommendations

As evidenced by the process report by Opie, et al (1977), the Opie and Coffin patent (1974) on roasting and solid state segregation reduction of sulfide concentrates, and the many other researchers referenced, a segregation process for the recovery of copper from chalcopyrite concentrates is discernible. The processing scheme and material flows are well defined from past research efforts. Based on this earlier information, the evaluation presented in this study clearly defines the process energy requirements. A presentation of a breakdown of the energy assessment and an evaluation of a "theoretical" energy total provides an indication of the extent of possible variances in energy requirements.

The total energy requirements for an operational process that includes no special features for economizing is 21.64 million Btu/ton product with 21.47 million Btu/ton product provided in the form of direct fuels, steam and electrical power consumption. A "theoretical" estimate considering the recovery and recycle of unreacted coal indicates the process has the potential for total energy requirements of 16.21 million Btu/ton product. The process energy requirements are sensitive to chalcopyrite concentrate composition in that changes in composition would affect the waste heat recovery from the roaster (e.g., lower sulfur levels) or increase coal consumption (e.g., greater fraction of gangue or reactions with constituents of the gangue).

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2.14 THERMO ELECTRON CHLORINATION PROCESS

2.14.1 Introduction

The following is a brief description and evaluation of the chalcopyrite chlorination process reported by Thermo Electron Corporation to U.S. Department of Energy (Thermo Electron, 1978).

2.14.2 Process Description

Chalcopyrite concentrates are reacted with chlorine gas, forming cuprous chloride, ferric chloride, and elemental sulfur. The cuprous chloride is drawn off the lower part of the reactor in molten form and electrolyzed to copper metal and chlorine gas for recycle. Ferric chloride and elemental sulfur vapors pass out the top of the reactor and are condensed to liquids and separated by decantation. The ferric chloride is then burned with oxygen to Fe_3O_4, chlorine again being recycled to the main reactor. Principal reactions are as follows:

$$CuFeS_2 + 2\tfrac{1}{2}\,Cl_2 \longrightarrow CuCl_2 + FeCl_3 + 2S \text{ -- Basic chlorination reaction} \qquad (2.14.1)$$

$$CuCl_2\ (c) \longrightarrow CuCl\ (1) + \tfrac{1}{2}\,Cl_2\ (g) \text{ -- In lower part of reactor} \qquad (2.14.2)$$

$$CuCl\ (1) \longrightarrow Cu\ (c) + \tfrac{1}{2}\,Cl_2\ (g) \text{ -- Molten salt electrolysis} \qquad (2.14.3)$$

$$3FeCl_3 + 2O_2 \longrightarrow Fe_3O_4 + 4\tfrac{1}{2}\,Cl_2 \text{ -- Burning of ferric chloride} \qquad (2.14.4)$$

2.14.3 Material Balance

A schematic flowsheet of the process is presented in Figure 2.14-1 and a material balance in Table 2.14-1. The material balance differs somewhat from the Thermo Electron report, as it is based on 1,000 tons of copper cathodes from feed assaying 25 percent copper, 29 percent iron, and 31 percent sulfur. Their flowsheet is based on 1,442 tons of concentrate assaying 24 percent copper, 21 percent iron, and 24 percent sulfur. Another difference is that the flowsheet given here omits a step where trace amounts of cupric chloride ($CuCl_2$) are water-leached from the gangue leaving the reactor. This step is shown in the Thermo Electron report but is not included in their material or energy balances. Note that 100 percent recovery of all products and 100 percent utilization of all reagents is assumed. The process is mostly conceptual at this time and is in a very early stage of development.

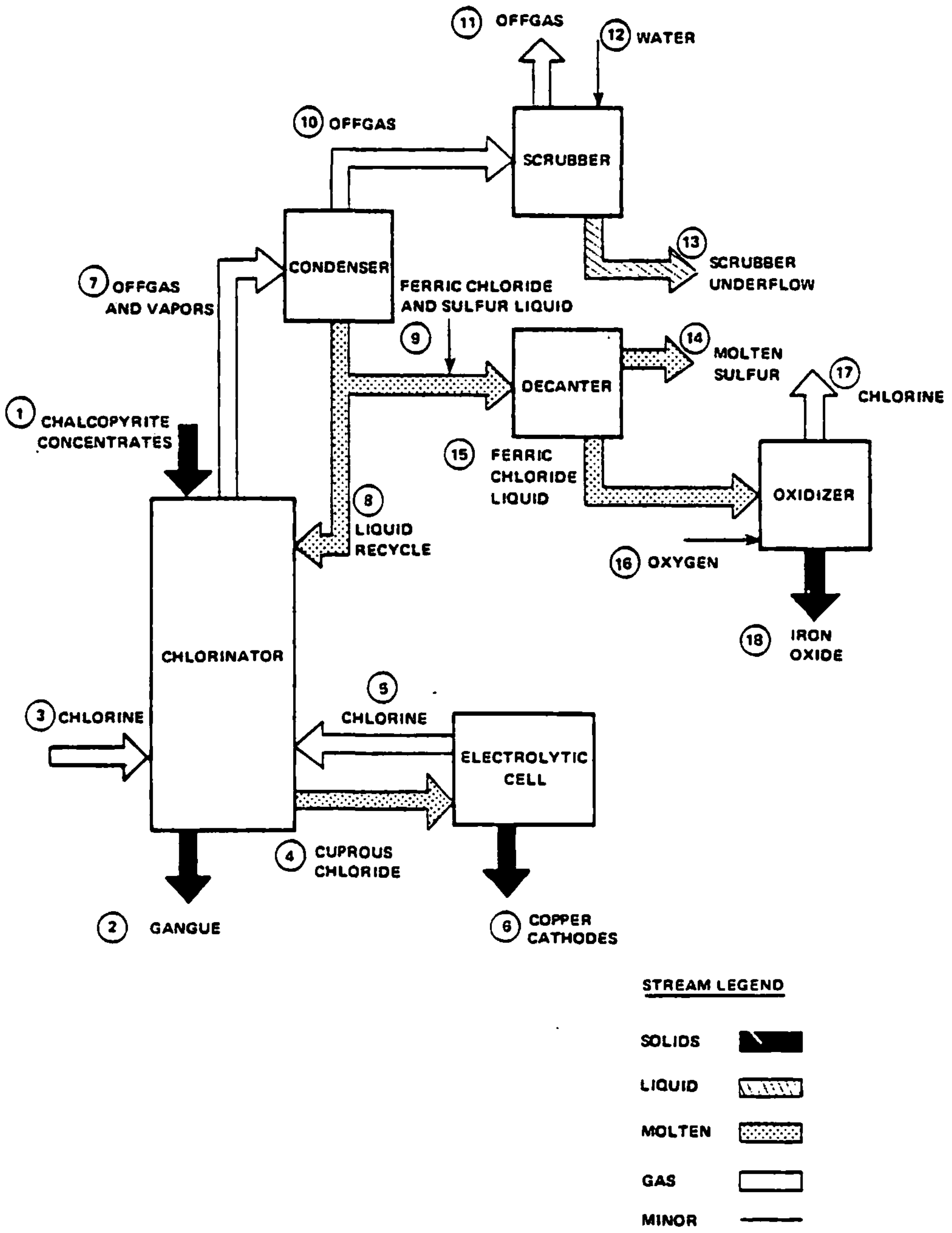

FIGURE 2.14-1 THERMO-ELECTRON CORP. PROCESS

TABLE 2.14-1

IDEAL MATERIAL BALANCE FOR 1000 TONS COPPER

Stream No.	Description	Tons/1000 Tons Copper
1	Feed 25% Cu, 29% Fe, 31% S, 15% gangue	4000
2	Gangue from reactor to waste	600
3	Chlorine gas recycled from oxidizer (17)	2210
4	Molten CuCl, feed to electrolysis	1560
5	Chlorine from cell, recycled to reactor	560
6	Copper cathodes	1000
7	Offgas containing ferric chloride and sulfur vapors	8350
8	Liquid $FeCl_3$ and S° recycled to reactor	3740
9	Liquid $FeCl_3$ and S° to decanter	4610
10	Offgas to scrubber	-
11	Offgas to atmosphere	-
12	Water to scrubber	-
13	Scrubber underflow to waste	-
14	Molten sulfur product	1240
15	Liquid $FeCl_3$ to oxidizer	3370
16	Oxygen gas to $FeCl_3$ oxidizer	440
17	Chlorine from oxidizer, recycled to reactor (3)	2210
18	Fe_3O_4 product	1600

2.14.4 Energy Requirements

Theoretically, the only energy inputs to the process are for electrolysis of cuprous chloride and for manufacture of oxygen to burn the ferric chloride. Thermo Electron reports that 11.0 megawatts is used for electrolytic production of 346 tons per day copper metal at 50 percent cell efficiency and 1.4 megawatts for manufacture of 116 tons per day separated oxygen. This is 763 kilowatt hours per ton of copper and 290 kilowatt hours per ton of oxygen. MSRD's analysis shows 774 kilowatt hours per ton of copper in electrolysis (a good check) but 405 kilowatt hours per ton of oxygen. The 405 figure was given to us by AIRCO and is for a new plant producing 150 tons per day oxygen gas at 95.5 percent purity, 200 pounds per square inch. Bringing everything to the consistent basis of the flowsheet in Figure 2.14-1 and using a conversion factor of 10,000 Btu's per kilowatt hour, the theoretical energy requirements are as follows:

TABLE 2.14-2

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 1 — THEORETICAL ENERGY REQUIREMENT

	Btu per Ton Copper Thermo Electron	MSRD
Electrolysis	7.6×10^6	7.7×10^6

TABLE 2.14-3

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 2 — THEORETICAL ENERGY REQUIREMENT

	Btu per Ton Copper Thermo Electron	MSRD
Oxygen Manufacture	1.3×10^6	1.8×10^6

This discrepancy is not major. However, since the chlorination process is being compared to actual operating processes, some practical assumptions will be made which will increase the real energy requirements. These assumptions are 90 percent recovery of copper, 10 percent makeup of chlorine, and 10 percent excess oxygen. In addition, 10 percent of the total energy will be assumed for operation of the scrubber and miscellaneous equipment.

Chlorine is manufactured in diaphragm cells at an energy cost of about 2,440 kilowatt hours per ton. At 10 percent excess and 90 percent copper recovery (see Figure 2.14-1 and Table 2.14-1), about 0.31 tons of chlorine will have to be made up per ton of copper recovered. This requires 756 kilowatt hours (7.6×10^6 Btu) per ton of copper recovered.

Energy requirements are now estimated as follows:

TABLE 2.14-4

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 1 — ASSUMED OPERATIONAL ENERGY REQUIREMENTS

	Btu per Ton Copper
Electrolysis	8.6×10^6
Miscellaneous	1.8×10^6
Total	10.4×10^6

TABLE 2.14-5

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 2 — ASSUMED OPERATIONAL ENERGY REQUIREMENTS

	Btu per Ton Copper
Oxygen Manufacture	2.2×10^6
Chlorine Manufacture	7.6×10^6
Total	9.8×10^6

Hypothesized in the Thermo Electron report is an energy recovery of 347 kilowatt hours per ton of copper by converting the heat from the ferric chloride-sulfur condenser to electric power. MSRD does not believe this to be feasible. It is difficult to evaluate the amount of ideal heat available, because it is not certain if sulfur is condensing from S^8, S^6, S^4, S^2, etc. Also, some of the specific heats are uncertain. Our judgment is that at most 3.0×10^6 Btu's per ton of copper might be available on an ideal basis (see Reactions 1 and 2 and Energy Balance Item No. 6). But conversion of this heat to electric power would be very inefficient due to the low temperature. A factor of 10,000 Btu's per kilowatt hour is reasonable for fossil-fuel steam power plants but unrealistic for utilization of waste heat at only 585 degrees Kelvin. A better figure would be about 24,000 Btu's per kilowatt hour, giving only 14 percent heat recovery efficiency or 0.4×10^6 Btu's per ton of copper. This is negligible in the energy balance.

No heat recovery at all should be assumed for this process in its present stage of development.

2.14.5 Discussion

Although 20 million Btu's per ton of copper is a relatively low energy requirement, the chlorination process may not be a practical approach. Most of the key steps have apparently not been demonstrated even in the laboratory. Of particular concern are the flow of solids and gas through the chlorination reactor, the drawoff of molten cuprous chloride ($CuCl$) from the reactor, molten salt electrolysis of cuprous chloride, separation of ferric chloride ($FeCl_3$) from sulfur (S), scrubbing of the offgas, and production of iron oxide (Fe_3O_4) by burning ferric chloride with oxygen. It is not known if all these steps, although theoretically interesting, will work with acceptable efficiencies, purities, etc. Dealing with the corrosive environments presented by chlorine gas and metal chlorides at elevated temperatures will also be challenging from the practical standpoint.

2.14.6 Reference

Dean T. Morgan, James Schad, Alexandra Zakak and Dae Sik Kim (Consultant). Thermo Electron Corporation, "Chlorine Extraction Processes for Energy-Conserving Recovery of Non-ferrous Metals." 101 First Avenue, Waltham, Mass. 02154. Contract No. EC-77-C-02-4532, U.S. Department of Energy, Director for Industrial Conservation, 20 Massachusetts Avenue, Washington, D.C. 20545, December 1978. Report Number TE4228-97-79.

2.15 OXY-FUEL REVERBERATORY SMELTING

2.15.1 Introduction

This variant on the matte smelting process was developed in Chile during the years after the Kennecott Caletones smelter had been nationalized, and is well described in papers presented at AIME meetings in New York and Atlanta (Schwarze, March 1977; Schwarze et al, March 1977 and Achurra et al March 1977).

Kennecott had built an oxygen plant at the smelter before relinquishing their facilities and the new management sought to utilize this to increase productivity of the plant. Over a period of several years they gradually replaced air-oil burners by oxygen-oil burners, until finally the reverberatory furnaces operated on oxygen-oil exclusively. Production rate doubled, oil consumption fell to half the old figure and while roof life decreased, its life per ton of product remained constant. Due to the large decrease in dilution by nitrogen, SO_2 content of the reverb gases was in the 8-10% range, ample for acid manufacture. Therefore the process is presented here as offering another option for a plant trying to meet environmental standards with minimum capital expenditure.

2.15.2 Process Description

The process outlined on the attached flow sheet, Figure 2.15-1, is almost identical to the standard reverb smelting process in that converter slags are returned to the reverb for cleaning, eliminating the costly slag cleaning methods needed by other new processes. While this is perhaps not essential, the concentrates were dried separately at Caletones, since they had been doing this before. It is doubtless a more efficient way to use energy since the waste gases from this operation leave at a lower temperature than from the reverb.

Referring to the tabulation of streams in the Reverberatory Furnace Smelting Section, Stream (1) has had the H_2O eliminated in the dryer. Stream (2) Silica flux, remains unchanged, as do (4) Reverb slag; (6) Matte; (7) Converter flux; (8) Converter slag; (9) Converter off-gas; (10) Converter air; and (11) Blister copper.

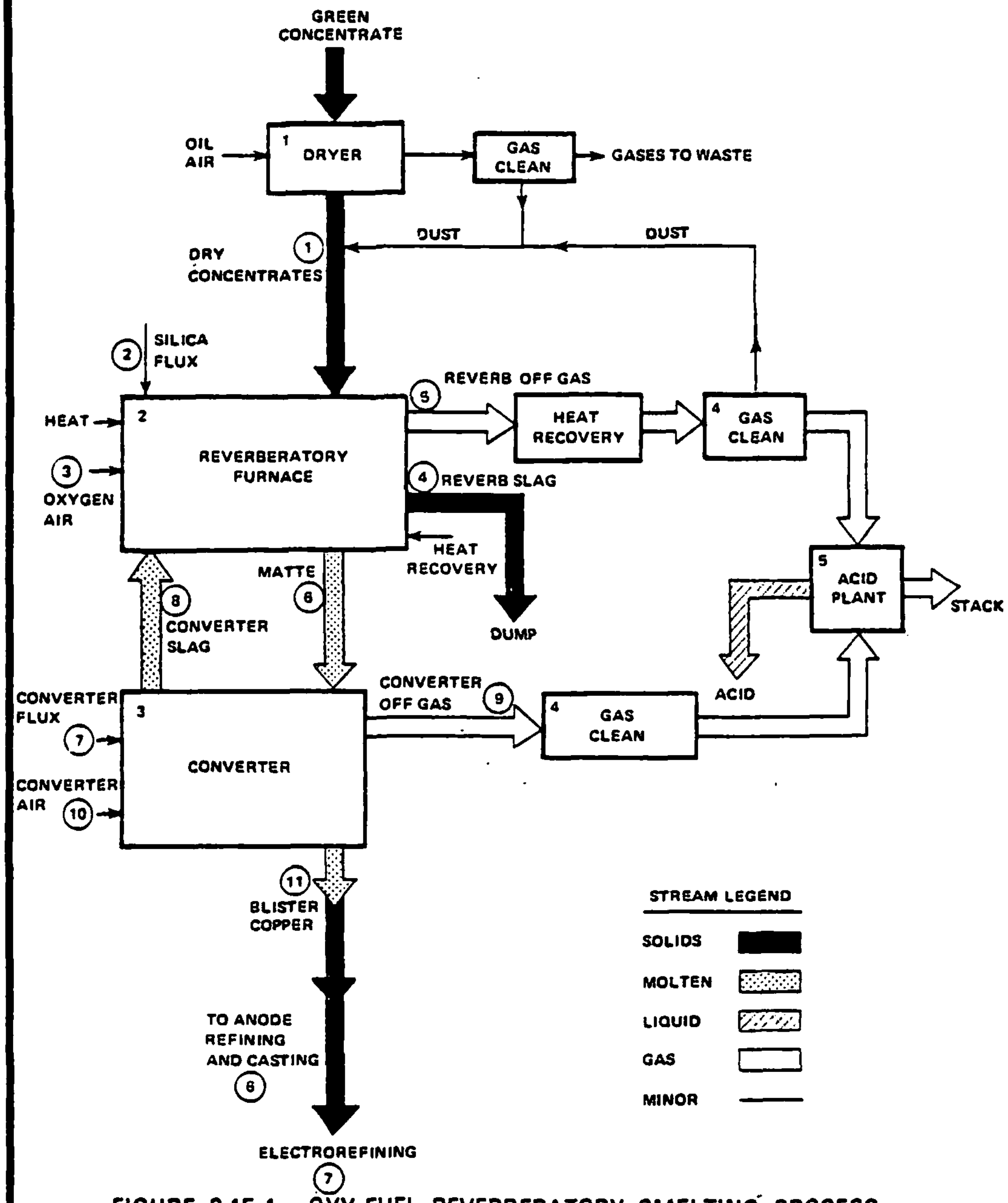

FIGURE 2.15-1 OXY-FUEL REVERBERATORY SMELTING PROCESS

It is only streams (3) NG & Air and (5) Reverb off-gas that change significantly, and are shown below. For the fuel input, oil is used, and 80% of the required oxygen for its combustion is supplied as technically pure oxygen; the rest is supplied by air infiltrating into the furnace. The latter also supplies the needs for oxidizing labile sulfur. In the Reverb off-gas, Stream 5, sulfur from fuel oil and from oxidation of labile sulfur are combined to estimate total gas volume based on an analysis of 9% SO_2 by volume, which explains the presence of some free oxygen in addition to the other gas species. This type of correction was not made in the Offgas Stream for the air-natural gas reverb. In spite of the omission of excess air in that tabulation the decrease in total gas is dramatic, and fully explains the decreased fuel requirements.

2.15.3 Comparison of Reverb Gas Streams with Oil Oxygen and Air Natural Gas

Item	Air Natural Gas		Oil Oxygen	
	(3) tons	(5) tons	(3) tons	(5) tons
H_2O	1,208	1,605	251	251
SO_2	—	1,239	13	1,252
O_2		?*		498
CO_2	1,584	1,584	810	810
N_2	7,379	7,379*	537	4,193
Total	10,171	11,807		7,004
Percent SO_2	2-3			9

* A sulfur balance was not used in conjunction with sulfur analysis to estimate dilution air. So the reported nitrogen is surely low.

2.15.4 Energy Requirements

Table 2.15-1 presents the Level I energy requirements for Oxy-Fuel reverberatory smelting. The analysis does not include oxygen enrichment of converter air. However, as an oxygen plant is present one would expect oxygen enrichment of converter air as well.

Table 2.15.-2 presents the Level II energy requirements for Oxy-Fuel reverberatory smelting.

2.15.5 Conclusion

The replacement of air-oil burners by oxy-fuel burners leads to a significant decrease in fuel usage in smelting. The effect of oxy-fuel operation on NO_x emissions is not known and needs to be studied.

2.15.6 References

Herman Schwarze: Oxy-fuel burners save energy at El Teniente's Caletones smelter, World Mining, May 1977, pp. 58-61.

H. D. Schwarze, G. B. Vera and O. F. Pino: Use of new technologies at Caletones smelter, TMS Paper No. A77-90, TMS-AIME New York, 1977.

H. J. Achurra, R. G. Espinosa, and L. J. Torres: Improvements in full use of oxygen in reverb furnaces at Caletones Smelter, Presented at AIME Meeting Atlanta, March 1977.

TABLE 2.15-1 **ENERGY REQUIREMENTS** Level 1

OXY FUEL SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Materials Handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
1	Dryer				
	A) Fuel	GAL	9.7	0.139	1.350
2	Reverb. Smelting				
	A) Fuel: Fuel Oil	GAL	66.7	0.139	9.270
	B) Electrical Energy	KWH	60.8	0.0105	0.638
	C) Waste Heat Recovery: Steam	LBS	2650	0.0014	-3.710
3	Converting				
	A) Electrical Energy	KWH	155	0.0105	1.628
	B) Fuel: Fuel Oil	GAL	3.6	0.139	0.500
4	Gas Cleaning				
	A) Hot Gas Cleaning				
	1- Reverb. (9% SO_2)	Thous. SCF	166.8	0.00336	0.560
	2- Converters (7% SO_2)	Thous. SCF	211.8	0.00336	0.712
	B) Cold Gas Cleaning				
	1- Reverb.	Thous. SCF	166.8	0.00126	0.210
	2- Converter	Thous. SCF	211.8	0.00126	0.267
	3- Fugitive Emissions Control	KWH	340.0	0.0105	3.570
5	Acid Plant				
	A) Reverb. & Converter Gas (7.9% SO_2)	Thous. SCF	378.6	0.0119	4.505
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095

TABLE 2.15-1 (cont.) **ENERGY REQUIREMENTS** Level 1

OXY FUEL SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	26.145

*Not shown on flowsheet.

TABLE 2.15-2

ENERGY REQUIREMENTS

Level 2

OXY FUEL REVERBERATORY

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb. Smelting				
	A) Silica Flux	TON	0.518	0.042	0.022
	B) Oxygen	TON	0.498	3.78	1.882
3	Converting				
	A) Silica Flux	TON	0.437	0.042	0.018
*	Water Pollution Control				
	A) Lime	LBS	30.0	0.0027	0.081
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	2.471

*Not shown on flowsheet

2.16 OXYGEN SPRINKLE SMELTING

2.16.1 Introduction

The oxygen sprinkle smelting process concept proposed by P. E. Queneau and R. Schuhmann, Jr. consists of modifying existing reverberatory furnaces by the installation of oxygen sprinkler burners. The oxygen sprinkler burner was developed in collaboration with Professor H. Richter of Dartmouth College. We understand that the burner has been designed, manufactured and a full scale prototype has been tested for solids flow and mixing at ambient temperatures. Full scale hot testing of the sprinkler burner began in November 1980. The sprinkler burner has been installed in the roof of an operating reverberatory furnace at the Morenci branch of Phelps Dodge Corporation and is being tested at this time. Under conditions of limited head room the design offers excellent gas-liquid-solid contact of reactants and dispersion of particulates over a wide area. The modification transforms an existing reverberatory furnace into an oxygen flash smelting unit with improved performance with respect to productivity, operating costs, energy conservation, higher metal recovery and environmental control.

2.16.2 Process Description

The process flowsheet is presented in Figure 2.16-1 and an isometric view of the oxygen sprinkle smelting furnace is presented in Figure 2.16-2.

An existing reverberatory furnace can be modified for "oxygen sprinkle smelting" by closing all unnecessary openings and installing four sprinkler burners. The burners are designed to accomplish several important functions within the existing structure. These include (a) the intimate mixing of finely divided concentrates with the oxygen-rich gas for flash smelting, and (b) uniform sprinkling of particulates over most of the bath surface. Provision is made for the admixture of a small percentage of pulverized coal with the solids feed, normally only to the burner nearest to the slag-tapping end to produce a lower grade matte for slag cleaning purposes. The slag is cleaned prior to discharge by drenching it with a shower of low grade matte produced by flash melting of the copper concentrates. Thus, in addition to flash oxidation of the sulfide concentrate, the burner design aims at optimizing interphase heat and mass transfer and the control of heat and mass distribution throughout the furnace volume. The accomplishment of these aims converts the reverberatory furnace which is primarily an inefficient melting reactor into a relatively efficient and flexible chemical reactor.

In addition to modifications of the reverberatory furnace, a concentrate dryer and an oxygen plant have to be added. Converting is carried out in Peirce-Smith converters as in conventional reverberatory smelters. The blister copper from converting is cast into anodes and finally electrorefined to produce cathode copper.

2.16.3 Energy Requirements

Table 2.16-1 presents the Level I energy requirements for "oxygen sprinkle" reverberatory smelting. The analysis does not include oxygen enrichment of converter air. However, as an oxygen plant is present, one would expect enriched air to be used for converting as well.

Table 2.16-2 presents the Level II energy requirements for "oxygen sprinkle" reverberatory smelting.

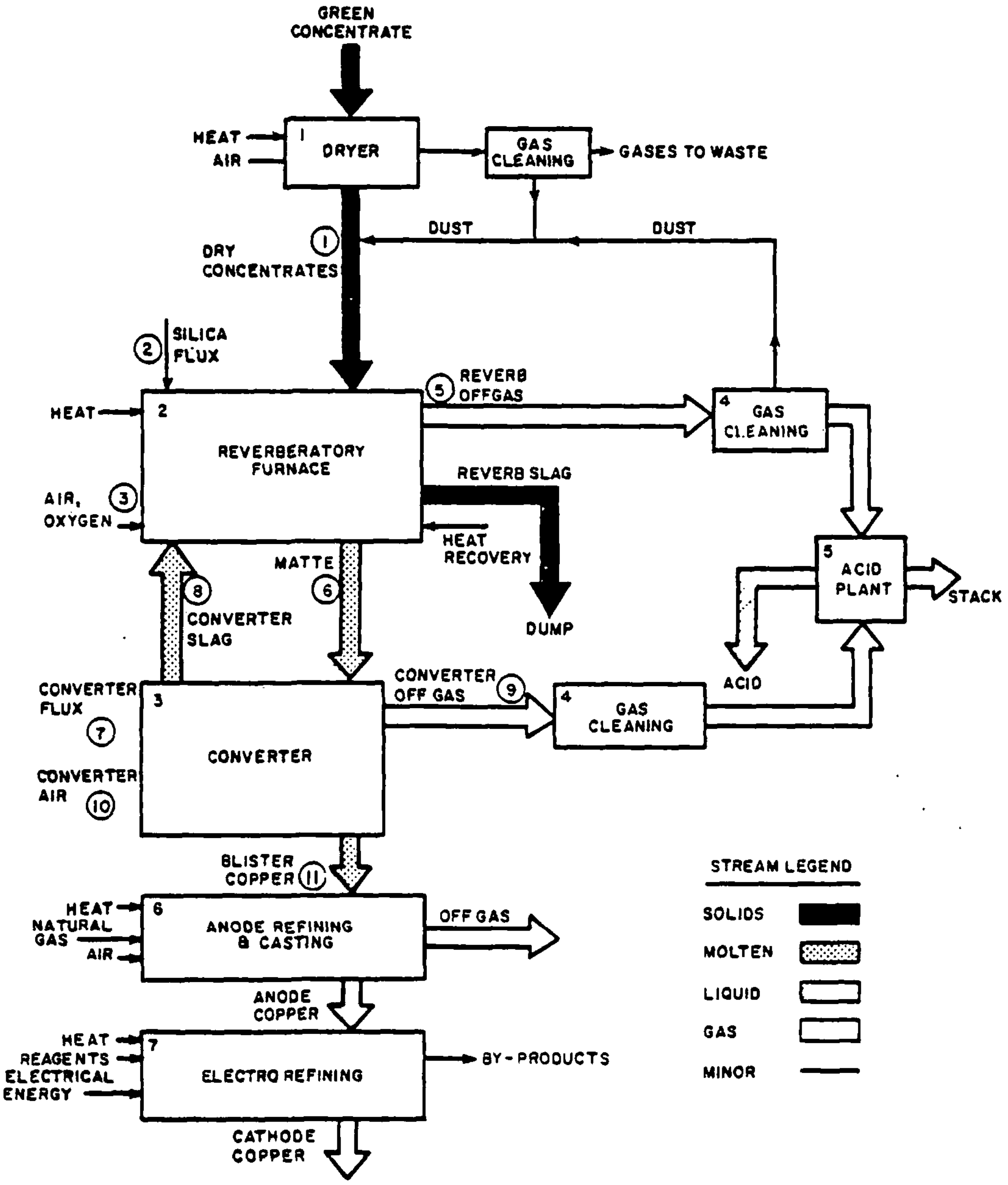

FIGURE 2.16-1 OXYGEN SPRINKLE SMELTING PROCESS

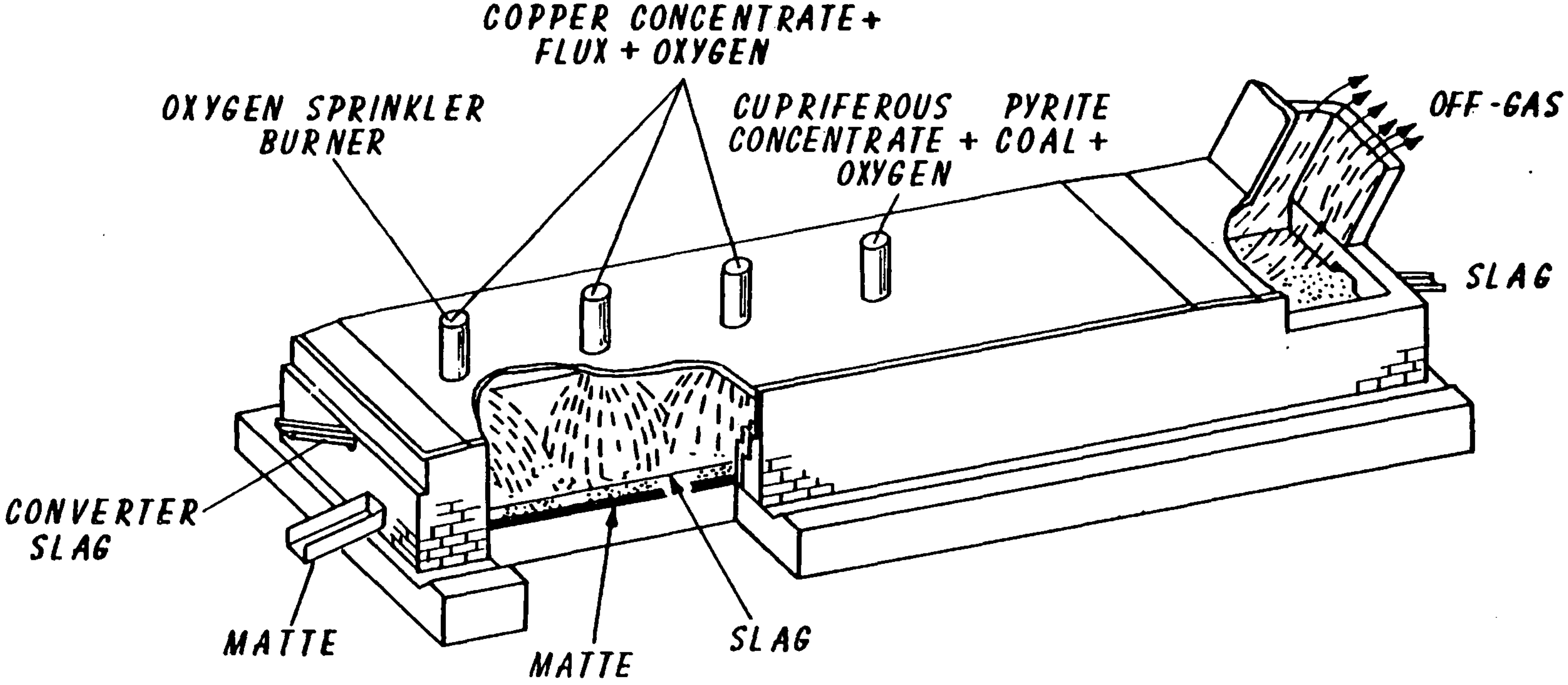

FIGURE 2.16-2 ISOMETRIC VIEW OF OXYGEN SPRINKLE SMELTING FURNACE (CONVERTED CONVENTIONAL COPPER REVERBERATORY FURNACE)

TABLE 2.16-1

ENERGY REQUIREMENTS

LEVEL 1

OXYGEN SPRINKLE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Materials Handling				
	A. Electrical Energy	KWH	69.1	0.0105	0.726
1	Dryer				
	A. Fuel: Fuel Oil	GAL	12.4	0.139	1.724
2.	Reverb Smelting				
	A. Fuel: Coal	TON	0.055	25.0	1.375
	B. Electrical Energy	KWH	60.8	0.0105	0.638
	C. Waste Heat Recovery	LBS	780	0.0014	-1.092
3	Converting				
	A. Electrical Energy	KWH	120	0.0105	1.260
	B. Fuel: Fuel Oil	GAL	2.3	0.139	0.230
4	Gas Cleaning				
	A. Hot Gas Cleaning				
	1- Reverb	THOUS. SCF	24.0	0.00336	0.081
	2- Converters	THOUS. SCF	167.3	0.00336	0.562
	B. Cold Gas Cleaning				
	1- Reverb	THOUS. SCF	24.0	0.00126	0.030
	2- Converters	THOUS. SCF	167.3	0.00126	0.211
	3- Fugitive Emissions Control	KWH	340	0.0105	3.57
5	Acid Plant				
	A. Reverb and Converter Gas (dilute to 9%)	THOUS. SCF	310.3	0.0126	3.909

TABLE 2.16-1 (Cont.) **ENERGY REQUIREMENTS** Level 1

OXYGEN SPRINKLE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Water Pollution Control A. Electrical Energy	KWH	9.0	0.0105	0.095
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	19.143

TABLE 2.16-2

ENERGY REQUIREMENTS

LEVEL 2

OXYGEN SPRINKLE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb Smelting				
	A. Silica Flux	TON	0.375	0.042	0.016
	B. Oxygen	TON	0.716	3.78	2.706
3	Converting				
	A. Silica Flux	TON	0.290	0.042	0.012
4	Water Pollution Control				
	A. Lime	LBS	30.0	0.0027	0.081
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	3.283

2.16.4 Discussion

The "oxygen sprinkle" reverberatory smelting concept results in decreased energy consumption due to flash oxidation of concentrates, with the use of oxygen and the energy savings due to decreased gas handling requirements. This analysis has been based on the available published information (Queneau and Schuhmann, 1979). Experimental data are needed to demonstrate adequate refractory life under actual operating conditions and to establish the quantity of air infiltration to the reverbs and the extent to which this will dilute the strong sulfur dioxide produced at the burner.

2.16.5 References

Queneau, P.E., and R. Schuhmann, Jr., "Metamorphosis of the Copper Reverberatory Furnace: Oxygen Sprinkle Smelting," Journal of Metals, December 1979, pp. 12-15.

3.0 HYDROMETALLURGICAL PROCESSES FOR TREATING CHALCOPYRITE CONCENTRATES

3.1 INTRODUCTION

The copper industry of the United States has in recent years been impacted by regulatory requirements relative to emissions standards. Of special concern have been sulfur, trace metal and particulate emissions. As a consequence, hydrometallurgical processing of copper concentrates has continued to attract attention. The ability of hydrometallurgical processes to scale-down to relatively small size is an attractive feature but capital and operating costs generally exceed those of new pyrometallurgical processes. Hydrometallurgical processes employing electrowinning are energy intensive and in general fail to compete in large scale operation with pyrometallurgical processes. Nevertheless, advantages in the handling of waste residues and the ability to compete for small scale operations continues to spur interest in the potential application of hydrometallurgical processes.

This study concerns itself with the energy requirements of selected, proposed or commercialized hydrometallurgical processes. These processes are sub-divided into four process categories as follows:

a) chloride leaching;
b) ammoniacal leaching;
c) acid leaching; and
d) pre-treated concentrates.

Of the chloride processes the Cymet Ferric Chloride Process and the Duval Process are examples. The Duval (CLEAR) Process is in operation and reportedly treated twenty-five percent of all of Duval's concentrate production in 1978[a]. Unfortunately we were not able to obtain sufficient information on the CLEAR process to include in this study. The extensively piloted Cymet Cupric-ferric chloride leach is included in this anaylsis. The Arbiter process is the only process developed using ammoniacal leaching chemistry. The commercial plant constructed in 1974 is not in operation currently. Two acid leach processes, the Nitric-Sulfuric Acid Leach Process developed by Kennecott Copper Company and the DuPont Company is considered as is also the Ferric Sulfate-Sulfuric Acid leach process proposed jointly by the University of Utah and Martin Marietta resulting from an NSF/RANN supported project.

Processes which include pre-treatment of concentrate prior to leaching are the Roast-Leach-Electrowin (RLE) Process, the Sulfite-Reduction Process and the Sherritt-Cominco Copper Process. The RLE, Lakeshore plant closed when the depressed price of copper rendered it uneconomic for continued operation. Most of the hydrometallurgical processes reviewed here use electrowinning. Exceptions are the Cymet process utilizing hydrogen reduction and the Sulfite-Reduction processes utilizing ammonium bisulfite as the reductant. Table 3.1-1 lists the above processes and includes the reviewing organization and such features as lixiviant, separation (purification), reduction and residues characteristic of each process. The reviewing sub-contractors are Arthur D. Little (ADL), Mountain States Research and Development (MS), and Ford Bacon and Davis (FBD).

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[a] Report given by R. W. Livingston at the Copper Hydrometallurgy Economics Panel Session, National A.I.M.E. Meeting, New Orleans, February, 1979.

TABLE 3.1-1 HYDROMETALLURGICAL PROCESSES INCLUDED IN THE ENERGY ANALYSIS

Process Name	Reviewing Sub-Contractor	Lixiviant(s)	Method of Separation-Purification	Reduction	Residue (other than undissolved residual solids)
Cymet Ferric Chloride Leach	ADL	cupric-ferric chlorides	centrifugal separation of crystallized cuprous chloride	fluidized bed hydrogen reduction	hydronium jarosite-ferric oxide
Arbiter Ammonia Leach	ADL	ammonia, oxygen	counter current deamtation (CCD) - solvent extraction	Electrowinning	gypsum, ferric oxide
Roast-Leach-Electrowin	*MS*	*spent electrolyte*	*CCD*	*Electrowinning*	*iron oxides*
Nitric-Sulfuric Acid Leach	FBD	nitric acid, sulfuric acid, oxygen	filtration	Electrowinning	ammonium jarosite, elemental sulfur
Sherritt-Cominco	ADL	Sulfuric acid, oxygen	filtration	Electrowinning	ammonium jarosite, ferric oxide, elemental sulfur
Ferric Sulfate-Sulfuric Acid	ADL	Ferric sulfate, oxgyen	filtration	Electrowinning	ammonium jarosite, gypsum, elemental sulfur
*Electroslurry	ADL	Ferric sulfate, oxygen	filtration	Electrowinning	ferrous sulfate (or calcium (arosite) gypsum, elemental sulfur
Sulfite-reduction	FBD	sulfuric acid	filtration	ammonium busulfite	gypsum, ferric oxides

*Analysis provided by Envirotech Corporation

3.2 ARBITER AMMONIA LEACH PROCESS

3.2.1 Introduction

This section contains an estimate of the material and energy requirements for the Arbiter Process, which utilizes countercurrent leaching techniques to extract copper by ammonia solution under oxygen atmosphere at low pressure and low temperature. This estimate is based on published information on the process, and on similar processes. The basis of these calculations is 1 ton of cathode copper from chalcopyrite concentrate. The process is, however, much more successful in extracting a high percentage of copper from chalcocite concentrates than it is with chalcopyrite concentrates used as a standard of comparison in this study.

A full-sized commercial plant using the Arbiter Process was built in 1974 at Anaconda's Montana smelter to produce 100 tons per day of cathode copper. The plant is not currently in operation due to the unavailability of concentrates with a high proportion of chalcocite which the process dissolves more readily than the chalcopyrite (McNulty, 1979).

3.2.2 Process Description

The Arbiter Process is an ammonia leach process using oxygen as an oxidizing agent under a pressure of 5 psig and a temperature of 60-90°C to extract copper from low grade or highly pyritic concentrates.

The process basically consists of five major steps as shown in Figure 3.2-1, the Arbiter Process flow diagram: (1) concentrate preparation, (2) countercurrent leaching, (3) organic solvent extraction and stripping, (4) copper electrowinning and (5) ammonia recovery and sulfate disposal.

The slurried concentrate is leached with ammonia under oxygen in a series of rubber-lined tanks with decantation and washing performed countercurrently. An organic-liquid-ion-exchange reagent is used to extract copper from the pregnant solution. The copper is, in turn, stripped from the organic solvent by an acid electrolyte and recovered by electrowinning. A portion of the barren raffinate is purged out of the system for the removal of sulfate by the addition of limestone producing gypsum slurry as a byproduct of the process. Ammonia is recovered for re-use.

3.2.3 Material Balance

The material balances are derived from the chemistry and knowledge of process conditions. The leaching chemistry of chalcopyrite can be described by the following equation:

$$CuFeS_2 + 4\tfrac{1}{4}O_2 + 4NH_3 + H_2O \rightleftarrows Cu(NH_3)_4^{++} + \tfrac{1}{2}Fe_2O_3 + 2SO_4^{=} + 2H^+ \qquad (3.2.1)$$

The liquid ion exchange steps are represented by the following general equation:

$$2RH_{(org)} + CuSO_{4(aq)} \rightleftarrows R_2Cu_{(org)} + H_2SO_{4(aq)} \qquad (3.2.2)$$

The gypsum production and ammonia recovery can be shown by the following equation:

$$(NH_4)_2SO_4 + CaO + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + 2NH_3 \qquad (3.2.3)$$

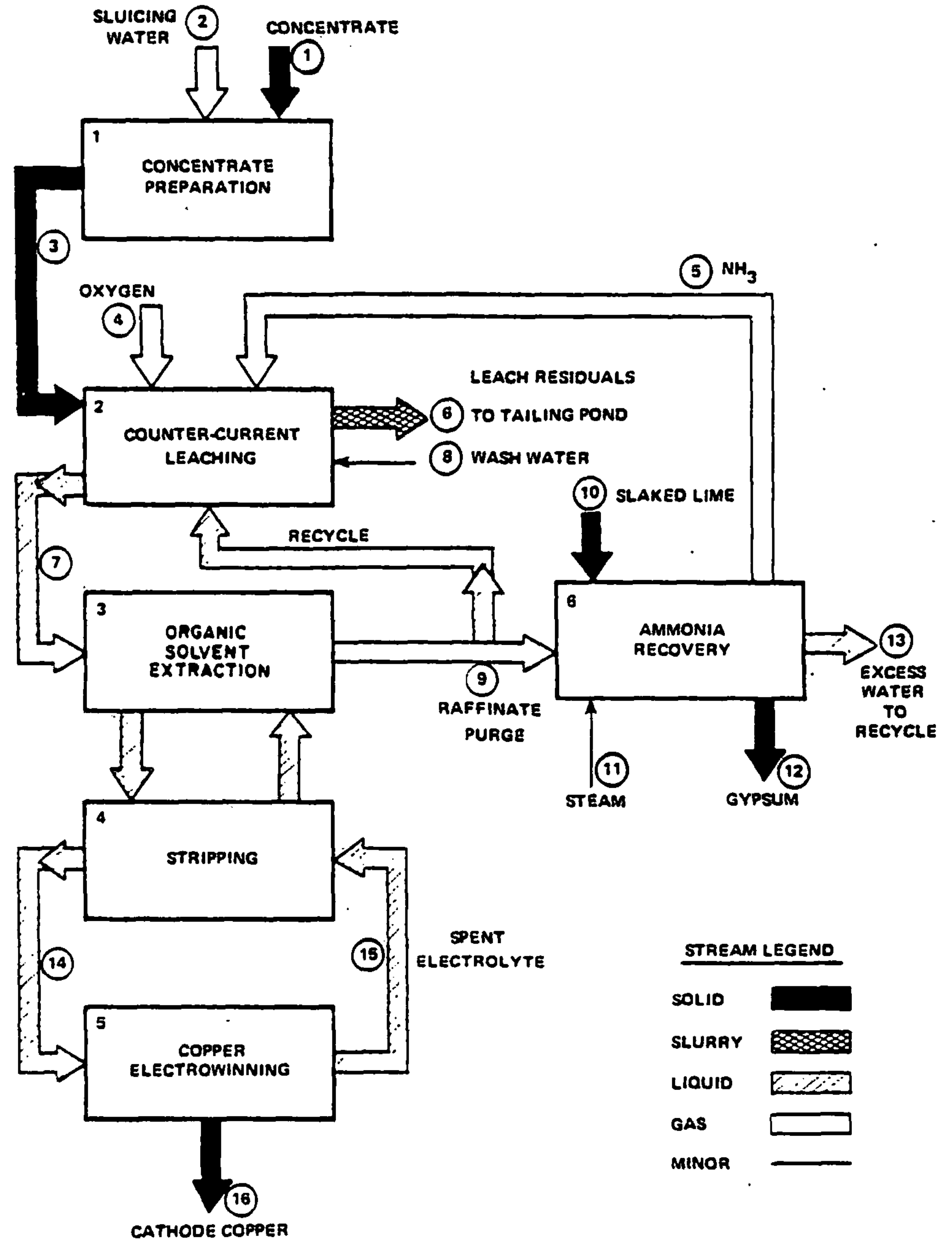

FIGURE 3.2-1 ARBITER AMMONIA LEACH PROCESS

Although the process is capable of achieving high recovery of copper, to the range of 95 to 97 percent by increasing the residence time in the leach circuit, recoveries in actual operation may be deliberately kept low (about 80 percent in the Montana operation) to enhance the recovery of precious metals contained in the concentrates (Kuhn, 1974).

Major effluents are the leach residues and gypsum slurry. These streams are sent to settling ponds. Overflows from these ponds can be used for water makeup. A material balance for this process is shown in Table 3.2-1.

The process does not generate any air pollutants but produces gypsum as a byproduct. Operating experiences indicate that the gypsum produced from the Arbiter Process, however, has not been of sufficiently high quality in physical characteristics and color to be suitable for wallboard manufacturing (McNulty, 1979). This may present a solid disposal problem to the plant operator.

3.2.4 Energy Requirements

The direct or Level I energy requirements for the Arbiter Process are shown in Table 3.2-2. The electrical energy includes all grinding, pumping, agitation and electrodeposition of copper, but does not include the energy for producing gaseous oxygen. The total electrical and thermal energy is equivalent to 37.9 million Btu per ton of copper ingot. The Level II energy required to produce the reagents used in the process, is presented in Table 3.2-3. An additional 25.5 million Btu per ton of copper is required to produce the reagents used in the process, largely in the form of oxygen, ammonia and lime.

3.2.5 Discussion

The Arbiter Process, using lime boil as a means to recover ammonia and to remove sulfate, as used at the Montana plant, requires substantially more energy than do the conventional smelting and refining plants equipped with sulfur dioxide emission control devices. According to the plant operator, the leaching, solvent extracting and electrowinning and lime boiling steps of the Arbiter Process would require 63 million Btu/ton of copper (McNulty, 1979). The high energy requirement of 35 million Btu/ton copper involved in the lime boil step is the result of a fairly dilute raffinate. A stronger raffinate can be produced but only at the expense of other upstream problems. Most other operators of hydrometallurgical plants have also found that the treatment of dilute discard streams require major energy use particularly in areas where solar evaporation is not an effective way of eliminating water.

Alternative methods for the disposal of sulfur and metal production have been studied by Anaconda.

Replacing the electrowinning step with copper cementation with iron was projected to save about 20 million Btu per ton of copper (McNulty, 1979).

3.2.6 References

Arbiter, N., "New Advances in Hydrometallurgy," Symposium for Efficient Use of Fuels in the Metallurgical Industries, December 9-13, 1974. Sponsored by IGT.

TABLE 3.2-1 ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		SLUCING WATER		FEED SLURRY		OXYGEN		AMMONIA	
COMPOSITION	wt.	wet wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.250	22.50			1.250	15.00				
Fe	1.33722	24.07			1.33722	16.05				
S	1.550	27.90			1.550	18.60				
SiO_2	0.43167	7.77			0.43167	5.18				
AL_2O_3	0.17222	3.10			0.17222	2.07				
FeO	0.03444	0.62			0.03444	0.41				
Fe_2O_3	0.05222	0.94			0.05222	0.63				
CaO	0.10333	1.86			0.10333	1.24				
MgO	0.04278	0.77			0.04278	0.51				
Others	0.02611	0.47			0.02611	0.31				
H_2O	0.55556	10.00	2.77777	100.00	3.33323	40.00				
NH_3									1.60503	100.00
O_2							2.14004	100.00		
$(NH_4)_2\ SO_4$										
$CaSO_4 \cdot 2H_2O$										
$H_2\ SO_4$										
$Cu(NH_3)_4\ SO_4$										
$Ca(OH)_2$										
$Cu\ SO_4$										
$Fe_2(SO_4)_3$										
TOTAL	5.55555	100.00	2.77777	100.00	8.33332	100.00	2.14004	100.00	1.60503	100.00

TABLE 3.2-1 (cont.) ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	LEACH RESIDUES*		PREGNANT SOLUTION**		WASH WATER***		BARREN RAFFINATE		SLAKE LIME	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.250	2.97								
Fe	0.45838	5.44								
S	0.54104	6.42								
S_iO_2	0.43167	5.12								
AL_2O_3	0.17222	2.04								
FeO	0.03444	0.41								
Fe_2O_3	1.30871	15.54								
CaO	0.10333	1.23								
MgO	0.04278	0.51								
Others	0.02611	0.31								
H_2O	5.05302	60.00	33.35404	85.49	38.54575	100.00	33.35404	87.66		
NH_3							0.53502	1.41		
O_2										
$(NH_4)_2\ SO_4$			2.07951	5.33			4.15608	10.93		
$CASO_4 \cdot 2H_2O$										
$H_2\ SO_4$										
$Cu(NH_3)_4\ SO_4$			3.58159	9.18						
$Ca(OH)_2$									2.33148	100.00
$CuSO_4$										
$Fe_2(SO_4)_3$										
TOTAL	8.4217	100.00	39.01513	100.00	38.54575	100.00	38.04514	100.00	2.33148	100.00

*Assume: Chalcopyrite 80% dissolved, Pyrite 0% dissolved

**Based on a copper concentration of 30 gpl in the strong solution(s)

***Amount calculated for water balance only

TABLE 3.2-1 (cont.) ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	STEAM		GYPSUM		EXCESS H_2O TO RE-USE		LOADED ELECTROLYTE*		SPENT ELECTROLYTE**	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe										
S										
SiO_2										
AL_2O_3										
FeO										
Fe_2O_3										
CaO										
MgO										
Others										
H_2O	0.050	100.00	8.12616	60.00	20.10359	100.00	220.7025	81.27	220.02508	81.32
NH_3										
O_2										
$(NH_4)_2\ SO_4$										
$CASO_4 \cdot 2H_2O$			5.41744	40.00						
H_2SO_4							28.70463	10.57	30.14116	11.14
$Cu(NH_3)_4\ SO_4$										
$Ca(OH)_2$										
$CuSO_4$							20.58478	7.58	18.85852	6.97
$Fe_2(SO_4)_3$							1.57509	0.58	1.54224	0.57
TOTAL	0.050	100.00	13.54360	100.00	20.10359	100.00	271.5670	100.00	270.5670	100.00

*Based on Reference 2: Cu: 37gpl Fe: 2.0 gpl H_2SO_4: 132 gpl

**Based on Reference 2: Cu: 34.0gpl Fe: 1.97gpl H_2SO_4: 137 gpl

TABLE 3.2-1 (cont.) ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)					
STREAM NAME	CATHODE COPPER					
COMPOSITION	wt.	wt.%				
Cu	1.000	100.00				
Fe						
S						
SiO_2						
AL_2O_3						
FeO						
Fe_2O_3						
CaO						
MgO						
Others						
H_2O						
NH_3						
O_2						
$(NH_4)_2 SO_4$						
$CASO_4 \cdot 2H_2O$						
H_2SO_4						
$Cu(NH_3)_4 SO_4$						
$Ca(OH)_2$						
$CuSO_4$						
$Fe_2(SO_4)_3$						
TOTAL	1.000	100.00				

TABLE 3.2-2 ENERGY REQUIREMENTS Level 1

ARBITER PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	<u>Electrical Energy</u>				
	A) Combined Amount for Electrowinning, Grinding, Pumping and Agitation	KWH	3000	0.0105	31.5
	<u>Fuel for Process</u>				
	A) Heating (Natural Gas)	SCF	1500	0.001	1.5
	B) Fuel for Lime Boil (Natural Gas)	SCF	4900	0.001	4.9
				TOTAL	37.90

TABLE 3.2-3 **ENERGY REQUIREMENTS** Level 2

ARBITER PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leaching				
	A) Oxygen	TON	2.14	3.78	8.089
	B) Ammonia Manufacture (5% loss/cycle)	TON	0.0805	41.73	3.359
6	Ammonia Recovery				
	A) Lime	TON	2.33	5.45	12.699
				TOTAL	24.147

Arthur D. Little, Inc., *"Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. VII. Ammonia Industry Report."* Report to Environmental Protection Agency, EPA 600/7-76-034g, December 1976.

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Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing, Phase VI., Bureau of Mines, December 1975.

Kuhn, M.S., et al, "Anaconda's Arbiter Process for Copper," *CIM Bulletin,* February 1974, pp. 62-73.

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Monhemiux, A.J., "Trends in Copper Hydrometallurgy," *Chem. & Process Engineering,* January 1970, Vol. 51(1), pp. 65-68.

3.3 THE ROAST-LEACH-ELECTROWIN (RLE) PROCESS

3.3.1 Introduction

All material and energy requirements described in this section are based on the pilot plant and commercial results of the roast-leach-electrowin (RLE) process. Included in the estimates are evaluation of material and energy flows developed by Hecla Mining Company and El Paso Natural Gas Company. (Griffith, Day, Jordan, and Nyman, 1973.) Included in the estimates are evaluation of material and energy flows for incoming process streams, outgoing process streams, and circulating streams.

The RLE process is not new. It has been extensively described in the metallurgical literature and the basic patent utilizing a fluid bed roaster was issued in 1957 (Foley, 1957). Prior to the Hecla Mining — El Paso Natural Gas development, the process had not been used commercially in North America. It was successfully piloted by Bagdad Copper Company and Dorr-Oliver, Inc. in 1957 (Howell, Grothe, and McLeod, 1957). Subsequent process development work abroad led to successful commercial installations in Zambia and Zaire, with over 300,000 metric tons of copper now being produced annually by this type of process in Zaire alone.

The process described by Griffith, et al., (Griffith, Day, Jordan, and Nyman, 1973) was piloted using concentrates from both Cyprus, Pima and Hecla Lakeshore operations. A full scale plant using a modification of the RLE process was the Hecla Lakeshore plant, a joint venture of Hecla Mining Company and El Paso Natural Gas Company, near Casa Grande, Arizona. The feed for the sulfide mill (and oxide mill, as well) came from an underground mine containing a large, complex deposit of both ore types (E/MJ, 1977). As a result of the decrease in copper prices the Lakeshore plant was shut down in 1978.

3.3.2 Process Description

The process is comprised of a fluid-bed sulfating roast (process step 1), followed by a leach (process step 4) and electrowinning of the copper to cathodes (process step 6). In the treatment of a typical chalcopyrite concentrate the major reactions are:

Fluid-bed sulfating roast

(1) chalcopyrite

$$CuFeS_2 + \frac{15}{4} O_2 \longrightarrow CuSO_4 + \frac{1}{2} Fe_2O_3 + SO_2 \qquad (3.3.1)$$

$$CuFeS_2 + \frac{13}{4} O_2 \longrightarrow CuO + \frac{1}{2} Fe_2O_3 + 2SO_2 \qquad (3.3.2)$$

$$CuO + \frac{1}{2} O_2 + SO_2 \longrightarrow CuSO_4 \qquad (3.3.3)$$

(2) pyrite

$$FeS_2 + \frac{11}{4} O_2 \longrightarrow \frac{1}{2} Fe_2O_3 + 2SO_2 \qquad (3.3.4)$$

Acid leach

$$CuSO_4 \text{ (solid)} \xrightarrow[\text{electrolyte}]{\text{spent}} CuSO_4 \text{ aqueous} \qquad (3.3.5)$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad (3.3.6)$$

The copper sulfide concentrate is slurry fed into the roaster wherein copper sulfides are converted to copper sulfate by controlling air flow rate and temperature. The iron sulfides in the feed are oxidized to hematite. The calcine is hot quenched and leached with dilute sulfuric acid to dissolve the copper sulfate. The leach slurry is separated into a clear pregnant solution and a leach residue by countercurrent decantation.

The copper is recovered from the pregnant solution in electrowinning by deposition on copper starter sheets. Spent electrolyte is divided between the agitation leach circuit and cementation for contact with metallic iron in a proportion that satisfies solution needs and overall copper recovery. Effluent liquor from the cementation step is rejected for the purposes of this analysis. Pregnant electrolyte contains about 49 gpl copper entering the starter section. Depletion of copper during electrolysis in the starter section reduces the solution concentration to 40 gpl copper. Current density in the electrowinning plant is designed to be in the range of 15 to 20 amps per square foot (E/MJ, 1977). In the test work performed by Griffith, et al., the following were established as the important variables in the RLE process:

(1) Roaster space rate
(2) Roaster temperature
(3) Roaster feed sulfur to air ratio
(4) Current density
(5) Spent electrolyte composition

The data used to construct the model of the RLE process were taken from the plant data of the Hecla Lakeshore operation. The Lakeshore process produced some cement copper which contains 40 percent copper. This was sent to a custom smelter where it was further processed into cathode copper. For this study the cementation process is followed by a redissolution step so that the final product from the RLE process is cathode copper.

The Lakeshore operation included a sponge iron plant. However, in this analysis, the preparation of sponge iron is not included in the heat requirement. It is assumed that the metallic iron for the copper cementation step would be provided from the most economical source.

The analysis of the concentrate from the Lakeshore operation was 25.92 percent copper, 25.55 percent iron, and 29.27 percent sulfur. Therefore, the data have been adjusted to the standard concentrate value of 25.00 percent copper, 29.00 percent iron, and 31.00 percent sulfur. The energy equivalents for some items were taken from Kellogg and Henderson (1967).

The flowsheet for the RLE process shown in Figure 3.3-1 is the original flow sheet and does not include a solvent extraction step which was to be added later. The material and energy requirements for the process are shown in Tables 3.3-1, 3.3-2, and 3.3-3. Table 3.3-2 includes all direct energy inputs and their contribution to the energy requirement for each process step. Table 3.3-3 includes the consumable materials and their energy contribution to the process.

It is evident from Table 3.3-2 that about 70 percent of the total energy for the process is in the form of electrical energy used in the electrowinning process. Large amounts of energy are also used in the production of acid. The cementation step requires a small amount of energy.

The process has basic limitations or disadvantages which are well known. Copper recovery (94.3 percent) is generally slightly lower than that achieved in reverberatory smelting, converting, and electrolytic refining. Precious metals in the sulfide concentrate are lost in the leach residue. Disposal of relatively large volumes of copper bearing acidic spent electrolyte is required, since more acid is generated in the electrolysis than is required in leaching. Although roaster gases are of a strength adequate for autothermal conversion to sulfuric acid, the gas strength is near the lower limit for autothermal operation. Because of the limitations, the process is applicable only where the limitations are not economically important or where low cost solutions to them can be developed.

3.3.3 Conclusions

The RLE process appears to be more efficient in energy utilization than the electric smelting process and as effective as conventional reverberatory calcine smelting. The overall energy consumption is 30.0 million Btu's per ton cathode copper as compared to 39.4 million Btu's per ton for electric smelting and 31.0 million Btu's per ton for the reverberatory calcine smelting. However, the process has basic limitations. Even with close control of the sulfate roaster, the exit

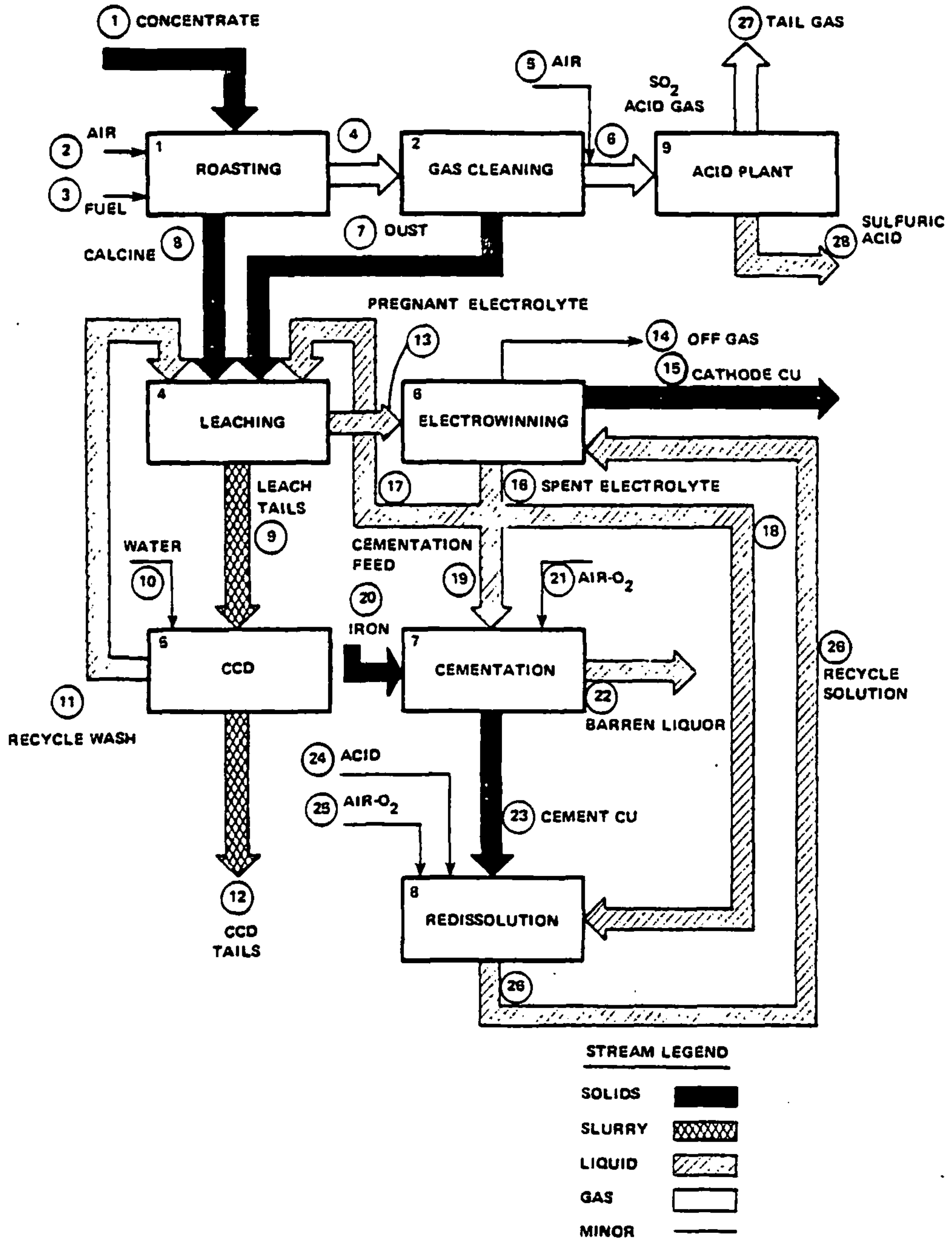

FIGURE 3.3-1 ROAST-LEACH-ELECTROWIN PROCESS

TABLE 3.3-1 ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		ROASTING AIR		FUEL		ROASTING OFF GAS		DILUTION AIR	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.061	25.001					.016	.101		
Fe	1.134	26.739					.013	.085		
S	1.315	30.997					.015	.098		
CuO							.732	4.644		
$CuSO_4$							.490	3.106		
FeO	.029	.690								
Fe_2O_3	.044	1.040					1.208	7.664		
$FeSO_4$							.090	.568		
SiO_2	.425	10.014					.319	2.022		
AL_2O_3	.146	3.450					.110	.697		
CaO	.088	2.070					.066	.418		
H_2O	.579						.579	3.675		
Fuel					.001	100.000				
O_2			2.750	23.000			.526	3.336	.383	23.000
N_2			9.206	77.000			9.206	58.420	1.282	77.000
CO_2							.002	.014		
SO_2							1.819	11.545		
SO_3							.568	3.607		
TOTAL	4.821	100.000	11.956	100.000	.001	100.000	15.759	100.000	1.665	100.000
TEMP. (F)	60		60		60		1274		60	
STATE	S		G		L		G		G	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	SO_2 ACID GAS		DUST RECYCLE		CALCINE		LEACH TAILS		WATER	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu			.016	.520	.005	.520	.021	.446		
Fe			.013	.436	.004	.436	.018	.373		
S			.015	.506	.005	.506	.021	.434		
CuO			.732	23.937	.244	23.937	.049	1.026		
$CuSO_4$			.490	16.010	.163	16.010	.257	5.407		
Fe_2O_3			1.208	39.497	.403	39.497	1.610	33.861		
$FeSO_4$			.090	2.928	.030	2.928	.042	.873		
SiO_2			.319	10.421	.106	10.421	.425	8.934		
AL_2O_3			.110	3.590	.037	3.590	.146	3.078		
CaO			.066	2.154	.022	2.154	.088	1.847		
H_2O	.579	4.031					2.073	43.589	8.322	100.000
H_2SO_4							.006	.131		
O_2	.909	6.325								
N_2	10.488	73.007								
CO_2	.002	.015								
SO_2	1.819	12.664								
SO_3	.568	3.957								
TOTAL	14.366	100.000	3.058	100.000	1.019	100.000	4.755	100.000	8.322	100.000
TEMP. (F)	600		1000		1112		123		60	
STATE	G		S		S		S		L	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	RECYCLE WASH		CCD TAILS		PREGNANT ELECTROLYTE		ELECTROWINNING OFF GAS		CATHODE Cu	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu			.021	.446					1.000	100.000
Fe			.018	.373						
S			.021	.434						
CuO			.049	1.026						
$CuSO_4$	.256	3.074	.001	.027	3.114	10.814				
Fe_2O_3			1.610	33.861						
$FeSO_4$	.041	.496	.000	.004	.503	1.746				
SiO_2			.425	8.934						
AL_2O_3			.146	3.078						
CaO			.088	1.847						
H_2O	8.019	96.355	2.376	49.968	25.101	87.177				
H_2SO_4	.006	.075	.000	.001	.076	.262				
O_2							.252	100.000		
TOTAL	8.322	100.000	4.755	100.000	28.793	100.000	.252	100.000	1.000	100.000
TEMP. (F)	74		74		123		104		104	
STATE	L		S		L		G		S	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	SPENT ELECTROLYTE		ELECTROLYTE RECYCLE		REDISSOLUTION LIQUOR		CEMENTATION FEED		CEMENTATION IRON	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Fe									.086	100.000
$CuSO_4$	.837	2.846	.602	2.847	.048	2.847	.187	2.847		
$FeSO_4$	.533	1.812	.383	1.813	.030	1.813	.119	1.813		
H_2O	26.350	89.582	18.946	89.578	1.504	89.578	5.899	89.578		
H_2SO_4	1.694	5.759	1.219	5.762	.097	5.762	.379	5.762		
TOTAL	29.415	100.000	21.150	100.000	1.680	100.000	6.585	100.000	.086	100.000
TEMP. (F)	104		104		104		104		60	
STATE	L		L		L		L		S	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	CEMENTATION AIR		BARREN LIQUOR		CEMENT CU		ACID		REDISSOLUTION AIR	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu					.075	100.000				
$FeSO_4$			.353	3.151						
H_2O			5.905	52.727			.007	7.000		
H_2SO_4			.344	3.071			.093	93.000		
O_2	1.059	23.000	1.053	9.402					.019	100.000
N_2	3.545	77.000	3.545	31.650						
TOTAL	4.603	100.000	11.199	100.000	.075	100.000	.100	100.000	.019	100.000
TEMP. (F)	60		104		104		60		60	
STATE	G		L		S		L		G	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)		(27)		(28)			
STREAM NAME	RECYCLE SOLUTION		ACID TAIL GAS		SULPHURIC ACID			
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%		
FeO	.235	12.559						
$FeSO_4$	.030	1.626						
H_2O	1.533	81.815			.262	7.000		
H_2SO_4	.075	4.000			3.482	93.000		
O_2			.454	4.151				
N_2			10.488	95.829				
CO_2			.002	.020				
TOTAL	1.873	100.000	10.945	100.000	3.744	100.000		
TEMP. (F)	157		100		100			
STATE	L		G		L			

TABLE 3.3-2 **ENERGY REQUIREMENTS** Level 1

ROAST - LEACH - ELECTROWINNING PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Fluid Bed Roasting				
	A) Electrical Power	KWH	110.61	0.0105	1.161
	B) Fuel (Start-Up)	GAL	0.212	0.1474	0.031
2	Roaster Gas Cleaning				
	A) Hot Gas Handling	MILLION SCF	296.11	0.00252	0.746
4	Leaching				
	A) Electrical Power	KWH	59.756	0.0105	0.627
5	CCD				
	A) Electrical Power	KWH	37.294	0.0105	0.392
6	Electrowinning				
	A) Electrical Power	KWH	2134.0	0.0105	22.407
7	Cementation				
	A) Electrical Power	KWH	30.675	0.0105	0.322
8	Redissolution				
	A) Electrical Power	KWH	16.275	0.0105	0.171
9	Acid Plant				
	A) Electrical Power	MILLION SCF	234.36	0.0113	2.648
	B) Cold Gas Cleaning	MILLION SCF	234.36	0.00132	0.309
				TOTAL	28.814

TABLE 3.3-3 **ENERGY REQUIREMENTS** Level 2

ROAST - LEACH - ELECTROWINNING PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
7	Cementation				
	A) Iron	TON	0.08625	18.00	1.553
8	Redissolution				
	A) Sulfuric Acid	TON	0.10125	.83	.084
				TOTAL	1.637

gas will contain excessive quantities of sulfur trioxide. Also, the recovery of copper as well as precious metals is lower, and disposal of large volumes of spent electrolyte is required. Moreover, the quality of cathode copper may not meet the electrolytic copper grade. Inclusion of the solvent extraction system appears to overcome some of these problems.

3.3.4 Recommendations

The RLE process is very well suited for mixed sulfide-oxide copper deposits. Because of some inherent disadvantages, the process needs additional research and development efforts. Of primary importance are the following:

(1) Recovery of precious metals
(2) Alternative methods for making the process suitable for all sulfide ores
(3) Alternate methods for sulfur removal other than excess acid production.

There appears to be little opportunity for major energy savings since electrowinning requires the major proportion of the total energy. However, if a method could be used for copper precipatation other than electrowinning considerable energy savings could result. For example, about 3×10^6 Btu per ton of cathode copper would be saved by utilizing the electroslurry electrowinning process.

3.3.5 References

Engineering and Mining Journal Operating Handbook of Mineral Process, McGraw Hill, Inc., pp. 21-22, 1977.

Foley, R.M., Method for Treating Copper Ore Concentrates, U.S. Patent No. 2,783,141, February 25, 1957.

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Kellogg, H.H. and J.M. Henderson, Extractive Metallurgy of Copper, Vol. 1, Ch. 19, American Institute of Mining, Metallurgical and Petroleum Engineers, Baltimore, MD, 1967.

3.4 CYMET PROCESS

3.4.1 Introduction

This process is analyzed for its material and energy requirements for extracting copper from chalcopyrite concentrate. The summary of material flows includes the raw materials and other process influents, internal process streams, and process effluents. The basis for all material and energy requirement is the production of one ton of cathode grade copper. The process in its present form has undergone extensive pilot plant testing since 1977 and the process at the pilot level is well understood.

3.4.2 Process Description

The process employs a cupric-ferric chloride to leach concentrates at 90° to 95°C to produce a solution rich in cuprous chloride as shown in Figure 3.4-1. The cuprous chloride is crystallized from solution by cooling to 38°C and separated from the solution in a centrifuge. The dried cuprous chloride crystals are fed to a fluidized bed reduction process that employs heated hydrogen as a reducing agent. After the copper nodules formed in the fluidized bed grow to a large enough size, they are removed by screening. The hydrogen chloride formed in the fluidized bed is removed by scrubbers and returned to the leach solution. The unreacted hydrogen is recycled back to the fluidized bed with the addition of make-up hydrogen. It is necessary to remelt the copper nodules in a refining furnace with an appropriate flux to remove any entrained sand and to fire refine the copper before casting into ingots.

The depleted liquor shown as stream 4 in Figure 3.4-1 is now rich in both cuprous and ferrous chloride. The liquor is regenerated back to ferric and cupric chloride with oxygen and by the addition of the hydrogen chloride recovered from the fluidized bed scrubbers. The reactions are exothermic and the solution leaves the step at 93°C. The excess iron in the regenerated leach liquor is precipitated as hydronium jarosite or ferric hydroxide. The major effluent streams from the process are the gangue minerals from the concentrate and the jarosite precipitates. These solid materials are sent to a tailings pond after recovery of the elemental sulfur and molybdenite they contain. The yield of copper metal in finished form from concentrate is 95 percent.

3.4.3 Material Balances

The material balances depend directly on the chemistry of the process. McNamara gave the following net reactions in his 1978 paper.

Cupric Leach

$$3CuCl_2 + CuFeS_2 \longrightarrow 4CuCl + FeCl + 2S^o \tag{3.4.1}$$

$$6CuCl_2 + S^o + 4H_2O \longrightarrow 6CuCl + H_2SO_4 + 6HCl \tag{3.4.2}$$

$$4FeCl_3 + CuFeS_2 \longrightarrow 5FeCl_2 + CuCl_2 + 2S^o \tag{3.4.3}$$

Ferric Leach

$$FeCl_3 + CuCl \longrightarrow FeCl_2 + CuCl_2 \tag{3.4.4}$$

$$4FeCl_3 + CuFeS_2 \longrightarrow 5FeCl_2 + CuCl_2 + 2S^o \tag{3.4.5}$$

Metal Reduction

$$2CuCl + H_2 \longrightarrow 2Cu^o + 2HCl \uparrow \tag{3.4.6}$$

Hydrolysis/Reagent Regeneration

$$4FeCl_2 + O_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O \tag{3.4.7}$$

$$4CuCl + O_2 + 4HCl \longrightarrow 4CuCl_2 + 2H_2O \tag{3.4.8}$$

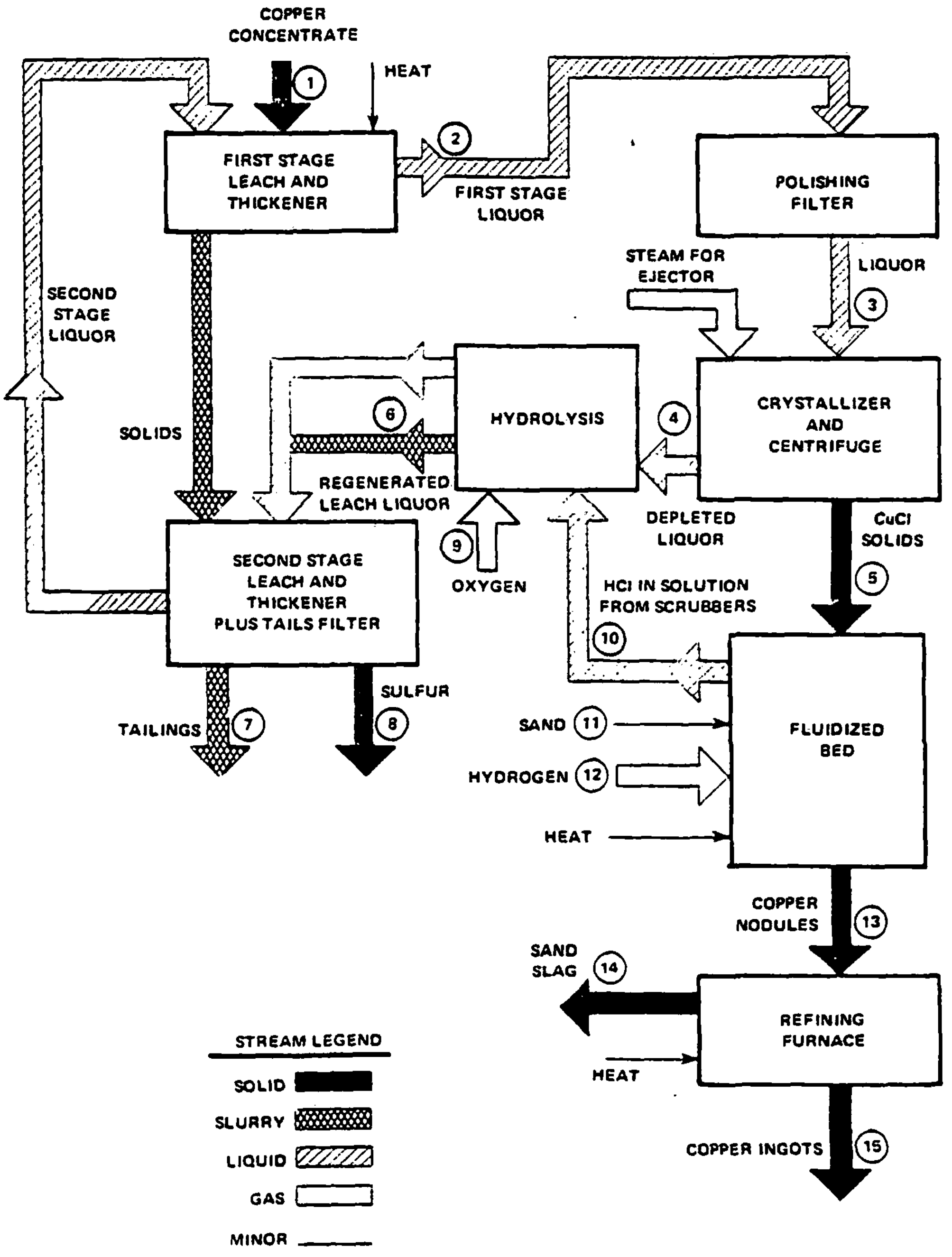

FIGURE 3.4-1 CYMET FERRIC CHLORIDE LEACH PROCESS

$$3FeCl_3 + 2H_2SO_4 + 7H_2O \longrightarrow (H_3O)\,Fe_3\,(SO_4)_2\,(OH)_6 \downarrow + 9HCl \tag{3.4.9}$$

$$FeCl_3 + 6H_2O \longrightarrow Fe\,(OH)_3\,(H_2O)_3 \downarrow + 3HCl \tag{3.4.10}$$

Summation

$$21O_2 + 18H_2O + 12CuFeS_2 \longrightarrow 12Cu^0 + 16S^0 + 4(H_3O)\,Fe_3\,(SO_4)_2\,(OH)_6 \tag{3.4.11}$$

$$9O_2 + 18H_2O + 12CuFeS_2 \longrightarrow 12Cu^0 + 24S^0 + 12Fe(OH)_3 \tag{3.4.12}$$

Material balance for the Cymet process is presented in Table 3.4-1. Since the process is still proprietary, many of the details on reaction times, temperatures, and concentrations are not known. The balances should present, however, a general idea of the material flows to produce one ton of copper.

The material balances and energy flows for the process are found in a number of references (McNamara, 1978), (McNamara, 1979), and (Bailey, 1978). Additional references to an earlier version of this process are found in earlier papers (Allen, 1974; Kruesi, 1973; and Kruesi, 1974).

3.4.4 Energy Requirements

The Level I energy requirements for Cymet Process for direct thermal and electrical energy are presented in Table 3.4-2. The electrical energy is reported to include all grinding, pumping, and agitation but not the energy used to produce oxygen by air separation. The total direct energy is 23.8 million Btu per ton of copper ingot. Looking at the energy needed to produce the chemicals consumed in the process, we find an additional 7.1 million Btu is consumed per ton of copper ingot. The energy content of the chemicals is presented in Table 3.4-3 with the production of gaseous oxygen and hydrogen requiring most of the energy input.

3.4.5 Discussion

The total energy for fuel, electricity and chemicals is equivalent to 30.9 million Btu per ton of copper ingot. The energy consumption is the lowest of all hydrometallurgical processes because of the use of the hydrogen fluidized bed for copper reduction. The energy consumption of 3.7 million Btu per ton of copper for hydrogen is considerably lower than energy consumption for electrowinning.

Extensive pilot plant testing has been completed by the Cyprus Metallurgical Process Corporation in Tucson, Arizona and the process has been evaluated both technically and economically. Cyprus plans to build a commercial plant using this process.

3.4.6 Conclusions and Recommendations

This process appears to be an attractive hydrometallurgical process with a relatively-low-energy consumption. The process is being actively developed and it may find several commercial applications. Like all hydrometallurgical processes, it may be most attractive at a smaller scale with a capacity of below 75,000 tons of copper per year where pyrometallurgical techniques are less attractive. It offers the potential of being a low-pollution method of extracting copper from chalcopyrite concentrates.

TABLE 3.4-1 CYMET HYDROMETALLURGICAL PROCESS

(TONS PER TON OF FIRE REFINED COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	COPPER CONCENTRATE		LIQUOR FROM CUPRIC LEACH		FILTERED LIQUOR		DEPLETED LIQUOR		CRYSTALLIZED CUPROUS CHLORIDE	
COMPOSITION	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%
Cu	1.050	25.0								
Fe	1.126	26.7								
S	1.305	31.0								
S_iO_2	0.365	8.6								
AL_2O_3	0.145	3.5								
FeO	0.029	0.7								
Fe_2O_3	0.044	1.0								
CaO	0.087	2.1								
MgO	0.036	0.9								
Others	0.022	0.5								
O_2										
H_2										
HCl										
$Fe(OH)_3$										
$NH_4Fe_2(SO_4)_2(OH)_6$										
Cu^{+1}			1.400	18.90	1.400	18.90	0.400	6.3	1.000	100.00
Cu^{+2}										
Fe^{+2}			5.997	80.10	5.997	80.10	5.997	93.7		
Fe^{+3}										
H_2O			14.000		14.000		14.000			
TOTAL	4.209	100.00	21.397	100.00	21.397	100.00	20.397	100.00	1.000	100.00

TABLE 3.4-i (cont.) CYMET HYDROMETALLURGICAL PROCESS

(TONS PER TON OF FIRE REFINED COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	REGENERATED LEACH LIQUOR		SOLID WASTE		SULFUR		OXYGEN OXYGEN GAS		HYDROGEN CHLORIDE	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%				
Cu			0.050	1.40						
Fe			0.044	1.20						
S			0.050	1.40	1.004	100.00				
S_iO_2			0.363	10.30						
AL_2O_3			0.145	4.00						
FeO			0.029	0.80						
Fe_2O_3			0.044	1.20						
CaO			0.087	2.40						
MgO			0.036	1.00						
Others			0.022	0.60						
O_2							0.909	100.00		
H_2										
HCl									0.575	100.00
$Fe(OH)_3$	0.813	10.1	0.813	22.90						
$NH_4Fe_2(SO_4)_2\text{-}(OH)_6$	1.884	23.5	1.884	52.80						
Cu^{+1}										
Cu^{+2}	0.400	5.0								
Fe^{+2}										
Fe^{+3}	4.915	61.4								
H_2O	14.000									
TOTAL	22.012	100.00	3.567	100.00	1.004	100.00	0.909	100.00	0.575	100.00

TABLE 3.4-1 (cont.) CYMET HYDROMETALLURGICAL PROCESS

(TONS PER TON FIRE REFINED COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	SAND IN FLUID BED		HYDROGEN GAS		COPPER NODULES		SAND SLAG		COPPER INGOT	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu					1.000	90.00			1.000	100.00
Fe										
S										
S_iO_2	0.110	100.00			0.110	10.00	0.110	100.00		
AL_2O_3										
FeO										
Fe_2O_3										
CaO										
MgO										
Others										
O_2										
H_2			0.0157	100.00						
HCl										
$Fe(OH)_3$										
$NH_4Fe_2(SO_4)_2(OH)_6$										
Cu^{+1}										
Cu^{+2}										
Fe^{+2}										
Fe^{+3}										
H_2O										
TOTAL	0.110	100.00	0.0157	100.00	1.110	100.00	0.110	100.00	1.000	100.00

TABLE 3.4-2 **ENERGY REQUIREMENTS** Level 1

CYMET HYDROMETALLURGICAL PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Refining Furnace				
	A) Fuel	SCF	6000	0.001	6.0
	Electrical Energy				
	A) For Overall Operations	KWH	1690	0.0105	17.8
				TOTAL	23.8

TABLE 3.4-3 **ENERGY REQUIREMENTS** Level 2

CYMET HYDROMETALLURGICAL PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Hydrolysis				
	A) Oxygen	TON	0.909	3.78	3.436
	Fluidized Bed				
	A) Hydrogen	TON	0.0157	234.00	3.674
	B) Sand	TON	0.11	0.042	0.005
				TOTAL	7.115

3.4.7 References

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3.5 SHERRITT-COMINCO PROCESS

3.5.1 Introduction

The unusual features of the Sherritt-Cominco process are an activating roast and an initial leach to reduce the iron content of the chalcopyrite concentrates. The estimates in this section include calculations of material flow for raw materials, internal process streams, and process effluents. A basis of one ton of cathode copper from a specified chalcopyrite concentrate is used in all calculations. The process has been extensively tested in a 9 ton per day pilot plant on a complex concentrate containing chalcopyrite, iron pyrite and recoverable zinc, gold and silver. A simpler process without zinc recovery is proposed for the purer chalcopyrite concentrate used in this comparison.

3.5.2 Process Description

The process for treating Arizona type chalcopyrite concentrates is a simplification of the process to treat the more complicated pyritic copper concentrates. As is outlined in Figure 3.5-1, the process employs a two-stage activating roast and a two-stage leach to produce a solution rich in cupric sulfate.

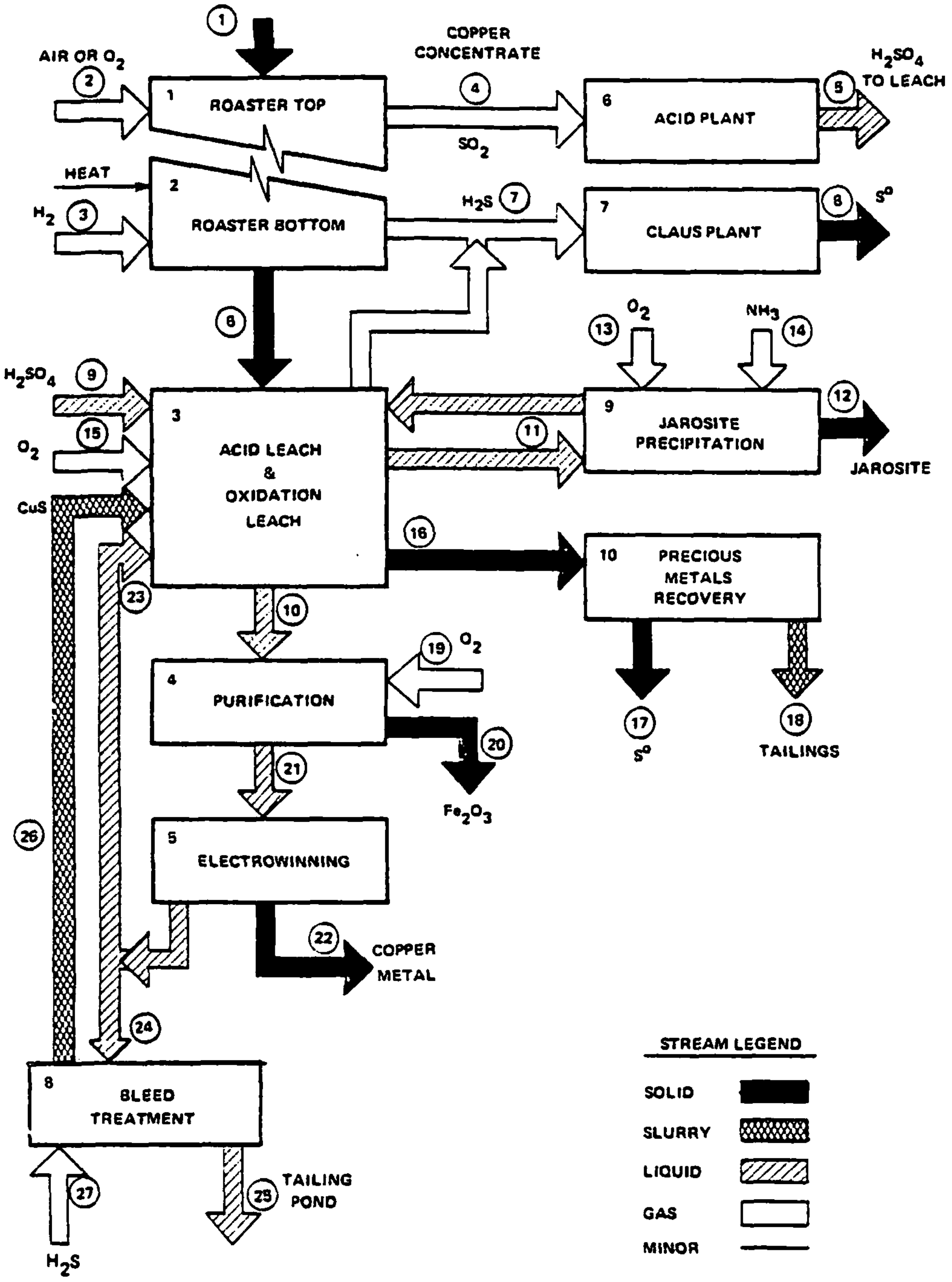

FIGURE 3.5-1 SHERRITT - COMINCO PROCESS

An oxidizing roast of the chalcopyrite concentrate followed by a reducing roast with hydrogen produce a calcine of bornite and troilite. All leaching steps are carried out in lead-clad-brick autoclaves at elevated pressures. The milder-first-stage sulfuric acid leach, conducted at 70°C and atmospheric pressure, dissolves the ferrous ion in troilite without dissolving the copper in the bornite. The dissolved iron is removed from the liquor as ammonium jarosite by first treating it with oxygen and ammonia and then by separating the precipitated jarosite from the liquid. In the stronger-oxidative leach, sulfuric acid and oxygen at 100°C and 13.5 atmospheres pressure dissolve 98 percent of the copper content. The leach liquor is purified of much of the iron and trace impurities in a pressurized oxygen reactor. The purified leach solution is sent to copper electrowinning cells for copper recovery.

In the electrolytic cells most of the electrolyte is recycled to the oxidative leach step. A small bleed stream of electrolyte controls the concentration of trace impurities not removed elsewhere in the process. The process employs a two-stage sulfuric acid plant to produce the acid required for leaching and a Claus plant to control the hydrogen sulfide produced in the reduction roast and first-stage leach. The major solid effluents from the process are the undissolved portion of the concentrate, the ammonium jarosite precipitate and a small amount of ferric oxide precipitate. Precious metals can be recovered from the oxidation leach residue, while elemental sulfur is recovered in the Claus plant and the precious metals circuit.

3.5.3 Material Balance

The material balances are derived from the chemical reactions involved. The chemistry is summarized below.

Destabilization Roast

$$5CuFeS_2 \xrightarrow{\text{Heat}} 5CuFeS_{1.8} + 1/2S_2 \tag{3.5.1}$$

$$7FeS_2 \xrightarrow{\text{Heat}} Fe_7S_8 + 3S_2 \tag{3.5.2}$$

Reduction Roast

$$5CuFeS_{1.8} + H_2 \rightarrow Cu_5FeS_4 + 4FeS + H_2S\uparrow \tag{3.5.3}$$

$$Fe_7S_8 + H_2 \rightarrow 7FeS + H_2S\uparrow \tag{3.5.4}$$

Acid Leach

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S\uparrow \tag{3.5.5}$$

Jarosite Precipitation

$$6FeSO_4 + 2NH_4OH + 3/2O_2 + 7H_2O \rightarrow 2NH_4Fe_3\,(SO_4)_2\,(OH)_6 + 2H_2SO_4 \tag{3.5.6}$$

Oxidation Leach

$$Cu_5FeS_4 + 6H_2SO_4 + 3O_2 \rightarrow 5CuSO_4 + FeSO_4 + 4S^o + 6H_2O \tag{3.5.7}$$

Electrowinning

$$2H_2O + 2CuSO_4 \rightarrow 2Cu^o + 2H_2SO_4 + O_2 \tag{3.5.8}$$

The material balances that result from this chemistry are shown in Table 3.5-1. Hydrogen reduction could replace the electrowinning but it has not yet been demonstrated on a large-pilot-plant basis (Maschmeyer, 1978). The background for material flow requirements was taken from a number of recent papers (Kawulka, 1978; Maschmeyer, 1978; and Swinkels, 1978).

3.5.4 Energy Requirements

The Level 1 energy requirements for the Sherritt-Cominco process are shown in Table 3.5-2. The electrical energy includes all grinding, pumping, agitating, and electrodeposition of copper, but does not include the energy for producing gaseous oxygen. The total electrical and thermal energy is 38.7 million Btu per ton of copper ingot. The Level 2 energy, which is required to produce the reagents used in the process, is presented in Table 3.5-3. An additional 9.4 million Btu per ton of copper is required to produce the reagents used in the process, largely in the form of oxygen, hydrogen and ammonia.

3.5.5 Discussion

The total energy for fuel, electricity and chemicals is 48.1 million Btu per ton of copper ingot. The energy consumption is in the mid-range of other hydrometallurgical processes analyzed in this study. The use of the hydrogen reduction version of this process could lower the total energy consumption when it is commercially proven.

The process has undergone extensive pilot plant evaluation with all materials of construction, process control, and operating procedures well defined. The companies believe they understand all parameters necessary to design a commercially viable copper refinery capable of treating a wide variety of concentrates. Other versions of this process can successfully treat mixed sulfide concentrates and recover zinc, molybdenum, precious metals as well as copper.

3.5.6 Conclusions and Recommendations

One of the major attractions of this process is its stage of development and its ability to process very complex concentrates. Its energy consumption is in the mid-range for hydrometallurgical processes analyzed in this study, and the hydrogen reduction version could result in lower energy consumption. Like all hydrometallurgical processes, it may be most attractive in smaller plants with a capacity of less than 75,000 tons per year.

3.5.7 References

Arthur D. Little, Inc., *Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. VII Ammonia Industry Report,* Interagency Energy-Environment Research and Development Program Report, EPA 600/7-76-034g, December 1978.

Energy Conservation Program Guide for Industry and Commerce, National Bureau of Standards Handbook 115, September, 1974.

Energy Use Patterns for Metal Recycling, U.S. Department of Commerce, Bureau of Mines Circular 8781, 1978.

Kawulka, P., C.R. Kirby and G.L. Bolton, "The Sherritt-Cominco Copper Process — Part II: Pilot-Plant Operations," *CIM Bulletin.* February 1978, pp. 122-130.

TABLE 3.5-1 SHERRITT-COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	COPPER CONCENTRATE		AIR		HYDROGEN		SULFUR DIOXIDE		SULFURIC ACID	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.02	25.00								
Fe	1.089	26.70								
S (Combined)	1.265	31.00								
S (Free)										
SiO_2	0.351	8.60								
AL_2O_3	0.143	3.50								
FeO	0.028	0.70								
Fe_2O_3	0.041	1.00								
CaO	0.086	2.10								
MgO	0.037	0.90								
Others	0.020	0.50								
NH_3										
O_2										
O_2 (In Air)			0.300	21.00						
H_2					0.014	100.00				
SO_2							0.600*			
N_2			1.130	79.00						
$NH_4Fe_2(SO_4)_2$-$(OH)_6$										
H_2O										
Cu^{+2}										
Fe^{+2}										
H_2SO_4									0.910	100.00
H_2S										
TOTAL	4.080	100.00	1.430	100.00	0.014	100.00			0.910	100.00

*Dry basis and SO_2 content only

TABLE 3.5-1 (cont.) SHERRITT-COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	ACTIVATED CALCINE		HYDROGEN SULFIDE		SULFUR		SULFURIC ACID MAKE-UP		OXIDATIVE LEACH LIQUOR	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.020	27.00								
Fe	1.089	28.80								
S (Combined)	0.960	25.40								
S (Free)					0.595	100.00				
S_iO_2	0.351	9.30								
AL_2O_3	0.143	3.80								
FeO	0.028	0.80								
Fe_2O_3	0.041	1.10								
CaO	0.086	2.30								
MgO	0.037	1.00								
Others	0.020	0.50								
NH_3										
O_2										
O_2 (In Air)										
H_2										
SO_2										
N_2										
$NH_4Fe_2(SO_4)_2$-$(OH)_6$										
H_2O									11.800*	
Cu^{+2}									1.246	82.08
Fe^{+2}									0.119	7.84
H_2SO_4							4.170	100.00	0.153	10.08
H_2S			0.632	100.00						
TOTAL	3.775	100.00	0.632	100.00	0.595	100.00	4.170	100.00	1.518*	100.00

*Water not included in totals

TABLE 3.5-1 (cont.) SHERRITT-COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	ACID LEACH LIQUOR		AMMONIA JAROSITE		OXYGEN		AMMONIA		OXYGEN	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe										
S (Combined)										
S (Free)										
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
CaO										
MgO										
Others										
NH_3							0.08	100.00		
O_2					0.305	100.00			0.429	100.00
O_2 (In air)										
H_2										
SO_2										
N_2										
$NH_4Fe_2(SO_4)_2-(OH)_6$			2.851	94.7						
H_2O	14.300*		2.500*							
Cu^{+2}			0.010	0.3						
Fe^{+2}	0.998	70.6								
H_2SO_4	0.415	29.4	0.150	5.0						
H_2S										
TOTAL	1.413*	100.00	3.011*	100.0	0.305	100.00	0.08	100.00	0.429	100.00

*Water not included in totals

TABLE 3.5-1 (cont.) SHERRITT-COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	OXIDATION RESIDUE		FREE SULFUR		TAILINGS		OXYGEN FOR PURIFICATION		FERRIC OXIDE PRECIPITATE	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.010	0.90			0.010	1.30				
Fe	0.091	8.10			0.091	11.80				
S (Combined)	0.017	1.50			0.017	2.20				
S (Free)	0.353	31.60	0.353	100.00						
S_iO_2	0.351	31.40			0.351	45.80				
AL_2O_3	0.143	12.80			0.143	18.70				
FeO	0.028	2.50			0.028	3.70			0.039	100.00
Fe_2O_3	0.041	3.60			0.041	5.40				
CaO	0.028	2.50			0.028	3.70				
MgO	0.037	3.30			0.037	4.80				
Others	0.020	1.80			0.020	2.60				
NH_3										
O_2							0.012	100.00		
O_2 (In Air)										
H_2										
SO_2										
N_2										
$NH_4Fe_2(SO_4)_2$-$(OH)_6$										
H_2O										
Cu^{+2}										
Fe^{+2}										
H_2SO_4										
H_2O										
TOTAL	1.119	100.00	0.353*	100.00	0.766	100.00	0.012	100.00	0.039	100.00

*Material quantities on a dry basis and major components only

TABLE 3.5-1 (cont.) SHERRITT - COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	PURIFIED SOLUTION		COPPER METAL		SPENT ELECTROLYTE RECYCLED		SPENT ELECTROLYTE TO BLEED		BLEED LIQUOR	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu			1.000	100.00						
Fe									0.002	1.5
S (Combined)										
S (Free)										
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
CaO										
MgO										
Others										
NH_3										
O_2										
O_2 (In Air)										
H_2										
SO_2										
N_2										
$NH_4Fe_2(SO_4)_2-(OH)_6$										
H_2O	11.80*				11.082		0.718		0.718	
Cu^{+2}	1.246	84.6			0.231	12.20	0.015	12.20		
Fe^{+2}	0.027	1.8			0.025	1.60	0.002	1.60		
H_2SO_4	0.200	13.6			1.637	86.20	0.106	86.20	0.129	98.5
H_2S										
TOTAL	1.473*	100.00*	1.000	100.00	1.893	100.00	0.123	100.00	0.131	100.00

*Water not included in totals

TABLE 3.5-1 (cont.) SHERRITT - COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)		(27)				
STREAM NAME	Copper Sulfide		Hydrogen Sulfide				
COMPOSITION	wt.	wt.%	wt.	wt.%			
Cu	0.015	66.4					
Fe							
S (Combined)	0.0076	33.6					
S (Free)							
S_iO_2							
AL_2O_3							
FeO							
Fe_2O_3							
CaO							
MgO							
Others							
NH_3							
O_2							
O_2 (In Air)							
H_2							
SO_2							
N_2							
$NH_4Fe_2(SO_4)_2$-$(OH)_6$							
H_2O							
Cu^{+2}							
Fe^{+2}							
H_2SO_4							
H_2S			0.008	100.00			
TOTAL	0.0226	100.00	0.008	100.00			

TABLE 3.5-2 **ENERGY REQUIREMENTS** Level 1

SHERRITT - COMINCO COPPER PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
5	Electrowinning and Process Use				
	A) Electrical Energy	KWH	3000	0.0105	31.5
	Total Fuel Requirement				
	A) Process Steam 1.25 Ton/Ton Copper	LBS	5143	0.0014	7.2
				TOTAL	38.7

TABLE 3.5-3 **ENERGY REQUIREMENTS** Level 2

SHERRITT - COMINCO COPPER PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Total Oxygen Use In System	TON	0.746	3.78	2.820
2	Roaster Bottom A) Hydrogen	TON	0.014	234.0	3.276
9	Jarosite Precipitation A) Ammonia	TON	0.08	41.73	3.338
				TOTAL	9.434

Maschmeyer, D.E.G., P. Kawulka, E.F.G. Milner and G.M. Swinkels, "Application of the Sherritt-Cominco Copper Process to Arizona Copper Concentrates," *Journal of Metals,* July 1978. pp. 27-31.

Maschmeyer, D.E.G., E.F.G. Milner and B.M. Parakh, "The Sherritt-Cominco Copper Process — Part III: Commercial Implications," *CIM Bulletin,* February 1978, pp 131-138.

Swinkels, G.M. and R.M.G.S. Berezowsky, "The Sherritt-Cominco Copper Process — Part I: The Process," *CIM Bulletin,* Feburary 1978, pp 105-121.

3.6 NITRIC-SULFURIC ACID LEACH PROCESS

3.6.1 Introduction

This evaluation of material and energy requirements is for a copper extraction process referred to as the nitric-sulfuric acid leach process ("NSL process" or "nitric acid process"). The evaluation includes calculations for raw materials, process steam, electrical power consumption, fuels, consumables, internal process streams, effluents, and heat losses. Energy requirements are assessed in two respects, (1) an operational requirement that does not include special processing features for economizing or recycling heat generated by the processing reactions and (2) a theoretical requirement that includes heats of the processing reactions, indicative of potential energy savings.

The nitric-sulfuric acid leach process is basically hydrometallurgical; the process design considered for this study is for the treatment of chalcopyrite concentrates recovered by froth flotation. The flow scheme is characterized by the hot vat leaching of the concentrates with an oxidizing lixiviant mixture of nitric and sulfuric acid. Following lixiviant purification, electrowinning is employed for copper recovery. A detailed description of the processing operations is presented by Brennecke, et al (1978). Improvements in the flowsheet are described by Davies, et al (1978). The experiments conducted to develop the process, and results of economic and energy evaluations by the staff of the Ledgemont Laboratory, Kennecott Copper Corporation, are discussed in these two papers. Some general conclusions drawn by the Kennecott investigators are:

1. The nitric-sulfuric acid leach process can produce electrowon copper capable of meeting typical chemical specifications for electrorefined-copper quality.
2. Energy requirements for the nitric-sulfuric acid leach process are higher than for equivalent pyrometallurgical extractions (as much as 2.5 times).
3. Operating costs of the nitric-sulfuric acid leach process are higher than for an equivalent pyrometallurgical extraction in medium- or large-size plants. Very small plants could have a slight cost advantage.

3.6.2 Process Description

The process design incorporates the improvement discussed by Davies, et al (1978). The major processing sections are an oxidizing nitric-sulfuric acid leach of the chalcopyrite concentrates, a series of purification steps (nitrate, iron and selenium removal) for the copper-rich lixiviant, and electrowinning to recover the copper as wire-grade cathodes. The oxidant for the leach, nitrogen peroxide (NO_2), is regenerated with oxygen via a gas-phase reactor (see flowsheet, Figure 3.6-1).

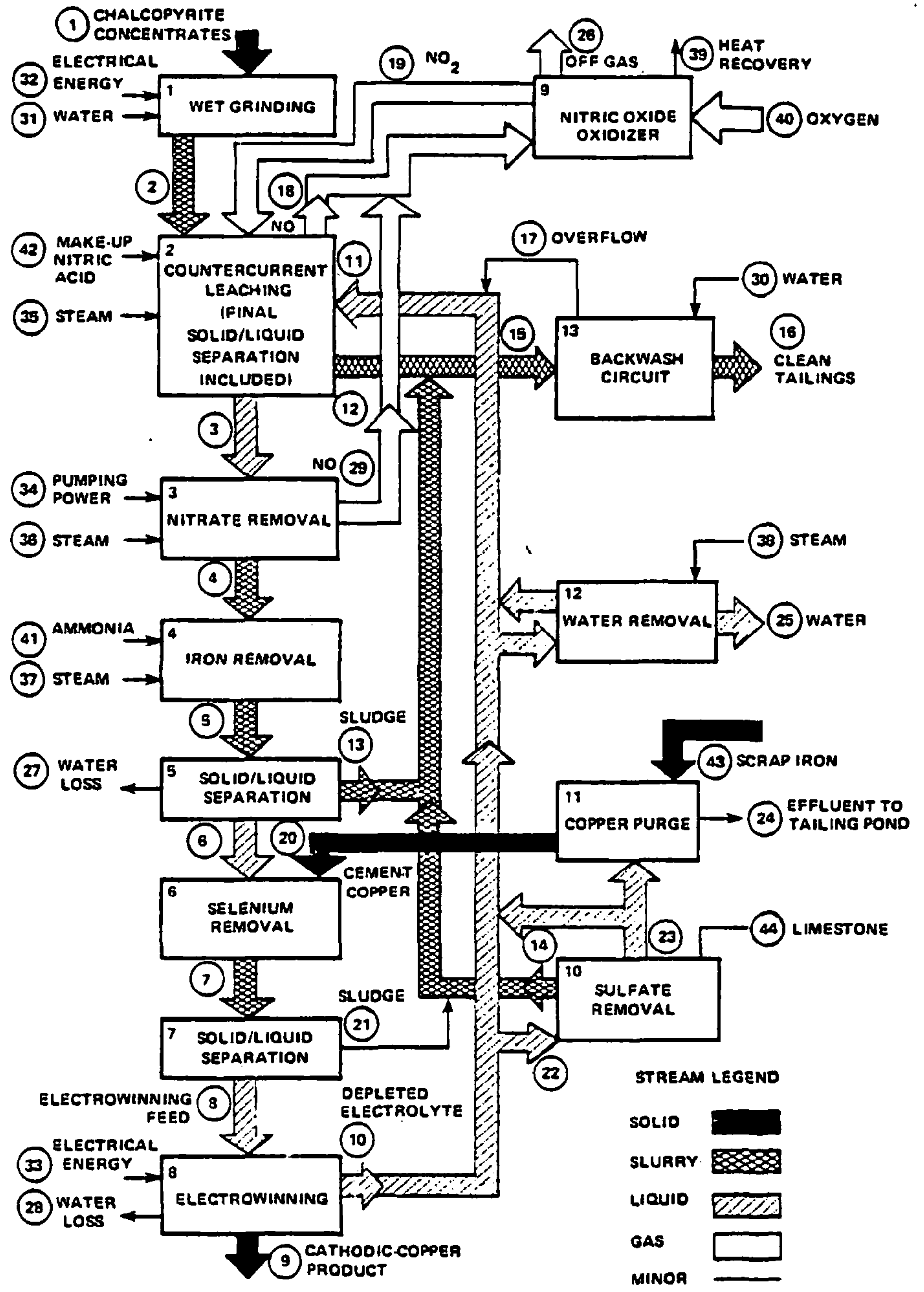

FIGURE 3.6-1 NITRIC-SULFURIC ACID LEACH PROCESS

Leaching is conducted in nonpressurized vats at 90°C. The nitrate-removal and iron-removal purification steps (Process Steps 3 & 4 in Figure 3.6-1) are conducted at 1350 kPa and 180°C. Oxidant regeneration (Process Step 14, NO Oxidizer) requires moderate pressures and some cooling. Other process steps are conducted at or near ambient conditions. Brief, but informative, descriptions of electrowinning and the other conventional hydrometallurgical process steps employed in the process design are given in Biswas and Davenport (1976). A short text on the nitrogen oxide chemistry is that by Jolly (1964).

The major stoichiometric relationships for the processing reactions are as follows:

Vat Leaching of Chalcopyrite Concentrates, Process Step 2

a. Copper dissolution

$$CuS + NO_2 + 2H^+ \longrightarrow Cu^{++} + S^0 + H_2O + NO \qquad (3.6.1)$$

b. Iron dissolution

$$FeS + NO_2 + 2H^+ \longrightarrow Fe^{++} + S^0 + H_2O + NO \qquad (3.6.2)$$

c. Sulfur oxidation

$$S^0 + 2NO_2 + H_2O \longrightarrow 2H^+ + SO_4^= + 2NO \qquad (3.6.3)$$

d. Nitrate formation

$$3NO_2 + H_2O \longrightarrow 2NO_3^- + 2H^+ + NO \qquad (3.6.4)$$

NO Oxidizer, Process Step 9

$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (3.6.5)$$

Nitrate Removal, Process Step 3

a. Iron oxidation

$$NO_3^- + 4H^+ + 3Fe^{++} \longrightarrow NO + 2H_2O + 3Fe^{+3} \qquad (3.6.6)$$

b. Hydrogen jarosite formation (incomplete)

$$3Fe^{+3} + 6H_2O + 2SO_4^= \longrightarrow HFe_3(SO_4)_2(OH)_6 + 5H^+ \qquad (3.6.7)$$

Iron Removal, Process Step 4

Ammonium jarosite formation

$$NH_3 + 3Fe^{+3} + 6H_2O + 2SO_4^= \longrightarrow NH_4Fe(SO_4)_2(OH)_6 + 5H^+ \qquad (3.6.8)$$

Selenium Removal, Process Step 6

a. Selenium precipitation

$$H_2SeO_3 + 4Cu^0 + 2H^+ \longrightarrow Cu_2Se + 2Cu^{++} + 3H_2O \qquad (3.6.9)$$

b. Iron reduction

$$2Fe^{+3} + Cu^0 \longrightarrow 2Fe^{++} + Cu^{++} \qquad (3.6.10)$$

As indicated above, the process has been laboratory tested and technically and economically evaluated by the staff of Kennecott Copper Corporation at their Ledgemont Laboratory. Further processing improvements could consist of the optimization of some of the processing steps; however, such improvements would probably have minor impact on the costs or energy requirements. Presently, development has not been attempted beyond the laboratory stage.

3.6.3 Material Balance

The evaluation of the material requirements is based on the process as described by Brennecke, et al (1978) and Davies, et al (1978). A water-removal step is added to maintain the water balance of the leaching-purification-electrowinning loop. A backwashing circuit is added to clean the tailings slurry and reduce copper loss. A wet grinding step is added for particle size control of the feed to the leach vats. The flowsheet employed is presented in Figure 3.6-1 with identifiers for each processing step and stream. The evaluation of material requirements is summarized in Table 3.6-1. For the evaluation, the production rate of cathodes is set at about 100,000 ton/yr and the copper recovery is 98%. The feed is considered to be a chalcopyrite concentrate recovered by froth flotation, to be non-refractory to the leaching process, and having a composition of 25% copper, 29% iron and 31% sulfur.

3.6.4 Energy Requirements

A summary for the energy requirements for the process is listed in Tables 3.6-2 and 3.6-3. The energy evaluation is based on the material evaluation presented above. Table 3.6-2 is a listing of Level 1 requirements. The listing is on a modular basis in sequential processing order. At Level 1, the chemicals and other consumables in the process are not included except for the fuel used. Table 3.6-3 is a listing of Level 2 energy requirements — chemicals, fluxes, refractories and other consumables used on a continuous basis in association with the process. Energy equivalent estimates are included in the tables and the equivalent fuel requirements are calculated and summed. This information supports the values given in the tables, but is too extensive for inclusion as footnotes.

The energy requirements presented in Tables 3.6-2 and 3.6-3 are evaluated for a process considered to be operated in a conventional manner. The totals are termed "operational" in the above summary table. The operational estimate does not consider special processing features for economizing or recycling heat generated by the processing reactions. The following is a discussion of a "theoretical" energy requirement for the process, that includes consideration of the heats of the processing reactions. The difference between the operational estimate and the theoretical estimate is indicative of the potential of the process for energy savings.

The following energy calculations were provided by Goel (1979). Thermochemical data for the calculations can be found in Barner and Schenerman (1978) unless noted otherwise.

TABLE 3.6-1 NITRIC-SULFURIC ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(3)		(8)		(9)		(16)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		PREMANT LEACH LIQUOR		ELECTROWINNING FEED		CATHODES		CLEAN TAILINGS SOLIDS	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.020	25.00	1.540	5.97	1.440	6.53	1.000	100.00	0.020	0.37
Fe	1.140	27.94	1.100	4.27					1.140	20.88
S	1.270	31.13							1.270	23.26
H_2O			16.910	65.57	15.500	70.33				
SO_4^{-2}			4.860	18.84	3.210	14.56				
NO_3^{-1}			0.410	1.59						
H_2SO_4			0.970	3.76	1.890	8.58				
Other	0.650	15.93							3.030	55.49
O_2										
HNO_3										
NH_3										
$CaCO_3$										
Scrap Iron										
Steam										
TOTAL	4.080	100.00	25.790	100.00	22.040	100.00	1.000	100.00	5.460	100.00

TABLE 3.6-1 (cont.) NITRIC-SULFURIC ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(20)		(35)		(36)		(37)		(38)	
STREAM NAME	CEMENT COPPER		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.05	100.00								
Fe										
S										
H_2O										
SO_4^{-2}										
NO_3^{-1}										
H_2SO_4										
Other										
O_2										
HNO_3										
NH_3										
$CaCO_3$										
Scrap Iron										
Steam			13.36	100.00	13.36	100.00	13.36	100.00	13.36	100.00
TOTAL	0.05	100.00	13.36	100.00	13.36	100.00	13.36	100.00	13.36	100.00

TABLE 3.6-1 (cont.) NITRIC-SULFURIC ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(40)		(41)		(42)		(43)		(44)	
STREAM NAME	OXYGEN		AMMONIA		NITRIC ACID		SCRAP IRON		LIMESTONE	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe										
S										
H_2O										
SO_4^{-2}										
NO_3^{-1}										
H_2SO_4										
Other										
O_2	1.770	100.00								
HNO_3					0.068	100.00				
NH_3			0.070	100.00						
$CaCO_3$									0.640	100.00
Scrap Iron							0.080	100.00		
Steam										
TOTAL	1.770	100.00	0.070	100.00	0.068	100.00	0.080	100.00	0.640	100.00

TABLE 3.6-2 **ENERGY REQUIREMENTS** Level 1

NITRIC - SULFURIC ACID LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Wet Grinding				
	A) Electrical Energy	KWH	21.42	0.0105	0.225
2	Countercurrent Leaching				
	A) Steam, Process Heating	TON	2.90	2.8	8.120
3	Nitrate Removal				
	A) Steam, Process Heating	TON	4.64	2.8	12.992
	B) Pumping (electrical energy)	KWH	7.15	0.0105	0.075
4	Iron Removal				
	A) Steam, Process Heating	TON	0.19	2.8	0.532
8	Electrowinning				
	A) Electrical Energy	KWH	2300	0.0105	24.15
12	Water Removal				
	A) Steam, Distillation	TON	5.63	2.8	15.764
*	Ancillary Loads				
	A) Electrical Energy	KWH	50	0.0105	0.525
				TOTAL	62.383

*Not shown on flowsheet

TABLE 3.6-3 **ENERGY REQUIREMENTS** Level 2

NITRIC - SULFURIC ACID LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Countercurrent Leaching				
	A) Nitric Acid	TON	0.068	14.2	0.966
4	Iron Removal				
	A) Ammonia	TON	0.0695	39.0	2.711
9	Nitric Oxide Oxidizer				
	A) Oxygen	TON	1.77	3.78	6.691
10	Sulfate Removal				
	A) Limestone	TON	0.64	3.6	2.304
11	Copper Purge				
	A) Scrap Iron	TON	0.08	2.0	0.160
				TOTAL	12.064

Energy generated by leaching reactions

$CuS + NO_2 + 2H^+ \longrightarrow Cu^{++} + S^o + H_2O + NO$ (3.6.11)

$\Delta H^o_{298} = -[2{,}800 + 7{,}900] + [15{,}500 - 15{,}300 - 57{,}800 + 21{,}600]$

$= -15{,}900$ cal/mole

Copper dissolved – 1.02 kg = 16.05 moles

Energy Generated = (16.05) (15,900) (3.60 x 10^{-6})

= .92 million Btu/ton product

$FeS + NO_2 + 2H^+ \longrightarrow Fe^{++} + S^o + H_2O + NO$ (3.6.12)

$\Delta H^o_{298} = -[-39{,}200 + 7{,}900] + [-21{,}300 - 15{,}300 - 57{,}800 + 21{,}600]$

$= -41{,}500$ cal/mole

Iron dissolved – 1.14 kg = 20.41 moles

Energy Generated = (20.41) (41,500) (3.60 x 10^{-6})

= 3.05 million Btu/ton product

$S^o + 2NO_2 + H_2O \longrightarrow 2H^+ + SO_4 + 2NO$ (3.6.13)

$\Delta H^o_{298} = -[15{,}300 + 3\,(7{,}900) - 57{,}800] + [-232{,}700 + 3\,(21{,}600)]$

$= -118{,}500$ cal/mole

Sulfur oxidized – all sulfur from FeS_2 + 35% from $CuFeS_2$ oxidized to sulfate
= .602 kg = 18.78 moles

Energy Generated = (18.78)(118,500) (3.60 x 10^{-6})

= 8.01 million Btu/ton product

$3NO_2 + H_2O \longrightarrow 2NO_3^- + 2H^+ + NO$ (3.6.14)

$\Delta H^o_{298} = -[3\,(7{,}900) - 57{,}800] + [2\,(-49{,}600) + 21{,}600]$

$= -43{,}500$ cal/mole

Nitrate formation – .42 kg = 6.8 moles

Nitrate production is kept to a minimum as required for complete oxidation of Fe^{++} to Fe^{+3}. Excess nitrate must be removed.

Energy Generation = (6.8) (43,500) (3.60 x 10^{-6})

= 1.06 million Btu/ton product

Total Energy Generation

by Leach Reactions = .92 + 3.05 + 8.01 + 1.06

= 13.04 million Btu/ton product

Heat evolution by NO oxidation

$NO + 1/2O_2 - NO_2$ (3.6.15)

ΔH°_{298} = −13,700 cal/mole

NO produced in the leach vessels – 3.01 kg = 100.3 moles

Heat Evolved = (100.3) (13,700) (3.60×10^{-6})

= 4.95 million Btu/ton product

50% credit from Heat Exchanger = 2.47 million Btu/ton product

Heat required in nitrate-removal reactions (Retention Time: 10 minutes at 180°C and 1350 kPa)

$NO_3^- + 4H^+ + 3Fe^{++} \longrightarrow NO + 2H_2O + 3Fe^{+3}$ (3.6.16)

ΔH°_{298} = − [49,600 + 3 (−21,300)] + [21,600 + 2 (−57,800) + 3 (−11,600)]

= −15,300 cal/mole

No heat credit given.

$3Fe^{+3} + 6H_2O + 2SO_4^= \longrightarrow HFe_3(SO_4)_2(OH)_6 + 5H^+$ (3.6.17)

ΔH°_{298} = − [3 (−11,600) + 6 (−57,800) + 2 (−232,700)] + [−796,570*]

= 50,250 cal/mole

Hydrogen jarosite formation – 40% of dissolved iron removed as hydrogen jarosite = 8.16 moles

Heat Required = (8.16) (50,250) (3.60×10^{-6})

= 1.48 million Btu/ton product

(*ΔH_f of hydrogen jarosite is from M.R. Spedden, Kennecott Copper, Nov. 1971; available from M.E. Wadsworth's personal file)

Heat required in iron-removal reactions (Retention Time: 85 min. at 180°C and 1350 kPa)

$NH_3 + 3Fe^{+3} + 6H_2O + 2SO_4^= \longrightarrow NH_4Fe_3(SO_4)_2(OH)_6 + 5H^+$ (3.6.18)

$\Delta H^\circ_{298} = 61{,}250$ cal/mole

Iron precipitated

Heat Required = $(12.25)\,(61{,}250)\,(3.60 \times 10^{-6})$

= 2.70 million Btu/ton product

($^\dagger\Delta H_f$ of ammonium jarosite assumed the same as for hydrogen jarosite)

Total Heat Generated by Processing Reactions

= 13.04 + 4.95 − 1.48 2 − 2.50

= 13.18 million Btu/ton product

The heat generated by the process reactions can, in theory, be employed to offset steam requirements necessary for process heating. Some special design considerations may be necessary to accomplish the savings in steam, however. Such is the case with vat leaching where the process streams must be heated prior to leaching. An equipment design that transfers heat from the leaching vats to the influent streams would be needed. The theoretical energy requirement for this special design is as follows:

Total Level 1 Energy Requirement — 62.38 million Btu/ton product (See Table 3.6-3)

Offset from Heat Generated by Processing Reactions — 13.18 million Btu/ton product

Steam Conserved by Improved Water Balance — 13.18 million Btu/ton product

Total Theoretical Level 1 — Requirement — 36.02 million Btu/ton product

Total Level 2 Energy Requirement — (unchanged, see Table 3.6-3) — 12.06 million Btu/ton product

Total Theoretical Energy — Requirement — 46.42 million Btu/ton product

3.6.5 Discussion

Highly significant aspects in the evaluation of material and energy requirements for the nitric-sulfuric acid leach process are ascertaining the compositions of the streams of the leaching-purification-electrowinning loop (streams with 20-25 times the mass flow of the product) and evaluating the control of the water balance (a control that is highly sensitive to the tailings backwash operation and the direct injection of steam for process heating).

The Level 1 energy requirements are dominated by the process heating for the countercurrent-leaching and nitrate-removal steps and by the energy required to remove water from the leaching-purification-electrowinning loop to maintain the water balance. Electrowinning is also a heavy energy consuming step. The energy required for electrowinning is determined by the production rate of cathodes and is fairly independent of process design considerations. Thus, electrowinning offers little potential for energy reduction via design improvements. The process heating energy requirements have potential for reduction via refinements in design that economize or recycle heat (with an increase in equipment complexity, of course).

The energy requirements for Level 2 are dominated by ammonia and oxygen consumptions. These requirements are dependent on the composition of the chalcopyrite concentrate feed, and thus, offer little opportunity for improvement via design refinement. Make up of nitric acid in the counter-current leaching step is a critical design consideration. The makeup of nitric acid is dependent on the gas-tight integrity of the leach vats, gas handling, and gas processing equipment (all design considerations). Nitric acid is also a strong energy consuming item (14.2 million Btu/ton, see Table 3.6-2); thus, potential energy requirement increases from design variances relevant to the gas-tight integrity of the equipment is discernible. Additional significance is placed on nitric acid make up if the energy required for air pollution control of NO losses were considered.

With the exception of electrowinning electrical energy and the ammonia and oxygen consumption, the energy requirement for the process is mainly in the form of low-pressure process-heating steam. Many opportunities are thus afforded for the economizing or recycling of heat and for utilizing waste heat from other processing activities. The extent to which these energy conservation measures might be carried would depend on the optimization of an operational design.

3.6.6 Conclusions and Recommendations

The processing energy requirements are significantly sensitive to process design factors that influence the utilization of heat generated by the processing reactions or the economizing and recycle of heat from the leaching and purification steps. Second to the process design factors, chalcopyrite concentrate composition differences causing variances in ammonia and oxygen consumption are most significant.

The six largest energy consuming items are electrowinning, water removal for control of the water balance of the leaching-purification-electrowinning loop, process heating steam for the nitrate-removal step, process heating steam for counter-current leaching, oxygen for NO oxidation, and ammonia consumption for iron precipitation, respectively. The total energy requirement for an operational process is 74.44 million Btu/ton product of which 62.38 million Btu/ton product (84%) is in the form of direct fuel, steam and electrical power consumption. The theoretical energy evaluation indicates that the effective use of heat generated by the processing reactions would significantly reduce the total energy required (38% reduction, from 74.44 million Btu/ton product to 46.42 million Btu/ton product). Both the operational and the theoretical assessments are significantly above the energy required for more conventional pyrometallurgical processing.

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3.7 UNIVERSITY OF UTAH-MARTIN-MARIETTA PROCESS

3.7.1 Introduction

This process, with attrition grinding of concentrate and ferric sulfate leach, is analyzed for its material and energy requirements for extracting copper from chalcopyrite concentrates. The estimates include calculations of material flow for raw materials, internal process streams, and process effluents. The basis for the calculations is the production of one ton of copper from chalcopyrite concentrates. The process was evaluated at a pre-pilot plant stage by the University of Utah, Salt Lake City, Utah and Martin Marietta of Baltimore, Maryland. This evaluation was supported by the National Science Foundation under NSF/RANN Grant Award No. GI 40538.

3.7.2 Process Description

The process requires attrition milling of concentrates to produce small particles necessary for efficient leaching. In an acid ferric sulfate leach, a layer of elemental sulfur builds up on the surface of the concentrate particles that inhibits the leaching process. The specified mean particle size of 1 micrometer is a trade-off between the desire to have particles as small as possible without expending an excessive amount of energy for the attrition milling. As shown in Figure 3.7-1, a two-step leach is employed with an intermediate step to remove the coating of sulfur from the concentrate particles so that the second leach step can proceed at a faster rate. The leaching processes are carried out at 90°C under atmospheric pressure: three stages at four hours per stage in step 1 and 3 stages at one hour per stage in step 2. The resulting solution rich in cupric sulfate is treated for iron removal by addition of ammonia and oxygen to form ammonium jarosite precipitate which must be separated from the solution. Selenium is subsequently removed by precipitation with metallic copper before the purified solution flows into electrolytic cells for the electrowinning of cathode copper. The spent electrolyte is recycled to the leaching stages after removing the excess liquid and precipitating excess sulfate as gypsum. The active ferric ion is regenerated in the electrolyte from the ferrous ion in the leaching vessels by the action of oxygen and sulfur dioxide.

3.7.3 Material Balance

The material balances were derived from the chemical reactions occurring during the extraction of copper. The chemistry may be summarized as:

Leach Stages

$$2CuFeS_2 + 3O_2 + 2SO_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 2FeSO_4 + 2H_2O + 4S^o \qquad (3.7.1)$$

$$FeS_2 + 4O_2 + 2H_2O + SO_2 \longrightarrow FeSO_4 + 2H_2SO_4 \qquad (3.7.2)$$

$$CuS + 3SO_2 + 2O_2 + 2H_2O \longrightarrow S^o \downarrow + CuSO_4 + 2H_2SO_4 \qquad (3.7.3)$$

Iron Removal

$$12FeSO_4 + 3O_2 + 4NH_4 + 18H_2O \longrightarrow 2\,(NH_4)_2\,Fe_6\,(SO_4)_4\,(OH)_{12} \downarrow + 4H_2SO_4 \qquad (3.7.4)$$

Selenium Removal

$$H_2SeO_3 + 4Cu^o + 2H_2SO_4 \longrightarrow Cu_2Se \downarrow + 2\,CuSO_4 + 3H_2O \qquad (3.7.5)$$

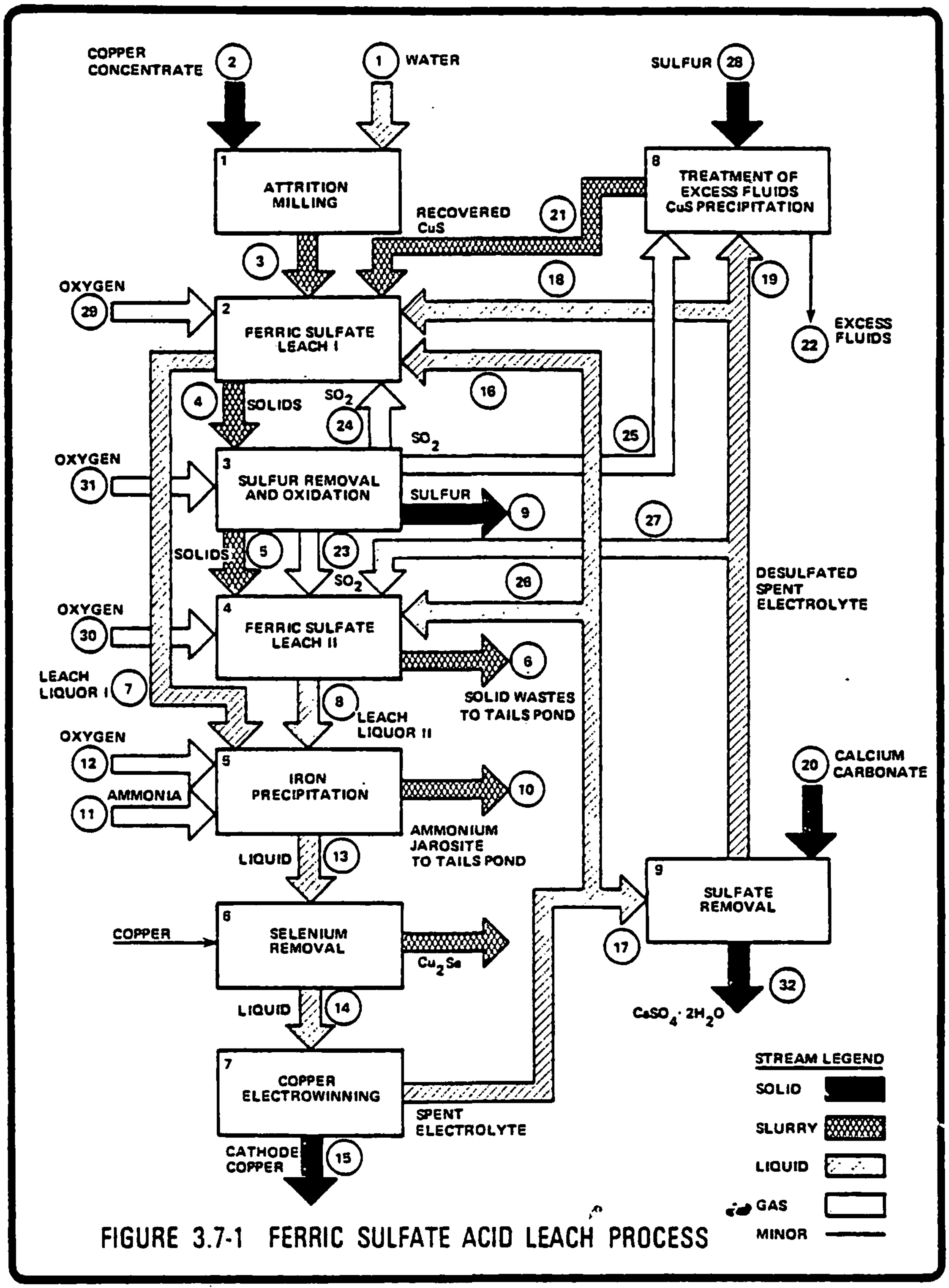

FIGURE 3.7-1 FERRIC SULFATE ACID LEACH PROCESS

Electrowinning

$$2CuSO_4 + 2H_2O \longrightarrow 2Cu^0 + 2H_2SO_4 + O_2 \quad (3.7.6)$$

Sulfate Removal

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O \downarrow + CO_2 \uparrow \quad (3.7.7)$$

Recovery of Copper Sulfate from Waste Solution

$$CuSO_4 + S^0 + SO_2 + 2H_2O \longrightarrow CuS \downarrow + 2H_2SO_4 \quad (3.7.8)$$

The material balances resulting from this chemistry are presented in Table 3.7-1. The quantities involved are sufficient to produce one ton of cathode copper. Stream numbers are the same as appeared in Figure 3.7-1.

The material flow requirements were taken from a flowsheet prepared by J. L. Sepulveda of the University of Utah and modified for a chalcopyrite concentrate composition consistently used in this report. The process reactions and kinetics are detailed in a recent paper (Beckstead, 1976). Other references, (Baily, 1978; Goel, 1979; and Rosswog, 1979), present energy estimates for electrowinning copper from a cupric sulfate solution and general process energy for the hydrometallurgical leaching.

3.7.4 Energy Requirements

The Level 1 energy requirements that include all direct thermal and electrical inputs are shown in Table 3.7-2. The electrical energy includes milling, pumping, agitation and electrodeposition of copper, but does not include the energy for producing gaseous oxygen or ammonia. The total energy which is all electrical, is equivalent to 55.3 million Btu per ton of cathode copper. The reasons for this relatively large energy requirement center around the energy intensive nature of the electrowinning step and the attrition milling step. The Level 2 requirements for chemicals consumed in the process are shown in Table 3.7-3 for a total of 10.0 million Btu per ton of copper. The major chemical contributors to the total energy load are gaseous oxygen used in several process steps, and the ammonia used for iron precipitation.

3.7.5 Discussion

The total energy for both fuel, electricity and chemicals is equivalent to 65.3 million Btu per ton of cathode copper. The energy consumption is in the upper range for hydrometallurgical processes because of the energy intensive attrition milling of concentrates and the electrowinning of copper. The energy consumption figures could change for this process as it is developed further since it is still in a laboratory testing stage. The process is currently being technically and economically evaluated at the University of Utah.

3.7.6 Conclusion and Recommendations

This process appears to have the attraction of being a low-pollution route for the extraction of copper from chalcopyrite concentrates. Its energy requirements are quite high at its present state of development. These energy figures might be improved as more is learned about the process. Like all hydrometallurgical processes, it may be more attractive in smaller plants with a capacity of around 75,000 tons per year.

TABLE 3.7-1 FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WATER		COPPER CONCENTRATE		CONCENTRATE SLURRY		LEACH I SOLIDS		SOLIDS FROM SULFUR REMOVAL	
COMPOSITION	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%
Cu			1.013	25.00	1.013	25.00	0.081	3.70	0.081	6.30
Fe			1.083	26.70	1.083	26.70	0.231	10.40	0.231	18.10
S (Combined)			1.256	31.00	1.256	31.00	0.264	11.90	0.264	20.70
S (Free)							0.943	42.5		
S_iO_2			0.350	8.60	0.350	8.60	0.350	15.80	0.350	27.40
AL_2O_3			0.140	3.50	0.140	3.50	0.140	6.30	0.140	11.00
FeO			0.028	0.70	0.028	0.70	0.028	1.20	0.028	2.20
Fe_2O_3			0.042	1.00	0.042	1.00	0.042	1.90	0.042	3.30
$NH_4Fe_2(SO_4)_2\text{-}(OH)_6$										
Others			0.140	3.50	0.140	3.50	0.140	6.30	0.140	11.0
NH_3										
O_2										
N_2										
SO_2										
H_2O	3.647	100.00	0.405		4.052					
$CaSO_4 \cdot 2H_2O$										
$Ca\ CO_3$										
Cu^{+2}										
Fe^{+2}										
CuS										
TOTAL	3.647	100.00	4.457	100.00	8.104	100.00	2.219	100.00	1.276	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	SOLID WASTES		LIQUOD FROM LEACH I		LIQUOD FROM LEACH II		SULFUR		AMMONIUM JAROSITE	
COMPOSITION	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%
Cu	0.008	0.70	1.226	57.91	0.171	59.40				
Fe	0.140	12.70	0.890	42.10	0.117	40.60				
S (Combined)	0.160	14.50								
S (Free)	0.092	8.40					0.296	100.00		
S_iO_2	0.350	31.80								
AL_2O_3	0.140	12.70								
FeO	0.028	2.50								
Fe_2O_3	0.042	4.00								
$NH_4Fe_2(SO_4)_2(OH)_6$									2.654	100.00
Others	0.140	12.70								
NH_3										
O_2										
N_2										
SO_2										
H_2O			21.133		5.321					
$CaSO_4 \cdot 2H_2O$										
Ca CO_3										
Cu^{+2}										
Fe^{+2}										
CuS										
TOTALS	1.100	100.00	23.249	100.00	5.609	100.00	0.296	100.00	2.654	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	AMMONIA		AIR		IRON PRECIPITATION LIQUOD		SELENIUM REMOVAL LIQUOD		CATHODE COPPER	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%
Cu									1.000	100.00
Fe										
S (Combined)										
S (Free)										
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
$NH_4Fe_2(SO_4)_2(OH)_6$										
Others										
NH_3	0.094	100.00								
O_2			0.133	21.00						
N_2			0.632	79.00						
SO_2										
H_2O					26.455		26.455			
$CaSO_4 \cdot 2H_2O$										
Ca CO_3										
Cu^{+2}					1.395	94.60	1.397	94.6		
Fe^{+2}					0.079	5.40	0.079	5.4		
CuS										
TOTAL	0.094	100.00	0.765	100.00	27.929	100.00	27.931	100.00	1.000	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	SPENT ELECTROLYTE TO LEACH I		SPENT ELECTROLYTE TO SULFATE REMOVAL		DESULFATED LIQUOD TO LEACH I		DESULFATED LIQUOD TO CuS PRECIP.		CALCIUM CARBONATE	
COMPOSITION	wt.	dry wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%
Cu										
Fe										
S (Combined)										
S (Free)										
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
$NH_4Fe_2(SO_4)_2(OH)_6$										
Others										
NH_3										
O_2										
N_2										
SO_2										
H_2O	14.799		11.656		3.534		3.647			
$CaSO_4 \cdot 2H_2O$										
$Ca\ CO_3$									.938	100.00
Cu^{+2}	0.222	83.50	0.175	83.5	0.053	83.5	0.055	83.5		
Fe^{+2}	0.044	16.50	0.035	16.5	0.011	16.5	0.011	16.5		
CuS										
TOTAL	15.065	100.00	11.866	100.00	3.598	100.00	3.713	100.00	.938	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COOPER)

STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	COPPER SULFIDE		EXCESS FLUID		SULFUR DIOXIDE TO LEACH II		SULFUR DIOXIDE TO LEACH II		SULFUR DIOXIDE TO CuS PRECIP.	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe										
S (Combined)										
S (Free)										
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
$NH_4Fe_2(SO_4)_2^-(OH)_6$										
Others										
NH_3										
O_2										
N_2										
SO_2					0.115	100.00	1.125	100.00	0.055	100.00
H_2O			3.647	100.00						
$CaSO_4 \cdot 2H_2O$										
$Ca\ CO_3$										
Cu^{+2}										
Fe^{+2}										
CuS	0.082	100.00								
TOTAL	0.082	100.00	3.647	100.00	0.115	100.00	1.125	100.00	0.055	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)		(27)		(28)		(29)		(30)	
STREAM NAME	SPENT ELECTROLYTE TO LEACH II		DESULFATED LIQUOD TO LEACH II		SULFUR		OXYGEN FOR LEACH I		OXYGEN FOR LEACH II	
COMPOSITION	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe										
S (Combined)										
S (Free)					0.0277	100.00				
S_iO_2										
AL_2O_3										
FeO										
Fe_2O_3										
$NH_4Fe_2(SO_4)_2(OH)_6$										
Others										
NH_3										
O_2							0.829	100.00	0.117	100.00
N_2										
SO_2										
H_2O	0.852		4.474							
$CaSO_4 \cdot 2H_2O$										
$Ca\ CO_3$										
Cu^{+2}	0.0128	83.5	0.067	83.5						
Fe^{+2}	0.0025	16.5	0.013	16.5						
CuS										
TOTAL	0.8673	100.00	4.554	100.00	0.0277	100.00	0.829	100.00	0.117	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(31)		(32)				
STREAM NAME	OXYGEN FOR SULFUR OXIDATION		CALCIUM SULFATE PRECIPITATE				
COMPOSITION	wt.	wt.%	wt.	wt.%			
Cu							
Fe							
S (Combined)							
S (Free)							
S_iO_2							
AL_2O_3							
FeO							
Fe_2O_3							
$NH_4Fe_2(SO_4)_2(OH)_6$							
Others							
NH_3							
O_2	0.648	100.00					
N_2							
SO_2							
H_2O							
$CaSO_4 \cdot 2H_2O$			1.613	100.00			
Ca CO_3							
Cu^{+2}							
Fe^{+2}							
CuS							
TOTAL	0.648	100.00	1.613	100.00			

TABLE 3.7-2 **ENERGY REQUIREMENTS** Level 1

FERRIC SULFATE ACID LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>Attrition Milling</u>				
	A) Electrical Energy (2 to 3 micron mean Particle size 4.05 ton concentrate/ton copper)	KWH	408.2	0.0105	4.286
7	<u>Copper Electrowinning</u>				
	A) Electric Energy	KWH	2445	0.0105	25.673
	<u>Process Pumping and Agitation</u>				
	A) Electrical Energy	KWH	900	0.0105	9.45
				TOTAL	39.409

TABLE 3.7-3 **ENERGY REQUIREMENTS** Level 2

FERRIC SULFATE ACID LEACH PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leach I A) Oxygen	TON	0.829	3.78	3.134
3	Sulfur Oxidation A) Oxygen	TON	0.648	3.78	2.449
4	Leach II A) Oxygen	TON	0.117	3.78	0.442
5	Iron Precipitation A) Ammonia	TON	0.094	41.73	3.923
9	Sulfate Removal A) Limestone	TON	0.938	0.104	0.098
				TOTAL	10.046

3.7.7 References

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3.7A THE ELECTROSLURRY™ — ENVIROTECH CORPORATION PROCESS

3.7A.1 Introduction

This process uses ferric sulfate leaching to extract the copper from chalcopyrite concentrates. An analysis will be made of the material balance for raw materials, internal process streams, and process effluents on the basis of 1 ton of copper product. The energy requirements are estimated on the basis of a commercial plant with a production rate of 50,000 tons per year of copper cathodes. In collaboration with Dr. Milton Wadsworth, Professor of Metallurgy and Metallurgical Engineering at the University of Utah, the process has been developed at the bench level at the Envirotech Research Center in Salt Lake City, Utah.

3.7A.2 Process Description

Overall, chalcopyrite concentrate is converted to covellite (CuS) and digenite ($Cu_{1.8}S$) and the converted solids are then processed through a slurry electrowinning cell to recover copper as electrowon cathodes. The slurry electrowinning cell offers a new concept in copper electrowinning in that it generates ferric iron at the anode instead of oxygen when compared to conventional copper electrowinning. This eliminates the oxygen over potential which is the major contributor to the high energy requirement in conventional electrowinning. The ferric iron, generated at the anode, is used to leach copper from the copper bearing solids which have been fed to the cell. Thus, leaching and electrowinning take place simultaneously.

The flowsheet is shown in Figure 3.7A-1. Copper concentrate is mixed with water to produce a slurry of 50 wt.% solids and is fed to an attritor milling circuit to produce a mean particle size of approximately 2 micron. This improves reaction rates in subsequent leaching and conversion circuits. 39% of the ground concentrate is leached in an acidic ferric sulfate solution to produce a copper sulfate, iron sulfate, sulfuric acid solution for feed to the conversion circuit. Ferric iron is generated "in-situ" by sparging the agitated slurry with oxygen gas. A 97% copper leach is obtained in 5 hours. The reaction is carried out at 90°C. 61% of the ground concentrate is mixed with the leach liquor and the resulting slurry is reacted with sulfur dioxide gas in an agitated vessel to convert the chalcopyrite to covellite and digenite. Retention times are approximately 2.5 hours and the reaction is carried out at 90°C. The converted solids are mixed with electrolyte from the slurry electrowinning circuit and processed in the electrowinning cells to produce copper cathodes. The conversion liquor contains ferrous sulfate and sulfuric acid and is sent to an iron removal step to remove iron as hydrated ferrous sulfate; after iron is removed, the acid liquor is returned to the leach circuit. A bleed stream is removed from the conversion liquor before iron removal to maintain a water and impurity balance. Iron removal is accomplished by adding the sulfuric acid required for leaching to the conversion liquor which is saturated with ferrous sulfate.

Sulfuric acid addition lowers the solubility of ferrous sulfate and hydrated ferrous sulfate precipitates out of solution and forms crystals which are easily filtered and washed. Approximately 85% of the copper contained in the conversion solids can be leached in the slurry electrowinning cells before an appreciable amount of iron begins to accumulate in the electrolyte. The cell circuit is controlled so that the electrolyte slurry exits the circuit at this point and goes to liquid solid separation where the electrolyte is recovered and returned to the electrowinning cells and the residual cells solids are directed to the leach step to recover residual copper. Sulfur contained in the feed concentrate is converted to elemental sulfur and reports to the tailings from the leach circuit. The elemental sulfur is recovered by pressure filtration, on plate and frame filter, with steam at 35 PSIG. Bleed streams and the hydrated ferrous sulfate (if it cannot be sold as by-product) are directed to a waste treatment and circuit where the acid is neutralized and iron is oxidized and precipitated as ferric hydroxide before being disposed to a tailings pond. Laboratory testing has shown a 98% copper recovery for the process.

3.7A.3 Material Balance

The process chemistry is shown by the following reactions:

Leaching

$$CuFeS_2 + 2Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 5FeSO_4 + 2S^0 \qquad (3.7A.1)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (3.7A.2)$$

Overall:

$$CuFeS_2 + O_2 + 2H_2SO_4 \longrightarrow CuSO_4 + FeSO_4 + 2S^0 + 2H_2O \qquad (3.7A.3)$$

Conversion

$$CuFeS_2 + 1.25CuSO_4 + 0.25SO_2 + 0.5H_2O \longrightarrow \qquad (3.7A.4)$$

$$1.7CuS + 0.3Cu_{1.8}S + FeSO_4 + 0.5H_2SO_4 \qquad (3.7A.5)$$

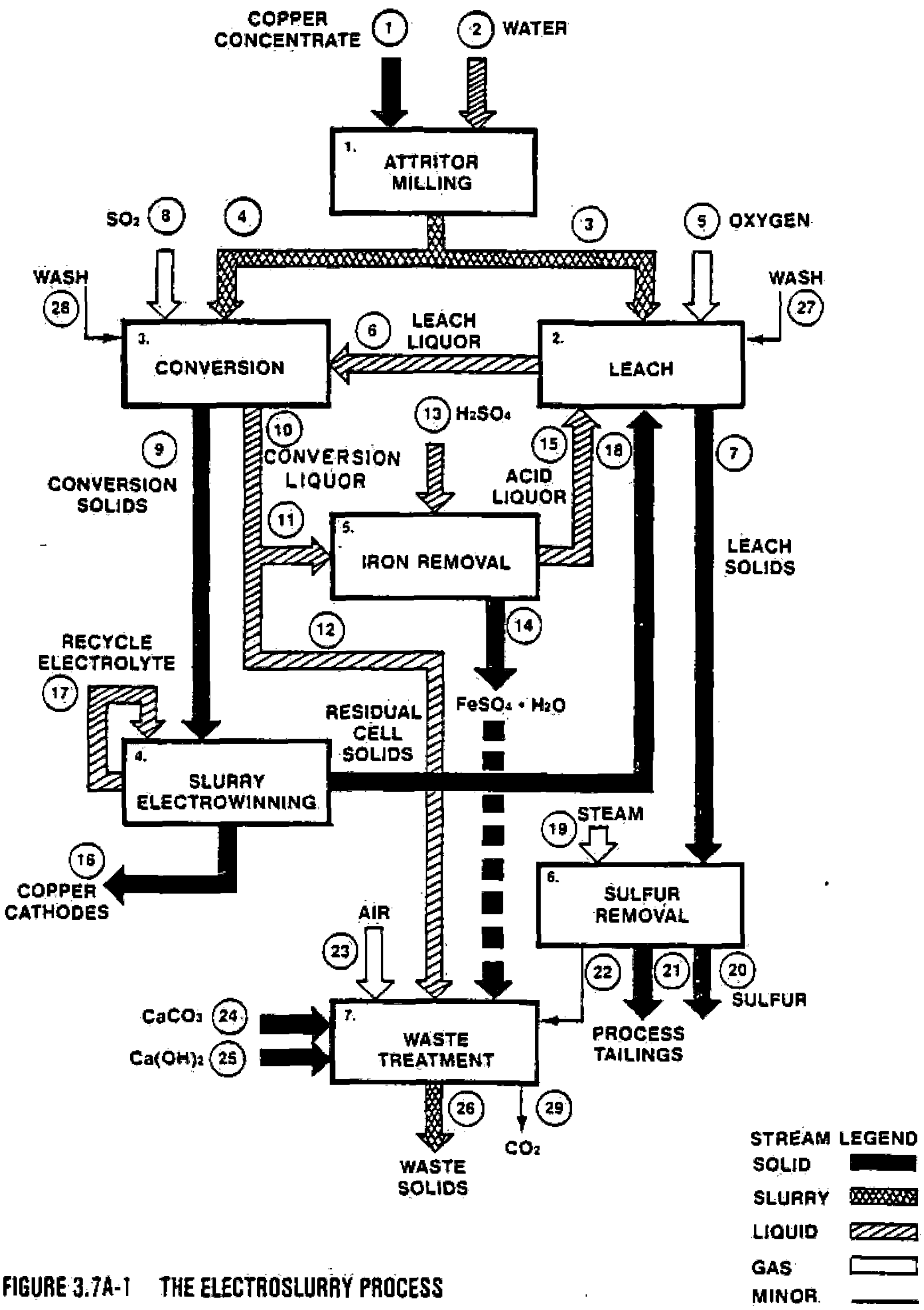

FIGURE 3.7A-1 THE ELECTROSLURRY PROCESS

Slurry Electrowinning

$$2Fe^{+2} \longrightarrow 2Fe^{+3} + 2\bar{e} \qquad \text{(Anode)} \qquad (3.7A.6)$$

$$CuS + 2Fe^{+3} \longrightarrow Cu^{+2} + 2Fe^{+2} + S^{0} \qquad \text{(Slurry)} \qquad (3.7A.7)$$

$$Cu_2S + 4Fe^{+3} \longrightarrow 2Cu^{+2} + 4Fe^{+2} + S^{0} \qquad \text{(Slurry)} \qquad (3.7A.8)$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu^{0} \qquad \text{(Cathode)} \qquad (3.7A.9)$$

Waste Treatment

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2 \qquad (3.7A.10)$$

$$FeSO_4 + Ca\,(OH)_2 + 0.25O_2 + 2.5H_2O \longrightarrow Fe\,(OH)_3 + CaSO_4 \cdot 2H_2O \qquad (3.7A.11)$$

Overall Process Chemical Reaction

$$CuFeS_2 + 0.555O_2 + .1104SO_2 + 0.8892H_2SO_4 + \text{ES CELL} \longrightarrow$$

$$Cu^{0} + 2S^{0} + FeSO_4 + .8892H_2O \qquad (3.7A.12)$$

The material balances resulting from the above chemistry are presented in Table 3.7A-1. The quantities involved are sufficient to produce 1 ton of copper product. Stream numbers are the same as appear in Figure 3.7A-1.

3.7A.4 Energy Requirements

The Level 1 energy requirements that include all direct thermal and electrical inputs are shown in Table 3.7A-2. The electrical energy includes milling, pumping, agitation, and electrodeposition of copper, but does not include the energy for producing gaseous oxygen. The total energy which is in the form of electricity, is equivalent to 31.2 million Btu per ton of copper cathode. The electrowinning step requires approximately 19.1 million Btu per ton of copper cathode (61.2% of the total). This is approximately 21% lower than that required by conventional electrowinning which is estimated to be 24 million Btu per ton of cathode copper. The Level 2 requirements for chemicals consumed in the process are shown in Table 3.7A-3 for a total of 8.4 million Btu per ton of copper. The major contributor to the Level 2 energy requirements is burnt lime which is used for iron precipitation.

3.7A.5 Discussion

The total energy for both fuel, electricity, and chemicals is equivalent to 39.6 million Btu per ton of copper cathode. The energy consumption is in the lower range for hydrometallurgical processes. This can be attributed mainly to the lower power requirements of the slurry electrowinning cells. Further reductions in energy requirements are possible since this process is still at the preliminary stages of development. The process has been checked at the bench scale level and the electroslurry cell has been studied extensively in continuous operation.

3.7A.6 Conclusions and Recommendations

As with all hydrometallurgical processes, this process offers a less polluting route for the extraction of copper from chalcopyrite concentrates. The estimated energy requirements show the

TABLE 3.7A-1 THE ELECTROSLURRY^{TM} PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	Copper Concentrate		Water		Concentrate Slurry		Concentrate Slurry		Oxygen	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%	wt.	wt.%
Cu	1.0204	25.0			0.39795	25.0	0.62245	25.0		
Fe	1.1430	28.0			0.4457	28.0	0.6973	28.0		
S (Combined)	1.2653	31.0			0.4935	31.0	0.7718	31.0		
S (Free)						16.0				
Others	0.653	16.0			0.2547	16.0	0.3983	16.0		
H_2O	0.5045		3.5772	100.00	1.5918		2.4898			
H_2SO_4										
$CuSO_4$										
$FeSO_4$										
$CaCO_3$										
$Ca(OH)_2$										
$Fe(OH)_3$										
$CaSO_4 \cdot 2H_2O$										
O_2									0.28	100.00
N_2										
SO_2										
CO_2										
TOTAL	4.5862	100.00	3.5772	100.00	3.18365	100.00	4.97965	100.00	0.28	100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY™ PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	Leach Liquor		Leach Solids		Sulfur Dioxide		Conversion Solids		Conversion Liquor	
COMPOSITION	wt.	wt.%	wt.	dry wt.%	wt.	wt.%	wt.	dry wt.%	wt.	wt.%
Cu	(0.5559)		0.0204	0.9			1.1784	44.4		
Fe	(0.7147)		0.264	12.0			0.3064	11.5	(1.106)	
S (Combined)			0.258	11.7			0.7718	29.1		
S (Free)			1.01	45.8						
Others			0.653	29.6			0.3983	15.0		
H_2O	8.3194	61.0	0.4667						10.7267	66.9
H_2SO_4	1.9718	14.5							2.3148	14.4
$CuSO_4$	1.3959	10.2								
$FeSO_4$	1.9431	14.3							3.006	18.7
$CaCO_3$										
$Ca(OH)_2$										
$Fe(OH)_3$										
$CaSO_4 \cdot 2H_2O$										
O_2										
N_2										
SO_2					0.112	100.00				
CO_2										
TOTAL	13.6302	100.00	2.6721	100.00	0.112	100.00	2.6549	100.00	16.0475	100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY^{TM} PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	Conversion Liquor To Iron Removal		Conversion Liquor To Waste Treatment		Conc. Sulfuric Acid		Ferrous Sulfate (Crystalline)		Acid Liquor	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu										
Fe	(0.6192)		(0.4865)				(0.3931)		(0.226)	
S (Combined)										
S (Free)										
Others										
H_2O	6.0069	66.9	4.7198	66.9	0.1258	5.0	0.1929	15.3	5.9399	58.0
H_2SO_4	1.2963	14.4	1.0185	14.4	2.3905	95.0			3.6868	36.0
$CuSO_4$										
$FeSO_4$	1.6834	18.7	1.3226	18.7			1.0689	84.7	0.6145	6.0
$CaCO_3$										
$Ca(OH)_2$										
$Fe(OH)_3$										
$CaSO_4 \cdot 2H_2O$										
O_2										
N_2										
SO_2										
CO_2										
TOTAL	8.9866	100.00	7.0609	100.00	2.5163	100.00	1.2618	100.00	10.2412	100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY™ PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	Copper Cathode		Recycle Electrolyte		Residual Cell Solids		Steam		Sulfur	
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	dry wt.%	wt.	wt.%	wt.	wt.%
Cu	1.0	100.00	1.2274	3.2	0.1784	10.8				
Fe			0.9196	2.4	0.3064	18.5				
S (Combined)					0.3234	19.5				
S (Free)					0.4484	27.1			.9086	100.00
Others			3.4351	9.0	0.3983	24.1				
H_2O			28.7395	75.7			0.315	100.00		
H_2SO_4			3.6784	9.7						
$CuSO_4$										
$FeSO_4$										
$CaCO_3$										
$Ca(OH)_2$										
$Fe(OH)_3$										
$CaSO_4 \cdot 2H_2O$										
O_2										
N_2										
SO_2										
CO_2										
TOTAL	1.0	100.00	38.0	100.00	1.6549	100.00	0.315	100.00	.9086	100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY^{TM} PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	Process Tailings		Water From Sulfur Removal		Air		Calcium Carbonate		Calcium Hydroxide	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	dry wt.%	wt.	dry wt.%
Cu	0.0204	1.6								
Fe	0.264	20.4								
S (Combined)	0.2581	19.9								
S (Free)	0.101	7.8								
Others	0.653	50.3								
H_2O			0.7817	100.00						
H_2SO_4										
$CuSO_4$										
$FeSO_4$										
$CaCO_3$							1.0393	100.00		
$Ca(OH)_2$									1.1654	100.00
$Fe(OH)_3$										
$CaSO_4 \cdot 2H_2O$										
O_2					0.126	21.0				
N_2					0.474	79.0				
SO_2										
CO_2										
TOTAL	1.2965	100.00	0.7817	100.00	0.6	100.00	1.0393	100.00	1.1654	100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY^{TM} PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)		(27)		(28)		(29)		
STREAM NAME	Waste Solids		Wash Water		Wash Water		Carbon Dioxide		
COMPOSITION	wt.	dry wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	
Cu									
Fe	(.8796)								
S (Combined)									
S (Free)									
Others									
H_2O	4.7986		0.9334	100.00	0.937	100.00			
H_2SO_4									
$CuSO_4$									
$FeSO_4$									
$CaCO_3$									
$Ca(OH)_2$									
$Fe(OH)_3$	1.6828	27.2							
$CaSO_4 \cdot 2H_2O$	4.4964	72.8							
O_2									
N_2									
SO_2									
CO_2							.4573	100.00	
TOTAL	10.9778	100.00	0.9334	100.00	0.937	100.00	4.573	100.00	

TABLE 3.7A-2 **ENERGY REQUIREMENTS** Level 1

THE ELECTROSLURRY^{TM} PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Attritor Milling				
	A) Electrical energy for grinding equip. (2-3 micron mean particle size. 4.0817 ton concentrate/ton copper product).	KWH	408.17	0.0105	4.2858
	B) Electrical energy for circuit pumping and agitation.	KWH	13.65	0.0105	0.1433
2	Leach				
	A) Steam for circuit heating.	BTU			2.4460
	B) Electrical energy for circuit pumping and agitation.	KWH	42.89	0.0105	0.4503
3	Conversion				
	A) Steam for circuit heating.	BTU			2.3630
	B) Electrical energy for circuit pumping and agitation.	KWH	93.88	0.0105	0.9857

TABLE 3.7A-2 (cont.) **ENERGY REQUIREMENTS** Level 1

THE ELECTROSLURRY^{TM} PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
4	Slurry Electrowinning				
	A) Electrical energy for electrowinning cells (to rectifiers and cell recirculation pumps)	KWH	1820	0.0105	19.1100
	B) Electrical energy for circuit pumping. agitation and cathode handling.	KWH	39.91	0.0105	0.4191
5	Iron Removal				
	A) Electrical energy for circuit pumping and agitation.	KWH	14.16	0.0105	0.1487
6	Sulfur Removal				
	A) Steam for circuit heating.	BTU			0.59
	B) Electrical energy for circuit pumping and agitation.	KWH	3.22	0.0105	0.0338
7	Waste Treatment				
	A) Electrical energy for circuit pumping and agitation.	KWH	23.82	0.0105	0.2501
				TOTAL	31.2258

TABLE 3.7A-3

Level 2

ENERGY REQUIREMENTS

THE ELECTROSLURRY^{TM} PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leach				
	A) Oxygen	TON	0.28	3.78	1.058
3	Conversion				
	A) Oxygen (for sulfur burner)	TON	0.056	3.78	0.212
5	Iron Removal				
	A) Sulfuric Acid	TON	2.3905	0.83	1.984
7	Waste Treatment				
	A) Limestone	TON	1.15	0.104	0.120
	B) Lime	TON	0.928	5.4	5.011
				TOTAL	8.385

process to be potentially competitive with conventional smelting. Removal of hydrated ferrous sulfate from the process as a by-product could lower the energy requirements by approximately 2.5 million Btu per ton of cathode copper. Research is currently underway at the bench level to further reduce the energy requirements of the slurry electrowinning circuit. Two approaches being studied are lower current density operation in the range of 60 amps per square feet and the use of more conductive lead alloys for anodes.

The slurry electrowinning concept may have application to the recovery of other metals. Tests conducted by Envirotech Corporation have shown recovery of chrome, zinc, nickel, and cobalt may be feasible with this technique.

3.8 ROAST/SULFITE-REDUCTION PROCESS

3.8.1 Introduction

This section contains estimates of the material and energy requirements for a copper extraction process referred to as the sulfite-reduction process. The estimate includes the evaluation of material flows of raw materials, other influents, internal process streams, and effluents. Energy values are evaluated for raw materials, fuels, steam, electrical power and other consumables. Energy requirements are assessed in two respects, (1) an operational requirement that does not include special processing features for economizing or recycling of heat between or within processing steps and (2) a theoretical requirement that includes improved heat transfer and utilization. The theoretical energy evaluation is indicative of potential energy savings.

The sulfite-reduction process is hydrometallurgical with the exception of the initial roasting step and the anode furnaces prior to conventional electrorefining of the copper product. The process design evaluated is for the treatment of chalcopyrite concentrates recovered by froth flotation.

A fairly detailed description of the novel processing steps is given by Bartlett (Feb.-Mar. 1978) in the report "A Process that Uses Sulfur From a Copper Concentrate to Reduce Leached Copper." The more conventional processing steps are described in standard texts on copper extraction such as that by Biswas and Davenport (1976). Some advantages claimed for the process are reduced energy and labor requirements by the elimination of electrowinning typical of hydrometallurgical copper extraction, low requirements for raw materials and utilities, and few corrosion problems. The process is fairly complex as is evident by the many process streams shown on the flow sheet (see Figure 3.8-1). The flow scheme consists of three recycle loops, interconnected: (1) The lixiviant recycle loop for the leaching and precipitation of copper, (2) the scrubber-liquor recycle loop for the adsorption of sulfur dioxide from the roaster gas and the removal of sulfate, and (3) the ammonia recycle loop for the adsorption of ammonia into the sulfite liquor (indicated as the Gas Scrubber Circuit, Process Step 7, in Figure 3.8-1).

3.8.2 Process Description

The main features of the sulfite-reduction process are a roasting of the chalcopyrite to oxidize the copper and iron sulfide minerals (Process Step 1, Fluid-Bed Roasting in Figure 3.8-1), a sulfuric acid leach of the calcine from the roaster (Process Step 2, Leach Circuit in Figure 3.8-1), and a copper reduction step (Process Step 3, Reduction Autoclaves in Figure 3.8-1), that utilizes a sulfite-rich liquor generated by the adsorption of sulfur dioxide from the roaster gas. The roasting

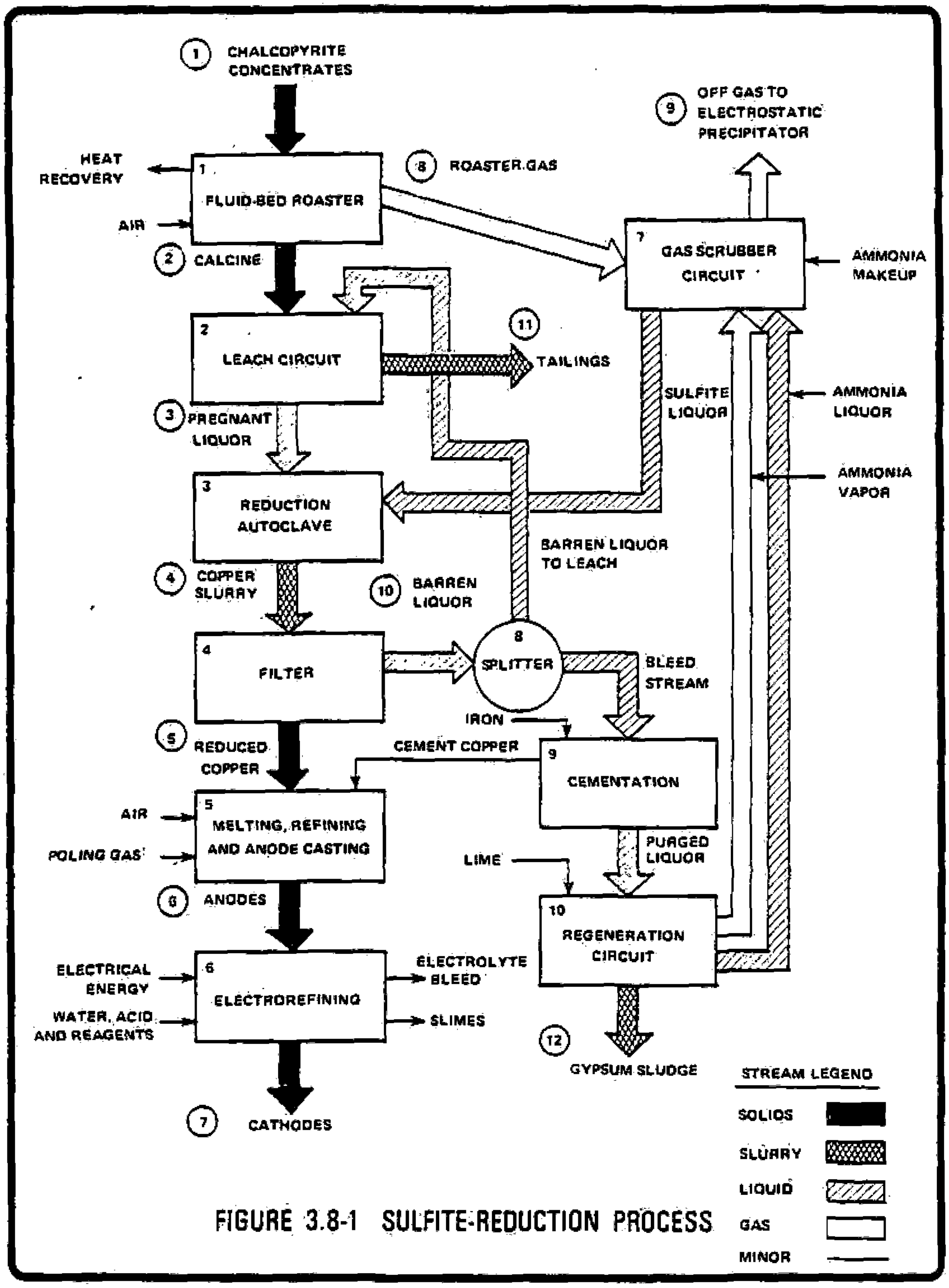

FIGURE 3.8-1 SULFITE-REDUCTION PROCESS

is controlled at 650°C to prevent the formation of ferrites — acid-insoluble, copper-containing compounds. Leaching is conducted in open vats at 85°C, and the reduction step is conducted under pressure at 160°C and 854 kPa. A roaster-gas sulfur dioxide concentration of 5% is sufficient for adsorption and sulfite-rich liquor generation. The fluid-bed roaster is capable of producing gases with sulfur dioxide levels well in excess of 5%.

The main stoichiometric relationships for the processing reactions are as follows:

Fluid-Bed Roasting, Process Step 1

a. Chalcopyrite oxidation

$$2CuFeS_2 + 6\tfrac{1}{2}\,O_2 \longrightarrow 2CuO + Fe_2O_3 + 4SO_2 \tag{3.8.1}$$

b. Pyrite oxidation

$$2FeS_2 + 5\tfrac{1}{2}\,O_2 \longrightarrow Fe_2O_3 + 4SO_2 \tag{3.8.2}$$

Sulfuric Acid Leaching, Process Step 2

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \tag{3.8.3}$$

Reduction Chemistry, Process Step 3

a. Reduction of copper by ammonium bisulfite

$$CuSO_4 + NH_4HSO_3 + H_2O \longrightarrow Cu^{o} + 1/2\,(NH_4)_2SO_4 + 1\tfrac{1}{2}\,H_2SO_4 \tag{3.8.4}$$

b. Reduction of copper by ammonium sulfite

$$CuSO_4 + (NH_4)_2SO_3 + H_2O \longrightarrow Cu^{o} + (NH_4)_2SO_4 + H_2SO_4 \tag{3.8.5}$$

Gas–Scrubbing and Sulfite Regeneration Chemistry, Process Step 7

a. Ammonium sulfite formation

$$(NH_4)_2SO_3 + SO_2 + H_2O \longrightarrow 2NH_4HSO_3 \tag{3.8.6}$$

b. Ammonia adsorption

$$NH_4HSO_3 + NH_3 \longrightarrow (NH_4)_2SO_3 \tag{3.8.7}$$

Sulfur Disposal and Ammonia Regeneration Chemistry, Process Step 10

a. Acid neutralization with limestone

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \tag{3.8.8}$$

b. Ammonia recovery with lime

$$CaO + (NH_4)_2SO_4 \longrightarrow 2NH_3 + CaSO_4 + H_2O \tag{3.8.9}$$

3.8.3 Material Requirements Evaluations

The evaluation of material requirements is based on the description of the process by Bartlett (Feb.-Mar. 1978). Melting of the copper precipitate from the reduction autoclaves; fire refining to remove iron, oxygen and sulfur; anode casting; and electrorefining have been added to provide a processing scheme comparable with conventional pyrometallurgical technology. The flow sheet is that of Figure 3.8-1 which shows the identifiers for the process steps and streams used in the material and energy requirements evaluations. A summary of the material flows is listed in Table 3.8-1. A complete accounting of pertinent supportive calculations, data and references for the material flows is given in Appendix 3.8-A. Considered for this evaluation is a cathode production rate of about 100,000 ton/year and a copper recovery of 98%. The feed is considered to be a chalcopyrite concentrate recovered by froth flotation having a composition of 25% copper, 29% iron and 31% sulfur that is amenable to the process.

3.8.4 Energy Requirements Evaluation

Tables 3.8-2 and 3.8-3 list a summary of the energy requirements for the process. The energy requirement evaluation is based on the above material requirements evaluation. Level 1 requirements for fuels, steam and electrical power (excluding chemicals and consumables) are listed in Table 3.8-2. Level 2 requirements for chemicals, fluxes, refractories and other consumables, are listed in Table 3.8-3. Equivalent fuel requirements are calculated and summed using appropriate energy equivalent estimates. Relevant calculations and descriptive information for the energy requirements tables can be found in Appendix 3.8-B if such information is too extensive for inclusion as footnotes.

The evaluation for Tables 3.8-2 and 3.8-3 is an "operational" estimate in that it reflects a process designed and operated in a conventional, operational mode. The bottom-line totals are termed "operational" in the above summary table. This operational estimate does not consider any special features for the economizing or recycling of heat within the process. The "theoretical" estimate discussed below includes such considerations. The main aspect of the theoretical estimate is the utilization of the heat generated by the processing reactions to offset process heating requirements. The difference between the operational and theoretical estimates is indicative of the potential of the process for energy savings.

The following energy calculations were provided by Goel (1979). Thermochemical data for the calculations can be found in Barner and Schenerman (1978).

Energy generated by the leaching reaction

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad (3.8.10)$$

$$H^o_{298} = (-37{,}600 - 232{,}700) + (15{,}500 - 232{,}700 - 57{,}800)$$

$$= -4{,}700 \text{ cal/mole}$$

Copper dissolved– 1.00 kg = 15.73 moles

Energy Generated = $(15.73)\,(4{,}700)\,(3.60 \text{ x } 10^{-6})$

= .27 million Btu/ton product

TABLE 3.8-1 SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		CALCINE		PREGNANT LIQUOR*		COPPER SLURRY SOLIDS		ANODES	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.02	25.06	1.02	29.74	1.00	7.23	0.99	100.00	0.99	100.00
Fe	1.14	28.01	1.14	33.24						
S	1.26	30.96	0.01	0.29						
Other	0.65	15.97	1.26	36.73	3.174	9.09				
NH_4HSO_3					0.097	0.28				
$(NH_4)_2SO_3$					0.0128	0.04				
$(NH_4)_2SO_4$					2.622	7.51				
H_2SO_4										
H_2O					26.48	75.85				
NH_3										
Scrap Fe										
$Ca(OH)_2$										
$Ca\ CO_3$										
SO_2										
$Ca\ SO_4$										
pH					3.0					
TOTAL	4.07	100.00	3.43	100.00	34.91	100.00	0.99	100.00	0.99	100.00

*Copper is figured as $CuSO_4$. 10% of the total weight is allowed for minor impuity buildup which is included as "Other".

TABLE 3.8-1 (cont.) SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	ANODES		CATHODES		ROASTER GAS		OFF GAS		BARREN LIQUOR*	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	1.00	100.00	1.00	100.00					0.01	
Fe										
S										
Other									3.803	9.09
NH_4HSO_3									0.140	0.33
$(NH_4)_2SO_4$									0.019	0.05
$(NH_4)_2SO_4$									3.763	9.00
H_2SO_4									2.235	5.34
H_2O									31.870	76.19
NH_3										
Scrap Fe										
$Ca(OH)_2$										
$CaCO_3$										
SO_2						5.0		3.0		
$CaSO_4$										
pH									0.95	
TOTAL	1.00	100.00	1.00	100.00					41.83	100.00

*Copper is figured as $CuSO_4$. 10% of the total weight is allowed for minor impurity buildup which is included as "Other".

TABLE 3.8-1 (cont.) SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)							
STREAM NAME	TAILINGS (SOLIDS)		GYPSUM SLURRY (SOLIDS)		CEMENT COPPER		SULFITE LIQUOR*		BARREN LIQUOR TO LEACH*	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	0.02	0.92			<0.01	100.00			<0.01	0.01
Fe	1.14	52.29								
S	0.01	0.46								
Other	1.01	46.33					0.702	9.09	2.652	9.09
NH_4HSO_3							1.443	18.69	0.097	0.33
$(NH_4)_2SO_3$							0.186	2.41	0.013	0.04
$(NH_4)_2SO_4$									2.622	8.99
H_2SO_4									1.557	5.34
H_2O							5.39	69.81	22.20	76.11
NH_3										
Scrap Fe										
$Ca(OH)_2$										
$CaCO_3$										
SO_2										
$CaSO_4$			2.12	100.00						
pH							3.3 - 3.5		0.95	
TOTAL	2.18	100.00	2.12	100.00	0.01	100.00	7.721	100.00	29.17	

*Copper is figured as $CuSO_4$. 10% of the total weight is allowed for minor impurity buildup which is included as "Other".

TABLE 3.8-1 (cont.) SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.										
STREAM NAME	BLEED STREAM*		PURGED LIQUOR*		AMMONIA LIQUOR*		AMMONIA VAPOR		AMMONIA MAKEUP	
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%	wt.	wt.%
Cu	<0.01	0.08								
Fe										
S										
Other	1.154	9.08	1.154	9.09	0.973	9.09				
NH_4HSO_3	0.043	0.34	0.043	0.34						
$(NH_4)_2SO_3$	0.006	0.05	0.006	0.05	0.058	0.54				
$(NH_4)_2SO_4$	1.142	8.99	1.142	9.00						
H_2SO_4	0.678	5.34	0.678	5.34						
H_2O	9.67	76.12	9.67	76.18	9.67	90.37				
NH_3							300	100.00	0.035	100.00
Scrap Fe										
$Ca(OH)_2$										
$CaCO_3$										
SO_2										
$CaSO_4$										
pH										
TOTAL	12.70	100.00	12.69	100.00	10.70	100.00	300	100.00	0.035	100.00

*Copper is figures as $CuSO_4$. 10% of the total weight is allowed for minor impurity buildup which is included as "Other".

TABLE 3.8-1 (cont.) SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.								
STREAM NAME	IRON		LIME		LIMESTONE			
COMPOSITION	wt.	wt.%	wt.	wt.%	wt.	wt.%		
Cu								
Fe								
S								
Other								
NH_4HSO_3								
$(NH_4)_2SO_3$								
$(NH_4)_2SO_4$								
H_2SO_4								
H_2O								
NH_3								
Scrap Fe	0.02	100.00						
$Ca(OH)_2$			0.71	100.00				
$Ca\ CO_3$					0.76	100.00		
SO_2								
$Ca\ SO_4$								
pH								
TOTAL	0.02	100.00	0.71	100.00	0.76	100.00		

*Copper is figures as $CuSO_4$. 10% of the total weight is allowed for minor impurity buildup which is included as "Other".

TABLE 3.8-2 **ENERGY REQUIREMENTS** Level 1

SULFITE REDUCTION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roaster				
	A) Waste Heat Recovery	BTU	-4.25	1.00	-4.25
	B) Fuel (Start Up only)	BTU	0.2	1.00	0.20
2	Leach Circuit				
	A) Electrical Power	KWH	59.756	0.0105	0.627
	B) Process Heating, Steam				
3	Reduction Autoclaves				
	A) Pumping, Electrical	KWH	8.04	0.0105	0.084
	B) Process Heating, Steam	LBS	8164	0.0014	11.43
4	Filter				
	A) Electrical	KWH	2	0.0105	0.021
5	Melting, Refining, and Anode Casting				
	A) Heating and Melting (Fuel Oil)	GAL	19.5	0.15	2.925
	B) Poling Gas	SCF	225	0.0010	0.225
6	Electrorefining				
	A) Electrical	KWH	272	0.0105	2.856
	B) Process Heating (Fuel Oil)	LBS	1300	0.0014	1.82
7	Gas Scrubber Circuit				
	A) Electrical	KWH	132.43	0.0105	1.39
	Ancillary Loads				
	A) Electrical	KWH	50.0	0.0105	0.525
				TOTAL	17.769

TABLE 3.8-3 **ENERGY REQUIREMENTS** Level 2

SULFITE - REDUCTION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
5	Melting, Refining, and Anode Casting				
	A) Flux	TON	0.1	0.71	0.076
6	Electrorefining				
	A) Acid and Reagents	TON	0.0165	0.83	0.014
7	Gas Scrubber Circuit				
	A) Make-up Ammonia	TON	0.035	39.0	1.365
9	Cementation				
	A) Scrap Iron	TON	0.02	18.0	0.36
10	Regeneration Circuit				
	A) Lime	TON	0.71	5.45	3.870
	B) Limestone	TON	0.76	0.24	0.182
				TOTAL	5.867

Energy generated by the reduction-autoclave reactions

(90% of copper is assumed to be reduced by bisulfite [NH_4HSO_4], and the remaining copper is assumed to be reduced by sulfite [$(NH_4)_2SO_3$] at a reduction efficiency at 99%)

$$CuSO_4 + NH_4HSO_4 + H_2O \longrightarrow Cu^o + 1/2\,(NH_4)_2SO_4 + 1\tfrac{1}{2}\,H_2SO_4 \qquad (3.8.11)$$

In an aqueous solution, this equation can be expressed as

$$Cu^{++} + HSO_3^- + H_2O \longrightarrow Cu^o + SO_4^= + 3H^+ \qquad (3.8.12)$$

$$\Delta H^o_{298} = (15{,}500 - 165{,}000 - 57{,}800) + (-232{,}700)$$

$$= -25{,}400 \text{ cal/mole}$$

Energy Generated = (15.73) (.90) (.99) (25,400) (3.6 x 10^{-6})

= 1.28 million Btu/ton product

$$CuSO_4 + (NH_4)_2SO_3 + H_2O \longrightarrow Cu^o + (NH_4)_2SO_4 + H_2SO_4 \qquad (3.8.13)$$

In an aqueous solution, this equation can be expressed as

$$Cu^{++} + SO_3^= + H_2O \longrightarrow Cu^o + SO_4^= + 2H^+ \qquad (3.8.14)$$

$$\Delta H^o_{298} = (15{,}500 - 167{,}200 - 57{,}800) + (-232{,}700)$$

$$= -23{,}200 \text{ cal/mole}$$

Energy Generated = (15.73) (.10) (.99) (23,200) (3.6 x 10^{-6})

= .13 million Btu/ton product

Total Heat Generated = .27 + 1.28 + .13
by Processing Reactions = 1.68 million Btu/ton product

With some special design features, the heat generated by the processing reactions can be utilized to heat the influents of the reaction vessels and, thus, offset a process heating requirement. Generally, the processing equipment is increased in either size or complexity to accomplish this heat transfer — e.g., employing bulkier continuous-stirred tanks as compared to more efficient tube or staged reaction vessels. The theoretical energy requirement is evaluated as follows:

Total Level 1 Energy Requirement — (see Table 3.8-3) — 35.40 million Btu/ton product

Offset from Heat Generated by Processing Reactions — 1.68 million Btu/ton product

Total Theoretical Level 1 Requirement — 33.72 million Btu/ton product

Total Level 2 Energy Requirement (unchanged, see Table 3.8-3) — 5.87 million Btu/ton product

Total Theoretical Energy Requirement — 39.59 million Btu/ton Product

3.8.5 Discussion

The sulfite-reduction process does not involve novel technology in that it integrates processing steps developed for other metallurgical or environmental pollution control purposes. The roasting of chalcopyrite concentrates is similar to the technology for autogeneous oxy-sulfate roasting developed by Hecla Mining Co. at their Lakeshore, Arizona property (Bartlett, Feb.-Mar. 1978) or equipment employed by Cities Service Co., Minerals Group at their Copperhill, Tennessee operation for roasting pyrite in the production of sulfuric acid. Roaster gas scrubbing is similar to the ammonia-based processes for sulfur dioxide removal from power-plant stack gases that have been developed by Nippon Kokan KK, a steel company in Japan; Ugine Kuhlmann in France; Smelter Control Research Association, U. S., and others (Slack and Hollinden, 1975, Radian Corp., 1976). The leaching circuit is typical of hydrometallurgical acid-leaching operations employed for metal extractions such as for copper and uranium (Biswas and Davenport, 1976, Ch. 13; Merritt, 1971). The copper reduction step is the Jamau 1907 patent (Jamau, 1907) and has been recently investigated and reported on by Parker and Muir (1976). Regeneration of ammonia (Process Step 10, Regeneration Circuit in Figure 3.8-1) has been shown to be effective in the Nippon Kokan KK process (Slack and Hollinden, 1975). The other process steps (cementation, melting, fire refining, anode casting, and electrorefining) are common to conventional copper production.

Each step of the sulfite-reduction process was extensively laboratory tested, and technically and economically evaluated by the staff of Kennecott Copper Corp. Research Center at Salt Lake City, Utah (Bartlett, Feb.-Mar. 1978 and Oct. 1978). Further development has been recommended by Bartlett (SRI International, 1977). Present development has not gone beyond attempting laboratory experiments.

The evaluations provided by this study clearly demonstrates the validity of combining the various processing technologies. Of particular interest if the interplay of reductant (sulfites) and acid levels in the lixiviant recycle loop (see calculations in Appendix 3.8-A). A significant element in the operation and control of this loop and the other two interacting recycle loops (see discussion in Introduction above) is the splitter (Process Step 8, Figure 3.8-1). Control of the flow of solution returned to the leach vats and the flow of the bleed stream to the ammonia regeneration circuit is intimately related to the chemistry of the leach circuit and reduction autoclaves. The material flow calculations show that operation and control are feasible.

3.8.6 Conclusions and Recommendations

The processing energy requirements are not significantly sensitive to processing design factors that influence the utilization of heat generated by the processing reactions (such theoretical considerations would produce an energy requirement reduction of 1.68 million Btu/ton product or 4% of the operational energy requirement estimate). The processing scheme is also fairly insensitive to the composition of the chalcopyrite concentrate feed. This insensitivity is the result of the energy requirements being dominated by process heating steam and other loads that are fairly independent of the feed composition. The roaster waste heat recovery is the energy value most dependent on feed copper, iron and sulfur levels. A reduction of 10% in roaster waste heat recovery would increase the total energy requirement by about 1% (see values on Tables 3.8-2 and 3.8-3).

The two largest energy consuming items are process heating steam for the reduction autoclaves, and process heating steam for the leach circuit. These two major energy items constitute 71% of the total. The operational energy requirement is estimated as being 41.32 million Btu/ton of copper produced with 35.45 million Btu/ton product (86%) in the form of direct fuel, steam and electrical power consumption. The theoretical energy requirement that considers the utilization of the heat generated by the processing reactions is estimated as 39.64 million Btu/ton product, only slightly less (4%) than the operational estimate.

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ACID-FREE REGENERATION OF GOLD-BEARING ANION-EXCHANGE RESINS

UDC 622.342:66.074.7

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Increased interest has recently been shown in acid-free methods of regeneration in the sorption extraction of precious metals from cyanide pulps and solutions, particularly in connection with the production of ferritized ion exchangers.

There are a number of alkaline methods of resin regeneration, but these are not entirely acceptable in practice[1] [1, 2].

The authors of this paper have have developed a new scheme for selective regeneration of gold- and silver-bearing anion-exchange resins with solutions of ammonium thiocyanate and alkali, based upon different speeds of element elution by ammonium thiocyanat solutions (Fig. 1).

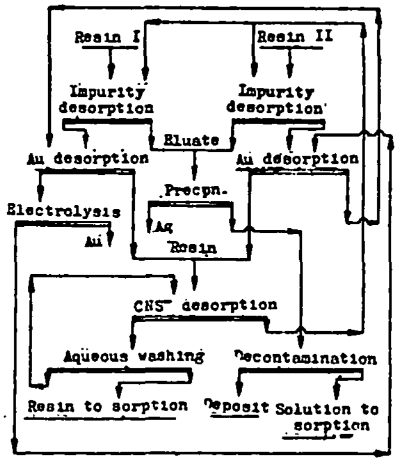

Fig. 1. Chart of thiocyanate alkaline scheme for selective regeneration of resin for a two-stage sorption process.

AM-2B anion exchangers of porous structure in magnetic and non-magnetic modifications saturated in cyanide pulps were taken for study (Table 1).

Table 1
Content in Resin, mg/g

Ionite	Au	Ag	Cu	Zn	Fe	Ni	Co	As	Total impurities
AM-2B	6.55	0.46	14.5	2.50	0.6	1.8	0.50	3.6	23.50
AM-2BP	5.25	12.30	5.7	4.08	—	0.51	0.13	0.2	10.62
AM-2BP	6.83	1.47	4.6	1.90	—	1.4	0.15	0.4	8.45

The investigations were conducted under dynamic process conditions. The elution of metal lower cyanide complexes from anion exchangers is caused by their displacement by the thiocyanate ion, due to the concentration effect and high polarizability of the latter.

Selectivity in the elution of sorbed elements by ammonium thiocyanate solutions (with the exception of zinc) is in accordance with the affinity series for metal lower cyanide ions, which is as follows for the AM-2B anion exchanger:

$$Au > Zn > Ni > Ag > Cu > Fe > CN^-.$$

Silver is close to copper and nickel in the selectivity series; it is therefore not possible to separate it from the impurities.

Alkali is a selective eluent for zinc, which can be separated either from the saturated or the degolded resin [3].

Speed and selectivity in elution depends upon the ammonium thiocyanate concentration in the solution and the temperature (Fig. 2).

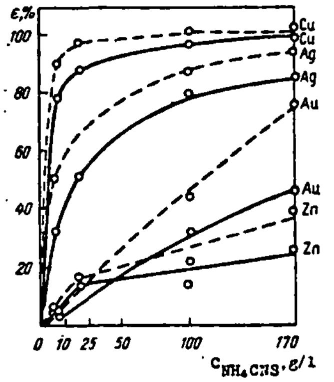

Fig. 2. Effect of temperature upon desorption of Au, Ag, Cu, and Zn (τ = 4 hr): —— – 20°C; --- – 50°C.

Raising the temperature from 20 to 50°C accelerates the completion of the copper desorption process appreciably and makes it possible to reduce the eluent concentration to 5-10 g/liter with a high (90-95%) degrees of copper desorption when gold extraction into the eluate is not higher than 8%.

Unlike gold, silver is easily eluted from anion-exchange resins, although the elution rate is less than for copper.

The addition of alkali (NaOH) to the thiocyanate eluent makes it possible to separate out the zinc with iron and copper, and fairly high figures for the separation of impurities (90-95%) and gold are achieved in 3-4 hr with thiocyanate-alkaline solutions of quite moderate concentrations: 10 g/liter NH_4CNS and 10-25 g/liter NaOH (Fig. 3).

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[1] British Patent No. 808909, 1952.

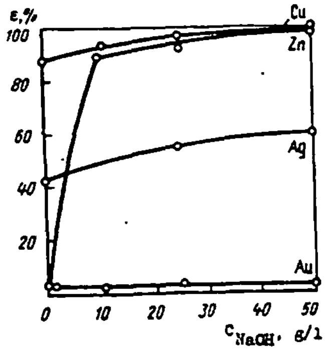

Fig. 3. Effect of NaOH concentration upon desorption of Cu, Zn, Ag, and Au by thiocyanate-alkali solution (τ = 4 hr; t = 50°C; c_{NH_4CNS} = 10 g/liter).

In these circumstances, 26-50% Ag passes into the thiocyanate-alkaline eluate, but complete extraction from the resin is possible with an excess of eluent and an increase in washing time (Fig. 4).

Together with the impurities, 2.6-3.8% Au is desorbed into the thiocyanate-alkaline eluate; this is at the level of gold extraction in purification operations in chloride-thiocyanate and acid-thiourea regeneration schemes.

The high efficiency of thiocyanate-alkaline solutions in relation to iron, copper, and zinc can be used in combination with the concentration capabilities of the eluent for selective regeneration of gold-bearing anion-exchange resins. This can be achieved by consecutive treatment of the resin, first with a thiocyanate-alkaline solution with a low thiocyanate concentration to desorb the impurities, then by eluting the gold with a concentrated thiocyanate solution.

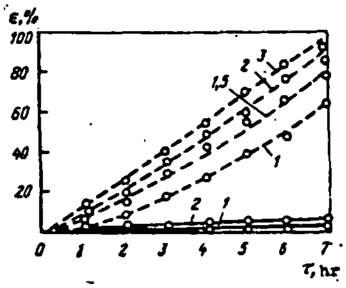

Fig. 4. Effect of unit loading upon elution of Au and Ag by thiocyanate-alkali solution with a concentration of 10 g/liter NH₄CNS+25 g/liter NaOH (t = 50°C):
—— - Au; --- - Ag.
The figures on the curves indicate the unit loading (in 1 hr) $\bar{w}$ = 1 liter/solution/1 liter resin.

During the process of eluting impurities by the thiocyanate-alkaline method, the resins are saturated with the thiocyanate ion, which helps to accelerate the subsequent process of selective gold elution.

Washing the sorbent between operations becomes superfluous when the same reagent us used to separate the impurities and gold; as a result, the total regeneration time is reduced and the gold concentration in commercial regenerate fractions increased by 20-25%.

However, the thiocyanate ion absorbed by the resin in the regeneration process has an adverse effect upon sorption of precious metals by recirculating resin, being a strong depressant.

It has been established that the reduction in the resin capacity for precious metals is proportional to the residual capacity of the ion exchanger in terms of the thiocyanate ion [4].

Complete restoration of the sorption properties of the anion-exchangers is therefore impossible without recharging them, to chloride or hydroxyl forms; this recharging takes longer than desorption of gold and impurities added together [4].

Among the desorbents for the thiocyanate ion, alkali is preferable to nitrate and chloride eluents, particularly for the AM-2B anion exchanger, because it can be used to combine the desorption of the thiocyanate ion, zinc, sulfur, silicon, aluminum, and arsenic with conversion of the resin to the hydroxyl form which is most selective in relation to gold [4], and the thiocyanate-alkaline eluates can be re-used in the regeneration process. Most of the ammonium thiocyanate expended on regeneration has to be neutralized because there are no economical methods for extracting thiocyanates from the eluates.

Neutralization of spent thiocyanate-alkali eluated by chlorination leads to salt pollution of effluents and industrial water, and makes complete water recirculation difficult.

A reagent-free method of breaking down thiocyanates with ozonized air in the eluates and directly in the process of eluting them from the ion exchanger has been used to eliminate this disadvantage.

The experiments were conducted in a laboratory installation consisting of an ozonizer and a column with a porous bottom.[2]

The investigations showed that complete breakdown of non-ferrous metal cyanides and thiocyanates by dispersed ozonized air in thiocyanate-alkaline and chloride-alkaline eluated of complex composition was achieved in 10-60 min (Table 2).

Approximate calculations showed that the cost of neutralizing cyaniferous thiocyanate-alkaline eluates by ozonizing will be 3-10 kopecks per ton of ore with a normal

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[2] E. K. Roshchin participated in the work.

APPLICATION OF FRAGMENTATION RESEARCH TO BLAST DESIGN: RELATIONSHIPS BETWEEN BLAST DESIGN FOR OPTIMUM FRAGMENTATION AND F

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INTRODUCTION

Recent research done jointly by the University of Maryland and Martin Marietta Laboratories (Fourney, et al., 1979; Holloway, et al., 1980; Barker, et al., 1979; Winzer and Ritter, 1980a,b; Winzer, et al., 1979a,b,c) has revealed a number of hitherto little recognized factors in the fragmentation process in explosively loaded rock. Blasting patterns are commonly designed with delays between boreholes, both to reduce ground vibration and to enhance fragmentation; however, research has shown that the delay times expected are not often achieved due to the high degree of irregularity in the firing times of the initiators (Winzer, 1978; Winzer, et al., 1979a).

Crack initiation and propagation have also been reevaluated. Work by Fourney, et al. (1979), Holloway, et al. (1980), and Winzer and Ritter (1980a,b) supported early theories of rock breakage by stress-wave-induced damage (e.g., Obert and Duvall, 1950; Duvall and Atchison, 1950, 1957; Hino, 1956; and others), which were later rejected because of energy considerations. However, the new studies went beyond those synthesizing gas-pressure and stress-wave breakage mechanisms (e.g., Field and Ladegaard-Pederson, 1971; Kutter and Fairhurst, 1971) in that they found new fracture mechanisms and provided data indicating that stress-wave breakage is the dominant fracture mechanism and is principally responsible for fragmentation.

The results of these research efforts have been integrated into an applications approach for use in field production blasting operations. Tests with these new approaches are discussed, and resulting changes in ground vibration, especially frequency, and their implications are presented.

EXPERIMENTAL METHODS

Production blasting tests were monitored using four 16-mm high-speed motion picture cameras and three, three-axis recording seismographs. To record actual firing times of boreholes in the blast pattern, a Redlake Locam and a Redlake Fastax were placed behind and above the active bench. To monitor face fragmentation and burden motion, a Fastax was placed in line with and slightly above the active face, and a Locam, as nearly perpendicular to the face as possible. This geometry varied somewhat from shot to shot. Framing rates varied from 500 to 3000 frames/s depending on exposure conditions. Environmental Technology three-axis recording seismographs were used to record the resulting ground vibration in the vertical, transverse, and longitudinal modes. The response of these seismographs is essentially flat from 2-100 Hz, the frequencies of most interest in blasting seismology. The seismographs were linked to the cameras through a radio transmitter that transmitted a continuous 1000-cycle timing pulse to three receivers (one for each seismograph) to be recorded on the seismograph tape. When one of the high-speed cameras gives the signal to fire the shot, this pulse is interrupted, resulting in a zero-time indication on the magnetic tape of each seismograph. In this manner, the shot parameters (firing times, delay, fragmentation behavior, etc.) can be related to the record of the seismic event.

RESULTS

Fragmentation Studies

Analysis of high-speed motion pictures of production blasts and reduced-scale block and bench blasts (Winzer, et al., 1979b; Winzer and Ritter, 1980a,b), as well as evaluation of the effects of errors in ms delay initiators on fragmentation (Winzer, 1978; Winzer, et al., 1979a), has changed both the technology of initiation of blasting patterns and the patterns themselves. Winzer, et al. (1979c) published results of a study of the effects of various factors (burden, spacing, structure, and timing) on fragmentation. For a given range of burden and spacing, timing and structure were found to be the most important factors affecting the success of the blasting operation.

Two aspects of timing were found to be basic to a successful blast: sequencing and proper firing interval. All boreholes must fire in the designed sequence. For example, in a single-row blast opening at one end, the holes should fire 1, 2, 3, 4, etc., from the opening end. Sequencing errors produce oversize, flyrock, backbreak, and tight muck, as has been clearly shown in high-speed films of more than 60 production blasts.

Less readily analyzed are the effects of timing errors that cause "crowding" (holes firing closer together than expected), thus changing the relief in a shot. Previous work (Bergmann, et al., 1974; Andrews, 1975) had established the optimum delay at about 1 ms/ft of burden, equivalent to about 1.2 ms/ft between holes in a row and ~ 5-6 ms/ft on the echelon, depending on the spacing and burden. Using high-speed films of production blasts, Winzer, et al. (1979a,b) determined that to reduce vertical motion to zero, en-echelon relief had to be at least 8.2 ms/ft. This, coupled with positive evidence of the deleterious effects of the firing errors found by Winzer, et al. (1979a), led to the development of more accurate initiators (see Table 1).

Similarly, advances in understanding the factors controlling fragmentation and resulting ground vibration led to the introduction of more sophisticated programmable sequential blasting machines to control the firing of a series of initiators. Although the availability of both new blasting machines and more

Table 1

Means and Standard Deviations of Firing Times for DuPont Experimental New Technology Initiators and Standard DuPont Initiators

Delay (ms)	New Technology Lab $\bar{X}$	1σ	Field $\bar{X}$	1σ*	Old** $\bar{X}$	1σ
75	74	1.3	99.5	6.6	86.2	4.2
100	97	2.6	117.9	6.1	111.7	5.6
125	120	2.8	144.7	8.9	140.4	7.8
150	149	3.9	171.5	5.8	173.4	6.0
175	180	2.9	197.3	5.4	185.1	5.9
200	196	5.1			183.4	9.6
250	245	4.8	302.4	---	279.2	9.6
300	305	3.0	330.0	---	307.0	11.7
350	346	5.5			362.4	34.4
400	395	4.6			428.1	19.8
450	458	9.1			440.8	18.6
500	514	4.5			523.7	24.0

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* Higher 1σ values reflect higher error in measurement of field data.

** From Winzer, et al. (1979a).

accurate initiators is still restricted, the combination of these two changes allows blasting patterns to be realistically designed with much longer delays and consequent higher relief (up to 17 ms/ft on active echelon burden vs 6.5 ms/ft in general practice). In addition, new delay guidelines for sequential blasting have recently been released by DuPont (Andrews, 1981, in press), reflecting the usefulness of long-delay patterns for improved fragmentation.

A combination of studies using Homalite models (Barker, et al., 1979; Fourney, et al., 1979), small rock plates (Holloway, et al., 1980) and large rock blocks and production blasting (Winzer and Ritter, 1980a,b) established the importance of structure to the overall fragmentation process, and quantified some of the mechanisms by which new fractures are initiated by the interaction of stress waves with structural discontinuities. Of current concern in the application of this research to blasting practice are large-scale discontinuities such as joints and bedding planes. These discontinuities influence the geometry of the borehole pattern, and perhaps also the optimum timing, although the latter influence is not yet clearly understood. These effects will be discussed below for individual cases.

Twenty production blasts were monitored in tests of five high-relief blasting patterns, and both fragmentation and ground vibration were assessed. Vibration effects will be discussed in detail in the next section.

Location 1. The tests in location 1, a limestone quarry, were the simplest conducted and also provided the most precise economic data. A single row of 6-1/8-in. holes was drilled on a 17-ft x 11-ft or an 18-ft x 14-ft pattern, depending on the ledge being shot. Bench heights were typically 40 to 45 ft. This pattern was unusual, i.e., the burden was larger than the spacing, but was determined by the spacing and character of major joints. Two sets of solution-weathered joints were prominent, 6 to 11 ft apart, one nearly parallel to the bench face, one at about 90°. Joints such as these, which are open or filled with material of very different properties than the surrounding rock, can severely attenuate the stress waves from the blast, and, as shown by Winzer, et al. (1979c), result in the production of oversize. Increasing the spacing aggravates the problem because more blocks of rock are insulated from stress waves by open joints, and decreasing the burden increases flyrock.

The original delay pattern used 17 ms between holes, and some shots were decked, with 25 ms between decks, for vibration control. The between-hole relief was 1.5 ms/ft. The new pattern tested used 42 ms between holes, increasing the relief to 3.8 ms/ft, which was within the range indicated by our earlier research.

Improved fragmentation due to the new pattern produced a savings of about 10% on the overall cost of production of a ton of stone from this quarry during a 4-month trial. The savings were based on changes in amount of secondary breakage required and in tons per hour of throughput at the primary crusher. The two major reasons for the improvement were: 1) increased relief, which decreased the amount of backbreak, resulting a straighter and smoother face and better performance for the next shot; and 2) somewhat more speculative, the additional time between holes, which allowed more time for fracture development around the detonated hole before the adjacent hole was fired. In the limestones at this location, crack propagation velocities are about 12% of the P wave velocity, or about 55 cm/ms (Holloway, et al., 1980), i.e., it takes about 10 ms for a crack to propagate the distance from the borehole to the free face with an 18-ft burden. Although the cracks are initiated throughout the burden by the P wave, they require time to grow and coalesce. Therefore, the total propagation time indicates the minimum time necessary for a significant crack network to begin to form. However, movement sufficient to open the cracks in blocks requires periods 2 to 4 times longer than to form the crack network, or 20-40 ms of delay for this location. If the hole is fired too soon, the stress waves from adjacent boreholes may not be able to fully interact with cracks formed or forming from previously fired boreholes, thus impeding fragmentation. Research is continuing on this question.

Locations 2, 3, and 4. At these three locations, more complex patterns were tested, in both granite and limestone. All tests were on multiple-row patterns, with between-row delays and high en echelon relief. The first set of tests used patterns similar to that shown in Fig. 1.

Between-hole delay in a row was 50 ms (fixed by the available delay intervals in the ms delay series); the sequential timer was set to an interval of 100 ms; bench height was 72 ft; burden was 10 ft and spacing was 12 ft, equivalent to a delay of 4.2 ms/ft between holes in a row and 10 ms/ft between echelons. These delays between holes and echelons were about 1 ms/ft and 2 ms/ft more, respectively, than those used in our earlier research.

The results from these tests were similar to those at location 1: oversize blocks were reduced or eliminated altogether, and backbreak was greatly reduced (see Fig. 2). In comparison with multi-row blasting

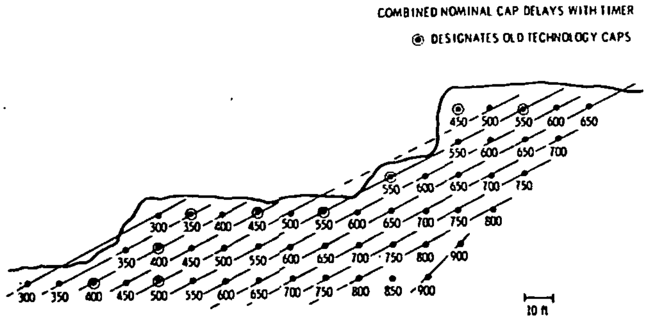

Figure 1 High-relief blasting pattern tested in a granite quarry. Sequential timer setting was 100 ms between individual circuits, and between-hole delays were 50 ms. Firing times shown are nominal.

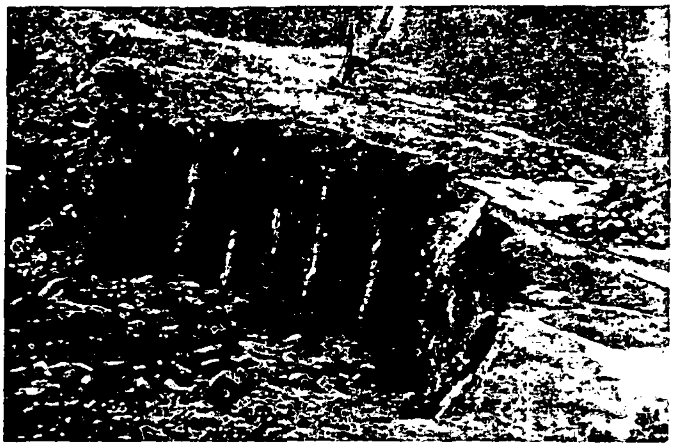

Figure 2. Photograph of wall conditions and part of the muckpile from the shot shown in Fig. 1. Note the absence of backbreak, and the displacement and height of the muckpile.

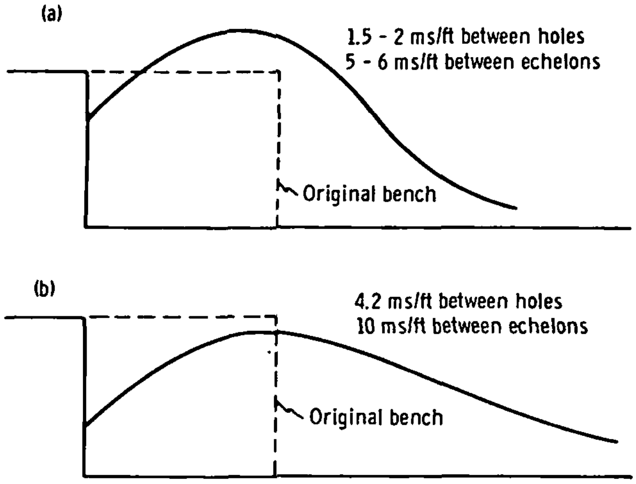

Figure 3. Sketches of muckpile cross sections for different delay patterns: a) typical shape of a muckpile for delay of < 2 ms/ft between holes and < 6 ms/ft en echelon; b) typical configuration for delay of > 3 ms/ft between holes and > 8 ms/ft en echelon.

patterns using less delay (1.7-2 ms/ft between holes, 5-6 ms/ft between echelons), vertical motion was reduced (flyrock or high-velocity venting of stemming), and the shape of the muckpile changed (Fig. 3) due to increased overall displacement of the fragmented material. The result was an economic advantage, especially where front-end loaders are used. In the case shown in Fig. 3a, the fragmented material is fairly "tight"; it resists shovel or loader penetration, increasing its handling time. In the situation shown in Fig. 3b, the fragmented material is looser and can be loaded more rapidly. Up to 30% reductions in loading time have been achieved using higher relief patterns.

The patterns described worked well for shots up to five rows, but beyond this point, vertical motion increased, and displacement and wall conditions deteriorated. In addition, high-relief shots with this design produce ground vibration with relatively high particle velocities in the 3-18 Hz range, the resonant frequencies of residential structures (Siskind, et al., 1980).

Earlier unpublished work at Martin Marietta Laboratories indicated that for shots using up to 10 rows, as much as 18 ms/ft on the echelon would be needed to reduce vertical motion to zero. The long between-row delays (125-150 ms) required to accomplish this type of relief would result in light burdens on the front rows, possibly causing cutoffs, noise, and front-row flyrock.

A sequential blasting machine, with variable intervals between circuits, can prevent too much relief on the front rows and too little deeper into the shot. Using machines built by Safety Devices of Lorton, Va., and Research Energy of Ohio, we could set the intervals between each of 10 circuits for any delay between 5 ms and 999 ms (Research Energy) or between 100 µs and 999 ms (Safety Devices). This flexibility allowed shot designs with progressively increasing delays between circuits and corresponding increases in en-echelon relief in deep shots.

This type of pattern -- decreased between-hole relief and increased en-echelon relief -- shown in Fig. 4, was tested in a limestone quarry in Iowa. Initial en-echelon relief was 14 ms/ft, increasing to 21 ms/ft in the rear rows. In addition, the between-hole relief was increased on the last row. A comparison of the results from this shot and a previous shot using standard sequential timer programs is shown in Fig. 5. The difference between these two

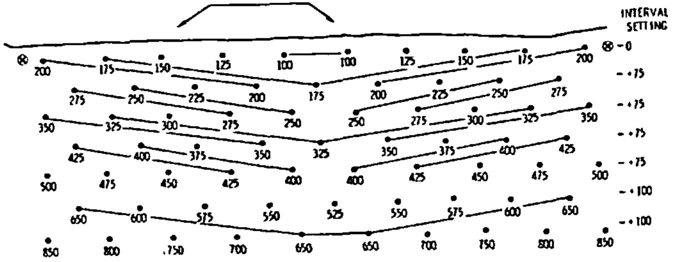

Figure 4. Variable relief blasting pattern tested in a limestone quarry in Iowa. Delay times shown were achieved by increasing the firing interval between circuits (rows) for the last two rows in the shot.

Figure 5. Photograph of muckpiles produced by the pattern given in Fig. 4 (background) and a fixed-interval, lower relief pattern using 5 rows (foreground). Part of the muck in the foreground has been removed. Muck from the new pattern obscures the wall from this angle, but the material is thrown clear of the wall to the base of the bench.

shots was principally in displacement and wall conditions. The fragmented material from the test blast was displaced from the wall nearly to the bottom of the bench, the muck profile was lower, and backbreak was reduced.

Results from all three test series established the success of application of the research results in delays and structural effects to field practice. Moreover, application was aided by new technology initiators and new blasting machines, themselves the result of earlier research. Significant savings in production costs were realized. One problem stemming from the use of new patterns remained to be addressed, that of ground vibration.

Vibration Studies

The problem of vibration is critical in the application of any blasting pattern, as more and more mining operations become surrounded by urban areas. New work on the effects of blast-induced ground vibration on residential structures (e.g., Medaris, 1977; Siskind, et al., 1980) established the importance of the frequency of the seismic waves, and presented new guidelines on the frequencies and amplitudes of ground vibration that can be expected to produce damage in residential structures. These new guidelines recommend considerably lower amplitudes than do previous ones, and take into account frequency.

Because of the importance of being able to predict seismic effects from these new blasting patterns, we have undertaken a study of the relationships between frequency and amplitude of ground vibration and input parameters such as the delay pattern. On each of the multi-row blasting patterns previously discussed, three or more three-axis recording seismometers were used to record the vibration produced by the blasting pattern. Each tape was digitized and processed for peak particle velocity for each of the three components. Frequencies present in each component were obtained by Fourier analysis.

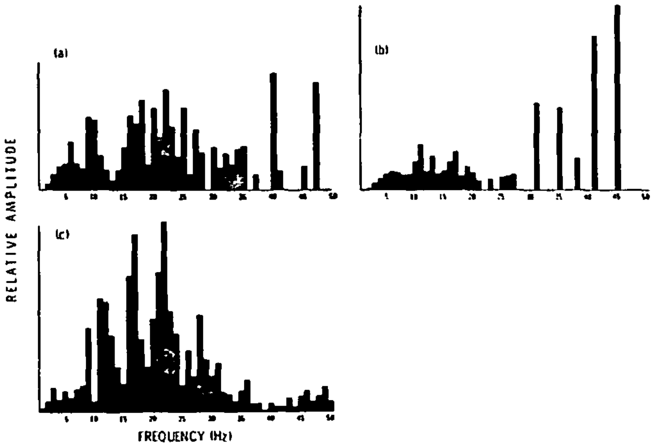

Figure 6. Calculated and measured frequencies for the shot shown in Fig. 1. a) Calculated from laboratory-derived initiator firing times; b) calculated from borehole firing times measured using high-speed cinematography; c) Fourier spectrum (longitudinal component) from the seismogram. The high frequencies shown in the calculated spectra from firing times measured in the field occur partly because only a small percentage of the firing times were obtainable; thus, the sampling statistics are not good. The match is better for the spectra calculated using measured firing times for the initiators. Higher frequency peaks (above 30 Hz) are present in the vertical and transverse components of the spectra from the seismogram.

Figure 6 presents results from 1 of the 12 shots monitored, obtained as follows. From the mean and standard deviations of the firing times for DuPont initiators given in Table 1, the intervals between the firing time of each hole and all others were calculated. The inverse of the intervals equals the frequency. The number of intervals corresponding to a particular frequency (Ω), multiplied by the square of that frequency, was plotted as a histogram. [This procedure provides the best correlation with the amplitudes in the Fourier spectra from the seismograms, but the physical meaning of the parameter (interval x Ω^2) is not yet known.] Figure 6 presents the frequencies obtained from the firing times measured in the laboratory (6a), the frequencies calculated from actual firing times in the shot (6b), and the Fourier analysis of the seismic data from the shot (6c). There is generally good agreement between the major frequencies obtained from the laboratory data and actual firing times and the actual frequencies found in the shot, suggesting that a relationship between delay design and resulting frequency of ground vibration exists.

This type of analysis can be used to design shots that shift frequencies out of the resonant frequency of residential structures. The shots discussed previously produced major peaks in the spectra between 5 and 20 Hz. Particle velocities at 500 ft ranged from about 0.5 to 1 in./s, and at 900-1000 ft, ranged from about 0.15 to 0.5 in./s. At the higher amplitudes, these shots therefore produced vibration that exceeded the lower limits of potentially damaging vibration (0.5 in./s at 10 Hz or less, as recommended in the most recent Bureau of Mines studies). Although there were no occupied houses within range of damaging vibrations at the locations where the test patterns were used, a problem was encountered at another location.

Location 5. This location is a granite quarry situated at the edge of a small town. The nearest residents are about 1000 ft from one or more of the active faces in the pit, and all residential structures are situated on poorly consolidated sandy siltstone which overlies the granite. The quarry experiences both poor blasting results and complaints from neighbors arising from ground vibration. Blasting patterns such as those tested at locations 2, 3, and 4 would produce low-frequency ground vibration, which could aggravate the problem. In addition, the area itself may be conducive to transmitting vibration at certain frequencies. To test this theory, a single 3.5-in. borehole was fired on one of the 60-ft benches at the quarry. The spectrum from this single hole was quite complex, containing frequencies around 6, 10, 15, 20, and 26 Hz. This result was not surprising since a columnar charge is not a point source. The additional complicating effects of delays and multiple columnar charges were eliminated, however.

Thus, it could be tentatively assumed that the transmission characteristics of the ground favored waveform energy at the frequencies found in the single-hole seismogram. The delay pattern for this site should therefore prevent generation of large amounts of energy at those frequencies, yet still meet the objectives of better fragmentation. Accordingly, a pattern was designed to shift the bulk of the seismic energy to frequencies above 20 Hz. Figure 7 is a plot of the expected frequencies for the new pattern design (from initiator firing times) and actual frequencies obtained for that pattern from the seismogram taken at the same location as that for the single hole. As can be seen, the pattern has succeeded in shifting the frequency above 20 Hz. Smaller peaks still appear at 6, 10, and 15 Hz, but they are lower than those produced by earlier patterns. The shot, consisting of three rows of 3.5-in. holes drilled on a 9-ft x 9-ft pattern, used 125-ms delays between rows 1 and 2, 136-ms delays between rows 2 and 3, and 50-ms delays between holes, i.e., 5.6 ms/ft between rows and up to 18.5 ms/ft on the echelon. The result was improved breakage, displacement, and wall conditions.

The subject of frequency of ground vibration from blasting and its control is complex, and has been treated here in a fairly simple, empirical manner. With suitable caveats, we can say that the input parameters, expressed in terms of interval firing times, are directly related to the output frequencies. This conclusion has some support from earlier studies (Frantti, 1963; Pollack, 1963) of seismograms taken at long distances. However, the relative amplitudes calculated from the firing times do not always agree with those from seismogram spectra, and their physical significance is unknown at this time. Complicating the interpretation of the spectra are the transmission characteristics of the ground itself, and the statistical nature of the input function, which is caused by scatter in initiator firing times. The successful application of these relationships to design blasting patterns that produce shifts in frequencies suggests that the relationships discussed are valid. Considerably more research must be done to understand the fundamental causes of the observed spectra.

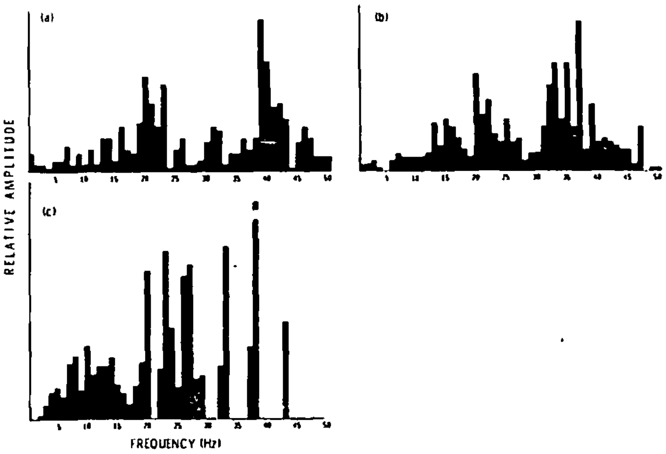

Figure 7. Calculated and measured frequencies for high-relief patterns designed to shift the frequencies above the resonant frequencies of houses (a, b, and c as in Fig. 6).

CONCLUSIONS

Application of discoveries from research on effects of delays on fragmentation, and on fundamental fragmentation mechanisms themselves, to the design of blasting patterns, has resulted in new, more efficient blasting patterns for use in open-pit mining. These new blasting patterns induce changes in the frequency, and possibly the amplitude, of ground vibrations, but preliminary research results indicate that frequency can be controlled by delay design, and that these designs can be implemented using new technology initiators and new programmable sequential blasting machines.

Acknowledgments

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Acid-Ferric Sulfate Solutions For Chemical Mining

PAUL H. JOHNSON

Chemical mining may be defined as the use of chemicals in extracting metal values from in situ broken or unbroken ores within a mine. The present means for the generation and regeneration of sulfuric acid or sulfuric-ferric sulfate solutions are inadequate for most applications. This report describes a pressure oxidation process for the generation and regeneration of these solutions from pyrites and spent iron sulfate leach liquors. While recent mining developments such as solution injection, caving, and conventional and nuclear blasting, have provided new and better means for the percolation of leach solutions through rock masses, little has been done to reduce cost and improve the quality of the leach solutions that are required.

A leach solution for chemical mining should meet certain requirements. It should be 1) inexpensive on either a small or large tonnage basis, 2) capable of selectively leaching the desired ore minerals contained in a particular ore, 3) of the proper strength or quality to do the job of leaching in an underground environment and 4) amendable to simple and inexpensive metal recovery steps. It is also important that the capital investment be low for the solution generation and/or regeneration plant.

Sulfuric acid and/or ferric sulfate solutions are the most likely candidates for chemical mining leach solutions. Most of the oxides and sulfides of copper, zinc and nickel and the oxides of uranium, vanadium, beryllium, etc., are soluble in one or both of these solutions. However, gangue materials that are high in lime, magnesia, iron or aluminum may interfere with their use.

Several processes have been introduced in the past for the generation and/or regeneration of acid-ferric sulfate leach solutions. Air oxidation of spent ferrous sulfate leach solutions under atmospheric conditions was found to be non-economical at Cananea, Mexico. Anodic oxidation was used at Inspiration, Arizona for several years to oxidize iron sulfate solutions. Various sulfur dioxide adsorption-oxidation processes, in specific applications, have met with some success. Bacterial oxidation of spent iron sulfate leach liquors has attracted a good deal of attention in recent years. Insofar as the generation and regeneration of acid-ferric sulfate solutions for chemical mining are concerned, each of these processes have their limitations. Some of them would be inefficient and too expensive, some would not do the complete job of solution generation and regeneration and some would not produce solutions of the proper strengths for efficient chemical mining.

A new process,* recently tested on a laboratory scale, makes use of pressure oxidation techniques to convert solutions of ferric and ferrous sulfates and/or pyrites to sulfuric acid and/or ferric sulfate solutions. Commercial scale application would probably require the use of an autoclave which retains pyrite at a high pulp density within the vessel until reacted. A description of the autoclave is appended to this article.

CHEMISTRY

The over-all process consists of:

1) acid-ferric sulfate generation and regeneration from pyrites and spent iron sulfate leach liquors at elevated pressures and temperatures and at high pulp densities;

2) adjustment of the ferric sulfate content of the leach liquor when the iron oxide reaction product is removed under atmospheric conditions;

3) heap, "in-situ" or "in-mine" leaching of ores under atmospheric conditions;

4) purification or adjustment of pregnant leach liquor;

5) metal recovery from pregnant leach liquor.

In the acid-ferric sulfate generation step, water or spent solution containing iron sulfates, pyrite and air are combined in an autoclave of special design to bring about the reaction,

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad [1]$$

PAUL H. JOHNSON is a graduate student, Dept. of Mining and Geological Eng., University of Utah. The paper was presented in May at the Pacific Southwest Mineral Industry Conf. of AIME at Reno, Nev.

* Patent applied for.

Concurrently, under the same conditions as those of the pyrite oxidation, sulfuric acid and ferric sulfate are regenerated from the iron sulfates contained in the spent leach liquors. The ferrous sulfate originally in the spent leach liquor, plus any obtained through pyrite oxidation, is oxidized to ferric sulfate, i.e.,

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O. \qquad [2]$$

In those cases where there is insufficient sulfuric acid present, a basic iron sulfate forms according to the equation,

$$4FeSO_4 + 3H_2O + O_2 \rightarrow Fe_4SO_9 + 3H_2SO_4. \qquad [3]$$

Ferric sulfate hydrolyzes in varying degrees according to the reaction temperature, to form sulfuric acid and a solid iron oxide product, i.e.,

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow 3H_2SO_4 + Fe_2O_3 \qquad [4]$$

A savings is effected in acid ferric sulfate regeneration from spent leach liquors. Much less air and autoclave volume is required in the regeneration of iron sulfates to acid than in the generation of acid from pyrites.

Iron oxide dissolves in the highly acid solution under atmospheric conditions according to the reaction,

$$3H_2SO_4 + Fe_2O_3 \rightarrow Fe_2(SO_4)_3 + 3H_2O. \qquad [5]$$

Upon removal and cooling of the regenerated, acid-ferric sulfate solution from the autoclave vessel, the iron oxide residue product is allowed to settle in a thickener and removed from the system. The temperature of the leach liquor-iron oxide pulp and the time of contact during separation should determine how much acid would be reconverted back to ferric sulfate.

In the atmospheric leaching of sulfide and oxide ores under atmospheric conditions with this acid-ferric sulfate leach liquor, both ferric sulfate and ferrous sulfates are added to the leach liquor. Typical leaching reactions are:

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow 2CuSO_4 + FeSO_4 + S$$
$$ZnS + Fe_2(SO_4)_3 \rightarrow ZnSO_4 + 2FeSO + S$$
$$3CuO + Fe_2(SO_4)_3 \rightarrow 3CuSO_4 + Fe_2O_3$$
$$Fe_2O_3 . nH_2O + 3H_2SO_4 \rightarrow nH_2O + Fe_2(SO_4)_3$$

When copper is precipitated from solution by cementation, the reaction is:

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

Again, ferrous sulfate is added to the system.

After metal recovery by standard metallurgical processes, most of the spent solution is combined with pyrite and returned to the autoclave.

LABORATORY EQUIPMENT

The major laboratory equipment used in this study consisted of a laboratory, high-pressure, high-temperature acid-ferric sulfate production autoclave. It was built almost entirely of titanium and had a considerable amount of accessory equipment. The vessel was tall (about 20 ft) and narrow (up to 9 in. diam). It was placed within a supporting structure and wrapped with an insulated shield. Controls and measuring equipment were used to measure and regulate the flow and pressure of air passing through the system, indicate the pulp level within the vessel and measure the rate of flow of circulating solution and the temperature within the vessel. The system had a means of adding water to make up for steam losses, for adding reagents if needed during a test, for external heating and for periodic sampling of the vessel contents. Air was supplied to the vessel via a large receiver tank by a compressor capable of compressing 6.75 standard cfm air to a pressure of 700 psi. A mercoid switch controlled the pressure of air in the receiver tank and the operation of the compressor.

This vertical, gas-agitated, laboratory autoclave was capable of batch leaching 5 to 9 lb of solids under conditions that are quite similar to what might be expected to exist in a commercial size vertical, gas-agitated autoclave. These conditions were a pulp density in the reaction zone of approximately 40%,* agitation by air-solution fluidization, circulating solution classification, air pressures as high as 700 psi, and temperatures to 230C. Air and circulating solution flow rates were controllable and measurable over a wide range.

LABORATORY MATERIALS

A pyrite flotation concentrate and commercial ferrous and ferric sulfates were used in this study. Table I is a screen analysis of the pyrite concentrate. It assayed 38.0% Fe, 43.0% S, 0.4% Cu, 1.0% Zn, 0.8% Pb and 0.082 and 2.5 oz of Au and Ag, respectively. The ferrous sulfate salt assayed 25.6% Fe^{++} and 44.7% SO_4. The ferric sulfate was composed of 24.0% Fe^{+++} and 42.2% SO_4. Tap water was used in all experiments.

EXPERIMENTAL PROCEDURE

In these studies, batch charges were added to the autoclave, the vessel was sealed and then heated up to temperature under running air flow conditions. It was then run under a given set of leach

TABLE I. Screen Analysis of Pyrite Flotation Concentrate

Mesh	% Retained
+20	0.0
−20 +28	0.6
−28 +35	1.0
−35 +48	3.5
−48 +65	8.8
−65 +100	36.9
−100 +150	5.7
−150 +200	1.6
−200 +270	24.8
−270	16.9
	100.0

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* The pulp density was limited in the laboratory titanium model to 40% solids because of solution recirculation limitations. These limitations would not be involved in a larger, continuous model having a more efficient means of recirculation.

conditions for approximately 3 hours. In some instances, ferrous and ferric sulfates and/or sulfuric acid were injected into the vessel when reaction temperatures were reached. Periodic sampling of the vessel contents provided a means of following the chemical reactions.

PYRITE OXIDATION

Numerous tests were conducted with pyrite and water charges to determine the effect of variables on pyrite oxidation rates.

Fig. 1 is a typical time versus leach liquor composition graph. The composition of the leach liquor contained in the autoclave (corrected for volume changes) is plotted versus time and temperatures from the time of startup to the finish of the tests. Sulfuric acid, SO_4, and ferrous and ferric iron compositions are plotted on this graph.

Table II shows data for a number of pyrite oxidation tests. The more pertinent test results obtained in this series of tests are described in this table as; (1) the rate of sulfate production during the given test period in terms of sulfate ion/liter of solution in vessel/hr (gpl SO_4/1/hr), corrected for volume changes; and (2) the total iron content of the leach liquor in the system at the end of two hours of leaching in terms of grams per liter (gpl) (uncorrected for volume changes).

TABLE II. Summary of Pyrite Oxidation Tests

	Tests Nos.							
	7	8	9	10	11	12	13	14
Temperature, °C	185	185	175	175	175	155	155	195
Air Pressure, psig	355	355	300	355	355	355	355	355
Air Flow, cfm/sq in.	.067	.067	.067	.067	.033	.067	.033	.067
Pyrite, grams	2500	3500	2500	2500	2500	2500	2500	4500
Addition of Water	x	x	x	x	x	x	x	x
Total Water, liters	14	14	14	14	14	14	14	14
1-2 hr SO^c_4 Prod. Rate	39	55	22	25	30	13	13	78
2 hr Fe^T gpl	6.5	11.5	3.8	6.2	5.0	1.0	1.0	23
2 hr H_2SO_4 gpl	40.5	62.5	27.0	29	64.5	11.5	14.8	62

Sulfate production rates were noted to increase with increases in the surface area, pulp density, oxygen partial pressure and to be independent of the solution compositions. Tests 7 and 8, which were run with pyrite charges of 2500 and 3500 g respectively, had 1-2 hour sulfate production rates of 18 and 25 gpl per hour respectively.

The sulfate production rate curves were noted to be essentially linear with time in each test, despite the fact that the composition of the leach solutions varied widely within each test. Solutions as high as 120 gpl H_2SO_4 were produced in 2½ hours of leaching at relatively low pulp densities.

These data correspond well with those obtained by earlier experimenters who worked with stirred, conventional autoclaves and weak solutions. They concluded that the over-all rate of pyrite oxidation was proportional to temperature, surface area, or pulp density and oxygen partial pressure and was independent of the solution composition.

Sulfate production rates were not influenced appreciably by air flow rates. The 1-2 hour sulfate production rate obtained in test 10 (25 gpl SO_4 per 1 per hr), which was run at 175°C and a pressurized air flow of 0.067 cfm per sq in., is comparable to the 30 gpl SO_4 per 1 per 1-2 hour value obtained in Test 4 wherein the temperature was held at approximately 182°C and the pressurized air flow was maintained at 0.02 cfm per sq. in. Likewise, tests 13 and 12, which were run at a temperature of 155°C and air flow rates of 0.033 and 0.067 cfm per sq in.[†], had identical sulfate production rates.

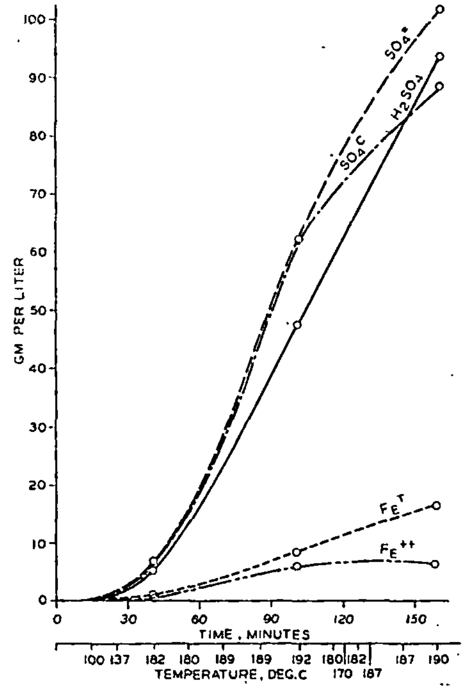


Fig. 1—Typical time vs. leach liquor composition graph for pyrite oxidation test No. 8.

Inasmuch as there was found to be little or no variation in sulfate production rates with increased air flow or increased agitation through the air-stirred autoclave, diffusional control is not indicated at low agitation levels. Activation energies obtained from experimental data also support this conclusion.

EFFECT OF IRON SULFATES

Since ferrous and ferric sulfate either accumulate in the leach solution during the leaching of pyrite or, in the case of an acid-ferric sulfate regeneration process, are added to the charge entering the autoclave, it was of interest to examine their possible effects on the over-all reaction at temperatures in the range of 155 to 175°C.

Table III summarizes the tests made on pyrite in solutions containing iron sulfates.

The curves of Fig. 2 are representative of those tests (Test 15) wherein ferric and/or ferrous sulfates were added to the charge initially.

Fig. 3 shows a typical test (Test 16) where iron sulfates were added to the system when it had attained reaction temperatures.

Characteristic of tests where iron was initially present in the leach liquor was;

(1) rapid formation of acid to a level dependent on the test temperature, i.e.,

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow 3H_2SO_4 + Fe_2O_3; \qquad [6]$$

[†] These two values of pressurized air flow probably represent the low and the medium range air flow rates for this type of air-stirred autoclave.

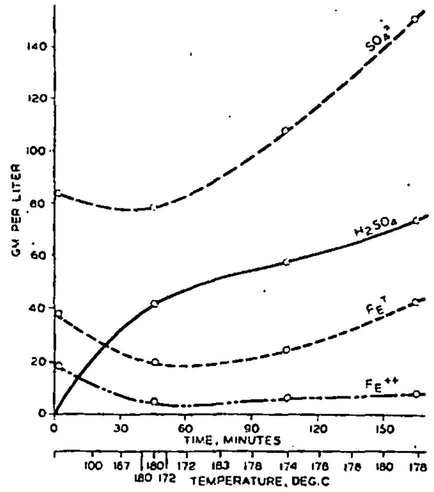


Fig. 2—*Leach liquor composition graph, iron sulfates initially present, Test 15.*

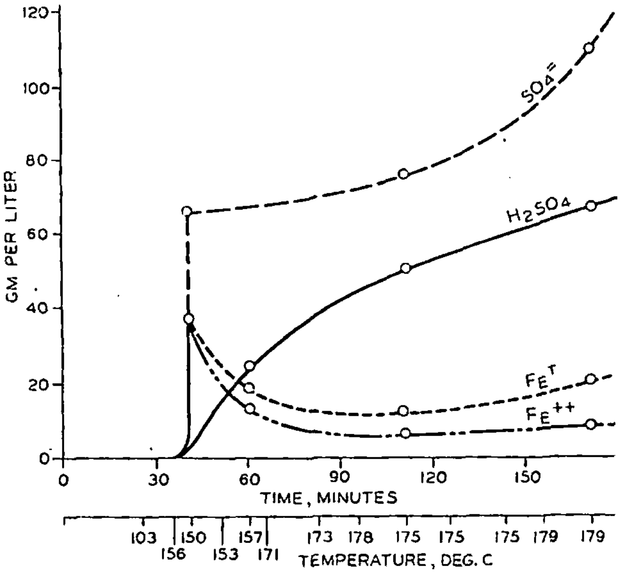


Fig. 3—*Leach liquor composition graph, iron sulfates injected, Test 16.*

(2) a rapid decrease in the total iron content of the system as a result of the above reaction;

(3) continued pyrite oxidation, i.e.,

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4,$$

at similar rates to those obtained in tests where iron was initially absent in the system, and;

(4) basic iron sulfate precipitation was found to interfere somewhat with the normal pyrite oxidation pattern in those tests wherein initial iron sulfates were present in the leach liquor. Early in the test, before the acid content of the leach liquor had a chance to build up, a yellow basic iron sulfate product would precipitate and cause the sulfate production rate to be somewhat less than normal, i.e.,

$$4FeSO_4 + 3H_2O + O_2 \rightarrow Fe_4SO_9 + 3H_2SO_4 \quad [7]$$

AUXILIARY REACTIONS

Due to operational differences between a commercial size continuous autoclave and the laboratory model in which testing was done, certain differences are to be expected in the chemistry. The heating or cooling of solutions in entering or leaving a large continuous vessel would take place much faster and under more reducing conditions than in the case of tests run in the laboratory model. Ferric sulfate, during the brief ingress period, would be partially reduced to the ferrous form by pyrite, i.e.,

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \rightarrow 15\,FeSO_4 + 8H_2SO_4 \quad [8]$$

and the liquor leaving the vessel would have a tendency to form ferric sulfate from acid and the solid ferric oxide product, i.e.,

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad [9]$$

TABLE III. Pyrite Oxidation Tests with Iron Sulfates

	Test 15	16	17	18	19	20	21	22
Temperature, deg. C	175	175	150	175	175	155	175	175
Air pressure, psig	355	355	250	355	355	355	355	355
Air flow, cfm/sq in.	.067	.067	.067	.067	.067	.067	.067	.067
Pyrite #1, gms	4300	2500	1000	2500	2500	2500	2500	1000
H_2SO_4, ml	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.9
Ferrous sulphate, gm	1061	2022*	1060	1061*	—	—	—	371
Ferric sulphate, gm	1072	—	1072	—	584	584	1072	368
Total water, liters	14	14	14	14	14	14	14	14
$SO^{=}_4$ prod. rate 1-2 hr	35	25	11	22	25	9	28	13
2 hr Fe^T, gpl	28	13	23	6.5	8.0	4.5	14	13
2 hr H_2SO_4, gpl	61.5	54	26	44	45	33.5	40	32

* Injected at end of warmup period

Evidence of the reducing effect of pyrite on ferric sulfate can be seen in the warmup periods of almost all of the tests run in the laboratory model of the air-stirred autoclave. In the early part of each of these tests, despite the fact that oxidizing conditions prevailed, the content of ferrous sulfate in the solution increased and that of the ferric sulfate decreased.

The effects of pyrite in reducing ferric sulfate were studied in a series of tests in which 100 g samples of minus 100 mesh pyrite #2 were contacted with 100 ml amounts of an acid-ferric sulfate solution containing 41.2 gpl total iron, 4.7 gpl ferrous iron, and 13.7 gpl sulfuric acid for one-half hour durations at variable test temperatures.

This reduction of ferric iron on pyrite at slightly elevated temperatures could possibly be used to good advantage in any cyclic acid-ferric sulfate generation or regeneration process wherein the presence of ferric iron in the pregnant liquor was a hindrance to the metal recovery step.

Often, in tests conducted in the laboratory autoclave model, it was noticed that if the leach liquor were allowed to set in the vessel at the end of the test, or was in contact with the ferric oxide slimes for a fairly long duration, sulfuric acid would dissolve the ferric oxide and form ferric sulfate in the leach liquor.

If, in the commercial production of a ferric sulfate lixiviant, a solution of high ferric sulfate content were desired instead of a solution of high acid content, slow settling of the ferric oxide residue at a somewhat elevated temperature would promote the reversion of sulfuric acid to ferric sulfate.

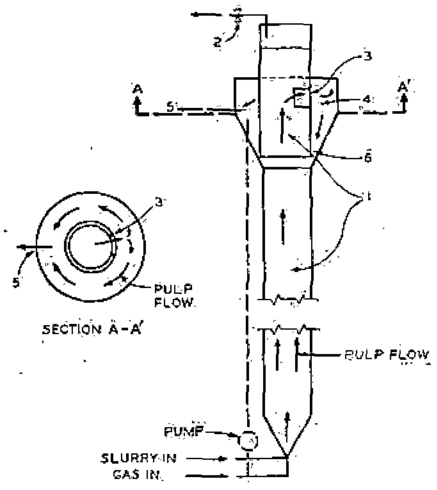
SUMMARY

Thus, in this process, compressed air is used to oxidize and hydrolyze pyrite and/or spent ferrous and ferric sulfate leach liquors to relatively strong solutions of sulfuric acid and/or ferric sulfate. The reactions, shown in Eq. 1 and Eq. 2, proceeded at reasonable rates in an air-stirred autoclave at temperatures above 140°C, at high pulp densities and, at air pressures above 200 psig. Under the same test conditions, and at the same time as these oxidation reactions, some (depending on temperature) of the ferric sulfate present was quickly hydrolyzed to sulfuric acid, as shown in Eq. 4.

The reverse of this reaction was shown to occur at atmospheric pressures and below-boiling temperatures. This reaction could be used to reconvert acid to ferric sulfate. Solutions with up to 12% sulfuric acid and/or 6% ferric iron were produced by this generation-regeneration process.

A similarity may be noted in the chemistry of pyrite oxidation in an air-stirred autoclave to that in a horizontal, impeller-stirred autoclave. The principal difference in the equipment, however, is that a single small, air-stirred vessel of the type described in this article would do the same job as numerous larger, conventional autoclaves in series arrangement. In this application, the new vessel design should be much less expensive and more efficient. •

—A Vertical, Gas-Agitated Autoclave—



Simplified diagram of autoclave. Note cone-shaped classifier compartment.

The accompanying drawing shows a new vertical, gas-agitated autoclave* in its simplest form. The long and relatively narrow chamber (1) represents the reaction zone where a bed of solids is agitated by a liquid-gas fluidization action. Gas, liquids and solids are pumped into the base of this zone and move upward in the chamber at different rates. In moving through the system, the gas agitates, helps to fluidize the solid bed and chemically reacts with the slurry. It leaves the system via a restriction valve at the top of the vessel at an outflow pressure somewhat less than its inflow pressure.

Liquids and solids move upward under conditions of violent agitation in the reaction zone to the vicinity of the window (3) leading to the internal classifier (4). In this cone-shaped compartment surrounding the reaction zone, slurry moves circumferentially from the entrance window (3) to a discharge port (5) where the leach liquid and selected solids leave the system. Most of the solids entering the internal classifier settle on the conical walls and then re-enter the reaction zone via the openings at the base of the internal classifier (6).

The most important features of the autoclave, with respect to its design, are the internal classifier, the reaction zone, the solution recirculation system and the injection ports located at the base of the reaction zone column.

The internal classifier has several purposes:

1) It serves to hold the contents of the reaction zone at a high pulp density (plus 55%) for more efficient chemical reaction;

2) It allows effluent pulp to be drawn from an area adjacent to the reaction zone, reducing frothing problems;

3) It retains solids in the reaction zone until they are fully reacted hence reducing volume and staging requirements;

4) It provides means for obtaining a classified leach liquor for internal recirculation or withdrawal.

The geometry of the reaction zone is dependent on a great number of factors, i.e., the optimum amount of gas required by the chemical reactions and for good agitation; staging; maintenance, construction and cost factors; the pulp volume required at a given pulp density and chemical reaction rate; flow rate of solution through the system.

Given sufficient information about these physical and chemical factors, it should be possible to design a vertical autoclave reaction zone for any given ore.

In any vertical air-agitated autoclave where pulp, or a more dilute recirculated solution, enters the reaction zone at the bottom of the column, it is important that the injection port(s) be of such design as to prevent the backflow of the high density pulp contained in the reaction zone. Pulp backflow would cause plugging of lines and trouble on startup after a shutdown period.

A laboratory vertical, gas-agitated autoclave was of a design which required a recirculation system consisting of a pipe running from the internal classifier to a point some distance below the autoclave proper and then back up to the injection port at the base of the reaction zone. No pump was used. In such a system, the length and diameter of the solution recirculation line, sufficient to cause the proper amount of solution recirculation, would depend on the pressure and temperature of the system, the height of the reaction zone, the density of the pulp in the reaction zone and in the recirculation system, the amount of recirculated solution required to maintain suspension of pulp in the reaction zone, the amount and density of gas passing through the system, and the fluidity of the solution.

A compartmented version of the autoclave, capable of treating 35,000 gal at a high pulp density and at a comparatively low operating cost, could be built at an estimated cost ranging from $140,000 to $190,000.

A significant advantage of this autoclave appears to be its ability to function in a different and more efficient manner. Its inherent ability to retain and react solids at high pulp densities, regardless of the character of the feed slurry and the available gas and liquid flow through the system, would lend to the treatment of the following types of materials:

1) Solids requiring complete dissolution that enter and/or leave the reaction vessel at either very dilute or medium pulp densities;

2) Applications where only limited gas and/or fluid flow is available to cause fluidization and agitation of coarse, dense or low reactable mineral content solids;

3) Flotation concentrates which have a tendency to float in an air-agitated autoclave.

The internal design of the new vertical gas-agitated autoclave has the potential of improving the fluidization and leaching efficiency of autoclaves and, consequently, of broadening their field of application. Underground installation of the vessel could reduce the plant capital investment and operating costs. •

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*Patent applied for

AUTOCLAVE LEACHING OF AURIFEROUS SULFIDE ORE

UDC 669.213.63

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Certain types of resistant auriferous ores cannot be processed by the classic methods of cyanidation and amalgamation because the gold finely dispersed in the sulfides is not sufficiently extracted.

An oxidizing roast is regarded as the most acceptable method of exposing such minerals [1]; a substantial disadvantage of this process is the formation of low-melting mixtures which coat the gold particles and prevent diffusion of the cyanide solution. On the other hand there are inevitable losses of gold in oxidizing roasting because of the considerable amounts of dust that are lost.

Mineralogical analysis of certain auriferous sulfide ores shows that the principal constituent minerals are pyrites, chalcopyrite, pyrrhotite, and (in part) arsenopyrite, in which gold is present in the crystalline lattices of sulfides disseminated in quartz and in the form of complex compounds with silver, tellurium, bismuth, and antimony. The greatest amount of gold is in the structurally free state, in associations in the quartz.

Processing such ores is more efficient when high temperatures and pressures are used.

A study was made of the process of autoclave separation of auriferous sulfide ore from the Koch-Bulak deposit, Uzbek SSR; ammonia solution, giving combined extraction of valuable constituents from the material, was used as the solvent [2-6]. The experiments were conducted in Vishnevskii type titanium autoclaves [7].

Relationship of Gold Extraction from Sulfide Ore to Solvent Composition

Solvent composition, g/l			Degree of Au extraction, %
NH_3	$(NH_4)_2SO_4$	Cu	
50	—	—	56.0
100	—	—	76.0
50	100	—	83.0
100	100	—	89.0
50	100	2.5	93.0
100	50	2.5	90.0

Test conditions; t = 180°C; τ = 5 hrs; liq:sol = 5:1

Chemical Composition, %

	Sample 1	Sample 2
As	Not detected	Not detected
Al_2O_3	9.65	4.29
Fe_2O_3	3.50	23.62
SiO_2	59.46	42.11
CaO	0.84	1.23
Cu	0.22	0.75
Zn	--	0.13
MgO	1.33	1.45
S	9.96	7.03
Na_2O	0.13	0.04
K_2O	3.0	0.96
Other admixtures	8.02	13.36
Σ	96.31	95.07

The experimental results showed that raising the temperature to 175-180° C increased the extent to which gold passed into solution; after this, temperature had no appreciable effect. Maximum gold extraction in these circumstances is 76% irrespective of the initial raw material content of valuable constituent (not more than 56% in the absence of an oxidizing agent).

Published data [3,4] and our own experiments showed that the presence of an oxidizing agent in the leaching of resistant sulfide ores helps to form a stable complex of $Au(S_2O_3)_2{}^{3-}$ type according to the reaction

$$2Au + 4S_2O_3{}^{2-} + H_2O + 1/2\,O_2 = 2Au(S_2O_3)_2{}^{3-} + 2OH^-.$$

The following proved to be the optimum leaching conditions: solvent composition (g/liter) 50 NH_3, 100 $(NH_4)_2SO_4$, 2.5 Cu; liquid-to-solid ratio 5 : 1; partial pressure of O_2 15-20 at; τ = 5-6 hr, size of material 90% -0.074 mm (see Table).

In spite of the high extraction of gold when rich ores are processed, considerable amounts of metal (7-8% Au) remain in the cakes. The causes of underleaching form the subject of further investigations.

CONCLUSIONS

A study was made of the possibility of using autoclave technology to process resistant auriferous sulfide ores. A non-toxic solvent ensuring a high degree of gold extraction into solution was selected, and an optimum leaching routine has been perfected and recommended.

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