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# LEACHING BEHAVIOUR OF COBALTOUS AND COBALTO-COBALTIC OXIDES IN AMMONIA AND IN ACID SOLUTIONS

C.VU*, K.N. HAN and F. LAWSON

*Department of Chemical Engineering, Monash University, Wellington Road, Clayton, Victoria, 3168 (Australia)*

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## ABSTRACT

Vu, C., Han, K.N. and Lawson, F., 1980. Leaching behaviour of cobaltous and cobalto-cobaltic oxides in ammonia and in acid solutions. *Hydrometallurgy*, 6: 75–87.

The dissolution behaviour of cobaltous oxide and cobalto-cobaltic oxide in ammonia and in acid solutions has been investigated. The dissolution reaction for cobaltous oxide was found to be chemically controlled with apparent activation energies of 54.0 kJ $mol^{-1}$ and 56.5 kJ $mol^{-1}$ respectively in ammonia and in acid solutions. The dissolution rate of cobalto-cobaltic oxide in ammonia-ammonium carbonate is very slow at low temperatures. At higher temperatures, the amount of cobalt remaining in solution is low, less than $2 \times 10^{-5}$ mol $dm^{-3}$ at 150°C, due to the precipitation of cobalt carbonate and cobalto-cobaltic oxide.

## INTRODUCTION

It is normal industrial practice to reduce cobalt oxide before attempting to take the cobalt into solution. Generally the reduction is continued until the oxide is converted completely to the metallic state and is carried out with any one of a number of different reducing agents. (For example hydrogen, carbon monoxide, coal or coke may be used.) The subsequent leaching step, is most frequently conducted using solutions of ammonia-ammonium carbonate in the presence of oxidising agents such as pure oxygen or air.

Very little has been published on the direct leaching of metal oxides in ammonia-ammonium carbonate solutions which are widely used as leachants in hydrometallurgy. Amongst those who have reported on ammonia leaching of oxides is Dean (1952) who studied the leaching behaviour of manganous oxide and found that the oxide was converted to manganese carbonate through an intermediate manganese ammine complex. In a further study on the leaching of manganese from low grade ores Welsh and Peterson (1957) reported the

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*Currently with ICI Aust. Ltd., Explosives Factory, Ballarat Road, Deer Park, Vic. 3023, Australia.

results when ammonium carbamate was used as the solvent. Wendt (1953) described the ammonia-ammonium carbonate leaching of low grade zinc ores, while Langston et al. (1957) used ammonium carbonate solutions under pressure in their investigation of uranium extraction from its ores. No data have been reported describing the leaching behaviour of cobalt oxides in ammonia solutions, although the dissolution of cobalt metal in both acid and ammonia solutions has been studied (Han and Lawson, 1974; Vu and Han 1977, 1979). In ammonia solutions under the conditions used in the study, the rate of dissolution of cobalt metal is controlled by the rate of diffusion of oxygen to the metal surface.

The Eh—pH diagram for the ammonia—cobalt—water system at 25°C has been drawn and shown as Fig. 1. The standard free energies of formation of each species are taken from the literature (Pourbaix, 1966; Yatsimirskii and Vasilev, 1960). Similar phase diagrams have been drawn by numerous investigators (Han et al., 1974; Osseo-Asare and Fuerstenau, 1978). From this it is seen that under the correct conditions of pH and oxygen potential, soluble cobalt ammines become the thermodynamic stable species and hence direct leaching of cobalt oxides in ammonia solutions should be possible. (It should be remembered that the Ep—pH diagram is a thermodynamic equilibrium diagram from which nothing can be said about the kinetics of reactions.)

The present paper reports the results of an investigation conducted to determine the leaching behaviour in ammonia and sulphuric acid solutions of cobalt oxides of different oxidation states as such a study could show whether it might be possible to obtain satisfactory cobalt recovery by the direct leaching of oxide ores containing cobalt without a preliminary reduction step.

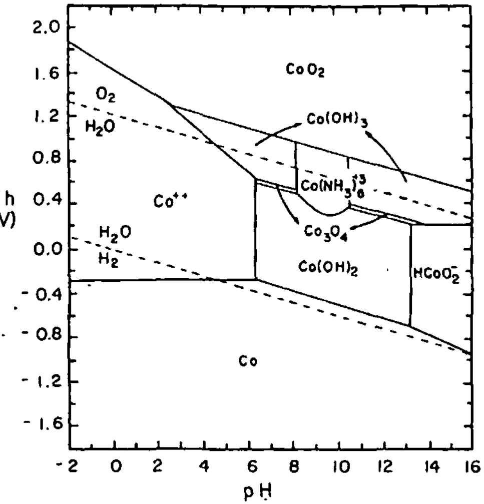

Fig. 1. Potential—pH diagram for the Co—$NH_3$—$H_2O$ system at 25°C and 1 atm total pressure. Activity of total dissolved ammonia species is unity and activity of cobalt ion species is unity.

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## THEORETICAL BACKGROUND

### *Stability of cobaltous and cobalto-cobaltic oxides*

Three cobalt oxides have at various times been reported. The existence of cobaltous oxide, CoO and cobalto-cobaltic oxide, $Co_3O_4$, has been well established; the existence of cobaltic oxide, $Co_2O_3$, is less certain. The equilibrium relationships between cobalt metal and the various cobalt oxides in the presence of oxygen have been reviewed by Gulbransen and Andrew (1951); the kinetics of oxidation of cobalt into cobalt oxides has been studied by many workers including Johns and Baldwin (1949), Gulbransen and Andrew (1951) and Mrowec and Przybylski (1977).

The standard free energies of decomposition of the cobalt oxides have been given by Gulbransen and Andrew (1951) and were used in this study to determine the equilibrium relationships between cobalt metal and the various cobalt oxides as a function of temperature and oxygen pressure. These are shown as Fig. 2.

The stable cobalt species under an oxygen pressure of 0.21 atm., i.e., air, and at temperatures greater than about 900°C is cobaltous oxide, but below this temperature under the same oxygen pressure cobalto-cobaltic oxide is stable. This result is in agreement with that reported by Wood et al. (1965), Morral (1969) and others, all of whom reported that the decomposition of $Co_3O_4$ to CoO occurred in air at about 900°C.

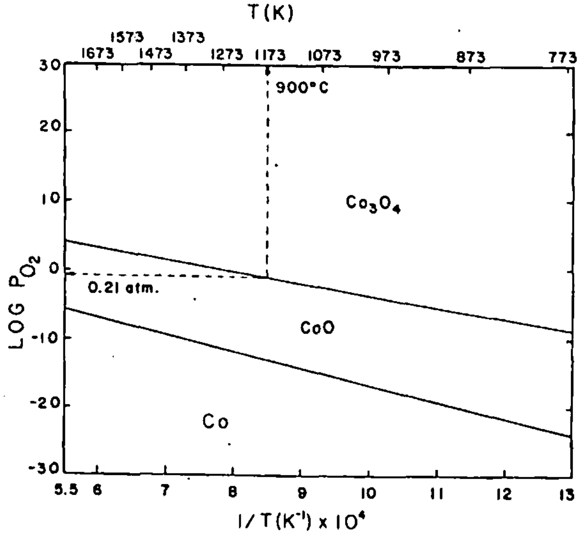

Fig. 2. Thermodynamic stability diagram for the system cobalt-oxygen.

### *Stability of cobalt in ammonia solution in the presence of carbon dioxide*

At room temperature and at atmospheric pressure, the vapour in equilibrium with ammonium carbonate solutions contains only small amounts of ammonia and carbon dioxide. At higher temperatures however the vapour pressures are quite large and cannot be neglected in any analysis. The Eh—pH diagram for the Co—$NH_3$—$H_2O$ system at 25°C in the presence of carbon dioxide is shown as Fig. 3 and should be compared with Fig. 1. Figure 3 shows the equilibrium conditions existing in a cobalt—ammonia—carbon dioxide system in which the activity of the uncomplexed ammonia species is unity, the activity of the total (aquo and ammonia complexed) soluble cobalt species is unity and carbon dioxide is present at a pressure equivalent to the average in dry air (ca. $3.16 \times 10^{-4}$ atm). In the analysis carried out, the only ionic species considered were $Co^{2+}$, $Co(NH_3)^{2+}$, $Co(NH_3)_2{}^{2+}$, $Co(NH_3)_3{}^{2+}$, $Co(NH_3)_4{}^{2+}$, $Co(NH_3)_5{}^{2+}$, $Co(NH_3)_6{}^{2+}$ and $Co(NH_3)_6{}^{3+}$. Carbonate ammine complexes were not considered. It is realised that the accuracy of the stability diagram could have been improved by taking such species into account. However, as far as can be ascertained standard free energy of formation and entropy data are not available for them.

At a pH of about 9.3, the major stable cobalt-bearing species are the cobaltic hexammine complex and solid cobalt carbonate depending on the solution oxidation potential. This is in contrast with the situation which occurs when there is no carbon dioxide present. In the presence of carbon dioxide, cobalt carbonate is thermodynamically more stable than the cobalt oxides.

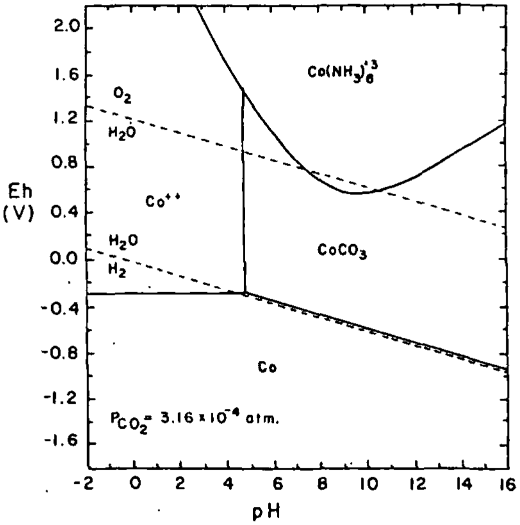

Fig. 3. Potential—pH diagram, for the Co—$NH_3$—$CO_2$—$H_2O$ system at 25°C and 1 atm total pressure. Activity of dissolved ammonia species is unity and activity of cobalt-bearing ionic species is unity.

## EXPERIMENTAL

### *Preparation of reagents*

The cobalt oxides used were all of analytical grade; the cobaltous oxide powders were prepared from cobalto-cobaltic oxide reduced under controlled conditions and freshly prepared before each experiment. If the cobaltous oxide was allowed to remain in contact with air, its leaching behaviour was significnatly modified; it leached more slowly in both ammonia solutions and sulphuric acid. Further the decrease in the rate of dissolution was essentially proportional to the time that the cobaltous oxide was in contact with the air. (As will be shown later, this behaviour is what would be expected if there was surface oxidation with the formation of cobalto-cobaltic oxide, $Co_3O_4$, the thermodynamically stable oxide phase at room temperature in the presence of oxygen at 0.21 atm pressure. This is shown in Fig. 2.) A.R. grade cobalto-cobaltic oxide was used as the source material and the method of preparation used is summarised below:

(i) Cobalto-cobaltic oxide powder contained in a ceramic boat was held for 24 h in a tube furnace set at 900°C and a steady flow of air was maintained through the furnace during this period.

(ii) The reduction product was allowed to cool in the furnace under a high purity nitrogen atmosphere. The nitrogen gas was deoxygenated by passing it slowly through a furnace held at 300°C containing turnings of pure copper. At this temperature, the equilibrium oxygen pressure above $Cu/Cu_2O$ is less than $10^{-20}$ mmHg! The purity of the cobalt-bearing material so formed was checked by X-ray diffraction (XRD) to ensure that the cobalto-cobaltic oxide had all been converted to cobaltous oxide (The colour of cobaltous oxide is a quite distinctive grey compared with the black of the cobalto-cobaltic oxide.) The surface areas of these preparations of the two oxides were measured using a Ströhlein Area Meter and were found to be 2.95 $m^2\,g^{-1}$ for cobaltous oxide and 1.96 $m^2\,g^{-1}$ for cobalto-cobaltic oxide.

A disc with a cobaltous oxide surface was prepared by holding a high purity cobalt metal disc at 900°C for 24 h in air and then cooling it quickly under an inert (oxygen-free nitrogen) atmosphere. The presence of the cobaltous oxide layer was confirmed by XRD analysis.

Leaching solutions were prepared by dissolving A.R. grade ammonium carbonate in distilled water. Immediately before the leach solution was used for an experiment it was saturated with a mixture of oxygen and nitrogen of the appropriate composition.

### *Equipment and experimental method*

For the low temperature experiments, the equipment used was that described previously (Vu and Han, 1977, 1979). Sample weights of cobalt oxide ranging from 0.2 to 1.0 g were used in each test and this was stirred with the ammonia leachant in a thermostatistically controlled vessel. Since the cobalt oxide particles were fully suspended at an impeller speed of 340 rpm, this stirrer speed was used throughout. The oxygen concentration in solution was maintained constant by passing a mixture of oxygen and nitrogen gas continuously through the solution at a rate of about 20 ml $s^{-1}$. Samples of the solution were withdrawn for analysis at regular intervals and the resulting change in volume of the solution was taken into account during the final analysis of the results.

For the high temperature experiments, a series 4500 autoclave manufactured by Parr Instrument Company, U.S.A. was used. This unit consists of a stainless steel pressure vessel fitted with an open top pyrex glass liner. The total actual volume of the vessel is 2000 ml and 1000 ml of solvent, measured at 25°C were used in each test. The stirrer and stirrer shaft are both made from titanium which is not attacked by the solvent under the reaction conditions used.

Each experiment was conducted in a similar fashion and details of the method are summarised below. Cobalt oxide and ammonia solution saturated with oxygen at the concentration required were rapidly heated together in the reaction vessel until the desired temperature was reached after which time the vessel was immediately sealed. No additional gas was introduced into the autoclave so the equilibrium pressure generated was produced by volatile species coming out of solution. When the pressure had stabilized, the stirrer was turned on and when the temperature had stabilised as well, the test was deemed to have commenced. A sample was withdrawn, analysed and taken as representing the initial conditions. All chemical analyses for metal ions were carried out using a Techtron AA5 atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

### *Leaching behaviour of cobaltous oxide in ammonia solutions*

#### *Stirred speed*

The cobaltous oxide disc, 1.91 cm diameter, was leached in solutions containing 0.8 mol $dm^{-3}$ total ammonia at disc rotation speeds from 300 rpm to 1500 rpm. The leaching rate was observed to be independent of the speed of rotation. This indicates that mass transfer plays little part in the rate controlling step at the temperature of the test, namely 25°C.

#### *Temperature*

Cobaltous oxide powder rather than the cobalt oxide disc was used in all studies reported subsequently since a larger reaction surface area was necessary in order to obtain concentrations of cobalt ions in solution high enough to give acceptable analytical accuracy in reasonable times. In no case was more than about 1% of the initially added cobalt oxide dissolved. The results from this series of experiments in which the temperature was varied from 15°C to 45°C are given as Fig. 4. The results show an initial slow rate of dissolution

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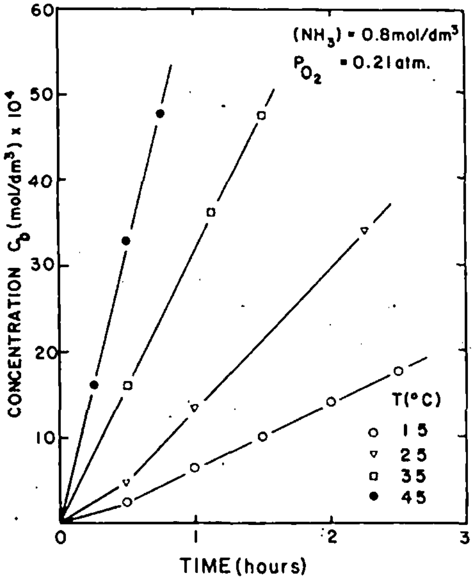

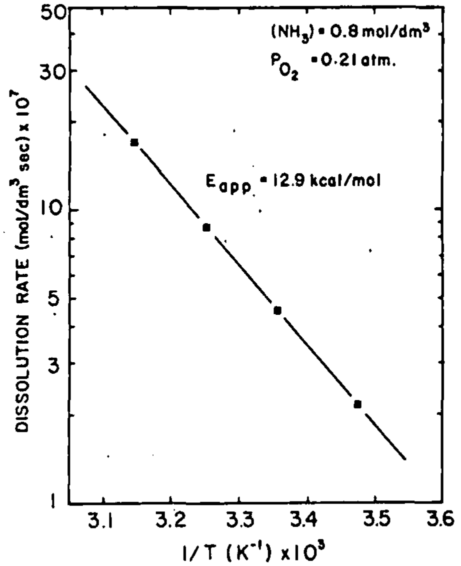

Fig. 4. Bulk concentration of cobalt in solution as a function of time for different leaching temperatures. 1 g of CoO powder used.

Fig. 5. Arrhenius plot for the dissolution rate of cobaltous oxide in ammonia solution. 1 g of CoO powder used.

due most probably to the presence of a thin layer of cobalto-cobaltic oxide covering the surface of the cobaltous oxide. This behaviour is most clearly seen at lower temperatures where the rates of solution are relatively low.

Figure 5 shows the relationship between the reciprocal absolute temperature and the dissolution rate in the constant rate region. The apparent activation energy for the dissolution reaction is 54.0 kJ mol$^{-1}$ (12.9 kcal mol$^{-1}$); an activation energy of this magnitude is indicative of a reaction that is controlled by surface chemical processes. This conclusion is consistent with that drawn from the rotating disc experiments.

*Ammonia concentration*

Solutions were prepared by dissolving AR ammonium carbonate in distilled water to give solvents containing total ammonia concentrations of from 0.08 to 0.8 mol dm$^{-3}$. The results obtained when these solutions were used as the leachant for cobaltous oxide at 25°C and in an air atmosphere are shown as Fig. 6. Under these conditions, the rate of dissolution of cobaltous oxide was directly proportional to the concentration of total ammonia in solution. This behaviour is quite different from that found when cobalt metal was leached (Vu and Han, 1977) and suggests that the mechanism of the dissolution of cobalt metal is quite different from that by which cobaltous oxide goes into solution.

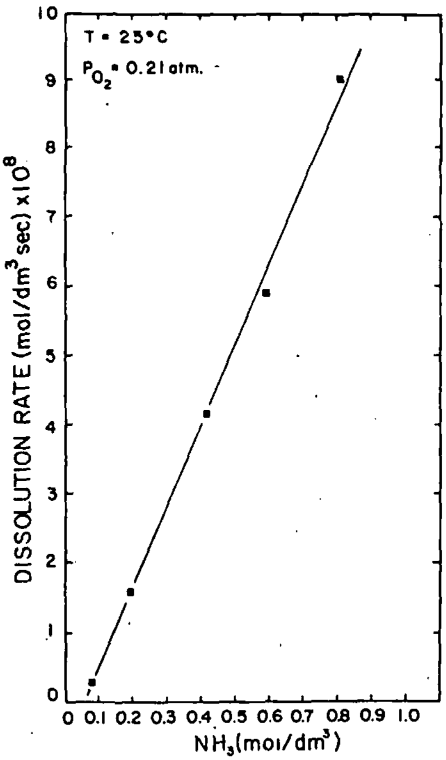

Fig. 6. Effect of ammonia concentration on the dissolution rate of cobaltous oxide powder. 0.2 g of CoO powder used.

### Oxygen concentration

The rates of dissolution of cobaltous oxide powder in a solution containing 0.8 mol dm$^{-3}$ total ammonia but containing different amounts of dissolved oxygen were determined and as expected the rate was found to be essentially independent of the oxygen concentration.

## Leaching behaviour of cobaltous oxide in acids

### Temperature

The results of leaching tests of cobaltous oxide at different temperatures in a sulphuric acid solution of 0.04 mol dm$^{-3}$ are given as Fig. 7. The reaction proceeds much more rapidly in acidic than in ammonia solutions. For a given mass of sample the initial high rates fall relatively quickly as the particle size (and hence the reaction surface area) decreases. Initial rates were used in the construction of the Arrhenius plot shown as Fig. 8. The apparent activation energy for the reaction was 50.5 kJ mol$^{-1}$ (13.5 kcal mol$^{-1}$), which suggests that acid leaching of cobaltous oxide is also controlled by the rate of the surface chemical reaction.

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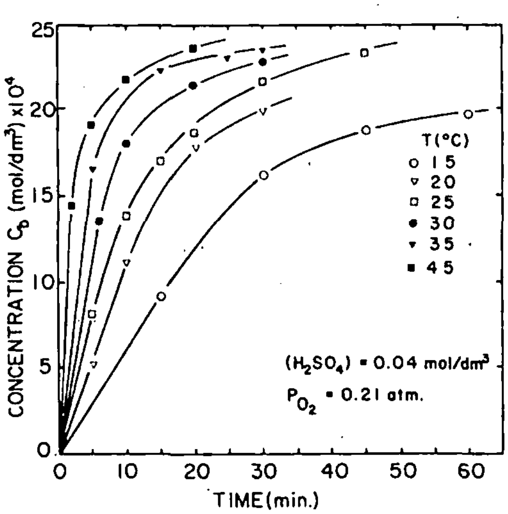

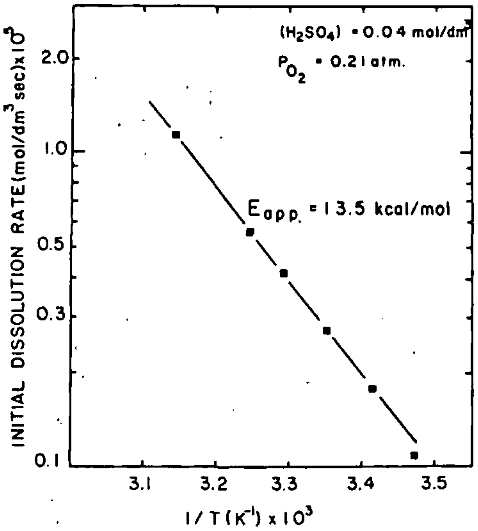

Fig. 7. Bulk concentration of cobalt as a function of time for different temperatures of acid leachant. 0.2 g of CoO powder used.

Fig. 8. Arrhenius plot for the dissolution rate of cobaltous oxide in acidic solution.

*Acid concentration*

A series of experiments was carried out in which cobaltous oxide was leached with different concentrations of sulphuric acid and the results are shown in Fig. 9. These data were statistically fitted using a least squares technique. The gradient was found to be 0.426 with 95% confidence limits of ± 0.040. The initial rate of dissolution then is proportional to acid concentration raised to the power 0.426, thus:

$$(dC_b/dt)_i = k'C_a^{0.426}$$

where $(dC_b/dt)_i$ = the initial rate of dissolution, $C_a$ = sulphuric acid concentration, $k'$ = the apparent rate constant.

### *Leaching behaviour cobalto-cobaltic oxide in ammonia*

The rate of leaching of cobalto-cobaltic oxide, $Co_3O_4$, in ammonia solutions is very slow at low temperatures. In an experiment in which 0.2 g $Co_3O_4$ powder was suspended in a solution containing 0.8 mol dm$^{-3}$ total ammonia for 7 h at 25°C, the concentration of cobalt ammine complexes found was less than 1 ppm! Consequently, all leaching tests conducted with $Co_3O_4$ were carried out at elevated temperatures.

Even at high temperatures, the rate of dissolution is still quite low. One series of experiments was carried out in which 0.2 g of cobalto-cobaltic oxide

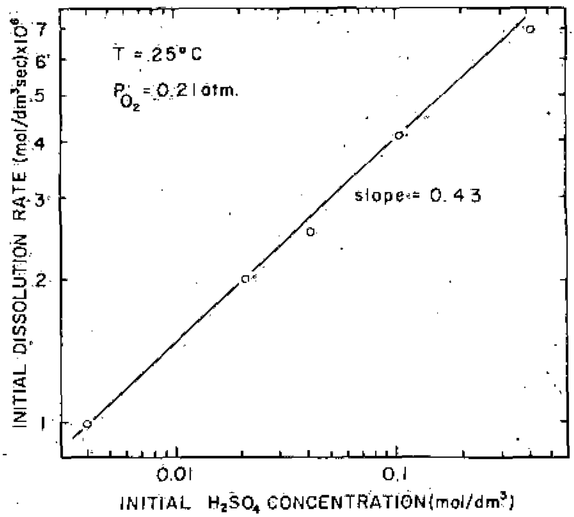

Fig. 9. The dissolution of cobaltous oxide in sulphuric acid.

suspended in a solution containing 0.8 mol $dm^{-3}$ total ammonia was heated to a temperature of 275°C and held at this temperature for several hours. At the end of the period, a sample was taken and the temperature reduced by about 50C degrees and procedures repeated in order to see the effect of temperature on the solubility of cobalt species. The results are shown in Fig. 10a. Another series of experiments was conducted in a manner similar to that described above except that the leachant contained cobalt ammine complexes at an initial concentration of $1.82 \times 10^3$ mol $dm^{-3}$ in addition to ammonia-ammonium carbonate. The results of these tests are shown in Fig. 10b.

It is clear from these two series of experiments that the amount of cobalt in solution depends on the temperature of the ammonia-ammonium carbonate solution and *not* on the concentration of cobalt initially present in solution. At these high temperatures, cobalt ions initially present hydrolyse and precipitate as cobalt carbonate and cobalto-cobaltic oxide. The same general behaviour was observed when solutions of cobalt ammine in ammonia-ammonium carbonate at concentrations in excess of $1.3 \times 10^{-2}$ mol $dm^{-3}$ were held at temperatures greater than 100°C. There is a rapid initial decrease in the cobalt ion concentration but after about 15 h the amount of cobalt in solution became essentially constant and depended only on the temperature, the higher the temperature, the lower the concentration. X-Ray analysis of the residue in all cases showed the presence of cobalt carbonate and cobalto-cobaltic oxide.

This behaviour whereby cobalt carbonate precipitates at elevated temperatures is not unknown as Schaufelberger (1955) described a process in which cobalt in ammonia solution was separated from nickel by heating the solution to 155—170°C in the presence of excess ammonium carbonate.

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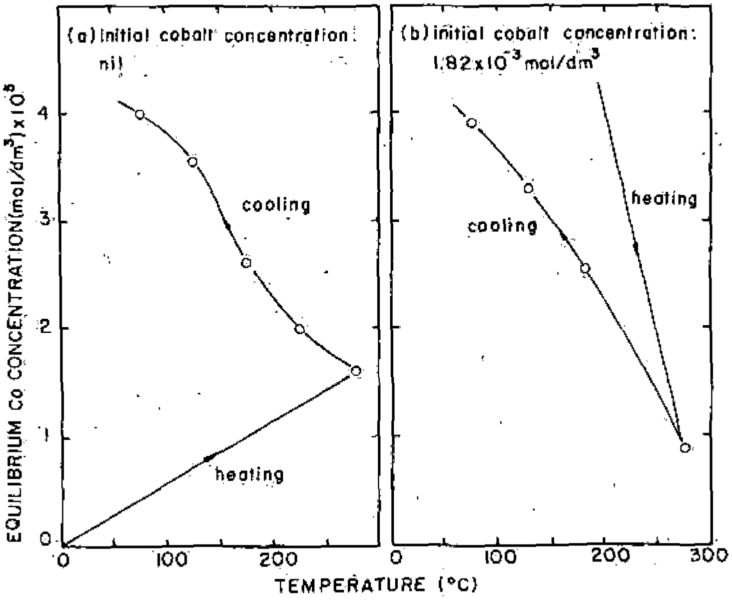

Fig. 10. Variation of cobalt concentration in ammonia-ammonium carbonate solution at elevated temperatures. Total ammonia concentration 0.8 mol dm$^{-3}$, 0.2 g of $Co_3O_4$ used. (a) Initial cobalt concentration — nil, (b) Initial cobalt concentration — 1.82 × 10$^{-3}$ mol dm$^{-3}$.

*Leaching behaviour of cobalto-cobaltic oxide in sulphuric acid*

The rate of dissolution of cobalto-cobaltic oxide in sulphuric acid solution is also very low. Only one milligram of cobalt was taken into solution after one hour at 25°C when one gram of $Co_3O_4$ was agitated with 1000 ml of 0.04 mol dm$^{-3}$ $H_2SO_4$. This behaviour is in direct contrast with that observed when cobaltous oxide is contacted with sulphuric acid.

*Leaching mechanism of cobalt metal, cobaltous oxide and cobalto-cobaltic oxide*

The rates of dissolution of these three substances are quite different, and it is contended that these differences are due to their different chemical structures. For cobalt metal, at temperatures above 500°C, the structure is cubic close-packed but at room temperature it is partly hexagonal (Wells, 1975). Cobaltous oxide has the normal NaCl structure, which has full cubic symmetry only at high temperatures but partly tetragonal at lower temperatures (Wells, 1975). Cobalto-cobaltic oxide has a spinel structure with 32 oxygen atoms and 24 cobalt ions in the unit cell, one third of the cobalt ions being $Co^{2+}$, the remainder $Co^{3+}$.

The mechanism by which cobalt metal dissolves in a leachant in the presence of oxygen is believed to be that an oxygen atom or more likely an oxygen molecule is adsorbed on to the cobalt metal surface and acts as an electron receiver. Under such conditions, the bonding between the oxygen and cobalt is very weak; the breaking of the bonds occurs easily during leaching and hence the metal dissolves fairly quickly. The overall reaction consists of two electrochemical steps which occur at separate and distinct locations on the metal surface. However, the anode and cathode sites can move with the consequence that the attack appears essentially uniform over the entire metal surface.

The bonding between oxygen and cobalt entities in both cobalt oxides is chemical and hence in comparison very strong. The breaking of these bonds requires significantly more energy and as a result, the rates of dissolution of the oxides are lower than the dissolution rate of the metal as evidenced from this study and the previous studies (Vu and Han, 1977). Furthermore the bonding of the oxygen in the cobalto-cobaltic oxide, with a spinel structure, is extremely strong and the rate of dissolution of this oxide is even slower than that of cobaltous oxide in the same solvent. In both of these cases, the dissolution is chemical rather than electrochemical in nature.

Since there is this great difference in rates of leaching, there is little prospect of an economic process being developed in which cobalt oxides are leached directly with either sulphuric acid or ammonia-ammonium carbonate solutions rather than the currently used scheme involving prereduction to the metallic state before leaching.

## CONCLUSIONS

1. The leaching reaction whereby ammonia-ammonium carbonate solutions dissolve cobaltous oxide is chemically controlled with an apparent activation energy of 54.0 kJ $mol^{-1}$ (12.9 kcal $mol^{-1}$).
2. The dissolution rate of cobaltous oxide is directly proportional to total ammonia concentration but is independent of the oxygen concentration.
3. The leaching of cobaltous oxide in sulphuric acid solutions is controlled by the rate of the surface chemical processes with an apparent activation energy of 56.6 kJ $mol^{-1}$ (13.5 kcal $mol^{-1}$).
4. The dissolution rate of cobaltous oxide in sulphuric acid is proportional to acid concentration to the power approximately 0.43.
5. The dissolution rate of cobalto-cobaltic oxide in ammonia-ammonium carbonate solutions is very slow at low temperatures. At higher temperatures, the amount of cobalt remaining in solution is low due principally to the precipitation of cobalt carbonate.
6. The leaching rates of cobalt oxides in both ammonia-ammonium carbonate and sulphuric acid are significantly lower than the equivalent rates observed when cobalt metal was dissolved in aerated leachants. Direct leaching of the oxides therefore does not appear to be economically practicable.

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ACKNOWLEDGEMENTS

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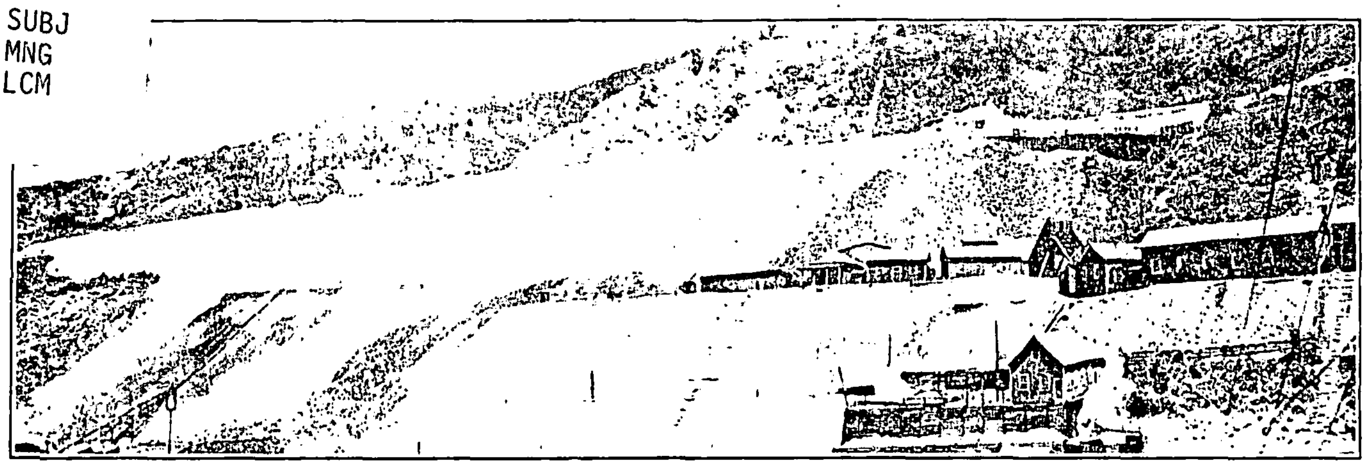

*The surface plant of the Ohio Copper Co.*

*The pump house and pipe line are on the left. Solution is discharged at the top of the embankment in a perforated launder. Headframe of inclined shaft to Mascotte tunnel is shown on right.*

# Leaching a Copper Mine

### *The Ohio Copper Co. Initiates a New Mining Method and Becomes an Exceptionally Low-cost Producer*

**By Felix Edgar Wormser**
Assistant Editor

LET A MAN SUGGEST anything new, untried, or revolutionary, and he will generally promptly be scoffed, criticised, and often ridiculed for his ideas. Samuel K. Kellock and Fred E. Turner, manager and superintendent, respectively, of the Ohio Copper Co., at Bingham, Utah, know that this is so, for they have successfully introduced into mining practice something which a few observers proclaimed visionary—the leaching of caved ore in place.[1] They were informed for one thing, when the subject was first broached, that the solutions would not percolate evenly throughout the orebody but would "channel" through it. They were also told that the action of the solutions would have a tendency to clog the caved area by the formation of talcose substances and would prevent the dissolution of further copper mineral. But none of these dolorous predictions has come to pass. At present the Ohio Copper Co. is producing copper by this unique method at a cost between 6½ and 7½c. per lb., against a cost a few years ago which caused the company to shut down tightly with but small hope of working the property profitably by ordinary methods of mining and milling in a normal copper market.

The most pleasing part of the story to the stockholders and directors of the company must be the fact that the experimental work and the installation of equipment necessary to insure continuous production by leaching was done without recourse to an appeal for funds. Mr. Kellock felt that by selling a few of the ore-dressing machines in the company's large and idle mill at Lark sufficient money could be raised to purchase the pumping equipment and apparatus needed to give the leaching scheme a thorough trial. He was authorized to do so, and with the $15,000 received from the sales bought a moderate-sized pumping plant and minor accessories. The work has been more than self-sustaining ever since.

The Ohio Copper Co. had never been successful in its attempt to work on large-scale regulation methods. The mill at Lark, a few miles away from the mine, failed to come up to expectations after it was built and operated, owing to the difficulties involved in treating the oxidized ores which are such an important part of the Ohio orebody. Extraction was low and costly, and it has been estimated that an 18c. copper market is required before the mill can make a profit. The very impediment of successful milling, however, is an advantage when it comes to leaching, as the oxides are readily soluble in the ordinary water used. Over 300,000 lb. of cement copper is being produced per month, an output that will be probably trebled by the present installation of larger pumping equipment.

The mine itself is on the east side of Bingham Canyon, directly opposite the huge open-pit Utah Copper operations. The surface plant is extremely unpretentious, as can be seen by an inspection of the accompanying photographs. The caved mine area is about 800 ft. long, 900 ft. wide, and 900 ft. deep along the dip. It was formerly worked through an inclined shaft dipping 50 deg. E., 1,400 ft. deep, sunk in the footwall, and connected at the bottom with the main haulage or Mascotte tunnel, through which the ore was trammed by electric motor about 2½ miles to the mill at Lark, on the other side of the Oquirrh range. The shaft has two compartments and is used to handle men and supplies.

Mining engineers will recall that the Ohio Copper mine in its "mining" days was famous for the unusually low cost of mining with the block-caving system used. The ore was low in grade, carrying about 0.8 per cent copper per ton, so that some cheap large-scale mining method had to be employed. Blocks 100x100 ft.

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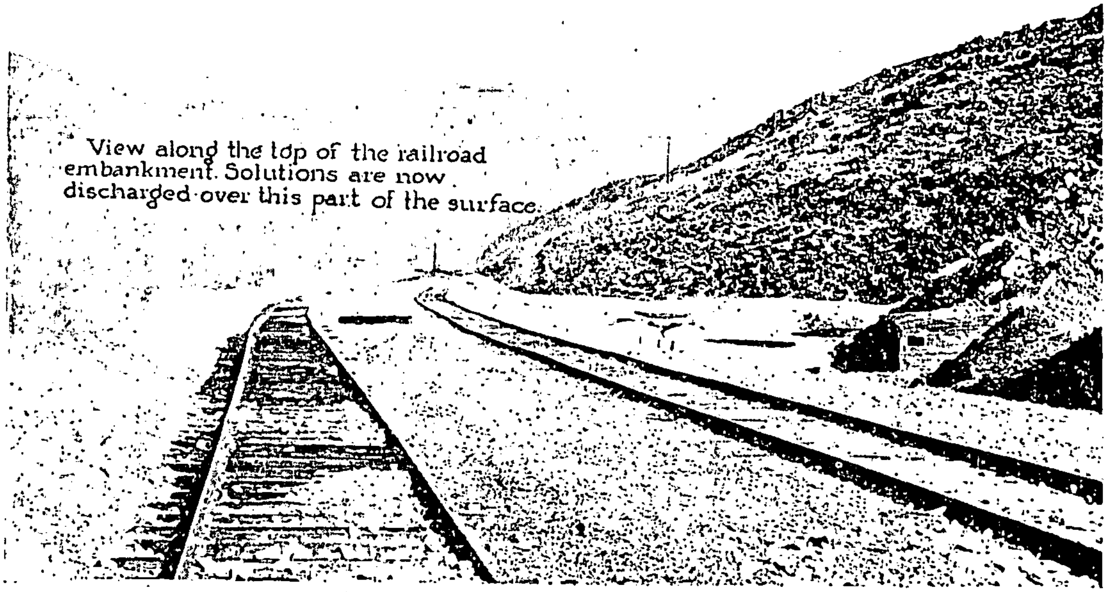
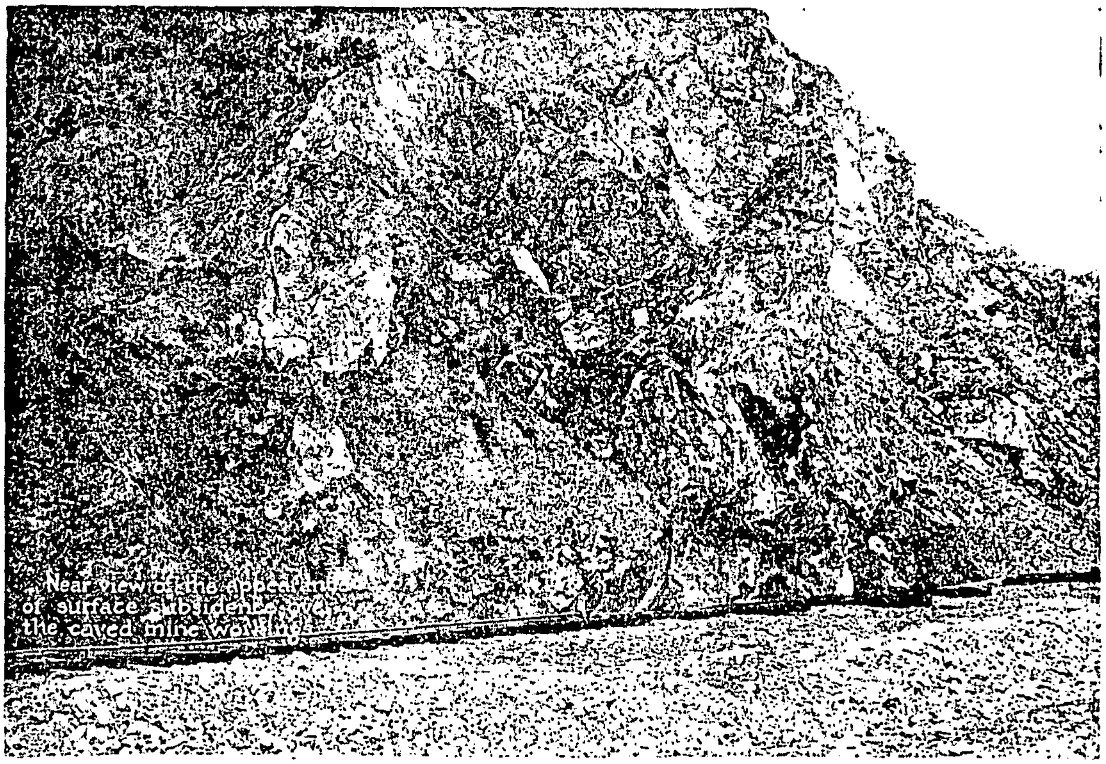
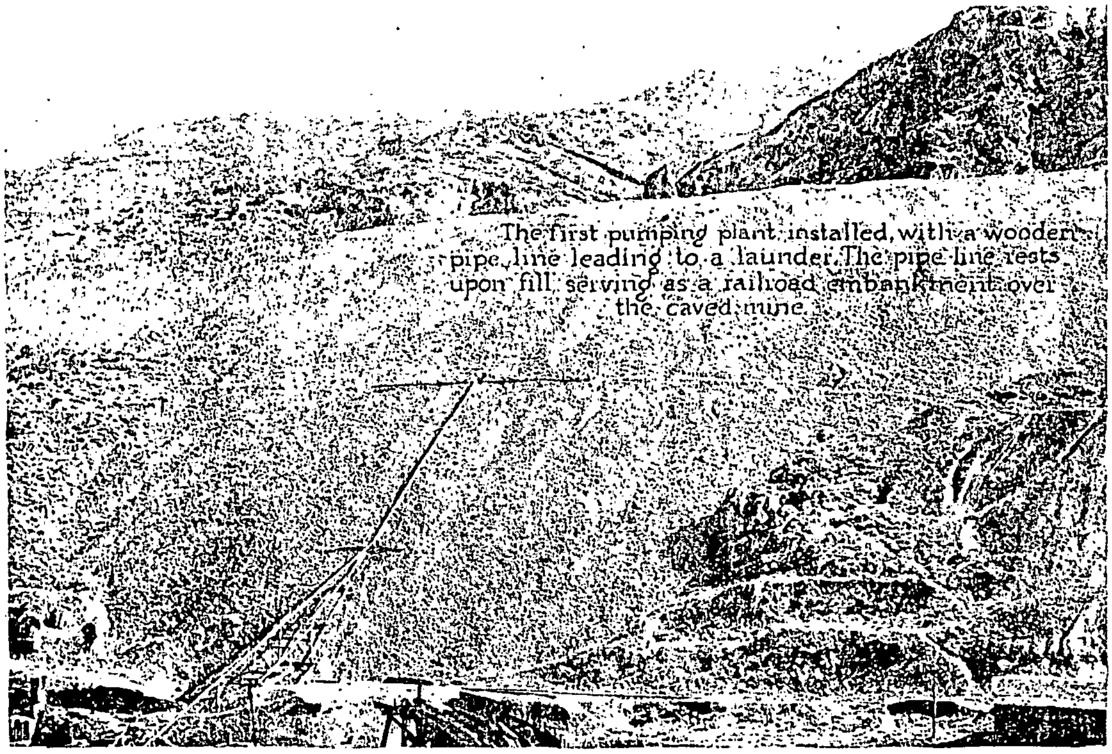
[1] Messrs. Varley and Oldright have also described this operation in a paper delivered before the Utah Metal Mining Institute at Salt Lake City, May 5, 1923, entitled "Leaching of Caved Areas of the Ohio Copper Mine."



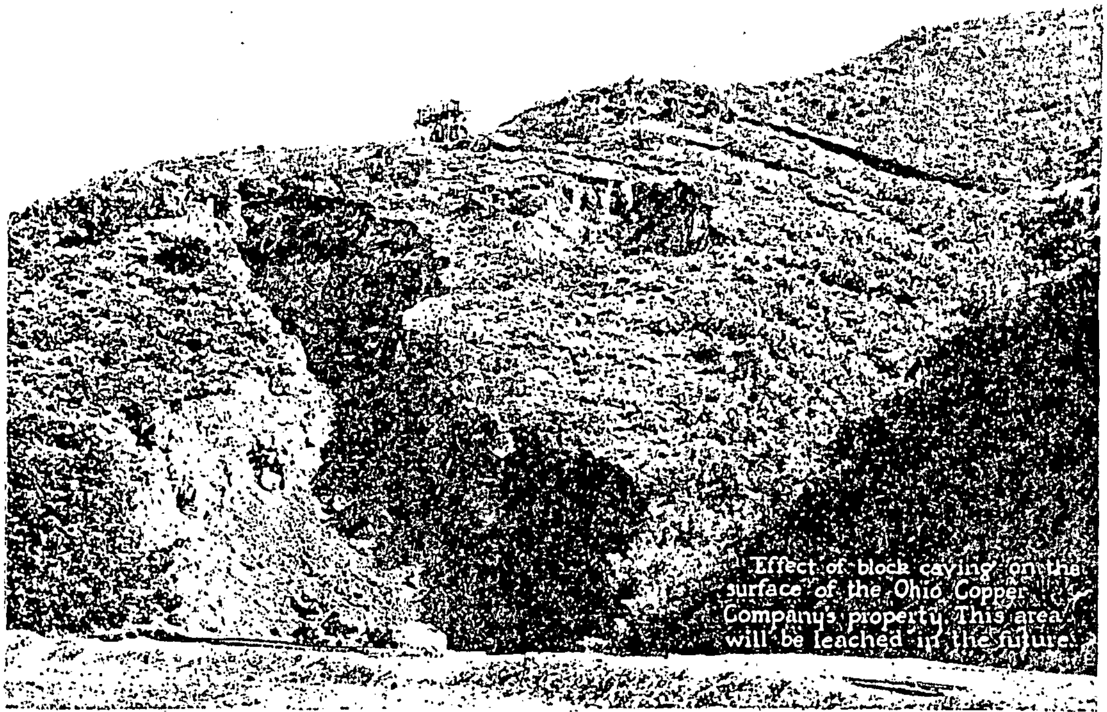
View along the top of the railroad embankment. Solutions are now discharged over this part of the surface.



Near view of the appearance of surface subsidence over the caved mine workings



The first pumping plant installed, with a wooden pipe line leading to a launder. The pipe line rests upon fill, serving as a railroad embankment over the caved mine

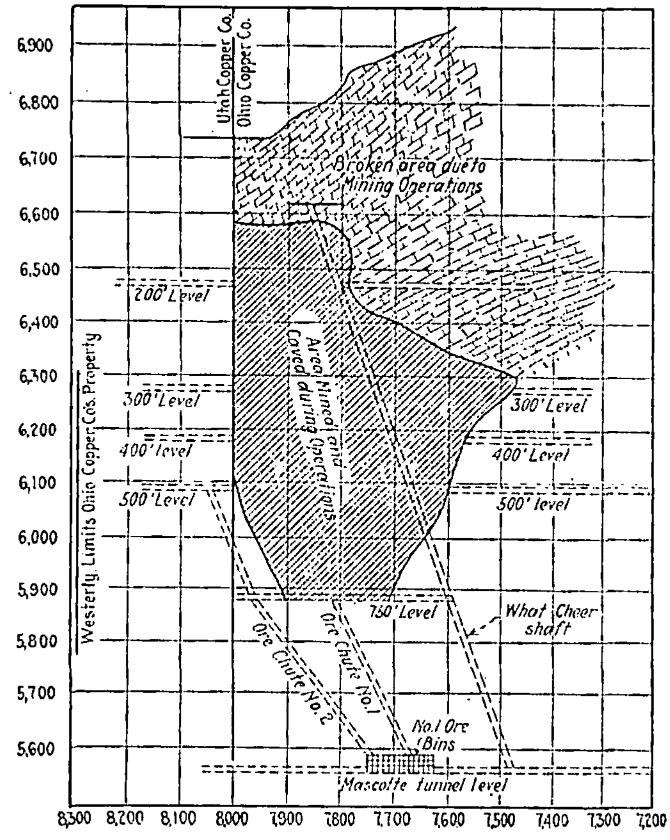


Effect of block caving on the surface of the Ohio Copper Company's property. This area will be leached in the future square and 60 ft. high were caved, and although the preliminary work generally consumed several months, mining of these blocks cost only about 22c. per ton before the war. The underground work naturally had its effect upon the surface, which subsided and caved, giving it the appearance shown in accompanying plates. The broken ore in the caved areas was drawn through raises to ore bins on the Mascotte tunnel level and hauled to the mill. These raises are excellent passageways for the solutions which now leach the caved mine workings.

## OXIDATION OF SULPHIDES TO SULPHATES

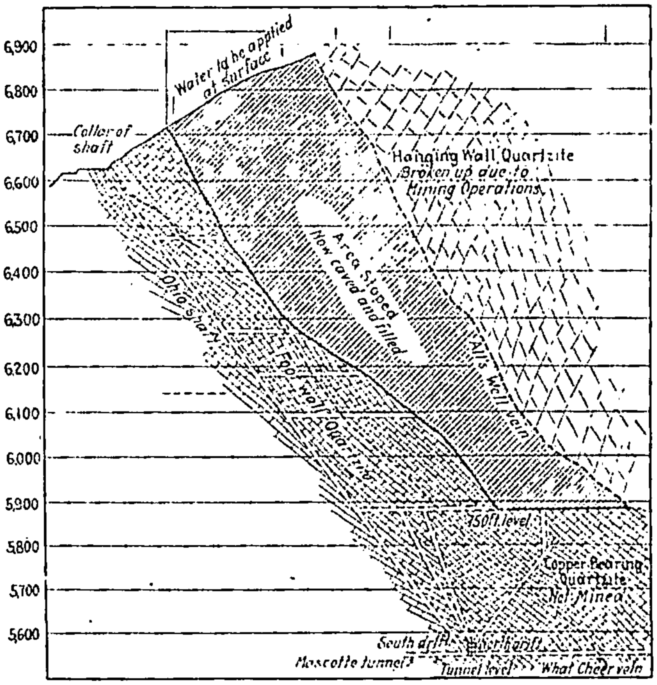
The orebody is a mineralized quartzite and quartz monzonite carrying oxidized copper minerals, chalcocite, and pyrite. The monzonite is considered to have intruded a bed of sandstones, altering them to quartzite. The richest parts of the deposit are found along the contact of the quartzite and monzonite. Both hanging wall and footwall are in quartzite, which is practically impervious to the solutions used and is ideally suited to prevent loss of solution through dissipation in the walls. The hanging wall is shattered from the caving that took place, whereas the footwall is unbroken. Caved sections are now difficult of access, but those mine workings which can be reached from the main shaft show strikingly the effect of oxidation on the copper minerals in the ore.

Surfaces of drifts and crosscuts in the orebody a few hundred feet from the shaft are covered with a fine lattice work of pale blue and green veinlets of oxidized copper ore. The air in these drifts is warm but not uncomfortably so. It readily circulates in the caved areas, rising from the tunnel level below to the surface and facilitating oxidation. If the surface appearance of these drifts is any indication of the condition of the caved stopes, they must be in an admirable condition for leaching. Oxidation of the ore is also aided by the presence of pyrite, which probably accounts for most of the heat in the drifts.



*East and west geological section—looking north*

*Precipitation boxes extend east along the Mascotte tunnel. Most*



*North and south geological section*

*Note the raises from Mascotte tunnel leading to caved stopes.*

The copper content of the ore is widely variable. The management estimate that reserves are about 38,000,000 tons of 0.3 per cent ore.

It was with considerable trepidation and interest that Kellock and Turner watched the progress of their experimental work in the fall of 1922. They first installed a 4-in. centrifugal pump driven by a 60 hp. electric motor, and laid a wooden pipe extending from it up the side of the canyon and over the caved surface for 150 ft., where a launder was built, in which the pipe line could discharge about 300 to 400 gal. per minute. Page 667 gives a view of the original installation and shows the pipe line extending halfway up the hill which covers a goodly part of the caved surface of the property. The dark, stained appearance of the surface is due to the discoloring and oxidizing matter in the water used for leaching purposes and shows the exact location of the original points of application.

In the meantime preparation was made to catch any solution which might percolate through the mine in a series of precipitation boxes filled with old iron junk. As only a few raises extended from the main haulage level to the caved stopes, it was felt that the enriched solution would have to emerge at these raises, and the boxes were therefore placed close to them. After the stage had been well set, common ditch water was pumped from Bingham Canyon at the rate of 300 gal. per minute to the launder, where it was distributed over the surface and quickly disappeared from view. The water was a rusty, cloudy brown, coming mainly from mine workings farther up the canyon. It contained no acid, and no outside reagent was added to it.

The effect of the experiment was anxiously watched, and it was only after about forty-eight hours of intermittent observation at the raises on the Mascotte tunnel level that the vigil was rewarded. At that time a stream of slightly clouded water began to issue from the raise, but it changed to a clear, deep, coppery blue after a short time. This was most encouraging, and steps were immediately taken to enlarge the precipitating plant and the scope of the experimentation. It was necessary to widen the Mascotte tunnel to make room for the precipitation boxes along each wall and leave space for a haulageway in between. By placing the boxes in the tunnel near the bottom of the shaft a working place is provided that is cool in summer and warm in winter, giving a more uniform temperature than could be obtained with an outdoor installation.

The boxes were built in ten sections of 320 ft. each. They are made of 2-in. planks 32½x32½-in. in cross-section by 16 ft. long, and are placed end for end in the tunnel in two rows along the walls. By-passes are furnished to permit the solution to be transferred from one row of boxes to that opposite, to facilitate dressing or repairing any particular section. Each box has a false bottom, consisting of a light, sturdy lattice-work which is nothing more than a series of ½-in. strips ¼ in. apart, on top of which another series of strips is placed at right angles ⅜ in. apart. This false bottom rests upon cleats 16 in. above the bottom of the box. Trouble was experienced for a time with leakage of solution from the precipitation boxes. This was remedied by "guniting" the interiors, which checked the leakage and increased production.

Loosely baled detinned scrap from Pacific Coast plants is used as a precipitating medium. It costs $20 per ton delivered, and although more expensive than the iron junk which might otherwise be used, is far more satisfactory, being easier to handle and more uniform in size and composition. It has been found that the first four sections of the precipitating plant make 50 per cent of the cement copper and that about 1 lb. of scrap is required for every pound of copper produced. The solution carries about 4.6 lb. of copper per ton, of which from 90 to 97 per cent is precipitated.

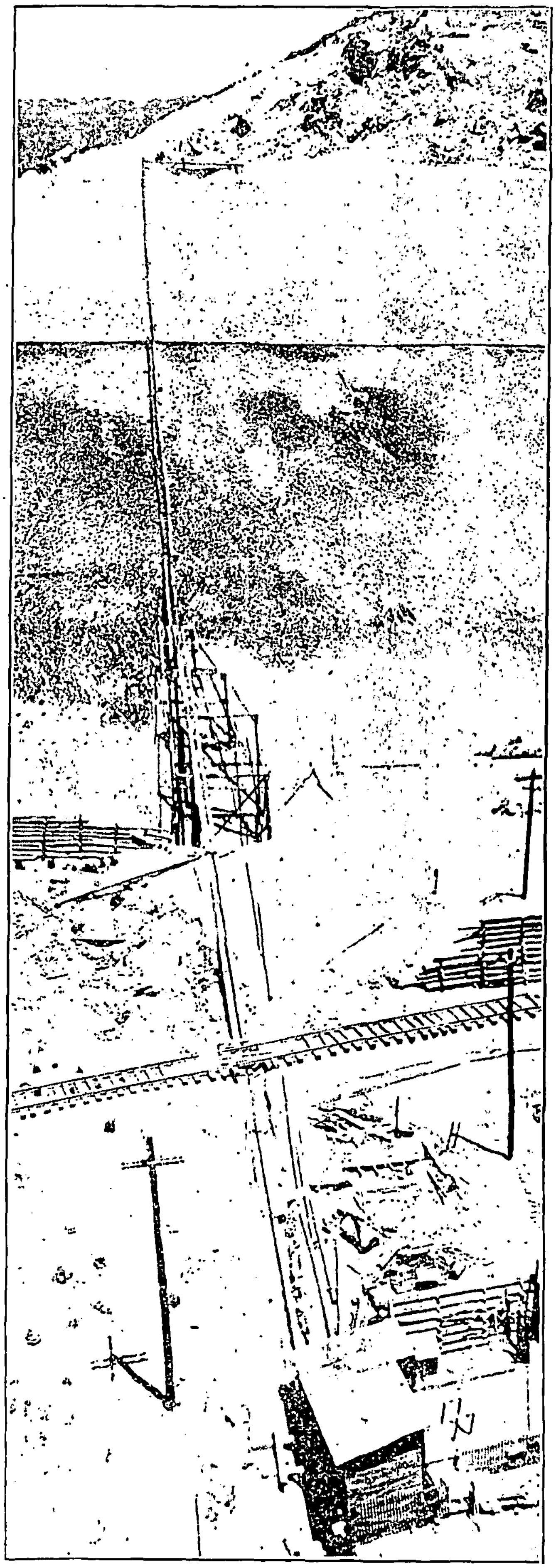
The high-grade cement copper produced assays between 90 and 94 per cent copper. Boxes were formerly dressed twice a week, but will be dressed every day when the new pumping plant is completed and operating. The copper is shoveled into mine cars and shipped to Garfield for smelting. The chief and only difficulty in precipitation is the tendency for the copper to adhere to the scrap. Efforts are being made to correct this trouble, which may arise from a number of causes, such as the presence of impurities, acid, or organic matter. In the initial stages of the work the water from the last boxes was allowed to go to waste, but owing to the dearth of adequate water supplies, it is planned to recirculate this solution, together with other water drained from the mine, and to leach with it again.

To present data as to the cost of operations, the following average financial results for the first five months of the year 1923 are given:

| | Cents Per Pound |
|---|---|
| Operating cost, office expenses and supplies, etc.. | 4.341 |
| Smelting and selling ........................ | 2.943 |
| Total ........................................ | 7.284 |
| Received for copper ........................ | 15.33 |

The operating profit up to July since the beginning of leaching operations is close to $100,000.

To increase production, which had been running around 300,000 lb. per month, it was decided to increase the volume of solution used for leaching to over three times its earlier quantity, or from a rate of 400 to a



*The original pump house and pipe line*

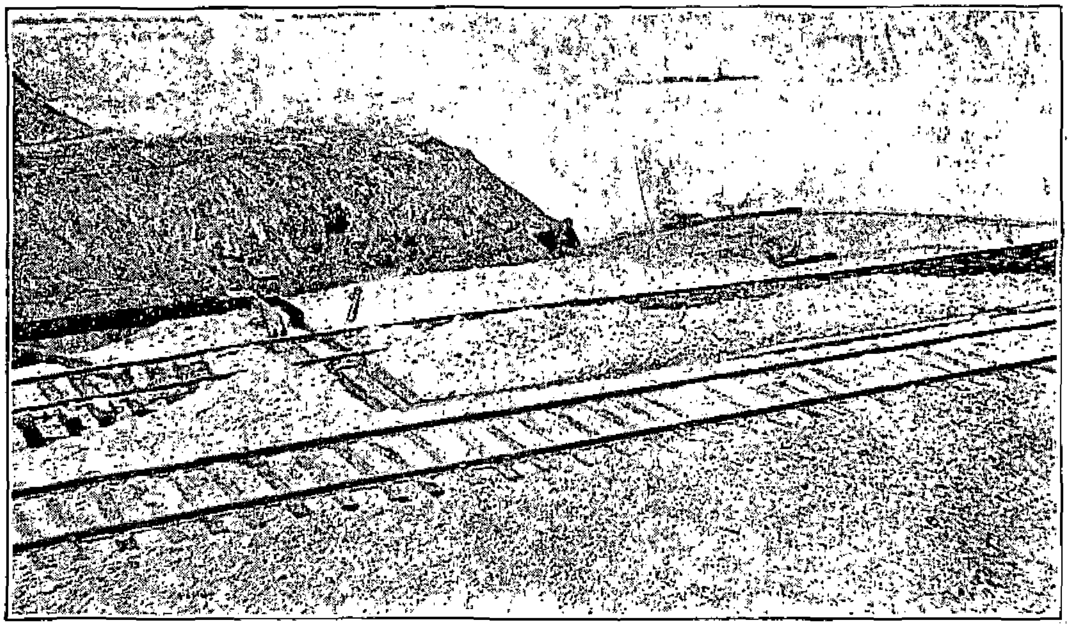
*Another unit has been erected in the Ohio shaft. Note the stained surface areas. They mark the places over which the solution was first allowed to percolate from the first launder used.*

rate of 1,500 gal. per minute. Water is none too plentiful in Bingham Canyon or on the property of the Ohio Copper Co. All of it available is carefully husbanded. A plant has been erected in the main shaft, capable of pumping all the water drained in the Mascotte tunnel, including that from the precipitation boxes, by stages to the surface. Four centrifugal pumps are being installed on the 100, 400, 750, and Mascotte tunnel levels, respectively. With the exception of the tunnel level pump, which is a two-stage machine, all the pumps are single-stage units, each with a capacity of 1,500 gal. per minute. Each one is partly constructed of acid-resisting bronze. A "booster" unit has also been installed, 500 ft. distant from the main pump on the tunnel level, to assist in furnishing it with solution from the last precipitation boxes.

Early experimentation showed that when the point of application of solution to caved area was moved only six feet the volume discharged into the precipitation boxes decreased for about thirty-six to forty-eight hours, until the solution from the new point of application arrived. Then it increased again. This would indicate that the tendency to "channel," which some critics thought would be a possible objection to the method, is not a source of trouble.

To date only a fraction of the mine has been treated. The accompanying photographs show the stained sections where the solution has been allowed to percolate over the surface and give an idea of the ground that remains to be treated. Careful computation of the surface of the caved area shows that it contains approximately 840,000 sq.ft. In the operations of the company up to July 31 about 1,000 sq.ft. of this surface had been covered, which leaves a large area still untreated.

The results that have been achieved were accomplished entirely with the poor quality of water available in Bingham Canyon. Some day, perhaps, acid will be added to increase dissolution, but no expense for chemicals has yet been found necessary. The present procedure is to treat a certain area of the mine, and then to abandon that portion temporarily while another section is being treated. This is done for the purpose of permitting further oxidation in the leached area. After which it is planned to return to the first section and re-leach it. The treatment of original ore in place will also receive attention at some future time.



*The top of the embankment*

*Water from the canyon below is discharging into the distribution launder. Utah Copper mine in background.*

## Comparative Advantages of Zinc-smelting Methods

Conditions being equal, the electrothermic process for the smelting of zinc may be said to have the advantage over the electrolytic process in the items of power, labor, metal recovery, cost of roasting, first cost of plant, and in its adaptability to smaller scale operations, according to B. M. O'Harra, associate metallurgist of the U. S. Bureau of Mines, who is studying the electrothermic metallurgy of zinc under a co-operative agreement between the Bureau and the Missouri process is superior to the retort process in the items of reduction, fuel, labor, metal recovery, ability to treat low-grade and impure ores, cost of roasting, first cost of plant construction and the cost of retorts and condensers.

The electrothermic smelter must be near cheap power, as must also the electrolytic, but as many retort smelters are now some distance from their supply of ore this is no great difficulty. Each of the three processes —retort, electrolytic, and electrothermic—has its particular field and there are undoubtedly places in this country where the electrothermic process could be

METALLURGY

# LEACHING CONVERTER MATTE WITH AN ACID, NICKEL-CONTAINING SULFATE-CHLORIDE SOLUTION

UDC 669.243.82

L. A. Sinev and S. A. Vilenchik

When copper-nickel converter matte is leached with a mixture of sulfuric and hydrochloric acids, a solution is obtained which contains 50 g/l Ni, 2-equiv/lit each of the chlorine and sulfate-ion, and 2.3 g-equiv/lit of free acid.

It is inadvisable to direct that kind of solution to conventional purification and separation processes since it leads to a high consumption of reagents. The most efficient method of processing the excess free acid is to use this solution to leach fresh converter matte while simultaneously blowing the pulp with air.

In order to intensify the mixing process in the tests, a vessel was used which was equipped with a diffuser having split partitions in the circular area. For the leaching operation, use was made of a sample of factory converter matte (0.06 mm in size), containing (in %): 39.15 Ni, 37.86 Cu, 0.91 Co, 2.87 Fe, and 18.5 S. The test conditions were as follows: batch of converter matte 20 g, liq:sol ratio of 3:1-6:1, a temperature of 60-90°C, air consumption of 7 lit/min, and a mixer rotation rate of 500-4000 rpm.

It was established that an increase in the blast will most substantially accelerate nickel dissolution during the 1st 1--1.5 hours of leaching. A 30°C temperature increase (from 60 to 90°C) accelerates the leaching process by 35-50%, which -- according to the Van't Hoff law -- corresponds to the diffusion process.

In this connection, a series of tests was organized in which the number of mixer revolutions varied from 500 to 4000 rpm. Simultaneously, in order to intensify the effect of the mutual particle collisions, the liq:sol ratio was changed to 1:1 in the entire series. Test results (Fig. 1) showed that a perceptible acceleration in dissolution was noted only where the number of mixer revolutions increased to 2,000 rpm. A further increase in the rate of mixer revolution is inadvisable in practice.

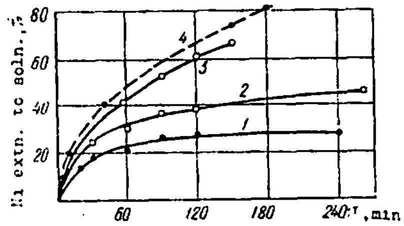


Fig. 1. Effect of mixing intensity on the dynamics of nickel passage into solution, at n (rpm):
1 - 500; 2 - 1000; 3 - 2000; 4 - 4000.

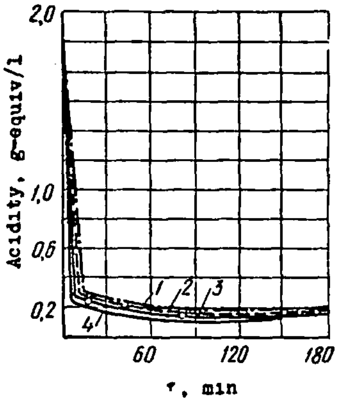
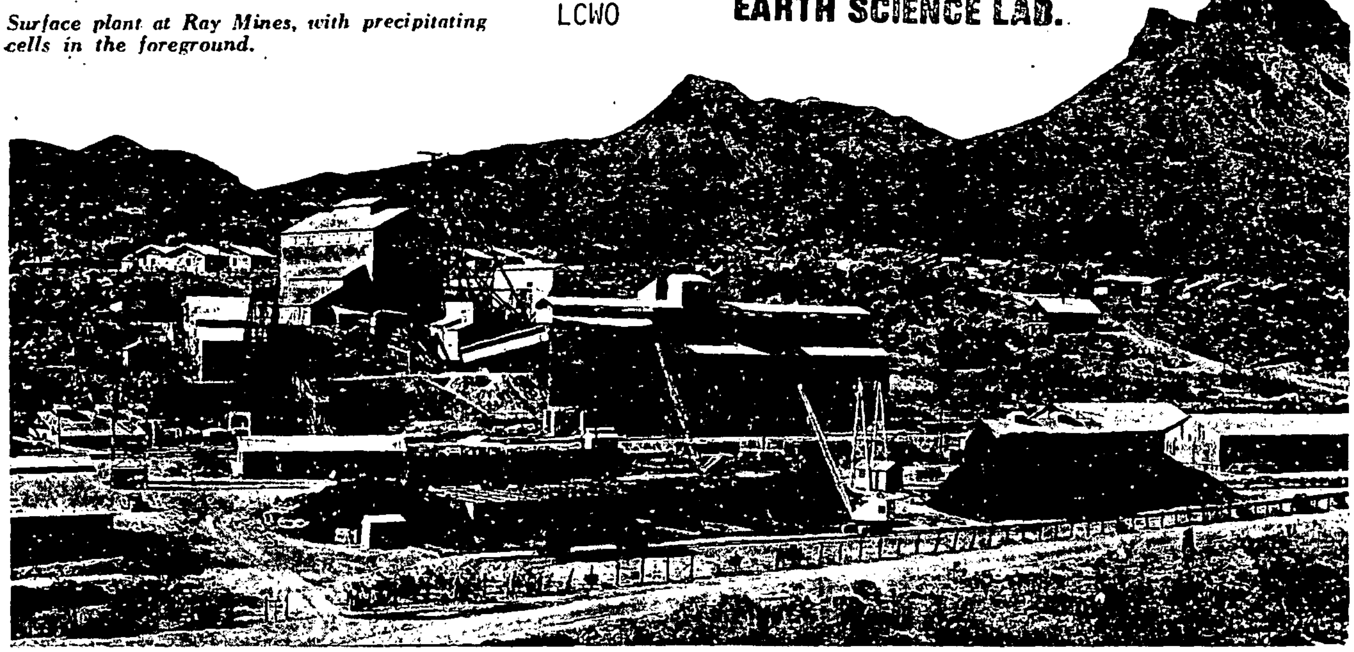


Fig. 2. Dynamics of acid consumption during leaching when employing air blowing, at temperatures (°C): 1 - 60; 2 - 70; 3 - 80; 4 - 90.

The effect of the original acidity was studied within a range of 1-4 g-equiv/lit of free acid, where the molar ratio for the sulfuric and hydrochloric acids was 1:1. As was expected, the greatest extraction of nickel to solution is noted at higher acidity, and the increase in nickel recovery was proportional to the increase in free acidity for the solution. It was found that an increase in l:s ratio from 3:1 to 6:1 will increase nickel extraction to solution, since there is also an increase in free acid required for the unit weight of the charged converter matte.

The following series of tests was conducted to study the dynamics of acid consumption during leaching. Results, shown in Fig. 2, indicate that most of the nickel dissolves in the first 10-15 min. It should be noted that leaching fresh converter matte with the obtained acid solution makes possible a drop of free acid in the obtained solution to 0.17-0.15 g-equiv/lit. Thus, research showed that the excess acidity of the starting solution can be reduced by leaching fresh, fine-ground converter matte during intensive mixing and simultaneous air-blowing the pulp at 900°C; the optimum l:s ratio is (4-5):1. To avoid copper passage to solution, neutralization should be aimed at an Ni extraction 50% of its amount in the charged converter matte. Leaching should be performed at a maximum air feed to the pulp, permitting a lower operating period.

When the original solution contains 50-60 g/l of nickel, the final solution will contain (g/l): 100-120 Ni, 2.2-2.6 Co, 6.2-8 Fe, and 0.03-0.01 Cu with 0.15-0.17 g-equiv/lit of free acid. The leaching residue is used to produce a starting acid solution.



*Surface plant at Ray Mines, with precipitating cells in the foreground.*

# Leaching Copper from Worked-Out Areas of the Ray Mines, Arizona

By Robert W. Thomas
General Manager, Ray Mines Division, Kennecott Copper Corp.; Member, A.I.M.E.

LEACHING of mined-out areas at the Arizona property of the Ray Mines Division, Kennecott Copper Corp., was started on Jan. 20, 1937, and by July 1, 1938, 10,000,000 lb. of copper had been produced by this method. Leaching operations at present are confined to the western portion of the ore body and over an area of approximately ten acres. The ore in this area was extremely high in pyrite and the copper content, which averaged slightly in excess of 1 per cent, was the result of incomplete secondary enrichment by solutions which apparently worked laterally from the main ore body. Above the ore was an unaltered zone of primary or protore averaging 125 ft. in thickness and containing approximately 0.6 per cent copper. Above this was the capping or leached zone averaging 50 ft. thick.

That this area would be particularly adaptable to leaching was recognized as early as 1922. Prior to a year's shutdown of the mine in 1921 a section had been prepared in this area for mining on the second level. Upon resumption of operations it was found that the oxidation of this broken ore had been so complete that it was necessary to abandon a considerable tonnage. This oxidation had also extended into the protore zone overlying the ore.

Evidence of the adaptability of this particular area for leaching was confirmed during 1935 and 1936. The mine was again closed down from April 1, 1933, to Jan. 1, 1937. Prior to this shutdown mining operations were again being conducted in this area on the third level, and just before the shutdown a dam and drain tunnel on the surface, installed to divert surface water from the caved ground, had been destroyed. During 1935 and 1936, both wet years, considerable water therefore made its way into the caved area. The copper content of this surface water after percolating through the broken ground averaged about 1 per cent, or the equivalent of 83.3 lb. per thousand gallons of water. At the time of the shutdown in 1933 mining operations within this area on the third level had not been completed and a small tonnage of comparatively low-grade ore still remained to be mined. However, experience gained in 1922 on the second level indicated that this broken ore would have to be abandoned as oxidation would be more complete than before owing to the longer shutdown period.

No further mining operations were contemplated at a lower horizon, so leaching was considered. An estimate was made of the copper content of the ore abandoned in this area on the second and third mining levels. This, plus the indicated copper in the primary or protore zone above the ore, indicated that the ground amenable to leaching contained over 50,000,000 lb. of copper. The probable extraction was unknown but it was felt that even with mediocre results the copper recovery would be sufficient to warrant the construction of a new precipitating plant together with such other expenditures as might be required.

To prepare this area for leaching entailed considerable work underground. Drainage drifts had to be driven and concrete dams installed in the various underground tunnels to prevent the flow of the solution into active

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A paper prepared for the Regional Meeting of the A.I.M.E., Tucson, Ariz., Nov. 1-5, 1938.

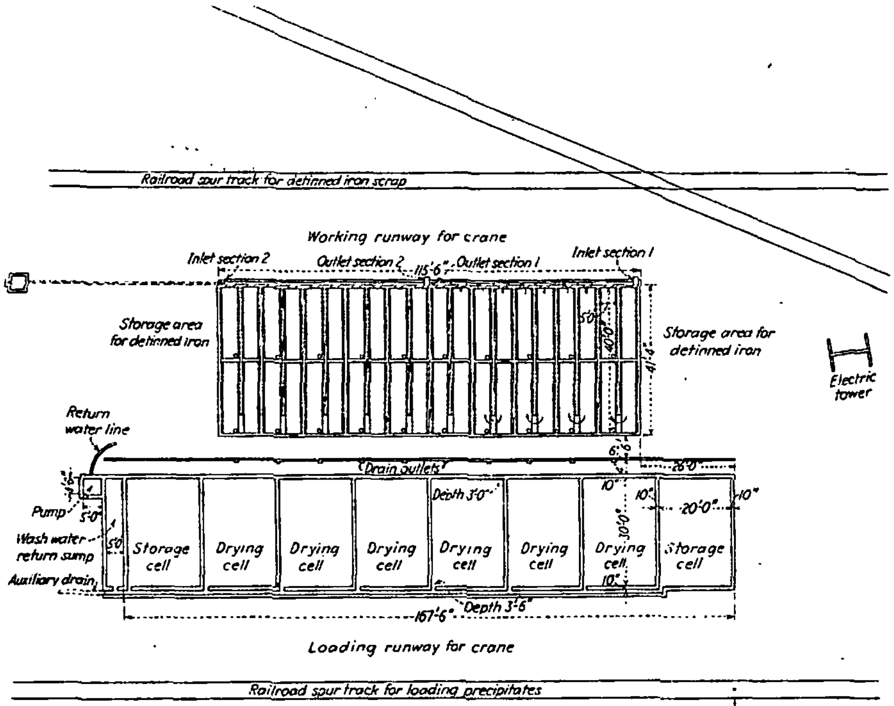


*Fig. 1. General plan of the precipitating plant.*

mining areas on the fourth level. It was also necessary to install on the third level a concrete ditch having a capacity of 500 g.p.m., together with the necessary pump station and pumps for handling the water.

Underground pumping equipment consists of two centrifugal pumps made of Duraloy, each having a capacity of about 325 g.p.m., with a combined capacity for both pumps of approximately 500 g.p.m. The pump suctions are submerged and the entire operation is automatically controlled. Water is conveyed from the mine to the precipitating plant on the surface through an 8-in. lead-lined pipe.

Water is pumped to the caved ground by a four-stage automatically controlled centrifugal pump, with a capacity of 340 g.p.m. This supply can be increased to 500 g.p.m. by the addition of another pump when water in this quantity is available. The water was originally distributed in the caved area through a system of pipe lines equipped with rotating sprinklers to effect a uniform distribution, but shortly after leaching operations were started it became quite evident, from the marked decrease in the copper content of the solution, that channels were being formed in the broken ground. This caused considerable concern, and the sprays were moved to another part of the caved area. Upon returning the sprays to their original location some two months later, the solutions were found again to be normal and remained so until the old, or probably new channels were again established. Therefore a definite program of moving the sprays was put in practice, one area being sprayed until the copper content of the water drops to 0.4 per cent, or approximately 33 lb. per thousand gallons, whereupon the sprays are moved to another location. Thus the caved area can be reworked repeatedly and draining of the broken ground between spraying periods permits the old channels to seal themselves. After about six months of leaching in the above manner a marked settlement of the caved ground occurred, resulting in slides of such magnitude that the pipeline system was destroyed. Since that time leaching has been confined to the use of sprays along the edge, together with a few hose lines into the cave. The pipe system will again be installed when the settling of the caved ground has ceased, as experience indicates that a uniform distribution of the water is most necessary for successful extraction.

Leaching has been done entirely by fresh water so far, which will be continued as long as a satisfactory extraction is obtained, which should be for a considerable time. Oxidation of the pyrite in this particular area should form sufficient ferric sulphate to convert a major portion of the copper. At some future date, however, a leaching agent may be required. Possibly the tailing water from the precipitation plant can be used, taking advantage of the ferric sulphate, formed by the oxidation of the ferrous sulphate, in this solution. Before this water can be used for leaching, however, it must be conditioned, for in oxidizing from ferrous to ferric sulphate a basic iron precipitate having the consistency of an extremely fine clay is formed, which would seal up the interstices in the broken ore, thus preventing the percolation of the solutions. A satisfactory conditioning of the tailing water would also be extremely advantageous as the supply of fresh water is limited, particularly during the summer.

Precipitation of copper from mine waters was not a new venture in practice at the Ray Mines, as precipitating plants had been in use since the inception of mining here. The precipitation of copper by these plants, however, was a minor operation as the normal flow of underground water did not exceed an average of 50 g.p.m., and only contained about 5 lb. of copper. The first precipitating plant consisted of a series of wooden launders in which scrap iron was used as the precipitant. In 1916 these launders were replaced by a series of redwood tanks 8 ft. in diameter and 10 ft. high, the total plant having a capacity of approximately 75,000 gal., or sufficient to handle the normal flow of the mine over a 24-hour period. Pumping operations were conducted once in 24 hours, which made it possible under this system for the mine water to be in contact with the scrap iron for one full day. The plant was satisfactory and proved entirely adequate for the volume of water then available.

In designing the new precipitating plant three major operating steps were considered, namely, handling of the iron precipitant, removal of the cement copper from the precipitating cells, and drying and loading the copper precipitate. Experience indicated that the satisfactory removal of the cement copper from the precipitating cells was the major problem. After visits to various plants it was felt that this particular operation was most satisfactorily handled at the plant of the Utah Copper Co. There the cells are equipped with false bottoms, consisting of specially constructed wooden grilles or screens of 3/8 by 1/2-in. mesh, through which the

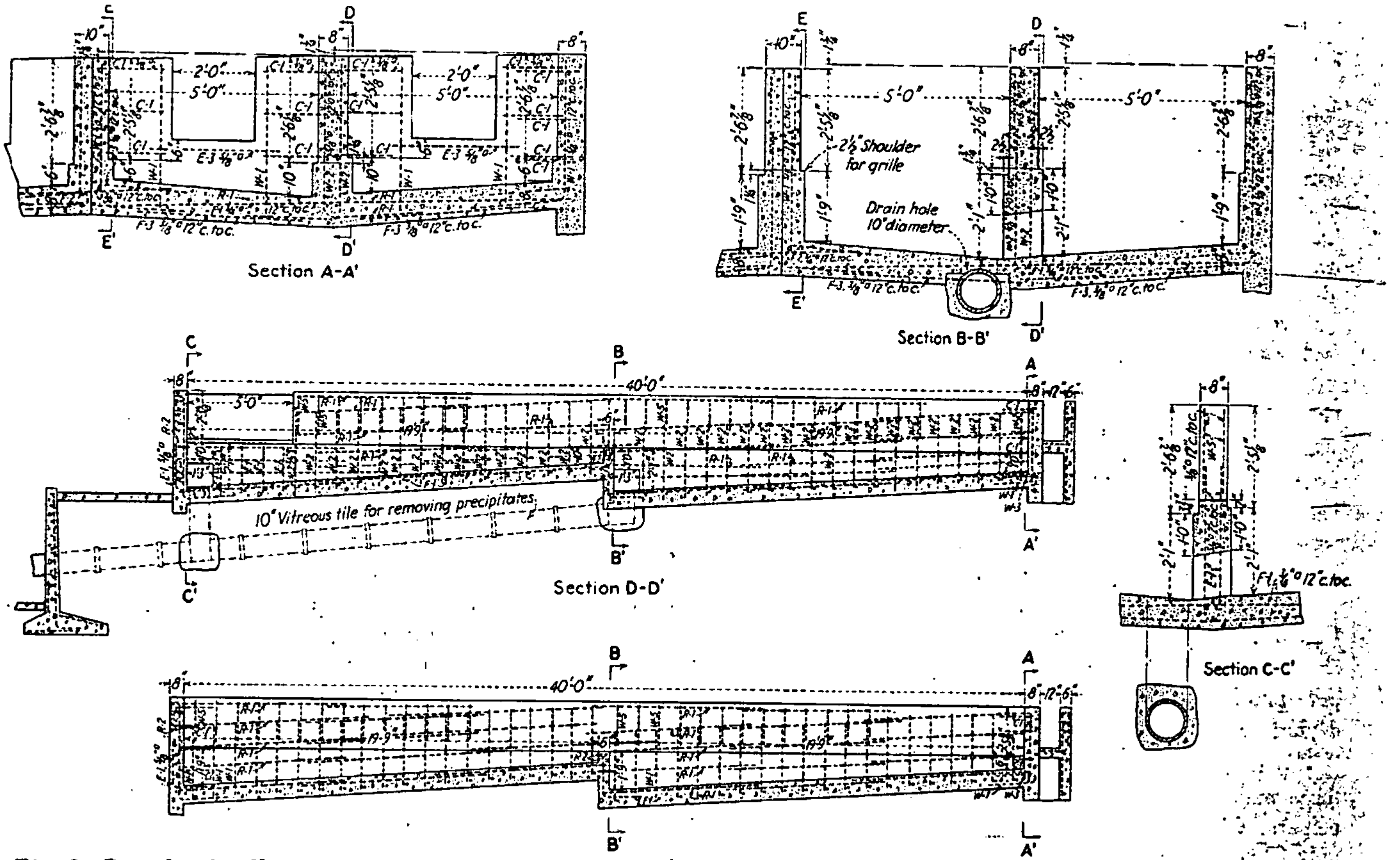


*Fig. 2. Details of cell construction.*

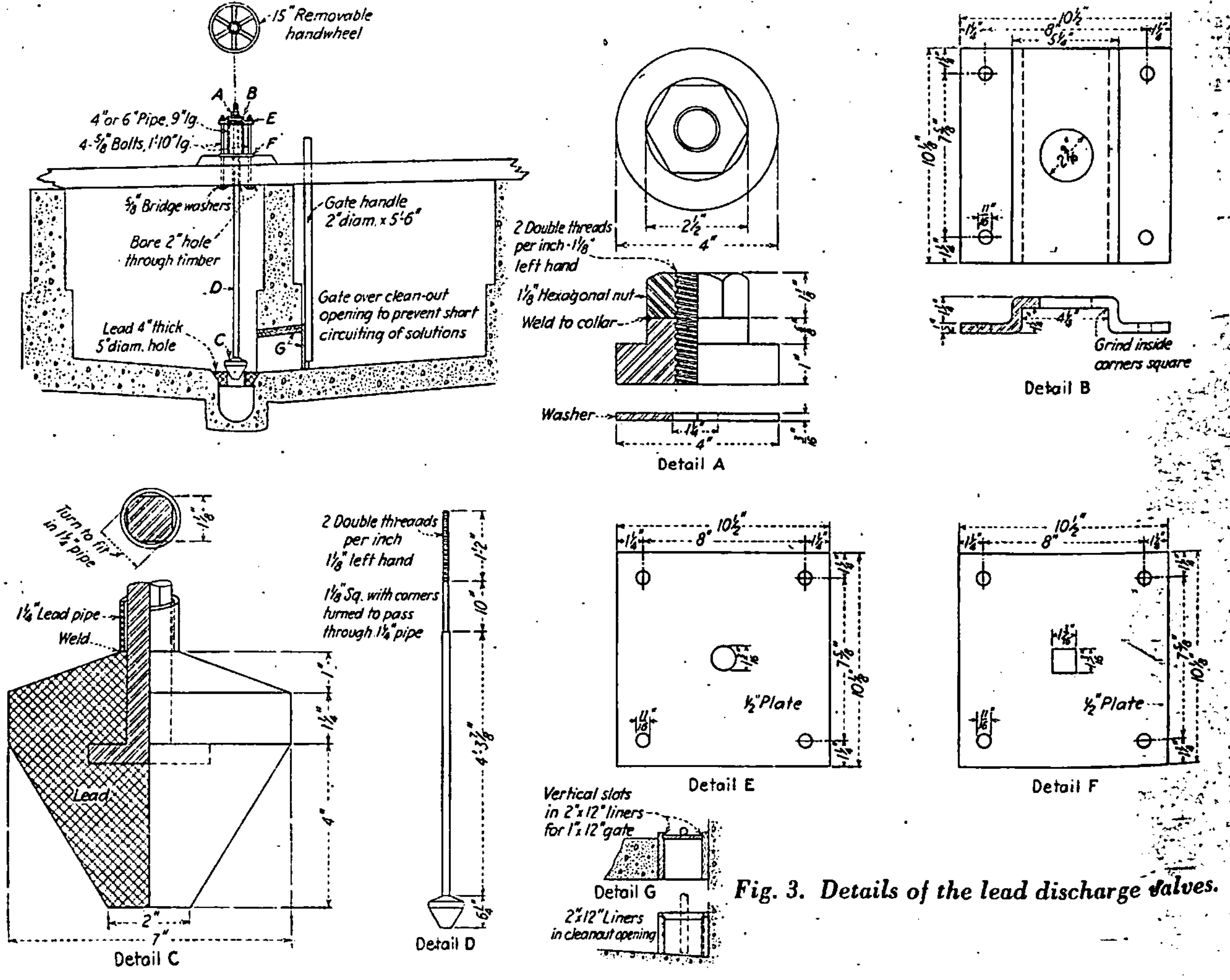
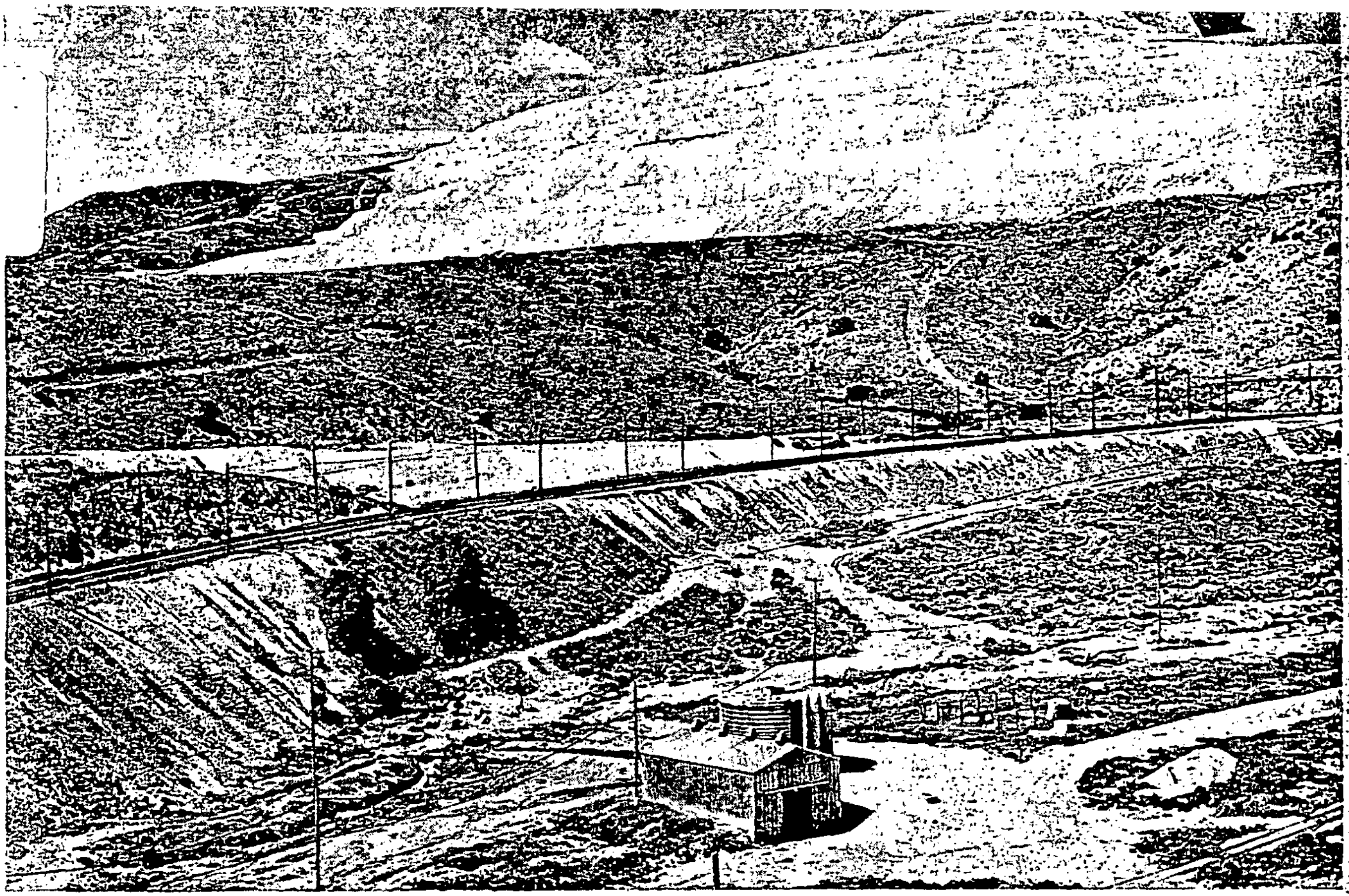


*Fig. 3. Details of the lead discharge valves.*



**THERE'S LOTS OF COPPER** in this Bingham Canyon dump. Seven-car waste train and electric locomotive under arrow show you how large this dump is. It is only one of several dumps being leached under Kennecott's expansion program.

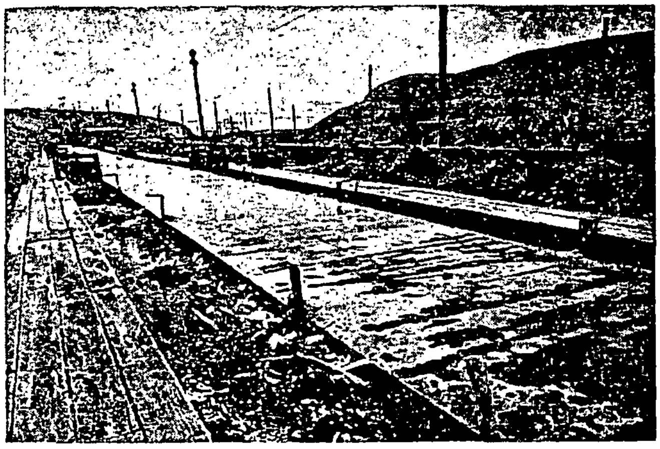
# LEACHING DUMPS to recover more

Part I of II parts

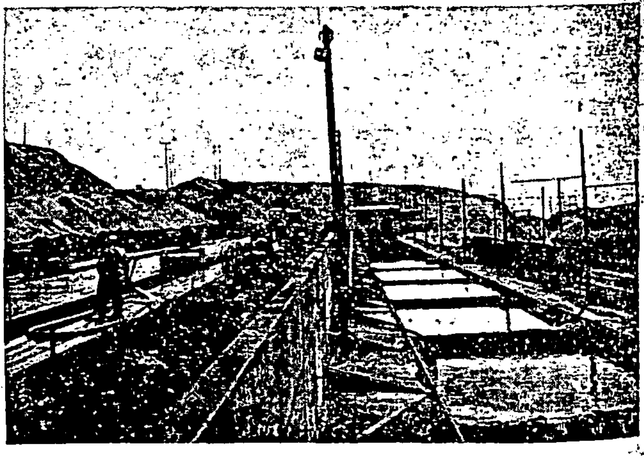
By George O. Argall, Jr.

SPECIAL REPORT

**Watch for the second part of this article on Southwest copper dump leaching. Specific details of leaching procedures, precipitation plants, pumps and pipe lines will be published in the November issue of MINING WORLD. Reports cover dump leaching at eight copper mines in Arizona, Nevada, New Mexico, and Utah.**



**SCRAP IRON** filled precipitation launders at Kennecott's Copperton precipitation plant below Utah open pit mine.



**WASHING CEMENT COPPER** from precipitation tanks into settling tanks at right. Flow is through inclined launders.

Leaching of low-grade copper bearing dumps in the Southwest is a very important source of copper today. More and more copper is being recovered every year by this process. Copper will be recovered long into the future by dump leaching.

Here is why copper leaching (sulphides primarily as distinct from oxide leaching at Inspiration or Yerington) is important:

Drive up Bingham Canyon with one at **Kennecott Copper Corporation's Utah Division** engineers and he will tell you, "There's more than a billion tons in these stripping dumps. Copper will be recovered from them by leaching long after the Utah open pit has closed down." Precipitate copper from leaching is of growing importance at Utah. In 1961, 9,438 tons of copper was recovered. This was raised to 16,678 in 1962 by increasing the volume of leaching solution and raising copper content of the pregnant solution.

Expansion, now underway, of the Utah mine dump leaching system, including construction of reservoirs, pipelines pumping stations, driving of pregnant solution collecting adits, and new cone-type precipitation units are scheduled to increase recovery to 72,000 tons of copper precipitate annually.

**Duval Corporation** started its new leaching operations at the Esperanza mine in the first half of 1962. Five percent of the total copper production for the year was by this method.

**Inspiration Consolidated Copper Company** recovered 5,174,374 pounds of copper in 1962 by leaching in place (total copper output was 104,581,211 pounds). Leaching was started on a new dump late in the year.

**Kennecott Copper Corporation's Nevada Mines Division** resumed leaching last year with the goal of obtaining 3.0 percent of the total copper recovered by the Division in the next five years at a lower cost per pound than mined copper.

**Bagdad Copper Corporation** started an extensive dump leaching program in 1961 with 1,005,616 pounds of copper being recovered. In 1962, 6,074,357 pounds were recovered (28,496,896 pounds for entire operation), at a direct cost of $0.0298 per pound. Goal is to increase recovery to 2,750,000 pounds per month.

**American Smelting and Refining Company** started leaching of two dumps in 1960 at its Silver Bell mine. Operations are efficient and profitable, and will be continued for many years.

Dump leaching has been practiced at the **Chino Mines Division of Kennecott Copper Corporation** since 1924. Water was first pumped to the dumps in 1936 and the flow was increased to 1,000 gallons per minute in 1939. Today, 10,000 gallons per minute are pumped to dumps.

Dump leaching at **Kennecott's Ray-Mines Division** has been underway for more than 25 years.

**Miami Copper Company** has been leaching dumps at its Castle Dome mine since January 1953. All mining ended in December 1953.

**Anaconda Company,** at its Berkeley pit in Butte mines ore, leach and waste. The leach material is placed in separate dumps for future leaching.

This preceding brief summary shows why dump leaching is proving to be an ever-increasing method of recovering copper from low-grade material necessarily moved during the mining cycle, but too low in grade to be milled at a profit in the respective concentrators.

# Southwest copper at lower cost

Dump leaching as now practiced is an old metallurgical process, starting with heap roasting and heap leaching in Germany in the 16th century. Leaching reached its greatest efficiency and usage in Europe at the famed copper-pyrite mines at Rio Tinto, Spain. Phelps-Dodge Corporation was one of the pioneers in the Southwest at Bisbee, Arizona and Tyrone, New Mexico, in the early 1920's. Leaching of broken ore-in-place was started in 1923 in Bingham Canyon, Utah, by the Ohio Copper Company.

The recent acceleration in leaching can be attributed to five main points.

First, the experimental work carried on by Kennecott Copper Corporation's Salt Lake City, Utah, Research Center, where it was found that leaching efficiency could be raised by growth of bacteria in solutions, regulation of solution temperature, control of oxygen in solution, and relationship of the iron salts.

Second, vastly increased leaching opportunities because of the great tonnages of low grade material mined and dumped each day at new mines and as a result of stripping ratios at the older mines.

**Third,** the relatively small investment in leaching facilities per pound of copper recovered in contrast to expansion of milling facilities to recover the same amount of copper by raising tonnage throughput.

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### Chemical Reactions for Copper Mineral Leaching in Dumps

**Pyrite:**
$4FeS_2 + 15O_3 = 2Fe_2(SO_4)_3 + 2H_2SO_4$

**Chalcopyrite:**
$CuFeS_2 + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 = CuSO_4 + 5H_2O + 2H_2SO_4$

**Chalcocite:**
$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$

**Covellite:**
$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$

**Azurite:**
$Cu_3(OH)_2(CO_3)_2 + 3H_2SO_4 = 3CuSO_4 + 2CO_2 + 4H_2O$

**Malachite:**
$Cu_2(OH)_2CO_3 + 2H_2SO_4 = 2CuSO_4 + CO_2 + 3H_2O$

**Cuprite:**
$Cu_2O + H_2SO_4 + Fe_2(SO_4)_3 = 2CuSO_4 + 2FeSO_4 + H_2O$

**Chrysocolla:**
$CuSiO_3 \cdot 2H_2O + H_2SO_4 = CuSO_4 + SiO_2 + 3H_2O$

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**Fourth,** low manpower requirements needed for leaching.

**Fifth,** the chemical process of both leaching and precipitation is simple, continuous, requires the addition of only a small amount of sulphuric acid, and does not require continuous, close supervision of trained operators.

Dump leaching is different at all mines, as is brought out in the following mine descriptions and series of tables. However, the success at all mines is due to several of the following factors:

1. Non-acid-consuming character of the dumps. One mine, Chino, lists one of its gangue minerals as siliceous limestone. Undoubtedly there is a small percentage of acid-consuming unsiliceous limestone in the dumps. Bagdad has some calcite.

2. A solid, impervious surface under the dumps.

3. The ability of the dump minerals (primarily pyrite) to form small amounts of sulphuric acid and ferric sulphate (see Chemical reactions above). The latter is a very active solvent for copper in chalcocite ($CuS$), which is found in many of the dumps.

4. Availability of adequate water at low cost.

5. Ability to recirculate water through dumps many times without appreciable loss.

6. The presence of some of the easily soluble oxide minerals—malachite, azurite, cuprite, and others—in the dump.

### Sulphide Copper Minerals and Percent Copper in Dumps Now Being Leached[1]

| *Minerals* | *Ray Division* | *Bagdad*[2] | *Chino Division* | *Silver Bell* | *Esperanza* | *Utah Division* | *Mine "A"* |
|---|---|---|---|---|---|---|---|
| Chalcopyrite | | X | X | X | X | X | X |
| Chalcocite | X | X | X | X | X | X | X |
| Pyrite | | X | X | X | X | X | X |
| Bornite | | X | | | | | X |
| Covellite | | | | | | | X |
| Percent sulphide copper | 0.24 | 0.30 | 0.27 | — | 0.25 | — | — |

[1] Copper oxides—azurite, malachite, cuprite, chrysocolla—are found in nearly all dumps, but their total copper content is so much lower than the sulphide content that this review is primarily concerned with sulphide leaching.

[2] Bagdad's oxide capping dumps contain malachite, azurite, and a little chrysocolla which are being leached at present time. These dumps require acid which is made in Bagdad's acid plant.

### Leaching-Solutions Charged to Dumps and Pregnant Recovered from Dumps

| | *CHARGED TO DUMPS* | | | | | *PREGNANT FROM DUMPS* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *Mine* | *pH* | *Ferrous Iron*[1] | *Ferric Iron*[1] | *Gallons per Minute* | *Copper*[1] | *pH* | *Ferrous Iron*[1] | *Ferric Iron*[1] | *Gallons per Minute* | *Copper*[1] |
| Ray | 3.4–4.0 | 3.5–3.8 | 0.1 | 4,500 | 0.1 | 2.3–2.5 | 0.8–1.2 | 1.3 | 4.000 | 0.5–1.5 |
| Bagdad | 2.0– | 4.5 | 0.2 | 3,300 | 0.2 | 2.5 | Negative | 2.8 | 3,200 | 1.0 |
| Chino | 3.5 | 3.5 | 0.2 | 10,000 | 0.3 | 2.5 | 0.9 | 0.6 | 9,000 | 2.3 |
| Silver Bell | 3.35 | 1.67 | 0.04 | 900 | 0.007 | 2.4 | 0.01 | 0.57 | 860 | 1.086 |
| Esperanza | 3.25 | 1.10 | 0.1 | 1,000 | Nil | 2.8 | 0.01 | 0.01 | 950 | 1.00 |
| Utah | 2.4 | 2.5 | 0.02 | 2,000 | 0.1 | 2.5 | 1.0 | 1.0 | 1,800 | 1.2 |
| Mine "A" | 2.5 | 5.0 | 0.7 | 600 | 0.21 | 2.0 | 3.3 | 1.1 | 500 | 1.35 |

[1] Expressed in grams per liter.

### Copper Precipitation from Pregnant Solution

| | *PREGNANT SOLUTION TO PRECIPITATION* | | | | | | *TAILING SOLUTION FROM PRECIPITATION* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Mine* | *Copper*[1] | *$H_2SO_4$* | *Ferrous Iron*[1] | *Ferric Iron*[1] | *pH* | *Pounds Iron per Pound Copper* | *Copper*[1] | *$H_2SO_4$* | *Ferrous Iron*[1] | *Ferric Iron*[1] | *pH* |
| Ray | 1.0 | 2.0 | 1.1 | 1.2 | 2.5 | 1.8 | 0.08 | 0.3 | 3.7 | 0.12 | 3.5 |
| Bagdad | 1.0 | 1.0 | 0.02 | 2.8 | 2.2 | 1.7 | 0.03 | 0.7 | 0.1 | 2.6 | — |
| Chino | 1.5–2.3 | 0.6 | 0.9 | 0.6 | 2.5 | — | 0.1–0.3 | 0.2 | 3.5 | 0.2 | 3.5 |
| Silver Bell | 1.09 | 0.6 | 0.01 | 0.57 | 2.3 | 1.5 | 0.006 | 0.08 | 2.08 | Trace | 3.6 |
| Esperanza | 1.00 | 0.2 | 0.01 | 0.1 | 2.8 | 1.35 | Trace | Nil | 1.1 | 0.01 | 3.75 |

[1] Expressed in grams per liter.

### Solution Pumping Details for Copper Dump Leaching

| *Mine* | *Type Pumps* | *Material* | *Horsepower* | *Gallons Pumped per Minute* | *Head in Feet* |
|---|---|---|---|---|---|
| Ray | Horizontal centrifugal | 316 SS | 125 to 200 | 1,000–1,500 | 300–475 |
| Bagdad | Vertical propeller[1] | Stainless steel | Two, each 400 | 2,000 each | 646 |
| Chino | 3 Horizontal<br>8 Vertical | Stainless steel | Four, each 200<br>Seven, each 250 | 1,000 each | 9, at 600<br>2, at 650 |
| Silver Bell | Vertical centrifugal 2, 6-inch; 2, 5-inch | 316 SS (Pregnant)<br>304 SS (Barren) | Two, 50 and 10<br>Two, 100 | 250 and 900<br>650 and 250 | 195 and 20<br>250 and 165 |
| Esperanza | Vertical centrifugal (15-inch) | 316 SS | 200 | 1,000 | 165 pounds per square inch |
| | Vertical centrifugal (2½-inch) | 316 SS | 1.5 | 1.00 | 25 PSI |
| | Centrifugal[2] (6-inch) | 316 SS | 10 | 1,000 | 10 PSI |
| Utah | Horizontal centrifugal | Stainless steel | 350 | 2,000 | 500 |
| Mine "A" | Centrifugal (10-inch) | Stainless steel | — | 1,000 | 400 |

[1] U. S. Pumps. [2] With Adjusto Speed Clutch.

7. Concentration of minerals along fracture planes in the rock, to allow circulating solutions to have direct contact with minerals.

8. Dumps located in a series of canyons or draws leading to a main canyon, so that pregnant solutions from several dumps can flow by gravity to a central collection dump in main canyon.

9. The higher dumps now being built with Diesel trucks, which raise height of leaching column to permit longer contact between solution and rocks.

10. A gangue rock which will not decrepitate to seal intra-rock cavities and block solution flow.

11. Adequate, but not excessive, formation of ferric sulphate in the dump which would make copper precipitation from pregnant solution costly or difficult.

At Miami Copper and Ray Mines Division, leaching of caved capping and low grade ore, essentially in-place, has been a copper source for some time. This material is broken, shifted, and fractured, and is similar to a dump in several respects. Procedures and methods are very similar, in most respects, to dump leaching. In fact, if these two mines were to be developed today by open pitting rather than by caving (used when they were started because of the difference in economics), much of the material now being leached would be leached anyhow after it was trucked to dumps. Leaching solution is sprayed over the top of the caved areas, and the pregnant solution is collected in old mine workings and pumped to surface precipitation plants.

Sulphides are found at various mines in the following types of rocks: Ray Division—schist, porphyry; Bagdad—monzonite porphyry, quartz, some calcite; Chino Division—highly altered granodiorite, shales, quartzites, and some silicated limestones; Silver Bell—alaskite, dacite porphyry, quartz monzonite; Utah—quartzite; Inspiration—porphyry; Esperanza—andesite, greywacke, quartz diorite, quartz monzonite; and Nevada Mines—monzonite porphyry.

Drilling of vertical holes in dumps to obtain samples, ascertain degree and rate of percolation and channeling, and to serve as solution injection points is always a problem because of the heterogeneous size and nature of the particles in the dump. Churn drills, rotary drills, and the Klam drill have all been used. Caving of holes and the problem of drilling through large boulders are two major difficulties in drilling. The new Klam drill, which makes a hole as large as 28 inches in diameter, offers the advantage of straight holes as deep as several hundred feet. Shallower holes can be drilled without casing, because the hole diameter is larger than the tool so that the walls are never touched or disturbed. No water or air are used for drilling and large rocks can be removed intact from the hole.

Rotary drills make holes fast for injection points and are readily available from the mining department.

### Kennecott Raises Bugs

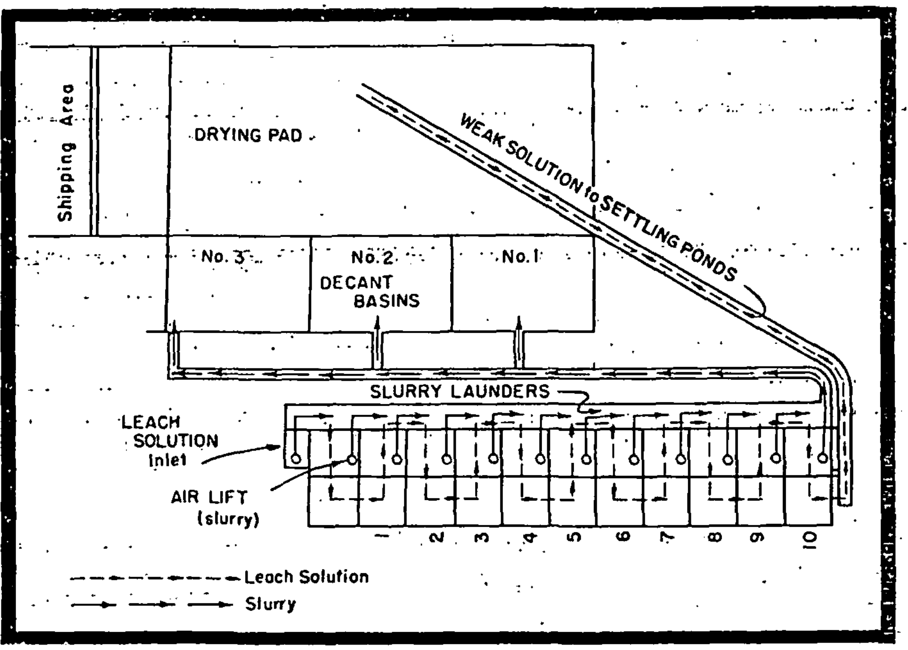
Thiobacillus thio-oxidans and thiobacillus ferro-oxidans bacteria are found in copper mine leaching waste waters. Brigham Young University metallurgists working under a Kennecott grant determined several years ago that these bugs were important for copper leaching. The more bugs the more efficient leaching. These bacteria, which thrive only in acid solutions under high humidity and temperature in the dark recesses of the dumps, oxidize pyrite to sulphuric acid and ferrous sulphate and simultaneously convert ferrous iron to ferric iron. The acid holds the ferric sulphate in solution until it comes in contact with copper sulphides, which are oxidized to soluble copper sulphate, while the ferric sulphate is reduced to ferrous sulphate to provide another batch of "food" for bacterial oxidation. Temperature of leach solution is important as efficiency rises with temperature. In one experiment, artificially heated solution (100 to 110° F.) doubled the copper content of the pregnant solution.

### Leaching control

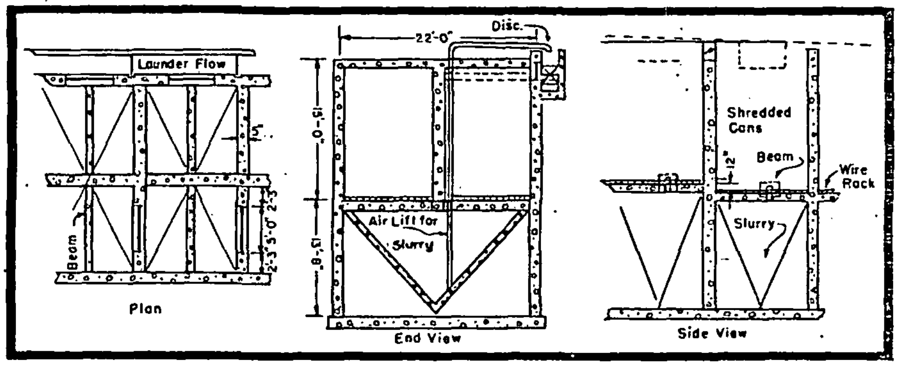
Copper content of the pregnant solution is the key to leaching control. When assays show a falling off in copper content, the normal procedure is to change input leaching pattern on the dumps. Those sprays, ponds, or ditches which have been leached longest are usually taken off, with the solution being directed to a new area. A constant trial and error method is used to maintain copper grade, as it is impossible to predict how often it will be necessary to change leaching pattern.

After a pond has been cut out of the circuit, it is allowed to set and dry for various intervals. A most important action takes place in the dump during this period as the solu-

## How Bagdad precipitates cement copper

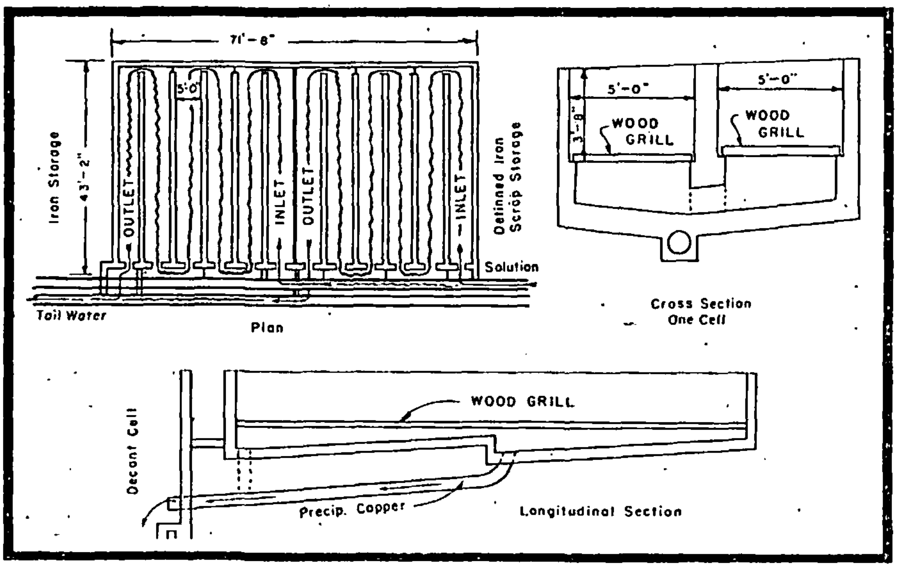


**PLAN** of precipitation plant. Pregnant solution enters at left, weak effluent overflows at right. Cement copper is drained, dried, and stored for shipment.



**BIG PRECIPITATION CELLS** have no gravity drain. Air lift elevates slurry of cement copper and solution into discharge launder during continuous precipitation.

## Details of Ray Mines' precipitation plant



**STEPPED BOTTOM** with double discharge. Note the scrap iron storage areas at both ends of precipitation area. Most mines store and charge from one side only.

tion adhering to rock faces creates a humid environment, under oxidizing conditions, to continue the conversion of the copper minerals to soluble salts. When solution is redirected to the area the leaching cycle is again started.

The importance of close pH control of leaching solutions has been demonstrated in the laboratory and on actual dumps. Addition of small amounts of sulphuric acid to the precipitation plant effluent prevents hydrolysis and resultant precipitation of iron salts to blanket and make the dump surface impervious. This iron precipitate masking was one of the early problems at Chino. Close pH control of leaching solution is practiced at Kennecott's operations. Silver Bell regulates pH control at head of precipitation cells to about 2.3. This results in better copper precipitation by preventing hydrolysis and the precipitation of hydrous iron salts from solution at tail end of cells where acid concentration is low.

### Iron for Precipitation

The so-called shredded tin can which is actually a tin can which has been burned to remove the tin coating, the label, any lacquer coating, solder from seams and scraps of original content is by far the most popular iron source for precipitating copper. The cans are not shredded, rather, or more accurately, they are crushed or crumpled.

Many years ago it was found that scrap from the making of cans and other similar stringy was not as efficient as the crumpled cans, because this material has a tendency to pack in the cells to hinder solution flow. Of course, any iron can be used, but the small surface area per pound of iron in a railroad rail does not make it suitable as an iron source. Several of the larger plants use a variety of iron scrap; other plants use only the cans. Economics of iron supply determine source and type of iron. There are several firms in California and Arizona which specialize in the production of the shredded cans for the copper industry.

### Precipitation Reactions

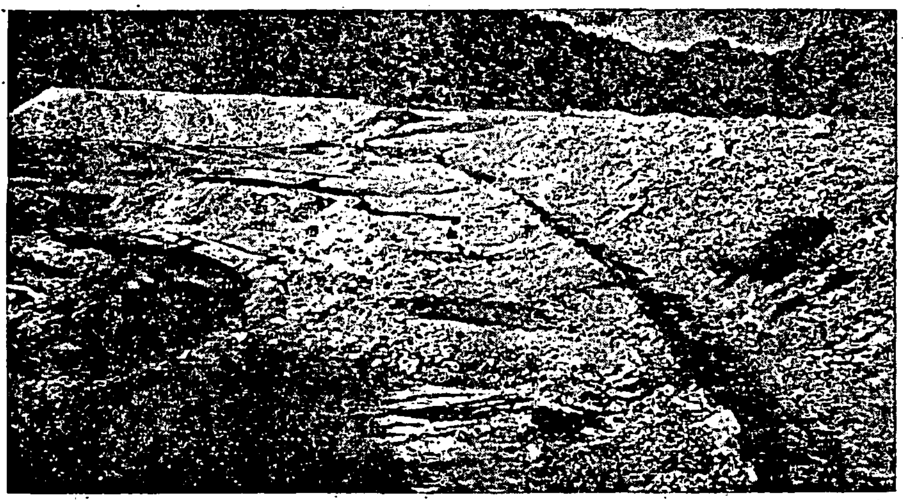
Iron in the cells reacts on three constituents of the pregnant solution as follows:

$$\begin{gathered}Fe + CuSO_4 = Cu + FeSO_4\\ Fe + H_2SO_4 = H_2 + FeSO_4\\ Fe + Fe_2(SO_4)_3 = 3FeSO_4\end{gathered}$$

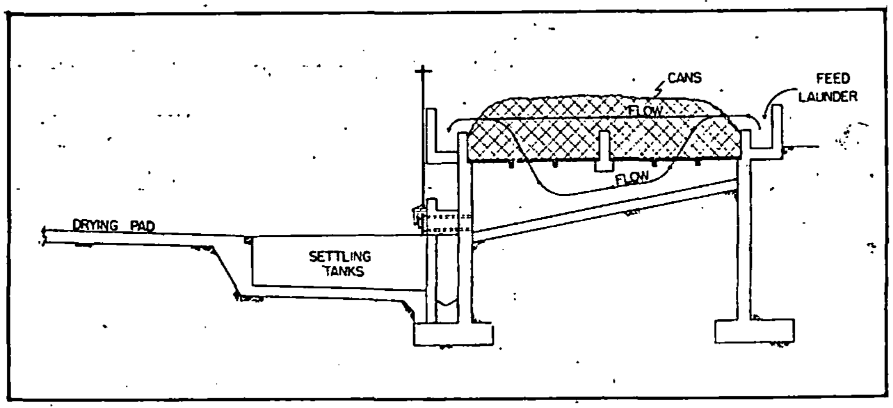
Reduction of the ferric iron to ferrous is the most rapid, next is the reduction to metallic copper which is the goal of the process.

To be continued in November 1963 issue.

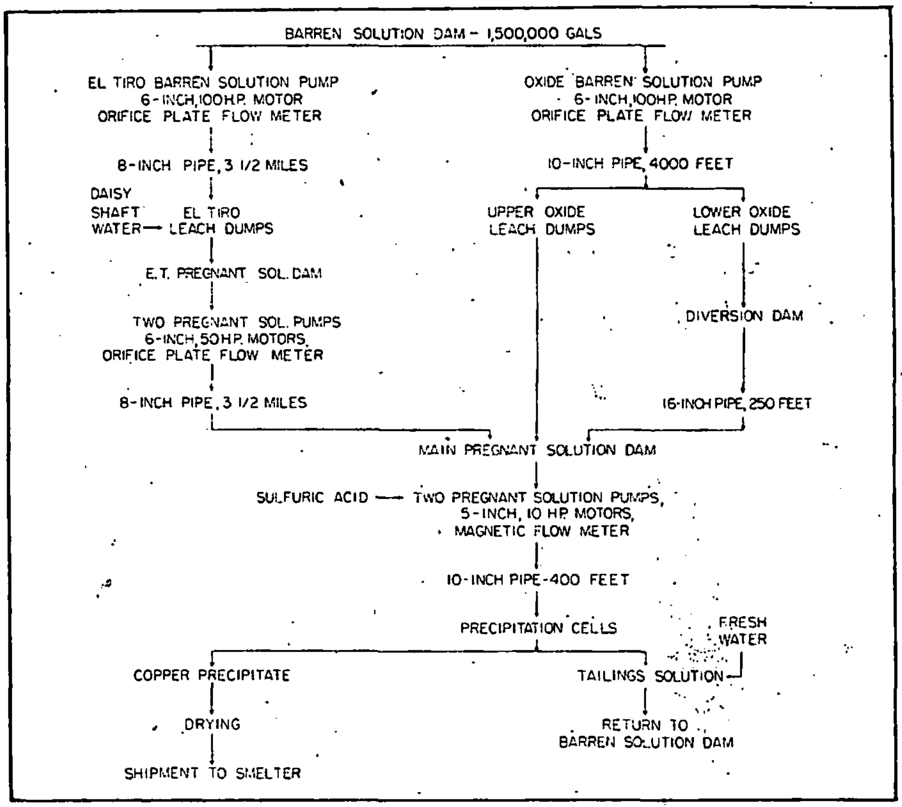
## Silver Bell's dump leaching circuit



**OXIDE MINE** dump leaching solution distribution system showing inlet ditch at right feeding solution into system of terraced ponds on top of dump.



**PRECIPITATION PLANT** cross section showing how cans are suspended in solution. Cement copper is washed through opened valve into settling tanks.



**FLOWSHEET** of the El Tiro and Oxide mines' dump leaching circuit designed by Asarco's milling department. Dumps are 3.5 miles apart.

# Experimental Leaching at Anaconda

BY FREDERICK LAIST AND HAROLD W. ALDRICH, ANACONDA, MONT.

(Salt Lake Meeting, August, 1914)

THE object of the construction and operation of the 80-ton leaching plant was to test out the leaching of sand tailings on a large scale and, if possible, determine a definite method of operation, and the best construction for the larger unit which is now being built. It was also of importance to obtain some practical data as regards cost items. The 80-ton plant was not expected to be a commercial success. A leaching process on such low-grade material necessitates the treatment of a very large tonnage. Such a cost item as labor, for instance, is entirely out of proportion in such a small plant. The amounts of acid, salt, scrap iron, and fuel for roasting, however, are the same per ton in an 80-ton plant as in a 2,000-ton plant. These costs were definitely established. Also the percentages of extraction and grade of tailings were definitely determined for a large-sized unit.

Following will be found the description of the plant, the method of operation and the results obtained. A general view of the plant is given in Fig. 1.

The bins consisted of one coal bin with a capacity of 30 tons, one salt bin with a capacity of 20 tons, and a "mill tailings" or feed bin which held 70 tons. The coal and salt bins were placed with their floor level even with the firing floor of the roasting furnace. The feed bin, to give it greater capacity, discharged about 12 ft. below this point, to a 12-in. conveyor belt, which in turn discharged into a pug mill. This fed another conveyor belt, which discharged into the top hearth of the furnace.

The furnace was an ordinary six-hearth MacDougall roaster, 20 ft. in diameter. It was equipped with two fire boxes, on opposite sides, the flames entering on the third hearth. An induced draft was obtained with a Buffalo blower, worked as an exhaust fan. Just above the top hearth was an annular flue around the whole circumference of the furnace. Slots at intervals of about 18 in. led from this flue down into the top hearth. The slots were 2 in. wide by 6 in. long. This annular flue proved rather unsatisfactory, as it tended to fill up with flue dust and choke the slots, thus cutting down the draft. The volume of gas through the furnace was 3,500,000 to 4,000,00 cu. ft. per 24 hr. at standard conditions of temperature and pressure. The temperature of the outgoing gases was about 180° C.

The furnace was air cooled, 15-lb. air entering the shaft through a 2½-in. pipe. The pressure in the arms themselves was 2½ lb. per square inch; 850,000 cu. ft. of cooling air at standard conditions of temperature and pressure was used for this purpose. This, we believe, was a great deal more than was necessary, but we did not want to take any chances on losing any furnace arms, before the experimenting was finished.

There were four drop holes in the wall between the second and third floors, and six between the fourth and fifth floors. Four holes seem to be ample. The discharge from the furnace to the cooler was an 8-in. pipe at the outer edge of the bottom hearth. A nearly dust-tight chute led into the cooler. All dust made in the cooler was, therefore, drawn back into the furnace.

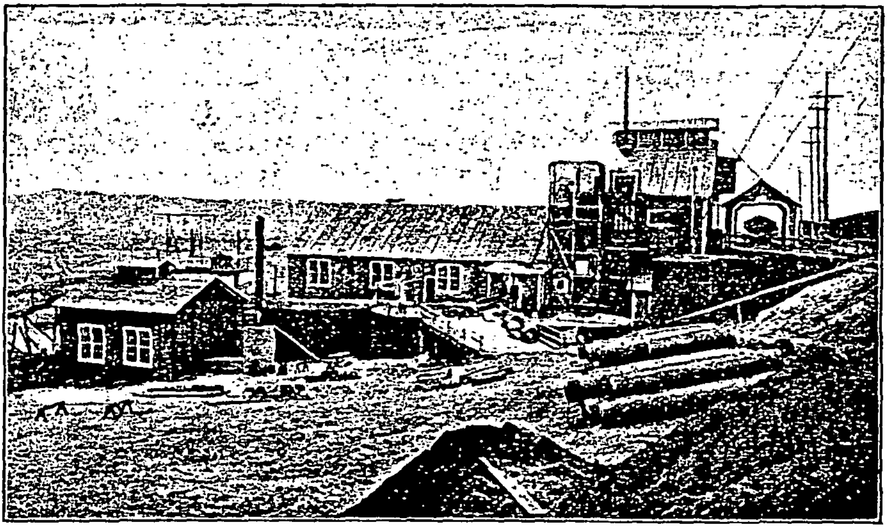


FIG. 1.—VIEW OF 80-TON LEACHING PLANT.

The cooler, shown in Fig. 2, was a rotating drum, built of ¼-in. boiler plate, 19 ft. long and 2 ft. in diameter. It had a slope of ¾ in. to the foot, and made 10 rev. per minute. At the lower end, cold water entered an annular chamber through a stuffing box, and from this chamber 26 iron pipes 1 in. in diameter carried the water to the upper end and discharged into a circular launder 18 in. from the end, and on the outside of the drum.

The calcine entered the cooler at 260° to 370° C., depending on the amount of sulphur in the feed, and was discharged at about 45° C. The rate of feed, of course, also affected the temperature of the dis-

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charged calcine.
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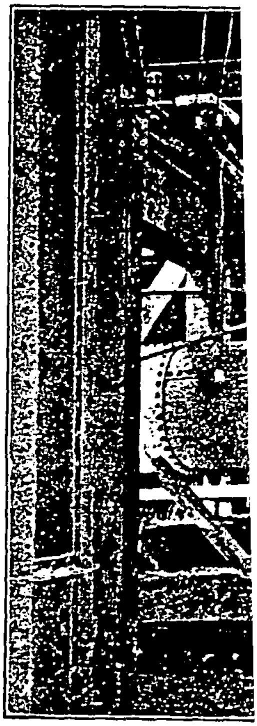

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charged calcine. At 80 tons of an average feed, the cooling water required to cool the calcine to 45° C. was 25,710 gal. per 24 hr. To cool the same to 37.5° C. required 34,666 gal. per 24 hr. The cooler discharged into a 6-in. screw conveyor, into which a water spray, to settle the dust, was turned. The screw conveyor discharged to a series of belt conveyors, which carried the moistened calcine to the hoppers of the distributing launder above the tanks.

The distributing launder extended from the center to the circumference of the tank, where it was supported by a small fiber wheel. It was driven from the conveyor belt, through a series of bevel gears. The distributor was an iron launder 6 in. wide by 8 in. deep, with slots in the bottom spaced 18 in. apart. There was a slide on each slot, so that any or all of them could be closed. A 6-in. screw conveyor, resting down in the launder, moved the calcine from the center of the tank, outward.

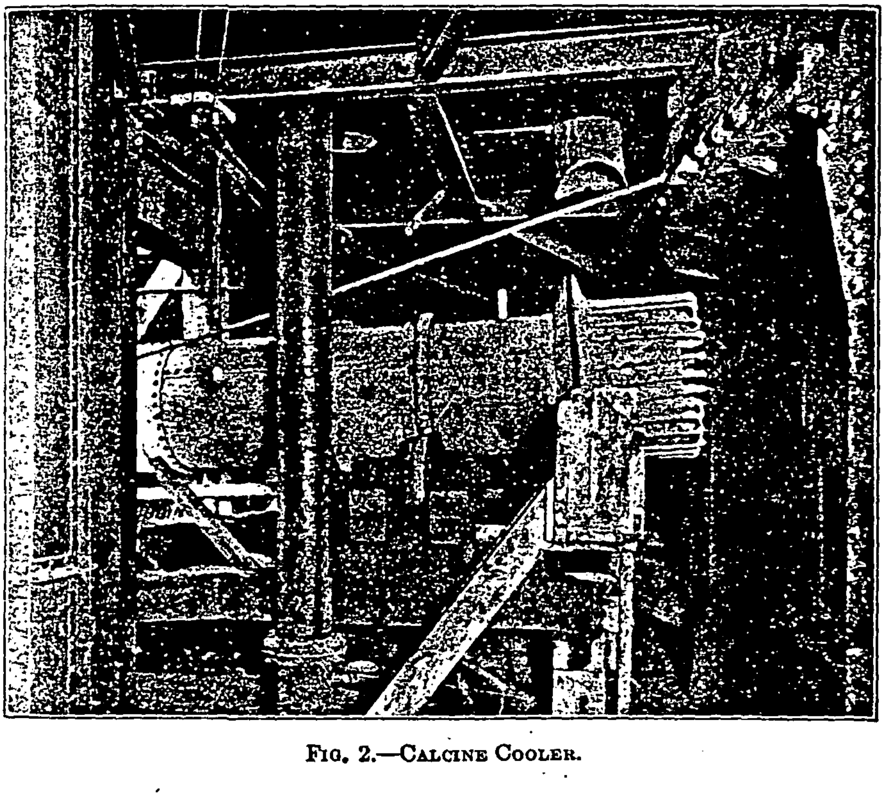

FIG. 2.—CALCINE COOLER.

Two leaching tanks, 32 ft. in diameter and 12 ft. deep, were placed in line with the furnace. A conveyor belt ran over each one, so that by moving the distributor from one tank to another, and by means of a switch gate, either tank could be filled. The tanks were of redwood. Each had five discharge gates, 12 in. in diameter, one in the center, and one in the center of each quarter of the tank. Suitable launders were provided underneath the tanks, for carrying away the leached tailings. Each launder had a stream of water entering through a 12-in. dirty-water main, from the concentrator. Valves were provided, so that all the water could be sent down one launder if necessary. Three-inch dirty-water pipes also led to the top of the tanks to furnish water for sluicing purposes. This was done with two 3-in. rubber fire-hose lines.

The filter bottoms were made with 2 by 4 in. pieces, spaced every 1 ft. across the tank, and 1-in. slats placed with 1-in. spaces across the tank in the other direction, and nailed to the 2 by 4 in. pieces with copper nails. Then the whole bottom was cut into sections convenient for handling, when taking the bottom up. A filter medium of two layers of coarse cocoa matting was spread over this. The bottom of the tank under the filter had a lead lining, which came up the sides 6 in. Suitable drains for the solutions were provided under the filter. Pipes for carrying concentrated acid were provided for each tank, and steam connections for heating the solutions, as they went on.

Two 10 by 10 ft. iron tanks were provided for holding the stock of concentrated acid. All connections and fittings for concentrated acid were of iron. As a safety, there was a lead plug which fitted into the discharge hole in the tank. This was operated from the top with an iron rod connected to the plug. There was a gauge on each tank, actuated by an air-tight iron float.

Two 28 by 10 ft. lead-lined redwood tanks held the stock solutions for leaching, and a third tank the copper solution. A heavy lead steam coil inside the tank was used to heat the solutions to prevent freezing in very cold weather. Drains from the tanks led to the air lifts, of which there were three, made of 5-in. lead pipe and lifting about 16 ft. The lower elbows were in a 16-ft. pit. The air lifts used 90-lb. air, but only because all of the available 15-lb. air was used for the furnace cooling. A very slight turn of the valve gave sufficient air. The discharge from the lifts was into a lead-lined box above the tops of all the tanks, leaching and solution. The launder system was such that it was possible to transfer solution from any tank to any other tank in the plant. A circulating air lift was provided for each leaching tank. It was not necessary to have a pit for these, however, as they only had to actually lift against a pressure of a few inches. They were connected to the bottom of the tank, under the filter, and discharged into the top, over the calcine. Each would handle 250 gal. or more per minute. Under the air-lift discharge box was a lead-lined heater box, into which live steam was injected to heat the solutions. Some of the launders were lead lined and others were not. In some places, the lead would creep and split at the seam. The wood launders with no lining were satisfactory for the time the plant was in operation, about six months, and are probably good for a long time yet. We did not try to protect them with paint in any way A 28-ft. Oregon fir tank was put up as a spare acid tank. It was slow in taking up, but for an unlined tank it did very well. It had been put up and taken down twice before this, so it was not in the best condition. The iron hoops for 4 ft. from the bottom were protected with lead strips.

A small 9 by 10 ft. wooden tank, with agitator equipment, was also put up for prospective sponge-iron precipitation. It was not lead lined and gave no trouble from leaks.

In two of the large lead-lined solution tanks we added salt directly to the solution. It settled to the bottom, and in a day or so the tanks commenced to leak. After repairing, we discontinued this method of adding salt and were troubled no more. It seems that the hydrochloric acid liberated attacked the lead very materially. If a leak does occur in a lead-lined tank the wood backing does no good whatever. It is so thoroughly dried, of course, that it has no holding power for the solution.

To each of the solution tanks, there was an acid pipe connection and a fresh-water connection. A 1½-in. lead pipe with a bend of 1 ft. of its length at the bottom of the tank furnished 90-lb. air for agitation and mixing. This did not work very well. The air came to the top of the solution at the point where it entered, and did not agitate a very large proportion of the tank. We could get no swirling effect at all.

The lead lining and piping showed no appreciable corrosion in the six months of operation, excepting, as was stated before, where a large amount of salt came in contact with the lead, and where live steam impinged on the lead in the presence of acid solution. A lead pipe carrying steam will not stand up in our solutions when they contain 3 to 4 per cent. acid, but in the solutions after precipitation, which carried 1 per cent. or less, no corrosion could be observed in a month's continuous running. The lead air lifts showed no appreciable wear at the elbows, where the most corrosion would be expected. The lead pans in the bottoms of the leaching tanks were of no benefit, when the scheme whereby the acid solution was sprinkled on, instead of the tank being saturated, was abandoned. The leaching tanks leaked pretty badly, but this was due to faulty construction, rather than to any fault of the wooden tanks. In several places it was necessary to protect the hoops with lead strips. The air lifts worked very satisfactorily, handling a large amount of solution very easily, except when they started "foaming." This was something which we could not account for definitely. At times, the solution coming up the air lift gave a great deal of trouble because of this foam. The solutions averaged about 1.22 sp. gr. and were more or less viscous. Cold solutions seemed to foam much worse than the warm ones, so it seems as though the viscosity was what caused the trouble.

The precipitation launders were two lead-lined troughs, side by side, each 75 ft. long, by 3 ft. wide by 2½ ft. deep. The copper solution entered the upper end of one launder and returned in the other to an air lift, which raised it into the copper-solution tank. It was circulated in this way until the copper content was low enough, say, 0.06 per cent., to be returned to the leaching system. The precipitating launders were equipped with false bottoms 4 in. above the floors to give room for the cement to settle and leave all of the iron free. A settling tank was provided and, when cleaning up, the end gates were removed and the cement washed or pushed out of the launders into it. With fresh, clean iron, this equipment will precipitate 8 to 10 gal. per minute from 2 per cent. copper to 0.1 per cent.

Owing to the entirely new and experimental nature of this work, it was found necessary to make a great many changes from the procedure which had been planned out in advance. This was true in the case of handling the material, the roasting, and the scheme of leaching.

As the plant was originally built, the feed to the furnace, as well as the calcine from the furnace to the leaching tanks, was to be handled in small bucket elevators. These gave a great deal of trouble. The nature of the material to be handled showed very soon that the elevators would not do the work. The feed has a good deal of fine material, though much coarser than slime, which tends to pack and build up as it drops to any surface. In the case of the feed elevator, the buckets would fill up and not discharge, and finally would have to be cleaned out. We endeavored to moisten the calcine as it came from the furnace, to settle the dust, and it acted much the same way as the feed. Unless the calcine was dampened as it came from the furnace, the elevator raised so much dust that it was almost impossible to work in the building. These elevators were then discarded and belt conveyors substituted. It was necessary to put in two belts to get the feed to the top of the furnace. A pug mill was installed between these two belts, to mix in a certain percentage of slime, which was to be roasted and leached with the sand.

As originally built the furnace was designed for oxychloride roasting and salt was added on the fourth floor. All the doors were machined and made air tight. There was a combustion chamber between the second and third floors. The flames entered this chamber from the fire boxes and then traveled down through six holes 8 in. in diameter, spaced around the floor of the combustion chamber, to the third floor, and up through the drop holes to the second and to the top and out. The third floor was sealed from the fourth. A 3-in. drop hole on each side of the shaft, near the center, formed the bottom of a small hopper, which was set down in the brick. There was an adjustable gate on this drop hole, which could be set so the hopper had sand in it all, or nearly all, of the time, thus preventing any gases from the fourth hearth being drawn above into the third hearth. A fan furnished the draft for the upper three floors, and another forced the gases from the lower four through a scrubbing tower. This was for the purpose of separating the chloride or copper- and silver-bearing gases from the sulphur or waste gases.

There was a seventh floor provided. This was nothing but a flat water jacket to cool the calcine. There were also copper rakes on the seventh floor, in case it was desired to use a water spray to assist in the cooling and also settle the dust.

The bottom floor discharged through a 6-in. hole into a cast-iron pipe which contained a screw conveyor. This closed conveyor carried the material from the center of the furnace to the calcine elevator. In this way no air could enter the lower or chloridizing floors, except what was allowed to go in through an open door regulated to suit conditions. Theoretically, this looked very good, but under operating conditions a great many difficulties arose. The use of the combustion chamber required much more fuel than direct firing into the third hearth. At the time the combustion chamber was taken out, the sealed drop holes between the third and the fourth floors were also discarded, and a regular center drop hole was put in. Then the upper fan was the only one used and all the gases were combined. The fuel percentage immediately dropped down to what it should have been. This was due to the greater efficiency without the combustion chamber, and also very largely to the benefit derived, on the top two floors, from the hot gases rising from the fourth, fifth, and sixth floors, where a large part of the oxidation went on. When the furnace was run with the fourth floor at 930° F., which temperature gave the best results, there was no oxidation on the second floor from the top. The sand was heated up, of course, and just about hot enough to ignite the sulphur as it dropped to the third or fired floor. The most of the oxidation took place on the fourth floor.

When the hot calcine dropped to the water-jacket floor the jacket bulged and the rakes cut through, causing it to leak. This caused a great deal of trouble, as the water-soluble copper in the calcine went into solution and precipitated out on the iron, taking it into solution. The water jacket was also a very inefficient cooler. It was discarded, and a discharge hole cut in the outer edge of the sixth floor.

Then the problem of an efficient calcine cooler presented itself. A water jacket 20 ft. long and 4 ft. wide was built, and connected to a Wilfley table motion. This scheme worked poorly in a mechanical way, as the weight of water in the jacket was considerable, and the jerk of the jacket caused a sort of a hydraulic-ram action inside it, which caused many leaks. Also, the cooling efficiency was not very good. A layer of the finer calcine formed on the jacket and the coarser material merely slipped down over the top of this, getting very little cooling. A coil of cooling pipes, the whole length and width of the jacket, was laid on top of it, and calcine allowed to run down over these pipes. In this scheme the calcine acted the same way, most of the calcine never touching the jacket, but sliding down over the top of the lower calcine layer. The next method tried was the rotary cooler described in the preceding pages. It worked very satisfactorily, giving an efficient cooling and requiring very few repairs. The cooler discharged into a screw conveyor. About 1 per cent. water was sprayed on the calcine at this point to settle the dust. Mechanically the screw worked very well, but the water-soluble copper ate out the iron rapidly, and made it necessary to replace it often.

A push conveyor was built to replace this screw. After proper adjustment, it worked quite well, mixing in the water nearly as well as the screw. In comparison with this, a rotating wooden drum 2 ft. in diameter and 12 ft. long, was also tried. This gave the best results of any arrangement so far, for a short conveyor, particularly where it was necessary to mix in a small amount of water, for dust settling or cooling purposes. No iron could come in contact with the moistened calcine, and the repairs were very low. It rotated slowly and mixed the water in perfectly, about 1 per cent. water being required to prevent the calcine from dusting.

The scrubbing tower for the chloridizing gases did not work very efficiently and an electrical precipitation unit was installed. It was put in by Linn Bradley, of the Research Corporation, and was designed to handle all of the gases, chloride, sulphur, and coal gases. The treater was built after the design of Dr. F. G. Cottrell, of the Bureau of Mines, and worked satisfactorily, as 90 per cent. of the copper and a considerable amount of acid were recovered from the fumes.

After a 50-day successful run, it was decided to discontinue the feeding of salt into the furnace, for a time, and see what results could be obtained. This method offered many advantages. No valuable metals were volatilized, and no accretions formed in the furnace to cause trouble. The results from the straight oxidizing roast proved to be so good that it was continued for 70 days. The extraction on the copper was even better than on the chloridizing roast, but the silver recovery was not so good. However, the excess silver that would be saved by roasting with salt would not pay for the increased expense and bother entailed by a salt roast. The leaching solutions carry salt, and a great deal of chloridizing is done in the tanks.

The results from the oxidizing roast have this advantage over those of the chloridizing period: The oxidizing period was the later one, and naturally everything ran more smoothly and better results were more easily obtained. Also there was a leaner feed to work on during the chloridizing period.

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mixture. The slime, dewatered on an Oliver filter, was carried by a conveyor belt to a pug mill, where it was mixed with the coarse tailings. The mixture was fairly uniform, but some pieces of slime the size of a walnut entered the furnace, did not break up, and were roasted on the outside only. The slime, even after roasting, decreases the percolation rate so much as to make its treatment by mixing with the sand impossible.

The operation of the furnace, after everything was systematized, was very simple. The firing takes a certain amount of skill and experience, and the regulation of the furnace also takes some practice. A pyrometer was used on the fourth floor, but an experienced man could regulate the furnace and keep it within 30° of the required temperature, by the appearance of the lower three floors. To do this, of course, the same grade of feed must be maintained. A marked change in the amount of sulphur in the feed necessitated a readjustment of conditions in the furnace. One point is rather important; that is, not to let the temperature get too low, say 880° F., on the fourth floor, for if it once starts down it is very hard to get it back without lowering the amount of feed. The fire caused by the burning sulphur seems to go out, and then it has to be ignited again, using a disproportionate amount of coal.

The feed averaged about 3.00 per cent. sulphur and the calcine about 0.6 per cent. sulphur.

It was our experience that the higher temperatures, say 1,000° or more, caused a large amount of ferrite or insoluble copper; that is, insoluble in any acid but hydrofluoric; 900° to 930° F. seemed to give the best results.

The feed to the furnace averaged about 5 per cent. moisture, but very often went as high as 8 or 10 per cent. When this happened, the material on the top floor would bank up over the arms, instead of going through between the rakes. This always made it necessary to shut the feed off and let the rakes clear themselves. This trouble often limited the amount of feed it was possible to put through the furnace. With three or four arms on this floor, and with a feed carrying 0.68 per cent. copper and a proportionate amount of sulphur, the furnace handled very close to 100 tons per day, dry weight. The rakes on the first or top hearth were the only ones which showed any appreciable wear during the six months' operation. They were replaced about every four or five weeks. The blades and blade holders should be used there, as replacing these is much cheaper than replacing the whole rake.

Fire brick was used in the fire boxes and in the construction of the second and third floors. All the rest of the lining and the floors were built of ordinary red brick. No special endeavor was made to increase the water-soluble copper. It seemed to affect the acid consumption very little and electrolytic precipitation is out of the question at present, since the solutions carry chlorides. About 40 per cent. of the copper was soluble in water.

To give a full idea of the experimenting and changing in the leaching schemes, it seems best to take them up separately and show what was done on each.

In the experimental work done in the summer and fall of 1912, in a small experimental plant, a leaching scheme was worked out which seemed to give excellent results. This method consisted of sprinkling the No. 1 or weak solution on the charge, then letting it stand a few hours and following with the No. 2 or strong solution in three portions. This was sprinkled on in the same way, much as a lawn would be sprinkled, except that a few hours were allowed to elapse before the addition of each portion. The solution was allowed to drain out as fast as it would and no hydrostatic pressure built up in the tank. The No. 1 solution was precipitated, made up in acid, and used as the No. 2 solution for the next leach. The No. 2 solution was returned and used for the No. 1 in the next leach.

Accordingly, an automatic sprinkler was designed for this plant, and a lead pan was put into the bottom of the leaching tank, to prevent leakage.

The first six leaches were all subjected to the sprinkling system, and were treated in much the same way, except variations in acid and salt strengths. These show in the table of tank leaches. As far as the "sprinkling system" goes, it seems to have done about as good work as the later "flooding system," considering the class of calcine used at that time. The furnace was not making very good calcine until Oct. 20, and the first four leaches had been completed at that time. However, the flooding system offers fewer difficulties and dispenses with all automatic sprinklers, and, if anything, does better work. When a tank is flooded with solution, all parts of the calcine are apparently more apt to be saturated with acid than by the sprinkler system. However, the average results of the first six leaches come as near to the results from the laboratory leaches as those of the later ones.

Leach No. 7, the first one in which the flooding system was used, gave rather poor results. This was due entirely to improper washing. The tailings sample after washing in the laboratory gave a result of 0.096 per cent. copper in comparison with 0.135 per cent. copper after the wash in the leaching tanks. Until this leach, at times there was a good deal of fine material and a good deal of slime in the feed. This hindered the percolation, and resulted in poor extraction and imperfect washing. Classifiers were installed in the mill to give a more perfectly deslimed feed. Leach No. 8 was very similar to leach No. 7. However, it gave a considerably better extraction percentage on the copper, but

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In leach No. 9, a new scheme was tried. Air under 90 lb. pressure was connected under the filter bottom of the tank. The No. 1 solution was added, circulated down to 0.5 per cent. $H_2SO_4$, and replaced with the No. 2 solution. This was then drained for about 8 hr. In that time, most of the solution which would drain had come off. The air was then turned on for 8 hr. This was repeated three times, the air coming up through the warm, moist calcine being about 40° C. and it seemed as though its oxidizing action on the calcine was sure to benefit the extraction. This was tried in some of the later leaches, but seemed to help them very little, if at all. Leach No. 9 gave an exceptionally good extraction. However, it is doubtful, from later results, whether the aeration was responsible, as the calcine was very good and also the percolation. In this leach, the top and bottom of the tank were sampled separately. The bottom showed about 1 per cent. poorer extraction than the top.

Leach No. 10 was made on a 6-ft. depth, or 224 tons, of calcine. An attempt was made to determine if the shallower bed would equalize the results in the top and bottom of the tank. The extraction on the bottom was 2 per cent. poorer than on the top. On leach No. 11, a copper and silver balance was made, in which the calcine, tailings, and all solutions were measured, sampled, and assayed. This leach was the first of the oxidizing-roasted material. It had the same treatment as leach No. 10, except that one portion of the No. 2 solution was added under the filter bottom and forced up through the calcine. This method gave the bottom of the tank the benefit of the first application of the warm strong acid. The results show a much better extraction at the bottom than at the top of the tank. There is such a wide variation in the other direction, that it looks as though perhaps there was an error in sampling or analysis. On none of the succeeding leaches where this was tried was the extraction better at the bottom than at the top of the tank. This method is worth consideration, at any rate.

Leach No. 12 had two portions of acid added at the bottom and two portions at the top. In this case, the top gave an extraction nearly 3 per cent. better than the bottom, in spite of adding the solution at the bottom. Aeration also was used on this tank and the air heated before going in. Leach No. 13 had no aeration and all of the solution was added at the top. Leach No. 14 was started with an $H_2SO_4$ solution with no salt. It was planned to run this solution through, and determine whether it would dissolve enough of the copper so that it could be precipitated on the scrap iron and all of it be discarded. In this way, the chloride solutions would not have so much copper to take up, and, therefore, when precipitated, would not take so much iron in solution or become so foul. This scheme would cut down the amount of discard solution and salt loss. The first soultion only dissolved about one-half of the copper and the cycle was prolonged to such an extent that it seemed advisable to abandon the idea. A balance was also made on this leach and 98.5 per cent. of the copper was accounted for. In this leach the silver extraction was poor. An attempt was made to put the wash water on at the bottom; it was then changed about and started on at the top. In this way, some silver which was held in solution by the salt was precipitated in the tailings, due to the dilution with the wash water. The silver results on this leach were thrown out when averaging the results.

Leach No. 15 gave the best results of all the leaches. It had rather a high calcine—0.713 per cent. Cu—and percolated very readily and had about a six-day treatment. In this case, the strong acid necessary to bring the solutions up to strength was added to the stream of solution as it went on to the charge; 55 lb. of acid per ton of calcine was added in this leach. The No. 2 solution was put on and drained, then another portion put on to re-saturate it, and to this portion enough acid was added so that a zone of 15 per cent. acid traveled down through the charge. The repeated draining and re-saturating seem to help considerably in the extraction. A new scheme was tried in the washing which seemed to give excellent results, and was continued through all the rest of the leaches. Salt, to the amount of 1 per cent. of the weight of the charge in the tank, was spread on top of the leached calcine just before the wash water was added. This strong zone of salt solution traveled down through the charge and dissolved or washed out any silver chloride remaining. The salt going down first, went into the solution tanks to take the place of the discard solutions; thus no, or very little, salt found its way into the wash-water tanks.

Leach No. 16 was a very successful one, the percolation being very good. About 50 lb. of acid was used per ton of calcine, and added to the No. 2 solution as it went on. Aeration was used. The No. 1 solution was added and circulated down to 0.6 per cent. $H_2SO_4$ from 4.2 per cent. Then it was replaced with one-half of the No. 2 solution. This first half was then drained, and followed down with the second half of No. 2 solution, this portion having part of the strong acid added to it. The tank was then drained to about 10 per cent. moisture and aerated for 8 hr. The air coming up through the calcine, moistened with, say, an 8 to 10 per cent. $H_2SO_4$ solution, was expected to give excellent conditions for oxidation and subsequent solution. The air may be, and probably is, of some advantage, but it is so small as to be almost inappreciable. Also, aeration tends to prolong the cycle considerably. The repeated draining and re-saturation are thought to be more beneficial than the aeration. When a charge is drained and then re-saturated, all particles are bound to get a fresh supply of acid, while circulation does not accomplish quite the same end. During circulation, the solution travels slowly down through the charge, taking the easiest course, and if there are any softer portions they get more than their share of the acid, and harder places get less. In this leach there was about 1 per cent. difference in extraction between the regular extraction and that using a laboratory washed tailings as a basis for calculation.

Leach No. 17 was treated the same as No. 16, with the exception that the whole amount of acid was added to the second half of the No. 2 solution as it went on. This brought the acid strength up to about 18 per cent. $H_2SO_4$ for this portion. This was allowed to travel down through the calcine, replacing the first half. The charge was then aerated and the first half of the No. 2 solution returned, and the total No. 2 solution circulated was down to the same acid value as the No. 1 solution had when it went on. There was rather a large difference between the extraction on the top and bottom, and the washing could have been improved upon also.

In leach No. 18, the same solutions which were used in No. 17 were used without precipitating out the copper. They were made up in acid strength, however. The idea was to see if it was possible to run the solutions higher in copper content, without interfering with efficient leaching. The results were not very satisfactory. Using the richer copper solutions made washing of the charge much more difficult and also the variation between extractions on the top and bottom was larger than it should have been.

Leaches 19 and 20 were run side by side and at the same time. Both were treated with No. 1 solution, and then one had No. 2 solution added to it, and its drainage of No. 2 solution was lifted to the top of the other charge. The two leaches were see-sawed back and forth in this way several times; that is, one was drained as fast as possible and the drainage put on top of the other tank, adding, of course, its proportion of strong acid. This was to accomplish the large number of drainings and re-saturations spoken of above, without the use of spare or sump tanks. The scheme worked very well as far as time and the handling of solutions went. It is possible to drain a 10-ft. depth of this material to about 10 per cent. moisture in 6 to 7 hr. Leach 19 had 49 lb. $H_2SO_4$ per ton added to it and 48 lb. was added to leach 20.

The sluicing of tailings is a very simple and cheap operation. Seven million gallons of water per 24 hr. will sluice and carry away all the tailings which two men can sluice out of five 12-in. gates in the bottom of a tank. This amount of water was available and used, but probably much less than this would be sufficient. The greatest difficulty is at the start, when a hole is first opened up. The sand caves in and it takes a very large amount of water to carry away this sudden influx of sand into the tail race. Two men could sluice 400 tons from one of the tanks used here in about 5 hr.

There is not much to be said with reference to the precipitating. The launders were filled with scrap iron and the solution circulated through them. At 30° C., a 2 per cent. Cu solution, carrying 0.7 per cent. $H_2SO_4$, was precipitated to 0.1 per cent. Cu when circulating at the rate of 8 to 10 gal. per minute.

This strong copper solution precipitated as a very good cement copper. It was flocculent, and, on wrought iron, merely touching the iron would break the copper off and leave a fresh iron surface. The cement ran from 75 to 85 per cent. copper.

The hard or cast scrap iron was also tried. At first, the copper seems to precipitate on it as fast as on the soft iron, but a layer of copper quickly plates on it, and the cleaning up is a pretty expensive operation. Every piece must be handled separately, brushed, and most often scraped, before the iron is fit for further precipitation. By using malleable iron scrap, sweeping is hardly necessary, if the iron can be moved a little occasionally. The copper drops off and to the bottom of the launder immediately. The iron consumption was about 1.15 lb. per pound of copper.

## General

A copper tube was used for all tailings sampling. Iron cannot be used because of the precipitation on it of any copper in solution. The copper tube was closed at the lower end and brought to a sharp point. A slot was cut its full length, and one side bent out a little to form a cutting edge. A piece of rubber hose was pushed into the sampler, just filling it, then it was driven down through the charge, the hose withdrawn and the tube turned several times. In this way, the cutting edge filled the tube with tailings representing that part of the tank. This sampler was checked several times, by opening up a hole to the bottom of the charge and sampling up the side of the hole with a wooden scoop. If there was any abrasion of the copper off the tube, it did not appreciably affect the sample.

It requires about 20 per cent. of the weight of the calcine in weight of solution to saturate the charge. This assumes the solutions at a specific gravity of 1.00, while in reality they have a specific gravity of about 1.25.

It requires about 40 per cent. of the weight of the charge in wash water for a reasonably good wash.

The acid consumption will not exceed 50 lb. $H_2SO_4$ per ton of charge and the salt lost in solution discard will not be more than 1 per cent. of the weight of calcine, probably much less. By figuring acid consumptions on each leach, and using acid content of each solution, before going on and after coming off the calcine, the acid consumption on the first

---

14 leaches averag
per ton was adde
not very much so.
lb. consumption
little effect on the

The silver has
extent. This wou
coated and precip
addition of water,
forms in the botto
to be cleaned up
in the scrap-iron l

The accompan
there is not much

The feed from
copper, about 5
Ninety tons per 24
furnace of the type
its dry weight. T
About 40 per cent.

On 14...
On 40...
On 60...
On 90...
On 110..
On 160..
On 200..
Through

Under conditio
that an 85 per cen
probably 86 or 87
of copper per ton
plant, and built fo
encountered, as th
plant, depended on
and cooling equip
were caused by tro

14 leaches averages about 25 lb. per ton. On the last six, 50 lb. of acid per ton was added. This may have given somewhat better results, but not very much so. It seems as though perhaps the extra acid of the 50-lb. consumption was used in taking up iron and alumina, and had very little effect on the copper remaining in the charge.

The silver has a tendency to precipitate on the lead linings to a small extent. This would not offer much difficulty, as the lead rapidly becomes coated and precipitation ceases. The solutions, on cooling and on the addition of water, drop some of the silver out as silver chloride. This forms in the bottom of the solution tank to more or less extent and has to be cleaned up periodically. All of the silver in solution precipitated in the scrap-iron launders with no trouble whatever.

## SUMMARY

The accompanying Tables I, II, and III speak for themselves, so there is not much to explain about results.

The feed from the mill averages between 0.65 and 0.70 per cent. copper, about 5 per cent. moisture, and about 3 per cent. sulphur. Ninety tons per 24 hr. of this feed can be roasted in a 20-ft. MacDougall furnace of the type used here with a coal consumption of 2.75 per cent. of its dry weight. The calcine will contain about 0.6 per cent. sulphur. About 40 per cent. of the copper is water soluble.

*Screen Analysis of the Feed*

| Mesh | Per Cent. | Cumulative, Per Cent. |
|---|---|---|
| On 14 | 4.50 | 4.50 |
| On 40 | 50.31 | 54.81 |
| On 60 | 15.33 | 70.14 |
| On 90 | 11.45 | 81.59 |
| On 110 | 6.54 | 88.13 |
| On 160 | 5.52 | 93.65 |
| On 200 | 2.86 | 96.51 |
| Through 200 | 5.31 | 101.82 |

Under conditions which would apply in a large plant, it is expected that an 85 per cent. extraction can be made on the copper, and very probably 86 or 87 per cent. A tailing carrying between 2 and 2½ lb. of copper per ton should be made. In a plant as small as this 80-ton plant, and built for temporary use, a great many petty annoyances are encountered, as the running of the furnace, and therefore of the whole plant, depended on so many small pieces of machinery in the conveying and cooling equipment. Not 10 per cent. of the furnace shutdowns were caused by troubles with the furnace itself. Naturally, the furnace does much better roasting, and with a less coal consumption, when it is running continuously or nearly so.

No salt is necessary in the roast for the better extraction of the copper. It would increase the silver extraction from 75 to 90 per cent., but this extra 15 per cent. of the silver recovered would not pay for increased cost of salt, installation, and operation of an apparatus to catch the values in the gases. This recovery of fume values would probably not be much over 90 per cent. The chloridizing of the silver is done in the leaching tanks.

### *Summary of Results from Laboratory Leaches During Oxide-Chloride Period*

The extraction percentages on both copper and silver assume complete recovery of volatilized values.

No silver assays were made on the feed, an average result of 0.55 oz. per ton being used in figuring extraction.

| | |
|---|---|
| Recovery of copper, per cent | 86.7 |
| Recovery of silver, per cent | 94.3 |
| Pounds copper per ton in feed | 12.48 |
| Pounds copper per ton in tailings | 1.64 |
| Pounds copper per ton recovered | 10.84 |
| Average feed per 24 hr., tons | 90.8 |
| Average salt consumption, per cent | 1.04 |
| Average coal consumption, per cent | 2.94 |

### *Summary of Results from Tank Leaches*

#### Oxide-Chloride Period

The extraction percentages of silver and copper during the chloridizing period are figured by using the copper and silver values in the feed and assuming all volatilized values recovered.

| | |
|---|---|
| Pounds copper in feed per ton | 12.04 |
| Pounds copper in tails per ton | 2.54 |
| Pounds copper recovered per ton | 9.50 |
| Per cent. extraction on copper | 78.9 |
| Oz. silver per ton in feed | 0.55 |
| Oz. silver per ton in tails | 0.15 |
| Per cent. extraction on silver | 72.9 |

#### Oxide Period

| | |
|---|---|
| Pounds copper in calcine per ton | 13.58 |
| Pounds copper in tails per ton | 2.12 |
| Pounds copper recovered per ton | 11.46 |
| Per cent. extraction on copper—top ½ of tank | 86.2 |
| Per cent. extraction on copper—bottom ½ of tank | 82.8 |
| Per cent. extraction on copper—total tank | 84.4 |
| Per cent. extraction copper—tails washed | 86.0 |
| Oz. silver in calcine per ton | 0.57 |
| Oz. silver in tails per ton | 0.15 |
| Per cent. extraction on silver | 70.9 |

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TABLE I.—

| Date | | Rate of Feed Dry Weight |
|---|---|---|
| Oct. | 21 | 84.7 |
| | 22 | 88.1 |
| | 23 | 101.2 |
| | 24 | 103.1 |
| | 25 | 102.0 |
| | 26 | 104.7 |
| | 27 | 104.6 |
| | 28 | 103.5 |
| | 29 | 103.8 |
| | 30 | 104.6 |
| | 31 | 109.9 |
| Nov. | 1 | 108.3 |
| | 2 | 104.1 |
| | 3 | 104.7 |
| | 4 | 105.0 |
| | 5 | 104.7 |
| | 6 | 103.5 |
| | 10 | 100.3 |
| | 11 | 103.6 |
| | 12 | 91.9 |
| | 13 | 91.3 |
| | 14 | 91.5 |
| | 15 | 93.7 |
| | 16 | 96.0 |
| | 17 | 86.5 |
| | 18 | 83.4 |
| | 19 | 80.1 |
| | 20 | 80.8 |
| | 21 | 80.2 |
| | 22 | 78.9 |
| | 23 | 77.0 |
| | 24 | 76.2 |
| | 25 | 75.2 |
| | 26 | 75.2 |
| | 27 | 79.5 |
| | 28 | 78.7 |
| Dec. | 2 | 81.4 |
| | 3 | 82.1 |
| | 4 | 78.4 |
| | 5 | 82.6 |
| | 6 | 82.0 |
| | 7 | 82.2 |
| | 8 | 75.7 |
| | 9 | 73.6 |
| Average | | 90.8 |

TABLE I.—*Oxide-Chloride Roast. Results from Laboratory Leaches.*

| Date | Rate of Feed Dry Weight | Per cent. Moisture in Feed | Per cent. Coal | Per cent. Salt | Per cent. Copper in Feed | Per cent. Copper in Calcine | Per cent. Volatilized Copper | Average Temperature of Roast | Per cent. Copper as $Cu_2S$ in Tails | Per cent. Copper as Ferrite in Tails | Per cent. Total Copper in Tails | Oz. Silver per Ton in Tails | Extraction per cent. on Copper | Extraction per cent. on Silver |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oct. 21 | 84.7 | 4.5 | 3.00 | 1.16 | 0.587 | 0.504 | 0.083 | 1,070 | 0.048 | 0.060 | 0.108 | 0.05 | 81.7 | 91.0 |
| 22 | 88.1 | 7.0 | 3.29 | 0.70 | 0.580 | 0.539 | 0.041 | 1,050 | 0.044 | 0.061 | 0.105 | 0.03 | 88.0 | 94.6 |
| 23 | 101.2 | 4.0 | 3.38 | 1.24 | 0.590 | 0.531 | 0.059 | 1,060 | 0.045 | 0.068 | 0.113 | 0.05 | 81.0 | 91.0 |
| 24 | 103.1 | 6.5 | 2.75 | 1.16 | 0.555 | 0.478 | 0.077 | 1,000 | 0.039 | 0.044 | 0.083 | 0.03 | 85.0 | 94.6 |
| 25 | 102.0 | 7.5 | 3.00 | 0.93 | 0.501 | 0.460 | 0.041 | 1,000 | 0.036 | 0.029 | 0.065 | 0.03 | 87.0 | 94.6 |
| 26 | 104.7 | 5.0 | 2.81 | 0.86 | 0.478 | 0.448 | 0.030 | 930 | 0.040 | 0.022 | 0.062 | 0.02 | 87.1 | 96.5 |
| 27 | 104.6 | 5.0 | 2.82 | 0.97 | 0.545 | 0.521 | 0.024 | 950 | 0.038 | 0.025 | 0.063 | 0.04 | 88.4 | 92.8 |
| 28 | 103.5 | 6.0 | 2.95 | 0.94 | 0.549 | 0.519 | 0.030 | 1,000 | 0.043 | 0.036 | 0.079 | 0.03 | 85.9 | 94.6 |
| 29 | 103.6 | 6.5 | 3.16 | 0.87 | 0.555 | 0.501 | 0.054 | 1,000 | 0.040 | 0.039 | 0.079 | 0.02 | 84.0 | 96.5 |
| 30 | 104.6 | 5.0 | 2.68 | 0.86 | 0.555 | 0.466 | 0.089 | 1,000 | 0.044 | 0.046 | 0.090 | 0.03 | 83.8 | 94.6 |
| 31 | 109.9 | 5.5 | 2.84 | 0.84 | 0.596 | 0.519 | 0.077 | 1,000 | 0.044 | 0.046 | 0.090 | 0.03 | 85.9 | 94.6 |
| Nov. 1 | 108.3 | 5.5 | 2.90 | 0.86 | 0.596 | 0.549 | 0.047 | 980 | 0.044 | 0.044 | 0.088 | 0.03 | 85.4 | 94.6 |
| 2 | 104.1 | 5.5 | 2.94 | 1.04 | 0.614 | 0.553 | 0.061 | 930 | 0.043 | 0.028 | 0.071 | 0.03 | 88.5 | 94.6 |
| 3 | 104.7 | 5.0 | 2.92 | 1.03 | 0.550 | 0.516 | 0.034 | 900 | 0.042 | 0.024 | 0.066 | 0.03 | 82.8 | 94.6 |
| 4 | 105.0 | 5.0 | 3.24 | 1.14 | 0.562 | 0.533 | 0.029 | 900 | 0.040 | 0.020 | 0.060 | 0.03 | 89.4 | 94.6 |
| 5 | 104.7 | 5.0 | 2.96 | 1.06 | 0.550 | 0.528 | 0.022 | 900 | 0.050 | 0.029 | 0.079 | 0.05 | 85.6 | 91.0 |
| 6 | 103.5 | 6.0 | 2.82 | 1.01 | 0.597 | 0.562 | 0.017 | 920 | 0.050 | 0.020 | 0.070 | 0.03 | 87.8 | 94.6 |
| 10 | 100.3 | 8.5 | 3.03 | 1.16 | 0.699 | 0.643 | 0.056 | 930 | 0.046 | 0.026 | 0.072 | 0.03 | 89.8 | 94.5 |
| 11 | 103.6 | 6.0 | 2.92 | 1.15 | 0.712 | 0.661 | 0.051 | 930 | 0.067 | 0.022 | 0.089 | 0.03 | 87.7 | 94.6 |
| 12 | 91.9 | 10.5 | 3.21 | 1.26 | 0.612 | 0.556 | 0.056 | 960 | 0.038 | 0.038 | 0.076 | 0.02 | 87.7 | 96.6 |
| 13 | 91.3 | 9.3 | 3.13 | 1.37 | 0.625 | 0.556 | 0.069 | 920 | 0.042 | 0.033 | 0.075 | 0.04 | 88.1 | 92.8 |
| 14 | 91.5 | 6.0 | 2.72 | 1.25 | 0.587 | 0.562 | 0.025 | 930 | 0.043 | 0.032 | 0.075 | 0.04 | 87.2 | 92.8 |
| 15 | 93.7 | 6.0 | 2.93 | 1.25 | 0.656 | 0.619 | 0.037 | 930 | 0.065 | 0.027 | 0.092 | 0.03 | 86.0 | 94.6 |
| 16 | 96.0 | 4.0 | 3.03 | 1.10 | 0.675 | 0.662 | 0.013 | 1,000 | 0.076 | 0.029 | 0.105 | 0.05 | 84.5 | 91.0 |
| 17 | 86.5 | 6.0 | 3.50 | 1.22 | 0.644 | 0.619 | 0.025 | 1,020 | 0.060 | 0.045 | 0.105 | 0.03 | 83.7 | 94.6 |
| 18 | 83.4 | 4.0 | 2.74 | 1.25 | 0.669 | 0.637 | 0.032 | 950 | 0.045 | 0.037 | 0.082 | 0.03 | 87.8 | 94.6 |
| 19 | 80.1 | 6.0 | 2.80 | 1.22 | 0.700 | 0.650 | 0.050 | 940 | 0.064 | 0.022 | 0.086 | 0.02 | 87.7 | 96.5 |
| 20 | 80.8 | 5.0 | 2.79 | 1.10 | 0.710 | 0.704 | 0.006 | 930 | 0.078 | 0.024 | 0.102 | 0.04 | 85.7 | 92.8 |
| 21 | 80.2 | 5.0 | 2.99 | 1.12 | 0.761 | 0.742 | 0.019 | 1,000 | 0.072 | 0.034 | 0.106 | 0.05 | 86.0 | 91.0 |
| 22 | 78.9 | 5.5 | 2.97 | 1.18 | 0.692 | 0.616 | 0.076 | 960 | 0.054 | 0.033 | 0.087 | 0.04 | 87.6 | 92.8 |
| 23 | 77.0 | 4.0 | 2.88 | 1.10 | 0.660 | 0.597 | 0.063 | 960 | 0.053 | 0.025 | 0.078 | 0.02 | 88.2 | 96.5 |
| 24 | 76.2 | 5.0 | 3.08 | 1.19 | 0.692 | 0.660 | 0.032 | 960 | 0.086 | 0.015 | 0.101 | 0.03 | 85.6 | 94.6 |
| 25 | 75.2 | 6.0 | 2.75 | 1.24 | 0.666 | 0.609 | 0.057 | 1,000 | 0.048 | 0.017 | 0.065 | 0.03 | 90.4 | 94.6 |
| 26 | 75.2 | 6.0 | 3.04 | 1.10 | 0.622 | 0.560 | 0.062 | 1,000 | 0.042 | 0.023 | 0.065 | 0.02 | 89.6 | 96.5 |
| 27 | 79.5 | 4.5 | 2.58 | 0.92 | 0.684 | 0.610 | 0.074 | 1,010 | 0.055 | 0.022 | 0.077 | 0.02 | 88.9 | 96.5 |
| 28 | 78.7 | 6.0 | 2.91 | 0.97 | 0.912 | 0.874 | 0.038 | 1,020 | 0.076 | 0.031 | 0.107 | 0.03 | 88.4 | 94.6 |
| Dec. 2 | 81.4 | 3.5 | 2.60 | 0.83 | 0.595 | 0.533 | 0.062 | 980 | 0.054 | 0.021 | 0.075 | 0.03 | 87.5 | 94.6 |
| 3 | 82.1 | 3.0 | 2.62 | 0.88 | 0.651 | 0.620 | 0.031 | 1,020 | 0.048 | 0.018 | 0.066 | 0.04 | 89.8 | 92.8 |
| 4 | 78.4 | 7.5 | 2.77 | 0.95 | 0.620 | 0.558 | 0.038 | 1,000 | 0.055 | 0.014 | 0.069 | 0.03 | 89.0 | 94.6 |
| 5 | 82.6 | 3.5 | 2.62 | 0.77 | 0.614 | 0.571 | 0.057 | 1,000 | 0.038 | 0.027 | 0.065 | 0.04 | 89.3 | 92.8 |
| 6 | 82.0 | 4.5 | 3.09 | 0.78 | 0.614 | 0.601 | 0.087 | 950 | 0.046 | 0.028 | 0.074 | 0.03 | 88.0 | 94.6 |
| 7 | 82.2 | 4.0 | 3.02 | 0.84 | 0.614 | 0.539 | 0.025 | 950 | 0.047 | 0.029 | 0.076 | 0.03 | 87.8 | 94.6 |
| 8 | 75.7 | 11.5 | 3.12 | 0.87 | 0.614 | 0.595 | 0.081 | 950 | 0.047 | 0.031 | 0.078 | 0.03 | 87.4 | 94.6 |
| 9 | 73.6 | 14.0 | 2.75 | 0.90 | 0.645 | 0.558 | 0.013 | 950 | 0.049 | 0.048 | 0.097 | 0.02 | 85.0 | 96.5 |
| Average | 90.8 | 5.9 | 2.94 | 1.04 | 0.624 | 0.578 | 0.046 |  | 0.050 | 0.032 | 0.082 | 0.03 | 86.7 | 94.3 |

### TABLE II.—*Oxide Roast. Results from Laboratory Leaches*

| Date | | Rates of Feed Dry Weight | Per cent. Moisture in Feed | Per cent. Coal | Per cent. Copper in Feed | Per cent. Copper in Calcine | Average Temperature of Roast | Per cent. Copper as CuS in Tails | Per cent. Copper as Ferrite in Tails | Per cent. Total Copper in Tails | Oz. Silver per Ton in Calcine | Oz. Silver per Ton in Tails | Extraction per cent. on Copper | Extraction per cent. on Silver |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dec. | 10 | 81.0 | 5.5 | 2.72 | 0.580 | 0.568 | 950 | 0.047 | 0.030 | 0.077 | 0.44 | 0.07 | 86.7 | 84.2 |
| | 11 | 81.8 | 4.5 | 3.11 | 0.600 | 0.605 | 950 | 0.044 | 0.019 | 0.063 | 0.45 | 0.07 | 89.4 | 84.5 |
| | 12 | 82.6 | 4.0 | 2.72 | 0.584 | 0.574 | 960 | 0.051 | 0.020 | 0.071 | 0.44 | 0.08 | 87.6 | 81.8 |
| | 13 | 82.7 | 4.0 | 2.80 | 0.642 | 0.660 | 950 | 0.055 | 0.017 | 0.072 | 0.48 | 0.08 | 89.2 | 83.3 |
| | 14 | 81.2 | 5.0 | 2.87 | 0.672 | 0.710 | 940 | 0.074 | 0.017 | 0.091 | 0.62 | 0.10 | 87.3 | 84.0 |
| | 15 | 77.2 | 5.5 | 3.54 | 0.735 | 0.722 | 950 | 0.078 | 0.015 | 0.093 | 0.59 | 0.10 | 87.0 | 83.2 |
| | 16 | 78.7 | 4.5 | 3.05 | 0.710 | 0.703 | 970 | 0.079 | 0.041 | 0.120 | 0.56 | 0.09 | 82.9 | 83.9 |
| | 17 | 78.6 | 5.5 | 2.69 | 0.641 | 0.641 | 940 | 0.050 | 0.032 | 0.082 | 0.52 | 0.09 | 88.1 | 82.7 |
| | 18 | 81.0 | 6.0 | 2.50 | 0.732 | 0.707 | 930 | 0.060 | 0.019 | 0.079 | 0.55 | 0.07 | 88.8 | 87.3 |
| | 19 | 78.7 | 7.0 | 2.73 | 0.700 | 0.713 | 930 | 0.073 | 0.018 | 0.091 | 0.53 | 0.08 | 87.0 | 84.9 |
| | 20 | 77.4 | 9.0 | 2.54 | 0.601 | 0.601 | 930 | 0.048 | 0.025 | 0.073 | 0.54 | 0.08 | 87.9 | 85.3 |
| | 21 | 79.0 | 4.0 | 2.31 | 0.583 | 0.583 | 930 | 0.051 | 0.017 | 0.068 | 0.48 | 0.08 | 88.2 | 83.4 |
| | 22 | 81.1 | 5.0 | 2.59 | 0.696 | 0.663 | 930 | 0.063 | 0.015 | 0.078 | 0.56 | 0.08 | 88.3 | 85.7 |
| | 23 | 80.9 | 4.5 | 2.82 | 0.626 | 0.632 | 930 | 0.050 | 0.033 | 0.083 | 0.54 | 0.09 | 86.9 | 83.3 |
| | 24 | 79.4 | 7.0 | 2.57 | 0.645 | 0.676 | 930 | 0.048 | 0.027 | 0.075 | 0.62 | 0.12 | 89.0 | 80.7 |
| | 26 | 68.7 | 5.5 | 3.74 | 0.626 | 0.632 | 940 | 0.062 | 0.012 | 0.074 | 0.59 | 0.09 | 88.4 | 84.8 |
| | 27 | 80.7 | 5.5 | 2.90 | 0.654 | 0.666 | 930 | 0.047 | 0.024 | 0.071 | 0.60 | 0.08 | 90.2 | 86.6 |
| | 28 | 80.9 | 5.0 | 2.87 | 0.616 | 0.635 | 930 | 0.063 | 0.013 | 0.076 | 0.51 | 0.08 | 88.1 | 84.4 |
| | 29 | 79.2 | 7.5 | 2.95 | 0.585 | 0.610 | 920 | 0.054 | 0.023 | 0.077 | 0.44 | 0.07 | 87.5 | 84.2 |
| | 30 | 80.4 | 6.5 | 2.54 | 0.660 | 0.672 | 920 | 0.054 | 0.020 | 0.074 | 0.47 | 0.08 | 89.1 | 83.0 |
| | 31 | 81.1 | 5.0 | 2.03 | 0.710 | 0.697 | 920 | 0.058 | 0.022 | 0.080 | 0.58 | 0.08 | 88.6 | 86.3 |
| Jan. | 1 | 81.1 | 5.0 | 2.69 | 0.753 | 0.741 | 930 | 0.079 | 0.017 | 0.096 | 0.63 | 0.09 | 87.04 | 85.7 |
| | 2 | 81.3 | 3.5 | 2.84 | 0.716 | 0.691 | 920 | 0.064 | 0.015 | 0.079 | 0.46 | 0.06 | 88.56 | 87.0 |
| | 3 | 83.5 | 4.0 | 2.49 | 0.691 | 0.685 | 910 | 0.061 | 0.023 | 0.084 | 0.41 | 0.05 | 87.74 | 87.8 |
| | 4 | 81.0 | 5.0 | 2.76 | 0.740 | 0.672 | 920 | 0.065 | 0.023 | 0.088 | 0.49 | 0.08 | 86.90 | 83.7 |
| | 5 | 80.1 | 5.0 | 2.88 | 0.722 | 0.729 | 920 | 0.078 | 0.022 | 0.100 | 0.56 | 0.09 | 86.28 | 83.9 |
| | 6 | 81.8 | 4.0 | 2.75 | 0.735 | 0.729 | 920 | 0.054 | 0.016 | 0.070 | 0.42 | 0.06 | 90.40 | 85.7 |
| | 7 | 81.1 | 5.0 | 2.59 | 0.645 | 0.676 | 920 | 0.061 | 0.022 | 0.083 | 0.46 | 0.08 | 85.08 | 82.6 |
| | 8 | 82.3 | 3.5 | 2.47 | 0.657 | 0.608 | 920 | 0.053 | 0.016 | 0.069 | 0.48 | 0.06 | 88.65 | 87.5 |
| | 9 | 82.1 | 4.0 | 2.50 | 0.707 | 0.701 | 920 | 0.065 | 0.019 | 0.084 | 0.56 | 0.10 | 88.02 | 82.2 |
| | 10 | 79.2 | 4.5 | 2.72 | 0.707 | 0.688 | 920 | 0.061 | 0.019 | 0.080 | 0.51 | 0.07 | 88.68 | 86.3 |
| | 11 | 80.8 | 4.5 | 2.62 | 0.732 | 0.756 | 920 | 0.095 | 0.016 | 0.111 | 0.56 | 0.07 | 85.32 | 87.5 |
| | 12 | 80.7 | 4.0 | 2.59 | 0.756 | 0.750 | 920 | 0.081 | 0.027 | 0.108 | 0.58 | 0.09 | 85.60 | 84.5 |
| | 13 | 78.0 | 3.5 | 2.94 | 0.750 | 0.775 | 930 | 0.085 | 0.012 | 0.097 | 0.55 | 0.10 | 87.48 | 81.8 |
| | 14 | 83.0 | 3.0 | 2.66 | 0.856 | 0.818 | 950 | 0.109 | 0.022 | 0.131 | 0.70 | 0.12 | 83.99 | 82.9 |
| | 15 | 75.8 | 4.5 | 3.29 | 0.781 | 0.832 | 950 | 0.107 | 0.035 | 0.142 | 0.70 | 0.15 | 82.93 | 78.5 |
| | 16 | 76.5 | 3.0 | 2.69 | 0.732 | 0.725 | 940 | 0.074 | 0.024 | 0.098 | 0.62 | 0.13 | 86.48 | 79.0 |
| | 19 | 84.1 | 5.5 | 2.61 | 0.756 | 0.738 | 950 | 0.084 | 0.023 | 0.107 | 0.75 | 0.12 | 85.50 | 84.0 |
| | 20 | 73.2 | 4.0 | 2.92 | 0.787 | 0.795 | 960 | 0.083 | 0.023 | 0.106 | 0.67 | 0.12 | 86.32 | 82.1 |
| | 21 | 72.2 | 4.5 | 3.00 | 0.769 | 0.756 | 960 | 0.107 | 0.011 | 0.118 | 0.71 | 0.13 | 84.39 | 81.7 |
| | 22 | 72.3 | 4.5 | 2.76 | 0.756 | 0.775 | 980 | 0.089 | 0.024 | 0.113 | 0.52 | 0.10 | 85.42 | 80.8 |

TABLE II.—*Oxide Roast. Results from Laboratory Leaches. (Continued)*

| Date | | Rate of Feed Dry Weight | Per cent. Moisture in Feed | Per cent. Coal | Per cent. Copper in Feed | Per cent. Copper in Calcine | Average Temperature of Roast | Per cent. Copper as $Cu_2S$ in Tails | Per cent. Copper as Ferrite in Tails | Per cent. Total Copper in Tails | Oz. Silver per Ton in Calcine | Oz. Silver per Ton in Tails | Extraction per cent. on Copper | Extraction per cent. on Silver |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Jan. | 23 | 71.7 | 4.5 | 2.53 | 0.763 | 0.781 | 1,000 | 0.063 | 0.026 | 0.099 | 0.65 | 0.17 | 87.32 | 73.8 |
| | 24 | 72.3 | 4.0 | 2.94 | 0.738 | 0.732 | 1,000 | 0.063 | 0.029 | 0.092 | 0.58 | 0.14 | 87.43 | 75.8 |
| | 25 | 71.5 | 5.0 | 2.83 | 0.692 | 0.717 | 1,000 | 0.048 | 0.033 | 0.081 | 0.70 | 0.18 | 88.70 | 74.3 |
| | 26 | 76.3 | 5.5 | 2.62 | 0.625 | 0.630 | 960 | 0.040 | 0.030 | 0.070 | 0.55 | 0.14 | 88.88 | 74.5 |
| | 27 | 83.8 | 5.0 | 2.70 | 0.655 | 0.643 | 950 | 0.043 | 0.021 | 0.064 | 0.48 | 0.08 | 90.05 | 83.3 |
| | 28 | 84.8 | 6.5 | 2.74 | 0.631 | 0.655 | 940 | 0.041 | 0.024 | 0.065 | 0.54 | 0.10 | 90.08 | 81.5 |
| | 29 | 83.4 | 5.5 | 3.28 | 0.576 | 0.643 | 950 | 0.046 | 0.018 | 0.064 | 0.58 | 0.12 | 90.05 | 79.3 |
| | 30 | 84.0 | 6.0 | 2.71 | 0.613 | 0.619 | 930 | 0.042 | 0.019 | 0.061 | 0.48 | 0.09 | 90.15 | 81.2 |
| | 31 | 80.6 | 6.0 | 2.82 | 0.668 | 0.625 | 930 | 0.053 | 0.012 | 0.065 | 0.57 | 0.10 | 89.60 | 82.5 |
| Feb. | 1 | 82.7 | 4.5 | 2.62 | 0.686 | 0.704 | 950 | 0.046 | 0.025 | 0.071 | 0.59 | 0.11 | 89.91 | 81.3 |
| | 2 | 80.0 | 6.0 | 2.33 | 0.695 | 0.775 | 970 | 0.057 | 0.025 | 0.082 | 0.66 | 0.12 | 89.42 | 81.8 |
| | 3 | 81.5 | 5.0 | 2.27 | 0.702 | 0.695 | 960 | 0.046 | 0.027 | 0.073 | 0.66 | 0.15 | 89.50 | 77.3 |
| | 4 | 78.5 | 7.0 | 2.50 | 0.691 | 0.683 | 970 | 0.046 | 0.027 | 0.073 | 0.78 | 0.19 | 89.31 | 75.7 |
| | 5 | 74.8 | 4.5 | 2.35 | 0.641 | 0.634 | 980 | 0.035 | 0.032 | 0.067 | 0.49 | 0.15 | 89.43 | 68.1 |
| | 9 | 81.5 | 4.5 | 2.56 | 0.653 | 0.671 | 980 | 0.038 | 0.021 | 0.059 | 0.48 | 0.08 | 91.21 | 83.3 |
| | 10 | 74.4 | 12.0 | 3.15 | 0.641 | 0.659 | 960 | 0.041 | 0.025 | 0.066 | 0.47 | 0.08 | 89.98 | 83.0 |
| | 11 | 81.0 | 5.0 | 2.44 | 0.666 | 0.691 | 920 | 0.046 | 0.020 | 0.066 | 0.67 | 0.12 | 90.45 | 82.1 |
| | 12 | 80.8 | 5.0 | 2.49 | 0.703 | 0.716 | 930 | 0.080 | 0.009 | 0.089 | 0.83 | 0.15 | 87.57 | 81.9 |
| | 13 | 81.7 | 4.0 | 2.59 | 0.635 | 0.660 | 930 | 0.053 | 0.019 | 0.072 | 0.68 | 0.11 | 89.09 | 83.8 |
| | 14 | 81.5 | 4.0 | 2.89 | 0.594 | 0.600 | 950 | 0.038 | 0.019 | 0.057 | 0.56 | 0.11 | 90.50 | 80.3 |
| | 15 | 81.2 | 4.5 | 2.92 | 0.643 | 0.643 | 960 | 0.041 | 0.023 | 0.064 | 0.67 | 0.14 | 90.05 | 79.1 |
| | 16 | 81.3 | 4.5 | 2.82 | 0.637 | 0.655 | 960 | 0.035 | 0.034 | 0.069 | 0.61 | 0.11 | 89.47 | 82.0 |
| | 17 | 79.9 | 5.5 | 2.78 | 0.625 | 0.637 | 930 | 0.043 | 0.030 | 0.073 | 0.54 | 0.09 | 88.54 | 79.6 |
| | 18 | 81.3 | 5.5 | 2.61 | 0.613 | 0.619 | 930 | 0.038 | 0.024 | 0.062 | 0.61 | 0.11 | 89.98 | 82.0 |
| | 19 | 80.0 | 6.0 | 2.73 | 0.588 | 0.606 | 920 | 0.040 | 0.023 | 0.063 | 0.53 | 0.09 | 89.60 | 79.2 |
| | 22 | 80.6 | 4.5 | 2.78 | 0.588 | 0.600 | 920 | 0.033 | 0.031 | 0.064 | 0.56 | 0.09 | 89.33 | 84.0 |
| | 23 | 80.6 | 4.5 | 2.87 | 0.662 | 0.643 | 920 | 0.044 | 0.024 | 0.073 | 0.58 | 0.09 | 88.65 | 84.4 |
| | 24 | 80.6 | 6.0 | 2.61 | 0.649 | 0.686 | 930 | 0.042 | 0.027 | 0.069 | 0.47 | 0.08 | 89.94 | 83.1 |
| | 25 | 89.6 | 5.5 | 2.77 | 0.637 | 0.662 | 930 | 0.042 | 0.023 | 0.065 | 0.38 | 0.04 | 90.18 | 89.5 |
| Ave. | | 79.8 | 5.1 | 2.75 | 0.675 | 0.680 | | 0.058 | 0.023 | 0.081 | 0.57 | 0.10 | 88.09 | 82.5 |

| | |
|---|---|
| Recovery of copper, per cent. | 88.09 |
| Recovery of silver, per cent. | 82.5 |
| Pounds copper per ton in calcine | 13.6 |
| Pounds copper per ton in tailings | 1.62 |
| Pounds copper per ton recovered | 11.98 |
| Average feed per 24 hr. (tons dry wt.) | 79.8 |
| Average coal consumption, per cent. | 2.75 |

TABLE III.—*Results from Tank Leaches. Oxide-Chloride Roast*

| Leach Number | Tons Calcine | Per cent. Copper in Feed | Per cent. Copper in Calcine | Top Half | | Bottom Half | | Total Tank | | Washed Clean | | Pounds Copper Recovered per Ton | Oz. Silver per Ton in Feed | Oz. Silver per Ton in Tails | Per cent. Extraction on Silver | Temperature Solution C.° | Per cent. $H_2SO_4$ in No. 1 Solution | Per cent. NaCl in No. 1 Solution | Per cent. $H_2SO_4$ in No. 2 Solution | Per cent. NaCl in No. 2 Solution |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Per cent. Copper in Tails | Per cent. Extraction Copper | Per cent. Copper in Tails | Per cent. Extraction Copper | Per cent. Copper in Tails | Per cent. Extraction Copper | Per cent. Copper in Tails | Per cent. Extraction Copper | | | | | | | | | |
| 1 | 309 | 0.580 | 0.540 | ..... | ..... | ..... | ..... | 0.202 | 65.2 | ..... | ..... | 7.56 | 0.55 | 0.23 | 5.82 | 20 | 3.03 | 4.70 | 5.10 | 4.90 |
| 2 | 391 | 0.569 | 0.500 | ..... | ..... | ..... | ..... | 0.151 | 73.5 | ..... | ..... | 8.36 | 0.55 | 0.17 | 69.1 | 20 | 3.72 | 5.16 | 6.15 | 7.17 |
| 3 | 390 | 0.560 | 0.506 | ..... | ..... | ..... | ..... | 0.140 | 75.0 | ..... | ..... | 8.40 | 0.55 | 0.15 | 72.7 | 20 | 4.70 | 7.05 | 6.33 | 8.50 |
| 4 | 380 | 0.592 | 0.526 | ..... | ..... | ..... | ..... | 0.113 | 80.9 | ..... | ..... | 9.58 | 0.55 | 0.20 | 63.6 | 65 | 5.20 | 8.26 | 7.40 | 9.09 |
| 5 | 385 | 0.541 | 0.491 | ..... | ..... | ..... | ..... | 0.097 | 82.1 | ..... | ..... | 8.88 | 0.55 | 0.08 | 85.5 | 65 | 5.30 | 5.00 | 8.90 | 7.80 |
| 6 | 360 | 0.536 | 0.491 | ..... | ..... | ..... | ..... | 0.111 | 79.3 | ..... | ..... | 8.50 | 0.55 | 0.12 | 78.2 | 65 | 5.95 | 6.93 | 8.60 | 7.96 |
| 7 | 457 | 0.575 | 0.540 | ..... | ..... | ..... | ..... | 0.135 | 76.5 | ..... | ..... | 8.80 | 0.55 | 0.19 | 65.5 | 65 | 4.30 | 7.50 | 7.50 | 8.40 |
| 8 | 370 | 0.680 | 0.654 | ..... | ..... | ..... | ..... | 0.136 | 80.0 | ..... | ..... | 10.88 | 0.55 | 0.17 | 69.1 | 65 | 4.30 | 7.90 | 9.10 | 7.00 |
| 9 | 368 | 0.683 | 0.631 | 0.077 | 88.7 | 0.085 | 87.6 | 0.081 | 88.1 | ..... | ..... | 12.04 | 0.55 | 0.08 | 85.5 | 65 | 2.90 | 7.00 | 6.00 | 6.90 |
| 10 | 224 | 0.701 | 0.662 | 0.092 | 86.8 | 0.106 | 84.9 | 0.099 | 85.9 | ..... | ..... | 12.04 | 0.55 | 0.10 | 81.8 | 65 | 3.40 | 8.20 | 5.00 | 7.50 |
| Ave | ... | 0.602 | 0.554 | 0.085 | 87.8 | 0.096 | 86.8 | 0.127 | 78.9 | ..... | ..... | 9.50 | 0.55 | 0.15 | 72.9 | .... | ..... | ..... | ..... | ..... |
| *Oxide Roast* | | | | | | | | | | | | | | | | | | | | |
| 11 | 370 | 0.616 | 0.629 | 0.097 | 84.8 | 0.072 | 88.5 | 0.085 | 86.5 | 0.081 | 87.1 | 10.88 | 0.53 | 0.15 | 71.7 | 65 | 2.13 | 8.91 | 4.68 | 7.53 |
| 12 | 410 | 0.686 | 0.681 | 0.104 | 84.7 | 0.124 | 81.8 | 0.114 | 83.3 | 0.101 | 85.2 | 11.34 | 0.53 | 0.26 | 50.9 | 65 | 2.90 | 8.16 | 7.13 | 7.59 |
| 13 | 430 | 0.636 | 0.648 | 0.091 | 85.9 | 0.157 | 75.8 | 0.124 | 80.9 | 0.105 | 83.8 | 10.48 | 0.56 | 0.15 | 73.2 | 65 | 2.18 | 11.06 | 6.50 | 9.62 |
| 14 | 400 | 0.713 | 0.710 | 0.129 | 81.8 | 0.146 | 79.4 | 0.138 | 80.6 | 0.122 | 82.8 | 11.44 | 0.54 | 0.42 | 22.2 | 65 | 2.58 | 10.30 | 5.33 | 7.17 |
| 15 | 375 | 0.718 | 0.713 | 0.082 | 88.5 | 0.087 | 87.8 | 0.085 | 88.1 | 0.077 | 89.2 | 12.56 | 0.51 | 0.08 | 84.3 | 65 | 5.02 | 11.61 | 6.60 | 9.18 |
| 16 | 390 | 0.761 | 0.759 | 0.096 | 87.4 | 0.105 | 86.2 | 0.100 | 86.8 | 0.095 | 87.5 | 13.18 | 0.66 | 0.18 | 72.7 | 65 | 4.18 | 7.11 | 9.20 | 9.84 |
| 17 | 410 | 0.656 | 0.660 | 0.071 | 89.2 | 0.100 | 84.9 | 0.086 | 87.1 | 0.075 | 88.6 | 11.48 | 0.56 | 0.17 | 69.6 | 65 | 2.82 | 8.44 | 18.00 | 8.72 |
| 18 | 385 | 0.677 | 0.686 | 0.097 | 85.9 | 0.139 | 79.7 | 0.118 | 82.8 | 0.101 | 85.3 | 11.36 | 0.60 | 0.21 | 65.0 | 65 | 2.85 | 7.72 | 6.50 | 8.80 |
| 19 | 395 | 0.654 | 0.670 | 0.086 | 87.2 | 0.122 | 81.8 | 0.104 | 84.5 | 0.097 | 85.5 | 11.32 | 0.60 | 0.15 | 75.0 | 65 | 3.78 | 7.29 | 7.05 | 8.59 |
| 20 | 395 | 0.610 | 0.629 | 0.086 | 86.3 | 0.115 | 81.7 | 0.101 | 84.0 | 0.096 | 84.7 | 10.54 | 0.58 | 0.15 | 74.1 | 65 | 4.65 | 10.15 | 7.05 | 9.50 |
| Ave. | ... | 0.673 | 0.679 | 0.094 | 86.2 | 0.117 | 82.8 | 0.106 | 84.4 | 0.095 | 86.0 | 11.46 | 0.57 | 0.17 | 70.9 | .... | ..... | ..... | ..... | ..... |

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# Leaching Experiments on the Ajo Ores

BY STUART CROASDALE, DENVER, COLO.

(Salt Lake Meeting, August, 1914)

Not long ago I was called upon to conduct some experiments on the treatment of ores from the New Cornelia copper mine, Ajo mountains, Arizona, for the Calumet & Arizona Copper Co. The problem was a very interesting one and contained some unusual features. Incidental with this problem was the utilization of a large amount of low-grade pyrite in the Bisbee mines of the company, provided this could be accomplished by any feasible method.

The New Cornelia mine is situated 45 miles south of Gila Bend, the nearest railroad point, on the Southern Pacific Railroad. It is about 160 miles, almost due west, from Tucson. This section is one of the most arid in the United States. The normal annual precipitation, as given by the United States Weather Bureau covering a period from 1870 to 1901, is 3 to 5 in. During June and July, 1913, the records kept by the company gave the following results. These are all I have available, but they show the enormous evaporation that can be expected, which may be a factor in leaching operations on a large scale.

| | Temperature, Degrees F. | | |
|---|---|---|---|
| | High | Low | Average |
| June | 112 | 62 | 84.0 |
| July | 115 | 71 | 87.8 |

| Evaporation | June | July |
|---|---|---|
| Concrete tank, inches | 11.7 | 10.72 |
| Iron tank, inches | 14.8 | 13.07 |
| Rainfall, inches | None | 0.77 |
| Cloudy days | None | 10.00 |

Aside from several springs about 10 miles from the property, the nearest known water in quantity at the time these experiments were made was the Gila river at Gila Bend, 45 miles distant. Part of the development of the property of course included drilling for water in the valley, which was in progress at the conclusion of my experiments.

The ore deposit itself is unusual. It consists of an intrusive plug of monzonite or granite porphyry. Chalcopyrite, bornite, and magnetite are finely disseminated throughout the magma in sufficient quantities to make the greater part of the mass commercial ore to a certain depth.

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Pyrite is also present, and when the proportion of pyrite has exceeded chalcopyrite in the oxidized zone the kaolinization of the porphyry has been greater, which has an important bearing on the ore treatment. Erosion has removed the surrounding country rock and left the plug sticking out at the base of the mountains as two or three cone-shaped buttes, without overburden of any description.

Oxidation has taken place *in situ.* Owing to the aridity of the country, there has been no leaching and no secondary enrichment. Instead of following the contour of the surface, as might be expected, the drill records (in the mine model) show oxidation to have taken place quite uniformly downward throughout the mass and the division between the oxidized and sulphide ores is almost a horizontal plane. The transition zone, or partly oxidized zone, between the oxidized and sulphide ores is likewise shown to be quite narrow—much narrower than would be expected.

The oxidized ores amount to about one-third of the total ore developed. The greater part of the copper exists as carbonate, although there is some silicate and some oxides, including cuprite. There is also a small percentage of sulphide as residual chalcopyrite and intermediate forms.

The oxidized iron exists in both ferrous and ferric condition, both soluble in acid.

While the chalcopyrite is quite generally disseminated throughout the magma, there seems to have been a tendency for it to segregate in some portions, thus producing a higher-grade ore. The average grade of ore used for experimental purposes was placed between 1.5 and 2.0 per cent. copper. What the ultimate average grade will be will depend upon the cost of treatment.

## METHODS OF TREATMENT

From the foregoing it will be readily seen that the conditions of the problem demand simplicity of process and large scale of operations. Of course a railroad will be built to the mine, but whether the ore will be brought to water or water will be brought to the ore are yet factors to be considered and may have their bearing to a certain extent on the method of treatment adopted, when freight and fuel costs are estimated.

Methods of leaching with solutions of reducible salts, like ferric sulphate, ferric chloride, and cupric chloride, have some advantage in their solvent power on cuprite and chalcocite or other intermediate sulphides, but have little action on chalcopyrite. These salts are expensive and their value as commercial solvents depends upon their regeneration by some cheap method of oxidation after the dissolved copper has been precipitated. This difficulty has not yet been overcome and the results from attempts to use these methods have been disappointing even in the hands of skilled metallurgists.

The same may be said of sulphurous acid and ammonia processes.

Two methods of treatment, however, are available, and both are entirely reliable and feasible under the conditions involved. One of these is the old Henderson process of roasting with salt, and the other is leaching the raw ore with sulphuric acid. Under the head of "Chloridizing Roast with Salt," I include the so-called sulphatizing roast of Mr. Wedge, in which he finds the addition of a small percentage of salt very beneficial; and also the modification used by Mr. Laist at Anaconda, in which he reduces the consumption of salt, as well as the losses by volatilization, by giving the ore a preliminary roast before adding the salt.[1]

A comparison of these two methods may be made briefly as follows:

By using the chloridizing roast, all ores on the property could be treated by the same process—oxidized, sulphide, and intermediate. This would mean the construction of only one plant. The average extraction of the copper would probably be higher than that obtained from acid leaching and the small amount of silver in the ore would be recovered to a large extent. By mixing the ores, little if any sulphur would have to be added as pyrite. The only chemicals required would be salt, to the extent of 5 to 10 per cent. of the ore treated, and possibly a small amount of pyritic ore. Both of these could be transported in ordinary freight cars. There would be less corrosive solutions to handle. There would be a minimum amount of iron and alumina passing into solution. There would be no appreciable absorption of copper by slimes.

On the other hand, this method would require dry crushing of the ore to 20 or 40 mesh, which would be troublesome if not prohibitive on the oxidized ores on account of the difficulty in controlling the poisonous dust, in addition to the expense of grinding. It would involve a roasting cost. It would mean a more expensive plant, and a more extensive plant for the same capacity, due to the slower percolation of the fine material, which would require a much larger vat area of less depth to hold the tonnage required. It would mean a supply of cheap salt. A chemical precipitant would probably have to be used to recover the copper.

By leaching with sulphuric acid, the oxidized ore can be treated raw and need not be crushed finer than ½ in. or 2-mesh size, or perhaps coarser, as the experiments will show. Owing to the high oxidation of the surface ores and apparently small zone of partly oxidized ores, a large tonnage can be expected to give a comparatively high extraction by this method. Sulphuric acid can be made as a by-product at the roasting

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[1] Stuart Croasdale: *Engineering and Mining Journal*, vol. lxxvi, No. 9, pp. 312 to 314 (Aug. 29, 1903); *Trans.*, xlvi, 378 (1913); *Mining Magazine*, vol. x, No. 3, pp. 200 to 204 (March, 1914).

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plant of the Calumet & Arizona Co. at Douglas, or if the calcines are converted into sponge iron and used as a precipitant for copper, the low-grade pyrite from Bisbee can be cheaply transported and acid made at the mine. If electrolytic precipitation can be used, a small percentage of the acid consumed can be regenerated. This method of extraction will permit of less expensive plant construction for the oxidized ores.

On the other hand, sulphuric acid alone will extract none of the copper existing as sulphide, only half of the copper existing as cuprite, and may be indifferent about the silicate of copper. It will extract none of the precious metals. Owing to the character of the oxidation of the ore, already mentioned, considerable iron and alumina pass into solution as readily as the copper, which will seriously interfere with any form of electrolytic precipitation and render the amount of acid regenerated a doubtful asset when compared with the amount consumed. As an offset to this objection, some of the iron is in a ferric condition, which assists materially in the solution of the minerals mentioned above.

If acid is made at Douglas, it will have to be transported several hundred miles in tank cars, which will have to be returned empty. If acid is made at the mine from low-grade pyrite, a gain will be made in transportation, but the cost of an acid plant will be added to the cost of the leaching plant and the calcines will have to be utilized. Almost an entirely new plant will have to be constructed for treatment of the intermediate and sulphide ores.

The problem is clearly one in arithmetic as well as metallurgy, so laboratory experiments were made on both methods.

## LABORATORY EXPERIMENTS

The ore furnished me for these experiments came from the earlier development of the property and the oxidized ores were from very near the surface, but were less kaolinized than those received later for the larger experiments.

The analyses of the ores were as follows:

| | Oxidized Per Cent. | Sulphide Per Cent. |
|---|---|---|
| $SiO_2$ | 66.23 | 66.08 |
| Fe | 6.40 | 4.50 |
| $Al_2O_3$ | 13.75 | 11.35 |
| CaO, total | 0.56 | 0.55 |
| CaO sol. in dilute acid | 0.31 | 0.15 |
| S, total | 0.19 | 2.09 |
| S as sulphate | 0.03 | 0.03 |
| Zn | 0.10 | 0.10 |
| Cu, total | 2.03 | 2.75 |
| Cu sol. in 10 per cent. $H_2SO_4$ | 1.84 | 0.22 |
| Au, oz. per ton | 0.01 | 0.01 |
| Ag, oz. per ton | 0.22 | 0.18 |

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On a 2 per cent. ore, a variation of 0.01 per cent. in the percentage of copper in the tailings makes a difference of 0.5 per cent. in the percentage of extraction. This must be kept in mind when comparing the results of these experiments, for several hundredths of 1 per cent. may be within the limits of error in sampling and chemical analyses.

### *Chloridizing Roast with Salt*

*Oxidized Ores.*—The ore was crushed to 20 mesh. The experiments were conducted in an assay furnace at a low red heat or at estimated temperatures of 1,000° to 1,300° F. No attempt was made to condense the volatile copper chloride fumes.

The roasted ore was leached 24 hr. with a 1 per cent. sulphuric acid solution which was supposed to correspond to the solutions from the condensing towers at the Pennsylvania Salt Works, Philadelphia, where this method of copper extraction has been in use for a long time.

In a Wedge, or other multiple-hearth furnace, a particle of ore remains in the roasting or chloridizing atmosphere several hours. My first experiments were on variation in time of roasting, which ranged from 1 to 6 hr.

Sulphur was added, in the form of pyrite, in slight excess of that necessary to combine with the copper as CuS, or 1.2 per cent; 10 per cent. salt was added, which is twice the amount necessary to form the normal chloride of copper, but this might be of some advantage, as will be mentioned later.

At the end of 1 hr., 11.8 per cent. of the copper had volatilized and 65.8 per cent. had been rendered soluble in the roasted ore, which gave a total extraction of 77.6 per cent.

At the end of 6 hr., 69.0 per cent. of the copper had volatilized and 7.3 per cent. remained soluble in the roasted ore, which gave a total extraction of 76.3 per cent.

The tests, at 1-hr. intervals between these extremes, showed a gradual increase in the percentage of copper volatilized, with substantially the same total extraction.

In the next series of experiments the sulphur was varied from 1.2 to 2.5 per cent. The salt was kept constant at 10 per cent. and the time of roasting in each case was 1 hr.

With 1.5 per cent. sulphur the results were 15.5 per cent. volatilization of the copper, and 70.3 per cent. soluble copper in the roasted ore, or a total extraction of 85.8 per cent.; 2.1 per cent. sulphur gave 21.1 per cent. volatilization and 64.7 per cent. soluble copper, or a total extraction of 85.8 per cent. Both higher and lower sulphur contents gave lower total extractions.

In the third series of experiments the sulphur was kept constant at

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1.5 per cent. and the time of roasting at 1 hr. The salt varied from 5 to 15 per cent.

The lowest volatilization and highest total extraction were obtained with 10 per cent. salt, which, as stated above, were 15.5 and 85.8 per cent., respectively.

The result with 5 per cent. salt was a volatilization of 46.2 per cent. and a total extraction of 71 per cent. This amount of salt is near the theoretical quantity necessary to form the normal chloride of copper. My previous work on the volatilization of metals as chlorides proved that, other conditions being equal, volatilization greatly increases as the relations between the metal, salt, and sulphur approach theoretical proportions.

The use of 15 per cent. salt gave 23.2 per cent. volatilization and a total extraction of 80 per cent. Other proportions of salt gave intermediate results.

The foregoing experiments gave the best results when the ore, containing a little more than 2 per cent. copper, was roasted 1 hr. with 10 per cent. salt and 1.5 per cent. sulphur.

As a final test, these factors were all raised as follows: salt, 12.5 per cent.; sulphur, 2 per cent.; time, 1.5 hr. The results were, 24.2 per cent. of the copper volatilized and 62.3 per cent. soluble, or a total extraction of 86.5 per cent., which is substantially the same as before. The tailings from this test were leached an additional 24 hr. with a 5 per cent. sulphuric acid solution containing 7 per cent. salt, which increased the extraction to 90 per cent. In all probability a total of 48 hr. leaching with the weaker acid would have accomplished the same result.

*Sulphide Ores.*—The average analysis of these ores has been given. The copper existed as chalcopyrite. The experiments were conducted in a manner similar to those on the oxidized ores. The ore was crushed to 20 mesh. No sulphur was added. The percentage of salt ranged from 10 to 15 per cent. and, the ore being higher grade, the time of roasting was extended to 1.5 and 2 hr., although this was probably unnecessary. Owing to difficulty in controlling the furnace, the temperatures used were higher than they should have been.

The results were:

| | 1<br>Per Cent. | 2<br>Per Cent. | 3<br>Per Cent. |
|---|---|---|---|
| Salt used | 10.0 | 12.5 | 15.0 |
| Copper volatilized | 68.8 | 44.1 | 56.0 |
| Soluble copper | 20.0 | 47.9 | 37.2 |
| Total extraction | 88.8 | 92.0 | 93.2 |

Leaching these tailings an extra 24 hr. with 5 per cent. sulphuric acid solution containing 5 per cent. salt, extracted no more copper. There was no difficulty in extracting all the soluble copper in the roasted ore with a 1 per cent. acid solution.

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While the temperatures, as stated above, were higher than they should have been, these results confirm those made a number of years ago, when I found that copper is more readily volatilized from chalcopyrite by the chloridizing roast than from any other mineral.

*Mixed Oxidized and Sulphide Ores.*—The following experiments were conducted by the Wedge Mechanical Furnace Co., at Philadelphia, to determine the merits of a sulphating roast. Their report is as follows:

Test No. 1. The oxidized ore was ground to 20 mesh and the sulphide to 40 mesh. Two parts of sulphide were mixed with one of the oxide and the mixture was roasted 3.5 hr. at temperatures increasing from 550° to 1,180° F. The roasted ore was leached with 2° B. sulphuric acid solution. The extraction was 85.5 per cent.

Test No. 2. The same mixture of ores was roasted 3 hr., with 5 per cent. salt added, at temperatures ranging from 400° to 990° F. The roasted ore was leached with 2° B. hydrochloric acid solution, which gave an extraction of 94.4 per cent.

Test No. 3. The same ore mixture was used as before, and 5 per cent. salt was added. The mixture was roasted 2.5 hr. at temperatures from 500° to 860° F. The acid wash was 2° B. hydrochloric acid. The extraction was 96.0 per cent. of the copper.

Test No. 4. The preceding test was repeated with the addition of 2 per cent. pyrite (containing 47 per cent. sulphur) to the mixture. The ore was roasted 2.5 hr. at 600° to 900° F. and the roasted ore leached with 3° B. hydrochloric acid. The extraction was 93 per cent.

Test No. 5. Equal parts of oxidized and sulphide ore were used and 5 per cent. salt added. Other conditions being the same, 94 per cent. extraction was obtained.

Test No. 6. Both ores were ground to 40 mesh and mixed in equal parts with the addition of 5 per cent. salt and 2 per cent. pyrite. The extraction was 94 per cent.

Test No. 7. Test No. 6 was repeated, except that 3 per cent. pyrite was added instead of 2 per cent. The mixture was roasted 2 hr. at temperatures from 400° to 900° F. The extraction was 98 per cent. of the copper.

*Summary of Results.*—These experiments are sufficient to show that an extraction of 90 to 95 per cent. of the copper can be expected by a chloridizing roast on all the ores whether mixed or treated separately, but it would be preferable to mix them in order to secure the advantage of an excess of sulphur in the sulphide ores. If they are not mixed, from 1.5 to 2 per cent. sulphur will have to be added to the oxidized ores in the form of pyrite.

The ores will have to be crushed to 20 mesh, or finer.

The salt required will be 5 to 10 per cent.

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The results were as

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| Per Cent. Acid in Lixiviant | Per Cent. Extracte |
|---|---|
| 3.0 | 46.8 |
| 4.0 | 54.7 |
| 4.7 | 56.1 |
| 10.0 | 81.8 |

Stan

| Per Cent. Acid in Lixiviant | Per Cent. Extracted |
|---|---|
| 3.0 | 42.9 |
| 4.0 | 44.3 |
| 4.7 | 48.3 |
| 6.3 | 58.2 |
| 10.0 | 78.4 |

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The temperature of roasting should not be above 900° F. to avoid excessive volatilization.

Large furnaces, where air supply and temperatures are under better control and where the benefits of mass action can be obtained, should give as good if not better results than the laboratory. At low temperatures, the slight volatilization losses are easily recovered by scrubbing towers, together with sufficient acid for washing the ore.

### *Leaching Experiments*

These were made only on the raw oxidized ores. The crushing varied from 8 to 2 mesh sizes. The experiments were conducted in glass and stoneware jars provided with small air-lift pumps for circulating the lixiviants. Both standing and circulating lixiviants were tested. The strength of acid solution varied from 3 per cent., or just enough to dissolve the copper in the ore, up to a 10 per cent. solution. Sulphuric acid was used. All references to this acid mean 100 per cent. $H_2SO_4$ and not commercial acid. Only enough lixiviant was used in each experiment to cover the ore.

The results were as follows on 24-hr. treatment:

*8-Mesh Ore*

| | Standing Lixiviant | | Circulating Lixiviant | |
|---|---|---|---|---|
| Per Cent. Acid in Lixiviant | Per Cent. Cu Extracted | Lb. Acid Used per Lb. Cu Dissolved | Per Cent. Cu Extracted | Lb. Acid Used per Lb. Cu Dissolved |
| 3.0 | 46.8 | 3.2 | 48.7 | 3.3 |
| 4.0 | 54.7 | 3.3 | 71.0 | 2.7 |
| 4.7 | 56.1 | 2.8 | 85.2 | 3.2 |
| 10.0 | 81.8 | 2.8 | 88.6 | 3.5 |

*4-Mesh Ore*

| | Standing Lixiviant | | Circulating Lixiviant | |
|---|---|---|---|---|
| Per Cent. Acid in Lixiviant | Per Cent. Cu Extracted | Lb. Acid Used per Lb. Cu Dissolved | Per Cent. Cu Extracted | Lb. Acid Used per Lb. Cu Dissolved |
| 3.0 | 42.9 | 2.4 | 70.4 | 2.0 |
| 4.0 | 44.3 | 2.4 | 74.4 | 2.3 |
| 4.7 | 48.3 | 2.3 | 82.3 | 2.4 |
| 6.3 | 58.2 | 2.3 | 80.8 | 2.8 |
| 10.0 | 78.4 | 2.2 | 85.7 | 2.8 |

These experiments showed that circulating the lixiviant increased the extraction of copper without seriously increasing the consumption of acid; that crushing to 8 mesh increased the consumption of acid without materially increasing the extraction of copper; and that increasing the

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strength of the lixiviant increased the extraction of copper and also the consumption of acid when the lixiviant was circulated through the ore. The fine ore produced in crushing to 8 mesh seriously interfered with the percolation of solutions.

Further experiments were made on 4-mesh material by increasing the time of leaching, with the following results:

| Time of Leaching, Hr. | 5 Per Cent. Acid Lixiviant: Per Cent. Cu Extracted | 5 Per Cent. Acid Lixiviant: Lb. Acid Used per Lb. Cu Dissolved | 10 Per Cent. Acid Lixiviant: Per Cent. Cu Extracted | 10 Per Cent. Acid Lixiviant: Lb. Acid Used per Lb. Cu Dissolved |
|---|---|---|---|---|
| 24 | 82.3 | 2.4 | 85.7 | 2.8 |
| 48 | 83.7 | 2.6 | 90.1 | 2.6 |
| 72 | 84.2 | 2.7 | 87.6 | 4.2 |
| 96 | 86.7 | ... | 89.1 | 4.0 |

Additional time with 5 per cent. acid lixiviant increased the extraction very slowly—probably from the fact that the acid was nearly neutralized. The 10 per cent. acid lixiviant always had plenty of free acid remaining after the copper was all dissolved.

By referring to the analysis of this ore, it will be seen that the copper soluble in 10 per cent. sulphuric acid solution is only 90.6 per cent. when the sample is crushed to pass 100-mesh screen, so that a 10 per cent. acid lixiviant on a 4-mesh material for 48 hr. extracted about all of the copper that could be expected.

The above experiment was repeated on ore crushed to pass 0.5-in. or 2-mesh screen. Only a 10 per cent. acid lixiviant was used. The results, given below, were as good as those obtained from finer crushing.

| Time of Leaching | Per Cent. Cu Extracted |
|---|---|
| 48 hr. without change of lixiviant | 86.0 |
| 48 hr. Lixiviant changed after 24 hr. | 87.5 |
| 72 hr. Lixiviant changed after 48 hr. | 90.0 |
| 96 hr. Lixiviant changed after 48 hr. | 87.0 |

As already stated, the oxidized ore contained some cuprite. When clean sulphuric acid is added to this mineral, one-half the copper is set free in metallic condition, which remains insoluble in the acid. As nearly as could be determined by averaging a number of analyses, the amount of copper thus set free was about 0.2 per cent. of the ore, or say 10 per cent. of the total copper.

Analyses of the lixiviants from a number of leaching experiments showed that a certain amount of iron passed into solution simultaneously with the copper. This averaged from one-third to one-half of the amount of copper in solution, or from 0.8 to 1.1 per cent. of the solution. Some-

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times, with high iron and much kaolinized ores, it amounted to more than this. The iron was about equally divided as ferric and ferrous sulphates.

Using 10 per cent. acid, the lixiviant passing from a charge of leached ore contained from 4 to 6 per cent. free acid in addition to the copper, iron, alumina, etc.

This combination of circumstances enabled me to use the partly neutralized lixiviant from a leached charge of ore for the first lixiviant on a new charge of ore and thereby not only neutralize the free acid in the lixiviant and at the same time enrich it in copper, but have a solvent for the cuprite (or metallic coppper if formed) in the form of ferric sulphate. Since ferric sulphate was always present and the lixiviants were always circulated, it is scarcely possible that any cuprite could escape solution.

As soon as the first lixiviant was neutral, it was sent to the precipitating vats. If it was left on the ore beyond the neutral point, some of the copper was reprecipitated in the ore. A new 10 per cent. acid lixiviant followed the first and finished leaching the ore, which in turn was neutralized on a new charge of ore.

## Experimental Plant Tests

### *The Chloridizing Roast*

The chloridizing roast and the subsequent leaching of the ore with water and scrubbing-tower solutions is a well-established metallurgical process and has been in commercial operation for a number of years on 2 per cent. copper ores.

Laboratory experiments told what could be expected from this process and there is little danger of unlooked-for difficulties in larger-scale operations. The questions involved are therefore more of relative costs of construction and operation than of metallurgical experiment, so, for the time being, no experiments were conducted on a larger scale.

### *Acid Leaching*

*Percolation Experiments.*—A pipe 10 in. in diameter and 18½ ft. in length was used for an experimental percolation vat. For convenience in testing the various columns of ore, it was made in sections. The lower end of this vat was closed with a plate in which there was a 3-in. opening which served as a discharge gate for the ore and also for pipe connections to measure the flow of solution. This could also be attached to a centrifugal pump for circulating the solutions to the top of the vat if desired and in this way the working conditions of a commercial plant

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could be produced. Aside from a small screen to protect the valves, no filter was used in the vat. The ore itself corresponded to the gravel filter that was expected to be used in practice.

The height of any ore column in this vat was the same as that used in any commercial plant. The filtering area was 78.54 sq. in., or 0.545 sq. ft., which corresponded to the same section of a full-sized vat. The area of any commercial vat divided by this area and the result multiplied by the number of gallons per minute flowing through a given column of ore would give the approximate amount of solution that would have to be handled by circulating pumps in a large plant.

All percolation experiments were continued for three or four days if possible, in order to detect any irregularity in the flow of solution by the segregation of slimes or from other causes.

Since 8-mesh ore was found to be of no advantage in the laboratory leaching experiments, it was not used in these experiments.

The facilities at Douglas for crushing ore for experimental purposes at that time were very poor. There was no opportunity for stage crushing with intermediate screening. The ore was reduced so that it would nearly all pass a 2-mesh screen in one operation with one crusher and one set of rolls. This undoubtedly produced a different product than would be obtained in the usual practice.

*With 4-mesh ore.* A screen analysis of this material gave

| Mesh | Per Cent. |
|---|---|
| 4 to 8 | 30.6 |
| 8 to 16 | 22.4 |
| 16 to 20 | 8.4 |
| 20 and finer | 38.6 |

Between 3 and 4 per cent. of this product was a colloidal slime that could be suspended in water. This slime assayed 4.5 per cent. copper.

Ore crushed to this size absorbed 11 per cent. of its weight in water or 26.4 gal. per ton. This amount of water will be lost in tailings.

The additional quantity of water required to fill the interstices and cover a given quantity of ore in the vat was 15 per cent. of its weight or 36 gal. per ton. This will be known as one volume of water, or solution, in the experiments which follow, and its complete replacement will represent one cycle in the circulation of lixiviant, or one washing of the ore with water.

Experiment No. 1. The ore was charged into water to get the coarser particles on the bottom and form a better filter bed. Height of ore column, 5 ft. Fine ore and slime soon settled on top of the charge and practically stopped the percolation.

Experiment No. 2. Ore was charged into the vat dry. Height of ore column, 5 ft. Water was added on top of ore. Rate of percolation, 1

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gal. in 15 min. To the charge, 2.5 ft. of ore was added, making the total column 7.5 ft. Rate of percolation, 1 gal. in 15 min. Another 2.5 ft. of ore was added, making the total column 10 ft. Rate of percolation, 1 gal. in 15 min. At the end of 72 hr. the rate was 1 gal. in 23 min., after which it gradually decreased.

When the charge was drawn, the fine ore was found to be more or less segregated, which was perhaps due to the method of charging.

Experiment No. 3. The above experiment was repeated. With a 5-ft. column of ore the rate of percolation was the same, 1 gal. in 15 min. The ore column was increased at once to 10 ft., in which the rate of percolation was 1 gal. in 10 min. The rate remained the same when the column was increased to 12 ft.

Experiment No. 4. The ore was charged dry and the height of the column was 18 ft. Water was introduced into the bottom of the vat until the ore was covered, in order to remove the air more quickly. It was then circulated from the bottom of the vat to the top by means of a centrifugal pump. Rate of percolation was 1 gal. in 8 min. At the end of 72 hr. it was still 1 gal. in 8 min. The height of the ore column was then reduced to 12 ft. and at the end of 120 hr. the rate of percolation was 1 gal. in 9 min.

Experiment No. 5. Upward percolation. The ore was charged dry. Height of column, 12 ft. Water was introduced from the bottom of the vat and upward percolation was maintained with a 9-in. head of water above the ore from a stand pipe outside the vat. The rate of percolation was 1 gal. in 6 min.

With an ore column of 15 ft. and a 10-in. head of water above the ore, the rate of percolation was 1 gal. in 7.5 min.

*With 2-mesh ore.* The screen analysis was

| Mesh | Per Cent. |
|---|---|
| 2 to 4 | 40.0 |
| 4 to 8 | 25.8 |
| 8 to 16 | 14.2 |
| 16 to 20 | 6.0 |
| 20 and finer | 14.2 |

The colloidal slime was about 2 per cent. of the ore.

This ore absorbed 6 per cent. of its weight or 14.4 gal. of water per ton.

The volume of water necessary to cover the saturated ore was 27.7 per cent. of its weight or 66.5 gal per ton.

Experiment No. 1. Height of ore column, 12 ft. Water was circulated from bottom of vat to top by means of pump. Rate of percolation was 1 gal. in 30 sec. At the end of 96 hr., it was 1 gal. in 35 sec.

*Summary.*—The height of the ore column with 4 and 2 mesh ore has no retarding effect on the rate of percolation, unless the ore is very much disintegrated and produces a good deal of slime. If anything, the rate is increased with increased height. Vats can therefore be constructed with any convenient depth, but will probably not be practicable beyond 10 or 15 ft., depending of course upon the character of ore and method of crushing.

The ore should be charged dry or only moist.

Lixiviants can be introduced best from the bottom of the vat or down one side of the vat from the top of the ore. This allows the free escape of air and carbon dioxide gas and permits a rapid saturation of the ore and filling of the vat. After the ore is covered, the percolation of the lixiviant through the ore should be downward. This permits better control of solutions and the washing of the ore with the minimum quantity of water.

By keeping the ore covered with solution and having the pumping or circulating capacity a little above the rate of percolation, channels through the ore can be detected and remedied.

The rate of percolation in this experimental vat may appear slow, but when the proper calculation is made for a large vat, it will be found that considerable pumping capacity will be required to take care of the solution.

### *Leaching Plant Construction*

To meet the conditions at Ajo, reinforced concrete seemed to offer many advantages for large-sized leaching vats. This material has been used for a long time at the works of the Pennsylvania Salt Co., at Natrona and at Philadelphia, for leaching small tonnages of chloridized copper ores. The solutions there are a mixture of sulphate and chloride of copper and contain from 1 to 2 per cent. of free acid. No protective coating or lining has been used for the concrete although the new vat constructed at Philadelphia is lined with chemical brick laid with cement.

The stronger acid solutions used in leaching the Ajo ores necessitated some protective covering for the concrete. A paint of this character is made by Toch Brothers. It is known as "R. I. W. No. 44" and is advertised to have the following properties:

"1. It stands heat up to the point of carbonization.

"2. It withstands sulphuric acid, 20° strength, for two months without showing the slightest sign of decomposition.

"3. It withstands the action of 15 per cent. sulphuric acid, 10 per cent. copper sulphate, at a temperature of 135° F., for six months, without showing any sign of decomposition. Withstands influence of caustic soda up to about 10 per cent. strength.

"4. Two coats will last for several years on the interior of stand pipes. Steel must be clean and dry before material is applied.

"5. Has a record of three years and four months on the interior walls, floors and

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ceilings of storage battery rooms where the vapors of sulphuric acid are condensed twice a day. Three coats were applied.

"The dates of its longevity are simply minimum dates, as the material lasts much longer than our statements indicate."

The protection of these concrete vats was submitted to Toch Brothers and they recommended the following specifications:

> "Make your concrete a 1 : 2 : 4 mix, using an aggregate graded up to 1½ in., adding 3 lb. of 'Toxement' for each bag of cement necessary to complete the operation. After the concrete has set up thoroughly dry, clean the surface and then apply one coat of R. I. W. No. 89, allow about 36 hr. for it to dry, then apply a second coat of R. I. W. No. 89. Care should be taken after the first coat is applied so that every particle of the surface is thoroughly and completely covered. R. I. W. No. 89 is constructed slightly different from R. I. W. No. 44 in order to meet your specifications."

To make a concrete vat acid proof, it must first be made waterproof. For this purpose they recommended "Toxement," a patented preparation of their own which is advertised to be "a colloidal double resinate and silicate of calcium and aluminum."

A second method of waterproofing concrete was obtained from *Bulletin* No. 46, U. S. Department of Agriculture. In this method crude petroleum or preferably residuum is mixed with the concrete as follows:

> "For most purposes where damp proofing is required, 5 per cent. of oil based on the weight of the cement in the mixture is all that is necessary. For each bag of cement (weighing 94 lb.) 4.7 lb. or about 2¼ quarts of oil are required.
>
> "Mix the concrete in proportions of 1 part cement to 2 of sand and 4 of broken stone or gravel. Add water and thoroughly mix until no trace of oil is visible on the surface. If oil-mixed mortar is desired, prepare in the same manner without the gravel.
>
> "The use of 5 per cent. of oil increases the time of the initial set by 50 per cent. and the time of the final set by 47 per cent.
>
> 'Concrete with 10 per cent. oil has 75 per cent. of the strength of plain concrete at 28 days. At the end of one year the strength of 1 : 3 mortar suffers but little from the addition of oil in amounts up to 10 per cent.
>
> "Oil-mixed mortar containing 10 per cent. of oil is absolutely water tight under pressures as high as 40 lb. to the square inch. Oil-mixed mortar is effective as a waterproofing agent under low pressures when plastered on either side of porous concrete."

Tests were also made on the acid-resisting qualities of the following bricks, which might be used for lining concrete vats: Ordinary wire-cut shale brick from El Paso; "acid-proof tile" from El Paso; low-temperature fire brick from El Paso; "Star" fire brick from Pueblo, Colo.; silica brick from Pueblo, Colo.

These bricks were allowed to stand three months in 10 per cent. sulphuric acid solution; 5 per cent. sulphuric acid and 5 per cent. copper sulphate solution; and 10 per cent. copper sulphate solution (10 per cent. $CuSO_4 + 5H_2O$).

There was no apparent disintegration or injury to the physical structure of any of these bricks at the end of the test.

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Chemical analysis of the solutions likewise showed that none of the bricks had been appreciably attacked by either acid or copper sulphate solutions. The solutions from the silica brick contained some gelatinous silica, which probably came from the decomposition of the sodium silicate used as a binder, but this did not weaken the brick.

Two concrete storage tanks were made for holding wash water, in order to bring it up to normal strength (about 10° B.) of acid to be used as a lixiviant. In practice it would be better to build these tanks of steel or wood and line them with lead, but in this experimental plant concrete was used to determine its efficiency as well as that of acid-proof paints. Both of these tanks were made of oil-mixed reinforced concrete. They were 5 ft. in diameter and 5 ft. in depth, with walls 8 in. thick. One was plastered inside with "Toxement" mortar and the other with oil-mixed mortar. Both were painted inside with R. I. W. No. 89 paint as specified. For better protection from abrasion, the bottoms of these tanks were covered with ½ in. or more of hot asphalt and sand, troweled smooth and compact with a hot iron like street paving.

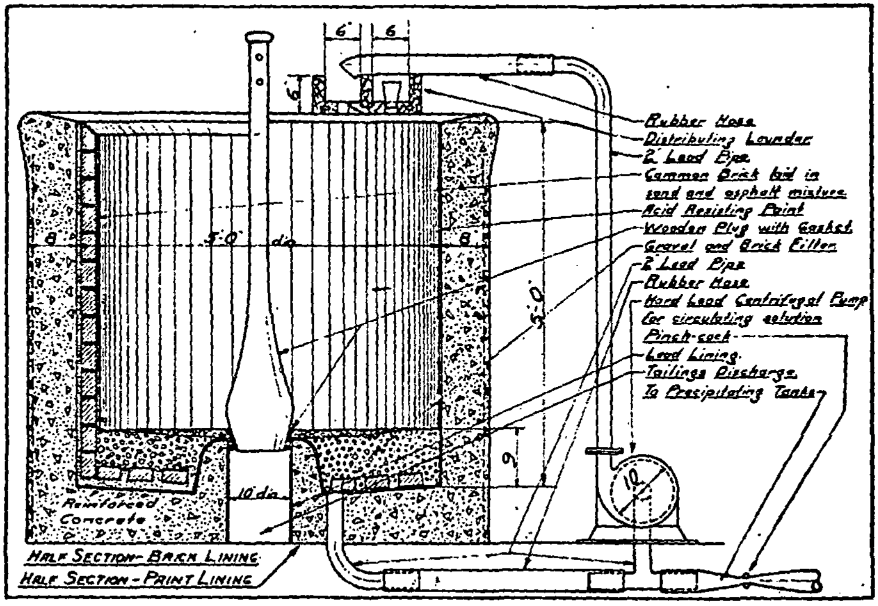

FIG. 1.—EXPERIMENTAL LEACHING TANKS.

Five leaching vats were constructed according to the general design shown in Fig. 1.

For convenience in subsequent work these vats were designated as *A, B, C, D,* and *E*, and their individual construction was as follows:

Vat *A*. Five feet in diameter and 5 ft. in depth. Concrete, mixed

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Vat *B*. Sam
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Vat *C*. Same
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Vat *D*. This
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with "Toxement" according to the Toch specifications. Plastered inside with cement mortar mixed with "Toxement." Painted inside with three coats of R. I. W. No. 89 paint. A false lining of wood was made to set inside this vat, but it was impracticable to retain this lining without scarring the paint, so it was abandoned at the start. It was also impossible to keep the paint from being worn off by the ore, so the vat was given one coat of asphalt dissolved in gasoline and then lined with El Paso common brick. The bricks were laid in hot asphalt, and hot asphalt and sand were poured between the brick lining and the concrete. The bottom was covered with asphalt and sand, troweled smooth while hot.

Vat *B*. Same construction and dimensions as Vat *A*. This was given two coats of hot asphalt, which was difficult to apply and on cooling it contracted and left pin holes of uncovered cement. A thin paint was then made by pouring hot asphalt into gasoline and a coat of this was applied to the above. The bottom was covered with asphalt and sand, troweled smooth while hot.

Vat *C*. Same dimensions as Vats *A* and *B*, but made of oil-mixed concrete and plastered inside with oil-mixed cement mortar. A priming coat of R. I. W. No. 89 paint was applied to the concrete. On top of this was placed a coat of hot asphalt followed by a coat of asphalt paint as described under Vat *B*. The bottom was made of hot asphalt and sand, as already described.

Vat *D*. This was rectangular, 5 by 8 ft. and 5 ft. in depth. It was made of oil-mixed concrete and plastered inside with oil-mixed cement mortar. The protective coatings were one coat of R. I. W. No. 89 and two coats of asphalt paint as described above. The bottom was covered with hot asphalt and sand.

Vat *E*. Made of oil-mixed concrete and plastered inside with oil-mixed mortar. Diameter 5 ft. and depth 10 ft. Protective coatings, one of R. I. W. No. 89 and one of asphalt paint. Bottom covered with hot asphalt and sand.

The capacity of Vats *A*, *B*, and *C* was between 3 and 4 tons, respectively. Vats *D* and *E* each held a little more than 8 tons.

Three solution or precipitating tanks, 5 ft. in diameter and 5 ft. in depth, were made and protected in the same manner as Vat *E*.

### *Leaching-Plant Operation*

These experiments were made on about 300 tons of oxidized ore shipped from the various shafts and test pits and during the development of the property.

*Test* 1.—This was made on two cars of ore, or Lots 1 and 2, which were crushed and mixed for treatment. As already stated, owing to

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limited crushing facilities, it was necessary to crush with one crusher and one set of rolls, as much as possible to 2 mesh and finer in one operation. The result of this was only 7.25 per cent. of oversize and probably a greater production of fines than would be obtained in practice.

Lot 1 was hard unaltered ore similar to that used in the laboratory experiments. Lot 2 was considerably altered by weathering and produced a great deal of fine material and slime.

A screen analysis of the mixture gave the following results:

| Mesh | Per Cent. |
|---|---|
| 2 to 4 | 29 |
| 4 to 8 | 14 |
| 8 to 16 | 18 |
| 16 and finer | 39 |

The chemical analyses of the two lots are given below:

| | Dry Weight, Pounds | Copper, Per Cent. |
|---|---|---|
| Lot 1 | 62,172 | 1.84 |
| Lot 2 | 94,570 | 1.37 |
| | 156,742 | 1.55 |

*Chemical Analyses*

| | Lot 1 Per Cent. | Lot 2 Per Cent. | | Lot 1 Per Cent. | Lot 2 Per Cent. |
|---|---|---|---|---|---|
| $SiO_2$ | 65.7 | 63.6 | Cu, total | 1.84 | 1.37 |
| Fe | 4.0 | 4.7 | Cu sol. in 10 per cent. $H_2SO_4$ | 1.66 | 1.27 |
| $Al_2O_3$ | 14.3 | 13.4 | $CO_2$ | 1.70 | 1.33 |
| | | | | Ounce | Ounce |
| CaO sol. in acid | 0.8 | 0.6 | Au | 0.01 | 0.01 |
| S, total | 0.3 | 0.4 | Ag | 0.20 | 1.18 |
| S as sulphate | 0.08 | 0.1 | | | |

The leaching was conducted in the manner described under laboratory experiments, namely, the partly neutralized lixiviant from finishing one charge of ore was neutralized and enriched by using it as the first lixiviant on a new charge of ore.

The details of this test are summarized as follows:

| | |
|---|---|
| Total ore leached, pounds | 125,857 |
| Average copper contents, per cent | 1.53 |
| Average time of acid leaching, hours | 70.6 |
| Average time of washing, hours | 5.0 |
| Final tailing, total copper, per cent | 0.30 |
| Final tailing, soluble copper, per cent | 1.12 |
| Copper extracted per ton of ore, pounds | 24.4 |
| Per cent. extraction | 80.0 |

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| | |
|---|---|
| Total weight of material extracted from the ore, per cent | 3.5 |
| Actual percentage of copper extracted | 81.0 |
| Percentage of available copper extracted | 91.0 |
| Lixiviant used per ton of ore, gallons | 132 |
| Average per cent. of acid in lixiviant | 9.24 |
| Acid consumed per pound of copper dissolved, pounds | 3.4 |
| Wash water used per ton of ore, gallons | 138 |
| Rate of percolation in inches per hour, measured in inches of solution above the ore in vat | 90 |
| Copper accounted for in solution, of the total amount extracted from the ore by difference between heads and tails, per cent | 92.2 |
| Average value of nearly neutralized lixivium sent to precipitating vats: | |
| Copper, per cent | 2.22 |
| Iron, per cent | 0.42 |
| Alumina, per cent | 0.47 |

The average grade of the ore in this test was lower than that used in the laboratory tests. There is, however, not likely to be a corresponding decrease in value of the tailing from a 1.5 per cent. ore, below that obtained from a 2.0 per cent. ore, so the percentage of extraction decreases rapidly in proportion to the decrease in the grade of the ore.

The ore was charged dry into the vats. The lixiviants were admitted on top of the ore but at one side of the vat, and no faster than could be absorbed by the charge. By making a little dam on top of the charge, the lixiviant passed immediately to the bottom of the vat and saturated the charge from below, thus permitting the escape of air and gas.

The soluble copper in the tailing was determined by boiling the laboratory sample (100 mesh) in 10 per cent. sulphuric acid. The copper not soluble by this treatment must exist as sulphide or as other minerals in the ore, not capable of being extracted by sulphuric acid and therefore is not available by this metallurgical process.

*Tests* 2 *and* 3.—These were made on car lots 3 and 4 treated separately. The ore was soft and much the same in character as Lot 2. It produced considerable fine material on crushing.

Lot 3 was crushed to ½-in. mesh.

Lot 4 under similar conditions crushed almost to ¼-in. mesh, as shown by screen analyses.

| Mesh | Lot 3 Per Cent. | Lot 4 Per Cent. |
|---|---|---|
| −2+4 | 16 | 6 |
| −4+8 | 27 | 27 |
| −8+16 | 17 | 21 |
| −16 | 40 | 46 |

| | Dry Weight Pounds | Copper Per Cent. |
|---|---|---|
| Lot 3 | 111,230 | 1.48 |
| Lot 4 | 89,670 | 1.44 |

*Chemical Analyses*

| | Lot 3 Per Cent. | Lot 4 Per Cent. | | Lot 3 Per Cent. | Lot 4 Per Cent. |
|---|---|---|---|---|---|
| $SiO_2$ | 64.00 | 63.30 | Cu total | 1.48 | 1.44 |
| Fe | 4.20 | 4.20 | Cu sol. in 10 per cent. | | |
| $Al_2O_3$ | 14.30 | 15.10 | $H_2SO_4$ | 1.32 | 1.30 |
| CaO sol. in acid | 0.45 | 0.60 | $CO_2$ | 1.42 | 1.43 |
| | | | | Ounce | Ounce |
| S, total | 0.20 | 0.20 | Au | 0.01 | 0.01 |
| S as sulphate | 0.04 | 0.06 | Ag | 0.19 | 0.17 |

The results from these tests are shown in the following table:

| | Test 2 | Test 3 |
|---|---|---|
| Pounds ore leached | 90,533 | 80,458 |
| Per cent. copper | 1.44 | 1.43 |
| Average hours acid leaching | 70 | 100 |
| Average hours washing | 7 | 23 |
| Final tailing, per cent. total copper | 0.27 | 0.40 |
| Final tailing, per cent. soluble copper | 0.23 | 0.38 |
| Pounds copper extracted per ton of ore | 23.3 | 20.6 |
| Percentage of copper extracted | 81.2 | 71.8 |
| Total per cent. of material extracted from ore | 3.0 | 3.0 |
| Actual percentage of copper extracted | 81.8 | 72.7 |
| Percentage of available copper extracted | 83.5 | 73.0 |
| Gallons lixiviant used per ton of ore | 123 | 137 |
| Average per cent. acid in lixiviant | 9.5 | 7.0 |
| Pounds acid consumed per pound copper dissolved | 3.5 | 3.3 |
| Gallons wash water used per ton of ore | 135 | 177 |
| Rate of percolation in inches per hour, measured in inches of solution above the ore in vat | 43 | 11 |
| Copper accounted for in solution | Combined with Test 4. | |
| Average value of nearly neutralized lixivium sent to precipitating vats: | | |
| Copper, per cent | 2.41 | 2.90 |
| Iron, per cent | 0.56 | 0.70 |
| Alumina, per cent | 0.53 | 0.73 |

These results show very clearly the effect of finer crushing on the same grade and character of ore. Both of these lots were substantially the same character of ore in every respect. They were very much altered by oxidation and contained practically no insoluble copper in the tailing, although the ore itself showed 0.08 to 0.10 per cent., probably as cuprite, which dissolved in the ferric salts extracted from the ore.

The extraction on the 4-mesh material was 9.4 per cent. lower and the rate of percolation dropped to one-quarter of that on the 2-mesh material. Hence much more time was consumed in leaching and washing the ore, with poorer results. Even on the 2-mesh ore the rate of percolation was only half that of the harder ore in Test 1, showing the effect of increased kaolinization of the ore.

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In order to determine the relative value of samples from the top, and other parts of the charge, and also to determine whether the charges were leaching uniformly or in channels, a number of samples were taken from different charges at each foot in depth. This was done by removing half the charge from the vat and sampling the standing face of the remaining half of the charge across each foot of vertical section at a point half way between the center plug and the side walls of the vat.

A general sample was also taken in this manner, to check, not only the sectional samples, but also the one-tenth portion of the entire charge which was quartered in the usual manner for a tailing sample.

These results show that the leaching is very uniform throughout the charge on evenly distributed 2-mesh material, and that samples taken from the top of the charge may be used for preliminary tailing.

| Lot 3, Test 2<br>Sample | Charge 22, Per Cent. Cu | Charge 24, Per Cent. Cu | Charge 25, Per Cent. Cu |
|---|---|---|---|
| First foot, top | 0.26 | 0.35 | 0.25 |
| Second foot | 0.27 | 0.30 | 0.25 |
| Third foot | 0.27 | 0.23 | 0.30 |
| Fourth foot | 0.29 | 0.26 | 0.35 |
| Average | 0.27 | 0.28 | 0.29 |
| One-tenth portion of charge | 0.26 | 0.27 | 0.26 |

Similar samples from the 4-mesh material (Car Lot 4, Test 3) did not give as uniform results. This contained not only much more fine material, but about 5 per cent. colloidal slime, as compared with 2 per cent. colloidal slime in the hard ore. Even though the ore was charged dry, this fine material was found to be irregularly segregated from the charging and apparently not from the action of the lixiviants. This segregation produced irregularities in the extraction by interference with the percolation and washing.

The results from the sectional sampling are given below:

| Sample | Charge 26, Per Cent. Cu | Charge 27, Per Cent. Cu | Charge 28, Per Cent. Cu | Charge 29, Per Cent. Cu | Charge 32, Per Cent. Cu |
|---|---|---|---|---|---|
| First foot, top | 0.24 | 0.31 | 0.23 | 0.46 | 0.24 |
| Second foot | 0.21 | 0.38 | 0.44 | 0.75 | 0.44 |
| Third foot | 0.33 | 0.40 | 0.27 | 1.10 | 0.34 |
| Fourth foot | 0.34 | 0.33 | 0.78 | 0.83 | 0.35 |
| Fifth foot | ...... | ...... | ...... | 0.31 | ...... |
| Sixth foot | ...... | ...... | ...... | 0.44 | ...... |
| Seventh foot | ...... | ...... | ...... | 0.46 | ...... |
| Eighth foot | ...... | ...... | ...... | 0.31 | ...... |
| Ninth foot | ...... | ...... | ...... | 0.75 | ...... |
| Average | 0.28 | 0.35 | 0.43 | 0.60 | 0.35 |
| General | 0.24 | 0.28 | 0.37 | 0.44 | 0.35 |
| One-tenth portion of charge | 0.26 | ...... | 0.37 | ...... | ...... |

The soluble copper in all of the tailings from these two lots of ore shows its weathered condition by the almost total absence of copper as cuprite or sulphide.

The difficulty in extracting this copper led to a more detailed analysis of the tailings to determine whether the copper was retained by the coarse material alone, or whether the colloidal slime also had a tendency to absorb and retain copper even after it had gone into solution.

These results are interesting since they show that the colloidal slime absorbs, or retains mechanically, as much copper as is held by the coarse material. As anticipated, there is also an increase in the percentage of alumina in the fine material.

*Screen and Chemical Analyses of Charge 25, Lot 3, Test 2*

| Size of Material, Mesh | Per Cent. of Weight | Per Cent. of Value | Per Cent. of Copper | Per Cent. Sol. Copper | Per Cent. of Silica | Per Cent. of Alumina |
|---|---|---|---|---|---|---|
| +4 | 9.3 | 15.2 | 0.47 | 0.39 | 68.0 | 12.6 |
| +8 | 32.5 | 30.6 | 0.27 | 0.20 | 69.6 | 12.7 |
| +16 | 23.2 | 19.5 | 0.24 | 0.18 | 68.5 | 13.9 |
| +30 | 14.0 | 10.8 | 0.22 | 0.17 | 66.0 | 14.0 |
| +60 | 4.7 | 4.3 | 0.26 | 0.19 | 66.9 | 13.5 |
| +100 | 7.0 | 6.6 | 0.27 | 0.21 | 66.3 | 13.1 |
| −100 | 9.3 | 13.0 | 0.40 | 0.37 | 63.3 | 16.4 |
|  | 100.0 | 100.0 | 0.28 | 0.22 | 67.7 | 12.6 |

*Screen and Chemical Analyses of Charges 29 and 30, Lot 4, Test 3*

|  | Charge 29 |  |  | Charge 30 |  |  |
|---|---|---|---|---|---|---|
| Size of Material, Mesh | Per Cent. Weight | Per Cent. Cu | Per Cent. Sol. Cu | Per Cent. Weight | Per Cent. Cu | Per Cent. Sol. Cu |
| +4 | 11.8 | 0.65 | 0.65 | 7.5 | 0.62 | 0.61 |
| +8 | 25.9 | 0.54 | 0.53 | 24.6 | 0.47 | 0.46 |
| +16 | 16.0 | 0.51 | 0.50 | 15.1 | 0.55 | 0.55 |
| +30 | 16.8 | 0.54 | 0.54 | 17.0 | 0.58 | 0.58 |
| +60 | 7.0 | 0.59 | 0.58 | 9.4 | 0.65 | 0.64 |
| +100 | 8.0 | 0.59 | 0.59 | 15.1 | 0.70 | 0.70 |
| −100 | 14.5 | 0.57 | 0.57 | 11.3 | 0.77 | 0.77 |
| Average........ | 100.0 | 0.56 | 0.55 | 100.0 | 0.60 | 0.59 |
| General samples | ..... | .... | 0.44 | ..... | 0.42 | .... |

This retention of the copper by the slime was also noticeable in washing the ore. Although the charges in Lot 4, Test 3, were washed a much longer time and with 50 per cent. more water than those in the previous tests, the analyses of the wash waters showed a very slow removal of the copper. Where the percolation was slow and the tailings high, even the sixth volume of wash water contained a high percentage of copper, while the acid was removed as readily as in previous tests. This confirms the well-known properties of colloidal or argillaceous material for retaining mineral salts.

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The rate of percolation in Test 3, Lot 4, dropped to one-eighth of the rate in Test 1.

The acid consumption in these two tests was substantially the same as in Test 1. The average strength of the acid used in Test 3 was 7 per cent. as compared with 9.25 per cent. and 9.5 per cent. in the preceding tests. In this test partly neutralized lixiviants were used on new ore in every charge, which could not always be done in the other tests. This had a tendency to lessen the consumption of acid, and neutral or nearly neutral solutions could be sent to the precipitating tanks. As stated before, if the acid contents of these lixiviants are too low and they become completely neutralized, part of the copper is reprecipitated in the ore. It would therefore be advisable to send the lixivium to the precipitating tanks slightly acid. Lixiviums containing relatively high percentages of ferric sulphate, and perhaps aluminum sulphate in the form of alum, show an acid reaction that corresponds to 0.2 per cent. to 0.5 per cent. of sulphuric acid.

*Test* 4.—This was made on Car Lot 5.

| | |
|---|---|
| Dry weight, pounds | 96,924 |
| Per cent. copper | 1.20 |

This ore was hard and contained more sulphides and cuprite than the previous lots except Lot 1.

*Chemical Analysis*

| | Per Cent. | | Per Cent. |
|---|---|---|---|
| $SiO_2$ | 65.50 | Cu, total | 1.20 |
| Fe | 3.90 | Cu, sol. in 10 per cent. $H_2SO_4$ | 1.04 |
| $Al_2O_3$ | 14.60 | $CO_2$ | 0.59 |
| CaO sol. in acid | 0.80 | | Ounce |
| MgO | 1.15 | Au | 0.01 |
| S, total | 0.44 | Ag | 0.17 |
| S as sulphate | trace | | |

The ore treated was screened through ½-in. or 2-mesh screen. Only 27.5 per cent. was finer than 16 mesh as compared with 40 per cent. in the preceding tests.

*Screen Analysis*

| Mesh | Per Cent. Weight | | Per Cent. Copper |
|---|---|---|---|
| +4 | 26.2 | | 1.04 |
| +8 | 30.3 | | 1.11 |
| +16 | 16.0 | | 1.28 |
| +30 | 11.3 | 27.5 | 1.40 |
| +60 | 5.5 | | 1.07 |
| +100 | 5.0 | | 1.92 |
| −100 | 5.7 | | 1.94 |
| | 100.0 | | 1.37 |

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The results from leaching this material are shown in the following table.

The oversize from Lots 3, 4 and 5, amounting to 4 per cent. of the total ore treated and ranging from ½ to 1 in. in size, was recrushed to pass a 2-mesh screen and leached separately. This oversize was substantially the same in character as the finer material but had passed through the rolls uncrushed due to the irregular hand feeding.

A screen analysis of the recrushed oversize gave the following results:

| Mesh | Per Cent. |
|---|---|
| +4 | 32.0 |
| +8 | 26.3 |
| +16 | 14.7 |
| −16 | 27.0 |

The leaching tests on this product are also shown in the following table:

|  | Test 4 | Recrushed Oversize Tests 2, 3 and 4 |
|---|---|---|
| Pounds ore leached | 77,636 | 10,300 |
| Per cent. copper | 1.29 | 1.49 |
| Average hours acid leaching | 77 | 90 |
| Average hours washing | 10 | 10 |
| Final tailings, per cent. total copper | 0.32 | 0.24 |
| Final tailings, per cent. soluble copper | 0.16 | 0.16 |
| Pounds copper extracted per ton of ore | 19.3 | 25.2 |
| Percentage of copper extracted | 75.0 | 83.8 |
| Total percentage of material extracted from the ore | 3.0 | 3.0 |
| Actual percentage of copper extracted | 75.8 | 84.4 |
| Percentage of available copper extracted | 82.9 | 91.2 |
| Gallons lixiviant used per ton of ore | 120 | 145 |
| Average per cent. acid in lixiviant | 9.3 | 10.8 |
| Pounds acid consumed per pound of copper dissolved | 4.3 | 3.8 |
| Gallons wash water used per ton of ore | 666 | 712 |
| Rate of percolation in inches per hour, measured in inches of solution above ore in vat | 161 | 75 |
| Per cent. of copper accounted for in solution, of the total amount extracted from the ore by difference between heads and tails. (Combined solutions from Tests 2, 3, and 4) | 99.8 | ...... |
| Average value of nearly neutralized lixivium sent to precipitating vats |  |  |
| Copper, per cent | 2.30 | ...... |
| Iron, per cent | 0.56 | ...... |
| Alumina, per cent | 0.66 | ...... |

The lower extraction in this test is due to the lower grade of the ore and the high percentage of sulphides in the ore. I have invariably

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| Size of Material Mesh |
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| −100 |
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found in experimenting with low-grade ores that the value of the tailing is a very constant factor, whether the value of the ore be $5 or $10 per ton.

In the analyses of the tailings in Tests 2 and 3 we found that practically all of the copper was soluble copper and that the extremely fine material carried more copper than some of the coarser sizes.

In this test several charges of the leached ore were washed with as much as 1,500 gal. of water per ton, or until the final wash water showed no copper or acid, which accounts for the high average volume of wash water in the results given above. This extra and complete washing had absolutely no effect on the soluble copper in the tailings, which remained as high as in charges washed with one-tenth of the water.

The following screen analyses on the tailings from two of these charges show that even the finest material retains copper soluble in sulphuric acid that will not wash out. Charge 41 came from *E* vat, 9 ft. in depth, and Charge 43 came from *A* vat, 4 ft. in depth.

| | Charge 41 | | | Charge 43 | | |
|---|---|---|---|---|---|---|
| Size of Material Mesh | Per Cent. Weight | Per Cent. Total Cu | Per Cent. Sol. Cu | Per Cent. Weight | Per Cent. Total Cu | Per Cent. Sol. Cu |
| +4.......... | 27.8 | 0.30 | 0.23 | 23.5 | 0.32 | 0.24 |
| +8.......... | 30.9 | 0.27 | 0.20 | 34.7 | 0.17 | 0.11 |
| +16......... | 16.6 | 0.32 | 0.21 | 16.5 | 0.12 | 0.08 |
| +30......... | 10.8 | 0.34 | 0.25 | 9.5 | 0.18 | 0.13 |
| +60......... | 4.6 | 0.49 | 0.30 | 5.2 | 0.34 | 0.19 |
| +100........ | 3.6 | 0.50 | 0.33 | 4.3 | 0.38 | 0.19 |
| −100........ | 5.7 | 0.55 | 0.36 | 6.3 | 0.55 | 0.32 |
| Totals........ | 100.0 | 0.33 | 0.23 | 100.0 | 0.24 | 0.16 |
| Original tailings | ..... | 0.30 | 0.13 | ..... | 0.24 | 0.15 |

This fact points to the importance of studying carefully the gangue of an ore, even if it may not be acid consuming. The ability of argillaceous and some colloidal material to absorb and retain mineral salts is well known and these experiments have shown it to be quite a factor in leaching raw oxidized porphyry ores with sulphuric acid.

An effort was made to determine the rate of extraction of copper from the ore by the several lixiviants. To do this the ore and lixiviant were sampled every 2 hr. The ore samples were taken from the top of the charge and the results obtained from them were not entirely satisfactory, but were the best obtainable.

The first charge tested in this way was Charge 20, Test 2. Two strong lixiviants were used on this charge—the first containing 14.2 per cent. acid and the second, 12.7 per cent. acid. The results are shown in the following table and are graphically presented in Fig. 2.

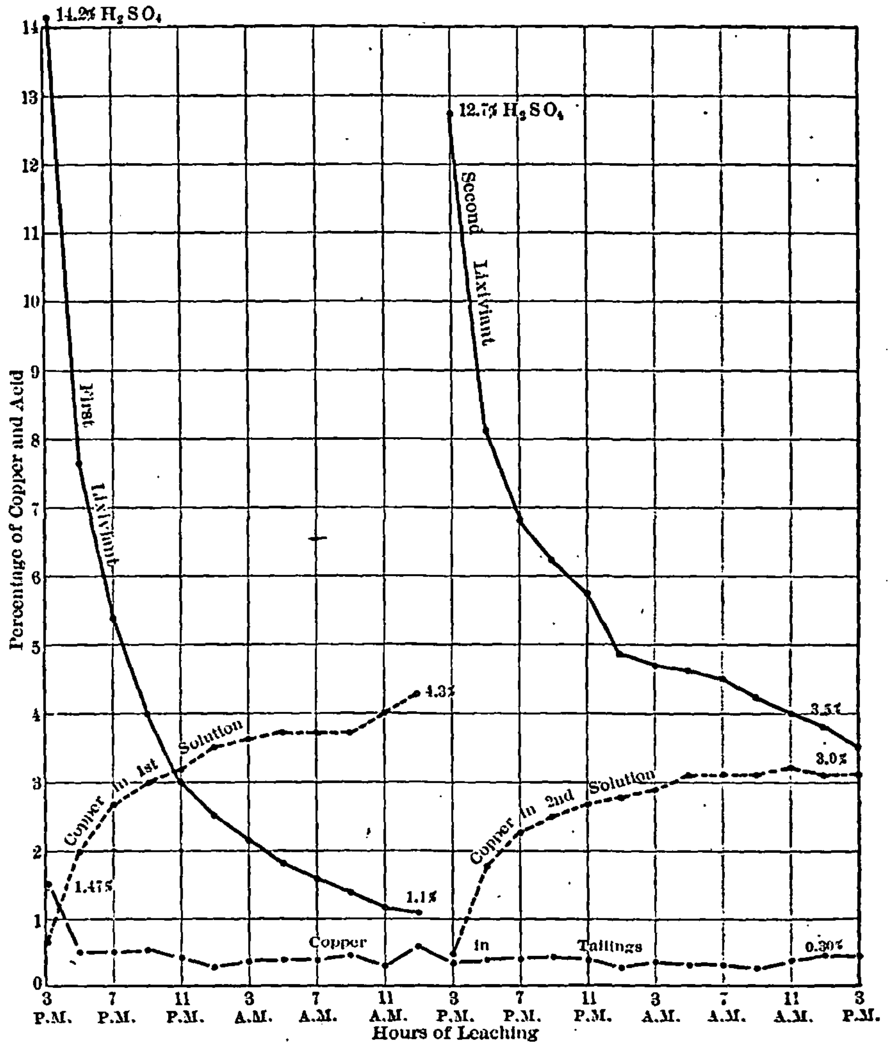

FIG. 2.—RELATIVE VARIATIONS IN COPPER AND ACID CONTENTS OF LIXIVIUM AND ORE, CHARGE 20, VAT *D*.

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5 a.m.........
7 a.m.........
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3 p.m.........

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Time of Sample

First Lixiviant
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3 p.m.........
5 p.m.........
7 p.m.........
9 p.m.........

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*Leaching Experiments on Charge 20, Vat D. Relative Variations in Copper and Acid Contents of Lixivium and Ore*

| Sample Time | Ore Per Cent. Cu | Solution Cu, Per Cent. | Solution $H_2SO_4$, Per Cent. |
|---|---|---|---|
| First Lixiviant | | | |
| 3 p.m. | 1.47 | 0.7 | 14.2 |
| 5 p.m. | 0.47 | 2.0 | 7.7 |
| 7 p.m. | 0.55 | 2.8 | 5.4 |
| 9 p.m. | 0.55 | 3.0 | 4.0 |
| 11 p.m. | 0.38 | 3.2 | 3.0 |
| 1 a.m. | 0.28 | 3.5 | 2.5 |
| 3 a.m. | 0.35 | 3.6 | 2.2 |
| 5 a.m. | 0.35 | 3.7 | 1.8 |
| 7 a.m. | 0.35 | 3.7 | 1.6 |
| 9 a.m. | 0.41 | 3.7 | 1.4 |
| 11 a.m. | 0.30 | 4.0 | 1.2 |
| 1 p.m. | 0.59 | 4.3 | 1.1 |
| Second Lixiviant | | | |
| 3 p.m. | 0.31 | 0.4 | 12.7 |
| 5 p.m. | 0.31 | 1.7 | 8.1 |
| 7 p.m. | 0.32 | 2.2 | 6.8 |
| 9 p.m. | 0.32 | 2.5 | 6.2 |
| 11 p.m. | 0.28 | 2.7 | 5.7 |
| 1 a.m. | 0.32 | 2.9 | 4.8 |
| 3 a.m. | 0.28 | 2.8 | 4.7 |
| 5 a.m. | 0.27 | 3.1 | 4.6 |
| 7 a.m. | 0.25 | 3.1 | 4.5 |
| 9 a.m. | 0.35 | 3.1 | 4.2 |
| 11 a.m. | 0.29 | 3.2 | 4.0 |
| 1 p.m. | 0.29 | 3.1 | 3.8 |
| 3 p.m. | 0.34 | 3.0 | 3.5 |

The next test was made on Charge 38, Test 4. This is more complete and shows the relative variations in the copper and acid contents of lixiviants and ore and also the quantities of iron and alumina passing into solution.

The first lixiviant used here was a partly neutralized one from a previous charge. This was followed by two new lixiviants, each containing 10 per cent. acid.

| Time of Sample | Per Cent. Cu in Ore | Lixiviums $H_2SO_4$ Per Cent. | Cu, Per Cent. | $Al_2O_3$ Per Cent. | Fe (Total) Per Ct. | Fe (Ferric) Per Ct. | Fe (Ferrous) Per Ct. |
|---|---|---|---|---|---|---|---|
| First Lixiviant | | | | | | | |
| 1 p.m. | 1.30 | 4.00 | 1.40 | ..... | ...... | ...... | ....... |
| 3 p.m. | 0.99 | 1.99 | 2.06 | 0.66 | 0.83 | 0.50 | 0.33 |
| 5 p.m. | 1.02 | 1.39 | 2.27 | 0.70 | 0.80 | 0.41 | 0.39 |
| 7 p.m. | ...... | 0.81 | 2.40 | 0.74 | 0.82 | 0.44 | 0.38 |
| 9 p.m. | 1.10 | 0.34 | 2.52 | 0.74 | 0.80 | 0.40 | 0.40 |

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| Time of Sample | Per Cent. Cu in Ore | Lixiviums | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_2SO_4$ Per Cent. | Cu, Per Cent. | $Al_2O_3$ Per Cent. | Fe (Total) Per Ct. | Fe (Ferric Per Ct. | Fe (Ferrous) Per Ct. |
| Second Lixiviant | ...... | 10.31 | 0.90 | 0.57 | 0.62 | 0.49 | 0.13 |
| 11 p.m. | 0.56 | 6.52 | 1.68 | 0.57 | 0.63 | 0.30 | 0.33 |
| 1 a.m. | 0.61 | 4.74 | 2.18 | 0.61 | 0.72 | 0.38 | 0.34 |
| 3 a.m. | 0.53 | 3.51 | 2.40 | 0.65 | 0.71 | 0.35 | 0.36 |
| 5 a.m. | 0.64 | 3.02 | 2.48 | 0.67 | 0.72 | 0.33 | 0.39 |
| 7 a.m. | 0.36 | 2.58 | 2.52 | 0.61 | 0.86 | 0.45 | 0.41 |
| 9 a.m. | 0.35 | 2.13 | 2.54 | 0.77 | 0.85 | 0.43 | 0.42 |
| 11 a.m. | 0.38 | 1.78 | 2.61 | 0.79 | 0.81 | 0.42 | 0.39 |
| 1 p.m. | 0.36 | 1.48 | 2.69 | 0.87 | 0.76 | 0.34 | 0.42 |
| 3 p.m. | 0.28 | 1.32 | 2.78 | 0.77 | 0.87 | 0.43 | 0.44 |
| 5 p.m. | 0.26 | 1.01 | 2.90 | 0.87 | 0.89 | 0.38 | 0.51 |
| 7 p.m. | 0.28 | 0.82 | 2.99 | 0.89 | 0.88 | 0.38 | 0.50 |
| 9 p.m. | 0.29 | 0.72 | 3.00 | 0.94 | 0.89 | 0.40 | 0.49 |
| Third Lixiviant | ...... | 10.00 | 0.40 | ...... | 0.42 | 0.16 | 0.26 |
| 11 p.m. | 0.32 | 6.35 | 1.38 | 0.58 | 0.60 | 0.28 | 0.32 |
| 1 a.m. | 0.47 | 4.70 | 1.84 | 0.62 | 0.67 | 0.31 | 0.36 |
| 3 a.m. | 0.29 | 3.88 | 2.02 | 0.67 | 0.70 | 0.29 | 0.41 |
| 5 a.m. | 0.38 | 3.44 | 2.03 | 0.76 | 0.74 | 0.33 | 0.41 |
| 7 a.m. | ...... | 3.06 | 2.32 | 0.77 | 0.83 | 0.42 | 0.41 |
| 9. a.m. | 0.28 | 2.68 | 2.40 | 0.87 | 0.87 | 0.46 | 0.41 |
| 11 a.m. | 0.31 | 2.30 | 2.47 | 0.89 | 0.88 | 0.47 | 0.41 |
| 1 p.m. | 0.24 | 2.00 | 2.54 | 0.93 | 0.96 | 0.53 | 0.43 |
| 3 p.m. | 0.29 | 1.80 | 2.54 | 0.96 | 0.98 | 0.43 | 0.55 |
| 5 p.m. | 0.35 | 1.64 | 2.54 | 0.99 | 1.00 | 0.49 | 0.51 |
| 7 p.m. | 0.32 | 1.48 | 2.54 | 1.03 | 1.04 | 0.51 | 0.53 |
| 9 p.m. | 0.33 | 1.44 | 2.54 | 0.98 | 1.09 | 0.55 | 0.54 |

The percentage of copper dissolved from the ore by the several lixiviants in this experiment, as accounted for by the copper in solution, was as follows:

| | Hours on Ore | Pounds Copper Taken into Solution | Per Ct. of the Total Copper Extracted |
|---|---|---|---|
| First lixiviant | 8 | 31 | 23.7 |
| Second lixiviant | 24 | 34 | 25.9 |
| Third lixiviant | 24 | 51 | 38.9 |
| Wash water | 7 | 15 | 11.5 |
| Totals | 63 | 131 | 100.0 |

The lixiviants slowly dissolved iron and alumina from the ore, reaching a maximum of about 1 per cent. of each constituent. About one-half of the iron was in the ferric condition, which is of value in dissolving copper, as has already been explained.

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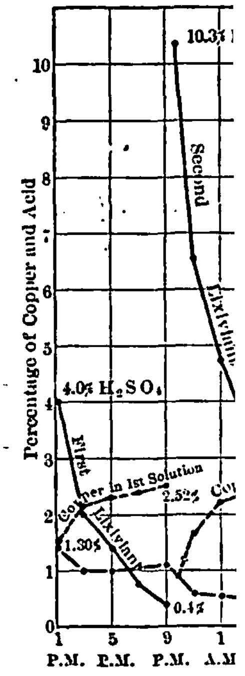

FIG. 3.—RELATIVE VA

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These results are graphically shown by Fig. 3.

In the foregoing tests the acid consumption was nearly 3.5 lb. instead of under 3 lb. as obtained in the laboratory experiments. While this was undoubtedly due to the more decomposed ore used in the larger experiments, yet it might be possible to secure a selective action of the acid for the copper by using weaker lixiviants and leaching the ore a longer time. If this is true, less iron and alumina would pass into solution and less acid would be consumed.

The reject from the charge samples of Tests 1, 2, 3, and 4 amounted to 30,345 lb. In order to test the advisability of leaching the ore with weaker acid and taking more time for the operation, this reject was treated in the experimental plant with an average of 5.25 per cent. acid lixiviant. The first lixiviant used on each charge was the partly neutralized lixiviant from a previous charge that had been treated with a 10 per cent. acid, and already contained 1.16 per cent. copper. Each charge was also saturated with water before putting on the lixiviant, to determine if this would effect any saving in acid.

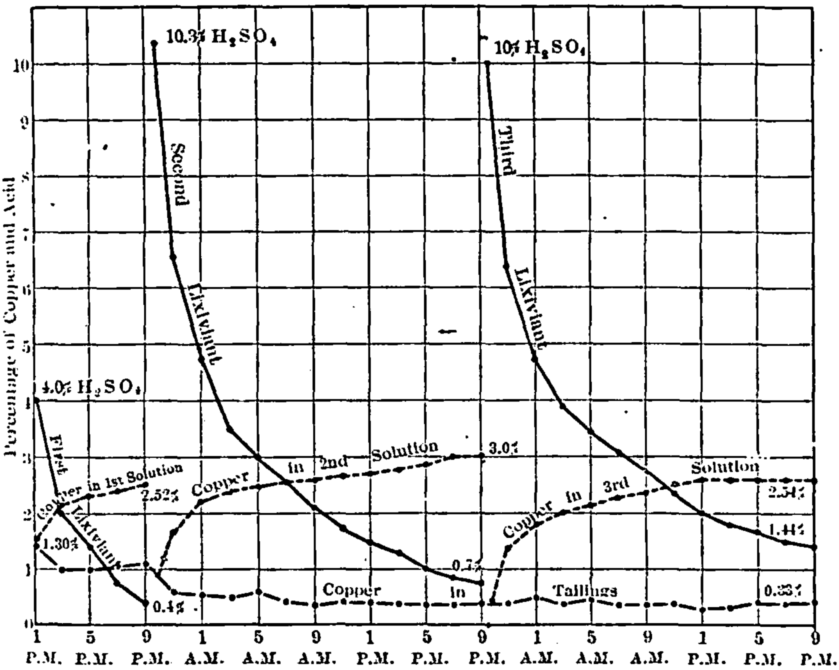

FIG. 3.—RELATIVE VARIATIONS IN COPPER AND ACID CONTENTS OF LIXIVIUM AND ORE, CHARGE 38, VAT *D*.

The results were:

| Vat. | Charges | | | Tailings | | | Extraction | | | Time of Leaching, Hours | Lixiviant Changed Every | Per Cent. Acid | | Lb. Acid Used per Lb. Cu Dissolved |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Weight, Lb. | Cu, Per Cent. | Cu, Lb. | Total Cu, Per Cent. | Sol. Cu, Per Cent. | Total Cu, Lb. | Total Cu, Lb. | Cu, Lb. per Ton | Per Cent. | | | Going On | Going Off | |
| A....... | 6,020 | 1.42 | 85 | 0.72 | 0.60 | 43 | 42 | 14.0 | 49.5 | 96 | 24 hr. | 5.50 | tr. | 3.0 |
| *B*....... | 7,825 | 1.40 | 109 | 0.32 | 0.23 | 25 | 84 | 21.5 | 77.0 | 120 | 24 hr. | 5.20 | tr. | 2.0 |
| *D*....... | 16,500 | 1.76 | 290 | 0.40 | 0.36 | 66 | 234 | 28.4 | 77.2 | 144 | 24 hr. | 5.10 | tr. | 2.0 |
| Total... | 30,345 | 1.60 | 484 | 0.44 | 0.37 | 134 | 350 | 23.0 | 72.3 | 120 | ..... | 5.25 | tr. | 2.1 |

The relative percentages of copper, iron, and alumina dissolved by the several lixiviants on each charge are shown below. Owing to the incomplete extraction and shorter time of leaching on Vat *A*, those results are not comparable and are omitted.

Vat *B*

| Extracted by | Hours on Ore | Per Cent. Acid | | Relative Percentages Dissolved | | |
|---|---|---|---|---|---|---|
| | | Going On | Going Off | Cu | Fe | $Al_2O_3$ |
| First lixiviant........... | 24 | 5.60 | trace | 1.0 | 0.0 | 0.0 |
| Second lixiviant......... | 24 | 5.40 | trace | 20.3 | 31.9 | 17.6 |
| Third lixiviant.......... | 24 | 5.40 | trace | 22.1 | 21.3 | 18.9 |
| Fourth lixiviant......... | 24 | 4.79 | trace | 28.3 | 21.3 | 29.7 |
| Fifth lixiviant.......... | 24 | 4.79 | trace | 27.3 | 25.5 | 33.8 |
| | | 5.20 | | 100.0 | 100.0 | 100.0 |

Vat *D*

| Extracted by | Hours on Ore | Per Cent. Acid | | Relative Percentages Dissolved | | |
|---|---|---|---|---|---|---|
| | | Going On | Going Off | Cu | Fe | $Al_2O_3$ |
| First lixiviant........... | 24 | 5.60 | trace | 1.0 | 0.0 | 0.0 |
| Second lixiviant......... | 24 | 5.40 | trace | 16.4 | 18.2 | 8.8 |
| Third lixiviant.......... | 24 | 5.40 | trace | 19.0 | 10.2 | 15.5 |
| Fourth lixiviant......... | 24 | 4.79 | trace | 21.9 | 21.6 | 26.3 |
| Fifth lixiviant.......... | 24 | 4.79 | trace | 20.9 | 21.6 | 25.5 |
| Sixth lixiviant.......... | 24 | 4.79 | trace | 20.2 | 28.4 | 23.9 |
| | | 5.10 | | 100.0 | 100.0 | 100.0 |

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The ore being saturated with water in each of these charges, each lixiviant put on represented one volume of solution, or enough to fill the interstices and cover the charge. The results in each case show that the first lixiviant, containing 5.60 per cent. acid, was but little more than enough to destroy the alkalinity of the ore and very little of the copper was dissolved. In fact, the first lixiviant coming from Vat *A* contained less copper than it did going on, showing that the acid was not sufficient to destroy the alkalinity of the ore and some of the copper was reprecipitated in the ore. This confirms the results already obtained in the experimental plant, where there was usually very little increase and sometimes a considerable decrease in the copper contents of the first lixiviant if the free acid and ferric sulphate in solution were not sufficient to destroy the alkalinity of the ore. Therefore it is a waste of time and expense to use lixiviants too weak to accomplish this purpose and to bring about a maximum solution of copper with the first lixiviant.

On the other hand, where a 10 per cent. or stronger acid was used, 75 or 90 per cent. of the total copper dissolved can be extracted by the first lixiviant in 36 to 48 hr.

Each succeeding lixiviant dissolved about the same amount of copper and a corresponding amount of iron and alumina. As in the laboratory tests, iron dissolved relatively as rapidly as the copper while the alumina dissolved in increasing proportions with each succeeding lixiviant.

The final lixiviants on each charge were made from new acid.

That the extraction was not completed, even at the end of the sixth day on Vat *D*, is shown by the complete neutralization of the acid in the final lixiviums and no decrease in their copper contents. Had the leaching been continued to the complete extraction of the copper, the increasing percentage of alumina, together with the iron passing into solution, would no doubt have increased the acid consumption to approximately that already obtained in the experimental plant.

It was found inadvisable to saturate the ore with water before applying the first lixiviant. This water must, of course, be replaced by the acid before the copper can be dissolved and the interchange takes place but slowly through the pores of the ore.

The acid lixiviants should be applied to the dry ore.

### *Summary of Operations*

Analysis of a composite sample of the five lots of ore treated gave the following results.

The average grade of this entire quantity of ore was much lower than anticipated and lower than that used for the laboratory experiments.

All of the ore treated passed through a 2-mesh screen except the oversize from Test 1, which amounted to 9,818 lb. This oversize

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ranged between 0.5 and 1 in. in size and was treated by itself as a special experiment to conform more closely to the practice of the Arizona Copper Co. at Clifton.

| | Calculated from Five Samples, Per Cent. | Composite Sample, Per Cent. | | Calculated from Five Samples, Per Cent. | Composite Sample, Per Cent. |
|---|---|---|---|---|---|
| $SiO_2$ | 64.27 | 63.29 | Cu, total | 1.44 | 1.45 |
| Fe | 4.18 | 4.20 | Cu sol. in 10 per cent. | | |
| $Al_2O_3$ | 14.73 | 14.30 | $H_2SO_4$ | 1.31 | 1.32 |
| CaO sol. in acid | 0.63 | 0.90 | $CO_2$ | 1.30 | 1.26 |
| MgO | ...... | 0.80 | | Ounce | Ounce |
| MnO | ...... | 0.14 | Au | 0.01 | 0.01 |
| S, total | 0.32 | 0.27 | Ag | 0.18 | 0.18 |
| S as sulphate | 0.05 | 0.10 | | | |

The first charge was leached only 20 hr. and gave an extraction of 51.7 per cent. The second charge was leached 39 hr. and gave an extraction of 71 per cent., making an average leaching time of about 30 hr. and yielding an average extraction of 61.3 per cent. If the time of leaching had been prolonged to 70 hr., corresponding to that of the 2-mesh material, the extraction of the whole lot would undoubtedly have been as good as that of the 2-mesh material alone, for by combining the results, we have:

| Size of Material, | Per Cent. Weight | Extraction | |
|---|---|---|---|
| | | Lb. Cu per Ton | Per Cent. |
| 1 to 0.5 | 7.25 | 21.6 | 61.3 |
| 0.5 and finer | 92.75 | 24.4 | 80.0 |
| Total | 100.00 | 24.2 | 78.4 |

Therefore in all probability the ore can be leached successfully if not crushed finer than will pass a 0.75-in. screen, which will avoid much of the fine material and slime.

The ore in Test 3, on the other hand, nearly all passed a 4-mesh screen. The fine material produced in crushing to this size very seriously interfered with the percolation of the lixiviants, and washing the ore; consequently it caused loss of time and gave low extractions.

Had the entire quantity of ore treated been thoroughly mixed and crushed to a uniform size, the results would have been better than the average of the results obtained by treating each lot separately, so the

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average results given below are probably not the best obtainable and are certainly on the safe side.

*Screen Analysis*

| Mesh | Per Cent. |
|---|---|
| +4 | 19 |
| +8 | 25 |
| +16 | 18 |
| −16 | 38 |
| | 100 |

| | |
|---|---|
| Total ore treated, pounds | 384,784 |
| Copper in ore, per cent | 1.43 |
| Total copper in ore, pounds | 5,526 |
| Available copper in ore (soluble in $H_2SO_4$ and lixiviant), pounds | 5,097 |
| Time of leaching, hours | 80 |
| Time of washing, hours | 10 |
| Copper in tailing, per cent | 0.32 |
| Total copper in tailing, pounds | 1,228 |
| Soluble copper in tailing, per cent | 0.21 |
| Total soluble copper in tailing, pounds | 799 |
| Copper in tailing insoluble in $H_2SO_4$, pounds | 429 |
| Total copper extracted from ore, pounds | 4,298 |
| Total copper extracted from ore, per cent | 77.8 |
| Copper accounted for in solution including that from oversize in Test 1, pounds | 4,269 |
| Copper accounted for in solution including that from oversize in Test 1, per cent | 97 |
| Total copper extracted from ore based on weight of tailing at 97 per cent. of ore, pounds | 4,336 |
| Total copper extracted from ore based on above weight of tailing, per cent. | 78.5 |
| Soluble or available copper extracted from the ore, per cent | 84.3 |
| Soluble or available copper extracted from the ore based on above weight of tailing, per cent | 84.7 |
| Copper extracted per ton of ore, pounds | 22.34 |
| Copper extracted per ton of ore based on above weight of tailing, pounds | 22.50 |
| Average strength of acid used, per cent | 8.9 |
| Acid used (100 per cent. $H_2SO_4$) per pound of copper dissolved, based on the difference in free acid in the lixiviants going on and going off each charge, as found by analyses, pounds | 3.6 |
| Acid used (100 per cent. $H_2SO_4$) per ton of ore on above basis, pounds. | 80 |
| Acid used (100 per cent. $H_2SO_4$) per pound of copper dissolved, based on the total combined acid found by analyses in all the solutions sent to precipitating tanks, wash waters, and lixiviants returned to storage, pounds | 3.15 |
| Acid used (100 per cent. $H_2SO_4$) per ton of ore on above basis, pounds. | 67 |
| Lixiviants used per ton of ore, gallons | 128 |
| Wash water used per ton of ore, gallons | 268 |
| Solution required to cover 1 ton of ore after saturation, equals one volume, gallons | 34 |
| Rate of percolation through ore, inches per hour | 78 |
| Rate of percolation per square foot of filter area, gallons per hour | 10 |

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*Summary of Construction*

Of the two methods recommended for waterproofing concrete viz., by the use of "Toxement" and by the use of crude oil, the concrete mixed with crude oil appeared to be less attacked by the acid solutions at the end of two months' service than that mixed with "Toxement," although the difference was scarcely noticeable.

Both methods require a much longer time for the concrete to set than when neither is used.

So far as could be observed, the acid-resisting qualities of concrete and plaster prepared with either "Toxement" or oil were not any better than those of ordinary concrete and cement plaster made with siliceous sand and gravel.

Acid-resisting paint known as "R. I. W. No. 89" prepared especially for this work was of no value whatever in protecting the concrete vats from the 10 per cent. sulphuric solutions, the weaker lixiviants in the leaching vats, or the neutralized copper sulphate solutions in the precipitating tanks.

Asphalt applied hot or as a paint was likewise useless as a protective covering for the cement plaster under any of the above conditions. One difficulty in retaining this on the walls of the vats was the high temperature of the water used for washing the ore, which averaged 100° F. or more.

The use of such warm wash water may be criticised and would have been changed under ordinary conditions, but there was a possibility of the water supply coming from hot springs or wells, if developed near the mine, so it was thought best to put the asphalt coverings to the severest test. Besides, a glance at the atmospheric temperatures during the summer months, as given in the beginning of this article, is sufficient to show that even this part of the experimental work required some care in manipulation. Asphalt that would soften and run from joints between bricks or from walls under the heat of the sun, might be brittle enough to crack at night and allow the acid solutions to get at the cement behind it.

With the exception of Vat *A*, all the leaching vats, acid and precipitating tanks may be considered as operated for the entire two months on the cement plaster alone, for at no time did the protective covering last more than 24 to 48 hr. on the leaching vats, and on the acid and precipitating tanks the paint would come off in patches after a few hours' or a few days' exposure to the solutions. At the end of two months the "Toxement" plaster, ½ in. thick, was disintegrated to the concrete in places on Vat *B* and the oil-mixed plaster of the same thickness was disintegrated nearly to the concrete on Vat C. In the acid storage tanks both the "Toxement" and oil-mixed plaster were dissolved in patches by the 10 per cent. acid solutions and the solutions leaked through the

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8-in. concrete walls. These holes were patched with ordinary cement and sand plaster and also with straight cement, both of which held the solutions successfully for several weeks.

One of the storage tanks was replastered with cement and sand and thoroughly coated with paraffin, which was forced into the plaster with a hot iron. When filled with dilute acid lixiviant, the paraffin came off immediately and was of no value whatever as a protective covering.

A plaster, recommended by the Standard Oil Co., was also tried on the acid storage tanks. It was composed, by weight, of 10 per cent. litharge, 20 per cent. short fiber asbestos, and 70 per cent. sand. These were mixed into a mortar with 40° silicate of soda and applied in the usual manner.

This plaster immediately disintegrated on filling the tank with water. The tank was then replastered with the same materials and filled with dilute acid. So long as the plaster remained covered with acid, it was a satisfactory protection, but on exposure to air it began to disintegrate.

Some of the leaching vats were plastered with ordinary cement and sand mortar and painted with several coats of crude petroleum. Each application of oil was allowed to soak into the cement and become perfectly dry before another coat was applied. This was done at the close of my experiments and I had no opportunity to test its merits.

The brick lining in Vat *A* proved to be very satisfactory. With the exception of where the asphalt was melted from the joints by the hot wash water, no deterioration could be noticed. This was due to the irregular size and shape of the common brick used for the lining and could be avoided by using pressed brick of uniform size which would permit of thin joints. In a large vat the brick would also be laid flat instead of on edge.

The sand and asphalt bottoms were entirely satisfactory when they were pressed solid with a heavy hot iron muller like that used in street paving. If this was not done, they were porous and spongy, and no protection against the solutions.

As now developed by the limited operation of the experimental plant, ordinary or oil-mixed concrete will be entirely satisfactory for leaching vats, wash-water and neutralized copper sulphate solution tanks. These can be made tight and acid resisting by lining with pressed brick of uniform size, laid in asphalt and backed with hot asphalt poured between the brick and concrete. Vitrified brick would be less porous and preferable if they can be obtained straight and uniform in size. The vats should be plastered inside with cement and sand mortar before putting in the brick lining.

The cement we used in construction came from the regular run of

Experim'tl leaching at

the mill at El Paso and contained more or less free lime. It is my belief that with cement and other materials containing *no* free lime, a concrete vat can be built and lined with brick, laid with thin joints of cement and sand mortar, that will be entirely satisfactory for acid leaching. After the brick soak full of mineral salts, there is very little if any transfusion of the corrosive solutions to the concrete back of the lining and they form a protective coating for both ore and solutions.

Oil-mixed cement plaster will last two or three months without patching or renewal. A brick lining laid in oil-mixed cement mortar would probably last longer than plaster, but the asphalt and brick lining is recommended if it can be held in place.

The cracks that form after construction are the most serious, if not a fatal defect in concrete for leaching vats. These are often so small that they are scarcely noticeable and yet are sufficient to start a leak that is almost impossible to stop. even with asphalt itself.

The shape of the vats is immaterial, although for economy of construction and operation a rectangular concrete vat is preferable. The tailings can then be removed from the top, and the bottom of the vat made solid with no openings.

The bottoms of the vats should be paved with sand and asphalt, thoroughly pressed down with hot iron mullers or otherwise to make a *compact* covering. On top of this should be a brick paving laid in asphalt.

The storage or acid mixing tanks for the 5 to 10 per cent. acid solutions should be made of steel or wood and lined with lead.

The hard-lead centrifugal pumps used for circulating the solutions showed no wear except the steel shafts. It was difficult to keep packing tight enough around the shafts to prevent the leakage of solutions, and at the same time not crack the lead casing or stuffing gland. The shafts on all the pumps were worn out in two months and were replaced with bronze. The wear on the bronze shafts is undetermined. The repairs on the pumps will not be a serious matter since new casings, runners and shafts are easily made.

Low-pressure air-lift pumps offer more advantages, on account of freedom from moving parts in the corrosive solutions, and are recommended.

The pure-rubber acid-proof hose used for the transfer of solutions showed no deterioration at the end of two months. While the initial cost is high, it is the only hose that will resist the corrosive solutions and it is indispensable for handling solutions from the pumps on top of the vats.

Lead-lined iron pipe is recommended for the rigid pipe connections and wooden, lead-lined or concrete launders provide the simplest means for the transfer of solutions from one leaching vat to another.

The tailings will have to be removed from the vats by machinery. No

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portion of them will run out by gravity unless they contain a high percentage of water.

Since the tailings will be discharged containing small percentages of free acid and copper sulphate, the kind of metal used for disks, plows or buckets in the excavating machinery was given consideration, although it is improbable that the quantity of acid or copper sulphate in the tailings will be sufficient to prohibit the use of cast iron, steel, or perhaps a high-silicon iron which has high acid-resisting properties.

Krupp bronze and "Monel" metal were both submitted to the following tests. Pieces of each metal were allowed to stand in acid solutions and in acidified copper sulphate solutions of varying strengths—the bronze for two and one-half and the Monel metal for three months.

The bronze precipitated the copper completely from all but the two strongest solutions. The Monel metal precipitated no copper, but passed into solution to a greater extent than the bronze. The results were as follows:

*With Sulphuric Acid*

| Strength of Acid | Per Cent. Loss in Weight | |
|---|---|---|
| Per Cent. $H_2SO_4$ | Bronze | Monel Metal |
| 0.12 | 3.22 | 3.89 |
| 0.25 | 3.26 | 5.92 |
| 0.50 | 3.77 | 8.86 |
| 0.75 | 3.54 | 7.62 |
| 1.00 | 3.64 | 7.55 |
| 1.50 | 4.55 | 10.07 |

*With Acidified Copper Sulphate Solution*

| Strength of Solution, Per Cent. Cu | Per Cent. Loss in Weight | |
|---|---|---|
| | Bronze | Monel Metal |
| 0.05 | 1.22 | 14.50 |
| 0.10 | 1.22 | 7.20 |
| 0.20 | 0.76 | 4.73 |
| 0.30 | 0.82 | 5.08 |
| 0.40 | 0.10 | 2.17 |
| 0.50 | 0.22 | 7.87 |

The Monel metal was also allowed to stand about six weeks in the following solutions:

| | Loss in Weight, Per Cent. |
|---|---|
| 10 per cent. sulphuric acid | 2.81 |
| 10 per cent. sulphuric acid and 10 per cent. copper sulphate (2.5 per cent. Cu) | 4.88 |
| 10 per cent. copper sulphate (2.5 per cent. Cu) | 1.99 |

A high-silicon iron, under the trade name of "Duriron," was tested in a similar manner by these solutions. So far as could be observed at

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the end of a few weeks this metal was not corroded in the least but the experimental work was closed before this test was finished. The acid-resisting quality of this alloy is well known but it has the disadvantage of being very hard and brittle.

## Precipitation of the Copper from Solution

I have purposely divided my subject into two parts because there have been almost as many methods proposed for precipitation of the copper from solution as there have for leaching it from the ore, and to-day there is probably more uncertainty and more difference of opinion concerning the methods of precipitation than there is concerning the methods of leaching. Of all the methods proposed there is just one that has been demonstrated a commercial success, and that is precipitation on metallic iron.

Lime or limestone was used in some of the earlier methods of hydrometallurgy, but this gave a precipitate that was little better than the ore itself.

Sulphurous acid came into prominence a few years ago, but it involved difficulties of manipulation that have not been overcome, even in small-scale operations. Hydrogen sulphide, produced from iron matte, has been tried but has not been developed on a large scale and is likely to prove a troublesome reagent under such conditions.

Electrolytic precipitation is always attractive and has probably received more attention and intelligent experimentation from skilled metallurgists than any other method While some small plants use this method from time to time, it cannot as yet be called a commercial success.

When working on a metallurgical problem, where the margin is narrow, one must always consider the materials at hand as the cheapest obtainable and most likely to permit profitable operations.

As possible precipitants for the copper, I considered the following in the order named: Natural sulphides of iron, artificial sulphide of iron, sponge iron, pig iron, and electric current.

### *Natural Sulphides of Iron*

If acid leaching is used for the oxidized ore some other process will have to be used for the sulphide ore. It is probable that this would be some form of mechanical concentration.

Tests had already been made by the ordinary methods of wet concentration at the University of Arizona before my arrival. These, by very careful manipulation, gave a recovery of 68 per cent. of the copper, 77 per cent. of the gold and 63 per cent. of the silver, but the concentrates carried only 10.2 per cent. copper from an ore that assayed 2.3 per cent. copper, 0.02 oz. gold and 0.22 oz. silver per ton.

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By a combination of flotation and concentration I was able to raise the recovery to over 76 per cent. and the grade of the concentrates to nearly 14 per cent. copper, although the flotation concentrates themselves assayed nearly 24 per cent. copper. As is often the case when chalcopyrite has its source in igneous rocks, it is intimately associated with magnetite. Even fine crushing to 40 mesh failed to separate the magnetite from the chalcopyrite in this ore and this destroyed the properties of the latter for flotation methods to a great extent, as well as lowered the grade of concentrates. However, by treating these concentrates on a magnetic separator I was able to raise the grade to 18.5 per cent. copper. The magnetite itself carried no value.

This, then, was the product, and probably the best that can be obtained from the sulphide ores by the usual methods of treatment. It must be shipped to the company's smeltery at Douglas for treatment, or it must be smelted into matte and blister copper on the ground. If shipped to the smeltery, it would certainly be advisable to raise its grade if possible either with or without removing the magnetite.

It is generally conceded among geologists that secondary chalcocite is formed by the action of copper sulphate solutions on pyrite. Barring the recognized but unknown intermediate reactions, the final result is supposed to be represented by this reaction:

$$5FeS_2 + 14CuSO_4 + 12H_2O = 7Cu_2S + 5FeSO_4 + 12H_2SO_4$$

While later investigators have found this reaction "incompatible with the actual volume relations observable," there seems to be no doubt about ferrous sulphate and sulphuric acid being formed when the chalcocite is deposited, and, if the above reaction is true, nearly all of the acid originally combined with the copper is regenerated.

The reaction with chalcopyrite might be very simple, producing cupric instead of cuprous sulphide, thus:

$$CuFeS_2 + CuSO_4 = 2CuS + FeSO_4$$

I had therefore a recognized precipitant for copper in the concentrates from the sulphide ores. Its efficiency as a precipitant was important but not essential, since any precipitation of the copper from solution and consequent enrichment of the concentrates would be a distinct gain. The only factor to make it a commercial success was the speed of the reaction and in this it failed. However, having secured sufficiently speedy reactions from other natural sulphides of iron on previous occasions, I am not prepared to say the last word has been spoken in this case.

### *Artificial Sulphide of Iron*

Two sources of this precipitant would be available. First, the matte produced by smelting the concentrates at the mine, and second, the matte that could be produced by smelting the low-grade pyrite at Bisbee. If soluble sulphides precipitate cupric sulphide from copper solutions and natural sulphides of iron precipitate cuprous sulphide, it is reasonable to expect the artificial sulphide of iron to do the same.

Earlier experiments had shown me that iron sulphide precipitates metallic copper and not sulphide of copper from solution. This investigation was carried further and I found the reaction to be, not a simple transposition of the metals, but the following:

$$4FeS + CuSO_4 = Cu + FeSO_4 + Fe_3S_4$$

I found also that the precipitation of copper stops at this point, although free sulphuric acid will readily decompose the $Fe_3S_4$ with the liberation of hydrogen sulphide. Therefore less than 25 per cent. of the iron in pure iron sulphide is available for the precipitation of copper and the resulting product cannot carry more than 17.7 per cent. copper.

Increase in the copper contents of a matte decreases its precipitating power so much that a matte containing over 30 per cent. copper precipitates practically no copper from solution. Nevertheless the iron from the matte passes into solution to an appreciable extent. The only explanation I can offer for this phenomenon is a reduction of the cupric sulphate to cuprous sulphate and an oxidation of the cuprous sulphide of the matte to cupric sulphide, according to the following reaction, but I am not prepared to say that this is correct.

$$FeSCu_2S + 2CuSO_4 = Cu_2SO_4 + FeSO_4 + 2CuS$$

I could produce no condition that would make a copper matte precipitate copper from solution within a reasonable length of time.

This method of precipitation was pronounced a failure. For further details see my original paper on this subject.[2]

### *Sponge Iron*

This was first used as a precipitant for copper in England in 1837, although Gossage, in 1859, was the first to use it in connection with the wet extraction of copper from ores. It was made by heating a mixture of finely crushed iron ore and coal in a reverberating furnace, with a reducing flame.

Since then a great deal of sponge iron has been produced by iron manufacturers and a number of furnaces have been invented for its production, all of which are described in books on the metallurgy of iron and steel. It is now produced commercially at Hoganas, Sweden, by heating a mixture of fine magnetic iron concentrates and coal in pots or retorts by means of producer gas.

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[2] *Engineering and Mining Journal*, vol. xcvii, No. 15, pp. 745 to 748 (April 11, 1914).

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According to Sir I. Lowthian Bell,[3] oxide of iron is easily reduced by solid carbon, but carbon monoxide gas is greatly preferred as a reducing agent.

The reduction of $Fe_2O_3$ begins at 420° F.

The reduction of FeO begins at 1,300° F. and is complete at 1,475° F.

Sponge iron readily combines with oxygen when exposed to the air at a red heat. It is also capable, at certain temperatures, of splitting up the carbon dioxide formed by its own reduction.

The necessary reaction for the reduction of iron oxide by carbon monoxide seems to be

$$Fe_2O_3 + 9CO = 2Fe + 3CO_2 + 6CO$$

or, that there is as much oxygen in the CO escaping as in the $CO_2$ formed. This reaction is not so simple as it appears, however, for carbon monoxide gas is split into carbon dioxide and carbon in the presence of iron oxide or metallic iron, thus:

$$2CO = CO_2 + C$$

Hydrogen greatly assists in the reduction of iron oxide.

Dr. Frankfurter of the University of Minnesota found that finely pulverized iron ore begins to reduce at about 300° F. in an atmosphere of hydrocarbon gas and is completely reduced below 1,000° F.

S. H. Stupakoff, in a paper read before the Engineering Society of Western Pennsylvania, states that carbon monoxide begins to reduce precipitated iron oxide at 285° F., roasted carbonate at 390° F., and is active on all ores at 750° F. It is most active at 1,000° F.

Solid carbon begins to reduce iron oxide at 800° F.

The reverse action, of $CO_2$ being reduced to CO by metallic iron, begins at 800° to 1,100° F., depending upon mass action, and is most active at 1,475° F.

A mixture of $3CO_2$ and 2CO is oxidizing at 1,000° F. and a mixture of $1CO_2$ and 2CO is oxidizing anywhere above 1,500° F.

My plan for the production of this precipitant was to manufacture sulphuric acid at the leaching plant from the low-grade Bisbee pyrite and then reduce the iron oxide in the calcines to sponge iron for precipitating the copper. The Bisbee pyrite contains about 38 per cent. iron and 1.5 to 2 per cent. copper. The copper would pay for the mining.

The freight rate on this material from Bisbee to Ajo would be very low and divided equally between the acid and precipitating departments. The acid plant would be constructed so as to have the same life as the oxidized ore in the mine. In this way the cost of acid made at the leaching plant should compare favorably with that made at the smelting plant at

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[3] *Principles of the Manufacture of Iron and Steel.*

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Douglas, when the cost and maintenance of acid trains and storage equipment are considered in conjunction with the high freight rates on this commodity.

The calcines from this pyrite would be in ideal condition for the production of sponge iron. They would contain a finely divided, porous, artificial oxide of iron which could easily be reduced at low temperatures. The product obtained from the reduction of these calcines would contain 60 to 65 per cent. metallic iron in a finely divided, porous condition that would present the greatest possible surface for the rapid precipitation of copper and the copper contained in the original pyrite would all be recovered.

Laboratory experiments were made by mixing iron ore with 30 to 35 per cent. coal, both crushed to 16 mesh, and heating in a closed clay crucible in an assay muffle for 1 hr. at a temperature of 1,600° to 1,800° F. From 75 to 77 per cent. of the iron in the ore was reduced to metallic iron.

These experiments were repeated by mixing calcines with 25 to 30 per cent. coal and heating in the same manner; 98 per cent. of the available iron was metallized.

Calcines were then placed in an iron tube and heated to a low red heat in an atmosphere of hydrocarbon gas for 1 hr. Over 90 per cent. of the available iron was metallized.

This experiment was repeated and the tube was heated to incipient redness for 90 min.; 93 per cent. of the available iron was metallized. The gas used for heating the tube in this experiment was the impoverished gas coming from the reduction of the calcines.

The available iron in these experiments was the iron existing as oxide and not that existing as sulphide.

These experiments were again repeated on calcines from Bisbee pyrite crushed to ½-in. mesh instead of 16 mesh. At the end of 1 hr. 76.6 per cent. of the available iron was metallized and at the end of 2 hr. 88.3 per cent. was metallized.

Sponge iron has been produced in quantity by iron manufacturers in small reverberatory furnaces and, as I have stated, is now produced commercially in Sweden from magnetite concentrates in intermittent furnaces of the brick or pottery kiln type, so there is no doubt about the metallurgical conditions necessary for its production, nor the feasibility of its production for the precipitation of copper.

The idea of using calcines as a source of iron is new, so far as I know, and was first proposed by me during the course of these experiments in the summer of 1912. The advantages of using this material are at once apparent from every view point.

My efforts, therefore, were not to determine if sponge iron can be produced commercially, but to devise a furnace that will receive the calcines hot from the roasting furnaces, reduce them continuously and

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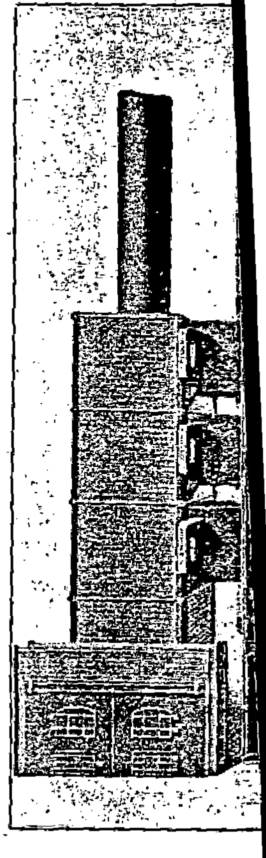

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deliver the metallized product or sponge iron to the precipitating department of the leaching plant. The problem is simply one of mechanical construction with no impossible or prohibitive features. The production of sponge iron is surprisingly easy, when the conditions are right.

After trying several small furnaces of different designs, I erected a Wedge double-function roasting furnace of special design to meet my conditions. This furnace was 9 ft. 9 in. in diameter, had six roasting hearths, one drying hearth and one cooling hearth. The three upper hearths were of the ordinary type for roasting sulphide ore. The three lower were muffle hearths heated with oil from outside fire boxes. The two sets of hearths were sealed from each other by automatic cast-iron valves. The entire furnace was sheathed with sheet iron except the top and bottom. Luting rings were placed around the center shaft, and every effort was made to make the furnace as air tight as possible. Each hearth was connected with the flue so the gases could be controlled as desired.

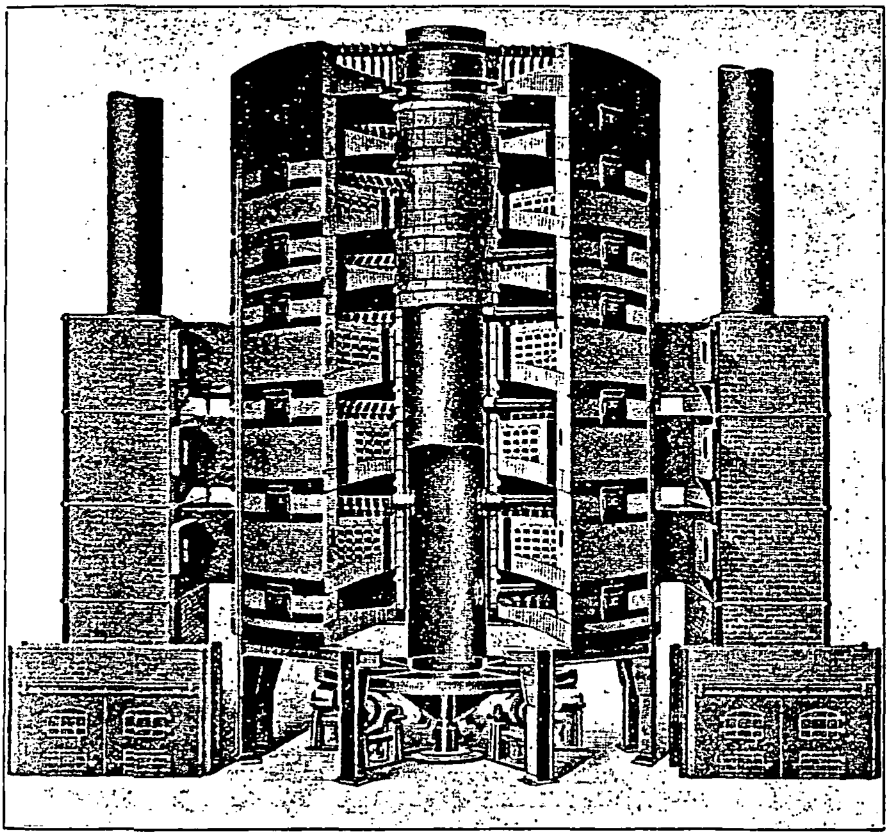

FIG. 4.—WEDGE DOUBLE-FUNCTION ROASTING FURNACE.

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A screw feeder was attached to the side of the furnace to deliver pulverized coal on the upper muffle hearth.

A general but incomplete idea of the furnace may be obtained from Fig. 4.

I expected to be able to roast Bisbee pyrite on the three upper hearths and deliver the red-hot calcines on the top muffle through the automatic valves, where they would be mixed with powdered coal from the feeder. In this way no heat would be lost and reduction would begin at once.

I soon found that I had made a serious mistake in trying to put two furnaces into one, for I had neither a roasting nor a metallizing furnace. With all six hearths for either purpose, I would have obtained better results.

The spaces for the passage of hot gases under the muffles were too small. In order to maintain the temperature that was desired on top of the muffle, the heat directly opposite the fire boxes was high enough to soften the clay tiles and cause them to warp. This allowed the calcines, already reduced to ferrous oxide, to drop into the joints and form a fusible slag which soon made a hole through the muffle and admitted air and products of combustion just where I wanted a reducing atmosphere.

My greatest trouble probably came from air leakage through the bottom or cooling hearth and around the central shaft. The bottom hearth was made of brick arched in the usual manner. It was plastered on the under side with cement, but with the constant contraction and expansion of the furnace it was impossible to make it air tight. I would frequently get metallization well started on the middle muffle hearth and the iron would oxidize again before discharging.

The luting rings around the central shaft, which were supposed to seal by dipping into the ore on the hearth, were not satisfactory for this purpose.

I endeavored to overcome these difficulties by producing a gas pressure inside the furnace from the combustion of the coal. In this I was partly successful, and for short periods of time, until something broke or temperatures fell, I got encouraging results.

The highest temperatures I was able to obtain on the muffles were as follows:

| | Degrees Fahrenheit |
|---|---|
| Top muffle | 1,000 |
| Second muffle | 1,320 |
| Third muffle | 1,460 |
| Cooling hearth | 1,040 |

but these were maintained only a short time before a muffle gave way.

When reducing with coal, I should have had higher temperatures or at least 1,400° on all the muffles. The soft coal used I thought

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had a tendency to deposit soot on the calcines at low temperatures, which retarded the reducing action. I tried lignite coal, but with so many other adverse conditions to contend with, I could not notice any difference. I also tried powdered coke, but at that time other conditions were unfavorable and the test was not completed.

I was anxious to use producer gas, but had no opportunity to do so. My own laboratory experiments and those of all other investigators have proved that iron oxide can be reduced much more easily with gas than with solid carbon, and producer gas made from lignite or oil (which would be the cheapest fuels obtainable at Ajo) would contain the most active reducing agents known for this purpose.

I regret that my work in this direction was stopped before it was carried to a conclusion, but enough was learned to satisfy me that it will be entirely feasible to metallize calcines for copper precipitation at a cost of not over $5 per ton of metallic iron. Our estimated costs at Ajo were not much more than this, and they included half the cost of the pyrite.

I believe a muffle type of furnace can be made practicable for metallizing calcines continuously, but it must be made gas tight. The top and sides should be sheathed with iron and the calcines fed through a double bell as on an iron blast furnace or through a screw feed that would always be kept full. The bottom of the furnace should be made of cast iron or, preferably, water-jacketed segments. The central shaft should be water-sealed top and bottom.

Other material than the 3-in. thick clay tiles used in the Wedge furnace could no doubt be found for the floors of the muffles. It should be some basic material. If producer gas is used for reduction, it might be possible to make these floors of cast-iron sections, because the temperature of reduction is much lower with gas than with solid carbon.

Producer gas should be used for reduction and the impoverished gas used for heating the furnace. The Mond Nickel Co. has been reducing nickel oxide by means of carbon monoxide for years in a similar type of furnace, without accident or difficulty of manipulation.

Subsequent experiments lead me to believe that a shaft furnace can be developed that will also do the work with much less complicated operation.

In any case the metallized product must be cooled in air-tight hoppers that will seal the furnace, or discharge from the furnace directly into water. The fine iron oxidizes immediately when exposed to the air at a red heat, but if cooled in a reducing atmosphere or in absence of air and kept dry, it will remain unaltered for months. If it is discharged from the furnace into water, it must be kept under water until used. It is difficult to take it from the water and dry it without some oxidation, but it will not oxidize under water within any reasonable time.

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### *Pig Iron*

When iron is mentioned for copper precipitation, no one in this country seems to consider anything but scrap iron as available for this purpose. It takes but a small amount of investigation, however, to find that pig iron is not prohibitive in cost at almost any point in the United States not remote from the railroad. It is reported that pig iron can be delivered on the Pacific coast from China or India at a cost of $10 to $12 per ton.

The use of ordinary pig iron requires long launders and more or less handling of the iron to effect complete precipitation of the copper. Of course the rapidity of precipitation depends upon the surface exposed, so I granulated the pig iron I used. This can be done best by shattering a small stream of molten iron with a jet of steam, and then cooling in a stream of water. The product was very hard and compact and most of it was in the form of shot or pear-shaped drops. It contained 93.5 per cent. iron. A screen analysis gave the following results:

| Mesh | Individual Percentages | Cumulative Percentages |
|---|---|---|
| +4 | 2.0 | 100.0 |
| +8 | 20.0 | 98.0 |
| +16 | 31.0 | 78.0 |
| +30 | 28.6 | 47.0 |
| +60 | 12.4 | 18.4 |
| −60 | 6.0 | 6.0 |

The relative precipitating values of the different sizes of this product were obtained by treating equal weights of each size with equal quantities of pure copper sulphate solution and also with lixivium obtained from leaching the oxidized ore. Each test covered the same period of time, at the same temperature, and was made under the same conditions.

| | Copper Sulphate Solution | | Lixivium | |
|---|---|---|---|---|
| Mesh | Grams Cu Precipitated | Relative Speed of Precipitation | Grams Cu Precipitated | Relative Speed of Precipitation |
| +4 | 0.050 | 1.0 | 0.06 | 1.0 |
| +8 | 0.105 | 2.1 | 0.11 | 1.8 |
| +16 | 0.385 | 7.7 | .... | .... |
| +30 | 0.540 | 10.8 | 0.59 | 9.8 |
| +60 | 0.925 | 18.5 | 1.05 | 17.5 |
| −60 | 1.175 | 23.5 | 1.31 | 21.8 |

At the Gumeshevesky mine in Russia 12 tons of granulated iron is reported to have the same precipitating capacity as 120 tons of iron plates.

The method of using granulated iron as a precipitant was also a

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small problem. Sponge iron from calcines or even from iron ore is attacked inside and out by the copper solutions and each particle, large or small, is soon a mass of cement copper. Granulated iron is attacked only on the surface and unless agitated continually during precipitation it soon cements together into a solid mass which retards further action.

To overcome this difficulty, I made a tube mill out of an iron pipe 10 ft. long and 20 in. in diameter. It was fitted with 6-in. openings at each end for the admission and discharge of solution. It was filled to these openings with granulated iron and revolved at the rate of 12 rev. per minute.

The solution going into this tube mill was a neutralized lixivium from leaching the oxidized ores. It contained

| | Per Cent. |
|---|---|
| Cu | 1.64 |
| Fe | 0.34 |
| Free acid | trace |

It was passed through at different rates of speed to get the precipitating capacity of the mill. The results obtained from the solution passing out of the mill were as follows:

| Rate, Gallons per Minute | 4 | 6 | 7 | 10 | 12 |
|---|---|---|---|---|---|
| Cu, per cent. | none | none | none | 0.06 | 0.09 |
| Fe, per cent. | ..... | ..... | 1.98 | 1.88 | 1.84 |
| Free acid, per cent. | ..... | ..... | trace | trace | trace |
| Iron (100 per cent.), pounds consumed per pound copper precipitated | ..... | ..... | 1.00 | 0.97 | 0.97 |
| Granulated iron, pounds consumed per pound copper precipitated | ..... | ..... | 1.07 | 1.04 | 1.04 |

The copper precipitate contained 73.6 per cent. copper. In a previous experiment, it contained 86.8 per cent. copper.

By this method of precipitation the iron remained in the mill, always bright and clean, while the precipitated copper passed out with the neutral solution, from which it settled rapidly and could be removed by decantation. The operation is continuous.

As seen by these results, the consumption of iron need not exceed 1 lb. for each pound of copper precipitated, provided the solutions are neutralized before precipitation.

In a large plant these mills should be made longer and of less diameter than an ordinary tube mill. The shell should be made of copper and lined with silex, to prevent abrasion. The galvanic current set up by the copper and iron would hasten the precipitation.

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### *Electrolytic Precipitation*

As usual, before starting a series of experiments, I compiled all the data available on this subject. These were obtained not only from published works, but from private notes and correspondence.

The vital factors governing this method of precipitation are cost of power, material for anodes, and interference of other metals.

The power required for deposition from clean copper sulphate solutions is about eight or ten times that required for refining purposes, or about 1 kw. per pound of copper deposited. The most economical current density is between 10 and 11 amperes per square foot and the voltage required is about 2 volts, although with magnetite anodes it is said a current density of 15 amperes can be used. With an average cost of electric power of not more than 1c. per kilowatt the power costs for this method of precipitation need not be prohibitive.

The anode material heretofore has been confined to lead or antimonial lead. Fused magnetite is now being tried and is said to be very satisfactory, although fragile and expensive. Its merits are yet to be demonstrated on a large scale. Lead anodes are gradually consumed, forming the peroxide of lead, which can be collected, reduced and used over again if necessary.

Interference of other metals has proved the chief stumbling block in most of the attempts to use the electrolytic method for the recovery of copper. Arsenic and antimony are troublesome, but are seldom found in appreciable quantities in leachable ores. Iron is the principal source of trouble and with it may be considered manganese if present, for its influence is substantially the same as that of iron. Iron, by its alternate oxidation and reduction, consumes electrical energy without the deposition of copper. It must, therefore, be rendered innocuous by one of the following methods: Removal by precipitation, the use of diaphragms, or the use of depolarizers.

Removal by precipitation on a large scale may be discarded at once as impracticable, for any effort in this direction would enable one to precipitate the copper direct by means of the same amount of chemical reagents and at about the same expense.

The use of diaphragms has been tried repeatedly, but never successfully, on long-continued, large-scale operations. Under the conditions involved, it is improbable that they can ever be made to operate successfully, for diaphragm material that does the work required, increases the electrical resistance beyond commercial limits.

The use of a depolarizer seems to offer a way out of this difficulty. The most feasible depolarizer and perhaps the only one sufficiently cheap for this purpose is sulphur dioxide. This has some advantages and some serious disadvantages. Theoretically, sulphur dioxide used in this

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manner will regenerate 3 lb. of acid for each pound of copper deposited. In experimental practice, 2 lb. has been the maximum obtained, owing to difficulties of manipulation. A certain amount of electromotive force is also generated in the direction of the current used, which reduces power consumption. These advantages, however, are more apparent than real. If much iron and alumina pass into solution from the ore, the actual acid regenerated in the electrolytic cells is relatively too small to be of any importance. On these Ajo ores, granting the best possible regeneration of acid from electrolytic cells, I estimated that 75 per cent. of the acid used will have to be made in an acid plant. In actual practice it would no doubt exceed this amount.

The mechanical difficulties in making the copper lixiviums absorb sufficient sulphur dioxide gas to produce the desired results have not been solved. Introduction of the gas into the electrolytic cells at the anode secures a very small absorption and renders the electrolytic plant uninhabitable for human beings. Acid makers of experience do not offer much hope of success for absorption of this gas by means of scrubbing towers.

Those who have tried to make sulphur dioxide act as a depolarizer on a commercial scale report these claims a fallacy.

Moreover, it has been found that when electrolytes containing sulphur dioxide are used the current density must be reduced to the neighborhood of 3 amperes per square foot in order to get a satisfactory deposition of the copper. This means an electrolytic plant installation three times the size ordinarily required.

It has been found impracticable to deposit copper from electrolytes containing less than 1 per cent. copper. The average lixivium including enough wash water and acid to maintain a standard electrolyte will average between 1.5 and 2 per cent. copper. Assuming then, for the sake of argument, that 35 to 50 per cent. of the copper can be deposited in good form by electrolysis (35 per cent. is actually the case in the only plant in operation), if relatively large quantities of iron and alumina pass into solution at each cycle of the lixiviant it will be necessary to discard the entire lixiviant in a short time or a portion of it at each cycle, in which the copper will have to be precipitated by a chemical reagent. This discarded lixivium will either be strongly acid or, if neutralized by fresh ore, will carry its full quota of copper. In any leaching operation, there will be also a gradual accumulation of wash water or weak solutions, which will have to be treated with a chemical precipitant.

The conditions governing the successful deposition of copper from solution by electrolysis have been determined quite conclusively after long and careful experimentation by men skilled in the art.

With ores that will yield lixiviums free from interfering elements, this method will no doubt prove a commercial success in spite of its expensive installation, but with ores like these where the iron passes into solution as readily as the copper, when the raw ore is leached with acid, it is doubtful if electrolytic precipitation can be made a commercial success or be used advantageously.

A much more feasible method of overcoming this difficulty with iron would be to keep it from going into solution in the first place.[4] This might be done by roasting the ore after crushing to the size required for leaching. The expense would be small. While there might be some danger of forming insoluble ferrites of copper, the iron and alumina would be rendered relatively insoluble in acid, the ore would be made more porous for leaching, there would be no argillaceous slimes to absorb valuable constituents, the copper sulphides and cuprite would be rendered soluble and the lixiviums might be clean enough for electrolysis.

My work was finished before this was tried.

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[4] See my discussion, *Engineering and Mining Journal*, vol. xcvii, No. 17, p. 871 (April 25, 1914).

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# LOCATION OF EXTRACTION BOREHOLES WHEN PHYSICOCHEMICAL METHODS ARE USED FOR WORKING MINERALS

V. G. Arens and I. L. Dem'yanova

UDC 622.277 : 622.366.1

By the system of working mineral deposits by physicochemical methods we mean the order of location, sinking (construction), and putting into operation of extraction boreholes [1]. Rational choice of a working system involves comprehensive analysis of the indices of possible alternative versions of the exploitation of the deposit, with an allowance for geological, hydrogeological, and economic factors.

The aim of a production process is to obtain the maximal effect for the minimal expenditure. However, in each case additional requirements must be satisfied. In particular, in some cases where mineral deposits are worked it is necessary to ensure a given level of mining out or to maintain a specific quality of the mined product, while in other cases one must attain minimal production cost or a given level of extraction of the mineral, etc. Efforts to increase extraction are a definite requirement for effective working of a mineral deposit [2].

Along with various methods promoting extraction of the product from the seam, the amount of mined-out mineral may be increased by denser location of the boreholes [3, 4]. In some cases, this is due to a decrease in the effect of seam nonuniformity on mining-out processes, in others to the characteristics of the processes arising when the boreholes are located closer to one another. Under natural conditions, both factors affect mining-out work, but in specific cases one or other factor will be predominant. This forms the basis of investigations of the effect of the parameters of the location pattern of extraction boreholes on mining-out work.

However, an increase in mining out of the mineral by denser location of the boreholes entails increased expenditure on extraction, because the working of deposits requires a great deal of capital. It is then necessary to determine the effective hole pattern. The effectiveness of simplified technical-economic calculations, based on qualitative assessments and dependences, becomes inadequate in the working of deposits by highly productive physicochemical methods. The location of extraction boreholes in a pattern which meets the requirements of efficient working of the deposit may be determined by analyzing a technical-economic model of the process. As the optimization criterion of the parameters of the hole pattern we may take the profit obtained by mining the deposit, because it takes account of the target indices – the coefficient of recovery and the extraction costs.

When examining the mathematical formulation of the problem of the most effective location of the boreholes which corresponds to the optimal expenditure and extraction, we take account of the effect of the combination of mining-geological and technical-economic factors on extraction and on expenditure for given types of borehole equipment.

The target function of this problem corresponds to the profit of the mine and is determined by the difference between the value of the mined product $V$ and its cost $C$:

$$P = V - C. \tag{1}$$

The value of the product is a function of a combination of constant and variable parameters, including the parameters of the extraction borehole pattern which have an effect on the coefficient of recovery. It may be expressed as:

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State Institute of the Mining of Chemicals, Moscow. Translated from Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh, No. 2, pp. 66-69, March-April, 1971. Original article submitted July 31, 1970.

$$V = v_0 B\,\eta., \tag{2}$$

where $v_0$ is the value of a unit of production, $B$ is the value of the balance reserves of the deposit being worked, and $\eta$ is the coefficient of recovery.

The cost of the mined product is determined by the outlay entailed on various classes of expenditure, which depend on the system used for working the deposit and on technological factors:

$$C = \sum_{i=1}^{m} c_i. \tag{3}$$

A marked effect is exerted on the production cost by the overall number of boreholes, which is determined by the borehole location pattern. The character of the effect of the number of extraction boreholes on the various classes of expenditure is determined in each case on the basis of the accepted procedure for determining the prime cost.

The mathematical problem of selecting the most efficient borehole pattern consists in maximization of the target function. The shortcoming of a maximized function, which is that no account is taken of the value of the unextracted part of the reserves of the deposit, may be eliminated by introducing into Eq. (1) the loss caused by underextraction of part of the balance reserves. The maximized function then becomes

$$P = V - C - L. \tag{4}$$

In a general case, the loss caused by underextraction may be expressed as

$$L = l B_p = l B(1 - \eta), \tag{5}$$

where $l$ is the loss caused by underextraction of 1 ton of balance reserves, and $B_p$ is the volume of the underextracted part of the reserves of the deposit.

To compile a technical-economic model of the process, we must establish a number of dependences, one of the most important of these being the dependence of the coefficient of recovery on the parameters of the borehole location pattern. As an example, we shall examine the problem of determining the extraction borehole location pattern when working sulfur deposits by the underground fusion method (UFS).

The losses incurred in UFS as a result of the location of the boreholes are due to formation of seam zones which do not undergo fusion. They are governed by nonuniformities of the seam to the strike and across its thickness and by the characteristics of propagation of the temperature field arising as a result of the difference between the densities of the injected water and the stratal water. The initial stage of investigation of the effect of the borehole location density on sulfur extraction is a study of the process in a homogeneous seam. For this purpose we performed a series of experiments on a UFS model of equivalent materials.

The characteristic of a tetragonal extraction borehole pattern was the ratio of the distance between the extraction boreholes b to the seam thickness h. Comparison of extraction was performed under conditions of equal expenditure on the heat carrier and equal duration of its effect on the seam.

The investigation of the fusion zones formed by this attack on the seam revealed that the uniformity of working of the seam increases with the density of location of the boreholes; this is clearly indicated by cross sections of the fusion zones and by calculation of the coefficient of recovery. The variation in this coefficient with the borehole density may be approximated by a linear equation. On the basis of this conclusion, we obtained a linear dependence of the coefficient of recovery, determined by the system of working [3], on the parameters of the borehole pattern:

$$\eta_p = 1 - \frac{b}{h}\,\frac{\mathrm{tg}\,\alpha}{3}, \tag{6}$$

which follows from a comparison of the geometrical forms of the fusion zones (characterized by the distance between the extraction boreholes and the mean value of the $\alpha$ between the generatrix of the fusion zone and the floor of the seam) with the volume of the part of the seam pertaining to one borehole.

This dependence is derived on the assumption of the absence of thermal and hydrodynamic interaction of the extraction boreholes, which may be possible if the proportion of the effect on the warmup of the seam due to interaction of the boreholes is negligible.

Examining the stationary problem, we assume that $\alpha$ is a constant value which is independent of time and t seam coordinate. In the proposed dependence, by $\alpha$ we mean the average value of the angle at the initial mome of attack on the seam.

With these assumptions, the dependence may be used for determining the optimal borehole pattern for worki sulfur deposits by the UFS method. By way of an illustration, we shall limit ourselves to a simple case, reducing th problem to an investigation of the function of one variable b. The expenditure on sulfur extraction may be divide into that dependent on the number of extraction boreholes and that independent of the latter. The establishment o the degree of effect of the number of extraction boreholes, n, on the different classes of expenditure is a matter of economic investigations; we will therefore confine our attention to arbitrary division of the overall costs. The cos dependent on the number of extraction boreholes, $c_0$, include the expenditure on drilling and equipping the extraction boreholes; the costs not dependent on these factors, $c_1$, include all other classes of expenditure:

$$C = c_1 + c_0 n. \tag{7}$$

After simplification, the target function, corresponding to the profit of the mine, assumes the form

$$P = v_0 B \eta_t\left(1 - \frac{b}{h}\frac{\operatorname{tg}\alpha}{3}\right) - (c_1 + c_0 n) - u B\left[1 - \eta_t\left(1 - \frac{b}{h}\frac{\operatorname{tg}\alpha}{3}\right)\right] \tag{8}$$

with

$$n = S/b^2; \; B = \sigma h S, \tag{9}$$

where S is the area of the deposit being worked, $\sigma$ is the sulfur content in tons/m$^3$, and $\eta_t$ is the technological coe ficient of recovery.

The optimal borehole pattern, characterized by the value of b, will correspond to the maximal profit:

$$b = \sqrt[3]{\frac{6c_0}{(v_0 + u)\,\sigma\,\eta_t \operatorname{tg}\alpha}}. \tag{10}$$

To determine the value of the losses for a particular borehole pattern, investigations must be performed. However, Eq. (10) may be used without taking account of the value of L; i.e., the equation assumes the form

$$b = \sqrt[3]{\frac{6c_0}{v_0\,\sigma\,\eta_t \operatorname{tg}\alpha}}.$$

The problem of the location of extraction boreholes for different physicochemical methods of working mineral deposits may be solved by analyzing technical-economic models of processes, compiled on the basis of physical and economic investigations.

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of calcium carbonate decreases in the presence of higher iron sulphides.

Phase composition of intermediate and final products according to Xray data

| System | No. of point | Temp. °C | Phase composition |
|---|---|---|---|
| FeS-CaO | 1' | 590 | CaO, FeS, CaS, FeO, $Fe_3O_4$ |
| | 2' | 750 | CaO, FeS, CaS, FeO, $Fe_3O_4$ |
| | 3' | 900 | FeS·CaO, $CaFe_2O_4$, $Fe_3O_4$, FeO, CaS, FeS |
| | 4' | 1200 | FeS·CaO, $CaFe_2O_4$, $Fe_3O_4$, FeO, CaS, FeS |
| $FeS_2$-CaO | 1' | 650 | $FeS_2$, $(Fe_7S_8+Fe_{11}S_{12})$, CaS, CaO, FeS |
| | 2' | 750 | $(Fe_7S_8-Fe_{11}S_{12})$, CaS, CaO, FeS |
| | 3' | 970 | FeS·CaO, FeS, CaS |
| | 4' | 1100 | FeS·CaO, FeS, CaS, $CaFe_2O_4$ |
| $FeS_2$-$CaCO_3$ | 1' | 700 | $CaCO_3$, FeS, $(Fe_7S_8-Fe_{11}S_{12})$, CaS |
| | 2' | 800 | $CaCO_3$, CaS, FeS, CaO |
| | 3' | 850 | $CaCO_3$, CaO, FeS, CaS |
| | 4' | 950 | FeS·CaO, CaS, $CaFe_2O_4$, $Fe_3O_4$ |

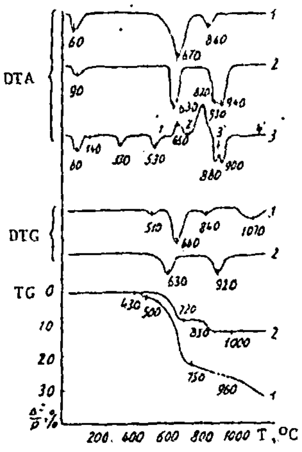

Fig.1
Derivatograms of the individual $FeS_2$ (1) and the $FeS_2$-CaO (2:3)(2) and FeS-CaO (1:1)(3) mixtures.

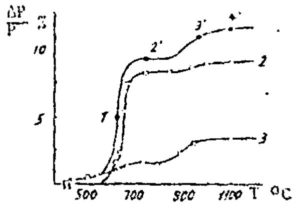

Fig.2
Curves for the weight loss in the $FeS_2$-CaO (2:3) system: $\Delta P_{tot}$ (1); $\Delta P_{S_2} = \Delta P_{tot} - \Delta P_{SO_2}$ (2); $\Delta P_{SO_2}$ (3).

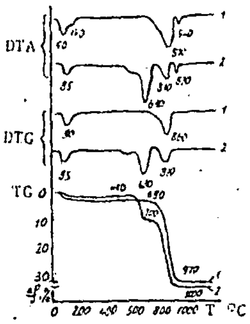

Fig.3
Derivatograms of the FeS-$CaCO_3$ (1:1) (1) and $FeS_2$-$CaCO_3$ (2:3) (2) mixtures.

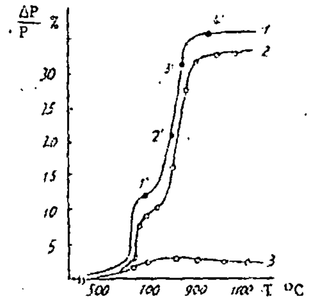

Fig.4
Curves for the weight loss in the $FeS_2$-$CaCO_3$ (2:3) system; $\Delta P_{tot}$ (1); $\Delta P_{S_2+CO_2} = \Delta P_{tot} - \Delta P_{SO_2}$ (2); $\Delta P_{SO_2}$ (3).

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UDC 669.712.1.054

# Leaching of hydrargillite bauxites having an increased kaolinite content with aluminate solutions having various caustic ratios

V I Fedoseev, F F Fedyaev, S I Kuznetsov and O S Tarasevich (Urals Polytechnic Institute - Department of the Metallurgy of Light Metals)

It is known that either the caking method or the consecutive variant of the Bayer-caking scheme is used for the extraction of alumina from low-grade bauxites having a silica ratio ($Al_2O_3$:$SiO_2$ ratio by weight) lower than 8. The cost of alumina produced by the above-mentioned methods is higher on account of the presence of the caking stage in the technological flow-sheet and the higher capital costs for the construction and equipment of the alumina plants[3]).

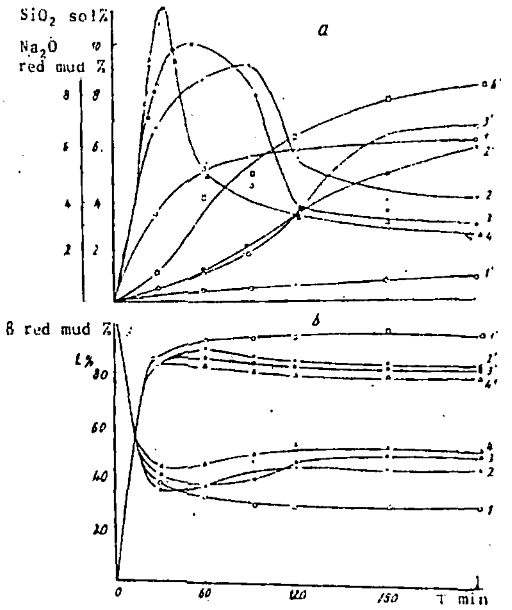
One of the main problems facing investigators is therefore the search for the possibility of processing low-grade bauxites to alumina by the simplest and most profitable Bayer process. It is necessary to find bauxite leaching conditions which the silica contained in the bauxite reacts little with the alkali, a low-alkali red mud is produced, but at the same time a high extraction of alumina into the solution is achieved. Such an attempt was made in the present work, in which the leaching of high-silica hydrargillite bauxites with aluminate solutions having various caustic ratios ($Na_2O_c$:$Al_2O_3$ molar ratio) was investigated.

Samples of bauxite from the Ayat' deposit of North Kazakhstan with $M_{Si}$ = 4.0 were used for the investigation. The particle size was -0.2 and -1.0mm. The bauxite was leached with aluminate solutions having a $Na_2O_c$ content of 240 g/l and various concentrations of $Al_2O_3$ g/l: 107, 132, 158, 197. The caustic ratios of the initial solutions amounted to 3.7, 3.0, 2.5, and 2.0. The amount of each solution was calculated to produce a caustic ratio of 1.7 after leaching. Leaching was carried out in steel vessels having an oil seal, which were placed in a glycerol-filled thermostate provided with agitation equipment. A constant leaching temperature of 105°C was maintained in all the experiments. After leaching the solid phase was separated from the aluminate solution and washed with hot distilled water. The composition of the solid and liquid media was determined by chemical analysis.

The results on the leaching of bauxite with a particle size of -0.2mm are given in the figure. In fig.(a) the kinetics of the passage of the silica into solution and the accumulation of alkali in the red mud are shown. With decrease in the concentration of alumina in the initial aluminate solution the silica content in the solution more rapidly reaches the so-called metastable equilibrium (where the rate of dissolution of the silica and the rate of its combination into the insoluble deposit are equal[2]).

Thus, during leaching with a solution having an $Al_2O_3$ concentration of 107 g/l the $SiO_2$ content reaches a maximum after 30 min and amounts to 11.6 g/l (curve 4): with an $Al_2O_3$ concentration of 197.0 g/l a maximum is not observed even after agitation for 4h. Here the concentration of $SiO_2$ amounted to only 6.3 g/l (curve 1). The alkali content of the red mud also differs. In the first case it contained 8.3% $Na_2O$, and in the second up to 1.0% $Na_2O$. Thus, it is possible to reduce the losses of alkali with the red mud greatly by leaching the bauxite with an increased $SiO_2$ content.

The kinetics of the extraction of alumina into the solution and the yield of red mud are shown in fig. (b). From the figure it is seen that the rate of passage of the alumina into solution during leaching is much higher than that of silica. The hydrargillite contained in the bauxite is leached almost completely by all the solutions after 30-40 min.



*The leaching of Ayat' bauxite having a silica ratio of 4 with aluminate solutions containing 240 g/l of alkali and the following concentrations of alumina g/l: 1 - 197; 2 - 158; 3 - 132; 4 - 107. a) The content of silica in the solution (1-4) and of alkali in the red mud (1'-4'); b) the yield of red mud β (1-4) and the extraction of alumina ε into the solution (1'-4').*

It is characteristic that higher extraction of alumina from the bauxite is observed during leaching with solutions having a low caustic ratio. Thus, with agitation for 4h the extraction of alumina into solution amounted to 94.0% with a solution having an alumina concentration of 197.0 g/l (alkali content 240.0 g/l) and 80.0% with a solution containing 107.0 g/l of $Al_2O_3$ (240.0 g/l $Na_2O$). The theoretical extraction of alumina from bauxite of such a quality is 81.0%. The higher extraction of alumina compared with the theoretical value when the low-ratio solution is used is explained by passage of alumina into the solution from the kaolinate together with the silica and by retardation of the desiliconising process.

Thus, during the leaching of low-grade hydrargillite bauxites with aluminate solutions having a low caustic ratio the hydrargillite passes completely into solution after agitation for only 30-40 min, and the silica remains in the solution for a long time. Here very little alkali accumulates in the red mud.

Analogous investigations were carried out into the leaching of the same bauxite but with a different particle size (-1.0mm). It was found that all the relationships observed in the leaching of the finer bauxite also hold in this case. The only difference lies in the slower dissolution of the hydrargillite, as a result of which complete dissolution takes 20-30 min longer.

The table gives a conversion of the chemical analysis of the red muds obtained during the leaching of bauxite with a particle size of -0.2mm to the mineralogical composition. An almost equal amount of kaolinite (12-20%) remains in the red mud in all cases, i.e., an identical amount of kaolinite dissolves in the solutions with various caustic ratios, but desiliconising takes place differently. The reason for this is the different concentration of alumina in the initial aluminate solution.

**The mineralogical composition of the red muds obtained after the leaching of Ayat' bauxite with aluminate solutions containing the following amounts of $Al_2O_3$ g/l: a) 197 ($\alpha_c$ = 2.0); b) 158 ($\alpha_c$ = 2.5); c) 132 ($\alpha_c$ = 3.0); d) 107 ($\alpha$ = 3.7)**

| Leaching time, min | $Na_2O$ in red mud | Kaolinite | HSAS | Gibbsite | Haematite | Rutile |
|---|---|---|---|---|---|---|
| | | | a | | | |
| 30 | 0.56 | 39.95 | 3.05 | 1.03 | 47.11 | 7.2 |
| 60 | 0.56 | 30.34 | 3.05 | - | 54.30 | 7.8 |
| 90 | 0.56 | 25.54 | 3.05 | - | 58.29 | 7.2 |
| 120 | 0.56 | 23.28 | 3.05 | 0.72 | 56.69 | 7.8 |
| 180 | 0.8 | 18.74 | 4.36 | - | 59.08 | 7.4 |
| 240 | 1.0 | 17.05 | 5.45 | 1.62 | 59.08 | 6.4 |
| 300 | 1.2 | 18.30 | 6.54 | 0.33 | 58.32 | 7.5 |
| 420 | 1.4 | 17.59 | 7.63 | 0.34 | 57.9 | 7.5 |
| | | | b | | | |
| 30 | 0.56 | 40.99 | 3.05 | 0.64 | 45.51 | 7.8 |
| 60 | 1.0 | 33.91 | 5.45 | 0.88 | 49.51 | 7.4 |
| 90 | 2.1 | 29.41 | 17.47 | 1.14 | 47.91 | 7.8 |
| 120 | 3.32 | 28.38 | 18.10 | 1.62 | 42.32 | 7.8 |
| 180 | 4.88 | 26.47 | 26.61 | 1.15 | 37.53 | 7.4 |
| 240 | 6.0 | 32.71 | 32.71 | 0.45 | 38.33 | 7.4 |
| | | | c | | | |
| 30 | 0.3 | 43.84 | 1.64 | - | 44.71 | 3.38 |
| 60 | 0.56 | 39.31 | 3.05 | 0.84 | 45.51 | 4.56 |
| 90 | 1.84 | 34.93 | 10.03 | 1.43 | 43.14 | 4.8 |
| 120 | 2.12 | 36.75 | 11.56 | 0.18 | 36.7 | 4.08 |
| 180 | 6.28 | 20.91 | 34.24 | - | 36.71 | 4.56 |
| 240 | 6.70 | 18.62 | 36.54 | 0.74 | 35.93 | 4.08 |
| | | | d | | | |
| 30 | 1.12 | 39.55 | 6.11 | 0.25 | 41.34 | 4.24 |
| 60 | 4.0 | 28.53 | 21.81 | - | 41.34 | 4.4 |
| 90 | 4.7 | 26.98 | 25.63 | 0.25 | 39.92 | 4.08 |
| 120 | 6.28 | 17.87 | 34.24 | 1.83 | 35.43 | 4.08 |
| 180 | 7.7 | 15.08 | 41.99 | 0.46 | 35.93 | 4.24 |
| 240 | 8.22 | 11.86 | 44.82 | - | 36.73 | 3.92 |

Kraus et alia[3]) have studied the solubility of hydrated sodium aluminosilicate in aluminate solutions and have shown that the equilibrium concentration of silica increases with increase in the alumina content of the solution more than 40-60 g/l. By comparison of the obtained data on the dissolution of the kaolinite contained in the bauxite in solutions with various concentrations of alumina with published data [3]) it can be seen that a silica content close to equilibrium was obtained in the solutions after agitation for 4h. Some authors[4-6]) have put forward the suggestion that aluminium-silicon-oxygen complexes, about the composition of which there is no common view, are formed when silica or its compounds are dissolved in aluminate solutions.

According to published data[3]), when hydrated sodium aluminosilicate is dissolved in alkaline solutions the alumina and silica pass into solution in a molar ratio close to unity i.e., complexes of the $Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot nH_2O$ type are formed in the solution. On this basis it can be supposed that in solutions with a high concentration of alumina the kaolinite reacts with the sodium aluminate during the first minutes of contact, and the compound is formed:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 2NaAl(OH)_{sol} + 2NaOH \rightleftarrows 2(Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot nH_2O)$$

Hydrated sodium aluminosilicate with the composition $Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot nH_2O$ is more soluble than the hydrated sodium aluminosilicate $Na_2O \cdot Al_2O_3 \cdot 1 \cdot 7SiO_2 \cdot nH_2O$ and is stable in solution. As shown by our experiments, the decomposition of this compound can be accelerated by the addition of sodium silicate:

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O + 0.7Na_2SiO_3 \rightleftarrows Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \times nH_2O + 1.4NaOH$$

## Conclusions

1. The kinetics of the transfer of silica and hydrargillite into solution from low-grade bauxite with an increased content

of kaolinite during leaching with aluminate solutions having various alumina contents were investigated.

2. It was established that in all cases the hydrargillite passes into solution completely after leaching for 30-40 min. During leaching with solutions having a high caustic ratio the silica content of the solution at first increases sharply and then decreases as a result of the precipitation of hydrated sodium aluminosilicate with the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$. A different pattern is observed during leaching with low-ratio solutions: the silica passes into solution more slowly and is retained in it for a prolonged period. In the latter case the losses of alkali with the red mud are small.

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UDC 669.2

## Kinetics of the oxidation of arsenic, tin, and antimony during the selective alkaline refining of crude lead

N S Krysenko and Yu P Fedorov (Zaporozh'e Industrial Institute)

### Summary

The kinetics of the oxidation of arsenic, tin, and antimony in the selective alkaline refining of crude lead, obtained from secondary lead raw material, by air alone, oxygen-enriched air, and oxygen were investigated. The oxidation rate of the impurity metals in the lead increases by 1.5-1.6 times with increase in the oxygen content of the blast from 21 to 99 vol.%.

The oxidation of the impurities takes place in the diffusion region and is mainly controlled by diffusion of the dissolved metals to the lead-alkaline melt interface. Equations are obtained for the dependence of the oxidation rate of arsenic tin, and antimony in binary alloys with lead on the oxygen content of the blast and on the temperature.

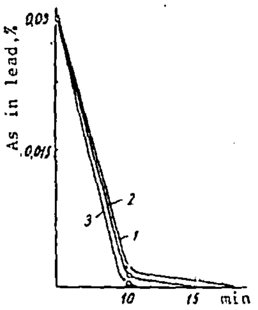

Fig. 1
Dependence of the content of arsenic in the lead on the length of the blast and on the amount of oxygen in the b blast (vol.% $O_2$): 1 - Air; 2 - 51.0; 3 - 99.0

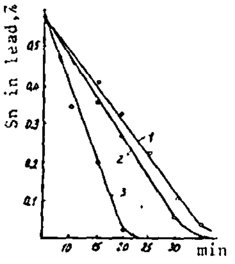

Fig. 2
Variation of the tin content of the lead on the length of the blast and on the oxygen content of the blast. The legend is the same.

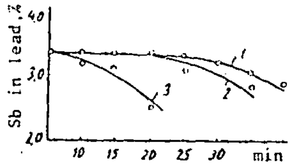

Fig. 3
The effect of the length and composition of the blast on the antimony content of the lead. The designations of the curves are the same.

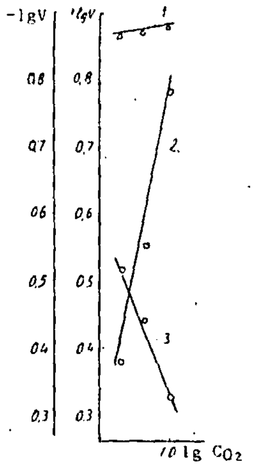

Fig. 4
Logarithmic dependence of the oxidation rate of arsenic (1), tin (2), and antimony (3) on the oxygen content of the blast.

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UDC 542.61:547.233:669.87

## Mutual effect of gallium, iron (III), and titanium in their extraction from hydrochloric acid solutions by the technical amine ANP-2 in kerosene

T I Voinarovskaya, N I Gavrilov, A M Reznik, and L D Yurchenko (Moscow Institute of Fine Chemical Technology - Department of the Chemistry and Technology of Rare and Trace Elements)

### Summary

Since gallium is present in hydrochloric acid solutions in the form of the anion $GaCl_4^-$, amines can provide the most effective means for its extraction. A radio-active tracer method was used to investigate the effective extraction of gallium from solutions containing large amounts of iron and titanium.

With the amine extractant exployed it is possible to concentrate the gallium and purify it from iron and titanium from solutions having a complex salt composition.

IN SITU, 1(4), 305-324 (1977)

# THE LIMITATIONS OF LABORATORY TESTING AND EVALUATION OF DUMP AND IN SITU LEACHING

Ronald J. Roman
Industrial Mineral Products, Inc.
P.O. Box 95, Ravensdale, WA 98051

## ABSTRACT

A general discussion of the modeling of dump and in-situ leaching is given, and a comparison of various fluid flow/reaction models and their underlying assumptions is presented. The need for laboratory work combined with model development in order to design field operations is demonstrated.

Dump and in situ leaching of copper has been practiced for many years. The recovery of copper by heap leaching at Rio Tinto is usually cited as the first commercial application of the leaching process.

In the 1880's old stopes were leached in copper mines in Ireland,[1] and in 1928 a patent[2] was granted for an in situ leaching process in which solutions are applied to the ground surface by a trench system, allowed to percolate through the ore and then collected by pumping from a shaft or by draining through an adit.

The early 1900's saw the establishment of copper dump leaching in the United States with Phelps Dodge at Bisbee and Tyrone and

Anaconda at Butte recovering copper from mine waters. In the 1920's and early 1930's John Sullivan, working at the U.S. Bureau of Mines in Tucson, conducted the first systematic scientific studies of leaching. Dump leaching was still being thought of as a poor cousin in conventional mineral beneficiation and it has just been during the last 10-20 years that there has been a major effort to more fully understand the process.

Uranium had received no attention before 1950 and it was during the boom years of the 1950's that Utah International developed and in 1967 was granted a patent for their "down hole" technique for in situ leaching.[3] With the weak demand for uranium in the early 60's, interest waned before the down hole techniques could be completely developed. Interest was renewed in the late 60's and experience in secondary oil recovery techniques and computer application produced rapid advances. Union Carbide used down hole leaching in Texas in 1968 followed by Anaconda in New Mexico in 1970 and Wyoming Minerals more recently.

The advances in copper in situ leaching have paralleled those for uranium, the first big operation in the United States being the Miami Mine in Arizona. The success of both the Old Reliable and Xonia mines has resulted in in situ leaching being now thought of as an alternative to conventional processing. As a result, accurate predictions are needed on the rate and extent of recovery possible from a deposit, given various operating conditions. When leaching was a secondary method of recovery, the economics of the venture was only slightly affected by the leaching results. However, if

leaching is to be the primary method used to recover the values, better forecasting procedures are needed.

The aim of any laboratory testing of an ore being considered for in situ leaching is to develop an estimate of the recovery versus time curve for some specified set of operating conditions. This estimate is then used together with the knowledge of the cost of the operation to generate the profitability of the proposed operation.

Scale-up equations or models are used to transform the laboratory data into the predicted field results. These models must account for any of the operating conditions in the laboratory which are different from those in the field. This implies that those factors which can affect the recovery versus time curve have been identified. If the in situ leaching process is examined, six sub processes are found to take part in the overall in situ process. These are:

(1) Flow of solution from an injection point to the rock to be leached.

(2) Diffusion of the leaching agent across a solution film boundary separating the fluid phase from the rock.

(3) Diffusion of the leaching agent through the reacted rock to the unreacted interior of that rock.

(4) Chemical reaction between the leaching agent and the mineral being dissolved.

(5) Diffusion of the dissolved metal back through the leach rock and back across the film boundary.

(6) Flow of the leach solution containing the dissolved metal out to a collection point.

The effect of changes in the operating conditions on each sub process can be predicted by applying known laws of physics and chemistry, and it is thus theoretically possible to develop a mathematical model to describe the in situ leaching process. Presently, no computer can satisfactorily solve a model of this process incorporating all that is known about in situ leaching. A solution to the algorithm for dynamic 2-phase (solution and air) flow is a major undertaking in itself, and must be reduced to a 2-dimensional problem. A solution to the 3-dimensional problem is theoretically possible, but the computer time necessary to solve the problem would exceed the real time simulated by the model.

Possibilities for simplifying the simulation of a complex phenomenon are threefold: (1) develop a faster computer, (2) develop new numerical or analytical methods for solving the complex differential equations that make up the model, and (3) accept assumptions that will reduce the complexity of the problem being studied. In the present state-of-the-art, the third alternative is most profitable.

Most researchers working on in situ leaching agree on a general model as a starting point. But differences appear in assumptions for solving the algorithm with a minimum loss in the model's accuracy. This disagreement results not from different theoretical interpretations of the problem, but from studying different problems. The relative rates and extents of the various processes occurring simultaneously within a heap will be different for different types of operations, and will dictate which assumptions can, or cannot, be made.

Making simplifying assumptions is not an easy task. The assumptions made can be verified as "good assumptions" only after the model is used to predict experimental data. One major assumption generally made is that all variables of no immediate interest have no effect on the process being modeled. For example, if the change in the solution composition is small as it flows through the heap, calculating this change (to include its effect on the leaching rate) may not be justified in terms of the small accuracy gained from the increased computer time. On the other hand, if the model does not include the change in solution composition, and it is large, then the results predicted by the model will not be valid. This type of omission can be disastrous to the model. Other types of omissions do not invalidate the model but merely limit its usefulness.

In order to be able to select valid simplifying assumptions it is best to examine each of the sub processes individually to determine if one or more of the sub processes is taking place at a rate which would cause it to be unimportant or very important. The sub processes can be taking place in parallel or in series.

Two distinct phenomena are of interest in the study of in situ leaching: fluid flow and the physicochemical reactions. These two phenomena can be studied separately if the extent of leaching an element of solution has participated in, and the extent of leaching an element of the deposit, do not influence the solution flow pattern. In other words, the solution flow pattern in the deposit is a function only of the initial conditions of the deposit. This assumption forces some questionable corollaries such as constant solution density, viscosity, surface tension, and limited decrepitation of the gangue rock as the solution flows through the deposit. If these assumptions are unacceptable, the solution flow and physicochemical phenomena must be studied together. "Practical usefulness" at this time, must be foremost in the model builder's mind--not "theoretical correctness." In many instances, assumptions will not affect the relative results the model forecasts, but will only alter the absolute value of each result. The model builder must decide which assumptions are legitimate and which destroy the usefulness of the model. Unfortunately, the effect an assumption has on the results given by a model is not known in advance; only after simulation of the process with the model--and in some cases pilot planting in an attempt to verify the model--does the invalidity of the assumption become apparent.

In general, researchers in in situ leaching have separated the fluid flow problem from the physicochemical problem. In addition, most researchers in one area have not crossed into the other area except to build simple models to simulate the entire system.

Most of the modeling work describing apparent fluid flow has been done by hydrologists in connection with natural recharge of ground water.[4-6]

In a leach dump fresh leach solution is either sprayed over the top of the heap or pumped into a pond on the top of the heap. Solution then flows downward, eventually exiting through springs near the bottom of the dump. A water table can build up in the dump; the

location of the water table is important in the chemical model of leaching. Dumps or heaps are generally built by the trucks hauling the broken rock from the pit to the dump site, unloading the rock over the edge of the dump. This process results in a size segregation in the dump in which the larger boulders are near the bottom of the heap while the finer materials remain near the top. The rock in the roadbed used by the trucks hauling the rock is pulverized and compacted. As a result, porosity and permeability can vary between wide extremes with short distances. A major problem in attempting to model the fluid flow within a heap, therefore, is obtaining porosity and permeability data for all segments of the dump. In in situ leaching, solution is usually injected into the ground water and the direction of flow established by pumping from a nearby well. The solution will flow following the path of least resistance which, in most cases, is not what would be considered ideal from a metallurgical point of view. The permeability of a segment of a uranium deposit is usually inversely related to its uranium content.

Some fluid flow modeling has been attempted by Jacobson.[7] The aim was to determine "relative" flow patterns in a heap under different operating conditions. Figure 1 shows a heap with an internal section of low permeability. The computer time needed to produce this figure was large. Yet many simplifying assumptions were made. One major assumption was that the flow of air up through the dump is spontaneous and does not influence the flow of leach solution down through the dump. Because most heaps are operated on a cyclic schedule (wetting and drying) and, hence, never attain a

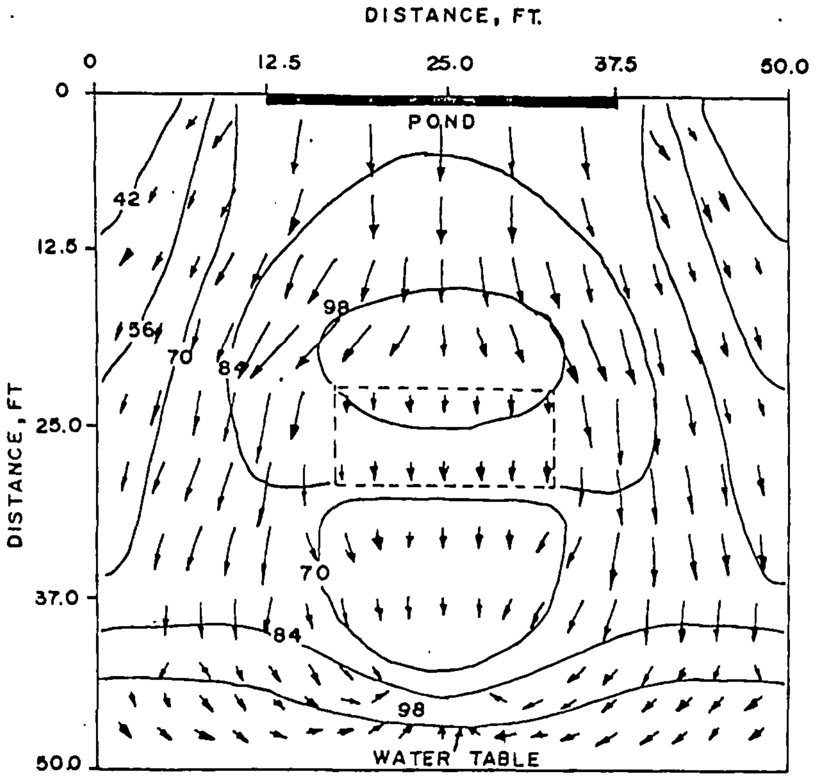


FIG. 1 Solution flow in a vertical section of a leach dump with a low permeability zone (dashed lines) in center. Contours showing equal saturation and flux vectors showing relative magnitude and direction of flow. Time about 10 hours after start of flow.

steady state flow, a dynamic fluid flow model is necessary. If the ore contains only oxide minerals, then the dump rest cycles are probably not necessary, and a steady state flow model would suffice. This model is much simpler and can, in fact, be solved for a 3-dimensional problem.

Fluid flow modeling has not received sufficient attention. The successful modeling of the fluid flow in dumps will be a major force in the development of new techniques for constructing heaps. Elimination of a water table and solution-channeling in sulfide dumps would improve significantly the performance of a dump.

There is an added problem in defining the solution flow. It is important to determine the position of the film boundary which separates the fluid phase from the rock. The film boundary then will define the effective particle size which, in turn, sets the length of the diffusion path through the particle. All the physico-chemical models now assume that individual particles (as determined by a screen analysis) are completely surrounded by the leach solution. This is definitely not the case in high bulk density zones. How does the difference in bulk density affect the scale up equations?

Increasing the bulk density can be expected to give more particle-to-particle contact; therefore, individual particles will be blinded by each other. As blinding increases with bulk density increase, the particles will behave like larger particles with a coarser apparent size distribution. The extreme will occur when the bulk density reaches that of the undisturbed rock, the entire dump behaving as a single particle with the dimensions of the heap itself. Harris[8] alluded to this phenomenon in his paper.

An alternative method of describing the same phenomenon is to consider the flow paths of the solution. At high bulk densities, leach solution no longer surrounds each particle, but flow paths are separated by several particles and channeling is said to take place (Figure 2). Instead of the particle radius being the maximum

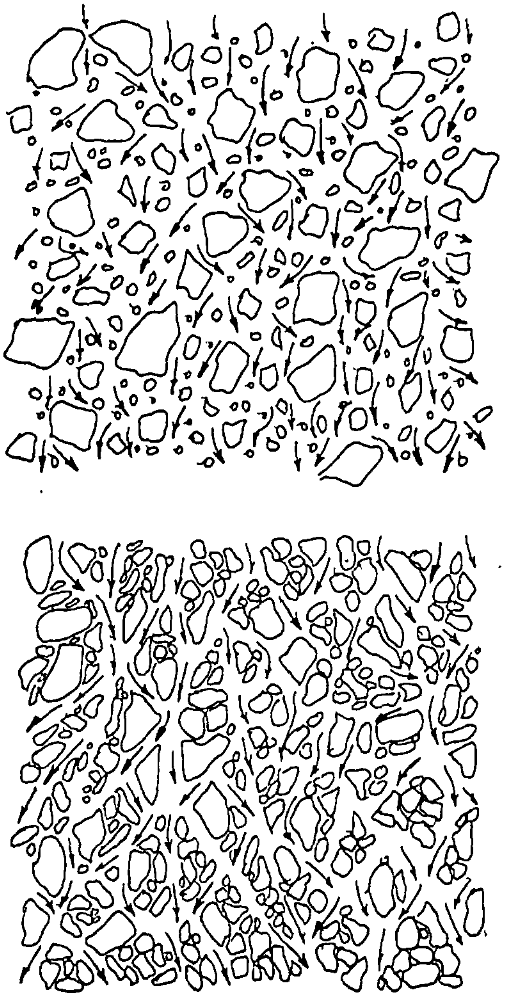


FIG. 2 Solution flow in low density and high density heaps.

distance through which the leaching agents must diffuse, the maximum distance is half the separation distance of the solution flow path. Particle size distribution must then be replaced in the models by the concept of channel separation distribution. Like size distribution, channel separation distribution specifies the cumulative

percentages of the rock in the dump situated less than a specified distance from a solution channel. Thus,

$$Y = \left(\frac{x}{d}\right)^{\alpha} \cdot 100 \qquad (1)$$

where $Y$ = percentage of rock less than $\frac{x}{2}$ meters from a channel,

$d$ = maximum spacing between channels (analogous to the Schulmann size modulus), and

$\alpha$ = constant (analogous to the Schulmann distribution modulus).

Distribution of the solution channel is a function of how the dump was built (among other things), and therefore it cannot be determined in the laboratory. Accordingly, it becomes necessary to determine a range for d and $\alpha$ in existing operations or measuring these parameters before leaching starts. Howard[9] gives a clue to one possible technique of measuring solution channel distributions. When his paper was published, little was known about the phenomenon of leaching; the importance of this type of data was not recognized. Figure 3 is a $\gamma - \gamma$ log for one hole drilled into a leach dump at Kennecott's Chino operation in New Mexico. The important feature of this log is that the dump can be divided conveniently into two lithologic categories based on the bulk density: one at 155 lb/ft$^3$ (250 kg/m$^3$) and the other <90 lb/ft$^3$(<1500 kg/m$^3$).

A reasonable assumption is that much of the solution flow will take place in the areas of <90 lb/ft$^3$(<1500 kg/m$^3$) bulk density (about 40 percent voids) whereas little flow will take place in the areas of 155 lb/ft$^3$ (2500 kg/m$^3$) bulk density (about 8 percent

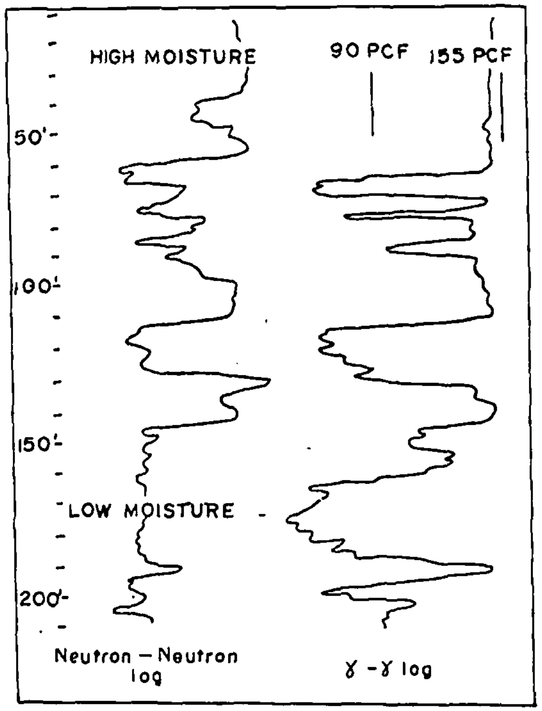


FIG. 3 Neutron-Neutron and Gamma-Gamma logs through a copper leach dump.

voids). Flow will occur in both parts of the dump. However, the fluid in the dense areas will not contribute to the total flow unless the low bulk density areas are completely saturated. From Figure 3 a distribution of solution channel separations may be determined if it is assumed that areas of <90 lb/ft$^3$ (<1500 kg/m$^3$) bulk density represent channels. The area between two neighboring channels behaves as a single particle (the only mechanism of transport through this area is diffusion). Comparison of the distribution of the distances of channel separation with the screen analysis of the material in the dump suggests that the ratio of distance of channel separation to particle size is about 30 to 1. To insure good leaching, this ratio should be kept as small as possible. Procedures for constructing dumps should be evaluated with this ratio in mind.

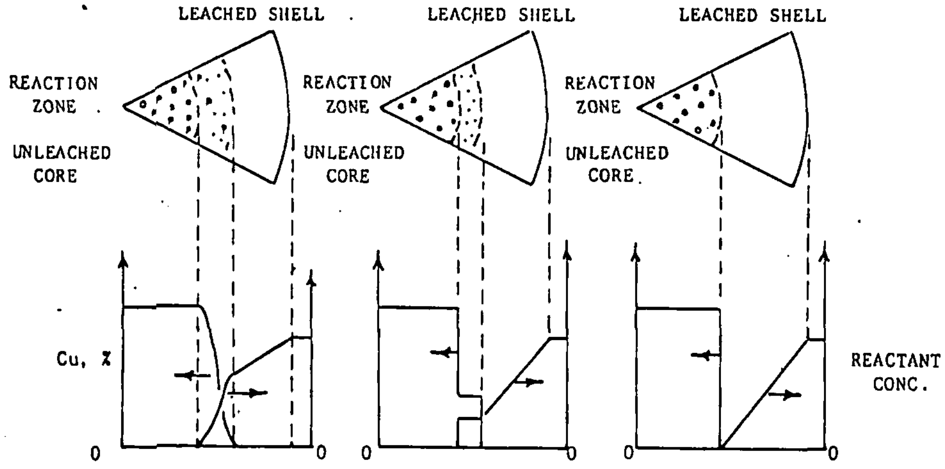
The constants in the solution channel distribution equation would change with time of leaching, but the use of this concept in place of a size distribution for scaling up dumps should give a more realistic estimate of dump performance.

When diffusion is not important, for example in new dumps or for very refractory mineralogy, the concept of channel separation becomes less important. The size distribution does not significantly influence the recovery time curve.

Defining the solution flow in an in situ or heap leaching operation is not the only problem. There are some problems still unsolved in describing the process within individual particles of ore.

Modeling of the physicochemical processes within a heap has come a long way from Taylor and Whelan's work at Rio Tinto.[10] Their work led to a simple model for predicting the copper extraction from a heap, given the past heap performance. Harris was next to propose a model for heap leaching, but like Taylor and Whelan's model, its only application appears to be in predicting future recovery from a heap given the past recovery.

More recent models have been developed for predicting the performance of a heap from laboratory tests. Three such models exist. They differ only in the assumptions made to solve the problem; each



STANFORD MODEL (a)

UNIVERSITY OF UTAH MODEL (b)

NEW MEXICO BUREAU MODEL (c)

FIG. 4 Three proposed models for individual particle leaching.

has its own area of application. Figure 4 shows the basic differences between the models; a segment of a single particle and the concentration of copper and reactant as a function of depth within the particle is shown. The model developed by Bartlett[11] (Figure 4-a) assumes a relatively slow chemical reaction rate. The result is a large reaction zone containing mineral grains at various stages of leaching. The model developed by Braun[12] assumes all the particles within the reaction zone are at the same state of leaching (Figure 4-b), thus, more applicable when the reaction zone is smaller (that is, the chemical reaction rate faster). The model developed by Roman[13] (Figure 4-c) goes one step further, assuming an instantaneous chemical reaction rate. The mathematical complexity of the models decreased from Bartlett's model to the Roman model.

TABLE 1

Acid Consumption Associated with the Dissolution of Rock Forming Cations

| ACID CONSUMPTION<br>CATION | GMS ACID/GM CATION |
|---|---|
| $Na^+$ | 2.1 |
| $K^+$ | 1.3 |
| $Ca^{++}$ | 2.5 |
| $Mg^{++}$ | 4.1 |
| $Fe^{++}$ | 1.7 |
| $Fe^{+++}$ | 2.6 |
| $Al^{+++}$ | 5.4 |
| Si (as $H_4SiO_4$) | 7.0 |

A second problem arises when reagents are not only consumed on the metal being leached. In acid solutions most minerals are unstable and will decompose to clays releasing calcium, iron, magnesium, potassium, and other rock forming elements into solution. Each element will be released at its own rate and because each consumes acid (Table 1) the leaching of each element will influence the rate of leaching of all of the other elements.

Figures 5, 6, and 7 give the solution compositions as a function of time from a column leaching test on an oxide ore. The ore was leached with sulfuric acid with no solution recycle. The metals leached by the acid solution can be divided into three groups. The first, containing calcium, lead, and silica, are generally present at a concentration limited by the solubility product of sulfate or, in the case of silica, amorphous silica. The second group, consisting of copper, manganese and zinc, appears to be released into solution following the diffusion controlled shrinking core model. The third group, iron, aluminum, potassium, etc., are released into

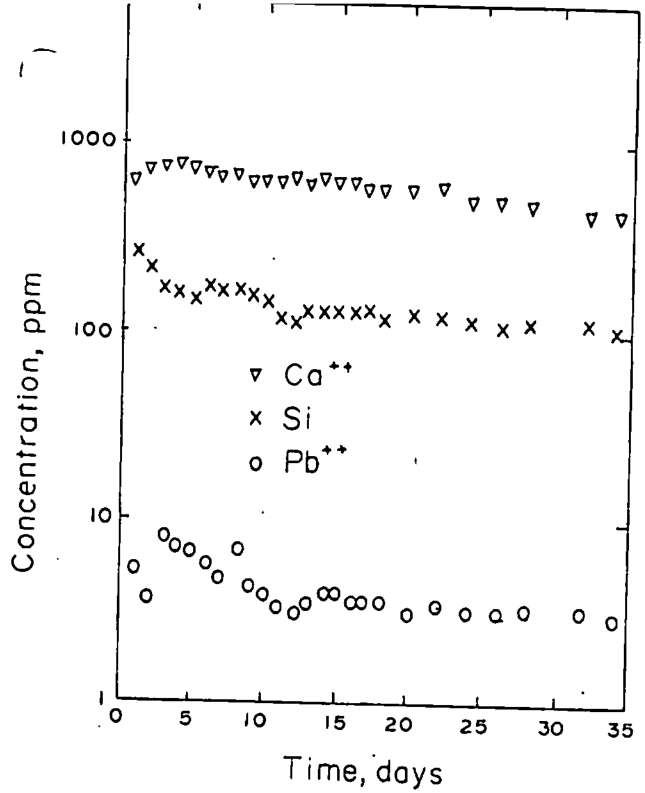


FIG. 5 Calcium, silicon, and lead concentrations in the pregnant solution from a column leach test on an oxide copper ore.

TABLE 2

Copper and Uranium Dissolution
From an Oxide Copper Ore

URANIUM RECOVERY-ORE A

| Sample, Days | Cu, ppm | U, ppm | Cu/U | Cum. Cu rec., % |
|---|---|---|---|---|
| 1 | 7740 | 1.9 | 4073 | 8.0 |
| 2 | 5380 | 1.1 | 4891 | 21.4 |
| 3 | 3910 | 0.91 | 4296 | 31.1 |
| 4 | 3140 | 0.68 | 4617 | 39.0 |
| 5 | 2250 | 0.50 | 4500 | 44.3 |
| 6 | 1850 | 0.40 | 4675 | 48.8 |
| 7 | 1250 | 0.29 | 4310 | 51.7 |
| 8 | 1050 | 0.29 | 3620 | 54.1 |
| 9 | 896 | 0.24 | 3733 | 56.2 |
| 10 | 744 | 0.16 | 4650 | 57.9 |
| 11 | 587 | 0.13 | 4515 | 59.4 |
| 12 | 544 | 0.10 | 5440 | 60.4 |
| 13 | 530 | 0.14 | 3785 | 61.9 |
| 14 | 530 | 0.14 | 3785 | 63.2 |
| 15 | 450 | 0.14 | 3214 | 63.9 |

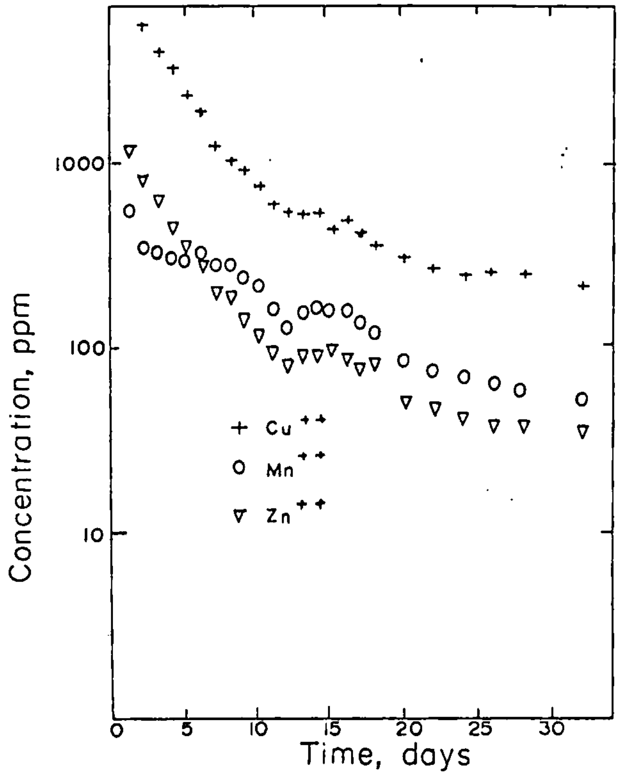


FIG. 6 Copper, manganese, and zinc concentrations in the pregnant solution from a column leach test on an oxide copper ore.

solution at a rate which appears to be both a function of diffusion and chemical reaction rate. Uranium from this oxide copper ore appears to follow the diffusion controlled rate as suggested in Table 2. The ratio of copper to uranium appears to be constant throughout the test. The proportionality constant is probably the ratio of the copper to uranium content of the ore.

It now can be seen that modeling the solution composition (acid content, in this case) as the solution flows through the material to be leached is a complex problem, not only a function of the metal being leached, but also a function of the gangue

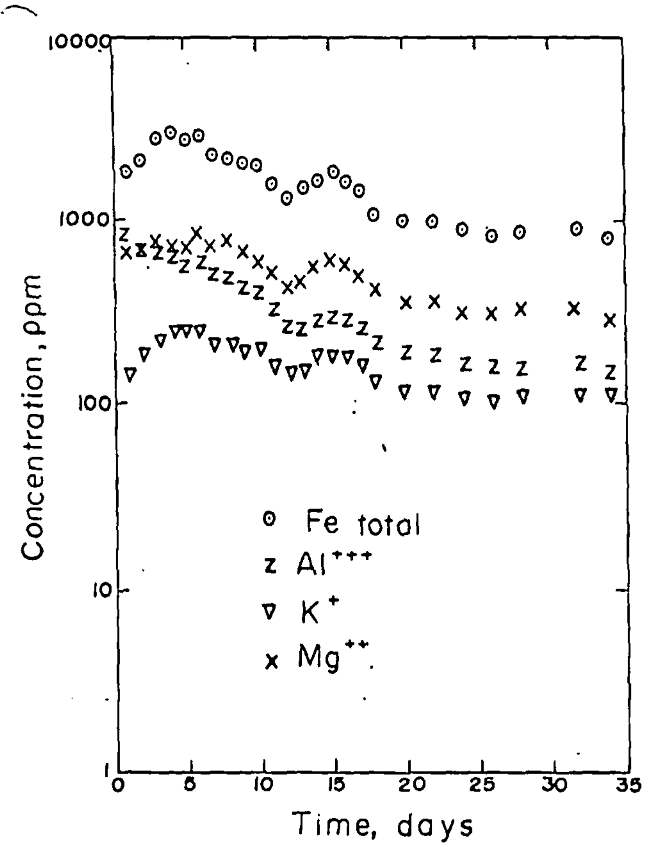


FIG. 7 Iron, aluminum, potasium, and magnesium concentrations in the pregnant solution from a column leach test on an oxide copper ore.

minerals present and the kinetics of the reaction between gangue minerals and the leach solution.

There are many other phenomena which are not included in published leaching models which may affect the validity of the predicted results. Temperature changes as a result of exothermic chemical reactions, air circulation cells within a heap, decrepitation of the rock as leaching progresses (resulting in both more

impermeable zone and maybe shorter diffusion paths), and precipitation of salts within the deposit causing changing flow characteristics are not at the present time being modeled. In some cases, these may not be important; in others they may be the controlling factor in the operation.

In spite of all the shortcomings, modeling based on laboratory test work should be carried out in any evaluation program. Modeling will, in most cases, give an idea of the best leaching results which can be obtained, thus setting an upper limit on production levels which can be expected. In addition, although the absolute values predicted by models may not be valid in many cases, the relative results from the prediction of two alternative operating procedures will be accurate. For example, although the rate of uranium production from a column of ore 10 meters in height will not be accurately known, you can determine that the rate of production from a column of ore 20 meters in height will be 1.5 times as great as for 10 meters. This type of information is invaluable in helping to design the leaching operation and the cost of obtaining it is not great.

As more experience is gained in leaching and modeling of leaching operations, it may one day be possible to evaluate a proposed leaching venture as easily as the mere evaluation of a heat exchanger.

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**United States Patent** [19]
**Coursen et al.**

[11] **3,986,430**
[45] **Oct. 19, 1976**

[54] **LOADING OF BOREHOLES WITH EXPLOSIVES**

[75] Inventors: **David Linn Coursen**, Mercersburg, Pa.; **Edmund Joseph Osterman**, Winchester, Va.

[73] Assignee: **E. I. Du Pont de Nemours and Company**, Wilmington, Del.

[22] Filed: **Mar. 21, 1975**

[21] Appl. No.: **560,712**

[52] **U.S. Cl.** .................................. **86/20 C**; 102/21; 102/23; 175/1; 175/72
[51] **Int. Cl.²** ......................... **F42B 3/00**; F42D 1/00
[58] **Field of Search** ................. 86/20 C; 102/20, 21, 102/23; 175/1, 72, 24, 48; 166/290, 51

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*Primary Examiner*—David H. Brown

[57] **ABSTRACT**

Explosive cartridges are loaded into boreholes at a rapid rate by guided descent through a retractable flexible tubing assembly through which a stream of water flows. The cartridges preferably are cut open just before their discharge from the assembly, and their passage through, or discharge from, the assembly is detected outside the borehole. The assembly is retracted incrementally until completion of the loading. Apparatus comprising a cartridge-guiding assembly through which a stream of water flows, and means associated with the assembly for sensing cartridge passage or discharge.

**24 Claims, 3 Drawing Figures**

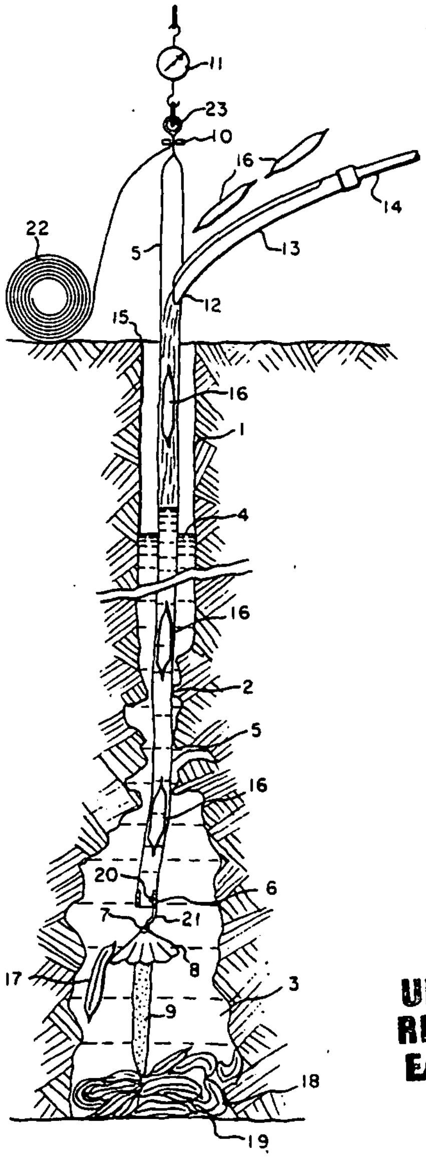
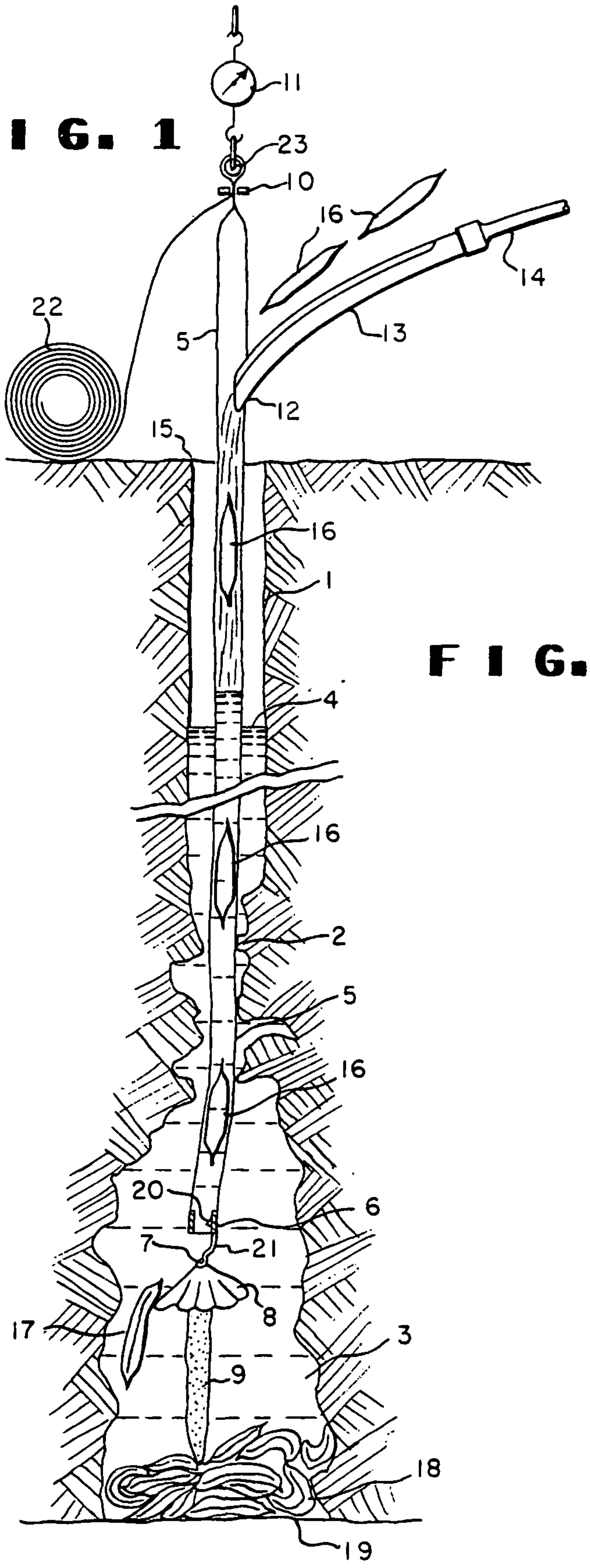


FIG. 1


11
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4
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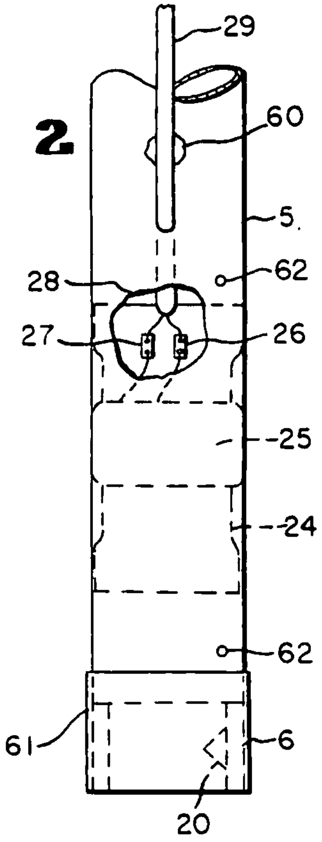
FIG. 2


29
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## LOADING OF BOREHOLES WITH EXPLOSIVES

### BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of emplacing explosive charges in deep boreholes and to an apparatus for carrying out the method.

2. Description of the Prior Art

Processes for explosively fracturing deep rock are becoming increasingly important as it becomes necessary to tap deep mineralized rock masses in order to supplement or replace dwindling energy sources and minerals supplies. Deep-blasting processes are needed, for example, in the treatment of oil and gas wells, the preparation of metallic ores for in situ leaching, and the preparation of oil shale for retorting or solvent extraction in place. To carry out such processes it is sometimes necessary to emplace and detonate explosives in boreholes ranging in depth from seveal hundred to several thousand feet.

Conventional procedures for loading boreholes are not adequate for loading boreholes of such depth. For deep boreholes, the explosive needs to be largely in cartridged form to avoid such problems as desensitization of the explosive by water and leakage of the explosive through fissures in the surrounding rock. Because deep holes are apt to be flooded with water, explosives which do not have good water resistance must be enclosed in a water-resistant wrapper. Even water-bearing explosives, known as water gels, which have a relatively high degree of water resistance and often are used in bulk form, preferably are cartridged for deep borehole loading. If a relatively fluid water gel explosive is simply dumped down the borehole, much of it may never reach bottom because it may stick to the walls of the borehole or dissolve in water on the way down. That which does reach bottom may be desensitized by admixture with water, and some may subsequently leak away through fissures in the rock. Also, water gel explosives that are sufficiently fluid to be pumped rapidly through a hose to great depths are likely to have insufficient viscosity to resist desensitization by water, and may leak away through fissures in the rock.

On the other hand, if an attempt is made to dump down a borehole a water gel which has a sufficiently high viscosity to resist desensitization by water, the explosive may bridge across the hole and never reach bottom. Or, even if it reaches bottom, it may fail to slump into a high-density load because of its high viscosity. Although it is possible to formulate water gel explosives so that they are very fluid while being pumped down a hose to the depths of a deep hole and then develop a high viscosity after being emplaced, the precise chemical control required in such a system is difficult to achieve consistently under field conditions. The use of cartridged water gels eliminates the problems caused by too high or too low a viscosity in the bulk explosive.

When conventional borehole loading procedures are employed to emplace explosive cartridges in boreholes, i.e., dropping or lowering the cartridges from the borehole collar, the borehole may become bridged by one or more cartridges before they have reached bottom, thereby blocking the hole causing a pile-up of cartridges above it. Such an occurrence, which, at the very least, adds greatly to the borehole loading time, becomes even more likely with boreholes of great depth, and also more difficult to remedy.

In addition to the above-described difficulties, other problems are encountered in cases in which the borehole has been chambered to permit the emplacement of a larger charge or if the composition of the charge is to be varied as a function of either vertical position in the hole or hole diameter. In such cases it is important to know the height of rise of the explosive load as a continuous function of the load emplaced, in order to confirm the size and shape of the chamber. Also, in response to this variable, it is often desired that the composition of the explosive being loaded by quickly changed, or loading be quickly cut off entirely.

Also, because of the large number of cartridges which may need to be emplaced in the borehole, it is important from the standpoint of economics that the loading method be as rapid as possible.

### SUMMARY OF THE INVENTION

This invention provides a method of loading a borehole with explosive cartridges comprising:

a. providing a cartridge-guiding assembly comprising a length of flexible tubing, preferably having inwardly projecting cutting means, e.g., a knife blade, mounted thereon in the vicinity of one of its ends, e.g., mounted on the inner wall of an open-ended, preferably somewhat rigid cylindrical member, such as a nozzle, which is coaxially joined to one end of the length of tubing so as to form a continuous channel therewith;

b. feeding the cartridge-guiding assembly into a substantially vertical borehole until the leading end of the assembly, e.g., the end of the tubing at which cutting means is mounted or the free leading end of the cylindrical member, is positioned at a location, short of the bottom of the borehole, where explosive cartridges are to be discharged, thereby leaving the cartridge-discharge space in the borehole, the assembly extending through substantially the remainder of the borehole, i.e., to substantially the collar of the borehole, and being sufficiently heavy, at least at its leading end, so as to be dragged downward against frictional forces produced at the borehole wall and through any water which may be present in the borehole;

c. directing a stream of water through the assembly, i.e., through the tubing and, when present, the cylindrical member;

d. feeding explosive cartridges into the length of tubing whereby the cartridges travel through the tubing together with the stream of water, preferably are cut open by passage past a cutting means, and are discharged from the leading end of the assembly, e.g., from the free end of the cylindrical member, into the cartridge-discharge space adjacent thereto;

e. sensing the passage of the explosive cartridges through, or their discharge from, the assembly, e.g., by measuring electrical or pressure transients, or tension in the tubing, caused by the presence or motion of the cartridges;

f. retracting the cartridge-guiding assembly when the space adjacent thereto is filled, as evidenced by the cessation of cartridge discharge, whereby additional cartridge-discharge space is created;

g. creating a cartridge-feeding opening in the retracted length of tubing in the vicinity of the borehole collar; and

h. repeating Steps (c), (d), (e), (f), and (g) as required until the desired number of cartridges have been discharged into the borehole.

Because deep boreholes are apt to be flooded with water and are expensive to drill, the explosive should have good water resistance and high energy per unit volume of loaded hole. For this reason, water gel explosives are preferred in the present process, in cartridged form while travelling through the guide assembly and thereafter released from the cartridges by cutting of the latter just prior to discharge from the assembly to allow the explosive to slump in the borehole to produce a high loading density. A preferred cartridge is a "chub," comprised of a tube of plastic film, filled with explosive, and gathered at both ends and closed, e.g., by means of closure bands around the gathered portions.

The present invention also provides apparatus for loading explosive cartridges into a borehole comprising:

a. a cartridge-guiding assembly comprising a length of flexible tubing and preferably inwardly projecting cutting means, e.g., a knife blade, mounted on the length of tubing in the vicinity of one of the tubing's ends, e.g., mounted on the inner wall of an open-ended, preferably somewhat rigid cylindrical member, such as a nozzle, which is coaxially joined to one end of the length of tubing so as to form a continuous channel therewith, the assembly (1) extending to a location inside, but short of the bottom of, a substantially vertical borehole from a location at the collar of, or outside, the borehole, the tubing end at which the cutting means, if present, is mounted, e.g., the cylindrical member, being in the foremost position, (2) being axially movable with respect to the borehole, and (3) having a stream of water flowing therethrough, i.e., through the tubing and, when present, the cylindrical member; and

b. means, e.g., load-detecting means, associated with said cartridge-guiding assembly, for sensing the passage of explosive cartridges through, or their discharge from, the leading end of the assembly, e.g., from the cylindrical member.

In addition, means for detecting and displaying the output of the sensing means may be associated with the sensing means.

In a preferred method and apparatus, a length of tubing extends outside the borehole and is longitudinally slit open in the vicinity of the borehole collar. The explosive cartridges are fed, and the stream of water is directed, into the length of tubing through the slit-open portion. As the tubing is retracted from the borehole, the slit-open portion is extended to the vicinity of the borehole collar, or a new slit is created near the collar.

## BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation in elevation of a borehole being loaded with explosive cartridges by the apparatus and method of the present invention;

FIG. 2 is a schematic representation in elevation of a portion of the apparatus of the invention wherein the means for sensing the passage of cartridges includes a wire coil whose inductance is changed by the passage of cartridges therethrough; and

FIG. 3 is a diagram of an inductance-monitoring circuit for use with the apparatus shown in FIG. 2.

## DETAILED DESCRIPTION

In the process of the invention, the loading of substantially vertical boreholes with explosive cartridges is accomplished at a rapid rate by the guided descent of the cartridges through a retractable tubing assembly through which a stream of water flows. The tubing provides a substantially uniform-diameter, smooth-wall passageway for the cartridges, thereby avoiding the problem of hole blockage due to cartridge hangup or bridging of the hole as may occur if the cartridges are dropped down rough-walled holes, possibly uneven in diameter. The stream of water washes the cartridges down the tubing, slowing them down and cushioning their fall while above the water table, and maintaining a flow of cartridges through the tubing assembly below the water table. Thus the cartridge-guiding assembly and water stream impart a degree of controllability to the borehole-loading process, a feature which is of greater importance with deeper boreholes.

The length of flexible tubing or hose is made of any material that is water-resistant and has sufficient flexibility to be handled conveniently in the length required for loading deep boreholes, e.g., several hundred to several thousand feet. As a practical matter, this means that the tubing will be adapted to be provided in folded or rolled-up form, from which it will be fed into the borehole. At the same time, the tubing should have a smooth inner wall, sufficient strength to withstand gross tearing which could result in the escape of cartridges through the walls of the tubing, and sufficient dimensional stability to preserve a substantially uniform cross-section throughout its length and thereby assure an uninterrupted cartridge descent therethrough.

The wall thickness of the tubing can vary depending on such factors as the strength of the tubing material and the diameter of the cartridges, a thinner wall being feasible with a stronger tubing material and a smaller-diameter cartridge. With many materials, the tubing wall thickness preferably is about from 0.1 to 0.7 percent of the cartridge diameter within the preferred cartridge diameter range of about from 1 to 6 inches (25.4 to 152 mm.), and optionally about from 0.3 to 0.4 percent of the cartridge diameter within the optimum cartridge diameter range of about from 1.5 to 3 inches (38 to 76 mm.), the lower end of the preferred thickness range being associated with the upper end of the preferred cartridge diameter range. In any case, the tubing wall thickness will be at least about 0.002 inch (0.051 mm.). There is no upper limit on the wall thickness so long as the desired flexibility of the tubing is maintained. Light-weight tubing is preferred, however, and therefore as a practical matter the tubing wall thickness usually will not exceed about 1 percent of the cartridge diameter. The inside diameter of the tubing is sufficient to allow easy passage of the cartridges to be used without providing so much clearance that the cartridges can override each other and jam, e.g., about 5–20 percent larger, but preferably about 10 percent larger, than the diameter of the cartridges. Naturally the outer diameter of the tubing has to be sufficiently small to permit insertion into and retraction from the borehole without deleterious abrasion of the tubing wall, or deformation from the approximately circular cross-section required to permit passage of the cartridges.

The tubing can be made of any material that will provide the necessary flexibility, strength, and dimensional stability in the selected wall thickness. Plastics and rubber, optionally laminated and/or reinforced with filaments such as metal or textile threads, can be used, for example.

In order that the tubing may be more easily handled in the long lengths required, it is preferred that it be as light in weight as possible. Light-weight tubing also is desirable if a load-detecting means is to be used to sense cartridge discharge from the assembly. For this reason, plastic tubing is preferred. Polymers such as polyethylene, polypropylene, plasticized polyvinyl chloride, polyvinylidene chloride, and polyethylene terephthalate can be employed, for example. Especially preferred is "Valeron" film, comprising two bonded cross-lapped sheets of oriented polyethylene film, which affords high strength, tear resistance, and dimensional stability in the form of thin-wall tubing, e.g., tubing having a wall thickness of about 0.003 to 0.006 inch (0.076 to 0.152 mm.).

The length of flexible tubing preferably has inwardly projecting cutting means mounted thereon in the vicinity of one of its ends. The purpose of the cutting means is to cut open the cartridges near their point of discharge from the assembly so that they are in a split-open condition when discharged into the borehole. This allows the explosive to fill in the voids which would otherwise exist between cartridges and thereby achieve a higher density. The preferred water gel explosives can be formulated to have a sufficiently high viscosity and sensitivity to afford good performance under high water pressure and still permit the slit cartridges to slump readily to a dense mass.

The cutting means, e.g., one or more slitting blades, can be mounted directly in the tubing wall, e.g., by insertion of a supported blade through the wall of a tube which is sufficiently firm to hold the blade in position and taping of the externally protruding blade support in place. With the preferred thin, light-weight plastic tubing, the cutting means can be mounted on the inner wall of an open-ended, preferably somewhat rigid cylindrical member, e.g., a nozzle or ring, which is coaxially joined to one end of the length of tubing so as to form a continuous channel therewith. The cutting means should be located no farther than ten, and preferably no farther than two, tubing diameters from the end of the tubing, e.g., the end of the cylindrical member, which is the discharge end of the assembly.

Preferred materials of construction for the cylindrical member are stainless steel or engineering plastics such as nylon, polyvinyl chloride, polycarbonate resin, or polyethylene. The cylindrical member can be joined to the tubing by any convenient method, e.g., force fit, clamping, etc. In a preferred method the outer diameter of an end of the cylindrical member is tapered down, the end of the tubing is slipped over the untapered end, and tight tape or banding is then put over the tubing-covered tapered portion of the cylindrical member. Likewise, the cutting blade can be mounted to the wall of the cylindrical member by any convenient method, e.g., by welding when a metal cylindrical member is used.

The cartridge-guiding assembly is sufficiently heavy, at least at its leading end, so as to be dragged downward in the borehole against the frictional forces produced at the borehole wall and so as to overcome the net upward buoyancy of any parts of the tubing which may be submerged in water in the borehole. With heavier tubing, the assembly may be sufficiently heavy of its own accord. However, to facilitate the passage of the tubing through constricted and possibly tortuous portions of the borehole, a weight preferably is secured to the leading end of the assembly, e.g., as shown in FIG. 1. Also, in the preferred assembly wherein the length of tubing is lightweight and buoyant in water, the assembly will be made heavy at its leading end by the attachment of a weight thereto. Usually a weight sized so as to provide a net downward drag of about from 1 to 20 pounds (0.4 to 9.1 kg.), when the tube is empty of cartridges and as felt at the borehole collar, is satisfactory.

The cylindrical member (e.g., nozzle), if suitably dense, can be suitable to weight the assembly, but preferably the weight is a deformable elongated member suitably suspended from the leading end of the tubing. Such a weight will be somewhat flexible and slithery to ease its descent and that of the entire cartridge-guiding assembly through uneven boreholes where localized constrictions could cause blockages to occur with rigid weights.

The method of loading explosive cartridges into a borehole according to the present invention by use of the apparatus of the invention will now be described with reference to FIG. 1 in which 1 is a substantially vertical borehole having a collar 15 and bottom 19. The diameter of borehole 1 is non-uniform, a constricted section of borehole being indicated by 2. The lower end of borehole 1 consists of cavity 3, a larger-diameter section of borehole produced by a springing or reaming procedure. Water is present in borehole 1 up to a level indicated by 4. The length of borehole 1 is, for example 465 feet (142 meters), and its diameter in the upper unconstricted portion thereof is 6 inches (152 mm.).

An assembly for guiding cartridges into borehole 1 comprises (a) a length of flexible tubing 5, e.g., made of a dimensionally stable polymer such as Valeron, coaxially joined, by tight taping 61 (FIG. 2), at one end to open-ended cylindrical member 6, e.g., a short rigid nozzle made, for example, of stainless steel, so as to form a continuous channel with tubing 5, and (b) cutting means 20, e.g., a knife blade, mounted to the inner wall of cylindrical member 6. The cartridge-guiding assembly has been positioned in borehole 1 with cylindrical member 6 in the foremost position, the leading end of cylindrical member 6 constituting the cartridge-discharge end of the assembly and being located short of the bottom 19 of borehole 1, leaving a cartridge-discharge space therein. Tubing 5 is 500 feet (153 meters) long, its inner diameter is 1.75 inches (44.4 mm.), and its wall thickness 0.006 inch (0.152 mm.).

Weight 9, secured to the leading end of the cartridge guiding assembly, is a deformable elongated member such as a cylinder coaxially suspended below cylindrical member 6. The weight is pivotably attached to one end of rod 21 at swivel 7, the other end of the rod being rigidly attached to the free end of cylindrical member 6. The shaft of rod 21 is inclined to the axis of cylindrical member 6 so as to provide an attachment for weight 9 that is on or near the axis of cylindrical member 6 but that does not interfere with the exiting of cartridges from the cylindrical member. Hanging the weight by swivel 7 allows the weight to pivot freely relative to cylindrical member 6, thereby preventing the flexible tubing 5 from becoming twisted. Weight 9 weighs about 10 pounds and is in the form of a long thin cylinder, e.g., a thin-walled rubber tube filled with dense fluid such as a dense slurry of red iron oxide, barium sulfate, ferrophosphorus, or ferrosilicon powder, or lead shot, suspended in water gelled with cross-linked polyacrylamide or guar gum. The slithery, flexible nature of weight **9** allows it to pass more readily through constricted borehole sections, e.g., the section denoted by **2.**

Secured to the top of cylindrical weight **9** is a cover disk **8**, e.g., a thin, flexible elastomeric disk having radial slits extending from its edge part of the way to its center. Disk **8** has a radius which is about from ½ to 2 inches longer than the distance from the center of the disk to the edge of cylindrical member **6** so that the disk can push member **6** away from obstructions and can also fold over the edge of member **6** as it is lowered through borehole **1** to prevent member **6** from being caught on obstructions, but can thereafter fall away from the edge of member **6** so that the mouth of the latter will not be obstructed as cartridges are to be discharged therefrom. Preferably, cylindrical member **6** is no longer than about three times its diameter so that it can more easily move up and down through curved and constricted sections of borehole.

Tubing **5** is fed into borehole **1** from reel **22** on which it is wound in flattened form. The flattened tubing from reel **22** loops around roller **23** and is held thereon by clamp **10**. Associated with the cartridge-guiding assembly is cartridge-discharge-sensing means **11**, in this case a spring balance. Roller **23** is suspended from spring balance **11**, hung from a tripod (not shown). Thus the portion of tubing **5** below clamp **10** is supported in axial position with the borehole. Weight **9** assists the movement of the assembly down through the borehole.

A cartridge-insertion means comprising flume **13** communicates with tubing **5** at a location in the vicinity of borehole collar **15**. Flume **13** is a tilted chute having a downward-curving spillway and a total length at least about twice the length of the carridge to be inserted. (The length of flume **13** can be equal to the cartridge length to accommodate inserting one cartridge at a time, or to two or more cartridge lengths depending on the number of cartridges one wishes to emplace substantially simultaneously.) The lower end of flume **13** is inserted into slit **12** in the wall of tubing **5** outside borehole **1** near collar **15**. Water is run into the upper end of flume **13** through hose **14** attached thereto.

Two explosive cartridges **16** are about to be fed into a running stream of water in flume **13**. The cartridges are chub film cartridges filled with a slumpable water gel explosive, and have a diameter, for example, of 1.5 inches (38 mm.). The water carries the cartridges down flume **13** and into tubing **5**. Other cartridges **16** are moving through tubing **5** in the water stream therein, and slit cartridge **17** has been discharged from the assembly and is shown dropping to the bottom of the borehole. A load of slit cartridges **18** is building up and slumping in the sprung portion of borehole **1**. Although the cartridges are slit open, the presence of the cartridge film wrapping minimizes the leakage of explosive through surrounding fissures.

The exit of the cartridges from cylindrical member **6** and possible blockages due to the buildup of cartridges in tubing **5** are monitored by observing the tension recorded on spring balance **11** (or an equivalent load detector). The depth to which this type of sensing means can be used depends on the friction of the tube against the borehole wall and therefore on both the roughness and verticality of the hole. This type of sensing means may be useful for boreholes as deep as about 1000 feet (305 m.) or more.

After the level of the slit cartridges in the borehole has reached cylindrical member **6**, the cartridge-guiding assembly, i.e., tubing **5**, is retracted to create additional cartridge-discharge space. To avoid extremely long cartridge drops with the cartridge slit and without the protection of the guiding tube, this retraction generally is performed in increments, with each retraction bringing the leading end of the assembly no more than about 100 feet (30.5 m.), and preferably no more than about 30 feet (9.2 m.), above the load of slit cartridges.

Tubing **5**, which is initially positioned so that the free end of cylindrical member **6** is typically about 15 feet (4.6 m.) from the bottom of borehole **1**, is now retracted about 15 feet (4.6 m.). Depth markings applied down the side of tubing **5** are useful for a more rapid determination of the length of tubing fed into and retracted from the borehole. Inasmuch as the retraction moves slit **12** and flume **13** as well, it is convenient either to extend slit **12** toward borehole collar **15** or to make a new slit near the collar, and to insert flume **13** in the new slit or in the extension. The steps of feeding cartridges into the assembly, sensing their discharge therefrom, then sensing the cessation of discharge and the buildup of undischarged cartridges when load **18** builds up to block the exit of cylindrical member **6**, and then retraction are repeated until the desired number of cartridges have been discharged into the borehole. At that time, the entire cartridge-guiding assembly is removed from the borehole.

The explosives initiation technique known as multiple priming, wherein a number of explosive primers are positioned throughout a charge in a borehole with spacings between them, can be used advantageously with the charge loaded by the present method. For example, a string of spaced primers, adapted to be detonated either by detonating cord or electrical blasting caps, can be lowered into the borehole along with the cartridge-guiding assembly. The cartridges are discharged with the primers in place and amass around the primers, and final removal of the cartridge-guiding assembly leaves the primed charge in the borehole.

When the cartridge-guiding assembly is in position for cartridge-discharging in the borehole, the length of tubing extends at least up to the borehole collar, i.e., to the mouth of the borehole, but preferably beyond the collar. The latter case is preferred not only because the tubing is more easily secured if it extends outside the borehole, but also because the wall of the portion of tubing outside the borehole can be slit open near the collar to allow faster cartridge insertion than can be accomplished through the exposed end of tubing whose diameter does not greatly exceed that of the cartridges.

If the tubing has a thin flexible wall, as preferred, it can easily be provided with a longitudinal slit in the portion outside the borehole, e.g., within about one foot of the collar, and, as described above, the slit extended toward the borehole collar with each retraction or a new slit made near the collar in the portion emerging from the borehole with each retraction. Alternatively, the tubing can be provided with an interlocking longitudinal seam adapted to be opened and closed repeatedly by a slide device, e.g., zipper tubing. Such tubing can be handled conveniently in the flat, unzipped condition, wound up on a reel from which it can be fed into the borehole by unwinding the unzipped tubing and zipping it closed as it is fed in so that the tubing wall is closed in the borehole up to the collar thereof. Outside the borehole the tubing remains unzipped to allow cartridge insertion. Each time the cartridge-guiding assembly is retracted, a portion of zipped tubing emerges from the borehole and this can be longitudinally opened up by unzipping substantially to the borehole collar to facilitate continued cartridge insertion. Because zipper tubing can be opened and closed repeatedly, it is reusable for loading more than one borehole without repairing slits made in the walls as is usually required when conventional tubing is reused.

The cartridges and water stream can be introduced into the tubing separately, e.g., by using a hose in the slit-open portion of the tubing to introduce the water and feeding the cartridges through the same or another slit. The flume technique described above, or a technique analogous thereto, is preferred, however, since entrainment of cartridges in the water stream outside the borehole increases the loading speed.

Using the loading method shown in FIG. 1, chub cartridges can be loaded into 465 feet (142 meters) deep holes at a rate of about 2500 cartridges per hour.

When the load of cartridges emplaced builds up to the extent that cartridge discharge and flow through the tubing stops, and the assembly is retracted, the cartridges could become seized in the tubing and it may be difficult to resume cartridge flow. This problem can be avoided by perforating the bottom portion of the tubing, e.g., at least about the bottom 100 feet (30.5 m.) of tubing, using, for example, about 0.125-inch (3.175 mm.) holes. Use of a pair of opposed holes about every foot (30.5 cm.) or so is suitable. This procedure prevents a vacuum from forming between the cartridges as a result of differences in their starting velocities, and the consequent seizing thereof. Such holes or perforations are denoted by the numeral **62** in FIG. **2.**

An important feature of the present process is the sensing and detection of the passage of the cartridges through, or their discharge from, the cartridge-guiding assembly. This feature provides information on whether the cartridges are being discharged or whether the flow has ceased due to blockage, e.g., by the build-up of cartridges in the borehole; and, together with measurements of the depth of the assembly before and after each retraction, permits an estimate to be made of the height of rise of the explosive load in the borehole as a continuous function of load emplaced. In this manner, one can determine the diameter of the borehole throughout its length and, if desired, change the composition of the explosive as a function of diameter or as a function of vertical position. The determination of the borehole diameter at different depths by this technique is especially useful when the boreholes have been chambered (i.e., expanded in order to accommodate a larger explosive charge), or if the borehole walls are unstable, inasmuch as an irregular diameter is apt to result in such cases.

The passage of individual cartridges through the lower end of the assembly can be sensed in various ways, using, for example, pressure, optical, or electrical transients caused by the presence or motion of the cartridges. For boreholes up to about 1000 feet deep, a load-detecting means such as that shown in FIG. 1 may be suitable, the load changing with the discharge of each cartridge. For deeper boreholes, an electrical transient measurement method is preferred. For example, the AC electrical resistance between two points near the inner wall of the cylindrical member, below the slitting knife, can be sensed. This resistance is high when no explosive cartridge is bridging the electrodes and is low when a slit cartridge is bridging them. Electrodes immersed in typical water gel explosive compositions are polarized by DC voltages, thus preventing clear detection of the presence or absence of an explosive cartridge. The use of AC voltages avoids this problem and AC frequencies of 60 Hz or more are satisfactory frequencies at which to detect changes in resistance caused by the passage of cartridges. A cartridge-slitting knife within the cylindrical member and an electrode downstream from the knife make a satisfactory pair of electrodes for the resistance-sensing procedure.

In a preferred embodiment, the passage of cartridges through the lower end of the assembly is sensed by measuring the inductance change in a wire coil coaxially mounted at the forward end of the tubing assembly. A material having high magnetic permeability, e.g., iron, magnetic iron oxide, or chromium dioxide, is located in each cartridge, e.g., in the explosive composition, in the packaging material enclosing it, or in a closure clip (an iron closure clip on a chub cartridge, for example). When the cartridge passes through the coil, the inductance of the coil changes, and is sensed and displayed by an inductance-monitoring circuit located outside the borehole and joined by wires to the coil. Preferably, the material of high permeability in each cartridge is contained in a single small locality, i.e., in a single iron clip on one end of the package so that the passage of each package produces only one pulse in the inductance-monitoring circuit.

In FIG. **2,** a 700-turn coil **25** of No. **34** copper wire is wound around the recessed portion of a spool-like, thin-walled plastic, hollow coil form **24.** Coil **25** has an outer diameter of 1.75 inches (45.4 mm.), and a height of 0.75 inch (19 mm.). The inner diameter of coil form **24** at the recessed portion is sufficiently large to allow the cartridges to pass through, and the largest outer diameter of the coil form is 1.75 inches (45.4 mm.). Coil form **24** is held in position in tubing **5** about a foot (30.5 cm.) above cylindrical member **6** by force fit. Metal tabs **26** and **27** are attached to the outer wall of coil form **24** by any suitable procedure. A temporary hole **28** in the wall of tubing **5** permits one end of the wire which forms coil **25** to be soldered to metal tab **26** and the other end to metal tab **27.** One end of one of the two 24-gage copper wires in insulated duplex wire **29** is also soldered to metal tab **26,** and one end of the other of the two wires to metal tab **27.** Coil **25,** tabs **26** and **27,** and the exposed portions of the wires are protected with a coating of a water-proofing agent, and a patch is placed over hole **28.** Duplex wire **29,** preferably affixed to the outer wall of tubing **5,** e.g., by intermittent applications of hot-melt adhesive **60,** extends to the surface where it is connected to an inductance-monitoring circuit such as that shown in FIG. **3.**

Referring to FIG. **3,** oscillator **30** generates approximately one volt a.c. at a frequency of one kilohertz. This furnishes power through coupling transformer **31** to the series combination of coil **25** and adjustable resistor **32,** one of the conductors of duplex wire **29** at the surface being connected to the junction of transformer **31** and resistor **34,** and the other to adjustable resistor **32**. This junction of coil **25** and resistor **32** is connected to the circuit common **33**, which preferably is also the circuit ground.

The voltages referenced to circuit common **33** appearing across coil **25** and adjustable resistor **32** are applied to precision rectifier circuits **58** and **59** through resistors **34** and **35**, respectively, with the outputs of the two rectifier circuits joined through summing resistors **40** and **45**.

Precision rectifier circuit **58** is composed of amplifier **36**, diodes **37** and **38**, and feedback resistor **39** connected so as to linearize the rectifier characteristic of diode **37**, i.e., force the circuit to behave as an ideal rectifier element. Such a circuit is known in the art, and is more fully described in the *Handbook of Operational Amplifier Applications*, Burr-Brown Research Corporation, Tucson, Arizona, Ed. 1, 1963, page 70. Similarly, precision rectifier circuit **59** is composed of amplifier **41**, diodes **42** and **43**, and feedback resistor **44**, and is arranged to rectify the negative-going half-cycle of the applied voltage, with reference to circuit common **33**, while circuit **58** rectifies the positive-going half-cycle.

The junction of resistors **40** and **45** is connected through capacitor **46** to provide AC coupling to amplifier **47**, whose gain and frequency response is determined by capacitors **46**, **48**, and **49**, and resistor **50**. In particular, capacitor **48**, in conjunction with resistors **40** and **45**, serves as a filter, eliminating the AC component of the summation of the rectified voltages appearing at the junction of resistors **40** and **45**.

The output of amplifier **47** drives a voltage level detector, consisting of amplifier **51** and resistors **52, 53, 54**, and **55**, with the triggering threshold determined by the value of variable resistor **54**. The level detector circuit is essentially a biased amplifier, as is more fully described in the aforementioned handbook, page 46.

In operation, the circuit is adjusted to a balanced condition throughout in the quiescent state, i.e., with no ferromagnetic material within coil **25**. Adjustable resistor **32** is used to balance the circuit so that the voltage across coil **25** is equal to the voltage across resistor **32**. Similarly, variable resistors **39** and **44** are adjusted to provide equality in the precision rectifier circuits, as denoted by zero voltage from the junction of resistors **40** and **45** to the circuit common **33**. Also, resistors **39** and **44** are further adjusted to provide maximum attainable amplification in rectifiers **58** and **59**, respectively, limited only by amplifier saturation and the above-mentioned equality requirement.

The cartridge whose passage is to be detected contains a material having high magnetic permeability. For example, the ends of a chub cartridge are closed with an iron clip at one end and an aluminum clip at the other so that only one signal is obtained from each cartridge. When such a cartridge passes through coil **25**, the latter's inductance and impedance change because of the presence of the ferromagnetic material (iron) within its field of influence, thus changing the voltage drop across coil **25**. This causes an imbalance in the circuit such that the positive rectified voltage no longer is equal to the negative rectified voltage, and the difference appears at the junction of resistors **40** and **45**, with relation to circuit common **33**. This transient difference voltage, after filtering, is amplified in amplifier **47**, and in turn actuates the voltage level detector, thus providing a signal which may be fed to a counter and visual display means **56** and also to an acoustic signaling means **57**.

We claim:

**1.** Method of loading explosive cartridges into a borehole comprising:

a. providing a cartridge-guiding assembly comprising a length of flexible tubing;

b. feeding said assembly into a substantially vertical borehole until the leading end of said assembly is positioned at a location, short of the bottom of the borehole, where explosive cartridges are to be discharged, thereby leaving a cartridge-discharge space in the borehole, said assembly extending through substantially the remainder of the borehole, and being sufficiently heavy, at least at its leading end, so as to be dragged downward against the frictional forces produced at the borehole wall and through any water which may be present in the borehole;

c. directing a stream of water through said assembly;

d. feeding explosive cartridges into said length of tubing whereby said cartridges travel through said tubing together with said stream of water and are discharged from the leading end of said assembly into the cartridge-discharge space adjacent thereto;

e. sensing the passage of said explosive cartridges through, or their discharge from, said assembly;

f. retracting said assembly when the space adjacent thereto is filled, as evidenced by the cessation of cartridge discharge, whereby additional cartridge-discharge space is created;

g. creating a cartridge-feeding opening in said retracted length of tubing in the vicinity of the borehole collar; and

h. repeating Steps (c), (d), (e), (f), and (g) as required until the desired number of cartridges have been discharged into the borehole.

**2.** A method of claim **1** wherein inwardly projecting cutting means is mounted on said length of tubing in the vicinity of the end thereof which is at said assembly's leading end, and said cartridges are cut open by passage past said cutting means.

**3.** A method of claim **2** wherein the passage of the cartridges through said assembly is sensed by measuring the electrical resistance change caused thereby.

**4.** A method of claim **1** wherein a portion of said length of tubing extends outside the borehole and is longitudinally slit open in the vicinity of the borehole collar, said explosive cartridges being fed, and said stream of water being directed, into said length of tubing through said slit-open portion.

**5.** A method of claim **4** wherein, after retraction of said assembly, said slit-open portion of said length of tubing is extended so as to reach the vicinity of the borehole collar.

**6.** A method of claim **4** wherein a new slit-open portion is created in said retracted length of tubing in the vicinity of the borehole collar.

**7.** A method of claim **4** wherein said explosive cartridges are fed into a stream of water in a flume, said flume having a downward-curving spillway and its lower end inserted in the slit-open portion of said length of tubing, whereby the cartridges are carried down the flume and into the cartridge-guiding assembly.

**8.** Apparatus for loading explosive cartridges into a borehole comprising:

a. a cartridge-guiding assembly comprising a length of flexible tubing, said assembly (1) extending to a location inside, but short of the bottom of, a substantially vertical borehole from a location at the collar of, or outside, said borehole, (2) being axially movable with respect to said borehole; and (3) having a stream of water flowing therethrough; and

b. means associated with said cartridge-guiding assembly, for sensing the passage of explosive cartridges through, or their discharge from, the leading end of said assembly.

**9.** Apparatus of claim **8** wherein said tubing is made of a dimensionally stable polymer.

**10.** Apparatus of claim **8** wherein a portion of said length of tubing extends outside the borehole and is longitudinally slit open in the vicinity of the borehole collar for feeding explosive cartridges and directing a stream of water into said length of tubing.

**11.** Apparatus of claim **8** wherein separated small perforations are present in the wall of the lower portion of said length of tubing.

**12.** Apparatus of claim **8** wherein inwardly projecting cutting means is mounted on said length of tubing in the vicinity of the end thereof which is at said assembly's leading end.

**13.** Apparatus of claim **12** wherein an open-ended cylindrical member is coaxially joined to one end of said length of tubing so as to form a continuous channel therewith, and said cutting means is mounted on the inner wall of said cylindrical member.

**14.** Apparatus of claim **8** wherein said means for sensing the passage or discharge of explosive cartridges is a load-detecting means from which said cartridge-guiding assembly is suspended.

**15.** Apparatus of claim **14** wherein said load-detecting means is a spring balance.

**16.** Apparatus of claim **8** wherein cartridge-insertion means communicates with said length of tubing at a location in the vicinity of the borehole collar, said cartridge-insertion means comprising a flume having a downward-curving spillway and its lower end inserted in said length of tubing whereby cartridges are adapted to be fed into the stream of water in said flume and carried into said cartridge-loading assembly.

**17.** Apparatus of claim **16** wherein the lower end of said flume is inserted in a slit-open portion of said length of tubing outside the borehole.

**18.** Apparatus of claim **8** wherein a weight is secured to the leading end of said cartridge-guiding assembly.

**19.** Apparatus of claim **18** wherein said weight is an elongated deformable member coaxially suspended from said assembly and secured thereto.

**20.** Apparatus of claim **18** wherein water is present in the borehole, said tubing is buoyant, and said weight is sufficient to overcome the buoyancy of any part of the tubing that is submerged in water.

**21.** Apparatus of claim **20** wherein said weight is sized to give a net downward drag on the assembly, when empty of cartridges and when felt at the borehole collar, of about from 1 to 20 pounds.

**22.** Apparatus of claim **21** wherein said weight is a sealed elastomeric tube filled with a dense fluid.

**23.** Apparatus of claim **21** wherein said weight is pivotably attached to one end of a rod having its other end rigidly attached to said cylindrical member, said rod having its shaft inclined to the axis of said cylindrical member.

**24.** Apparatus of claim **23** wherein a flexible, radially slit elastomeric disk is secured to the top of said weight.

* * * * *

**SYNOPSIS**

# Leaching of Oxide Copper Ore With Ammonium Hydrogen Sulphate: Bench-Scale Testing

**John C. Stauter** and **Anthony G. Fonseca,**
Continental Oil Company,
Ponca City, Oklahoma, U.S.A.

Two chemical problems occur with the use of sulphuric acid as a leaching reagent: (1) plugging and/or sealing of portions of vats or columns by hydrous iron and aluminum oxide precipitation, which reduces copper extraction; and (2) the fact that the copper-containing solution has a high metal ion impurity content, which can complicate copper recovery from solution.

Copper extraction from oxide ores by $NH_4HSO_4$ leaching has been found to be as good as that obtained by sulphuric acid leaching; and, at the same time, the amount of solubilized iron and aluminum, which is the major cause of the above problems, is considerably less than that obtained with sulphuric acid leaching.

TABLE 1 — Leach Test Summary

| | Test 1 | Test 2 | Test 3 | Test 4 |
|---|---|---|---|---|
| Leach Reagent | $NH_4HSO_4$ | $NH_4HSO_4$ | $NH_4HSO_4$ | $H_2SO_4$ |
| Recovery Per Cent | 65.5 | 72.4 | 77.4 | 76.0 |
| Leach Time (hours) | 45.1 | 72.0 | 80.5 | 79.0 |
| Flow Rate (ml/min.) | 2.6 | 1.6 | 1.45 | 1.5 |
| Material Balance (%) | 100.0 | 104.0 | 94.7 | 99.2 |
| $H_2SO_4$ Consumption (lb/ton) | 24 | — | — | 60 |
| $NH_3$ Consumption (lb/ton) | 2.6 | 2.6 | 2.7 | 0 |

Table 1 summarizes the results of the three ammonium hydrogen sulphate recycle column leach tests and the third recycle sulphuric acid leach test. All tests were conducted with 4500 g of -$\frac{3}{8}$-in. oxide ore, leached with 7 liters of solution. Copper extraction increases with the length of test and is comparable to extractions obtained with 5 wt. % sulphuric acid for equivalent leach times. The only difference between the two leach reagents is the production of a higher-concentration initial effluent with sulphuric acid. The copper solution profiles for the two leach reagents are shown in Figure 1.

Sulphuric acid consumption in the $NH_4HSO_4$ system was based on the amount of acid required to adjust all recycle leach solutions to the original pH of 0.80. Acid consumption for Test 1 was 24 lb per ton of ore; although not listed, Tests 2 and 3 were comparable. Acid consumption for the sulphuric acid leach system averaged close to 60 lb per ton in the control leach tests.

Ammonia consumption for the three recycle tests averaged 2.6 lb per ton; it is believed to be consumed due to ion exchange processes occurring in the ore clay fraction, because these fine ore fractions are known to exhibit appreciable exchange capacities(1). Ammonia analysis of the leach tails provided excellent agreement with ammonia losses observed in the leach liquors.

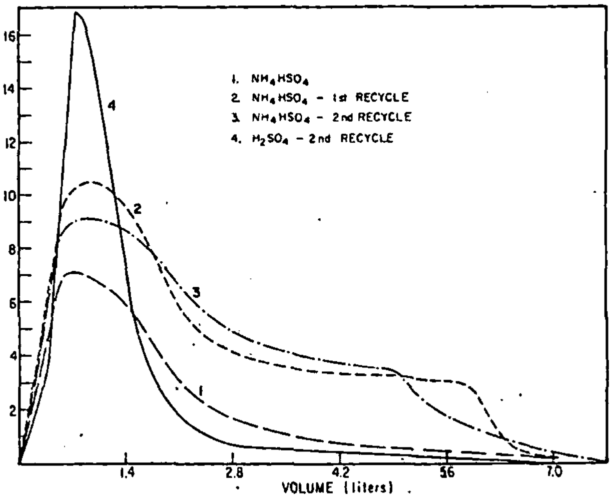

FIGURE 1 — Copper Concentration vs Solution Volume.

In small-scale bottle agitation tests, the ammonium hydrogen sulphate system produced a leach liquor with a markedly decreased iron content(2). This same trend was observed in the bench-scale column tests. The total amounts of iron and aluminum in the resultant $NH_4HSO_4$ leach liquor after three recycle tests is much lower than that of the $H_2SO_4$ leach systems. The data are shown in Table 2. The lowered amounts of iron and aluminum in solution could translate to increased copper extraction by reducing the possibility of sealing portions of the ore bed due to salt precipitation. Additional benefits may be obtained during copper recovery due to the lowered non-copper metal salt content of the leach liquor.

TABLE 2 — Iron and aluminum in solution after three recycle tests for both the $NH_4HSO_4$ and $H_2SO_4$ leach system

| | $NH_4HSO_4$ (g/liter) | $H_2SO_4$ (g/liter) |
|---|---|---|
| Fe | 0.45 | 2.43 |
| Al | 0.87 | 2.0 |

The ammonium hydrogen sulphate system showed a sulphuric acid saving of approximately 35 lb per ton. A rough economic comparison was made between the $NH_4HSO_4$ and $H_2SO_4$ leach systems based on the assumption that sulphuric acid is charged at $8 per ton and ammonia at $50 per ton, and also that extractions are virtually the same for each system. This comparison is shown in Table 3 and is based on the

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Synopsis of paper presented at the 12th Annual CIM Conference of Metallurgists, Quebec City, August 1973.

# CIM MEMBER APPLICATIONS

THE INSTITUTE is growing at a very healthy rate, and applications for Membership are welcomed at any time from anyone connected in any way with the mineral industries. The following applied for CIM Membership during the preceding month.

## As Corporate Member

**Lawjack Equipment Ltd., Montreal, Que.**

## As Members

**Alexander, F. Arthur, Vancouver, B.C.**
***Baumgartner, Peter, Cassiar, B.C.**
**Bigelow, C. C., Anchorage, Alas., U.S.A.**
**Bowser, Alan, Brampton, Ont.**
**Brindle, John E., Ottawa, Ont.**
**Brokx, Emile J., Granisle, B.C.**
**Brydges, James W., Arnprior, Ont.**
**Caley, William, Halifax, N.S.**
**Carlson, Nels R., Calgary, Alta.**
**Cordahl, George, Bralorne, B.C.**
**Cowling, Richard, Godsworthy, Western Australia.**
**Davenport, John W., Salisbury, Rhodesia.**
**Derouin, Ronald R. J., Calgary, Alta.**
**Geist, Elton W., Cleveland, Ohio, U.S.A.**
**Ghoneim, Salah A. A., Murdochville, Que.**
**#Hall, Richard B., St. Hippolyte, Que.**
**Harr, K. J. V., Wayne, N.J., U.S.A.**
**Hill, David W., Willowdale, Ont.**
**Iliffe, Michael J., Wabush, Labrador, Nfld.**
**Jones, Robert L., Schefferville, Que.**
**Johnston, Brian G., Calgary, Alta.**
**Khan, Shahid N., Islamabad, Pakistan.**
**Klingmueller, L., Anchorage, Alas.**
**Komura, Akiyoshi, Vancouver, B.C.**
**Kruesi, Paul R., Wheat Ridge, Col., U.S.A.**
***Lefebvre, Gaetan, Sept-Iles, Que.**
**Lewis, Richard, Tegucigalpa, Republic of Honduras.**
**Lister, Donald, Surrey, B.C.**
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**Malhotra, Subhash, White Pine, Mich., U.S.A.**
**Manthey, Thomas J., Cleveland, Ohio, U.S.A.**
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**Norman, Norval E., Houston, Texas, U.S.A.**
**Oolup, Jaan, Scarborough, Ont.**
**Pawliw, Paul A., Lynn Lake, Man.**
**#Rajicic, Milos, Edmonton, Alta.**
**Ramseier, Frederic N., Britannia Beach, B.C.**
**Rodger, William J., Terrasse Vaudreuil, Que.**
**Roy, Amalendu, Lidsdale, N.S.W., Australia.**
**Salisbury, William J., Honduras, C.A.**
**Van Meurs, Anton P. H., Ottawa, Ont.**
**Viste, H. Dwight, Calgary, Alta.**
**Wray, Robert J., Scarborough, Ont.**
**Wurster, Daniel Ch., Noranda, Que.**
**Yawnghwe, Hso H. P., Montreal, Que.**

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(*) On Transfer
(#) By Re-Election

## As Associate

**Pfeiffer, Robert R., Winnipeg, Man.**

## As Junior Members

**Chaykowski, Alexander, St. Leonard, Que.**
**Gambles, Graham J., Faro, Y. T.**

# CIM NEW ADDRESSES

MANY MEMBERS of The Canadian Institute of Mining and Metallurgy have moved in recent weeks and the CIM BULLETIN is pleased to list their new addresses below.

**Anderson, Frank W.**, Apt. 403, 725 - 15th Ave. S.W., Calgary, Alta. T2R 0R8. M-56
**Archibald, D. E.**, 355 Jane Street, Newcastle, N.B. M-73
**Bailey, Lawrence F. W.**, 340 Victoria Ave., Montreal, Que. H3Z 2M8. M-61
**Balfour, George C.**, 85 Tremoy, Noranda, Que. M-71
**Balogh, Alex G.**, 14 Armand Frappier, Valleyfield, Que. J6T 4L5. JM-58-66;M-68
**Bardswich, John**, Devco, Coal Div., P.O. Box 2500, Sydney, N.S. MSNS-71
**Bates, Gerald C.**, 31 Hickory, Thompson, Man. R8N 0R7. M-72
**Baudais, F. W.**, P.O. Box 194, Port Hardy, B.C. M-73
**Bedford, Clay P.**, Kaiser Engineers, 300 Lakeside Drive, Rm. 2553, Oakland, Calif. 94604, U.S.A. M-70
**Bell, Douglas H.**, Ministry of Natural Resources, Min. Res. Br., Div. of Mines, Rm. W1611, Whitney Block, Queen's Park, Toronto, Ont. M7A 1X3. M-66
**Bell, John A. M.**, Canadian Industries Limited, P.O. Box 836, Edmonton, Alta. T5J 2L4. JM-57-66;M-67
**Bettiol, Edward I.**, Jordan River Mines Ltd., 701-744 W. Hastings St., Vancouver, B.C. JM-51-58;M-59

## SYNOPSIS (continued) . . .

TABLE 3 — Comparative reagent consumption and cost for the $H_2SO_4$ and $NH_4HSO_4$ leach methods

| | $H_2SO_4$ Leach | $NH_4HSO_4$ Leach |
|---|---|---|
| Acid Consumption, lb/ton........ | 60 | 25 |
| Ammonia Consumption, lb/ton.... | — | 2.7 |
| Acid cost per ton ore............ | 24¢ | 10¢ |
| Ammonia cost per ton ore........ | — | 6.75¢ |
| Total regeant cost per ton ore..... | 24¢ | 16.75¢ |

reagent consumption results of Table 1. For an ore assaying 0.50 wt. % copper with an average 75% recovery, a saving of 1 cent per pound of copper is realized with this ore.

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(1) Grunig, J. K., Some Factors of Ore and Solution Chemistry in the Heap Leaching of Copper Ores, paper presented at Pacific Northwest Minerals and Metals Regional Conf., AIME, 1966.
(2) Fonseca, A. G., and Stauter, J. C., Leaching of Oxide Copper Ore with Ammonium Hydrogen Sulphate, paper submitted for publication in SME Transactions, AIME.

1977 v18 no 8

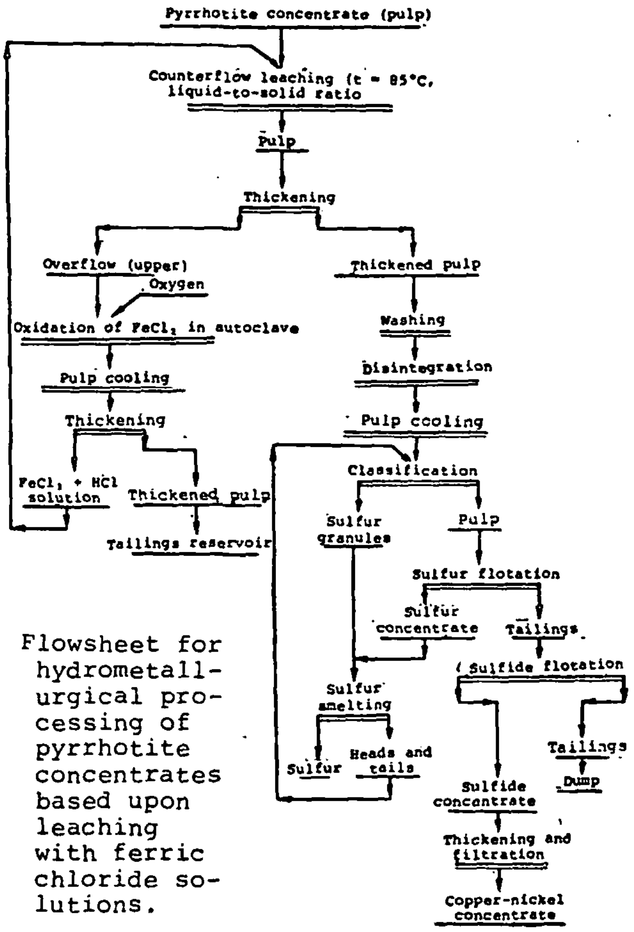
# LEACHING PYRRHOTITE CONCENTRATES WITH FERRIC CHLORIDE SOLUTIONS

UDC 669.2.053.4

A. L. Krestan

This work examines the possibility of using ferric chloride to process pyrrhotite concentrates. The technology is based on oxidation of pyrrhotite in aqueous pulp by the reaction $FeS + 2FeCl^3 = 3FeCl_2 + S^\circ$, followed by separation of elementary sulfur and production of a rich copper-nickel sulfide concentrate. Oxidizing hydrolysis of the ferrous chloride solution by the reaction $6FeCl_2 + 1.5O_2 = 4FeCl_3 + Fe_2O_3$ makes it possible to regenerate the reagent and to separate the pyrrhotite iron into an independent product.

Experiments were conducted on laboratory and enlarged laboratory scales, using the scheme shown in the Figure. The initial pyrrhotite concentrate contained (in %): 43.86-48.26 Fe, 1.82-3.60 Ni, 0.94-3.23 Cu, 0.06-0.17 Co, 24.16-29.32 S. The iron in the samples was represented mainly be hexagonal and partly by monoclinic pyrrhotite, with a small amount of magnetite; nickel was represented by pentlandite and copper by chalcopyrite and cubanite. The initial solution contained 120 g/liter $Fe^{3+}$ and 30 g/liter HCl, and the pulp density corresponded to a liquid-to-solid ratio of 1:6; this is governed by the solubility of $FeCl_2$. The presence of hydrochloric acid in the initial solution arose from the following circumstances: a) our previous kinetic studies had shown that reducing the solution pH value accelerates the oxidation of pyrrhotite appreciably; b) a more acidic final solution promoted the evolution of free hydrogen sulfide and the reverse precipitation of the non-ferrous metals which had dissolved.



Flowsheet for hydrometallurgical processing of pyrrhotite concentrates based upon leaching with ferric chloride solutions.

The concentrate was leached in a special glass reactor of 6 liters capacity with a mechanical mixer, at 85°C for 30-45 min. The final solution contained $\sim$ 200 g/liter $Fe^{2+}$, with 96-97% Fe extracted. Ni losses with the solution were 2-3%, and almost all the Cu concentrated in the leaching residue. After thickening and settling for 30 min, the ferrous chloride solution separated from from the undissolved residue and subjected to oxidizing hydrolysis in a titanium laboratory autoclave. Conditions were: T = 150°C, $P_{O_2}$ = 7 at, $\tau$ = 1.5-2 hr. Leaching residues were sent for disintegration after 2-stage washing, because direct extraction of elementary sulfur by flotation did not yield good results. Disintegration was conducted in a laboratory autoclave at 125°C, a liq:sol ratio of 1, for 20-30 min. Sodium sulfide, at a rate of 20-25 kg/ton was used to make the sulfides hydrophilic. Sulfur particles increase in size by coagulation during the operation, permitting preseparation of elementary sulfur by classification. Most of the elementary sulfur ($\sim$ 75%) was separated out as granules on a screen with a 0.25 mesh opening.

Sulfur flotation with emulsified kerosene was used to extract elementary sulfur residues. Kerosene consumption was 1 kg/t, using T-66 (100 g/t) as the frother. The S concentrate and the S granules were then combined. The S content of this product was at least 80%, with a total 95% S extraction into the product. S was obtained from this product under conditions similar to disintegration with respect to temperature and pulp density. The operation lasted 60 min. There was 80% S direct extraction of S to the commercial product. The sulfur flotation tailings were refloated to produce a higher-grade non-ferrous sulfide concentrate. Butyl xanthate (300-350 g/t) was the collector; T-66 (50-80 g/t) the frother. The sulfide concentrates contained (in %): $\sim$ 30 (Ni+Cu), 15 Fe, and 35 S. Extraction from the initial raw material was at least 95% each for Cu and Ni and 90% for Co.

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# LEACHING PRACTICES AT SMOKY VALLEY MINE

C. Arthur Lefler

Smoky Valley Mining Division
Copper Range Company
Round Mountain, Nevada

For presentation at the AIME Annual Meeting
Chicago, Illinois - February 22-26, 1981

## Desorption (Stripping) Section

One ton (.9 tonne) of carbon is withdrawn from the first reactor and passed daily to the desorption or stripping section which consists of a conditioning tank and three desorption tanks. The carbon is placed in the conditioning tank and raised to about 180°F (82°C) in the stripping solution and held for one day. It is then transferred to one of the three desorption vessels and leached for three days with sodium cyanide and sodium hydroxide solutions at a temperature of 180°F (82°C). The stripping solution at the rate of about 18 gpm. (1.14 L/sec) is passed through the three vessels in series fashion - into the oldest and out of the newest and the stripping effluent, containing about 2 oz Au/ton (68g Au/tonne) of solution, is fed continuously to the electrowinning section.

## Electrowinning

The electrowinning section consists of three 2' x 3' x 4' (.6m x .9m x 1.2m) cells with parallel solution flows of 6 gpm (0.4 L/sec). Each cell has three 2' x 3' (.6m x .9m) stainless steel anodes and six steel wool cathodes. The cells operate at 3 volts and 140 amps or about 4 amperes per square foot (43 $A/m^2$). Usual pulling schedule for each cell is as follows: The two cathodes closest to input side are pulled each week, the remaining four are shifted toward the input side of the cell and the new steel wool cathodes are then put into the spaces left at the output side of the cell. The dore' precipitates with residual iron from the steel wool cathodes are removed and dried to prepare for fire refining.

## Refining

The dried precipitate from the electrowinning cells is weighed and nitre, borax and silica reagents are added in the proper proportions for the refining furnace charge. The furnace is then charged and a temperature of 2100°F (1150°C) is obtained and held for 1.5 hrs. Each charge produces 200 to 400 oz (6200 to 12400g) dore' metal buttons. The buttons are then accumulated and melted in the casting furnace and dore' bars of 1000 to 1150 oz (31100 to 35800g) are cast.

Slag from button production is pulverized and then screened to remove the coarse trapped dore'. The screen undersize is tabled to remove fine trapped dore'. These two products are returned to subsequent melts.

## Leach Solution Heating

Temperatures during the winter in the Big Smoky Valley commonly fall well below freezing causing shutdown of the leaching heaps for the most of December, January and February each year. In order to mitigate losses due to freeze ups, submerged combustion burners capable of providing 25 million BTU's per hour ($26.4 \times 10^9$ joules/hr) to the leaching solution have been installed and are used as necessary to allow operation of the leaching system when temperatures are as low as 15°F (-10°C). Even in the worse cases where shutdown cannot be prevented, resumption of production is much more rapid.

## Carbon Treatment

We have experienced a considerable build-up in the carbon of calcium carbonate. The effect of the build-up caused a decrease in adsorption efficiency resulting in high plant tails. We are now washing the carbon with nitric acid and are operating at former levels of recovery. Tails from the plant are at .002 troy oz per ton (.07g/tonne) of solution. The technique employed is to place one ton (.9 tonnes) of stripped carbon, after kiln reactivation, in a fibreglass vessel and acid solution (10% $HNO_3$) is circulated through the carbon until a constant PH of 6 is achieved. Carbon is then washed and made basic with sodium hydroxide and reinserted into the adsorption circuit. Since we reactivate one ton (.9 tonnes) of carbon per day, we wash and hold the carbon for the 24 hour period.

# LEACHING PRACTICES AT SMOKY VALLEY MINE

The Smoky Valley Mine is jointly owned by Louisiana Land and Exploration Company, Felmont Oil Corporation and Case Pomeroy Company. Copper Range Company, a subsidiary of L.L. & E. is the operator of the mine.

The mine is located about 60 miles (100 km) north of Tonopah, Nevada on Highway 376 (formerly 8A) in the Big Smoky Valley on the western flank of the Toquima Mountain Range in the shadow of Mount Jefferson.

The mine is at an elevation of about 6100 ft. (1860m) and is situated on the southwestern flank of Round Mountain, the hill for which the town of Round Mountain is named. The ore is a rhyolitic ignimbrite with coarse gold occurring along fractures and with fine microscopic gold disseminated in the rock mass. Minor silver is associated with gold.

Annual mining is planned at 5.8 million tons (5.3 million tonnes) per year with 2.2 million tons (2 million tonnes) as ore (7,000 tons or 6,400 tonnes per day).

## Material Handling

After drilling and blasting the ore is loaded on fifty (50) ton (45 tonnes) trucks with rubber tired loaders or an electric power shovel and transported to an open circuit crushing system where it is reduced in size to a normal - 1/2 inch (1.25cm) product. The crushed material is belt conveyed to a storage pile and is then withdrawn as required and conveyed to a truck loading bin. The crushed ore is transported to the leaching pad area by the 50 ton (45 tonnes) trucks and stacked to a height of 13 feet (4m) using Loaders.

The material after leaching, washing and draining, is excavated from the leach pads with a loader and transported by trucks to an adjacent dump area.

## Leaching Pad Construction

The leaching pad is constructed of Hydraulic asphalt concrete over a carefully compacted base. The build-up of the pad includes a two inch (5cm) layer of asphalt which is covered with an asphalt rubber membrane and two additional 2½ inch (6.4 cm) layers of asphalt concrete. This provides an impermeable barrier to the downward percolating solutions.

The leach pad is 2525 feet (770m) long and 282 feet (86m) wide. The width includes a common drainage ditch which collects all effluent solutions and conducts them to a pregnant solution pump sump.

## Application of Leaching Solution to Heaps

Current practice for application of leach solution includes use of polyethylene piping for conveying barren solution from the plant effluent sump to the leach pads and the use of removable PVC piping for the spray distribution systems on the heap surface.

The barren solution is applied to the heaps by spraying - using "Bagdad Wigglers" 12" (30.5cm) lengths of 1/4" (0.64cm) surgical rubber tubing. The "Wigglers" are arranged in a 35 ft. x 35 ft. (10.7 x 10.7m) square pattern on the surface of the heaps with output of each spray at 5 gpm. (.3 L/s). The current application rate is .004 gpm/ft$^2$. (.0027 L/s/m$^2$). We are planning to increase the application rate to .005 gpm/ft$^2$ (.0034 L/sec/m$^2$) to improve coverage. We are now distributing 2200 gpm (.139m$^3$/s) of solution on the heaps but will increase this shortly to 3000 gpm. (.189m$^3$s).

## Heap Leaching Metallurgy

Metallurgical treatment consists of application of an aqueous solution of sodium cyanide and sodium hydroxide to the ore heaps to dissolve the gold and silver values.

Leaching solution concentrations to the heap are maintained nominally at 0.05% cyanide and 0.03% NaOH and solution PH is maintained at 11.0.

The leaching cycle is nominally 48 days distributed as follows:

| | |
|---|---|
| Leaching Time | 40 days |
| Washing Time | 2 days |
| Draining Time | 2 days |
| Loading, Unloading and Open | 4 days |

The leaching solutions are in closed circuit and the only make-up water is for evaporation and moisture in leached tails. The usual source of make-up in the system is the wash water which essentially balances with the losses for evaporation and tailings moisture. All solution from the leach pads is collected in a common ditch and by gravity to a pregnant solution sump.

The composition of pregnant solution is commonly from .020 to .030 troy oz Au/ton (.7 to 1.0g Au/tonne) of solution and from .4 to .6 lbs (181 to 272g) cyanide/ton of solution at a PH of 9.5 to 10.0.

## Process Plant

Recovery of gold and silver from solution is by activated carbon adsorption, desorption and then electrowinning and fire refining. The final product is dore' metal typically containing 65% gold 34% silver, and minor amounts of copper, nickel and iron.

## Adsorption Section

Pregnant solution at the rate of about 1600 gpm. (.101m$^3$/s) is pumped from the pregnant solution sump to an elevated plant inlet screening station. The solution then flows by gravity through a series of five 12 ft. (3.65m) diameter x 8 ft. (2.44m) deep open top adsorption reactor vessels which contain activated carbon. Flow through each tank is upward through the expanded carbon bed. Each reactor contains four tons (3.6 tonnes) of 12 x 30 mesh coconut carbon.

Carbon transfers are made counter to the solution flow in one ton (.9 tonnes) batches each day into the reactor system, between reactors and from the reactor system.

The carbon transfers are accomplished by eduction using barren solution as the transfer medium. Carbon is loaded during the five stages of adsorption to approximately 200 troy oz Au/ton (6900g Au/tonne) of carbon.

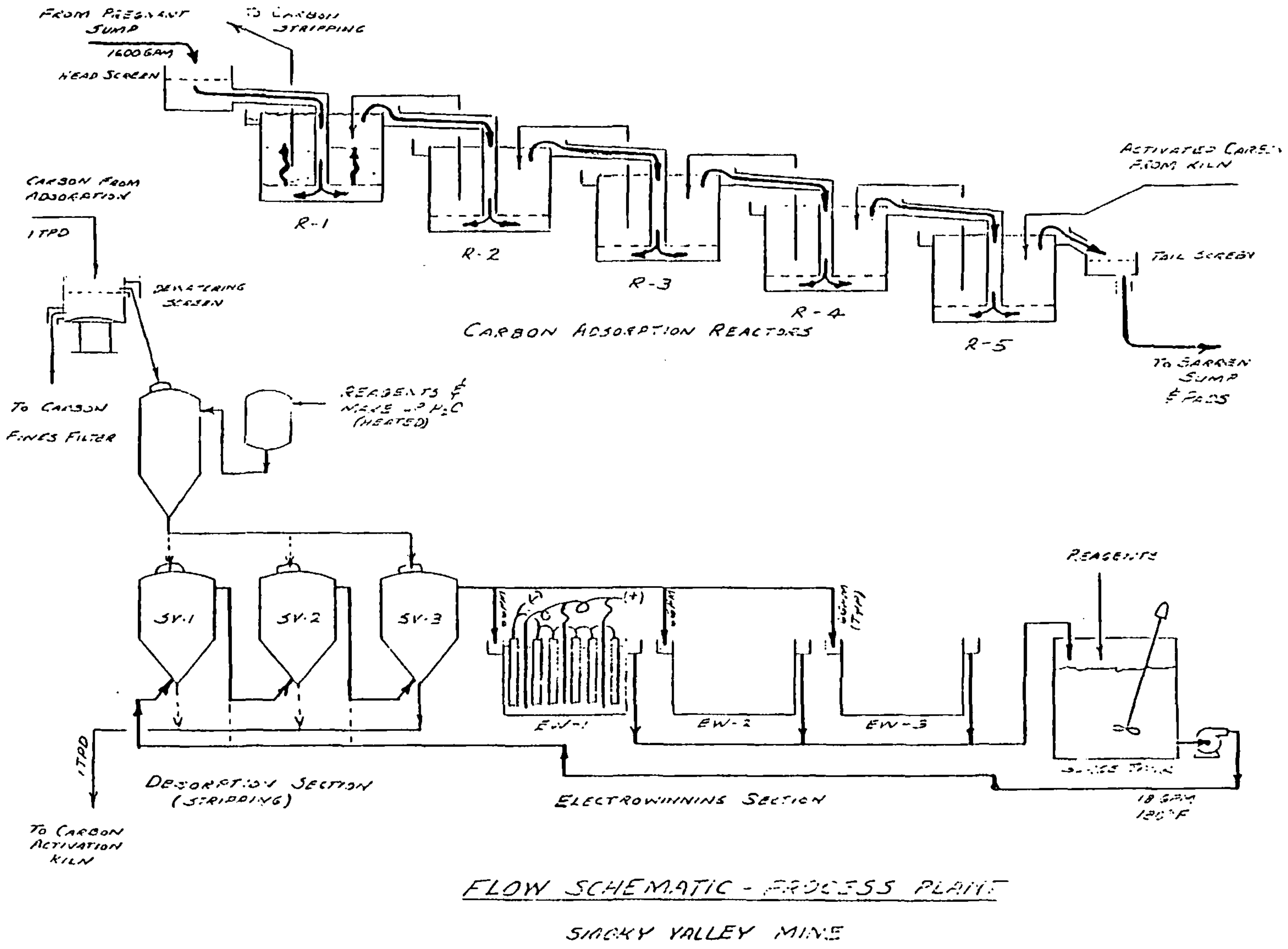

Figure 1.
FLOW SCHEMATIC - PROCESS PLANT
SMOKY VALLEY MINE

*Hydrometallurgy*, 5 (1980) 243—254

# THE LIQUID SURFACTANT MEMBRANE SEPARATION OF COPPER, COBALT AND NICKEL FROM MULTICOMPONENT AQUEOUS SOLUTIONS

J. STRZELBICKI and W. CHAREWICZ

*Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, 50-370 Wroclaw (Poland)*

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## ABSTRACT

Strzelbicki, J. and Charewicz, W., 1980. The liquid surfactant membrane separation of copper, cobalt and nickel from multicomponent aqueous solutions. *Hydrometallurgy*, 5: 243—254.

The separation of the cations of copper(II), cobalt(II) and nickel(II) from their mixed aqueous solutions, by liquid surfactant membranes containing di-(2-ethylhexyl)phosphoric acid (D2EHPA), lauric acid, caprylic acid, LIX-70 and Kelex-100 as ion exchangers and sorbitan monooleate as emulsifier has been studied. The effects of composition and acidity of the external feed solution on the separation of each metal are established. The multistage separation with fresh and reused liquid surfactant membrane was also applied to copper, cobalt and nickel mixed aqueous solution. D2EHPA liquid membranes appeared to be effective for nitrate and chloride systems, while Kelex 100 and LIX 70 membranes allow the separation of the metals studied, even from aqueous sulphate solutions. The process can be strongly competitive with liquid—liquid extraction, in particular in applications to the hydrometallurgical processing of low grade raw materials.

## INTRODUCTION

Hitherto published works on the liquid surfactant membrane separation of metal ions from aqueous solutions [1—10] have been concerned with the optimization of process variables for separation and concentration of chromates [1—3] and copper(II) [4—6], cobalt(II) [4,7] and nickel(II) [4] cations as well as for the removal of chromates, copper(II), mercury(II) and cadmium(II) cations from industrial wastewaters [3].

The system studied in this work is similar to that used for copper(II) [4,5] and cobalt(II) [4,7] separation where two aqueous solutions i.e. an internal-aqueous mineral acid solution and another mixed aqueous solution of copper, cobalt and nickel salts (external one) were separated by an organic solution (liquid membrane). The liquid membrane consisted of an emulsifier and an extractant (ion-exchanger) dissolved in an organic solvent. Such a liquid surfactant membrane exists as a water-in-oil-in-water type emulsion obtained by mixing the internal aqueous solution-in-organic membrane emulsion with the external aqueous solution.

The separation process is based on the selective permeation of metal-extractant complexes formed on the "external" side of the membrane through the organic membrane. The complexes decompose after reaching the "internal" membrane side and the released protonated extractant molecules remain in the organic membrane. Finally the internal solution is enriched in metal value, while the external solution becomes more acidic.

## EXPERIMENTAL

Mixtures of nitric, sulphuric or hydrochloric acid with a solution of an emulsifier (sorbitan monooleate (SPAN), International Enzymes Ltd., technical grade) and commercial extractants (Table 1) in kerosene of density 0.844 were stirred at the rate of 33 rps, by means of a magnetic stirrer (25 mm long, $\varnothing = 8.5$ mm) plated with teflon. The resultant water-in-oil type emulsion was then mixed with the (external) aqueous solution of copper(II), cobalt(II) and nickel(II) salts in a glass vessel (110 mm high, $\varnothing = 60$ mm) using a glass stirrer (spatula: length = 21 mm, width = 14 mm, thickness = 2 mm, deviation angle = 65°).

Experiments on the multistage liquid membrane separation with and without reuse of the organic membrane have also been conducted. In the first case a freshly prepared "internal" aqueous-in-organic membrane emulsion was mixed at each stage with the same initial "external" solution. In the second case a fresh portion of the "external" feed solution was mixed at each stage with the emulsion prepared from fresh "internal" solution and the recovered organic membrane. The organic membrane was recovered from the final emulsion after the previous stage of separation by addition of 2 cm$^3$ of $n$-butanol and separation of the resultant phases.

The acidity of the external solution was controlled during the experiments and maintained at a constant level by addition of aqueous potassium hydroxide. The concentrations of the metals separated in the external solution were monitored by a radiotracer technique using the $^{58}$Co, $^{64}$Cu and $^{63}$Ni radioisotopes and a multichannel gamma radiation analyzer (Nuclear Data ND-1200) or a beta-scintillation counter (for nickel).

Based on the mass balance for each experiment the following values were determined. Per cent recovery of each metal from the external solution

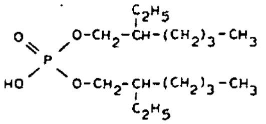
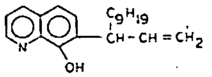
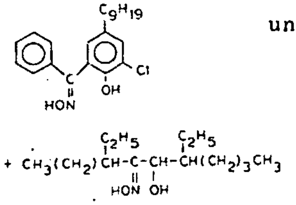
$$R = [1 - (c_r^e V_r^e / c_o^e V_o^e)]\ 100$$

the separation factor for metals A and B

$$\phi(\mathrm{A/B}) = (c_r^i / c_r^e)_A (c_r^e / c_r^i)_B$$

TABLE 1

Extractants used for liquid membrane separation of Co(II), Cu(II) and Ni(II) cations

| Compound | Chemical formula | Molecular weight | Purity | Producer | $pH_{0.5}$ for liquid—liquid extraction | | |
|---|---|---|---|---|---|---|---|
| | | | | | $Cu^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ |
| Di-(2-ethylhexyl) phosphoric acid (D2EHPA) |  | 321.5 | 95% | Institute of Organic and Polymer Technology Wroclaw (Poland) | 2.25 [11] | 3.1 [11] | 3.6 [11] |
| 7-Dodecenyl-8-hydroxyquinoline (Kelex 100) |  | 287.5 | technical | Ashland Chemicals Co. (U.S.A.) | 1.8 [12] | 3.2 [13] | > 3.2 [13] |
| Mixture of 5.8-diethyl-7-hydroxy-6-dodecanone oxime and 3-chloro-5-nonan-2-hydroxybenzophenone oxime (LIX 70) |  | unknown | technical | General Mills Chemicals Inc. (U.S.A.) | 2.6 [12.14] | 4.3 [13] | > 4.3 [13] |
| Caprylic acid ($C_8$) | $CH_3(CH_2)_6COOH$ | 144.2 | pure | Reachim (U.S.S.R.) | 3.14 [15]<br>3.37 [16] | 4.68 [15]<br>5.1 [17]<br>4.4—6.6 [18] | 4.56 [15]<br>4.9 [17]<br>4.3—5.9 [18] |
| Lauric acid ($C_{12}$) | $CH_3(CH_2)_{10}COOH$ | 200.3 | pure | Reachim (U.S.S.R.) | 3.4 [13] | 5.3 [13]<br>5.35 [17] | 5.1 [13] |

and the metal enrichment ratio

$$E = (c_r^i/c_o^e)$$

where $c$ (g m$^{-3}$) and $V$ (m$^3$) are the concentration and volume of solution, respectively, subscripts o and r refer to the initial and residual values, while i and e refer to the internal and external membrane solutions.

The residual volume of the external solution $V_r^e$ is equal to $1.1 \times 10^{-4} - \Delta V$. $\Delta V$ (m$^3$) describes the change of external solution volume caused by the emulsion instability ($\Delta V < 0$) or by the external solution permeation to the internal solution ($\Delta V > 0$). The value of $V_r^e = 1.1 \times 10^{-4}$ m$^3$ — maintained constant in all the experiments — is the sum of the initial volume of the external solution and of the aqueous potassium hydroxide added as a pH regulator.

## RESULTS

Separation of individual cations from aqueous solutions by a liquid surfactant membrane containing D2EHPA was investigated earlier. Based on the results obtained for copper [4,5], cobalt [4,7] and nickel [4] the above membrane was studied for a multicomponent aqueous solution of copper, cobalt and nickel salts, including multistage separation as well as the organic membrane reuse. Other commercial liquid ion-exchangers: LIX 70, Kelex 100, lauric and caprylic acids, were likewise studied. The experimental results are illustrated in Fig. 1 and summarized in Tables 2—9. These do not include the final content of metal in the organic membrane. In most cases this amounted

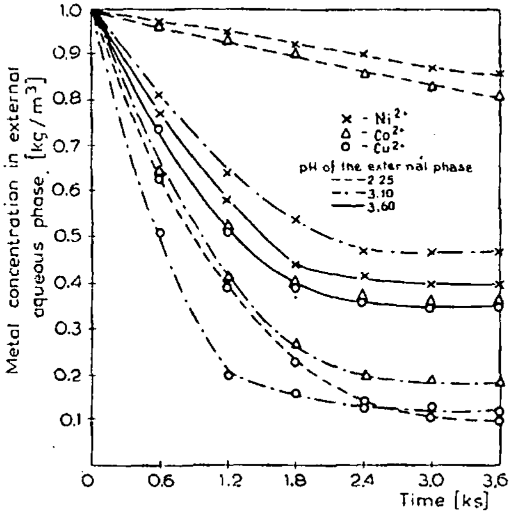


Fig. 1. Separation of copper, cobalt, and nickel cations by liquid surfactant membranes at varying acidity of the external feed solution. Membrane, solutions and stirring as for Table 2).

TABLE 2

Liquid surfactant membrane separation of copper, cobalt and nickel cations at various acidity of the external feed solution. Membrane: 3.0% (v/v) of Span 80, 6.3% (v/v) of D2EHPA in kerosene of density 0.844; stirring: 10.8 rps for 2.4 ks; initial metals concentration as nitrates in external solution 1 kg m$^{-3}$ for each; internal solution: 2.0 kmol m$^{-3}$ aqueous nitric acid

| pH of external solution | Recovery, *R* (%) | | | Separation factor, $\phi$ | | | Enrichment ratio, *E* | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | Co | Ni | Cu/Co | Cu/Ni | Co/Ni | Cu | Co | Ni |
| 2.25 | 89 | 11 | 4, 3 | 70.8 | 228 | 3.22 | 8.65 | 0.99 | 0.33 |
| 3.10 | 86 | 79 | 34 | 1.56 | 11.6 | 7.47 | 8.32 | 7.81 | 3.3 |
| 3.60 | 60 | 60 | 56 | 1.00 | 1.17 | 1.17 | 5.79 | 5.79 | 5.5 |

TABLE 3

Liquid surfactant membrane separation of copper, cobalt and nickel at various compositions of external-feed solution. Membrane and stirring as for Table 2. pH of the external solution equals 2.25

| Composition of the external solution | Composition of the internal solution | Final concentration in internal solution [kg/m$^3$] | | | Recovery R[%] | | | Separation factors $\phi$ | | | Enrichment ratio E | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cu | Co | Ni | Cu | Co | Ni | Cu/Co | Cu/Ni | Co/Ni | Cu | Co | Ni |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as nitrates | 2.0 kmol/m$^3$ $HNO_3$ | 8.4 | 0.53 | 0.33 | 88 | 6.5 | 4.3 | 122 | 201 | 1.6 | 8.4 | 0.53 | 0.33 |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as nitrates<br>1.0 kmol/m$^3$ $KNO_3$ | | 7.6 | 1.2 | 0.77 | 79 | 13 | 8.7 | 26 | 43 | 1.6 | 7.6 | 1.2 | 0.77 |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as chlorides | 2.0 kmol/m$^3$ HCl | 8.5 | 0.88 | 0.22 | 89 | 9.8 | 3.2 | 79 | 340 | 4.3 | 8.5 | 0.88 | 0.22 |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as chlorides<br>1.0 kmol/m$^3$ KCl | | 7.6 | 0.88 | 1.32 | 80 | 9.8 | 14 | 39 | 25 | 0.63 | 7.6 | 0.88 | 1.32 |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as sulphates | 150 kg/m$^3$ $H_2SO_4$ | 6.6 | 0.66 | 0.44 | 69 | 7.6 | 5.4 | 30 | 46 | 1.5 | 6.6 | 0.66 | 0.44 |
| 1.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as sulphates<br>0.35 kmol/m$^3$ $K_2SO_4$ | | 4.1 | 1.00 | 1.00 | 45 | 11 | 11 | 6.6 | 6.6 | 1.0 | 4.1 | 1.0 | 1.0 |
| 0.1 kg Cu/m$^3$<br>0.8 kg Co/m$^3$<br>0.8 kg Ni/m$^3$<br>as nitrates | 2.0 kmol/m$^3$ $HNO_3$ | 0.44 | 0.42 | 0.20 | 58 | 6.5 | 3.8 | 17 | 37 | 2.2 | 4.4 | 0.53 | 0.25 |
| 0.8 kg Cu/m$^3$<br>0.2 kg Co/m$^3$<br>0.2 kg Ni/m$^3$<br>as nitrates | | 8.6 | 0.13 | 0.08 | 86 | 6.5 | 1.0 | 113 | 194 | 1.7 | 11 | 0.85 | 0.90 |
| 8.0 kg Cu/m$^3$<br>1.0 kg Co/m$^3$<br>1.0 kg Ni/m$^3$<br>as nitrates | | 20 | 0.66 | 0.55 | 26 | 7.6 | 6.5 | 4.7 | 5.7 | 1.2 | 2.5 | 0.84 | 0.85 |

to 1% of the cobalt and nickel and to about 2.5% of the copper introduced to the liquid membrane system with the initial external solution.

In external solutions of various acidity the lowest values of the separation factors of copper, cobalt and nickel with the D2EHPA containing membrane were found at the highest pH (Fig. 1, Table 2). One-stage liquid membrane separation allows separation of copper from both cobalt and nickel or separation of nickel from both copper and cobalt. In the first case the separation is significantly improved.

Since the course of a liquid membrane separation depends on the composition of the external solution the behaviour of external solutions containing $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $K^+$ cations (in the form of nitrates, chlorides or sulphates) and the liquid membrane containing D2EHPA (Table 3) was studied. For the nitrate and chloride systems the separation factors of copper from both cobalt and nickel are relatively high, and, in general, are lower for sulphate solutions. On the other hand, the separation factor for cobalt from nickel does not exceed 2 in most cases. The effectiveness of separation decreased with the ionic strength of the external solution. The enrichment ratio of copper in the liquid membrane system studied reaches 11 for a one-stage separation and proves the applicability of this process to dilute multicomponent aqueous solutions of nonferrous metals.

Multistage liquid membrane separation was also studied. The same feed solution was mixed with the freshly prepared emulsion at each stage (Table 4). This method of operation permits high copper recovery as well as separation of copper from cobalt. From the practical point of view it was important to know whether the reuse of liquid membrane influences the effectiveness of the separation. To this end freshly prepared feed solution was mixed at each stage with emulsion prepared from a fresh internal solution and the organic phase which had been recovered after decomposition of emulsion used at the previous stage by the addition of 2 cm³ of *n*-butanol (Table 5). No significant

TABLE 4

Four-stage liquid surfactant membrane separation of copper from cobalt. Membrane, external solution and internal solution as for Table 2. Stirring 10.8 rps for 1.8 ks and pH of external solution 2.25

| Stage number | Final concentration in internal solution (kg m$^{-3}$) | | Total recovery, $R$ (%) | | Separation factor, $\phi$(Cu/Co) | Final $C_{Co}/C_{Cu}$ ratio | |
|---|---|---|---|---|---|---|---|
| | Cu | Co | Cu | Co | | external solution | internal solution |
| I | 8.7 | 0.99 | 89 | 11 | 71 | 8.1 | 0.11 |
| II | 0.54 | 0.52 | 95 | 38 | 17 | 16 | 0.96 |
| III | 0.21 | 0.38 | 97.1 | 51 | 15 | 27 | 1.8 |
| IV | 0.15 | 0.70 | 98.6 | 79 | 11 | 50 | 4.7 |

TABLE 5

Three-stage liquid surfactant membrane separation of copper from cobalt with the membrane reuse. Membrane, feed and internal solutions, stirring and pH as for Table 4

| Number of stage | Final concentration in internal solution (kg m$^{-3}$) | | Recovery, $R$ (%) | | Separation factor, $\phi$(Cu/Co) | Final concentration ratio | |
|---|---|---|---|---|---|---|---|
| | Cu | Co | Cu | Co | | internal solution $C_{Cu}/C_{Co}$ | external solution $C_{Co}/C_{Cu}$ |
| I | 8.6 | 1.0 | 89 | 11 | 64 | 8.7 | 7.4 |
| II | 8.7 | 1.7 | 89 | 18 | 35 | 5.1 | 6.8 |
| III | 8.9 | 1.6 | 90 | 16 | 45 | 5.6 | 8.0 |

effect of membrane reuse on metal recovery has been observed at varying though still high values of the separation factor.

Copper can be easily separated from cobalt or nickel, whereas the separation of cobalt from nickel is difficult owing to their chemical similarity. Table 6 shows results of cobalt and nickel separation from their mixed aqueous solutions. In most cases the cobalt/nickel separation factor exceeds 4.0 for one stage with a weak dependence on the external solution composition.

With a multistage liquid membrane separation process in which freshly prepared emulsion is used at each stage for the same feed solution, cobalt was effectively separated from nickel (Table 7). The final cobalt/nickel separation factor after three stages reached 6.1, and the final recovery of cobalt and nickel were 99% and 73%, respectively.

Four other commercial extractants were used for the separation of copper, cobalt and nickel (Table 8) as well as for mixtures of cobalt and nickel (Table 9) aqueous feed solutions of various compositions. The acidity of these solutions was chosen to equal a pH value 0.5 for the corresponding liquid—liquid extraction systems (see Table 1). The lowest recovery as well as the lowest separation factors were observed for membranes containing carboxylic acids. For the Kelex 100 and LIX 70 membranes these two parameters were

TABLE 7

Three-stage liquid surfactant membrane separation of cobalt from nickel with the membrane reuse. Membrane and initial solution as for Table 6. Stirring 10.8 rps for 1.5 ks

| Number of stage | Final concentration in external solution (kg m$^{-3}$) | | Final concentration in internal solution (kg m$^{-3}$) | | Recovery, $R$ (%) | | Separation factor $\phi$(Co/Ni) | Final $C_{Ni}/C_{Co}$ ratio in | |
|---|---|---|---|---|---|---|---|---|---|
| | Co | Ni | Co | Ni | Co | Ni | | external solution | internal solution |
| I | 0.36 | 0.68 | 6.0 | 2.4 | 61 | 25 | 4.8 | 1.9 | 0.40 |
| II | 0.070 | 0.42 | 3.1 | 2.4 | 92 | 50 | 7.7 | 6.0 | 0.77 |
| III | 0.011 | 0.21 | 0.70 | 2.2 | 99 | 73 | 6.1 | 19.0 | 3.1 |

TABLE 6

Liquid surfactant membrane separation of nickel and cobalt at various composition of external solution. Membrane and stirring as for Table 2. Initial concentration of separated metals in the external solution 1.0 kg $m^{-3}$ and pH 3.1

| Composition of the external feed solution | Composition of the internal solution | Final concentration in internal solution (kg $m^{-3}$) | | Recovery, *R* (%) | | Separation factor, $\phi$(Co/Ni) | Enrichment ratio, *E* | |
|---|---|---|---|---|---|---|---|---|
| | | Co | Ni | Co | Ni | | Co | Ni |
| Metal nitrates | 2.0 kmol/m³ $HNO_3$ | 9.0 | 6.3 | 91 | 64 | 5.8 | 9.0 | 6.3 |
| Metal nitrates and 1.0 kmol/m³ $KNO_3$ | | 7.3 | 4.0 | 75 | 38 | 4.4 | 7.3 | 4.0 |
| Metal chlorides | 2.0 kmol/m³ HCl | 8.3 | 4.4 | 84 | 45 | 6.3 | 8.3 | 4.4 |
| Metal chlorides and 1.0 kmol/m³ KCl | | 3.9 | 1.5 | 40 | 15 | 3.6 | 3.9 | 1.5 |
| Metal chlorides and 3.0 kmol/m³ KCl | | 0.77 | 1.7 | 8.7 | 17.5 | 0.41 | 0.77 | 1.7 |
| Metal sulphates | H 150 kg/m³ $H_2SO_4$ | 4.9 | 0.89 | 49 | 9.8 | 9.8 | 4.9 | 0.89 |
| Metal sulphates and 0.35 kmol/m³ $K_2SO_4$ | | 3.4 | 1.0 | 35 | 11 | 4.7 | 3.4 | 1.0 |

## TABLE 8

Liquid surfactant membrane separation of copper, cobalt and nickel at various compositions of the membrane. Stirring and initial metals concentration in the feed external solution as for Table 2. ($C_8$ = n-caprylic acid, $C_{12}$ = lauric acid)

| Composition of the external solution | Composition of the membrane | | Composition of the internal solution | Recovery R[%] | | | Separation factor ϕ | | | Enrichment ratio E | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Emulsifier | Extractant (ion-exchanger) | | Cu | Co | Ni | Cu/Co | Cu/Ni | Co/Ni | Cu | Co | Ni |
| metal nitrates<br>pH = 1.8 | 6.0% (v/v) Span 80 | 5.4% (v/v) Kelex 100 | 2.0 kmol/m$^3$ $HNO_3$ | 47 | 3.2 | 7.6 | 25 | 11.2 | 0.45 | 4.2 | 0.31 | 0.66 |
| metal nitrates and<br>1.0 kmol/m$^3$ $KNO_3$<br>pH = 1.8 | | | | 45 | 4.3 | 2.1 | 23 | 70 | 3.1 | 4.3 | 0.33 | 0.11 |
| metal sulphates and<br>0.35 kmol/m$^3$ $K_2SO_4$<br>pH = 1.8 | 7.0% (v/v) Span 80 | | 150 kg/m$^3$ $H_2SO_4$ | 31 | 3.2 | 2.1 | 18 | 36 | 2.0 | 2.8 | 0.22 | 0.11 |
| metal nitrates<br>pH = 1.6 | 1.0% (v/v) Span 80 | 5.0% (v/v) Lix 70 | 2.0 kmol/m$^3$ $HNO_3$ | 35 | 2.1 | 1.0 | 45 | 10.1 | 2.2 | 3.3 | 0.11 | 0.05 |
| metal nitrates and<br>1.0 kmol/m$^3$ $KNO_3$<br>pH = 1.6 | | | | 49 | 25 | 23 | 2.9 | 3.3 | 1.1 | 4.7 | 2.4 | 2.2 |
| metal sulphates and<br>0.35 kmol/m$^3$ $K_2SO_4$<br>pH = 1.6 | | | 150 kg/m$^3$ $H_2SO_4$ | 43 | 4.3 | 2.1 | 20.1 | 62 | 3.1 | 4.0 | 0.33 | 0.11 |
| metal sulphates and<br>0.35 kmol/m$^3$ $K_2SO_4$<br>pH = 3.5 | 5.5% (v/v) Span 80 | 3.0 % (v/v) $C_8$ | | 11 | 3.2 | 3.2 | 4.2 | 4.2 | 1.0 | 0.84 | 0.22 | 0.22 |
| metal nitrates<br>pH = 3.5 | 5.5% (v/v) Span 80 | 3.0%(v/v)$C_8$ | 2.0 kmol/m$^3$ $HNO_3$ | 64 | 31 | 30 | 3.9 | 4.1 | 1.1 | 6.1 | 3.0 | 2.9 |
| metal nitrates and<br>1.0 kmol/m$^3$ $KNO_3$<br>pH = 3.5 | | | | 36 | 13 | 12 | 3.9 | 4.3 | 1.1 | 3.4 | 1.2 | 1.1 |
| metal nitrates<br>pH - 3.5 | 3.0% (v/v) Span 80 | $1.87 \times 10^{-3}$ kmol/m$^3$ $C_{12}$ | | 20 | 2.1 | 1.0 | 19 | 42 | 2.2 | 1.7 | 0.11 | 0.05 |
| metal nitrates and<br>1.0 kmol/m$^3$ $KNO_3$<br>pH = 3.5 | 2.5% (v/v) Span 80 | | | 42 | 6.5 | 5.4 | 15 | 12 | 1.0 | 3.9 | 0.54 | 0.44 |
| Metal sulphates and<br>0.35 kmol/m$^3$ $K_2SO_4$<br>pH = 3.5 | 3.0% (v/v) Span 80 | | 150 kg/m$^3$ $H_2SO_4$ | 4.3 | 1.0 | 1.0 | 3.7 | 3.7 | 1.0 | 0.18 | 0.05 | 0.05 |

TABLE 9

Liquid surfactant membrane separation of cobalt and nickel at various compositions of the membrane. Stirring and the initial metals concentration in the feed external solution as for Table 2. ($C_8$ = n-caprylic acid, $C_{12}$ = lauric acid)

| Composition of the external solution | Membrane composition | | Composition of the internal solution | Recovery R [%] | | Separation factor $\phi_{Co/Ni}$ | Enrichment ratio E | |
|---|---|---|---|---|---|---|---|---|
| | Emulsifier | Exstractant | | Co | Ni | | Co | Ni |
| metal nitrates<br>pH = 3.2 | 7.5% (v/v) Span 80 | 5.4% (v/v) Kelex 100 | 2.0 kmol/$m^3$ $HNO_3$ | 4.3 | 6.5 | 0.59 | 0.33 | 0.55 |
| metal nitrates and<br>1.0 kmol/$m^3$ $KNO_3$<br>pH = 3.2 | | | | 9.8 | 1.0 | 25 | 0.92 | 0.04 |
| metal sulphates and<br>0.35 kmol/$m^3$ $K_2SO_4$<br>pH = 3.2 | | | 150 kg/$m^3$ $H_2SO_4$ | 4.3 | 3.2 | 1.5 | 0.33 | 0.22 |
| metal sulphates and<br>0.35 kmol/$m^3$ $K_2SO_4$<br>pH = 5.8 | 1.5% (v/v)<br>Span 80 | 5.0% (v/v) Lix 70 | | 12 | 7.6 | 1.6 | 1.1 | 0.72 |
| metal nitrates<br>pH = 5.8 | 2.0% (v/v)<br>Span 80 | | 2.0 kmol/$m^3$ $HNO_3$ | 11 | 7.6 | 1.4 | 0.99 | 0.72 |
| metal nitrates and<br>1.0 kmol/$m^3$ $KNO_3$<br>pH = 5.8 | 1.5% (v/v)<br>Span 80 | | | 12 | 15 | 0.76 | 1.1 | 1.4 |
| metal nitrates and<br>pH = 5.1 | 6.0% (v/v) Span 80 | 3.0% (v/v) $C_8$ | | 47 | 26 | 2.6 | 4.6 | 2.5 |
| metal nitrates and<br>1.0 kmol/$m^3$ $KNO_3$<br>pH = 5.1 | | | | 48 | 49 | 0.96 | 4.7 | 4.8 |
| metal sulphates and<br>0.35 kmol/$m^3$ $K_2SO_4$<br>pH = 5.1 | 5.5% (v/v)<br>Span 80 | | 150 kg/$m^3$ $H_2SO_4$ | 25 | 20 | 1.4 | 2.4 | 2.9 |
| metal sulphates and<br>0.35 kmol/$m^3$ $K_2SO_4$<br>pH = 5.1 | 3.0% (v/v) Span 80 | $1.87 \times 10^{-3}$ kmol/$m^3$ $C_{12}$ | | 20 | 15 | 1.4 | 1.9 | 1.4 |
| metal nitrates<br>pH = 5.1 | | | 2.0 kmol/$m^3$ $HNO_3$ | 41 | 24 | 2.2 | 4.0 | 2.3 |
| metal nitrates and<br>1.0 kmol/$m^3$ $KNO_3$<br>pH = 5.1 | 2.5% (v/v)<br>Span 80 | | | 37 | 37 | 1.0 | 3.6 | 3.6 |

high, which is of particular importance for the sulphate feed solutions which prevail in most hydrometallurgical processes. The separation factors of copper from cobalt and copper from nickel for liquid membranes containing Kelex 100 reached 18 and 20 and for LIX 70, 36 and 62, respectively. These values were obtained when potassium sulphate was present in the external solution.

For commercial extractant liquid membranes the separation factors of cobalt from nickel were lower than those obtained for D2EHPA membranes.

## DISCUSSION

From this study it is clear that the acidity of the external solution strongly influences the liquid surfactant membrane separation of copper, cobalt and nickel cations from multicomponent aqueous solutions. A proper choice of this acidity moreover allows selective permeation of the metal cations (Fig. 1, Table 2). The best permeation of copper, cobalt and nickel cations was achieved for D2EHPA containing liquid membranes at a pH of the external (feed) solution equal to pH 0.5 of the corresponding liquid—liquid extraction systems.

It has been stated that with decreasing acidity of the external solution the permeation rate increases for all the metal cations, thereby decreasing the selectivity of this process. This observation supports the results obtained previously [5,7].

The separation rate through liquid surfactant membranes depends on the kinetics of the reaction of metal ions with extractant molecules which probably occurs at the "external" interface of the membrane. At the given operating variables, when this reaction is optimized for certain ions, one observes a high permeation selectivity. When copper, cobalt and nickel mixed feed solution contains electrolyte in addition, the separation selectivity of the liquid membrane is decreased. The separation of the metals by liquid membrane containing D2EHPA (Table 3) is particularly inhibited by sulphates. This effect is probably connected with the interaction of separated cations and with the excess of electrolyte added. The interaction of copper cations with sulphates leads to complex formation [19], while with an excess of inert ions (e.g. sodium, potassium) sone D2EHPA-alkali metals cation complexes are formed. Both phenomena result in a decrease in their rate of reaction with D2EHPA and thus of the rate of the liquid membrane separation process.

The D2EHPA liquid surfactant membrane appears to be a highly effective means for the separation of copper, cobalt and nickel cations from slightly acidic and dilute aqueous solutions. It has been observed that, when Kelex 100 and LIX 70 containing liquid surfactant membranes are used, the separation factors of copper, cobalt and nickel cations are satisfactory even for sulphate feed solutions. Moreover, in the multistage liquid membrane separation process, both the recovery and the separation factors of the metals were substantially higher than those for the one-stage liquid membrane process. Consequently, membrane reuse does not affect the effectiveness of the separation of copper, cobalt and nickel cations from their mixed aqueous solutions through the liquid membrane.

Therefore, a separation process based on liquid surfactant membranes will compete strongly with liquid—liquid extraction, particularly for potential applications in the contemporary hydrometallurgical processing of low grade ores and other raw materials.

## ACKNOWLEDGMENTS

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# Laboratory Tests for Chloride Blast Roasting and Leaching

## *Important Factors Include Size of Crushing, Degree of Temperature, Time of Contact, and Percentage of Salt, Sulphur, and Carbonates*

By Theodore P. Holt
Metallurgical Engineer, Pulacayo, Bolivia


*Theodore P. Holt*

LITTLE has been published on the subject of chloride blast roasting and leaching since Mr. Keep's excellent article prepared in 1915.[1]

Since then much experience has been gained in treating various ores and in checking laboratory results with mill operations. A detailed description of the laboratory methods now in use should be of interest, especially to metallurgists experimenting on this and similar methods of ore treatment. I will therefore give in detail the practice as now followed, the method of analysis used, and some metallurgical notes bearing on the adaptability of ores in general to this treatment.

### PREPARING THE TEST CHARGE

For preliminary laboratory tests a representative sample of 150 to 200 lb. of the ore is desirable. This is crushed to ½ in. and quartered down in the usual way for the head sample. Aside from the usual determinations, the sample should be run for "fire" sulphur and carbon dioxide (analysis given later). Assuming that the sulphur determination shows 4 per cent sulphide-sulphur (roughly equivalent to 2.4 per cent of a good grade of coal), 1 per cent more sulphur or 0.6 per cent coal should be added to obtain the proper chloridizing temperature. Also, 8 per cent of salt should be added and the charge ground to $\frac{1}{16}$ in. It is then well mixed and water added until the ore will just adhere slightly when pressed in the hand. The desirable amount of water will vary from 5 to 12 per cent, depending on the character of the ore; the best amount will require some experimentation.

### THE TEST ROASTER

Various types and sizes of roasting furnaces have been tried out, as well as numerous methods of igniting the charge. I find the type of furnace shown in Fig. 1 very satisfactory. It has the advantage of simple construction, and can be operated anywhere if air at 2 oz. pressure or over is available.

The operation is as follows: First, the combustion chamber is half filled with wood cut to ½-in. size. The fire is started with a little fuel oil and a light blast through the valve *A*. The screen and roasting chamber are put in place, and the joint is sealed with a little plastic clay. Valve *A* is now opened further, the fire being urged until the screen is red hot. The blast is then reduced and the charge quickly added. Then the blast is again slowly increased, until the smoke rises slowly from the surface of the charge. After about one minute, *A* is closed and valve *B* is opened, the adjustment being judged, as before, by the smoke. Some prefer a water gage on the firebox for the air adjustment, but as the resistance of every charge varies, this is of limited value. On an average ore crushed as above described, anywhere from 2 to 5 in. water pressure is required. The roasting zone should reach the surface in from forty minutes to one hour.

The roasting cylinder is then moved to the side of the firebox and lifted from the charge, which will adhere sufficiently to stand alone. The sides are scraped off and the top half of the core is taken for the leaching tests. This part of the charge will be found to approximate the calcines of the commercial furnace.

### LEACHING TESTS

Percolators similar to those used in the old-time cyanide plants serve well for the leaching tests. Ten 2½-liter acid bottles with the bottoms cut off and mounted in a suitable frame make a satisfactory laboratory unit. They each hold a kilogram of charge, allowing ample room for solution. Cheesecloth over a perforated wooden disk gives a satisfactory filter. The rate of solution flow is best regulated by a small screw clamp. The leaching period varies from two to six days.

Battery jars holding slightly over two liters receive the solutions from the percolators. These should be marked at the one- and two-liter level, for convenience in

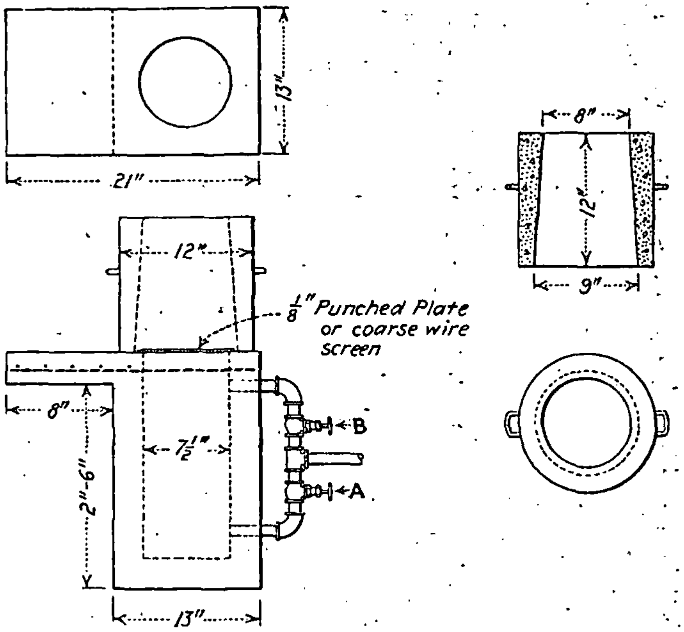

*Fig. 1. Laboratory roaster of reinforced concrete*

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[1] *Engineering and Mining Journal*, Feb. 6 and 15, 1915.

measuring the solution. A half-dozen ten- or twelve-quart enameled buckets are convenient for handling the solutions.

The roasted sample is broken to ¼ in. or so and a head sample cut out. Avoid contact with iron, as this will dechloridize the sample. One kilogram of the ore is weighed into a percolator and leached with from 6 to 20 liters of acid-chloride solution, carrying 5 lb. per ton of sulphuric acid and about 22 per cent of salt. In mill operations the temperatures of the leaching solutions vary greatly, especially where no effort is made to keep the solutions hot. When sluicing the calcines from the roasters the solution reaches the boiling point, whereas near the lower end of the iron boxes it may be as low as 20 deg. C. About 30 to 40 deg. C. is satisfactory for laboratory tests. In general, the higher the temperature the shorter the leaching period required.

The time of treatment will likewise vary from two to six days, depending mainly on the grade of the ore. If a high lead recovery is sought, it will be well to raise the salt content of the leaching solution close to saturation. If the ore is high in silver, some care is necessary, as the solubility of the silver is depressed, and a low extraction may result. If the ore carries no copper or soluble iron, a little ferric chloride will often improve the silver extraction. In mill practice iron enters the solution as ferrous chloride in the scrap-iron boxes, and is oxidized by contact with the air to ferric chloride.

It is well to measure 100 c. c. of solution from each two liters of the effluent as a solution sample. The solution should be thoroughly mixed and kept in a stoppered bottle. This gives a good check on the head and tailing assay, which is used as the basis of extraction.

### VARIATION FACTORS IN ROASTING

The leaching test is washed with ½ liter of water, dried, weighed, and assayed. The assays are corrected for the loss of weight in leaching, and this corrected tailing plus the solution should equal the head within experimental limits.

It is well to vary the size of crushing in roasting charges from four mesh to twenty mesh. Then, keeping the size factor constant, vary the percentage of salt. Also, the percentage of sulphur and the temperature are other factors to be investigated.

If the ore is low in carbonates, and carries 3 per cent or more of sulphur, it will be safe to assume that the roasters will produce ample acid for leaching. Otherwise the condenser can be connected and the acids collected in a given volume of chloride solution.

### VARIATION FACTORS IN LEACHING

Except with lead ores, where a nearly saturated chloride solution is desirable, a solution testing from 20 to 24 deg. is satisfactory for leaching. Acid may be varied up to 1 per cent. Acid chloride solutions are active solvents of native silver, silver sulphide, and other compounds, which accounts for the superior recovery obtained compared with that when using hyposulphite solution.

The effect of temperature, time of contact, and presence of cupric and ferric salts are other factors to be studied. The re-use of a precipitated solution will often show a higher recovery than a fresh solution.

One of the percolators as used for leaching also makes a very good scrap-iron precipitator. The small iron or steel lathe-turnings should be packed to a depth of 6 in. and the flow of the solution regulated by a small screw clamp. The solutions from the leaching tests are passed through at a rate to give fairly complete precipitation.

After 100 grams or so of the product has been secured it is cleaned up and a sample washed and dried for assay. About 50 grams of the undried product is transferred to a 2½-liter bottle and agitated with pregnant solution from the leaching tests. The product is allowed to settle, the barren solution decanted, and fresh silver solution added. This operation is repeated until the silver fails to precipitate. It is then filtered and washed and dried for assay.

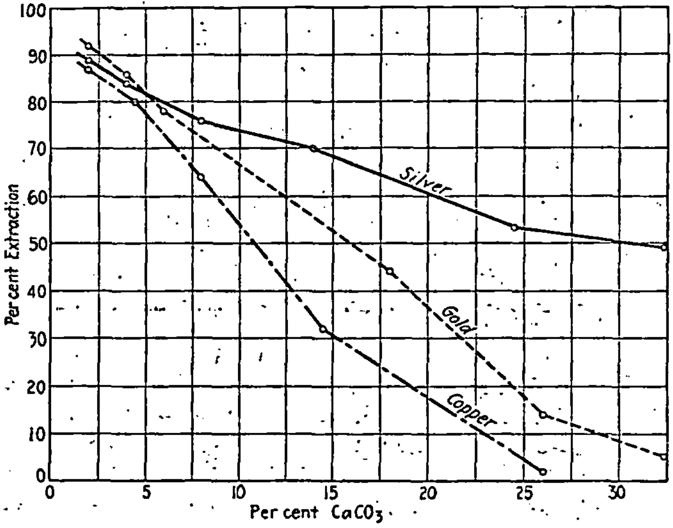


*Fig. 2. Effect of calcium carbonate on the gold, silver, and copper recovery*

The progress of the precipitation can be determined by diluting a sample of the solution with five volumes of clear water, the density of the silver chloride precipitate formed indicating the quantity of silver present. If much lead is present it will be necessary to allow this to settle before the silver chloride can be observed.

The results of a recent precipitation test of this kind are given below:

| | Scrap-iron Precipitate | Silver Precipitate |
|---|---|---|
| Silver, oz. per ton | 3,693.5 | 22,262.0 |
| Copper, per cent | 54.3 | 2.9 |
| Lead, per cent | 13.8 | Trace |

The silver precipitate is easy to reduce to fine doré bullion. If it is desired to carry this test further, the decanted solution can again be passed through the scrap-iron precipitator, or a small electric cell, and the remaining metals recovered.

### SALT CONSUMPTION

The principal reagent used in chloride roasting and leaching is common salt. It is found necessary to carry from 5 to 15 per cent in the roasting charge, and often this is a heavy item of expense. In many instances I have found that the salt actually consumed is a very small part of the amount necessary in the roasting charge for good chloridization. It is therefore feasible under some conditions to recover this unconsumed salt from the waste mill solutions and return it to the roasters.

The salt consumption determination consists in dissolving the soluble chlorides with warm distilled water from the roasted calcines, and determining the chlorine by a standard method. The water-soluble chlorine may be assumed as being available for chloridizing and fig-

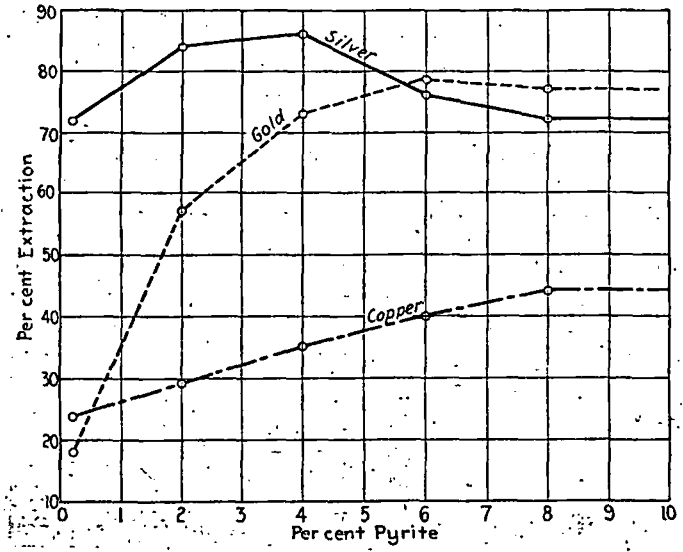


*Fig. 3. Effect of increasing the percentage of sulphur, with 4 per cent calcium carbonate*

ured as sodium chloride. The change in weight in roasting must of course be taken into the computation.

One ore upon which a complete series of tests was run, recovering the salt from the waste solution by solar evaporation, gave the following rather remarkable result:

Roast A. New salt (98 per cent NaCl) gave 4.3 per cent NaCl consumption.

Roast B. Evaporated mill solution (83 per cent NaCl) gave 1.1 per cent NaCl consumption.

The silver and copper recovery for Roast B was slightly higher than for Roast A. The chemical mass action in the roasting charge, it would appear, is responsible for the decrease in the salt decomposed. In other words, the presence of sodium sulphate in the roast limits the further decomposition of salt.

### LIMESTONE AND SIMILAR CARBONATES

Limestone and similar carbonates are the chief interfering minerals to chloride roasting and leaching. Their effect on the recovery of the metals is readily seen by reference to Figs. 2, 3 and 4. Fig. 2 shows the effect of an increasing percentage of calcium carbonate on the gold, silver, and copper recovery. Here the sulphur content of all roasting charges was 3 per cent. A similar series of tests on a silver-lead ore gave a lead curve slightly above the silver curve.

Fig. 3 shows the effect of increasing the sulphur in the roasting charge, all the roasts carrying 4 per cent calcium carbonate.

Fig. 4 shows a similar series in which all of the roasts carried 8 per cent calcium carbonate. The reason for the peculiar form of the silver curve in this case is obscure, but another series of experiments checked the first results closely. A double roast with this percentage of calcium carbonate present brought the recovery up to 90 per cent, showing that it is possible to sulphate the carbonates present effectively if sufficient sulphur is available.

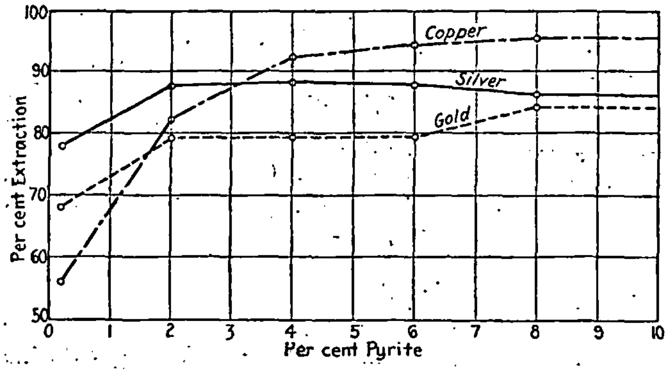


*Fig. 4. Effect of increasing the sulphur, with 8 per cent calcium carbonate*

In the metallurgical control of the mill, and also the laboratory experimental work, certain analyses and methods of assay have been found useful. These have been developed by the chemical staff of the Tintic mill and the Tintic Standard plants, and the Salt Lake station of the Bureau of Mines. So far as I know they are not available for reference, so I include them here.

### THE FIRE SULPHUR ASSAY

In the control of the roasting furnaces it is very important that the operator know the calorific value of the ores entering the charge. This determination consists in finding the reducing power of the ore on lead oxide. The stock flux is made up as follows:

Sodium carbonate, 10 lb.
Litharge, 25 lb.
Borax glass, 5 lb.

Use 10 grams of ore and 90 grams of the above flux when the sulphur is estimated to be less than 10 per cent. When over 10 per cent increase the litharge in the charge gradually to a maximum of about 50 grams. For ores containing over 25 per cent sulphur, cut the ore sample to 5 grams. Fuse for forty-five minutes, increasing the temperature gradually as in the standard lead assay. The calorific value of the lead button in terms of fire sulphur is given in the following table:

**California Value of Lead Button in Terms of Fire Sulphur**

| Grams Pb | Per Cent S | Grams Pb | Per Cent S | Grams Pb | Per Cent S | Grams Pb | Per Cent S |
|---|---|---|---|---|---|---|---|
| 1.0 | 0.4 | 9.5 | 4.2 | 18.0 | 8.1 | 26.5 | 12.0 |
| 1.5 | 0.75 | 10.0 | 4.5 | 18.5 | 8.3 | 27.0 | 12.1 |
| 2.0 | 0.90 | 10.5 | 4.7 | 19.0 | 8.6 | 27.5 | 12.3 |
| 2.5 | 1.2 | 11.0 | 5.0 | 19.5 | 8.8 | 28.0 | 12.6 |
| 3.0 | 1.4 | 11.5 | 5.2 | 20.0 | 9.0 | 28.5 | 12.9 |
| 3.5 | 1.6 | 12.0 | 5.4 | 20.5 | 9.2 | 29.0 | 13.1 |
| 4.0 | 1.8 | 12.5 | 5.7 | 21.0 | 9.5 | 29.5 | 13.3 |
| 4.5 | 2.0 | 13.0 | 5.9 | 21.5 | 9.8 | 30.0 | 13.5 |
| 5.0 | 2.25 | 13.5 | 6.1 | 22.0 | 10.0 | 30.5 | 13.8 |
| 5.5 | 2.5 | 14.0 | 6.3 | 22.5 | 10.1 | 31.0 | 14.0 |
| 6.0 | 2.8 | 14.5 | 6.6 | 23.0 | 10.3 | 31.5 | 14.2 |
| 6.5 | 3.0 | 15.0 | 6.8 | 23.5 | 10.6 | 32.0 | 14.4 |
| 7.0 | 3.1 | 15.5 | 7.0 | 24.0 | 10.9 | 32.5 | 14.7 |
| 7.5 | 3.3 | 16.0 | 7.2 | 24.5 | 11.1 | 33.0 | 14.9 |
| 8.0 | 3.6 | 16.5 | 7.5 | 25.0 | 11.2 | 33.5 | 15.1 |
| 8.5 | 3.9 | 17.0 | 7.8 | 25.5 | 11.5 | 34.0 | 15.3 |
| 9.0 | 4.1 | 17.5 | 7.9 | 26.0 | 11.8 | 34.5 | 15.6 |

### SOLUTION ASSAYS

For the determination of gold and silver take five assay tons of the solution in a beaker. Add 60 grams of test lead, put on the hot plate, and bring to boiling. Filter and transfer the lead filter paper and all to a scorifier. Add 2 grams of borax glass and reduce to the proper size button for cupellation.

For the determination of copper and lead take a 10-c.c. pipette of the solution, or more if very low-grade. Add about 10 c.c. of sulphuric acid and evaporate to white fumes. Then proceed as with the standard assay.

On account of the complex character of the commercial acid chloride solutions, the usual indicators are of no value. The cupro-ammonium sulphate method has been found best for this determination.

Dissolve copper sulphate in distilled water and dilute to one liter. Add ammonia until the heavy precipitate of copper hydroxide has almost, but not entirely, disappeared. Filter and titrate against a standard solution of acid.

Sometimes the freshly precipitated cupro-ammonium sulphate will become cloudy, owing to a little copper hydrate which has passed through the filter. A second filtration will give a clear solution. Or, if the solution is allowed to stand overnight before filtering, this trouble will be avoided.

A good strength for mill solutions commonly used is 12 grams of copper sulphate per liter. With 10 c.c. of the solution sample, each cubic centimeter will equal approximately 2.5 lb. of sulphuric acid per ton. For stronger acid solutions, this strength can be increased, although the weaker the cupro-ammonium sulphate, the more delicate the end point. This end point is the first slight precipitate or turbidity in the solution.

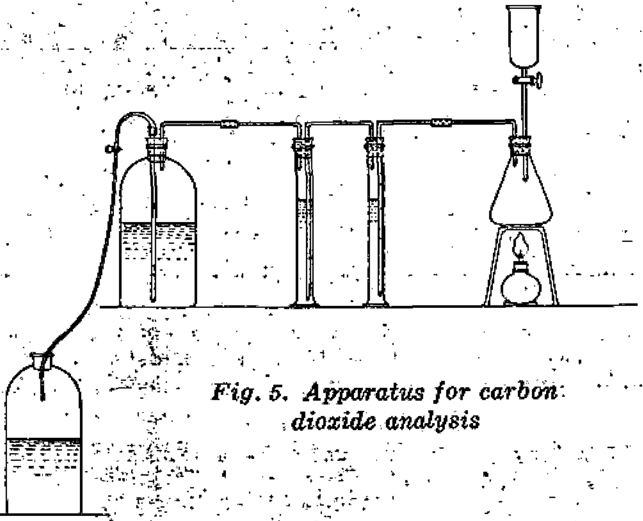


*Fig. 5. Apparatus for carbon dioxide analysis*

This determination is better understood by reference to Fig. 5.

Dissolve 20 grams of barium hydroxide in 1 liter of water, shake well, and allow to stand for three days. Make up a one-tenth normal hydrochloric acid solution and obtain its exact strength by titrating against either a standard sodium hydroxide solution or silver nitrate. Weigh 1 gram of ore into an Erlenmeyer flask. Measure into the two tubes. Connect up the tubes to the aspirator bottles and to the flask. See that all connections are airtight. Now run into the flask from the thistle tube a solution of hydrochloric acid (one part acid to three parts water). It is well to add a little copper sulphate to the acid to precipitate any hydrogen sulphide which may be generated. Aspirate the gas through the train and heat the flask to boiling over the alcohol lamp until the gas has been driven into the tubes and only steam is formed. Disconnect the tubes, wash them out quickly and thoroughly into a beaker, add a little phenolphthalein indicator, and titrate with the standard hydrochloric acid to a colorless solution.

From the equations below, figure the percentage of carbon dioxide.

$$Ba(OH)_2 + 2\,HCl = BaCl_2 + 2\,H_2O.$$
$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$
$$CO_2 + CaO = CaCO_3.$$

◆

# Production of Platinum and Allied Metals Declined in 1923

The quantity of crude platinum produced in the United States in 1923 was 609 troy ounces, of which Alaska produced 7 oz., California 578 oz., and Oregon 24 oz., according to a statement prepared from mine reports by James M. Hill, of the U. S. Geological Survey. This is a considerable decrease from the 1,008 oz. produced in 1922.

The platinum produced in Alaska was largely a by-product from gold mined in placers in the Chisna district, in the Copper River region. A little more than 53 per cent of the output in California was mined by dredges in Butte, Calaveras, Sacramento, Stanislaus, and Yuba counties, the greater part of the remainder was mined by dredges in Shasta County; and less than 1 per cent was mined from small placers on tributaries of Trinity River in Trinity County. The platinum produced in Oregon was practically all recovered by the beach miners in the vicinity of Bullards, Coos County, and Sixes, Josephine County.

The statistics show that refiners of platinum in the United States purchased in 1923 29 oz. of crude platinum from Alaska, 707 oz., from California, 63 oz. from Oregon, and 1 oz. from Washington, a total of 800 oz., as compared with 1,058 oz. purchased in 1922. They also purchased 54,741 oz. of crude platinum mined in foreign countries, of which 48,727 oz. was shipped from Colombia and 4,997 oz. from Russia.

**New Platinum Metals Recovered by Refiners in the United States 1919-1923**

(In Troy Ounces)

| Year | Platinum | Palladium | Iridium | Osmiridium | Others | Total |
|---|---|---|---|---|---|---|
| 1919...... | 40,220 | 3,807 | 401 | 402 | 279 | 45,109 |
| 1920...... | 36,015 | 4,309 | 418 | 409 | 393 | 41,544 |
| 1921...... | 51,791 | 2,686 | 286 | 581 | 1,026 | 56,370 |
| 1922...... | 54,142 | 1,943 | 210 | 1,301 | 122 | 57,718 |
| 1923...... | 46,780 | 1,934 | 280 | 787 | 16 | 49,797 |

**Platinum Metals Imported for Consumption in the United States, 1922 and 1923**

| | 1922 | | 1923 | |
|---|---|---|---|---|
| Metal | Troy Ounces | Value | Troy Ounces | Value |
| Platinum or crude platinum and unmanufactured products, ingots, sheets and wire.......... | 94,939 | $7,790,898 | 86,417 | $8,923,037 |
| Platinum, manufactured products, vases and retorts............... | (a) 45 | (b) 11,464 | 103 | 4,769 |
| Iridium........................... | 1,899 | 298,567 | 1,611 | 276,539 |
| Osmiridium......................... | 2,165 | 242,637 | 1,174 | 150,074 |
| Osmium............................ | 1,012 | 81,231 | 1,462 | 147,144 |
| Palladium.......................... | 9,754 | 537,684 | 14,578 | 857,071 |
| Rhodium........................... | 111 | 16,227 | 805 | 86,569 |
| Ruthenium.......................... | 100 | 4,839 | 487 | 21,492 |
| | 110,025 | $8,983,547 | 106,637 | $10,466,695 |

(a) Incomplete. Includes 18 oz. in vases and retorts, valued at $2,813, and 27 oz. in other products not specified, valued at $1,916.

(b) Includes articles to the value of $6,735 (quantity not given) imported under duty in 1922 prior to Sept. 22.

**Platinum Metals Consumed in the United States as Reported by Refiners, 1922 and 1923, by Industries**

(In Troy Ounces)

| Industry | Platinum | Iridium | Palladium | Others | Total | Percentage of Total |
|---|---|---|---|---|---|---|
| 1922 | | | | | | |
| Chemical........ | 8,834 | 172 | 458 | 271 | 9,735 | 5 |
| Electrical........ | 24,988 | 1,537 | 2,735 | ...... | 29,260 | 16 |
| Dental........... | 11,651 | 83 | 5,535 | ...... | 17,269 | 10 |
| Jewelry.......... | 108,527 | 2,588 | 9,852 | 1,190 | 122,157 | 67 |
| Miscellaneous..... | 2,838 | 1,064 | 636 | ...... | 4,538 | 2 |
| Totals......... | 156,838 | 5,444 | 19,216 | 1,461 | 182,959 | 100 |
| 1923 | | | | | | |
| Chemical........ | 8,637 | 190 | 485 | 266 | 9,578 | 5 |
| Electrical........ | 18,596 | 1,675 | 3,666 | ...... | 23,937 | 13 |
| Dental........... | 16,288 | 153 | 10,116 | ...... | 26,557 | 14 |
| Jewelry.......... | 105,699 | 3,073 | 14,948 | 190 | 123,910 | 65 |
| Miscellaneous.... | 3,156 | 1,403 | 986 | 1,256 | 6,801 | 3 |
| Totals......... | 152,376 | 6,494 | 30,201 | 1,712 | 190,783 | 100 |

**Stocks of Platinum Metals in Hands of Refiners in the United States, Dec. 31, 1919-1923**

(In Troy Ounces)

| Metal | 1919 | 1920 | 1921 | 1922 | 1923 |
|---|---|---|---|---|---|
| Platinum........................ | 29,228 | 46,747 | 38,514 | 41,900 | 36,554 |
| Iridium......................... | 3,359 | 4,196 | 4,991 | 7,559 | 5,208 |
| Palladium....................... | 10,235 | 16,565 | 21,042 | 24,975 | 26,266 |
| Others.......................... | 610 | 216 | 3,113 | 1,583 | 2,697 |

TSVETNYE METALLY / NON-FERROUS METALS N8, 1975

# LEACHING OF SECOND-GRADE ORES FROM THE KOUNRADSK DEPOSIT

UDC 669.334.43

B. D. Khalezov, B. M. Tokmin, and L. Z. Khrustalev

Samples of sulfide, mixed, and oxidized ores were taken to study the heap leaching of second grade ores from the Kounradsk deposit. The ores are represented by secondary quartzites or quartz porphyries. The principal rock-forming minerals are quartz, andalusite, and sericite. The sulfide minerals content does not exceed several parts of one per cent. They form sparse and small disseminated structures evenly scattered through the rock. The principal ore minerals are chalcopyrite, covellite, chalcocite, malachite, and azurite.

Table 1
Rational Composition of Copper Compounds in Ore, %

| Type of ore | Sulfates | Oxides | Secondary sulfides | Primary sulfides |
|---|---|---|---|---|
| Sulfide | Traces | 10,2 | 82,0 | 7,8 |
| Mixed | » | 15,1 | 83,0 | 1,9 |
| Oxidized | 0,6 | 39,9 | 45,7 | 13,6 |

It is apparent from the rational analysis (Table 1) that all three sorts of second grade ore contain an insignificant amount of primary copper sulfides. They differ little in their content of other constituents (Table 2).

The composition of the ores is favorable for copper extraction by leaching with sulfuric acid solutions. The ferric sulfate formed in the process of leaching when the iron salts in the ore dissolve serves as an oxidizing agent.

As a preliminary, the ore was crushed to -30 mm in size. The particle-size composition of all three types of ore was:

| | | | |
|---|---|---|---|
| Fraction, mm . . . . . . . . . . . . . . . | -30 + 10 | -10 + 5 | -5 |
| Content, % . . . . . . . . . . . . . . . . | 52-58.3 | 12.8-15.9 | 29-33 |

Prior to charging the percolator, each sample (weight 15-20 kg) was made up from the individual size classes in proportion to their yield, which maintained a constant ore particle-size and material composition. Percolator dimensions: diameter, 150 mm, height 700 mm.

Table 2
Chemical Composition of Ores, %

| Type of ore | Zn | Fe | S | $SiO_2$ | $Al_2O_3$ | CaO | MgO | Pb |
|---|---|---|---|---|---|---|---|---|
| Oxidized . . . | Traces | 2,1 | 1,08 | 69,78 | 16,08 | 0,27 | 0,45 | — |
| Mixed . . . | 0,001 | 3,3 | 2,85 | 74,76 | 16,2 | 0,03 | 0,04 | 0,08 |
| Sulfide . . . | 0,01 | 2,52 | 2,1 | 65,14 | 14,3 | 0,86 | 0,33 | — |

The ore charged into the percolator was moistened until "completely" saturated. Water consumption ranged from 76 to 98.5 ml per kg of ore.

The ore was sprayed with sulfuric acid solutions. Spray density was varied from 18 to 280 ml per kg of ore, the interval between spraying operations was varied from 1.5 to 9 days, and the acid concentration ranged from 5 to 100 g/liter.

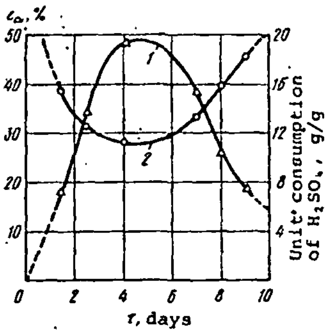
After leaching, the copper was precipitated from the solutions on scrap iron, the precipitate was separated out, and the tailings solutions were returned to the ore spraying operation. A proportion of the tailings solutions was withdrawn for neutralization, to reduce the concentration of salts accumulating in the circulating solutions.

Altering the interval between consecutive spraying operations from 1.5 to 4-5 days sharply increases the rate of copper extraction into solution. An interval of 4-5 days gives the maximum acid consumption. A further increase in the length of interval increases the unit consumption of acid and reduces the copper leaching rate, because the ore becomes too dry and the speed of the oxidizing process is drastically reduced.

At a spray density of < 20 ml/kg practically no solution emerges from the percolator, being used up in compensating for evaporation losses of moisture by the ore. An increase in spray density right up to 280 liters per ton, although it does increase copper extraction, also increases acid consumption by 1.5-2 times because the speed of solution of gangue elements increases.

In practice a spray density as high as 280 liters per ton is unacceptable, because it would necessitate the pumping of enormous amounts of solution.

Copper extraction rises sharply when the sulfuric acid concentration is increased; the unit consumption of acid increases in these circumstances. The results of leaching samples of oxidized and mixed ores from the Kounradsk deposit differ little from the results of sulfide ore leaching. We observe that a somewhat shorter interval (1-2 days or less) is required for the oxidized ore, because 40% of the copper in it is represented by oxidized minerals, which dissolve after a shorter contact with the solutions than is required for sulfide minerals.



Relationship of copper extraction (1) and unit acid consumption (2) to the interval τ between sprayings with a leaching duration of 75 days, an acid concentration of 25 g/liter, and a spray density of 140 ml/kg.

Analysis of our data leads to recommendation of the following average parameters for the process of leaching Kounradsk deposit ores: spray density 30-50 ml/kg; interval 2-6 days; sulfuric acid concentration in spray solutions 5-20 g/liter.

The upper or lower limits of the parameters found should be selected having regard to the production of "standard grade" solutions containing $\geq$ 0.5 g/liter Cu and 0.5-1 g/liter $H_2SO_4$.

The results of the experiments showed that the initial size of the ore did not affect copper extraction. After the experiment, no lumps > 10 mm in size were found in the solid residues from leaching. Consequently there will be no necessity in the industrial leaching of the ore for preliminary crushing of the large pieces.

The experiments established that the use of 70% tailings solutions in the recirculating water in oxidized ore leaching caused no deterioration in the basic process results.

It was established that the unit consumption of sulfuric acid was fairly high in the initial stage of leaching, reached a minimum at the stage of extraction of 25-30% copper, and then gradually rose again (see Fig.).

The results obtained made it possible to work out the initial data for the design and construction of a pilot heap leaching installation at the Kounradsk mine.

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# LOW-TEMPERATURE OXIDATION OF PYRRHOTITES

UDC 669.2.046.42

A. V. Vanyukov, Yu. B. Voitkovskii, N. N. Razumovskaya, and V. N. Bruek

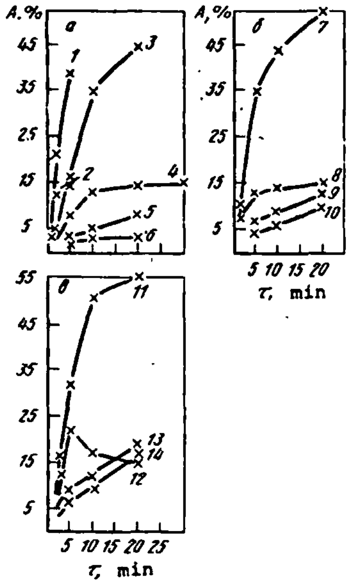
Studying the process of oxidation of the pyrrhotites which account for a considerable part of sulfide ores is of interest both in theoretical metallurgy and in designing processes and apparatus for pyrrhotite processing. The experimental findings [1-4] are somewhat contradictory, because the chemical mechanism of the process alters according to roasting conditions. The problem of formation of sulfates as primary products in the iron monosulfide oxidation reaction has not been solved up to the present. The available research methods (chemical and x-ray analysis, infrared spectrometry) cannot be used for quantitative comparison of reaction products, and it is even difficult to identify the products qualitatively. New methods, in particular, nuclear $\gamma$-resonance spectroscopy (the Mossbauer effect) are of interest in studying the oxidation process.

The object of the present work was to use nuclear $\gamma$-resonance spectroscopy to study the oxidation of iron monosulfides of various compositions. The research was carried out with synthetic iron sulfides produced by direct reaction of class V-3 iron with extra-high purity sulfur. The sulfides, which correspond precisely in composition to the borders of the pyrrhotite homogeneity region, were produced by diffusion through the vapor phase as a result of isothermal annealing of the synthesized material in equilibrium with corresponding two-phase mixtures with subsequent quenching in water.

X-ray analysis established that the materials produced had a similar composition to that prescribed [5]. Grains in a narrow size fraction, +0.1-0.08 mm, were isolated to study oxidation; this made it possible to stabilize the oxidation surface. The fine sulfide grains were oxidized in a fluidized bed of inert material to come as close as possible to isometric conditions. Samples for analysis were taken from the reactor fluidized bed at various stages of oxidation using a sampler with a vacuum intake and practically instantaneous quenching.

The Mossbauer studies were carried out with a spectrometer operating at variable speed using an NTA-512M multichannel analyzer. The source was $Co^{57}$ in a chromium matrix with an effect probability f = 0.70. The apparatus width, measured on sodium nitroprusside, was 0.24 mm/sec. All the measurements were made at room temperature on powder samples.

A six-peak spectrum consisting of single lines was observed only in specimens of stoichiometric composition. When the sulfur content of the specimens increases the spectra become more complex; the spectral lines either broaden or split. The spectra of pyrrhotites at an S content of > 37% (by mass) can be represented as the superposition of several six-peak spectra; this is apparently due to the presence of a corresponding number of non-equivalent positions of iron in the pyrrhotite structures.



Kinetics of iron oxide formation in oxidation of pyrrhotites: a) $FeS_{stoich}$ at t, °C: 1,2 - 600; 3,4 - 500; 5,6 400; b) $Fe_{0.89}S$ at t, °C: 7,8 - 500; 9,10 - 400; c - $Fe_{0.85}S$ at t, °C: 11,12 - 500; 13,14 - 400. 1, 3, .... 13 - formation of $Fe_2O_3$: 2, 4, .... 14 - formation of $Fe_3O_4$. The Fe (in %) which reacted with oxygen is shown on the A axis.

Oxides and sulfates of iron may be the principal oxidation products at oxidation temperatures of 400-600°C. The formation of these compounds should lead to the appearance of new spectral lines. A comparison of spectra obtained from oxidized materials with spectra characteristic of oxygen-bearing iron phases showed that the compounds $Fe_3O_4$ and $Fe_2O_3$ were formed as a result of oxidation; this led to the appearance of characteristic lines and to their superimposition on the initial spectrum. Iron sulfates, giving spectra in the form of pronounced doublets, were not detected in the reaction products.

The nuclear γ-resonance spectra were processed: the quantitative yield of reaction products was calculated by reference to the appropriate maxima, taking into account the overlapping the magnetite and hematite spectra. It is apparent from the Figure that the speed of oxidation and the quantitative relationship between the reaction products varies in pyrrhotites of different compositions. The kinetic characteristics obtained in the owrk have been processed according to equations for sulfide oxidation in a compressing nucleus model to define the limiting stage of interaction. It was apparent that the process of oxidation took place under kinetic conditions for most values of the degree of oxidation $\alpha$. At 500°C and with an oxidation time of > 10 min, diffusion difficulties in the access of oxygen to the reaction surface increase due to the increase in the layer of reaction products, and the oxidation process passes into the internal-diffusion region. The activation energies for oxidation proved to be 28.7 kcal/mole for FeS, 20.2 for $Fe_{0.89}S$, and 18.4 for $Fe_{0.85}S$, which agrees with the published findings [6].

Analysis of the Mossbauer absorption spectra indicates changes in the composition of the solid sulfide in the direction of an increased sulfur content. Sulfide enrichment with sulfur is due to the fact that the oxide coating grows due to iron diffusing from the sulfide through the layer of oxides to their outer boundary; the number of vacancies in the iron sublattice increases, and the pyrrhotite structure is disordered and rearranged.

The study of sulfide oxidation by nuclear γ-resonance spectroscopy made it possible both to identify the qualitative composition of the reaction products and to find that there were no sulfates in them and also to establish the quantitative relationship between a large number of oxidized and sulfide phases of iron. The results illustrate the considerable potential of the Mossbauer spectroscopy method for studying the kinetics and mechanisms of heterogeneous processes.

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decenyl acetate in mating communication than females of *T. ni*.

Five traps, each of which was baited with an evaporator (*9*) that released *cis*-7-dodecenyl acetate (*10*) at a different rate, were simultaneously placed in a field supporting a mixed population of both species. On each of 30 consecutive mornings, the moths caught in the traps were identified, sexed, and counted, and each trap was randomly moved to a new position. The number of *T. ni* males caught per trap increased with each increase in the rate of evaporation of *cis*-7-dodecenyl acetate (Fig. 1). On the other hand, *A. californica* males were caught only in the traps that released this compound at those low evaporation rates which were largely unattractive to *T. ni* males. These data indicate that the release of the same sex pheromone by females at different rates is a probable mechanism of reproductive isolation between these two species.

Only over a very narrow range of evaporation rates of *cis*-7-dodecenyl acetate will *T. ni* males enter traps baited with this chemical (*11*). Few males are captured in traps releasing the pheromone at rates tenfold above or below the optimum. We believe that the optimum release rate may be that which causes the pheromone concentration near the entrance of the trap to be similar to the concentration found in the immediate vicinity of a free-living, pheromone-releasing female. We further propose that a male encountering this critical concentration stops its long-distance pheromone-orientation behavior and engages in a short-range "searching" behavior, causing it to enter the trap. If these hypotheses are correct, then *T. ni* males responding to the low quantity of *cis*-7-dodecenyl acetate released from *A. californica* females would not reach their critical concentration and thus would neither terminate their long-distance orientation behavior nor enter traps. On the other hand, *A. californica* males approaching a receptive *T. ni* female would presumably reach this concentration, and thus terminate their long-distance orientation behavior, at some point downwind from the female.

It can be seen that reproductive isolation based on prevention of males orienting to the females of the related species is not complete (Table 1). Essentially no *A. californica* males were captured in traps baited with *T. ni* females. On the other hand, a fairly large number of *T. ni* males was captured in the traps baited with females of *A. californica*. Also, at certain intermediate evaporation rates of *cis*-7-dodecenyl acetate, males of both species were captured. However, previous laboratory research (*8*) has shown that an additional mechanism can operate at very close range, causing the female to reject copulation attempts made by males of the wrong species.

Table 1. Capture of males in traps baited with ten virgin noctuid females.

| Bait species | No. of males captured per trap* | |
|---|---|---|
| | *T. ni* | *A. californica* |
| *T. ni* | 1861 | 1 |
| *A. californica* | 37 | 79 |

* Based on 30 trapping nights.

R. S. KAAE*

H. H. SHOREY, LYLE K. GASTON

*Division of Toxicology and Physiology, Department of Entomology, University of California, Riverside 92502*

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6. Near identical retention times for the biologically active compound in extracts from female pheromone glands of *T. ni* versus *A. californica* were recorded with a flame ionization detector after gas-liquid chromatographic separation on each of three different columns (Carbowax 20 M, neopentylglycol adipate, and SF 96). Based on the previous identified structure of *T. ni* pheromone, these data limit the structure of *A. californica* phermone to several closely related straight chain 12-carbon monounsaturated acetates. T. L. Payne, H. H. Shorey, L. K. Gaston (*Ann. Entomol. Soc. Amer.*, in press) obtained electroantennograms (EAG) from *A. californica* and *T. ni* in response to *cis*-7-dodecenyl acetate and three closely related compounds (*cis*-$\Delta x$-dodecenyl acetate, $x = 6$, 8, and 9). Significant EAG responses were obtained with both *T. ni* and *A. californica* males for all compounds. However, from 100- to 10,000-fold more (compared to *cis*-7-dodecenyl acetate) of each compound was required to obtain the response. In addition, *trans*-7-dodecenyl acetate does not attract males of either species at any of several release rates that we have tested in the field.
7. Double-cone traps [R. K. Sharma, H. H. Shorey, L. K. Gaston, *J. Econ. Entomol.* 64, 361 (1971)] were baited with ten virgin females of *T. ni* or *A. californica*. Based on earlier experimentation with *T. ni* [R. S. Kaae and H. H. Shorey, *Ann. Entomol. Soc. Amer.* 65, 436 (1972)], we estimate that no more than two or three of these females were releasing pheromone at any one time.
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9. The construction and calibration of the evaporators is described by H. H. Shorey, R. S. Kaae, L. K. Gaston, J. R. McLaughlin, *Environ. Entomol.* 1, 641 (1972). Five evaporators were designed to release *cis*-7-dodecenyl acetate at 1, 3, 10, 30, and 100 ng/min under constant laboratory conditions of 18°C and 0.4 m/sec airflow. Temperatures and air velocities in the field were lower than these values during the conduct of the experiment, and actual release rates probably varied between one-tenth and one-half of the above-stated rates. Therefore, release rates in Fig. 1 are given as relative, rather than absolute, values.
10. The *cis*-7-dodecenyl acetate used gave only one peak on gas-liquid chromatography (lower limit of detection of other compounds was 0.5 percent), indicating that the material was at least 99.5 percent 7-dodecenyl acetate. An upper limit of 10 percent for the *trans* isomer was estimated by nuclear magnetic resonance ($\delta$ and $J$ are slightly different for the *cis* and *trans* olefinic protons).
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12. This is paper No. 36 of a series entitled "Sex pheromones of Lepidoptera." We thank B. Wilk and S. U. McFarland for their assistance. This research was supported in part by a grant from the Rockefeller Foundation.

* Present address: Department of Plant and Soil Science, California State Polytechnic University at Pomona.

11 October 1972

## Leaching: Use of a Thermophilic and Chemoautotrophic Microbe

*Abstract.* *A chemoautotrophic, thermophilic, and acidophilic microorganism capable of oxidizing reduced sulfur and iron compounds and leaching concentrates of molybdenite and chalcopyrite at 60°C has been characterized by transmission and scanning electron microscopy. This constitutes the first direct observations of microorganisms on ore fines.*

Field studies indicate that temperatures within low-grade copper ore dumps may reach 80°C (*1*). These elevated temperatures undoubtedly inhibit the leaching activity of strains of sulfur- and iron-oxidizing bacteria whose optimum temperature range is 25° to 45°C (*2*, *3*). Thermophilic organisms have not previously been considered in leaching activities. We therefore report the characterization of a chemoautotrophic, thermophilic, and acidophilic microorganism, possibly related to *Sulfolobus* (*4*), with the capa-

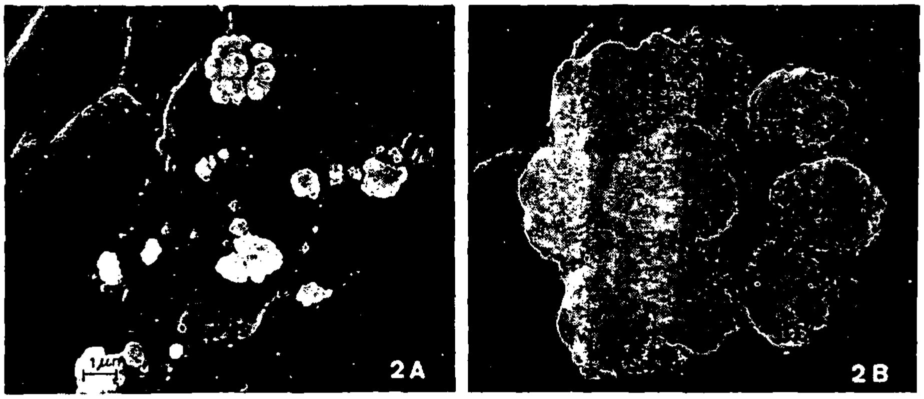

Fig. 1 (left). Transmission electron micrograph of a thin section of the chemoautotrophic isolate showing the intracellular body (*IB*). Fig. 2 (below). Scanning electron micrographs of the isolate on molybdenite fines: (A) localized segregation of isolate clusters; (B) magnified view of a single cluster in (A).

bility of oxidizing reduced sulfur and iron compounds between 45° and 70°C. The information presented here indicates that this organism may be useful as a biological leaching agent in regions of high temperature within dumps.

The organism was isolated by J. A. Brierley (*5*) from an acid, hot spring in Yellowstone National Park and recently has been described in more detail (*6*). Morphologically, the isolate is pleomorphic, varying in diameter from 1.0 to 1.5 μm. A rigid cell wall structure, typical of most bacteria, is not present. A membrane surrounds the cell; an amorphous layer is evident outside the membrane. The isolate possesses a dense, intracellular body of unknown composition and function (Fig. 1) (*7*).

The chemoautotrophic isolate grows aerobically. The source of energy can be either elemental sulfur or ferrous iron in a basal salt medium (*3*) containing 0.02 percent yeast extract. After 2 weeks of incubation at 60°C, the inoculated medium, containing elemental sulfur, was turbid and the total acidity had increased by 0.54 meq. Incubation of the isolate for 2 weeks in a basal salt medium containing 2.0 mg of ferrous iron per milliliter of solution resulted in the oxidation of 1.9 mg of the ion per milliliter of the solution and microscopically visible growth. Growth also occurs on either sulfur or iron in the absence of yeast extract; however, the growth is much slower.

Leaching studies showed that 98.5 percent molybdenite ($MoS_2$) with a particle size of 12 to 62 μm is also oxidized by the thermophilic isolate at 60°C. Molybdenum is solubilized at a rate of 6.6 mg liter$^{-1}$ day$^{-1}$ over a 30-day period for a yield of 3.3 percent in 100 ml of the inoculated acid medium, *p*H 2.5 (*3*) when shake flask extractions are used. When 0.02 percent yeast extract is added to the medium, the rate of dissolution is increased to 16.6 mg liter$^{-1}$ day$^{-1}$ (yield after 30 days, 8.3 percent); the addition of both 0.02 percent yeast extract and 1 percent ferrous sulfate increases the rate of dissolution to 26.5 mg liter$^{-1}$ day$^{-1}$ (yield after 30 days, 13.3 percent). In all cases the solubilization of molybdenum in uninoculated controls proceeded at a rate of 0.2 mg liter$^{-1}$ day$^{-1}$ over a 30-day period for a yield of 0.1 percent (*8*). Microscopic observation of inoculated flasks, containing 800 parts per million (ppm) of solubilized molybdenum, after 30 days of incubation, revealed the presence of a dense population of the organism; continuation of the leaching for another 30 days yielded further solubilization of the molybdenum, but at a decreased rate. A manometric measurement of respiration indicated that sulfur oxidation is not inhibited for 1 hour by the addition of 2000 ppm of molybdenum (*9*); however, growth of the isolate on sulfur is slowed by the addition of 1000 ppm of molybdenum (*10*). The tolerance to high concentrations of soluble molybdenum is unique to this organism—other investigators have reported a maximum tolerance of chemoautotrophic bacteria to molybdenum of about 5 to 90 ppm (*11*). Thus, where molybdenum is present, the use of other chemoautotrophic bacteria is necessarily limited.

Although there have been several attempts to investigate the disposition and distribution of bacteria on ore fines by replication electron microscopy (*12*), direct observations have not been made. Figure 2 illustrates several examples of direct observations of the thermophilic isolate on molybdenite fines in which the scanning electron microscope was used in the secondary emission mode (*13*). In Fig. 2A it may be observed that morphologically the isolate consists of clustered (colony) structures, each with an overall shape compatible with that shown in Fig. 1. Several observations of individual isolate clusters similar to that shown in Fig. 2B were made at various imaging angles in order to study the isolate-mineral interface. Apparently the isolate in many cases attaches to the mineral surface. In addition, nondispersive x-ray analysis of isolated organisms showed them to contain trace amounts of copper, detectable above the background in characteristic x-ray maps.

Preliminary evidence indicates that the isolate also oxidizes a chalcopyrite concentrate under the same conditions that it leaches a molybdenite concentrate. The copper is solubilized at a rate of 10 to 16 mg liter$^{-1}$ day$^{-1}$ from a chalcopyrite concentrate (27.6 percent copper; particle size; 74 to 105 μm) over a 30-day period in an inoculated acid medium, *p*H 2.5 (*3*). The solubilization of copper in uninoculated flasks occurs at a rate of 1 to 1.8 mg liter$^{-1}$ day$^{-1}$ over a 30-day period.

These properties, coupled with the isolate's ability to tolerate high concentrations of molybdenum, indicate that it may be a useful agent for leaching in dump regions where temperatures exceed the optimum (25° to 45°C) for most chemoautotrophic microorganisms.

CORALE L. BRIERLEY
*New Mexico State Bureau of Mines and Mineral Resources, Socorro 87801*
L. E. MURR
*Department of Metallurgical and Materials Engineering, New Mexico Institute of Mining and Technology, Socorro 87801*

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7. Thin sections were prepared as follows: the cells were cultured in basal salt medium with 0.02 percent yeast extract and colloidal sulfur; thin sections fixed with glutaraldehyde and osmium tetroxide were examined in an electron microscope (Hitachi HU-11B).
8. The intial concentration of molybdenum in all cases was 6000 ppm.
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13. The samples were prepared for scanning electron microscopy as follows: molybdenite fines from inoculated acid media placed on aluminum specimen stubs were air-dried and metallized with a mixture of gold and palladium (60 : 40) in vacuum to a thickness of roughly 150 A. Observations were made in a scanning electron microscope (Hitachi HHS-2R) operated at 20 kv and in a scanning electron microscope (Cambridge Stereoscan Mark II) fitted with a nondispersive x-ray analyzer (Princeton Gamma-Tech) operated at an accelerating potential of 20 kv. L. E. Murr, *Electron Optical Applications in Materials Science* (McGraw-Hill, New York, 1970).
14. Research at the New Mexico Bureau of Mines and Mineral Resources was supported in part by U.S. Bureau of Mines grant GO122123. We thank Dr. J. V. Scaletti, University of New Mexico Medical School, for preparing the transmission electron micrograph.

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# Lack of Tolerance to $\Delta^9$-Tetrahydrocannabinol in Chimpanzees

Abstract. *Five chimpanzees were given $\Delta^9$-tetrahydrocannabinol ($\Delta^9$THC): 1.0 milligram per kilogram of body weight for 21 days and 4.0 milligrams per kilogram of body weight for 42 days. Although accuracy and speed of performance on a delayed matching-to-sample task were significantly affected by both doses, tolerance to $\Delta^9$THC did not develop. No long-term behavioral effects of $\Delta^9$THC were observed after termination of the drug regimens.*

Although the short-term (acute) effects of marihuana have been determined, the long-term effects of marihuana have not been well defined (*1*). For example, the issue of whether marihuana tolerance develops in man has not been settled experimentally, and some discrepancy still exists regarding the effects of repeated marihuana administrations in nonhuman species. In those animal experiments where the effects of marihuana on unlearned behavior or on learned shock-avoidance behavior have been studied, no consensus as to the occurrence of marihuana tolerance has been reached (*2*, *3*).

In contrast, the development of a marked tolerance to the effects of marihuana on simple behavioral tasks maintained by appetitive rewards has been consistently demonstrated in a wide range of animal species (*2*, *4*, *5*). Most of these behavioral tasks have involved situations of the "go, no-go" type in which delivery of reward is made dependent on the repeated occurrence, as compared to the nonoccurrence, of a simple learned response. We now report a lack of tolerance in the chimpanzee to the behavioral effects of $\Delta^9$-*trans*-tetrahydrocannabinol ($\Delta^9$THC), the major active constituent of marihuana, on a conditional discrimination task which makes reward dependent on correct choice responses.

The effects of repeated $\Delta^9$THC administrations on short-term memory have not been studied in animals or man. We chose the delayed matching to sample task for our chimpanzee experiments since this task has proved useful for the study of conceptual processes and short-term memory in nonhuman primates, as well as for the study of short-term effects of psychotropic drugs (*6*). In addition, both the delayed matching to sample performance of nonhuman primates and human short-term memory have been shown to be impaired by $\Delta^9$THC (*7*, *8*).

Each of the three male and two female adult chimpanzees had extensive behavioral and $\Delta^9$THC histories (*5*, *8–10*) but had not been given drugs for approximately 3 weeks prior to the experiments reported below. The indoor area of the chimpanzee's living cage was modified to hold a stimulus-response panel containing three horizontally aligned choice-response keys and a sample response key located above the middle choice key. A delayed matching-to-sample trial was initiated by illuminating the sample response key with one of three white geometric forms (Δ, ×, or –) or one of three colors (green, red, or blue). The chimpanzee was required to make ten consecutive responses to the sample key after which the sample stimulus was turned off and a 20-second delay period was initiated. After the delay period, each of the three choice keys was simultaneously illuminated with a different choice stimulus. Although the positions of the choice stimuli were determined randomly, the choice stimuli for a given trial were from the same stimulus dimension as the sample stimulus for that trial. A response to the choice stimulus, which was the same as the previously presented sample stimulus, produced a reward consisting of a 1-g banana pellet (Ciba) and terminated the trial. A response to either of the two incorrect choice stimuli simply terminated the trial. Successive trials were separated by 15 seconds. Each daily experimental session consisted of 100 trials or 85 minutes, whichever came first.

After the behavior of individual chimpanzees appeared stable over seven consecutive sessions, the chimpanzees were given six control sessions in which the drug was not given, 21 consecutive $\Delta^9$THC sessions at 1.0 mg/kg, and 21 recovery sessions in which no drug was given. Finally, 42 consecutive $\Delta^9$THC sessions at 4.0 mg/kg were followed by 33 recovery sessions during which no drug was given. The $\Delta^9$THC (*11*) was orally administered 2.5 hours before each drug session in a vehicle consisting of water, corn syrup, and orange extract. The drug vehicle alone was administered 2.5 hours before each session in which no drug was given.

Since no systematic differences were obtained between color and form stimuli, the percentage of correct matching responses was plotted as an average for color and form trials (Fig. 1). Separate *t*-tests indicated that the initial $\Delta^9$THC doses of 1.0 mg/kg and 4.0 mg/kg produced significant ($P < .01$) decreases in matching accuracy as compared to the immediately preceding sessions without the drug. The magnitudes of these performance decrements were apparently not dose related. More importantly, no significant decrease in the drug effect on matching accuracy was observed during either long-term drug regimen. Recovery after the drug was more rapid after termination of the 1.0 mg/kg dose. In fact, a significant ($P < .05$) decrease in matching