lead compounds presented by Professor Forward and his colleagues at the International Mineral Processing Congress, I.M.M., London, 1960. In this discussion, the authors refer to the "oxygen carrier" nature of iron salts to explain their catalytic effects. Is it possible that a series of nitrogen species of which NH_3 and NH_4^+ represent the lowest oxidation state; i.e. NH_4^+, NO_2^-, NO_3^-, may also act as oxygen carriers and account for the difference between NH_3 and NH_4^+, since these would yield NO_2^- at different rates on oxidation by the same partial pressure of oxygen.

A. Vizsolyi, H. Veltman, and F. A. Forward: In oxidizing galena and other sulphides such as sphalerite, chalcopyrite or pentlandite in solutions containing free NH_3 we have never detected the formation of NO_2^- or NO_3^- although sulphamates containing NH_2 are produced consistently. In view of the irreversibility of the oxidation of nitrogen-containing species under the conditions existing it is thought unlikely that those mentioned by Dr. Leja are in effect "oxygen carriers." The sulphamate reaction may however play some role, although not as an oxygen carrier.

The Gaseous Reduction of Metals from Aqueous Solutions

B. MEDDINGS* and V. N. MACKIW†

Abstract

This paper deals with the use of gases to reduce aqueous solutions of metal salts. While the main emphasis is on systems where the reduced state is the metallic element the scope of the paper also embraces those systems where gaseous reduction produces a precipitate of the metal in a lowered valency state.

The physical-chemical parameters controlling the gaseous reduction of such dissolved metal species, thermodynamic feasibility, thermodynamic equilibria, reaction kinetics, reaction mechanism and catalysis, are discussed within a broad general framework. More detailed, specific, discussion is given for the hydrogen reduction of solutions of metals such as cobalt, copper, molybdenum, nickel and tungsten.

The state of knowledge of the subject is reviewed and particular areas where future research work would probably be most rewarding are indicated and discussed.

INTRODUCTION

Until recent times metals have been obtained either by direct mining or by pyrometallurgical processes. It is only comparatively recently that metal recovery processes based upon the properties of metal ions in aqueous solution have achieved commercial importance. The first of these processes was electrolysis and this was introduced as a final purification step appended to an old-established pyrometallurgical operation. During the last decade advances in the hydrometallurgical industry have been made by which the metals are brought into solution, separated, and precipitated out of solution by more extensive and specific utilization of the chemical properties of the metal ions in

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aqueous solutions. In general these reactions have been carried out in aqueous solutions and temperatures above 100°C have been used to achieve useful reaction rates, as a result pressurized equipment has been mandatory.

The details of the leaching processes by which useful metals contained in ores are brought into solution and the solutions purified have been well described by Mackiw and others.[47,17,23]

The main emphasis of this paper will be on the use of gaseous reducing agents to reduce aqueous solutions of metal ions to precipitate metallic powder. However, some consideration will also be given to those cases where gaseous reducing agents cause the precipitation of a chemical species of reduced valency which can then be converted to metal in no more than one further processing step.

These reactions will be considered in terms of their thermodynamic probabilities, their kinetic characteristics, their feasibility on a commercial scale, and the probable extension of such hydrometallurgical operations.

THERMODYNAMICS

A study of the thermodynamics of a reaction system can decide how *far* the reaction may proceed, it cannot decide how *fast* the reaction will proceed. Such a statement is a truism but it is still worth emphasizing that although thermodynamics may indicate that gas A can reduce Me^{n+} to metallic Me it does not necessarily follow that the reduction can be made to proceed at a useful rate under available conditions.

The Equilibrium Constant

The extent to which a reaction such as

$$A + B \rightarrow C + D \tag{2}$$

will proceed is given by the equilibrium constant K which is defined as

$$K = \frac{[C]\,[D]}{[A]\,[B]} \tag{3}$$

Very often the square bracket terms are equated to the analytical concentrations of the various species but from the thermodynamic viewpoint, with which we are now concerned, the square brackets refer to the effective chemical concentrations, i.e. the activities of the species. Equation (3) should therefore be re-written as

$$K = \frac{a_C a_D}{a_A a_B} \tag{3a}$$

where a_C signifies the activity of C. The thermodynamic equilibrium constant K is related to the standard free energy change, $\Delta F°$, of the reaction by the van't Hoff isochore

$$\Delta F° = -RT \ln K \tag{4}$$

The standard free energy change, $\Delta F°$, for the reaction can also be expressed in another form. If the reaction in (2) is considered to be the basis of a perfectly reversible electrochemical cell then the maximum net work obtainable from it is n.E.F. where n is the number of Faradays passing through the cell to complete the reaction, E is the potential of the cell in volts and F is the Faraday (96,487 coulombs). This maximum net work must equal the standard free energy change of the reaction, hence

$$-\Delta F° = n.F.E. \tag{5}$$

Thus although the extent to which a reaction will proceed is given most directly by the equilibrium constant K there are three equivalent ways in which this tendency to completion can be assigned a numerical value, these are interrelated by

$$\Delta F° = -n.F.E. = -RT \ln K$$

Care must be taken to express the constants F and R in compatible units. If R is expressed as 1.987 cal. deg^{-1}. $mole^{-1}$, as is usual, then F which is defined as 96,487 abs. coul. g. $equiv.^{-1}$ must be expressed as 96,487 × 0.2390 since one international volt-coulomb is equivalent to 0.2390 of a standard calorie. Using compatible units,

$$\Delta F° = -n.E.\ 23{,}060 = -2.303\ RT \log_{10} K \tag{6}$$

The interdependence of these three expressions of the thermodynamic probability of a reaction has also been given by Schaufelberger.[1]

The Use of Electrode Potentials

It will be seen later that the most widely used reducing gas for precipitating metals from solutions is hydrogen. For this reason most attention will be given to the thermodynamics of the general reaction

$$\mathrm{Me}^{n+} + \frac{n}{2}\,\mathrm{H}_2 \rightarrow \mathrm{Me} + n.\mathrm{H}^+ \qquad (7)$$

The equilibrium position of this reaction could be calculated from use of the standard Gibbs Free Energy values but it is found to be more convenient to use electrode potentials. In any case much of the tabulated free energy data has been calculated from electrochemical potentials.

The reaction described by equation (7) can be viewed as two opposing reactions, each with their own potential,

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + n.\mathrm{e} \qquad \text{Potential} = E_{\mathrm{Me}} \qquad (7a)$$

and

$$\mathrm{H}_2 \rightarrow 2\,\mathrm{H}^+ + 2\mathrm{e} \qquad \text{Potential} = E_{\mathrm{H}_2} \qquad (7b)$$

Clearly if E_{Me} exceeds E_{H_2} then the metal will liberate hydrogen from water and pass into solution but if E_{H_2} exceeds E_{Me} the hydrogen will reverse reaction (7a) and precipitate metal Me from solution. The potentials denoted by E_{Me} and E_{H_2} are single electrode potentials and are defined in the usual electrochemical nomenclature by,

$$E_{\mathrm{H}_2} = E^\circ_{\mathrm{H}_2} - \frac{2.303\ RT}{F} \cdot \log_{10} a_{\mathrm{H}^+} \qquad (8a)$$

and

$$E_{\mathrm{Me}} = E^\circ_{\mathrm{Me}} - \frac{2.303\ RT}{n.F} \cdot \log_{10} a_{\mathrm{Me}^{n+}} \qquad (8b)$$

(i) The Hydrogen Electrode Potential

The potential of the hydrogen electrode is governed by the concentration of hydrogen ions and hydrogen molecules in solution in contact with the electrode and is therefore a function of both pH and hydrogen gas pressure. Equation (8a) should therefore be re-written as

$$E_{\mathrm{H}_2} = E^\circ_{\mathrm{H}_2} - \frac{2.303\ RT}{F} \cdot \log_{10} a_{\mathrm{H}^+} + \frac{2.303\ RT}{2F} \cdot \log_{10} P_{\mathrm{H}_2}{}^* \qquad (8c)$$

where $P_{\mathrm{H}_2}{}^*$ is the fugacity of the hydrogen. However, between 1 and 100 atmospheres the effect of using fugacity in place of hydrogen partial pressure is negligible, at 100 Ats hydrogen pressure the fugacity is 106.1 atmospheres[2] and this only alters the last term in (8c) by 1%. By definition pH is defined as $-\log_{10} a_{\mathrm{H}^+}$ and since the standard electrode potential of hydrogen, $E^\circ_{\mathrm{H}_2}$ is defined as zero, equation (8c) reduces to

$$E_{\mathrm{H}_2} = 0.05916\ \mathrm{pH} + 0.02958 \log_{10} P_{\mathrm{H}_2} \qquad (8d)$$

at 25°C where P_{H_2} is the partial pressure of hydrogen expressed in atmospheres.

(ii) The Metal Electrode Potential

The single electrode potential for a metal ion in aqueous solution is controlled by the standard electrode potential for that ion and the activity of that ion in the solution

$$E_{\mathrm{Me}^{n+}} = E^\circ_{\mathrm{Me}^{n+}} - \frac{2.303\ RT}{n.F} \cdot \log_{10} a_{\mathrm{Me}^{n+}}$$

By definition

$$a_{\mathrm{Me}^{n+}} = f_{\mathrm{Me}^{n+}} \cdot [\mathrm{Me}^{n+}]$$

where $f_{\mathrm{Me}^{n+}}$ is the activity coefficient of the ion Me^{n+} and $[\mathrm{Me}^{n+}]$ is the analytical concentration of the ion. Hence at 25°C.

$$E_{\mathrm{Me}^{n+}} = E^\circ_{\mathrm{Me}^{n+}} - \frac{0.05916}{n} \cdot \log_{10} [\mathrm{Me}^{n+}] - \frac{0.05916}{n} \cdot \log_{10} f_{\mathrm{Me}^{n+}} \ldots. \qquad (8d)$$

At low concentrations the activity coefficient approaches unity and the last term in (8d) vanishes. But in 1 molal solutions, which are commonly used in hydrometallurgical operations, it is seldom possible to use $E_{\mathrm{Me}^{n+}} = E^\circ_{\mathrm{Me}^{n+}}$ since although the $\log_{10} [\mathrm{Me}^{n+}]$ term in (8d) becomes zero under these conditions the activity coefficient can be so much less than unity that the last term in (8d) becomes appreciable. This is shown by Table I which lists the variation of $f_{\mathrm{Me}^{n+}}$ with $[\mathrm{Me}^{n+}]$ for some typical divalent metal sulphates and chlorides, the values being taken from Latimer.[4]

Thus if the activity coefficient of a 1 molal solution of divalent metal sulphate is taken to be 0.05 one obtains

$$E_{\mathrm{Me}^{++}} = E^\circ_{\mathrm{Me}} - \frac{2.303\ RT}{2} \cdot \log_{10} 0.05$$

which at 25°C gives

$$E_{\mathrm{Me}^{++}} = E^\circ_{\mathrm{Me}} + 0.04 \qquad (9)$$

The value of $E_{Me^{n+}}$ clearly depends upon the value taken for the standard electrode potential and in all that follows the values of $E^{\circ}_{Me^{n+}}$ will be those quoted by Latimer[4] except for those of Ni^{++} and Co^{++}. The standard electrode potentials used by Schaufelberger[1] were also those of Latimer except for Ni^{++} and Co^{++}. But whereas Schaufelberger[1] used the values of Haring[5,6] for Ni^{++} and Co^{++} the present discussion uses the values for Ni^{++} and Co^{++} taken from the National Bureau of Standards circular "Selected Values of Chemical Thermodynamic Properties." The values of these potentials for comparison are:

TABLE I

Activity Coefficients in Some Metal Salt Solutions

Salt	Activity coefficients in solutions of molality									
	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0
$MgSO_4$	—	—	—	0.40	0.32	0.22	0.18	0.13	0.088	0.064
$NiSO_4$	—	—	—	—	—	—	0.18	0.13	0.075	0.051
$CuSO_4$	0.74	—	0.53	0.41	0.31	0.21	0.16	0.11	0.068	0.047
$ZnSO_4$	0.70	0.61	0.48	0.39	—	—	0.15	0.11	0.065	0.045
$MgCl_2$	—	—	—	—	—	—	0.56	0.53	0.52	0.62
$FeCl_2$	0.89	0.86	0.80	0.75	0.70	0.62	0.58	0.55	0.59	0.67
$CuCl_2$	0.89	0.85	0.78	0.72	0.66	0.58	0.52	0.47	0.42	0.43
$ZnCl_2$	0.88	0.84	0.77	0.71	0.64	0.56	0.50	0.45	0.38	0.33

	Ni/Ni^{++}	Co/Co^{++}
Haring	0.231 volt.	0.278 volt.
N.B.S.	0.241	0.267
Latimer	0.250	0.277

(iii) The Use of E_{H_2} and $E_{Me^{n+}}$ Potentials

In Fig. 1 the hydrogen potential at 25°C and 1 and 100 Atmospheres is plotted against pH while the potential ordinates are also used to plot the values of $E_{Me^{n+}}$ in 1.0 and 1.0×10^{-3} molal solutions. This figure is essentially the same as that used by Schaufelberger[1] but differs from it in that the metal potential values have been calculated taking activities into account. Because these corrections have a much larger effect in 1.0 molal solutions the slopes of the $E_{Me^{n+}}$ lines from 1.0 to 1.0×10^{-3} molal are much flatter than indicated by Schaufelberger.

It is thermodynamically possible to reduce a metal from solution by hydrogen if the E_{H_2} line in Fig. 1 lies above the $E_{Me^{n+}}$ line. Thus it is clearly possible to reduce cupric ions to copper at all normal pH values but to reduce cobaltous ions to cobalt it is necessary to maintain a pH above 5.6 using 1 atmosphere of hydrogen or above pH 4.4 with 100 atmospheres of hydrogen. It should be noted that Fig. 1 ignores effects such as hydrogen overvoltage. Although the hydrogen overvoltage will have a definite influence on reduction by hydrogen in heterogeneous systems the available information is too sparse for a full thermodynamic treatment at present.

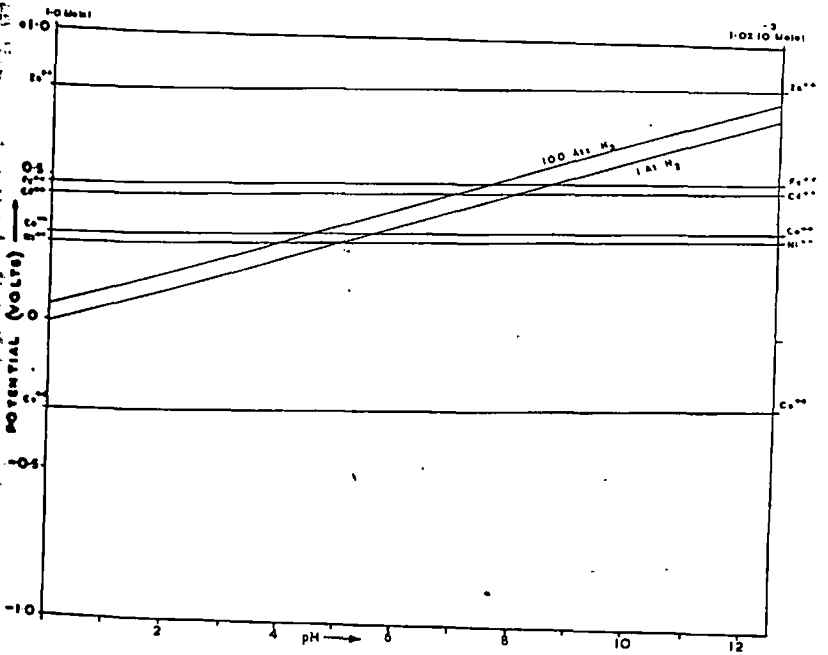

Fig. 1. Hydrogen and metal electrode potentials.

From Fig. 1 and Eq. (8d) it is possible to calculate the hydrogen pressure necessary to reduce a given metal at a given pH. Thus if the potentials required to reduce Zn^{++}, Fe^{++} and Cd^{++} are taken to be 0.83, 0.50 and 0.47 volts respectively then it follows that these are 0.47, 0.14 and 0.11 volts above the hydrogen potential at pH 6 and 1 atmosphere at 25°C. This difference in potential can be made up by increasing the hydrogen pressure but the pressure required is given by

$$\Delta E = 0.02958 \log_{10} P_{H_2}$$

Hence to reduce Zn^{++} at pH = 6 where $\Delta E = 0.47$, $\log_{10} P_{H_2} = 15.9$, a hydrogen partial pressure of 8×10^{15} atmospheres would be required.

The corresponding pressures for reduction of Fe^{++} and Cd^{++} at a pH of 6 would be 5.4×10^4 atmospheres and 5.2×10^3 atmospheres. If the same reductions were attempted at pH = 10 it would be found that $E_{H_2} > E_{Fe^{++}}$ or $E_{Cd^{++}}$ but that $E_{Zn^{++}}$ still exceeded E_{H_2} by 0.283 volts which corresponds to a required hydrogen pressure of 1.1×10^9 atmospheres. Clearly it is most improbable that Zn can ever be reduced from aqueous solutions by hydrogen. It may be possible to reduce ferrous solutions with hydrogen above pH 8.5 but it must be emphasized that this is more of a thermodynamic possibility than a practical chemical possibility. At pH 8.5 ferrous ions are unstable with respect to hydrolysis and it will probably not be possible to reduce such a system even by attempting to reduce the small amount of ferrous ion in equilibrium with the hydroxide and so displacing the equilibrium. When the ferrous ion concentration becomes very low the potential of the Fe/Fe^{++} couple is rapidly raised by the term $-0.02958 \log_{10} [Fe^{++}]$ and this could only be counterbalanced by a corresponding increase in the pressure term $+0.02958 \log_{10} P_{H_2}$ for the hydrogen potential. The solubility product of ferrous hydroxide is reported to be 1.64×10^{-14} and hence at pH 9 (pOH = 5) the ferrous ion concentration must be about 10^{-9} molar, this would increase the metal potential to the point where about 10^5–10^6 atmospheres of hydrogen would be required for reduction.

From a combination of Fig. 1 and the expressions for $E_{Me^{n+}}$ and E_{H_2}

$$E_{Me^{n+}} = E^{\circ}_{Me} - \frac{0.05916}{n} \log_{10} a_{Me^{n+}}$$

$$E_{H_2} = 0.05916 \text{ pH} + 0.02958 \log_{10} P_{H_2}$$

it is possible to derive a great deal of information about the thermodynamic possibility of various reduction reactions.

The pH at which reduction is carried out determines the minimum concentration of metallic ions which can be obtained since at equilibrium E_{H_2} must equal $E_{Me^{n+}}$.

Thus at 1 atmosphere H_2 and 25°C

$$E_{H_2} = 0.05916 \text{ pH} = E^{\circ}_{Me} - 0.05916 \log_{10} a_{Me^{n+}} = E_{Me^{n+}}$$

Since we are now considering equilibria in which the metal ion concentration is low we may replace $a_{Me^{n+}}$ by $[Me^{n+}]$, rearrangement then gives,

$$-\log_{10} [Me^{n+}] = n.\ \text{pH} - \frac{n.E^{\circ}_{Me^{n+}}}{0.05916} \qquad (11)$$

This identity is also given by Dobrochotov[8] who plots $\log_{10} [Me^{n+}]$ against pH down to values of $\log_{10} [Me^{n+}] = -14$. However in commercial hydrometallurgy metal concentrations below 10^{-2} molar are not of significant interest and hence it is equally useful to solve (11) for $\log_{10} [Me^{n+}] = -2$ and tabulate the pH values so obtained. These are given in Table II. From Table II it is obvious that if a 1.0 molal solution is to be reduced to 10^{-2} molal then precautions must be taken to prevent the n moles of H^+ produced from decreasing the pH below the equilibrium values shown in Table II. In general it is clear that metals with negative E° values can be reduced without such precautions but that metals with positive E° values will require the addition of neutralizing agents to maintain the pH values above the equilibrium value. This requirement becomes increasingly severe as E° increases and once again it seems that the reduction of Zn^{++} to Zn by hydrogen from aqueous solutions is a practical impossibility. From the practical viewpoint, solutions of uncomplexed Zn^{++} or Fe^{++} ions in solutions of pH greater than 6–7 are not possible and the mathematical solution of (11) does not correspond to chemical reality.

TABLE II

Equilibrium pH Values at $Me^{n+} = 10^{-2}$ Molar

Ion	E°	pH
Zn^{++}	0.762	13.9
Fe^{++}	0.440	8.5
Cd^{++}	0.403	7.8
Co^{++}	0.267	5.5
Ni^{++}	0.241	5.1
Cu^{++}	−0.337	−4.7
Ag^{++}	−0.799	−11.5

It is also possible to calculate how far hydrogen will reduce a solution of a metal salt.

Consider the following reaction of 25°C and a constant hydrogen pressure of 1 atmosphere:

$$Me^{n+} + \frac{n}{2} H_2 \rightarrow Me + nH^+$$

Let the fraction of Me^{n+} reduced be x, then

$$Me^{n+} + \frac{n}{2} H_2 \rightarrow Me + n\,H^+$$

$$(1 - x) \rightarrow x + n \cdot x$$

Hence

$$E_{Me} = E^\circ_{Me} - \frac{0.05916}{n} \log_{10} [1 - x] \text{ (neglecting activity coefficients)}$$

and $E_{H_2} = -0.05916 \log_{10} (n \cdot x)$

and for equilibrium

$$E^\circ_{Me} - \frac{0.05916}{n} \cdot \log_{10} [1 - x] = 0.05916 \log_{10} nx \qquad (12)$$

Equation (12) can then be solved to give a quadratic in x from which x can be determined. Solution of (12) for Cu^{++} gives $x = 1$ which agrees with Fig. 1 and Table II. Solution for the case of Ni^{++} proceeds as follows:

$$E^\circ_{Me} = +0.241, n = 2$$

Hence

$$0.241 - 0.02958 \log_{10} (1 - x) = -0.05916 \log_{10} \cdot 2x$$

$$\therefore \quad \frac{0.241}{0.02958} = 8.15 = \log_{10} (1 - x) - 2 \log_{10} 2x$$

$$= \log_{10} \frac{(1 - x)}{4x^2} = \log_{10} P$$

$$\therefore \quad P = 10^8 \times 1.41 = \frac{1 - x}{4x^2}$$

$$\therefore \quad 5.64 \times 10^8 \cdot x^2 + x - 1 = 0, \quad \therefore x = 4.21 \times 10^{-5}$$

This value of x corresponds to a hydrogen ion concentration of 8.4×10^{-5} i.e. a pH of 4.075 and from Fig. 1 it will be seen that at this pH the hydrogen potential is 0.42 i.e. the same as E° for nickel. However, Schaufelberger and Roy[9] have shown that nickel can be reduced by hydrogen from acid-sulphate systems down to a pH of 2.75. This is very probably another result of the influence of activity coefficients, the activity coefficient of H_2SO_4 is markedly low, being only 0.54 in 0.01 molar solutions,[4] hence the production of H^+ ions by the reduction of Ni^{++} does not decrease the hydrogen potential by the amount indicated by (8d). It is of interest that Schaufelberger and Roy[1,9] also found that cobalt could be reduced down to a pH of 3.3. This difference between pH 2.75 and 3.3 corresponds to a difference in hydrogen potential, from Fig. 1, of 0.033 volt and this should then be equal to the difference between the E° values for nickel and cobalt. The N.B.S. values[10] used in this paper give a difference for $E^\circ_{Co} - E^\circ_{Ni}$ of 0.026 v, the values of Latimer[4] give a difference of 0.027 v while the values of Haring[5,6] give a difference of 0.048 v. Hence the results of Schaufelberger and Roy[9] seem to indicate some inaccuracy in the results of Haring, most probably in the value of E° for nickel.

It is clear from Fig. 1 that the driving force for reduction increases as the pH increases and on this basis the conditions for reduction become more favourable as the solution becomes more alkaline. However, above pH 7 the rate of hydrolysis of transition metal cations becomes appreciable and in order to retain homogeneous solutions it is necessary to complex these ions. But the potentials of the metal-bearing species in such complexed solutions are not those shown in Fig. 1, those were calculated on the basis of the bare metal cations, Me^{n+} (actually, hydrated Me^{n+}). As a result Fig. 1 must be modified to take account of the altered metal potentials arising from the use of complexing agents.

For metals such as cobalt, nickel, copper and zinc, the simplest method of both raising the pH and complexing the metal ions is the addition of ammonia which causes the formation of the metal ammines $[Me(NH_3)_x]^{++}$. This effect is best exemplified by the case of nickel.

The addition of ammonia to a solution of a nickel salt results in the sequential formation of ammines as follows:

$$Ni^{++} + NH_3 \rightleftharpoons [Ni(NH_3)]^{++}$$

$$[Ni(NH_3)]^{++} + NH_3 \rightleftharpoons [Ni(NH_3)_2]^{++}$$

. . . .

$$[Ni(NH_3)_5]^{++} + NH_3 \rightleftharpoons [Ni(NH_3)_6]^{++}$$

For each of these step-equilibria there is a corresponding equilibrium constant given by:

$$k = \frac{[Ni(NH_3)_x]^{++}}{[Ni(NH_3)_{x-1}]^{++} \cdot [NH_3]}$$

The standard electrode potential for the couple $Ni^\circ/[Ni(NH_3)_x]^{++}$ is given by the sum of the standard electrode potentials for the two separate stages

$$Ni^\circ \rightarrow Ni^{++} + 2 \cdot e$$

$$x \cdot NH_3 + Ni^{++} \rightarrow [Ni(NH_3)_x]^{++}$$

The first is merely the standard electrode potential for nickel while the other is the standard electrode potential for the complex $[Ni(NH_3)_x]^{++}$ and is derived from the equilibrium constant by the use of

$$n.\,E.\,23{,}060 = 2.303\ RT \log_{10} k$$

The equilibrium constant for the reaction

$$x \cdot NH_3 + Ni^{++} \rightleftharpoons [Ni(NH_3)_x]^{++}$$

is the product of all the equilibrium constants $k_1, k_2 \ldots k_x$.

The equilibrium constants for the Ni^{++}—NH_3 system have been determined by Bjerrum[11] and are given below together with the standard electrode potentials calculated for each ammine. To avoid confusion E°_{Me} will always refer to the standard electrode potential of the metal Me while ${}^xE^\circ_{Me}$ will refer to the standard electrode potential of the ammine $[Me(NH_3)_x]^{++}$.

TABLE III

Potentials for the Nickel Ammines

$E^\circ_{Ni} = 0.241$ v[10]

Equilibrium constant[11]	${}^xE^\circ_{Ni}$
$\log_{10} K_1 = 2.80$	${}^1E^\circ_{Ni} = 0.324$ v
$\log_{10} K_2 = 2.24$	${}^2E^\circ_{Ni} = 0.390$ v
$\log_{10} K_3 = 1.73$	${}^3E^\circ_{Ni} = 0.441$ v
$\log_{10} K_4 = 1.19$	${}^4E^\circ_{Ni} = 0.477$ v
$\log_{10} K_5 = 0.75$	${}^5E^\circ_{Ni} = 0.499$ v
$\log_{10} K_6 = 0.03$	${}^6E^\circ_{Ni} = 0.499$ v

For any given ammoniacal nickel solution, in which all the nickel ammine species are necessarily in equilibrium, there will be only one nickel ammine potential but the absolute values will depend upon both the absolute nickel concentration and the ratio of ammonia to nickel present in the solution.

The potential of a solution of any ammine, such as $[Ni(NH_3)_x]^{++}$, is given by

$${}^xE_{Ni} = {}^xE^\circ_{Ni} - 0.02958 \log_{10} \frac{a_{\text{ammine}}}{(a_{NH_3})^x}$$

Where a_{ammine} represents the activity of the ammine $[Ni(NH_3)_x]^{++}$ and a_{NH_3} represents the activity of ammonia in solution. Since no activity coefficient data are available for the nickel ammines the usual approximation of substituting concentrations for activities must be made and hence

$$E_{Ni} = E^\circ_{Ni} - 0.02958 \log_{10} \frac{[Ni(NH_3)_x]^{++}}{(a_{NH_3})^x}$$

Bjerrum[11] has determined the variation of concentration of each ammine species with the overall NH_3/Ni ratio and from these results it is possible to calculate the potential of a 1 molal nickel solution as ammonia is added. These results are tabulated in Table IV and shown in Fig. 2.

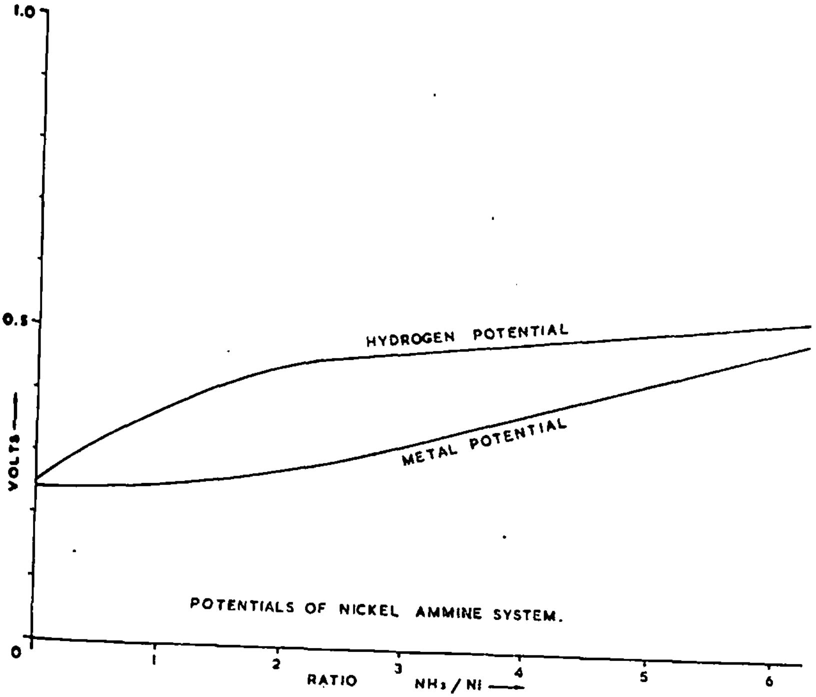

Fig. 2. Potential of Ni^{++}—NH_3 system.

TABLE IV

Concentrations and Potentials for the Ni/NH$_3$ System at 25°C
Total Nickel Concentration = 1.0 Molal

NH$_3$/Ni ratio	Ammine concentrations							potential
	Ni^{++}	Ni(NH$_3$)$^{++}$	Ni(NH$_3$)$_2^{++}$	Ni(NH$_3$)$_3^{++}$	Ni(NH$_3$)$_4^{++}$	Ni(NH$_3$)$_5^{++}$	Ni(NH$_3$)$_6^{++}$	$^{x}E_{Ni}$
0.064	0.940	0.059	0.001	0				0.242
0.184	0.826	0.165	0.009	0				0.243
0.50	0.573	0.361	0.063	0.003				0.248
1.12	0.233	0.466	0.256	0.043	0			0.260
1.50	0.166	0.393	0.372	0.109	0.009	0		0.269
1.99	0.040	0.251	0.437	0.234	0.036	0.002		0.282
2.52	0.010	0.115	0.375	0.379	0.110	0.012	0	0.300
2.97	0.002	0.047	0.258	0.438	0.215	0.038	0.001	0.318
3.56	0	0.011	0.114	0.379	0.362	0.126	0.008	0.346
4.01		0.003	0.050	0.270	0.418	0.235	0.025	0.370
4.73		0	0.009	0.108	0.356	0.429	0.099	0.411
5.02			0.003	0.057	0.278	0.494	0.168	0.460
6.22			0	0.006	0.092	0.461	0.440	0.497
15.91				0	0.001	0.085	0.913	0.517

Figure 2 also shows the hydrogen potential line, this being derived from the observed pH of ammoniacal nickel solutions. From this figure it is clear that the greatest driving force for the reduction occurs at about an ammonia/nickel ratio of 2.0–2.5. This is in agreement with the findings of Wadsworth[13] that in the hydrogen reduction of cobaltous sulphate solutions the maximum rate of reduction occurs at a ratio of NH$_3$/Co = 2, it is also the ratio of NH$_3$/Ni chosen in commercial hydrometallurgy.

Bjerrum has also determined the equilibrium constants for the Co^{++}–NH$_3$ system and the same calculations of the change of metal potential with ammonia/metal ratio have been carried out and tabulated in Tables V and VI. These results are very similar to those for the Ni^{++}–NH$_3$ system.

TABLE V

Potentials for Cobaltous Ammines
$E^{\circ}_{Co} = 0.267$ v[10]

Equilibrium constant	$^{x}E^{\circ}_{Co}$
$\log_{10} K_1 = 2.11$	$^{1}E^{\circ}_{Co} = 0.329$ v
$\log_{10} K_2 = 1.63$	$^{2}E^{\circ}_{Co} = 0.378$ v
$\log_{10} K_3 = 1.05$	$^{3}E^{\circ}_{Co} = 0.409$ v
$\log_{10} K_4 = 0.76$	$^{4}E^{\circ}_{Co} = 0.431$ v
$\log_{10} K_5 = 0.18$	$^{5}E^{\circ}_{Co} = 0.436$ v
$\log_{10} K_6 = -0.62$	$^{6}E^{\circ}_{Co} = 0.418$ v

In general the use of alkaline solutions for hydrogen reduction of metals from such solutions is thermodynamically justifiable only for those metals whose standard electrode potentials exceed 0.25 volt. The use of complexing agents to suppress hydrolysis above pH 7 or 8 can also prevent hydrogen reduction by increasing the metal potential to too high a level. Thus if ethylenediamminetetracetic was used to complex nickel salts in order to operate in alkaline solutions it is clear from the Ni^{++}–EDTA equilibrium constant, $\log_{10} K = 18.62$, that the metal potential would be increased to 0.77 v and this is only exceeded by the hydrogen potential at a pH of 12 and a pressure of 100 At.

Also, the corrosive conditions encountered when using hydrogen atmospheres under acid conditions in stainless steel equipment are severe enough that in commercial practice alkaline conditions are

TABLE VI

Concentrations and Potentials for the Co/NH₃ System at 25°C
Total Cobalt Concentration = 1.0 Molal

NH_3/Co ratio	Ammine concentration							Potential $-E_{Co}$
	Co^{++}	$Co(NH_3)^{++}$	$Co(NH_3)_2^{++}$	$Co(NH_3)_3^{++}$	$Co(NH_3)_4^{++}$	$Co(NH_3)_5^{++}$	$Co(NH_3)_6^{++}$	
0.124	0.882	0.113	0.005	0	0	0	0	0.269
0.509	0.575	0.350	0.071	0.004	0	0	0	0.275
0.901	0.345	0.444	0.189	0.021	0.001	0	0	0.280
1.520	0.126	0.380	0.380	0.100	0.014	0.0005	0	0.293
2.571	0.013	0.123	0.388	0.323	0.138	0.016	0	0.323
2.879	0.006	0.075	0.320	0.359	0.207	0.031	0.0007	0.333
3.643	0.001	0.017	0.148	0.332	0.381	0.115	0.0055	0.360
3.687	0.001	0.016	0.140	0.326	0.389	0.122	0.0061	0.362
4.429	0	0.003	0.044	0.198	0.455	0.274	0.026	0.394
4.998		0.001	0.016	0.114	0.414	0.395	0.060	0.419
5.288		0	0.010	0.084	0.377	0.445	0.083	0.430
5.663			0.005	0.057	0.326	0.494	0.118	0.445
7.042			0.001	0.016	0.180	0.544	0.260	0.488
8.428			0	0.006	0.106	0.505	0.383	0.519
10.466				0.002	0.056	0.428	0.514	0.550

always preferred. The solutions are usually made alkaline with ammonia. For metals with negative potentials, such as copper, the use of a base such as ammonia is solely to counteract the acid produced during reduction so as to maintain non-corrosive conditions within the equipment.

From the foregoing thermodynamic considerations it is clear that hydrogen reduction of metals such as Cu^{++}, Ni^{++} and Co^{++} should proceed at 25°C under a pressure of one atmosphere of hydrogen. That these reactions do not proceed under these conditions shows that thermodynamic arguments cannot indicate how fast these reactions will proceed and that kinetic factors must now be considered.

KINETICS

Consideration of the reaction

$$Me^{n+} + \frac{n}{2} H_2 \rightarrow Me + n\,H^+ \qquad (13)$$

enables the equilibrium constant to be formulated as

$$K = \frac{a_{Me} \cdot a_{H^{+n}}}{a_{Me^{n+}} \cdot a_{H_2{}^{n/2}}} \qquad (14)$$

and the value of the K can be calculated from a knowledge of the free energies of formation of the species involved or the heats of formation and entropy values. This is thermodynamics.

The rate at which the reaction proceeds is given by the rate constant k,

$$\text{Rate} = -\frac{d[Me^{n+}]}{dt} = k.\ \text{(some function of reactants)} \qquad (15)$$

which is not calculable from equation (13). This is kinetics.

The value of the rate constant k is determined by experiment and is expressed as a function of the factors and concentrations involved in the rate-determining step. For the reaction summarized in equation 13 the rate constant might be expressed by any of the following;

$$\text{Rate} = \frac{d[Me^{n+}]}{dt} = \frac{2}{n} \cdot \frac{d[H_2]}{dt} = k[Me^{n+}]$$

$$\text{or} = k[Me^{n+}] \cdot [H_2]$$

$$\text{or} = \frac{k[Me^{n+}][H_2]}{[H^+]}$$

$$\text{or} = \frac{k[Me^{n+}][H_2]^{\frac{1}{2}}}{[H^{+2}]}$$

In general

$$\text{Rate} = k[Me^{n+}]^a \cdot [H_2]^b \cdot [H^+]^c \cdot [Me]^d$$

where the values of a, b, c, and d must be determined by experiment and usually lie within the range ±2 and may, less often, include fractional terms such as $\frac{1}{2}$ or $\frac{3}{2}$. The hydrogen reduction of metal ions from solution to produce elemental metal often involves highly specific factors, such as surface area, which cannot be generalised. For this reason some of the kinetic factors in the hydrogen reduction of Ag^+, Cu^{++}, Ni^{++} and Co^{++} species will be considered separately and compared and contrasted.

SILVER SALTS

It has been shown by Halpern and Webster[13] that aqueous solutions of silver salts can be reduced to metallic silver by hydrogen. Using solutions of silver acetate it was found that the rate was first order with respect to silver concentration. The rate with respect to hydrogen was not determined but was assumed to be first order and the rate law was therefore expressed as

$$-\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[Ag^I]}{dt} = k[Ag^I][H_2] \qquad (16)$$

The use of Ag^I indicates that univalent silver is involved in the rate determining step but the precise nature of the species involved is not specified. When using acetate solutions the possible $Ag^{(I)}$ species are Ag^+, AgOAC and $Ag(OAC)_2^-$. Halpern and Webster[13] found that the rate of reduction to silver was increased by the addition of sodium acetate but not by the addition of the very weakly dissociated acetic acid. They therefore concluded that acetate ions increased the rate by making the acetate complexing of the Ag^+ ions more complete, the AgOAC and/or $Ag(OAC)_2^-$ species being more readily reducible than Ag^+.

COPPER SALTS

Like the Ag^+ ion, cupric ions have a negative electrode potential (−0.337 v) and should therefore be reducible by hydrogen in both acidic and alkaline solutions.

The hydrogen reduction of cupric salts in aqueous solutions has been studied by a number of workers.[1,14,15,16]

Halpern and Macgregor[15] studied the reduction of cupric perchlorate in perchloric acid solution for the overall reaction

$$Cu^{++} + H_2 \rightarrow Cu + 2\,H^+$$

and derived a rate expression given by

$$\frac{-d[Cu^{++}]}{dt} = \frac{k_1[H_2][Cu^{++}]^2}{[Cu^{++}] + (k_{-1}/K_2)[H^+]}$$

and deduced the following reaction mechanism:

$$Cu^{++} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad (17)$$

$$CuH^+ + Cu^{++} \xrightarrow{k_2} 2\,Cu^+ + H^+ \qquad (18)$$

$$2\,Cu^+ \longrightarrow Cu + Cu^{++} \qquad (19)$$

In this scheme (19) is rapid while (17) and (18) are rate controlling. This reaction path and rate equation is thus able to account for the observed fact that the reduction slows down very rapidly and virtually ceases at little more than 50% reduction even although thermodynamic considerations, as given in the preceding section, clearly indicate that the equilibrium position corresponds essentially to 100% reduction. These workers also studied the reduction of cupric sulphate in sulphuric acid solution and obtained a rate expression of the same form as above but in this case the reduction was both more rapid and more complete. Addition of sodium sulphate to the system pushed the equilibrium position even further towards complete reaction and it was concluded that the hydrogen ions produced in the reduction were being bound up by the sulphate ions to form the weakly dissociated bisulphate ion and this therefore retarded the back reaction of equation (17). In these acidic conditions it was also found that the rate of reaction was independent of the amount of copper powder in suspension in the system and the reduction was therefore a homogeneous reduction as opposed to a heterogeneous one.

The reduction of acidic cupric sulphate solutions has also been described by Schaufelberger[1] in some detail. No rate expression was derived but it was determined that the rate of reduction was increased by an increase in temperature, hydrogen partial pressure and ammonium sulphate concentration and was independent of the available surface area of copper powder. These results are in full qualitative agreement with those of Halpern and Macgregor described above.

The reduction of cupric sulphate solutions by hydrogen under ammoniacal conditions has been described by Evans, Romanchuk and Mackiw.[16] Under these conditions various insoluble species are precipitated from the reacting solution at various times and the whole system becomes too complex for detailed kinetic interpretation. However the effects of certain variables on the rate of reduction and final equilibrium position can be studied in isolation.

As in the acidic system the rate of reduction was increased by an increase in temperature and in sulphate salt concentration, ammonium sulphate in this case. It was also found that after an initial fast reduction, which reduced approximately half the copper, the rate of reaction slowed considerably and became independent of the copper concentration and proportional to the hydrogen pressure.

The amount of ammonia added to the system also influenced the rate of reduction. High NH_3/Cu molar ratios i.e. 2.5–3.0/1 resulted in slow reductions and high equilibrium concentrations of copper in solution. Ratios of NH_3/Cu below 2/1 resulted in faster reductions and complete reduction of the cupric ions to copper metal. However the most marked difference between the acidic and ammoniacal systems was that in the ammoniacal solutions the rate of reduction was accelerated by an increase in the amount of copper powder in suspension in the solution. It was determined that nucleation of copper particles also occurred throughout the reduction and that therefore the reduction was both homogeneous and heterogeneous.

COBALT SALTS

The hydrogen reduction of cobaltous salt solutions has been practised on a commercial scale by several companies i.e. National Lead Company of Fredericktown, Calera Mining Company of Garfield, Sherritt Gordon Mines of Canada and the Freeport Nickel Company. The operations of these companies have been surveyed in a paper by Benz and Mackiw[17] but very little detailed work appears to have been done on this system. It is usually assumed that it is so similar to the nickel/hydrogen reduction system that the results for nickel can be applied to cobalt with very little inaccuracy. Some detailed kinetic studies of the cobalt system have, however, been carried out by Wadsworth and co-workers[12,18] and Courtney[19], apart from the work reported by Schaufelberger and Roy.[9]

Kaneko and Wadsworth[12] reported on the hydrogen reduction of ammoniacal cobaltous sulphate solutions using colloidal graphite as a nucleation catalyst. It is found experimentally that in ammoniacal solutions nickel and cobalt will only reduce at a solid surface. This pre-requisite for reduction means that either some solid nuclei must be provided in the reaction system at the start or else the system must be caused to nucleate by some chemical means. Kaneko and Wadsworth used colloidal graphite as a source of nuclei for reduction. These workers found that the maximum rate of reduction occurred when a molar ratio of $NH_3/Co = 2/1$ was employed and therefore concluded that the cobaltous diammine sulphate complex was the most readily reducible. The rate of reduction in any experiment was constant at a constant hydrogen pressure, indicating a reaction of zero order with respect to cobalt. The dependence of rate on hydrogen pressure was unusual and was an exponential function of the gas pressure.

The rate of reduction was proportional to the amount of colloidal graphite present and a reaction mechanism was proposed in which a cobalt species was adsorbed on to a phenolic site on the graphite and then transformed to a cobalt species containing two added hydrogen atoms which decomposed to cobalt metal.

The results of Kaneko and Wadsworth were commented upon by Courtney.[19]

Wimber and Wadsworth[18] later studied the hydrogen reduction of cobalt sulphate—ammonium acetate solution and obtained results indicating catalysis of the reduction reaction by stainless steel and pyrex glass.

NICKEL SALTS

Nickel is produced in larger quantities and greater purity than any other metal by hydrogen reduction and a great deal of knowledge has been accumulated about this reaction.[1,9,20,21,22,23,24,25,26]

Schaufelberger and Roy have shown[9] that nickel can be reduced from slightly acidic solutions but because of the relatively unfavourable thermodynamics of acid reduction for nickel most work on this reduction has been carried out in ammoniacal solution and it is this work which will now be discussed.

The hydrogen reduction of nickel, like that of cobalt, is strictly heterogeneous and solid nuclei must be present for the reduction and deposition of nickel from solution. Accordingly it is possible to differentiate three cases of reduction according to whether the initial reduction solution contains pre-existing nickel nuclei, nuclei other than nickel, or is induced to nucleate during the reduction reaction. The latter case will be dealt with later and because the second case reverts to the first case at some time during the reduction/deposition reaction only the first case will be considered in some detail.

When an ammoniacal solution of a nickel salt is reduced by hydrogen in the presence of nickel nuclei the overall reaction is

$$\mathrm{Ni(NH_3)}_x + \mathrm{H_2} \xrightarrow{\text{Ni surface}} \mathrm{Ni} + 2\,\mathrm{NH_4^+} + (x - 2)\mathrm{NH_3} \qquad (20)$$

From equation (20) it is clear that if $x = 2$ the molar ratio $\mathrm{NH_3/Ni}$ will not change during reduction. In normal commercial practice x is maintained in the range 1.9–2.2 and in all subsequent discussion it will be assumed that $x = 2$ unless otherwise specified.

If such ammoniacal solutions are reduced by hydrogen in the presence of nickel powder suspended in the agitated solution it is found that the reaction is strictly heterogeneous, the reduced metal being deposited upon the surface of the pre-existing nickel seed. The kinetics of this relatively simple reduction-deposition reaction will now be considered.

The rate of reduction is found to be independent of the nickel concentration, at least down to 85% reduction, and first order with respect to both the hydrogen pressure and nickel seed surface area.[22] The reaction is therefore fitted by the rate expression

$$\text{Rate} = \frac{-d[\mathrm{Ni^{++}}]}{dt} = \frac{-d[\mathrm{H_2}]}{dt} = k.A.[\mathrm{H_2}]$$

where A is the surface area of the nickel seed and $[\mathrm{H_2}]$ is a measure of the hydrogen concentration, the partial pressure of hydrogen in the gas phase being almost invariably used, while k is the specific rate constant.

The variation of k with temperature had also been determined[27] and the apparent activation energy found to be 10.2 K.cal. mole^{-1}. It should be noted that in this determination of the activation energy, E_A, the variation of Henry's Law constant, relating hydrogen partial pressure to the solubility of hydrogen, with temperature was taken into account. The data for this correction were taken from the paper by Pray, Schweickert and Minnich[46] on the solubilities of hydrogen, oxygen, nitrogen and helium in water.

From the rate expression

$$\text{Rate} = \frac{-d[\mathrm{H_2}]}{dt} = k.A.[\mathrm{H_2}]$$

it follows that if the reduction is carried out within a closed and isolated autoclave the pressure within the autoclave will fall according to the above expression. Integration of that expression gives

$$k.A.\text{t.} = 2.303 \log_{10} [\mathrm{H_2}]^{\text{initial}} - 2.303 \log_{10} [\mathrm{H_2}]$$

where $[\mathrm{H_2}]^{\text{initial}}$ is the starting hydrogen pressure. From this a plot of $\log_{10} [\mathrm{H_2}]$ against t will give a straight line whose slope, $\log_{10} [\mathrm{H_2}]/t$, gives $k.A./2.303$ from which k can be evaluated if A is known.

It therefore follows that no further analysis of the kinetic data is possible until the surface area, A, of the nickel seed is known. Unfortunately the area A refers to the surface area on which deposition actually occurs and this is not necessarily the same as the surface area of the nickel powder measured by some arbitrary means such as the B.E.T. method. It is in this context that the discovery of a class of catalysts which accelerate the hydrogen reduction of nickel offers hope of circumventing the difficulty of evaluating A.

It has been found that anthraquinone, and a number of structurally related compounds, will accelerate the rate of hydrogen reduction of nickel solutions. This is true for both solutions containing nickel nuclei and solutions containing "foreign" nuclei. Moreover, it is found that the deposition of reduced nickel on to both classes of nuclei is remarkably uniform, the whole surface of the nuclei being evenly covered with freshly reduced nickel. The difference between the deposition of nickel in the absence or presence of anthraquinone is shown by Figs. 3 and 4. Figure 3 shows a cross-section through a nickel particle which has been produced by approximately forty successive depositions of nickel by hydrogen reduction of nickel solutions. Figure 4 shows a nickel particle produced in the same manner but with anthraquinone present during each deposition. Clearly the use of anthraquinone has led to a very uniform rate of nickel deposition over the whole surface of the particle shown in Fig. 4. Rather surprisingly the use of anthraquinone does not alter either the rate expression or the apparent activation energy, which remains at 10.2 K.cal. mole^{-1} even although the rate may be increased by a factor of twenty when using anthraquinone.

On the basis of these observations the following crude physical model may be proposed. It is assumed that the surface of the nickel nuclei is covered by a strongly adsorbed layer of nickel ions (or nickel ammine ions) and that these are so strongly adsorbed that the number of adsorbed ions only begins to fall off appreciably when more than 85% of the nickel ions originally in solution has been reduced. Under these conditions the rate of reduction will be governed by the rate at which

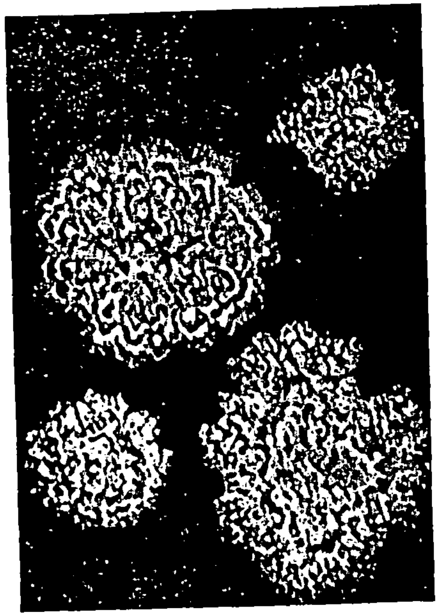
No Anthraquinone

Fig. 3. Nickel powder × 320

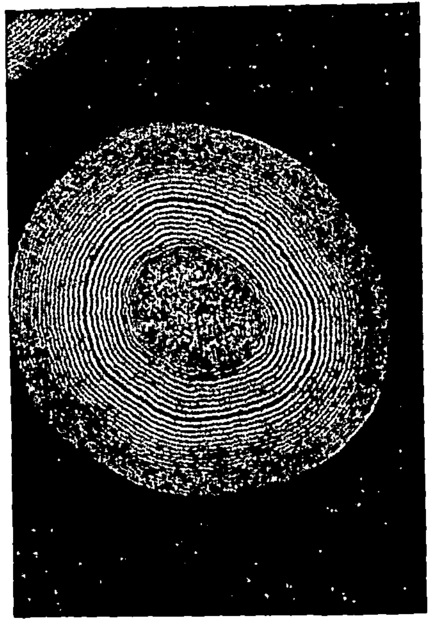
Anthraquinone Used

Fig. 4. Nickel powder × 320

hydrogen molecules can be adsorbed on to the nickel nuclei surface and this will be proportional to both the hydrogen partial pressure and the nickel nuclei surface area. The form of the rate equation fits such a model. It is further assumed that the actual rate determining step, probably between an adsorbed nickel ion and an adsorbed hydrogen molecule, can only take place at certain unusually reactive sites i.e. at "active centres". The function of the anthraquinone is then to increase the number of these active centres and thereby increase the observed rate of reduction without altering either the rate expression or the apparent energy of activation.

In conformity with this model it has been found that the acceleration in reduction rate brought about by anthraquinone varies with the nickel powder used as nuclei. For some very fine and highly active nickel powders the ratio "Rate with anthraquinone"/"Rate without anthraquinone" can be as low as 1.04 while the same ratio can be as high as twenty for some relatively coarse and poorly active nickel powders. If it is assumed that 100% of the exposed nickel surface acts as "active centres" when anthraquinone is present then the above range

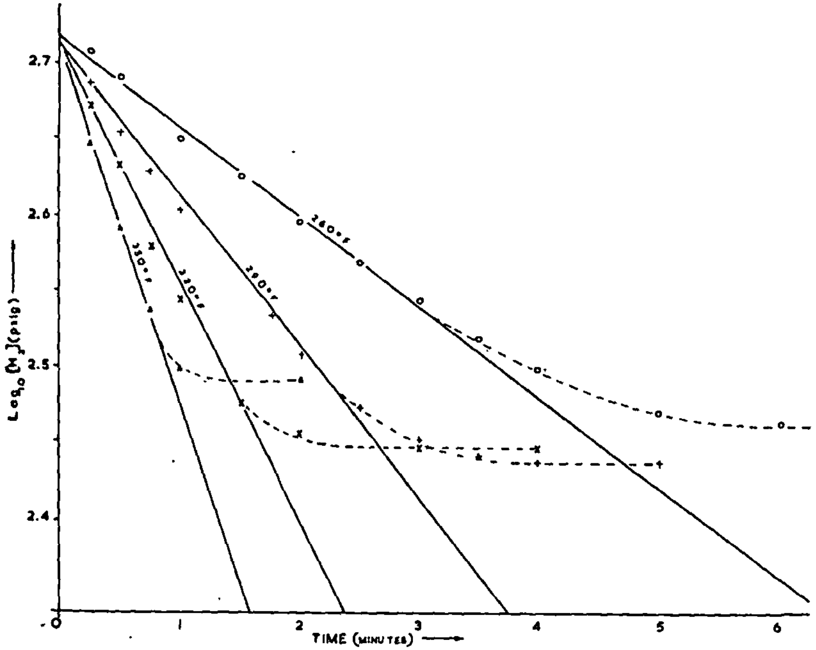

Fig. 5. Reduction rates at various temperatures.

of ratios would indicate that the fraction of total surface covered by active centres is about 95% for very fine, active powders and decreases to about 5% for poorly active powders. Such a range seems reasonable.

The above model also suggests that for a relatively inactive nickel powder there should be a range of anthraquinone additions in which the rate of reduction increases as the anthraquinone addition is increased but that above a certain level, corresponding to complete activation of the nickel nuclei surface, the addition of further anthraquinone should fail to increase the reduction rate. Such a situation has been found.

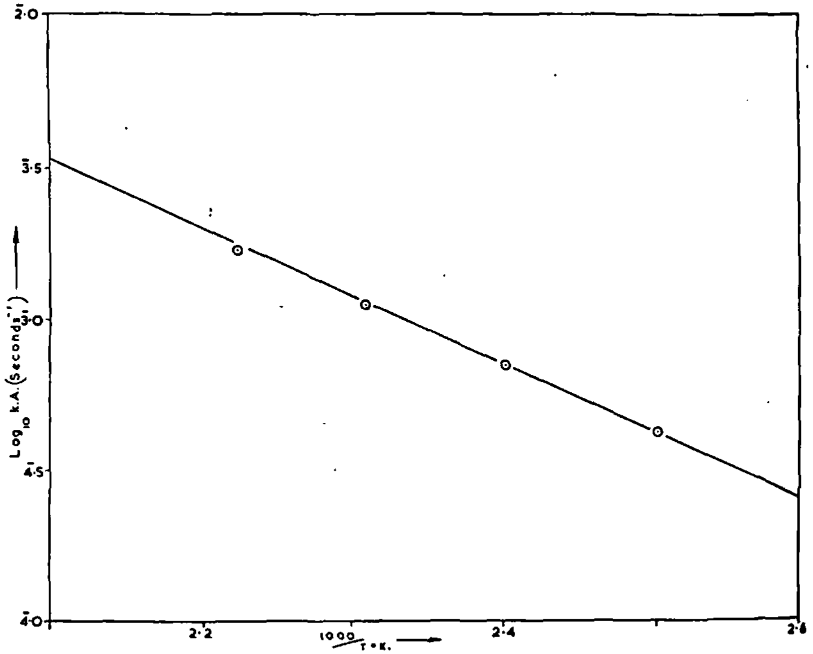

Fig. 6. Arrhenius plot $E_A = 10.2$ K.cal. mole^{-1}.

Figures 5 and 6 show some typical reduction plots obtained by following the fall in pressure within a sealed autoclave and plotting $\log_{10} [H_2]$ against time. Figure 6 then shows the Arrhenius plot obtained from these results.

Figures 7 and 8 show some results obtained with a special nickel powder as nuclei. Figure 7 shows the rate plots, $\log_{10} [H_2]$ versus t, for fixed conditions of temperature, initial hydrogen pressure, initial nickel ion concentration and weight of nickel powder nuclei while the amount of anthraquinone catalyst is varied. From this plot the slopes are used to obtain values of $k.A.$ which are then plotted against the anthraquinone addition in Fig. 8. By making the assumption that the maximum value of $k.A.$ in Fig. 8 corresponds to a value of A equal to the exposed surface area of the nickel powder it is now possible to proceed further with the kinetic analysis of the hydrogen reduction of nickel solutions.

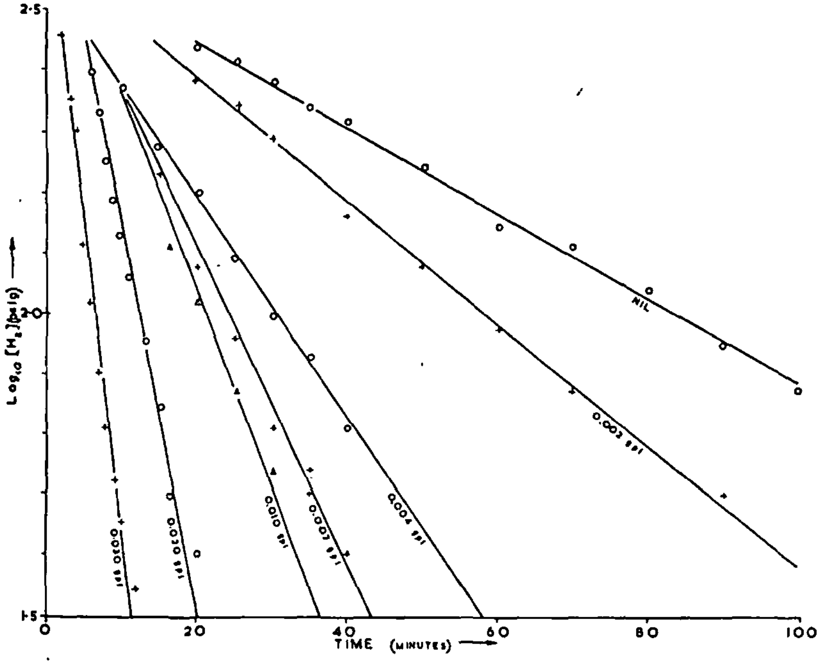

Fig. 7. Reduction curves at various anthraquinone concentrations.

Under normal conditions even the value of $k.A.$ at the plateau in Fig. 8 would be insufficient to fix the effective surface area since the area measured by a method such as the B.E.T. adsorption would probably include fine pores and capillaries which would not be available to nickel ammine ions in solution. However the nickel powder used as nuclei in the experiments represented in Figs. 7 and 8 consisted of the very smooth, spherical powder whose cross section is shown in Fig. 4. The particle size in this powder was very uniform and the average diameter was 198 microns (1.98×10^{-2} cm.) giving a surface area of 34.0 cm^{2}g^{-1}. It seems improbable from the appearance of this powder in Fig. 4 that the "surface roughness" correction factor would be large enough to alter significantly this value of the surface area per gram of powder. The amount of this powder used as nuclei was 100 g. per litre and the amount of nickel nuclei surface in the solution was therefore 3.4 cm^2 per cc. However, in the presence of anthraquinone the stainless steel interior surfaces of an autoclave are uniformly plated with nickel during a reduction and the total surface area for reduction and deposition of nickel in the experiments shown in Figs. 7 and 8 was therefore 3.9 cm^2 per cc. of nickel solution.

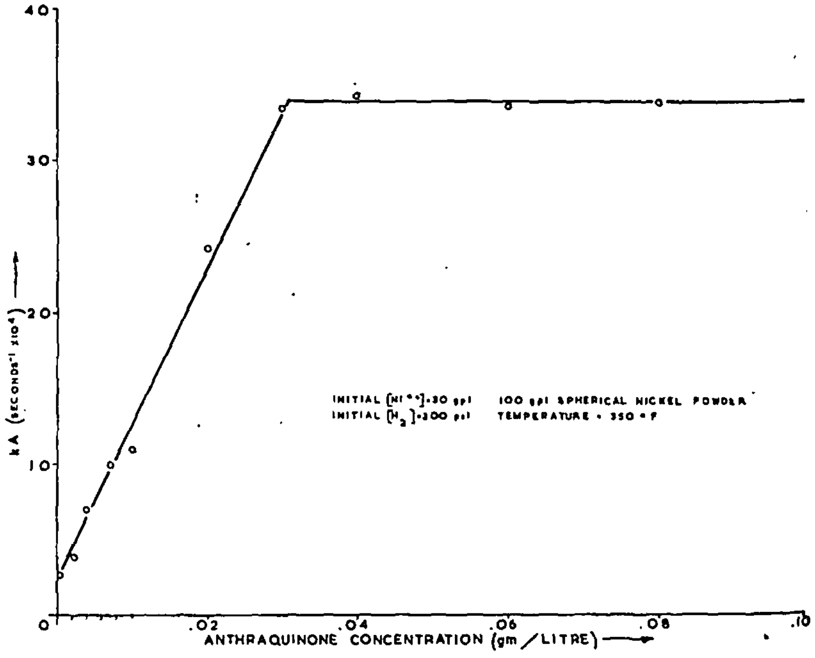

Fig. 8. Values of *k.A.* versus anthraquinone concentration.

From Fig. 8 the maximum value of *k.A.* was 3.4×10^{-3} seconds^{-1} and if $A = 3.9$ cm^{-1} it follows that $k = 0.872 \times 10^{-3}$ cm. seconds^{-1}.

From the relationship

$$\text{Rate} = \frac{-d[\text{H}_2]}{dt} = k.A.[\text{H}_2]$$

it follows that the rate of reaction of hydrogen molecules, under the standard conditions of 1 gm. mole of hydrogen per cc. and 1 cm^2 of nickel surface per cc., would be 0.872×10^{-3} gm. moles per cc. per second. Expressing this rate in molecules reacting per cm^2 of surface per second the rate is 5.25×10^{20} molecules per cm^2 per second. Making the assumption that one surface nickel atom can act as a site for the adsorption of one hydrogen molecule the number of adsorption sites per square centimetre of nickel surface is 2.07×10^{15} since the radius of the nickel atom is 1.24×10^{-8} cm. The rate of reaction is therefore 2.54×10^5 molecules site^{-1} second^{-1}. By using equation (178) in Chapter IV and Eq. (114) in Chapter VII of Glasstone, Laidler and Eyring's "Theory of Rate Processes"[30] the above specific rate constant can be equated to

$$k_1 = e \cdot \frac{\text{RT}}{\text{Nh}} \cdot e^{-\text{E}_\text{A}/\text{RT}} \cdot e^{\Delta\text{S}^\dagger/\text{R}}$$

By substituting $k_1 = 2.54 \times 10^5$, $\text{E}_\text{A} = 10.2$ K.cal. mole^{-1} and $\text{T} = 450$°K (350°F) the entropy of activation can be evaluated and is found to be $\Delta\text{S}^\dagger = -13.9$ e.u.

The dependence of the specific rate constant on temperature can be expressed in three ways, two of which are equivalent.

$k = \text{A}^* \cdot e^{-\text{E}_\text{A}/\text{RT}}$ where A^* = Frequency factor

$k = \text{P.Z.}\ e^{-\text{E}_\text{A}/\text{RT}}$ where Z = Collision number
P = "Probability" factor

$k = e \cdot \dfrac{\text{RT}}{\text{Nh}} \cdot e^{\Delta\text{S}^\dagger/\text{R}} \cdot e^{-\text{E}_\text{A}/\text{RT}}$ where $\Delta\text{S}^\dagger$ = Entropy of activation

These relationships can be used to discuss the effect of anthraquinone on the hydrogen reduction of nickel solutions. Using frequency factors, the rates derived from Fig. 8 for the reductions without anthraquinone and with sufficient anthraquinone to give the maximum rate yield frequency factors of 5.78×10^2 and 0.93×10^2 respectively. The corresponding probability factors are 1.06×10^{-4} and 1.7×10^{-3} while if the effective surface area, *A*, is assumed to be constant irrespective of anthraquinone concentration then the entropies of activation are -19.5 e.u. and -13.9 e.u.

The acceleration of the rate of nickel reduction by anthraquinone can therefore be correlated either to an increase in the Probability factor, using the collisional theory of chemical kinetics, or by an increase in the entropy of activation using the absolute theory of reaction rates. The former correlation can be interpreted as an alternative formulation of the crude physical model in which anthraquinone is envisaged as rendering the whole of the nickel seed surface active for reduction-deposition of nickel. The correlation of rate with entropy of activation is, however, deficient in this instance in that there is no immediately obvious reason why increasing amounts of anthraquinone should increase $\Delta S^{\dagger}$ up to a certain level and then cease to have any further effect upon the activation entropy. It seems therefore that the most satisfactory explanation of the effect of anthraquinone is that it increases the effective surface area of the nickel seed surface. How ever this increase in effective surface is achieved is not clear from the data at present available. From Fig. 8 the maximum rate of reduction occurs at 0.030 gpl of anthraquinone for 3.9×10^3 cm^2/litre of seed surface. The amount of seed surface is therefore only about 0.5 sq. Angstrom per anthraquinone molecules and it therefore seems unlikely that adsorption of the anthraquinone on to the seed surface is responsible for the catalysis. Adsorption of anthraquinone could account for the catalysis if the area of seed surface was increased to give about 50 sq. Angstroms per catalyst molecule but it seems unlikely that the observed surface of the very smooth nickel spheres used as seed is only one per cent of the true surface area. It should also be noted that 0.030 gpl of anthraquinone for 3.9×10^3 cm^2./litre of seed surface corresponds to about ten anthraquinone molecules per adsorption site. However one of the most remarkable aspects of the catalytic effect of anthraquinone is that it appears to be without effect on the hydrogen reduction of cobalt solutions. Apart from the possibility of a very specific interaction between anthraquinone and nickel the simplest explanation would be that a cobalt surface is always 100% effective for the reduction-deposition of cobalt. This seems rather unlikely even if only because hydrogen reduction of cobalt solutions is appreciably slower than that for nickel solutions. It seems probable that an elucidation of the detailed mechanism by which anthraquinone, and similar catalysts, accelerate nickel reductions would be most useful.

It has already been stressed that the hydrogen reduction of nickel is heterogeneous and proceeds at a solid surface, this solid surface being nickel powder in normal commercial production of nickel metal by hydrogen reduction. However, ammoniacal solutions of nickel can be reduced by hydrogen if the solutions can be induced to nucleate, the reduction then proceeding heterogeneously on these nuclei. One of the simplest and most efficient nucleating agents for the nucleation of nickel solutions is ferrous sulphate and the kinetics of this system have been described by Mackiw, Lin and Kunda.[22]

When ferrous sulphate is used as the nucleating agent and hydrogen reduction of nickel solutions carried out it is found that the reduction curves i.e. gpl Ni^{++} versus time, are parabolic in shape. This was explained by these workers on the hypothesis that during these reductions the rate of formation of nuclei was constant and the rate of nickel reduction was proportional to the number of nuclei present.
Thus

$$\frac{dN}{dt} = k_1 \qquad \text{and} \qquad \frac{-d[\mathrm{Ni}^{++}]}{dt} = k_2 \cdot N$$

where N = number of nuclei present.

$$\therefore \qquad N = k_1 t \qquad \text{and} \qquad \frac{-d[\mathrm{Ni}^{++}]}{dt} = k_1 \cdot k_2 \cdot t$$

Integration of this and substitution of $[\mathrm{Ni}^{++}]^{\mathrm{initial}}$ at $t = 0$ gives

$$\mathrm{Ni}^{++} = [\mathrm{Ni}^{++}]^{\mathrm{initial}} - \frac{k_1 \cdot k_2 \cdot t^2}{2}$$

and a plot of Ni^{++} versus t will therefore be parabolic, as is found by experiment.

Studies of various nucleating agents for the reduction of nickel solutions have been carried out by Schaufelberger and Courtney[25] who conclude, "nucleation of the Ni (II)—H_2 reaction usually seems to involve a mixed salt of Ni (II) and the reducing agent with only transient nucleation effectiveness, and the elucidation of the nucleation mechanisms will be difficult." The over-riding difficulty in any study of the kinetics of the nucleation of the Ni (II)—H_2 reduction lies in the difficulty of differentiating between reduction of nickel to form nuclei and the reduction of nickel on to existing nuclei. Until an adequate experimental technique is developed very few definite conclusions can be drawn about the nucleation of ammoniacal nickel solutions under hydrogen pressure.

In contrast to the heterogeneous nature of ammoniacal reductions, it has been found[1,9] that acidic solutions of nickel salts can be reduced by hydrogen without the necessity of adding specific nucleating agents to induce the formation of nuclei. This may indicate that the reluctant nucleation of ammoniacal nickel solutions is related to the lower concentration of uncomplexed Ni^{++} ions in these solutions compared to acidic solutions. However the extreme corrosion problems encountered with acidic solutions under hydrogen pressure make commercial operation under these conditions much less favourable than the use of ammoniacal solutions even though special nucleation techniques must be employed.

So far the hydrogen reduction of aqueous solutions to precipitate metallic powders has been considered. In the next section the use of gaseous reducing gases other than hydrogen and the recovery of reduced metallic compounds other than elemental metal will be considered.

REDUCING GASES OTHER THAN HYDROGEN AND INDIRECT METAL PRODUCTION

For all practical purposes the only alternatives to hydrogen on a commercial scale are carbon monoxide and sulphur dioxide. Of these it is normally easier to produce carbon monoxide pure, or mixed with other gases, normally hydrogen and nitrogen. One of the first processes outlined for the recovery of metal values from solution by reducing gases under pressure was described in patents issued to Mueller, Schlect and Schubardt in 1927 and assigned to I. G. Farbinindustrie.[31] This patent claimed that silver, copper, nickel, cobalt and zinc could be precipitated from solution as the metals by water gas or carbon monoxide or hydrogen or mixtures thereof under conditions of elevated temperature and pressure. While it is highly doubtful that zinc was ever reduced by this method or nickel or cobalt metal produced by gases containing carbon monoxide the patent examples do exemplify the reduction of silver and copper solutions, to metal, by the use of water gas under 130 atmospheres and various temperatures.

The use of carbon monoxide, and the kinetics involved, in the reduction of silver and copper solutions have been described by F. Pawlek and his co-workers.[32,33] These workers[33] found that the use of solutions buffered by 5% ammonium acetate resulted in a much faster reduction and lower activation energy than the use of unbuffered solutions for the carbon monoxide reduction of silver sulphate solutions. However the form of the rate expression was unchanged and in each case was

$$\frac{-d\,[\mathrm{Ag}]}{dt} = k \cdot [\mathrm{Ag}^+]^2 \cdot [\mathrm{CO}]$$

$$= A \cdot [\mathrm{Ag}^+]^2 \cdot [\mathrm{CO}] \cdot e^{-\mathrm{E_A}/\mathrm{R}}$$

where $A = 12.8 \times 10^5$ for unbuffered solutions; $= 6.02 \times 10^4$ for

buffered solutions. $\mathrm{E_A} = 14.1$ K.cal. mole^{-1} for unbuffered solutions; $= 9.3$ K.cal. mole^{-1} for buffered solutions.

Unfortunately a lack of knowledge of the solubility of carbon monoxide in the silver solutions employed precludes any estimations of any of the more fundamental equantities associated with the rate constant k, activation energy $\mathrm{E_A}$, and rate of reaction. All that can be done is to designate the numerical value of k after specifying $[\mathrm{Ag}^+]$, usually in gm. moles per litre, and [CO] usually as the partial pressure in atmospheres, from this the rate is then known for all other combinations of silver concentration, gas pressure and temperature. It should be noted that there is no indication that Pawlek, Bauch and Plieth[33] found the rate of reaction to be increased by the silver metal produced, the reaction is therefore presumably a true homogeneous reduction as was the case for the hydrogen reduction of silver solutions as studied by Halpern and Webster.[13]

Pawlek, Bauch and Plieth[33] also studied the use of carbon monoxide to reduce solutions of cupric sulphate but found that technical difficulties, such as the deposition of cupric oxide and copper deposits and corrosion of agitators, compelled them to use dilute unbuffered solutions of $\mathrm{CuSO_4}$. Under these conditions they found the rate expression to be

$$\frac{-d[\mathrm{Cu}]}{dt} = 2.56 \times 10^{13} \cdot [\mathrm{Cu}]^2[\mathrm{CO}] \cdot e^{-33{,}500/\mathrm{RT}}$$

where $-d[\mathrm{Cu}]/dt$ represents the rate of decrease of ionic copper in solution and [Cu] represents the concentration of ionic copper in solution. Again the solubility of CO in the solutions is unknown and hence k can only be expressed in arbitrary units. These workers also found that reproducible kinetic measurements could not be obtained unless the autoclave contained a sheet of etched copper sheet throughout the reduction. This strongly suggests that, as in the hydrogen reduction of ammoniacal $\mathrm{CuSO_4}$ investigated by Evans et al.[16] the reduction of copper solutions by carbon monoxide is both homogeneous and heterogeneous and that the variable results obtained in the absence of the copper sheet were due to differences in the rate and extent of nucleation in each experiment.

The relative rates of reduction of silver and copper solutions using carbon monoxide, hydrogen and mixtures of the two gases were also determined by Pawlek and his co-workers.[33] For both metals the rate of reduction with carbon monoxide was only about 20% of the rate with hydrogen but the decrease of rate with increasing CO content in hydrogen was much more rapid for copper than for silver. Thus a gas mixture containing 50 volume % CO still gave a rate of reduction 85% of that for pure hydrogen in silver reduction but in copper reduction a 50 volume % CO gas mixture gave a rate of reduction only 22% of that with pure hydrogen. These observations correlate well with some unpublished work carried out by Sherritt Gordon Mines on the effect of carbon monoxide on the hydrogen reduction of nickel solutions in which it was found that only 1% of CO in the hydrogen was sufficient to halt the reduction reaction under normal commercial conditions.

Carbon monoxide can be utilized to obtain metallic nickel from aqueous ammoniacal solutions of nickel salts by an indirect route involving nickel tetracarbonyl. The very thorough researches of Reppe on the chemistry of acetylene and carbon monoxide during the Second World War have been summarized by Reppe.[34] In that summary, and a subsequent reply to a criticism by Prof. Fierz-David.[35] Reppe described the production of nickel tetracarbonyl by the action of carbon monoxide under 100 atmospheres pressure, on highly ammoniacal solutions of nickel salts at 150°C. Reppe dissolved nickel salts in 30% ammonia solutions and obtained quantitative conversion to $Ni(CO)_4$ according to the following equation

$$[Ni(NH_3)_6]Cl_2 + 5\,CO + 2\,H_2O \rightarrow Ni(CO)_4 + 2\,NH_4Cl + (NH_4)_2CO_3 + 2\,NH_3.$$

Reppe was convinced that if the carbonyl formation proceeded via metallic nickel, as postulated by Prof. Fierz-David,[36] this intermediate would have been noticed by himself and his co-workers. Since metallic nickel was not detected in these experiments Reppe believed that the conversion to $Ni(CO)_4$ did not involve the formation of metallic nickel as an intermediate. Clearly this use of carbon monoxide to convert solutions of nickelous salts to nickel tetracarbonyl could form the basis of a method for winning nickel metal from solution by decomposing the tetracarbonyl to metal and recycling the carbon monoxide. Rather similar reactions with iron and cobalt salts were also described by Reppe.[34,35] Both iron and cobalt salts in aqueous 30% ammonia solutions react at 80°C under 100 At. of CO to give the dihydride of the tetracarbonyl or its ammonium salt

i.e. $$[Fe(NH_3)_6]SO_4 + 6\,CO + 4\,H_2O \rightarrow Fe(CO)_4 \cdot H_2 + (NH_4)_2SO_4 + 2(NH_4)_2CO_3$$

However the iron carbonyl decomposes in excess CO to yield hydrogen and volatile iron pentacarbonyl while the cobalt analogue is stable in alkaline solutions. The cobalt derivative can be recovered from the reaction solution by cautious acidification followed by vacuum distillation to collect the tetracarbonyl hydride in a cold trap. If this condensate is allowed to warm up slowly it melts and below 0°C it decomposes to yield hydrogen and the solid dimer of cobalt tetracarbonyl

$$2\,Co(CO)_4 \cdot H_2 \rightarrow 2\,H_2 + [Co(CO)_4]_2$$

Attention should also be drawn to a note published by Harkness and Halpern[37] on the reduction of various cationic species by CO in aqueous solution although these reductions do not result in metal powder production.

Comparatively little work has been carried out on the use of sulphur dioxide to reduce solutions of metals and it is not proposed here to do more than indicate some typical patents utilizing SO_2 as a reducing gas.[38,39,40,41,42] Early unpublished work in the laboratories of Sherritt Gordon showed that copper solutions could be completely reduced to the metal by SO_2 from ammoniacal solutions of controlled composition.[23]

In some cases the reduction of solutions of some metal species results in the formation of insoluble oxide or hydroxide species of lower valencies. Solutions of hexavalent molybdenum and tungsten exhibit this form of reduction and it is possible that a hydrometallurgical process for the separation and recovery of these metals can be based upon this reaction. It was first shown by Schaufelberger and his co-workers of Chemical Construction Company that hydrogen would reduce solutions of hexavalent uranium and pentavalent vanadium. Some studies on the kinetics of these reductions were subsequently published by Forward and Halpern[43] and O'Brien, Forward and Halpern.[44] In both these cases the reduction was heterogeneous and the rate of reduction was proportional to the amount of heterogeneous catalyst added, this catalyst being nickel powder. The uranium solutions contained the uranium carbonate complex $UO_2(CO_3)_3^{4-}$ and were buffered with sodium carbonate. The vanadium solutions contained sodium metavanadate and were also buffered by sodium carbonate. For both metals the rate of reduction was independent of metal concentration in solution but while the reduction of uranium was first order with respect to hydrogen the vanadium reduction was proportional to the square root of the hydrogen pressure. The rate expressions obtained for these reductions were;

$$\frac{-d[U_3O_8]}{dt} = k_1 \cdot [\mathrm{Ni}] \cdot [H_2] \cdot e^{-9800/RT}$$

and

$$\frac{-d[V]}{dt} = k_2 \cdot [\mathrm{Ni}] \cdot [H_2]^{\frac{1}{2}} \cdot e^{-7850/RT}$$

where $[U_3O_8]$ and [V] are the concentrations of uranium and vanadium in solution expressed as grams per litre of U_3O_8 or vanadium respectively and [Ni] represents the surface area of the nickel catalyst used in cm^2. per litre. It should be noted that the surface area of the nickel catalyst is the surface area as measured by the B.E.T. method and the effective catalytic area may differ from this so that any given value of the rate constants k_1 or k_2 may be valid for only one sample of nickel powder.

The essential characteristic of these two reductions is that relatively dilute leach solutions can be used and the metal values obtained in a convenient and pure form by the simple application of heat and hydrogen pressure. The uranium reduction yielded uranium dioxide according to the following equation,

$$UO_2(CO_3)_3^{4-} + H_2 \rightarrow UO_2 + CO_3^{2-} + 2\ HCO_3^-$$

while the vanadium reduction was claimed to produce V_2O_3 by;

$$2\ VO_3^- + 2\ H_2 \rightarrow V_2O_3 + 2\ OH^- + H_2O$$

The vanadium solutions were observed to change from colourless to a deep reddish brown colour before precipitation occurred and it was postulated that the reduction of pentavalent vanadium to the trivalent state proceeded in two stages, the first reduction from V^{V} to V^{IV} being fast and accounting for the initial colour change and the final step, V^{IV} to V^{III}, being rate determining.

Following this early work on uranium and vanadium by Halpern and his co-workers the same type of hydrogen reduction was applied to molybdenum and tungsten solutions by Soviet workers. The use of hydrogen reduction to precipitate molybdenum dioxide from sodium molybdate solutions has been studied by Lyapina and Zelikman.[45] These workers used solutions of sodium molybdenum made acid by the addition of sulphuric acid in order to neutralize the alkali produced during the reaction

$$MoO_4^{2-} + H_2 \rightarrow MoO_2 + 2\ OH^-$$

No precise kinetic data were presented for the reaction but it was shown that the reduction was accelerated by the addition of molybdenum or molybdenum dioxide powder to the solution before reduction. In other respects the rate of reduction varied with conditions in a manner to be expected from the overall equation given above, the rate was increased by an increase in hydrogen pressure and temperature and by a decrease in the pH of the solution. This work has been largely confirmed and extended to ammoniacal solutions within the research laboratories of Sherritt Gordon Mines and fuller details of the hydrogen reduction stage will be given in a later paper. The molybdenum dioxide produced by this hydrometallurgical process can be reduced to metallic molybdenum very conveniently by reduction with hydrogen in a furnace.

CONCLUSION

At the end of a survey of this nature it is possible to look back and see that the most commonly used reducing gas in modern hydrometallurgy is hydrogen. The reasons for this are not difficult to discover. Hydrogen is simple and cheap to produce on a large scale and can be readily purified. Because of its molecular weight a reduction can be carried out with less weight of reducing gas using hydrogen than any other reducing gas and this is reflected in all the mass transfer machinery within a plant designed to utilize gaseous reduction of aqueous solutions to recover metals. From the chemical point of view the reaction products from aqueous hydrogen reductions are either hydrogen or hydroxyl ions so that in effect there are no by-products to contaminate the product or solution. Other reducing gases such as CO or SO_2 either produce gaseous or aqueous reaction products which must be recovered or separated and in specific cases may tend to contaminate the product.

The great advantage of gaseous reduction of metal solutions lies in the high reaction rate with which solutions of even low metal contents can be rapidly depleted of metal values and processed. The method also offers the very attractive possibility of separating two or more metals from the same solution if their reduction potentials are sufficiently far apart. It should be noted that the pure nickel powder produced by Sherritt and which contains only 0.07% cobalt is obtained by hydrogen reduction of solutions in which the cobalt content is 2.5% of the total metal concentration.

The future potential of gaseous reduction of aqueous solutions in hydrometallurgical operations stems from its inherent amenability to the methods of process control, methods of analysis, research and modification which are employed in the chemical industry.

One of the major limitations of gaseous reduction of metal solutions is that it is not applicable to all metals. The prospects of obtaining iron powder by hydrogen reduction of aqueous ferrous or ferric solutions seem remote. On the other hand metals such as copper, silver, gold, platinum and palladium which can easily be reduced to the metal by hydrogen reduction from aqueous solutions are not produced in this manner to any significant extent at the present. It is reasonable to expect that the application of gaseous metal reduction will find more extensive application in this field of metallurgy.

It is also probable that some of the more amphoteric transition metals, such as molybdenum and tungsten, will be produced by processes involving hydrometallurgy and hydrogen reduction techniques.

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Discussion

F. E. Pawlek:* I congratulate the authors on their excellent presentation of the theoretical foundation, especially that of thermodynamics and the pressure reduction of metal salt solutions. It is consoling for us on the other side of the ocean to hear that in spite of so many efforts the kinetics of the reduction is not completely solved yet. In the case of acceleration of the reduction by Anthraquinone one perhaps would think of a true interreaction catalysis which could be determined by the quantity of hydrogen dissolved and by the velocity of the H_2/anthraquinone reaction.

B. Meddings and V. N. Mackiw: There is no doubt that the anthraquinone is itself reduced during the course of reaction. In some cases it has been possible to isolate some of the degradation products from the reduction solution and to determine that the solid so isolated contains Anthrone (by X-ray diffraction) and some other, as yet unidentified, material. But whether this H_2/anthraquinone reaction is a necessary, or the only, condition for the acceleration of the reduction process is another question. It is difficult to believe that anthraquinone, added to a cobalt solution under the same conditions as a nickel solution, should not react with hydrogen as it does in a nickel solution—yet it has not been convincingly shown that anthraquinone accelerates the rate of reduction of a cobalt solution.

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PART III

LIQUID-SOLID SEPARATION

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GOLD AND SILVER ASSAY METHODS IN THE MINING AND METALLURGY INDUSTRY

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Introduction

The history of gold and silver analyses shows an interesting duality. On one hand, classical chemical and instrumental methods have evolved to meet changing needs, but on the other hand, the age-old and somewhat empirical fire assay has remained a popular tool. Inasmuch as gold and silver generally have been present in ores at low concentrations, methods have been challenged by a need for sensitivity and selectivity coupled with reasonable assay time. A progressive increase in the importance of low grade materials as ore sources has led to the need for improved methods. Assays of these materials are required for process control and accounting in operating plants as well as for guiding research and development activities. The analytical response to these needs is evidenced by numerous reviews published through 1977--e.g., cf Kolthoff and Elving (1966), Beamish and Van Loon (1966, 1972, and 1977), Young (1971), Mallett (1970), and Sen Gupta (1973).

In this paper we present a brief sketch of the history and status of various gold and silver methods. A more detailed summary of atomic absorption spectroscopy (AAS) is given, as this method has gained in popularity more than other assay methods. AAS methods currently in use are summarized and discussed briefly. This paper is not meant to be a detailed review, as are the above mentioned publications. Rather, we borrow from those works and more recent papers to report trends in gold and silver analyses (particularly in AAS). Also, we discuss some selected potential problems, and problems that have been experienced by this laboratory.

Status of Au and Ag Methods

Table 1 summarizes the status of the more important gold and silver methods. All of these have found use in the industry at some time, and most are probably used occasionally by those laboratories which are set up for ready application. However, fire assay and AAS account for most quantitative work at present.

Fire assay has been the time-honored method for gold and silver determinations. Applied properly, it combines a very efficient metal collection or preconcentration technique with the primary detection method of weighing the gold bead. Other methods can be used to ascertain its purity. Accuracy for gold assays is usually acknowledged to be high, even though the claim is made occasionally that an ore contains values which fire assay has missed. (After forty years of research in the field, Beamish (1972) claimed that he had not experienced a single example of failure of the classical assays to find a paying ore!). By combining lead buttons from various sample collections, very large samples can be analyzed with acceptable precision and good representation of heterogeneous materials. The vitality of fire assay is attested to by the fact that it is still the most used method for umpire and accounting purposes. Also, a book has been published very recently by Smith (1979) which details procedures for fire assay.

Additional and newer methods have been and are important to laboratories which have applicable instrumentation, which have no fire assay equipment or analyst, or which find fire assay cumbersome--e.g., as in the case of liquids, few samples per day, or very low grade solid samples. These methods also have contributed significantly to the general state of analytical quality control, by proving the accuracy of the more routine methods with changing sample type. Thus, most laboratories at gold and silver mines use atomic absorption as well as fire assay.

Unless the fire assay losses are determined (which is quite lengthy), silver assays are more accurately made by other means. These fire assay losses, which are of the order of several percent for typical ores (see references in Mallett [1970] and Walton [1973]), have been accepted possibly because toll smelters expect to lose a comparable fraction of the silver during processing. With hydrometallurgical processes, toleration of these errors cannot be justified.

Fire assay is not sensitive enough for the practical assaying of many low grade ores or of small samples of nominally low grade material, which result from many laboratory or exploration studies. In these cases, fire assay collection is often combined with the more sensitive detection methods of atomic absorption or emission spectrography.

Before the development of AAS, most of the methods in Table 1 found some mining or metallurgical aplication. Gravimetric and titrimetric methods were used when richer ores were considered. They still find some use for higher grade intermediate and end metallurgical products when good precision is needed (e.g., copper anode sludges). Spectrophotometric (i.e., colorimetric) methods were very popular for trace levels of Au and Ag in the 1950's and 1960's. Electrometric methods also are very sensitive and are also very precise, but require more sophisticated instrumentation, so are used mostly where equipment is available and used for other purposes. X-ray methods and emission spectrography are useful, where applicable, because of their multi-element capabilities and accommodation of solid samples. Both suffer from variable matrix interference and, therefore, are quantitative only if complemented by adequate standards. Emission spectrography has been used as a quantitative method both for fire assay products and for noble metals which were separated from the base metals by precipitation. It continues to be used for semiquantitative determinations of noble metals in many materials, and for quantitative assays in relatively simple matrices for which enough reliable standards are available (e.g., in copper). Neutron activation is uniquely applicable to small (e.g., 1 g) samples which contain ultratrace levels of Ag or Au. As such, it appears to have more application in geologic than mining and metallurgical applications.

Atomic absorption started to find application in the early and middle 1960's. Since that time it has gained wide usage for all types of mining and metallurgy samples. Today it is the mainstay method for gold and silver in many or most laboratories and is important with regard to these assays in nearly all laboratories.

Some laboratories use rapid but probably incomplete sample digestions coupled with AAS procedures to yield quick, semiquantitative results. However, with the appropriate sample and standard preparation, AAS regularly gives gold results rivaling fire assay accuracy, and silver results which exceed it, considering the slag and cupel losses in fire assay (e.g., see Mallett [1970], Tendall [1965], and Fishkova, et al. [1972]). Although fire assay is heralded for its greater precision than other methods, proper sample preparation coupled with AAS yields equal or better precision on typical ores. This was demonstrated by Brandvold (1979) and in other recent literature. Brandvold's tests involved eight commercial laboratories which used fire assay and seven laboratories (commercial, industrial, and government) which used AAS. Both interlaboratory and intralaboratory results, for gold and silver (at 0.25 oz/ton and 17 oz/ton, respectively) were at least as precise for AAS as for fire assay. At much higher ore grades, it is recognized that fire assay has the advantage over AAS. Tests conducted by our laboratory confirmed this conclusion in assays of copper refinery slimes, which contained gold and silver at levels several orders of magnitude higher than those in ores. The fire assays were up to several hundred percent more precise than AAS in this test.

Au and Ag Atomic Absorption Methods

General

AAS gained in popularity over other nonfire methods because of its low cost, versatility, simplicity of operation, and specificity. Many aqueous samples can be aspirated into the flame with no pretreatment or with just a water dilution, and many solids require little more than a simple mixed acid digestion. Matrix effects from base metals and the solvents are usually much less than in the case of other instrumental methods. Modifications to the direct AAS procedures came about largely for low grade materials in which the gold or silver signal was nearly the same as background. Table 2 gives an overview of atomic absorption methods for the most frequently encountered sample types, over a wide range of silver and gold concentrations. Table 3 details some solvent extraction methods.

Discussion of Methods and Potential Problems

Sample Preparation: Aqua regia with, occasionally, the addition of hydrofluoric acid is the most-used lixiviant, and is applicable to most ore types. Other combinations of acids as well as cyanides are also used, and preroasting is sometimes applied.

Digestion time and amount of reagent vary, quite naturally, with the amount of acid-consuming materials in the sample. Thus, raw ores are usually simpler than base metal and pyrite concentrates. In the latter case, reagents in addition to aqua regia are often added to completely oxidize the sulfide; otherwise, sulfur beads may form on the reaction mixture. However, tests in this laboratory with such concentrates, at low Au and Ag levels, showed that destruction of the sulfur was not necessary in order to achieve recovery of the Au and Ag.

Detailed digestion procedures vary with the sample type, size of gold particulate, and laboratory. No one precedure or even reagent combination is optimum for all types of samples. This was demonstrated within our laboratory, where aqua regia is the standard lixiviant for most solid samples. However, silver in a carbon bed (used to remove the Ag from cyanide leach liquors) could not be dissolved quantitatively with either an aqua regia or a cyanide leach. It was finally dissolved quantitatively after the carbon was completely destroyed with hot, concentrated, $HClO_4$.

After digestion, the sample is redissolved in the solvent from which AAS measurements or solvent extraction is to take place. The sample is usually boiled or baked before the final solution makeup. General consensus is that this is done to remove NO_x. The reasons for this are not altogether clear, but it has been reported that NO_x interferes with AAS silver readings (Tindall, 1977), and some gold methods also have included baking. However, methods for both Au and Ag are used which do not include such baking, and the excess nitric acid does not interfere with subsequent extraction of gold into MIBK (Ichinose, 1971). Therefore, the general need for baking appears to be an unresolved question at present.

Independent of the above question, it has been reported that boiling samples to dryness and then baking at high temperatures can reduce Au(III) to Au(I) and Au, which do not extract into ketones such as MIBK (Tindall [1977]). Therefore, Tindall recommends that the sample be kept moist and NO_x be removed by boiling from, e.g., 50% HCl. Some authors add oxidants such as bromine or permanganate to the final makeup solution to counteract any prior reduction of Au(III).

Both AAS measurements and extraction can be performed from HCl or aqua regia solutions, the same components used in digestion. Although Au (III) is sufficiently soluble in even dilute HCl, silver may be lost to precipitation if the HCl is not concentrated enough. Figure 1 gives the solubility of Ag+ ions as a function of HCl concentration. This figure does not take into consideration chloride used in complexing other metal ions such as Fe^{3+}, Al^{3+}, and Pb^{2+}. Common practice is to make the final dissolution in 25 to 50% HCl which, according to the literature, is sufficient to hold at least 50 ppm Ag in solution. Ammonium acetate (NH_4Ac) is often added to the HCl solution when silver is determined in the presence of high lead. Although this improves the solubility of silver slightly (cf. Fig. 1) and prevents $PbCl_2$ precipitation (which can coprecipitate silver, cf Tindall [1965]), the value of ammonium acetate is not accepted by many.

Leach solutions such as cyanides may be aspirated directly into the flame. Standards should match the samples quite closely both in the case of solution samples and digest-makeup samples. Reliable background correction is essential for quantitative work, especially in the case of gold, unless both the standards and sample matrices are nearly identical. This is difficult to accomplish inasmuch as different samples usually contain different, unknown levels of the base metals and solvents. Background correction is practically a necessity with flameless AAS.

Air-acetylene flames and wavelengths of 328.1 nm (for Ag) and 242.3 nm (for Au) are employed almost universally. Typical sensitivities* are approximately 0.05 ppm for Ag and 0.3 ppm for Au.

Solvent Extraction: As Au and Ag concentrations decrease and additional sensitivity is needed, solvent extraction (SX) is usually employed. This serves to concentrate the sample, remove interferences (discussed later), and enhance the AAS signal for a combined sensitivity increase of up to 200 times. A suitable organic solvent provides quantitative extraction from the digestate or solution sample at a small organic/aqueous ratio, low solubility in the aqueous phase, selective extraction of Au or Ag over the other ions present, a flame transparent at the wavelengths involved, and enhancement of the absorption. The better and more popular solvents in these respects are listed in Table 3. Many others have been studied, however, as evidenced by the more than 100 SX schemes for gold and more than 20 for silver which were published from 1970-80.** Most of these references can be found readily in the reviews by Sen Gupta (1973) and Das and Bhattacharyya (1976), and in the biannual bibliographies of Atomic Absorption Newsletter. The great differences in these numbers is no doubt due to the greater sensitivity of the AAS response for silver, coupled with the fact that commercially interesting silver deposits are of higher grade than their gold counterparts.

Most gold extraction is done from HCl or aqua regia solutions containing chloride, 10 to 60%, but a few extractants function in cyanide or both cyanide and acid solutions. Silver may be extracted from similar solutions, but often requires additional treatment. Although the TOPO method of Burke (1974) was originally developed for Ag in metallic nickel, the authors have successfully applied it to ores and other mining materials. Cyanide leachates have been converted to HCl systems, preceded by oxidation of the Au(I) to Au(III) with such oxidants as, $KMnO_4$, aqua regia, and Br_2.

Although pre-equilibration of the extraction solution and the aqueous acidic media is deemed advisable by some authors, it has not been practiced universally (e.g., cf Tindall [1965]). Pre-equilibration, however, ensures constant recovery of the organic phase, when the solvent system solubility is not negligible--e.g., MIBK.

Ion Exchange: Resins also have been used for purifying and concentrating Au and Ag solutions prior to AAS analysis. A review of silver work is given by Kolthoff and Elving (1966) and one for gold work is given by Beamish and Van Loon (1977). This laboratory has recently used Rohm and Haas' XAD-7 to concentrate gold from mining samples, dissolved in aqua regia and brought up in HCl solutions. The gold was then stripped with an acetone-ethanol mixture or 40% HNO_3 and aspirated into the flame.

Flameless AAS

Flameless AAS provdes a means to increase flame AAS sensitivity, by up to 200 times. Interferences from aqueous leachates and digestates are so great, however, that flameless AAS has found application mainly after organic extraction. Thereby, the analytical sensitivity is increased far beyond that of the SX/flame-AAS methods.

Interferences: Interferences from other elements have been reported as minimal in many cases, but matrix difficulties and precautionary steps to avoid them are also prevalent in the literature (see Mallett [1970] and Sen Gupta, [1973]). High salt content, from some elements more than others, causes AAS interferences from broad band spectra and light scattering--i.e., Fe^{3+}, NaCN, KCN, Zn, Se, Te, Ni, Co, and Cu in the case of gold and Fe^{3+}, NaCN and KCN in the case of silver. Unless the salts are very concentrated, e.g., as when several grams of soluble sample are dissolved in 100 ml, we have found that background correction eliminates such interferences. Without background correction, we have found that quantitative results are difficult to attain. As reliable background correctors were not common until the late 1960's, it may be assumed that many problems reported were, in fact, due to the lack of this important AAS accessory. Even when a background corrector is used, we strongly recommend that its functionality be tested frequently with a matrix blank which matches the sample. This sould read zero if the background corrector is working.

At very high salt concentrations, the background corrector often cannot do its job; the high viscosity of concentrated solutions also impedes aspiration. In the extreme, salts may collect on the burner head. Although complexing agents have sometimes been added to increase solubilities of some species, solvent extraction appears the more common remedy. Even then, some species, e.g., Fe, may extract into the organic, rendering its properties unsuitable for aspiration. For this reason, the MIBK is given several washes with dilute (e.g., 1.5 M) HCl to remove interferent, the gold remaining in the organic phase.

Determination of Gold and Silver from a Single Sample Preparation: Gold and silver are often determined from the same sample, so a single sample preparation prior to AAS measurement offers substantial time savings. Single sample preparation is, of course, easily accomplished when both metals dissolve in the digest

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*The sensitivity is usually defined as the concentration which produces a 1% absorption.

**Not all of these schemes are coupled with AAS detection.

(e.g., aqua regia) or the leach solution (e.g., cyanide) at levels measurable with flame AAS.

Often the gold/silver ratio dictates that gold must be extracted but that silver can be determined directly from the digest. Tindall (1965) accomplished this from an aqua regia digest with 25% HCl makeup, and solvent extraction of gold into MIBK. Silver was determined from the HCl before the gold extraction (this is necessary as silver extracts incompletely into the MIBK), and gold was determined from the MIBK. The gold standards were prepared by extraction into the ketone from 25% HCl.

It would be advantageous to extract both the gold and silver from a common lixiviant (e.g., aqua regia), and aspirate them from a common organic solvent. This has been done (see Konovalov and Gureva, 1979) for high levels of Au and Ag in Sb-Pb alloys using petroleum sulfides in toluene as the extractant. Considering flame characteristics of this solvent, it would appear more suitable for ores to use some of the extractants in Table 3 which are common to both silver and gold--e.g., TOPO in MIBK or Aliquat 336 in DIBK. Such a method could not be found in the literature. It also appears possible to dissolve these metals, after aqua regia digestion and baking, with a NaCN solution and to either extract both metals in Aliquat 336/DIBK from that solution or directly aspirate the silver and extract the gold.

RECENT TRENDS IN SILVER AND GOLD METHODS

Literature of the last several years shows that strong effort is continuing in expanding, improving, optimizing, and evaluating analytical methods for gold and silver in mining and metallurgical applications. Well over 100 articles have been published since 1973 dealing just with atomic spectroscopy. A complete listing is beyond the scope of this article; again the reader is referred to the biannual bibliographies of At. Absorpt. Newsl. and Atomic Spectroscopy.

The accuracy, sensitivity and precision of AAS, applied properly, are at least as good as those for fire assay. Therefore, the choice between these methods would appear mainly to be one of assay time and available analyst skills. Flameless AAS is receiving more attention, and the result is nanogram or picogram sensitivities. Most separation techniques are still being considered--i.e., conventional ones such as solvent extraction, precipitation and fire assay, and also recent ones (e.g., see Kahn and Van Loon, 1978, who used ion exchange chromatography).

The state of present methods probably leaves assay time as a more important problem in the mining industry than sensitivity or method availability, per se. Therefore, innovations to eliminate assay steps are being pursued. For example, the organic extractant has been mixed directly with the dissolution reagent. In a more exploratory vein, both flame and flameless AAS have been attempted directly on solid samples.

In the flame AAS case, see Karmenova and Pogrebuysk, 1979, the sample was diluted with powdered graphite and this mixture aspirated into the flame.

Multielement analysis from both the raw sample, digests, and digest/extracts of the sample are probably the most considered time-saving procedure. Emission spectrography is far from dead, and several recent publications have applied it to the raw samples, so as to omit time-consuming separations. As discussed previously, single solvent extractions and also precipitations are developed to separate and concentrate several elements simultaneously. Publications applying this procedure are most prevalent for gold in conjunction with the platinum metals.

Perhaps the greatest time saving innovation developed during the '70's will be inductively coupled plasma (ICP) spectroscopy. Although applications to gold and silver are still sparse (e.g., see Motooka, et al., 1979, and Wemyss, et al., 1978), increased use is expected. ICP offers linear response over a much wider concentration range than AAS and, with the higher temperature, offers added spectral lines and sensitivity. Therefore, it is conceivable that samples soon may be determined by reading them with ICP after a simple digestion, and later the solids may be determined directly. With such capabilities the high cost of ICP equipment could be justified for many laboratories.

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Table 1. Status of Major Gold and Silver Analytical Methods

Method	Status
Fire Assay	Routine quantitative for most sample types; umpire; also used as collector for AAS and spectrographic methods.
Atomic Absorption Spectroscopy (AAS)	Routine quantitative for all sample types; probably most-used method.
Emission Spectrography	Quantitative for some applications; semiquantitative for others; more popular before AAS developed.
Inductively Coupled Plasma Spectroscopy	Just getting started; great potential.
Spectrophotometric	Popular trace-level method in '50's and '60's; backup and confirmatory.
X-ray (XRF, EDX)	Special applications; usually qualitative
Neutron Activation	Best method for ultra-trace levels in small samples; preseparations make method slow.
Gravimetric	Formerly used for higher grade samples.
Titrimetric	Formerly used for higher grade samples; some high grade applications (e.g., anode sludges).
Electrometric (polarographic, amperometric and coulometric)	Special applications; good sensitivity and precision.

Table 2. Selected Atomic Absorption Methodology for the Determination of Gold and Silver

			Flame AAS		Flameless AAS		
Sample	Sample Size (g)	Sample Preparation	Minimum Concentration in Original Sample	Concentration in Final Solution (mg/L)[a]	Minimum Concentration in Original Sample	Concentration of Final Solution (mg/L)[b]	Reference[c]
Au/solids	1-10	Aq. Reg.[d]/	34 g/t[e]	0.5-2	---	---	M, SG
Ag/solids	1-2	1-6 MHCl	10 g/t	0.05-4	0.1 g/t	0.001-0.025	M, SG
Au/solids	1-10	Roast/ CN^- leach	3 g/t	0.5-2	0.3[f] g/t	0.05-1.5	M, SG
Ag/solids	1-2	HNO_3/ 5% NaCN- 0.2% NaOH	10 g/t	0.05-4	0.1 g/t	0.001-0.025	M, SG
Ag/solids	0.1-0.2	Aq. reg./ NH_4OH	10 g/t	0.05-4	0.1 g/t	0.001-0.025	P
Au/solids	1-10	Aq. reg./ xtn[d]	0.2 g/t	0.5-2	0.02[f] g/t	0.005-0.5	T3
Ag/solids	*1-2*	*or Aq. reg./* HCl/xtn	*0.6 g/t*	*0.05-1*	*0.001 g/t*	*0.001-0.025*	T3
Au/solids	1-10	Aq. reg./ 1-4 MHCl/ resin sep'n	3 g/t	0.5-2	0.3[f] g/t	0.05-1.5	S
Au/CN^-	(g)	Dilution	0.5 mg/L	0.5-2	0.005 mg/L	0.05-1.5	M, SG
Ag/CN^-	(g)	Dilution	0.05 mg/L	0.05-2	0.005 mg/L	0.001-0.025	M, SG
Au/ aq. reg.	≤250	Dilution or evap/HCl/xtn	0.5 mg/L 0.01 mg/L	0.5-2 0.5-2	0.005 mg/L 0.001 mg/L	0.05-1.5 0.005-0.5	M, SG M, T3
Ag/aq.	≤250	HNO_3 to paste/5% NaCN-0.2% NaOH	0.01 mg/L	0.05-2	0.001 mg/L	0.001-0.025	M, SG
Au/CN^-	≤250	Acid/oxidant/ xtn	0.01 mg/L	0.5-2	0.0001 mg/L	0.005-0.5	M, SG
Au/other aq. sol'ns (thiourea, thiocyanates, etc.	≤250	Dilution or oxdn/vol redn/HCl/ xtn	0.5 mg/L 0.01 mg/L	0.5-2 0.5-2	0.005 mg/L 0.0001 mg/L	0.005-1.5 0.005-0.5	M, SG T3
Au/ organics	(g)	Dilute with solvent	0.5 mg/L	0.5-2	0.005 mg/L	0.005-0.5	M, SG, T3

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a)ppm = mg/L divided by the specific gravity of the solution at ambient temperatures.
b)Values assume single injection of 25 μL.
c)M = Mallett(1970); SG = Sen Gupta (1973); T3 refers to Table 3 references; S = Sukiman (1976); P = Perushottam, et al. (1972)
d)Aq. reg. = aqua regia; xtn = extraction.
e)1 g/t = 1 ppm = 0.0292 troy-oz/short-ton.
f)Based on 10 g sample and 50 ml final volume.
g)Needs only enough liquid for aspiration.

Table 3. Gold and Silver Extraction Methods

Solvent	Extractant	Aqueous Phases Reported	Metal Extracted	Selected References
MIBK	MIBK-Cl^-	Aqua Regia; 3-8 M HCl; 5% $HCl+HBr+Br_2$; Aqua Regia + permanganate + 3-8 M HCl	Au	Tindall (1965 and 1966), Hall (1979), Greaves (1963)
DIBK Toluene Xylene	DBS	Aqua Regia; 1-3 M HCl	Au	Rubeska, et al. (1977) Parkes and Smith (1979)
MIBK DIBK	TBP	Aqua Regia; 1-8 M HCl 8 M HNO_3	Au	Das and Bhattacharyya (1976)
MIBK DIBK Toluene	TOPO	HCl	Au	Das and Bhattacharyya (1976)
DIBK	TOA	NaCN, Aqua Regia	Au	Groenewald (1968, 1969), Mallett, et al. (1966)
DIBK	TOMA	NaCN, Aqua Regia	Au, Ag	Viets (1978), Groenewald (1968, 1969)
MIBK	Aliquat 336			Tsukahara (1980)
MIBK DIBK	5% TOPO	Aqua Regia + KI + ascorbic acid	Ag	Burke (1974)
MIBK DIBK	30% TOTP	Nitric acid	Ag	Bratzel, et al. (1972)
MIBK Butyl Acetate	0.5% DPT in Acetone	$HClO_4$, HNO_3, AF digest in 20% tartaric acid	Ag	Aruscavage and Campbell (1979)

Aliquot 336 = tricaprylmethylammonium chloride
DBS = dibutyl sulfide
DIBK = disobutyl ketone
DPT = diphenyl thiourea
IAA = isoamyl alcohol
MIBK = methyl sobutyl ketone

TBP = tributyl phosphate
TOA = trioctyl amine
TOMA = tri-n-octyl methyl ammonium chloride
TOPO = tri-n-octyl phosphine oxide
TOTP = triisooctylthiophosphate

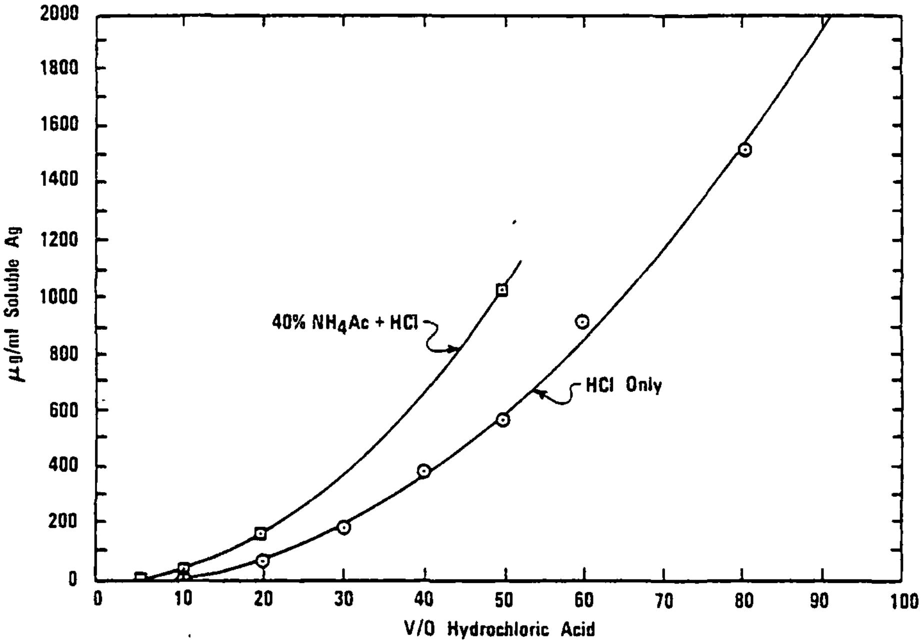

Figure 1. Solubility of silver in HCl—ammonium acetate solutions as determined experimentally

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Gold and Silver Extraction from Sulfide Ores

The allure of gold and silver to the mining industry has become more pronounced in recent years, primarily as a result of exceptionally high prices but also, in part, because of generally uninspiring base metal prices. Finding new ore bodies which are easily amenable to direct gravity and cyanide processing has not been that successful. Many of the newer precious metal ore finds are in sulfide ores, and such ores often present considerable resistance to metal recovery.

Assessment of ore treatment viability of these sulfide ores is difficult, particularly the category of complex sulfides. Such ores are seldom uniform and ore within any particular zone may often require more than one form of process procedure. To develop a process scheme necessitates an understanding of the relationship of ore type of current commercial processes and also of the particular difficulties that can occur in each unit process.

ORE TYPES

From a mineral processing standpoint, it is not possible to group both gold and silver ores together in one classification. Thus, gold and silver ores are grouped separately for the purposes of this discussion although there is some limited overlap of the two groups. Classification of an ore as belonging to either the gold or silver category is dependent on the value of the contained metal in the ore rather than the weight or volume proportion of the respective metals. A listing of ore types is presented in table 1.

Gold ores

A useful classification for gold ores was published by McQuiston and Shoemaker.[1] An abbreviated summary of those categories which apply to sulfide ores follows:

Free gold ores. These are ores in which the gold is in the elemental state and not locked in other sulfide minerals. Part of the gold may be sufficiently coarse to require the application of gravity separation. Cyanidation is normally used in conjunction with gravity separation or, if the precious metals are particularly fine, as the only process of precious metal extraction. Content of sulfides is low (usually less than 2 percent) and generally limited to pyrite.

Gold ores	Silver ores
1) Free gold ores	1) Silver with copper porphyrys
2) Gold with iron sulfides	2) Silver with lead and zinc minerals
3) Gold with arsenic and/or antimony minerals	3) Silver with vein copper minerals
4) Gold tellurides	4) Silver with cobalt and nickel minerals
5) Gold with copper porphyries	5) Silver with minor gold
6) Gold with lead and zinc minerals	
7) Carbonaceous ores	

Table 1. Types of gold and silver ores categorized according to mineralogy and processing method

Gold with iron sulfides. Gold occurs external to and disseminated within sulfides. Some sulfides, particularly pyrrhotite, tend to decompose in solution, consuming cyanide and inhibiting precious metal extraction. Aeration with lime prior to cyanidation is often practiced. Pyritic flotation concentrates are sometimes made and this concentrate may be shipped to a smelter if of very high grade but is more normally reground and cyanided or calcined and cyanided.

Gold with arsenic and/or antimony minerals. The presence of ores containing these minerals usually makes them refractory to direct amalgamation or cyanidation. Treatment requires flotation concentration, roasting and washing of the calcine, followed by cyanidation.

Gold tellurides. These are the only gold minerals, other than metallic gold, that are of economic significance. They usually occur with native gold and with sulfides. The ore or flotation concentrate normally requires some form of oxidation (by roasting or chemical oxidation) prior to cyanidation.

Gold with copper porphyries. Substantial quantities of gold ore are recovered, together with copper, in sulfide concentrates produced from porphyry copper deposits. Contained gold follows the copper through smelting and is recovered during electrolytic refining.

Gold with lead and zinc minerals. As for the previous category, the gold is usually recovered together with sulfide concentrates. In certain instances, however, the flotation tailings are cyanided for additional gold recovery.

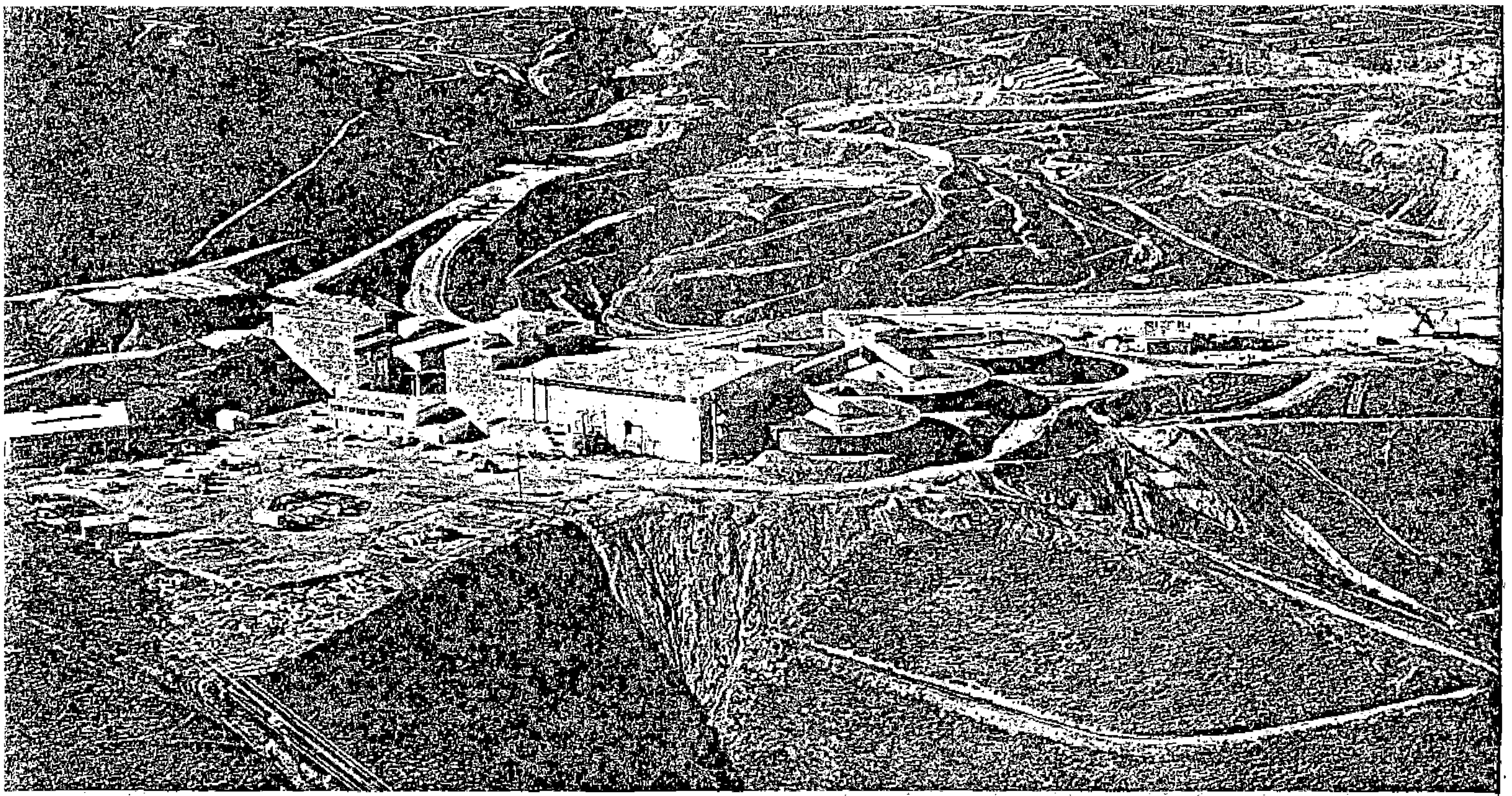
Carbonaceous ores. These ores contain carbon which adsorbs dissolved gold during leaching, resulting in premature precipitation. The gold adsorbed in the carbon is lost to tailings. Such ores also often contain sulfides. Treatment requires oxidation of the ore prior to cyanidation although, in some instances, it is possible to float out the detrimental material and in others to blanket the carbon with light fuel oil.

Silver ores

Most of the world's silver is produced as a by-product of base metal mining and, even when silver is of major economic importance in an ore, it is usually produced in conjunction with base metals. Thus, silver ores frequently constitute complex sulfides in the narrowest definition of this term. Classification of silver ores from a treatment standpoint is thus principally related to metals associated with the silver as indicated in the following listing:

Silver with copper porphyries. These deposits are the major source of silver. Although the silver content of the ores is low, the very large tonnages mined produce large quantities of the metal. Silver minerals are floated along with copper and recovered in smelting and refining.

Silver with lead and zinc minerals. Almost all lead-zinc and copper-lead-zinc ores contain silver. Silver occurs as the na-



Carlin mine of Carlin Gold Mining Co. in Nevada, where pyritic, carbonaceous gold ores are pretreated by slurry oxidation

tive metal, as argentite or a wide variety of sulfo-salts in distinct mineral masses or, more frequently, as argentiferous galena. Silver is recovered by gravity separation and flotation and the concentrates are smelted and refined to extract the silver along with lead and zinc. Flotation tails are sometimes cyanided.

Silver with vein copper minerals. Silver occurs with copper in massive hydrothermal sulfide veins as well as in the disseminated porphyries. Silver in these ores occurs primarily as argentiferous tetrahedrite. The silver is thus produced as a copper-silver flotation concentrate which is sold to smelters.

Silver with cobalt and nickel minerals. Silver in these ores occurs primarily as massive native silver together with arsenic, cobalt, nickel and iron and, occasionally, copper. Processing is by gravity and flotation concentration with subsequent smelting and refining. Flotation tailings are cyanided.

Silver with minor gold. This type of ore usually occurs in the form of low grade disseminated deposits. Silver is generally not associated with base metal sulfides but instead as distinct silver minerals. Total sulfide content of these ores is low. Treatment is by direct cyanidation though recoveries are often poor.

Extraction process depends on ore type

The type of process employed for extracting precious metal from an ore depends on the ore type. However, even when the relationship is clear, it does not follow that the process will be free of difficulties. Processes used for these ores are as follows.

Gravity separation/amalgamation. Generally, gravity separation is included as an adjunct to other processes in the processing of sulfide ores and may be included as a part of any of the listed processes. It is usually applied as part of the grinding circuit and thus is used ahead of any other extraction step. Gravity concentrates are usually amalgamated and retorted. Whenever any proportion of the precious metals occur as free coarse particles, this process is used and so may apply to about any of the ore types listed but is particularly applicable to free gold ores.

Direct cyanidation. The most straightforward process is direct cyanidation and entails simple leaching of the ore in a cyanide slurry after grinding. This can be applied to the low sulfide/free metal ores and to those ores associated with iron sulfides where the precious metals are not locked in pyrite. For some ores minor treatment of the ground ore prior to cyanidation is required, such as preaeration with lime to oxidize and precipitate pyrrhotite.

Oxidation/cyanidation. Oxidation of the entire ore is required prior to cyanidation. Such treatment is required on low sulfide/free metal ores when active carbon or carbon compounds are present in the ore that cannot be inactivated by light oil or easily removed by flotation. The process can also be applied to telluride ores to oxidize these minerals so that the precious metals may be leached by cyanide. The oxidation process employed is an alkaline chlorine slurry reaction and is followed by cyanide leaching.

Flotation/grinding/cyanidation. This system is applied to ores associated with iron sulfides where the precious metals are locked in sulfides. The process is reasonably simple.

Flotation/oxidation/cyanidation. Of all the ore processing systems this is the most complex. It is required for some telluride ores, some of the sulfide ores and for practically all ores containing sulfides in association with arsenic and antimony. With these ores the precious metals are concentrated by flotation and the concentrate is oxidized, almost always by roasting, and the oxidized concentrate is then cyanided. A wash step is generally required between oxidation and cyanidation.

Flotation/smelting. This is the normal practice for ores in which the precious metals are inseparable from base metal sulfides. It is the usual process for most sulfide ores mined principally for silver.

The preceding description of the relationship between processing method and ore type is necessarily an oversimplification. In reality there is considerable overlapping and intercombination of process methods. Problems that can occur in the processing schemes are best discussed in relation to the unit processes involved rather than the particular process scheme used. The unit processes may be listed and classified as follows:

Gravity separation Cyanidation Flotation	Primary extraction processes
Amalgamation Roasting Chlorine oxidation	Ancillary extraction processes
Fire refining Smelting	Metal production processes

The application and problems associated with these processes is discussed in the following paragraphs.

Gravity separation

Gravity separation is rather limited in application and is never used alone in the treatment of sulfide ores. Problems with gravity separation in its application to precious metal ore are the same as occur in its application to any other ore. Fortunately, however, gravity separation in this context need not be concerned with recovery of fine particles since these may be recovered by other processes. Thus, where gravity separation is employed, there are no special problems peculiar to gold not common to other applications of the process except that security precautions are required to protect the high value product from theft.

Cyanidation

It is interesting that the cyanide process came to the fore essentially in its application to sulfide ores on the Witwatersrand.[2] Ores mined initially on this gold field were the upper oxidized portions of the reef which were easily amenable to gravity and amalgam treatment. As mining progressed to lower levels, gold recoveries fell. The deeper ores were found to be successively less oxidized and, with increasing depth, were found impossible to process. To some extent the chlorination process was used on the deep ores but recoveries were erratic and operating expenses high. Fortunately, the cyanide process became known just in time and was found to work remarkably well, giving consistently good recoveries and reasonable operating costs.

Although the cyanide process works well on Witwatersrand ores and on many other sulfide ores it cannot be universally applied. This is the cause of much frustration. The problems that occur in cyanidation are as follows.

- Locking of precious metals so that cyanide solutions cannot penetrate and dissolve the precious metals.
- Existence, or formation during leaching, of strongly adherent films on the surface of native gold and silver, inhibiting or preventing further dissolution of the metals.
- High cyanide consumption which is often accompanied by high lime consumption.
- Long leach time required because of very slow reaction of precious metal minerals with cyanide.
- Leach solution fouling, rendering it inactive for precious metal dissolution and often giving difficulties in metal precipitation from pregnant solution.
- Readsorption or reprecipitation of precious metal from solution after initial dissolution.
- Toxic arsine gas formation on precipitating precious metal from pregnant solution.

Flotation

Flotation is frequently used for complex sulfide ores of precious metals. Where precious metals occur as minor values in base metal mines, they are recovered by flotation together with base metal sulfides. Flotation is almost universally used for processing ores where silver is the metal of principal value, and such concentrates are subsequently treated by smelting. There are also many plants, where gold is the metal of principal value, that use flotation but such concentrates are seldom smelted directly. Where gold is concentrated by flotation, the concentrate is usually too low in value to ship to a smelter and it is more often further processed at the mine site.

Serious difficulties are seldom encountered in flotation recovery of silver in sulfide ores but with gold the following problems can be encountered:

- Low precious metal recovery into concentrate.
- High bulk and low concentrate grade. Attempts to clean the concentrate through reflotation are often not successful.
- Poor flotation selectivity. Unwanted sulfides and associated minerals are recovered with precious metal bearing minerals.

Amalgamation

Amalgamation of raw sulfide ores has gradually diminished and is now seldom used. Use of amalgamation for the whole ore necessitates the application of amalgam plates which is a very labor intensive process, easily subject to theft. Plate amalgamation also results in mercury losses and consequent environmental problems. Particularly with sulfide ores, "sickening" of the plates can be a serious problem. Where amalgamation is presently used it is applied as batch treatment of gravity concentrates. With batch treatment it is easy to modify the process to minimize difficulties. However, special problems related to the mineralogy of the material treated do occur, including:

- Locking of gold and silver so that it is not exposed to the mercury.
- Tarnishing or surface coating of the precious metals so that it cannot be wetted by mercury.

Roasting

Roasting is a process of last resort in the treatment of precious metal ores. It is a process of many difficulties but, in some instances, it is the only alternative available. Roasting is now usually done in fluo-solid roasters but multiple hearth and Edwards roasters, in particular, have been extensively used in the past. Roasting is usually applied to flotation concentrates and results in oxidation or volatilization of harmful components and, in the case of ores where locking in pyrite is a problem, renders the pyrite porous so that subsequent cyanidation of the calcine will give good recovery of the gold.

Problems with roasting are not all strictly technical. Some severe problems are related to compliance with environmental pollution regulations. Relevant problems are listed below:

- Clinkering or fusing of the calcine. This can cause plugging of the roaster and also results in poor metal recovery from the calcine.
- Silver recovery after roasting is usually worse than that obtained by direct cyanidation.
- Sulfur dioxide is given off by the roaster. The gas concentration is seldom high enough to warrant making sulfuric acid. In some areas environmental regulations will not permit discharge of the gas.
- Arsenic trioxide is volatilized and collected from the gas stream. Disposal of the arsenic collected may be a problem, again as a result of pollution regulations.
- Control of reducing/oxidizing conditions within the roaster and of operating temperature is critical. The required parameters are also different in different zones of the roaster. To obtain close control is difficult, requiring very uniform feed assay and size consistency and skilled furnace operation.

Chlorine oxidation

Chlorine oxidation is used to oxidize carbon or carbon compounds in the ore which would otherwise adsorb precious metal from solution in the leach circuit. Chlorine is also used to oxidize gold and silver tellurides so that they will become amenable to cyanidation. The form of chlorine used for oxidation is based on cost. The forms in current use are chlorine gas and calcium hypochlorite. In some instances, chlorine oxidation is practiced for the whole ore and, in others, on flotation concentrates. It is also possible to use other forms of strong chemical oxidants, such as hydrogen peroxide or ozone, but these are more expensive than chlorine and are therefore not used commercially.

Problems that can occur with chlorine oxidation are:

- High chlorine consumption, particularly if substantial quantities of sulfide are present.
- High lime consumption, which is related to the preceeding item, in that oxidation of sulfides results in the formation of sulfuric acid which consumes lime.
- Chlorine will solubilize components of the ore which can result in fouling of the solution and difficulties in precipitation of precious metals.
- If base metals are dissolved by the chlorine, they will be cemented out of solution in zinc precipitation and result in difficulty in obtaining acceptable dore fineness when refining the precipitate.

Fire refining

Treatment of retorted amalgam and zinc precipitate from processing of complex sulfide ores to extract marketable metal is done by fire refining, which is essentially a smelting process on a small scale. Material recovered from the treatment of sulfide ores usually contains impurities which interfere with the fire refining process. Where impurities in zinc precipitate cause serious difficulties, it is possible to minimize the problem by acid leaching and/or calcining the material prior to refining. However, even with such treatment, it is sometimes not possible to produce bullion of high purity and slags of low precious metal content. Problems that occur in fire refining are:

- Low bullion purity.
- High precious metal losses in slags.
- Evolution of mercury vapour.

Smelting

Smelting is a subject of its own and peculiarities of this topic will not be dealt with at length here. Smelter recoveries of both gold and silver from concentrates are excellent. Some impurities in the concentrates do result in heavy penalties, however. In some instances it may be worth removing such impurities from the concentrate prior to shipment to a smelter. Accompanying metals will affect whether the concentrate is sent to a lead smelter or a copper smelter.

Difficulties with impurities in smelting may be grouped in the following categories:

- Most toxic substances are taken into the gas phase in smelting and recovery and disposal of these is difficult.
- Certain elements are recovered in the metal phase and give rise to difficulties in subsequent refining.

MINERALOGY

Having an understanding of ore types and processes, it is now possible to proceed to discuss the steps of mineralogical examination and ore testing that are required to develop a process for any particular mineral deposit.

Cyanidation plant at Pueblo Viejo mine in Dominican Republic. Facility was designd to treat 8000 tpd of gold and silver bearing oxide ores

Prior to any mineralogical examination of an ore, it should be assayed for elements of gangue components that may result in treatment problems in addition to those elements of economic significance. Normally, analysis of the elements listed below will be required:

Metallic elements			Amphoteric and nonmetallic elements		
Fe	Co	Ni	C		
Au	Ag	Hg	As	Sb	Bi
Cu	Pb	Zn	S	Se	Te

The analyses mentioned are best done for a number of samples from different locations within the ore body so that an idea of how pervasive the elements of concern are in the ore body.

Using the analyses, together with macroinspection of ore samples, it will be possible to roughly determine the form of sulfide and sulfo-salt minerals present. Generally, most of the metallic minerals are sulfides and arsenides and it is possible to roughly ascertain the form of these minerals from the stochiometric ratios of the elements determined in the chemical analysis. A listing of the more common sulfide minerals of concern in processing these ores is presented in table 2.

To further define the ore mineralogy, it is necessary to prepare polished sections for microscopic examination. The making of thin sections is not necessary except for exhaustive evaluations. The prepared sections are then examined with an optical microscope which will show the relationship between various minerals present. Of particular interest are inclusions and intergrowths.

To define the precious metal mineralogy, it is usually worthwhile, although sometimes not too successful, to physically concentrate the precious metals into a product for mineralogical examination. This may be done by flotation and by heavy liquid separation. The concentrate is then mounted in a plastic medium and polished sections prepared. Where the precious metals are relatively coarse, it may be possible to see them using an optical microscope. Should it not be possible to find the precious metals with an optical microscope it will be necessary to use an electron microscope/microprobe unit.

Gold content of ores is generally less than one part per million in terms of volume and to find it microscopically is difficult even using the best electron microscope/microprobe units available. To obtain a fair idea of the precious metals mineralogy requires persistence and takes a considerable amount of time and money. At times knowledge of such mineralogy may be of academic interest only, particularly if there are no serious problems in processing the ore and, in such cases, it is probably not worthwhile doing a very thorough investigation.

Relating ore mineralogy to process problems, mineralogical factors contributing to these problems may be grouped in the following categories:

- Locking of precious metals within sulfide minerals.
- Existence of tarnish or coatings on elemental precious metals.
- Presence of iron and base metal sulfides.
- Presence of arsenic, antimony and bismuth minerals.
- Occurrence of precious metal selenides and tellurides.
- Presence of carbon.

Each of these categories is discussed in detail below.

Locking of precious metals within sulfide minerals

This is one of the most frequently encountered problems, particularly of gold within pyrite. Using optical microscopes it

	Elemental	Sulfides	Arsenides	Antimonides	Selenides	Tellurides
Iron		FeS pyrrhotite FeS_2 pyrite/ marcasite	FeAsS arsenopyrite			
Cobalt			CoAsS cobaltite			
Nickel		$(Fe, Ni)_9S_8$ pentlandite				
Gold	Au native gold Au, Ag electrum			$AuSb_2$ aurostibite		$AuTe_2$ krennerite/ calaverite
Silver	Ag native silver Ag, Au electrum	Ag_2S argentite (Pb, Ag)S argentiferous galena	Ag_3AsS_3 proustite $(Cu, Fe, Ag)As_4S_{13}$ argentiferous tennantite	Ag_3SbS_3 pyrargyrite $(Cu, Fe, Ag)Sb_4S_{13}$ argentiferous tetrahedrite	Ag_2Se naumannite	Ag_2Te hessite
Mercury		HgS cinnabar				
Copper	Cu native copper	Cu_2S chalcocite CuS covellite Cu_5FeS_4 bornite $CuFeS_2$ chalcopyrite	Cu_3AsS_4 enargite $(Cu, Fe)As_4S_{13}$ tennantite	$(Cu, Fe)Sb_4S_{13}$ tetrahedrite		
Lead		PbS galena				
Zinc		ZnS sphallerite				
Carbon	C graphite/ amorphous C					
Arsenic		AsS realgar As_2S_3 orpiment				
Antimony		Sb_2S_3 stibnite				
Bismuth	Bi native bismith	Bi_2S_3 bismuthinite				Bi_2Te_2S tetradymite

Table 2. Common and important minerals associated with precious metals in sulfide ores

is frequently impossible to see any gold within the pyrite although assays definitely show it to be present. This has often led to the conjecture that gold occurs in solid solution in pyrite. Whether this does, in fact, occur is not of such vital concern in processing. Where gold is so fine that it cannot be seen microscopically obviously precludes grinding for liberation. The reason for the very frequent association of gold and pyrite occurs because of the cotectic precipitation of gold and pyrite from hydrothermal solutions, as explained by Helgeson and Garrels.[3] Where gold occurs in other sulfide minerals, the inclusions are usually larger and locking is not such a serious problem.

Locking of silver within sulfide minerals is frequent; in fact, most silver produced is mined as argentiferous lead and copper sulfides (primarily argentiferous galena and argentiferous chalcopyrite, tetrahedrite or tennantite). Very rarely silver occurs in sphalerite, or in pyrite, except for the relatively small portion that generally accompanies gold in such instances. The silver in the argentiferous lead and copper minerals is often in such intimate association with the base metal sulfides that they cannot be separated by mineral processing methods. However, this is not a problem since a reasonable smelter return is obtained for contained silver in such concentrates.

Locking of precious metals also occurs within minerals other than sulfides. Gold, for instance, is sometimes found locked in quartz though it is generally not as serious as the locking in sulfide minerals.

Where locking is limited, it may be dealt with by fine grinding, particularly if it is possible to concentrate the precious metals. Where locking is severe, oxidation is necessary, normally by roasting.

Tarnish or coatings on elemental precious metals

The existence of surface coatings on gold and silver particles is difficult to determine, particularly where the metal particles are extremely fine. In amalgamation, coatings may prevent wetting of the precious metals by mercury but the relatively coarse size of gold submitted to amalgamation is such that grinding can usually adequately clean the metal surface for efficient extraction. Cyaniding of ores containing coated precious metals generally results in requiring longer leach times rather than precluding the use of the process. Pretreatment of such ores with various chemicals, particularly acids, can usually overcome the difficulty. Where flotation of free gold and silver is practiced, coatings can interfere and impair the efficiency of the process. As for cyanidation, chemical removal of the coatings prior to the process may be required.

Presence of iron and base metal sulfides

Amalgamation, where iron and base metal sulfides are present, often results in some flouring and sickening of the mercury. However, in batch treatment this can be controlled by fine pregrinding of the concentrate with lime or other alkali and, in some instances, by addition of oxidizing agents prior to amalgamation. Cyanidation of ores containing a small proportion (2 percent or less) of iron and base metal sulfides is generally no problem. However, at greater concentrations considerable difficulties can occur. Frequently such ores cannot be cyanided directly. To do so results in high cyanide and lime consumption, particularly where copper sulfides are present. The dissolved copper is a further problem in that it can inhibit dissolution of the precious metals and in that it is precipitated with them in zinc cementation, constituting an impurity which is difficult to remove in fire refining. Mercury sulfides can be a problem, not because of cyanide consumption or effect on precious metal extraction, but because the mercury is precipitated in zinc cementation and constitutes a toxic impurity in the precipitate.

Lead and zinc sulfides are not particularly deleterious, nor, generally, is pyrite. The other iron sulfides, marcasite and pyrrhotite, however, result in high reagent consumption. The marcasite and pyrrhotite present in an ore can usually be rendered innocuous by aerating the ground slurry with lime prior to cyanidation. If base metals are present the precious metals may be conveniently concentrated by flotation with the base metals for sale to a smelter.

Where little base metals are present, and it is necessary to concentrate precious metals through pyrite flotation, recoveries are often poor and concentrate grades low. These difficulties may be related to the mineralogy of the ore as a consequence of the precious metals being contained in very fine pyrite which is not easily floated or because the pyrite content of the ore is so high that the ratio of concentration is low. The ore may also contain nonprecious metal bearing pyrite which dilutes the grade of the concentrate.

Presence of arsenic, antimony, and bismuth minerals

Whenever these minerals are present, particularly as their simple sulfides, processing problems are likely to result. Direct amalgamation of native gold and silver in the presence of arsenic, antimony or bismuth sulfides is generally impossible. To do so usually results in serious sickening and flouring of the mercury, substantial losses of mercury and poor precious metal recoveries.

Cyanidation of ores containing arsenic and antimony minerals is usually a problem. Association of gold with arsenopyrite, in particular, is relatively common. While gold occurs in the elemental form in association with and as inclusions in arsenic, antimony and other sulfide minerals, silver often occurs chemically combined with arsenic and antimony to form important ore minerals known as ruby silver.

The precise effect of arsenic and antimony minerals in cyanidation is not fully understood. Some contend that the presence of these minerals results in the formation of a coating on gold particles, preventing dissolution; and others that the minerals oxidizing in the slurry so reduce the oxygen content that cyanidation cannot occur. On precipitating solutions containing arsenic, arsine gas is formed and must be considered in design of plants treating arsenic containing ores. Where these minerals are present it is usually necessary to roast the ore prior to cyanidation. Roasting ores containing antimony can be troublesome because the presence of these minerals results in partial fusion of the charge causing clinker formation and, if not controlled, plugging of the furnaces. A further problem with arsenic and antimony minerals is that their presence in cyanide solutions interferes with the precipitation of precious metals from the solution.

Where flotation concentrates are made for shipment to a smelter, the presence of arsenic, antimony or bismuth generally results in substantial smelter penalties. in such instances it may be worthwhile extracting the antimony by leaching with alkaline sodium sulfide prior to shipment to the smelter.

Occurrence of precious metal selenides and tellurides

Although there are no naturally occurring gold selenides, elemental gold and gold tellurides are occasionally found with selenium minerals, generally in association with other sulfides. As with the arsenic-antimony-bismuth group, silver forms certain silver-selenium minerals. Except where other deleterious minerals are present, ores containing selenium present no particular problems in amalgamation and cyanidation except for higher than normal cyanide consumption because of the formation of selenium-cyanides and, in some instances, the selenium is cemented out of solution in zinc precipitation and may report as an impurity in the final metal product.

Gold, silver and tellurium form a ternary sequence of minerals, and gold/silver telluride minerals are more common in precious metal deposits than is generally realized. These telluride minerals are also often found locked as fine dispersions within sulfide minerals in the same way as the elemental forms of the precious metals. Telluride minerals need to be oxidized before they may be cyanided. Some telluride ores are faster oxidizing than others, which is probably related to the particular telluride minerals present and to the particular size of the minerals. Thus, some telluride ores may be oxidized and cyanided simultaneously while others oxidize so slowly that prior chemical oxidation or roasting is required to render them amenable to cyanidation. For some ores it is worthwhile concentrating the precious metals by flotation before further treatment. This can present difficulties because of locking of tellurides in other minerals and, where tellurides are free, because of overgrinding. (Tellurides are very soft, generally in the range of $1^1/_2$ to 3 on Mohs' hardness scale.)

Presence of carbon

Carbon in the ore can be determined by direct analysis, although it is often difficult to obtain consistent assays from different laboratories, particularly where it is present to the level of a few percent. Carbon analyses are presented in a confusing variety of forms including total carbon, organic carbon, inorganic carbon, mineral carbon and carbon as carbonates. Essentially, inorganic carbon, mineral carbon and carbon as carbonates mean the same thing. Elemental carbon and hydrocarbons are reported as organic carbon (i.e., total carbon minus the forms previously mentioned). It is sometimes worthwhile to also determine the humic acid content of the ore (which constitutes part of the organic carbon) since humic acids can, apart from reducing metal recovery in the same way as elemental carbon, have additional effects in ore processing. Carbon analysis is, however, not a positive indication of problems; some forms of organic carbon may be present in the ore without any resulting ill effect.

Where carbon is present, particularly in the form of graphite, it results in difficulties in amalgamation. The graphite tends to collect at the mercury surface, sickening the amalgam. In some instances it is possible to float it from the ore prior to amalgamation.

In cyanidation the presence of carbon may result in adsorption of dissolved precious metals from solution. This property is the basis of cyanide extraction processes using commercially prepared activated charcoal. As for amalgamation, it is sometimes possible to float the carbon from the ore prior to extraction of the precious metals. Where flotation of the carbon does not work, it is possible to counteract the deleterious effect of the material by oxidizing the ore with chlorine in a slurry or by roasting ahead of cyanidation. With some ores it is possible to mitigate the effect of carbon through addition of a light oil such as kerosene which coats the surface of carbon particles. Where humic acids occur in an ore they can adsorb gold from solution and then adsorb onto lime particles in the slurry, effectively reducing recovery. Humic acids also react with some flocculants to form a gum which can plug solution filters and precipitate presses.

ORE TESTING

Following the mineralogical examination of an ore it will be evident what problems are likely to occur in processing. The first step in developing a processing technique is to try simple gravity separation, cyanidation and flotation tests. Should these give reasonable recovery it is then a matter of optimizing conditions to maximize recovery. If a gravity or flotation concentrate is made, the treatment of the concentrate will require additional investigation.

Should the initial tests not give acceptable metal recovery it may be worthwhile conducting a comprehensive test program. Such a program should be arranged to briefly test as wide a variety of methods as possible before investigating any in depth. These tests may be grouped under four major headings, as follows: Chemical pretreatment, oxidation, physical processing and solvents other than cyanide.

These tests are briefly described below. Detail test parameters are not given since particular conditions such as reagent quantities, temperature, time, etc. are closely related to the type of ore tested. However, in initial testing of these methods it is worthwhile being on the generous side when setting reagent quantities.

Chemical pretreatment

These tests involve the treatment of the ground ore with a variety of different chemicals that may make the precious metals amenable to processing in one or more of the following ways:

Precipitation of harmful dissolved components
Removal of coatings on the surface of gold particles
Coating or loading the adsorption sites on active carbon

Evaluation of the effectiveness of chemical pretreatment is done by treating the ground ore slurry separately with each of the following reagents prior to cyanidation:

Lime with air
Sulfuric acid
Ammonium chloride
Sodium sulfide
Lead nitrate
Kerosene
Wetting agents (e.g. Aerosol OT)
Carbon adsorbed chemicals (e.g. phenol, iodine)

Following chemical pretreatment the ore should be given a standard cyanide test. It may be advantageous to filter the pulp and wash the filter cake prior to cyanidation, particularly where sulfuric acid is used, but, for initial testing of this procedure, it is acceptable to go directly to cyanidation as long as the pH is made alkaline prior to cyanide addition.

Oxidation

Oxidation of an ore or concentrate may be done in either of two basic ways, either by addition of oxidants to a slurry or by roasting.

Pouring gold bars at a South African refinery

Where the material is oxidized as a slurry, possible forms of oxidation may be classified as indicated below:

Pressure oxidation
  —using air
  —using oxygen
Atmospheric oxidation with chemical oxidants
  —permanganate and manganese dioxide
  —chlorate, hypochlorite, salt electrolysis or chlorine gas
  —nitric acid
  —Persulfates
  —Hydrogen and sodium peroxides
  —Ozone gas

The slurry should always be filtered and washed after an oxidation step. The cake is then subjected to a standard cyanidation test.

Roasting the ore may also be done in a number of ways. The principal basic alternatives are:

Straight oxidation roast
Reducing roast followed by oxidation roast
Salt roasting (adding sodium chloride)

With roasting tests, the latitude for variation in experimental parameters is wider than for most other tests; it is also generally more difficult to obtain repeatable data. Extensive studies on roasting of gold ores have shown that the optimum temperature is in the range of 550 to 600° C and this should be used in initial testing of any of the forms of roasting listed. After roasting the ore should be pulped with water, filtered and washed. The washed cake is then cyanided.

Physical processing

This group of tests involves physical separation of ore through standard mineral processing methods. Methods that should be tested are:

Fine grinding
Gravity separation
Amalgamation
Flotation
Rapid leaching and solution transfer
Carbon-in-pulp and resin-in-pulp
Magnetic separation

A standard grind for the test procedures given is generally around 70 percent minus 200 mesh, about average for most cyanide processing. However, to check whether particle size may be a factor in processing the ore, a grind series of three sequentially finer grinds should be made and cyanided.

For gravity separation the ground ore may be hand panned or treated on a laboratory vanning unit. With this and other physical process tests the respective products should be assayed and, if the bulk is sufficient, separately cyanided.

To test for amalgamation the ore should first be ground with lime and then with mercury in a laboratory mill to amalgamate any free precious metals. The amalgam and free mercury are separated from the ore by hydraulic separation and then retorted and assayed. The remaining material is assayed and cyanided.

Although flotation provides a wide diversity of procedures, it is not practical to test more than a few in initial testing of the ore. Flotation tests that should be included are a simple oil flotation to remove carbonaceous materials and a simple xanthate float to separate sulfides. The flotation concentrate and nonfloat product should be separately assayed and cyanided.

Because certain components in some ores can cause adsorption or precipitation of precious metal values dissolved during cyanidation, it is worthwile testing the effect of a series of short duration cyanidation periods followed by rapid solution removal. This may be tested in the laboratory by keeping the cyanidation period to 1/2 hour or less followed by filtration of the pulp; the filter cake is then repulped and cyanide leached following the initial procedure and so on for perhaps four stages. Assay of solution and final solids will give an indication of the efficiency of this procedure.

The rationale for using carbon-in-pulp or resin-in-pulp where the ore is refractory to direct cyanidation is that carbon and resins can rapidly adsorb dissolved precious metal values from solution before other substances in the pulp have an opportunity to adsorb or precipitate them. For these tests the ore is ground substantially finer than the resin or carbon used and standard cyanidation tests are then done on the slurry to which the resin or carbon is added. After leaching, the resin or carbon is removed by screening; it is then dried, ashed and assayed. The remaining solution and solids are assayed as for normal cyanide tests.

The last listed physical process to be tested on the ore is magnetic separation. This should be tested in a laboratory WHIMS (wet, high intensity magnetic separation) unit. As for the other tests, both products should be assayed and subjected to standard cyanidation tests.

Solvents other than cyanide

In the commercial leaching of gold and silver ores, no solvents other than cyanide are presently used. It generally appears that if cyanide will not leach the precious metals from the ore, other solvents are even less effective. However, there have been some reports to the contrary, so, if an ore does not respond well to simple cyanidation, it is worth trying them. Solvents that have been shown to dissolve gold and silver are:

Bromocyanide
Chlorine (as a gas or various chlorine compounds)
Thiourea
Malanonitrile
Acetone cyanohydrin
Ammonium thiophosphate
Ammonium thiosulfate
Ammonium monosulfide
Calcium cyanamide

As for cyanide, these reagents have an optimum pH band of operation. Testing is done using the standard bottle roll leach procedure used for cyanidation.

CONCLUSION

Development of metallurgical treatment processes for sulfide precious metal ores can be difficult, expensive and time consuming. Some ores of good grade prove uneconomic to treat and, for others, attainable recoveries are dissapointingly low. Often relatively complex process systems are required.

However, where the investigation of ore treatment is approached logically and thoroughly and with a good understanding of interrelating factors, the chances of developing a viable process for most ores is reasonably good. As with many endeavors, rewards are commensurate with effort, and the rewards, particularly from the processing of precious metal ores, can be very worthwhile.

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Hydrofluoric Acid Stimulation of Sandstone Reservoirs

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ABSTRACT

Hydrofluoric-hydrochloric acid mixtures have been successfully used to stimulate sandstone reservoirs for a number of years. Hydrofluoric acid (HF) has a specific reactivity with silica which makes it more effective than HCl for use in sandstone. Kinetics of the reactions of HF have been studied to determine the related effects of reservoir composition, temperature, acid concentration and pressure on the spending rate of HF. Secondary effects from by-product formation are noted and described. Predictions are made concerning the improvement in productivity resulting from HF treatment of skin damage.

The kinetic order of HF reaction in sandstone was experimentally determined to be first order, i.e., the reaction rate is proportional to concentration. HF reacts faster on calcite than on clay, which, in turn, is faster than the reaction rate of HF on sand. Static conditions retard the HF reaction rate. As HF is forced into cores, there is a temporary reduction as a function of flow rate and acid concentration.

Extensive deposition of calcium fluoride in acidized cores was not observed. Although some CaF_2 was detected, it was not considered a major source of damage in cores containing moderate amounts of carbonate. Other fluosilicates could be potentially more dangerous than CaF_2 in reducing permeability.

INTRODUCTION

Hydrofluoric acid has been widely used in stimulation treatments since 1935, when mud acid was introduced to the petroleum industry. Originally, this hydrochloric-hydrofluoric acid mixture was intended to remove mud filter cake, but it has since been successfully applied to many other oilfield problems. Mud acid treatments have been unusually successful in sandstone reservoirs where hydrochloric acid is unreactive due to a lack of enough calcite in the formation. The relatively small amount of hydrofluoric acid present (2.1 per cent) reacts with sand grains, clays and traces of calcite which are generally present in sandstone reservoirs. Since hydrofluoric acid (HF) is the key to mud acid success, this research effort has been dedicated to gaining a more thorough understanding of the basic chemical and physical principles involved as HF reacts.

Hydrofluoric acid's reactivity with silica makes it unique in application. Other mineral acids such as hydrochloric, sulfuric or nitric are unreactive with most silicious materials which comprise sandstone formations. A typical sandstone reservoir may contain 50 to 85 per cent silicon dioxide, more commonly called sand or quartz. Hydrofluoric acid reacts as follows:

$$4HF + SiO_2 \rightarrow SiF_4 \uparrow + 2H_2O$$

The silicon tetrafluoride (SiF_4) is a soluble gas, in some ways similar to CO_2, and is capable of undergoing further reaction when held in solution by pressure. These reactions will be considered in detail later.

Kinetics of the reactions of HF have been studied to determine the effect of reservoir composition, temperature and pressure on the spending of the acid. Secondary effects from by-product formation have been noted and described. The individual reactions of HF on quartz, glass and clay are reported. Mathematical correlations have been drawn, then applied to studies of HF spending in cores obtained from actual producing sandstone formations. The research reported herein is only the beginning of a continuing approach to better understanding and use of HF in petroleum reservoirs.

THEORY AND DEFINITIONS

Through the years, a concentrated effort has been made to understand the effects of many variables on hydrochloric acid (HCl) spending in limestone. Hendrickson *et al.*, have given mathematical relationships for HCl reactions which made possible the engineered approach to acidizing.[1] The same variables—temperature, acid concentration, formation composition, pressure and permeability-porosity relationships—which affect HCl behavior in limestone also govern HF behavior in sandstone. Insoluble by-products of HF reaction have been isolated and identified. Their effect on fluid flow has been measured under varying conditions in an attempt to evaluate the extent of possible damage and means of eliminating it.

In general, HF follows the same reaction paths as HCl. It will react with limestone and dolomite with speed and ease. Thin sections of acidized cores show the reaction of HF with limestone or calcite faster than its reaction with either clay or sand. When HF reacts with calcite ($CaCO_3$), theoretically, calcium fluoride (CaF_2) is precipitated, and has been blamed as a major cause of reduced permeability. On the other hand, pH and pressure such as that encountered in an underground formation under acid treatment definitely retard CaF_2 formation,[2] so the whole question of CaF_2 deposition in wells is a subject for study.

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[1] References given at end of paper.

While HF and HCl have equal affinity for reaction with calcite, HCl is more highly ionized and will be spent at a faster rate than HF. Since calcite is a minor constituent of most sandstone, this means that adding HCl with, or before, HF will greatly reduce HF spending on calcite where HCl could just as effectively do the job. HCl is a most effective spearhead for HF, because it reacts quickly with the calcite and thus exposes clay in the formation for the selective reaction with HF.

Once calcite is reacted, the HF will spend in clay and sand. The relationship involving clay deposition and total area now becomes quite important in determining the relative amount of clay to be dissolved. Under optimum conditions, 350 lb of clay (drilling mud) will be dissolved by 1,000 gal of acid containing 2.1 per cent HF.[3] However, since some of the HF can react on calcite and sand in the rock matrix, the amount of clay actually dissolved is a function of clay location and concentration.

Natural clays, such as illite and montmorillonite, are either located interstitially between sand grains in flow channels or in stringers. If the clay is uniformly deposited in flow channels, it may be attacked by HF. While the acid would attack both sand and clay, the attack on clay would be faster than the reaction with sand. However, since there may be a much larger surface area of sand present, only about half of the acid could be spent on the clay, while the remainder was reacting with the sand grains. The clay and acid must be in intimate contact before reaction can take place. Since damage to flow can result from clay swelling in flow channels, it is quite evident that reaction and removal of these clays (usually less than 10 per cent by weight) is sufficient to give large increases in permeability.

Again, when considering the flow of acid into a reservoir, it is important to determine the existence of major flow channels. These channels are related to the pore size distribution within the reservoir. The effect of pore size on flow distribution has been reported in the literature by several authors.[4-6] For example, assume a sandstone matrix may have the pore size distribution in Table 1.

Hence, 75 per cent of the fluid is flowing through 15 per cent of the rock. If those channels are open, adequate production will result. If damage exists in these critical areas, even though they represent only 15 per cent of the rock, there will be a large reduction in permeability, and productivity will be low. These factors must also be considered as an integral part of the approach to matrix acidizing.

The flow of fluid in a rock matrix has been a major subject of study in reservoir engineering for many years. An application of the principles of fluid flow to acidizing has been made by Hendrickson, Hurst and Wieland.[7] Principles of HF acidizing are closely related to those of HCl in limestone. The areas of reaction are most important. Skin damage is frequently the major source of production failure in new wells. This problem is the result of plugged flow channels in the area surrounding the wellbore. The area can range from fractions of an inch to several feet in diameter.

Damage is a function of the natural permeability allowing the forceful encroachment of drilling mud, cement filtrate and other solids and fluids added in the course of drilling and workover operations. In production, skin damage acts as a tight collar around the wellbore and reduces delivery rate of fluid or gas into the borehole. Damage from naturally occurring fines and clay within the matrix may also be subject to HF treatment. Building a skin from injection fluids or migration of fluids and solids in the course of production may also cause a skin effect subject to treatment. Hydraulic fracturing offers a means of overcoming skin damage in some cases, but treatment with HF offers increased production at generally reduced cost. A new technique of matrix treatment using HF acid is outlined in a recent paper by Ross, Pierson and Coulter.[8] Skin damage treatments with HF are especially effective in formations which are not subject to good fracture treatments or to fracture pressure requirements.

TABLE 1

Diameter of Pore	Pore Volume (%)	Flow Through These Pores (% of Total Flow)
Less than 1 micron	60	10
1 to 2 microns	25	15
2 to 5 microns	12	30
5 microns and above	3	45

The actual increase which may be expected by removing damage to restore permeability to the original or greater value is illustrated in Fig. 1, and can be determined by the equation:

$$\frac{Q_x}{Q_o} = \frac{\log \frac{r_e}{r_w}}{\frac{k_e}{k_x} \log \frac{r_x}{r_w} + \log \frac{r_e}{r_x}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q_x = flow rate in altered state
Q_o = flow rate in original state
r_e = radius of effective reservoir
r_x = radius of permeability change
r_w = radius of wellbore
k_e = reservoir permeability
k_x = altered permeability.

The decreasing effect of a 3-in. damage collar on productivity at increasing distances from the wellbore is illustrated in Fig. 2. The effect of such a restriction is greatest at the wellbore.

VARIABLES AFFECTING HF REACTIONS

Extensive studies have been conducted to evaluate the variables which affect the reaction rate of HF with a formation rock. This information is necessary for predicting the effectiveness of a particular treatment and selecting the optimum treating conditions.

As HF is forced into a sandstone matrix, there are three major paths of reaction open. The first is the previously described HF reaction with calcite. The reaction is analogous to spending of HCl in limestone and is a first-order

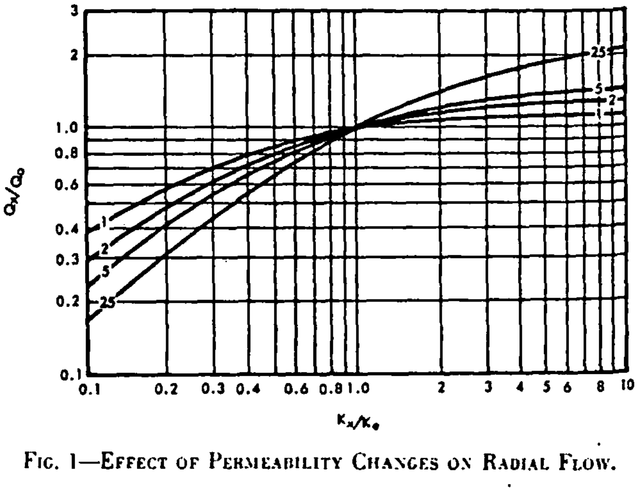

FIG. 1—EFFECT OF PERMEABILITY CHANGES ON RADIAL FLOW.

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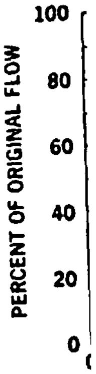

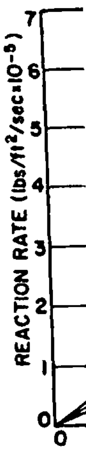

reaction. More important, HF is also capable of chemical reaction with clays and sand. These are the reactions that give HF its utility over HCl in sandstone reservoirs.

Some of the basic factors which control the relative reaction rates of HF within the matrix are temperature, concentration of acid, chemical composition of the matrix, pressure, and the area-volume ratio of the rock to the acid. Each of these factors will be considered independently to pinpoint the effect of the controlling variables and their contribution to over-all reaction rate. Experimental studies were conducted using glass and quartz slides to determine the relative reaction rates of HF with sand (represented by quartz) and with clay (represented by the flat drawn glass).

EFFECT OF TEMPERATURE

HF concentrations ranging from 2.1 per cent to maximum of 8.4 per cent were studied to determine the effect of temperature on the basic reaction rate. The results of these tests on glass slides are shown in Fig. 3. The amount of reaction taking place at the end of two hours at 80F is approximately one half of that reaction taking place at 125F. Likewise, the incremental reaction taking place at 175F is twice that of the reaction at 125F. This shows the dependence of reaction rate on temperature. Duplicate reaction conditions using quartz showed a similar increase in reactivity with temperature. Addition of excess HCl had no measurable effect on the reaction rate with either quartz or glass. Likewise, there was no significant difference in reaction rate if the HF solutions were prepared from the reaction of HCl with ammonium bifluoride or if the HF was simply diluted from a more concentrated solution.

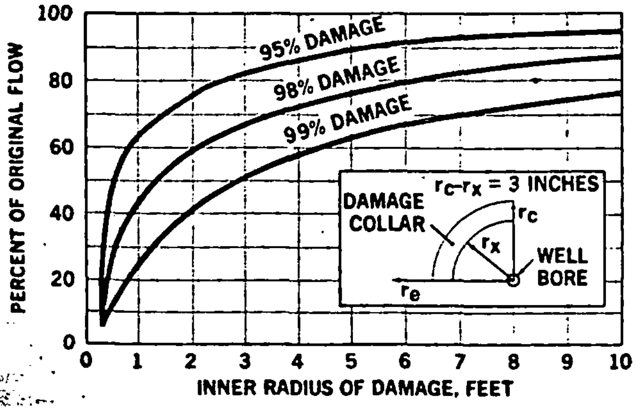

Fig. 2—Effect of Shifting Damage Collar.

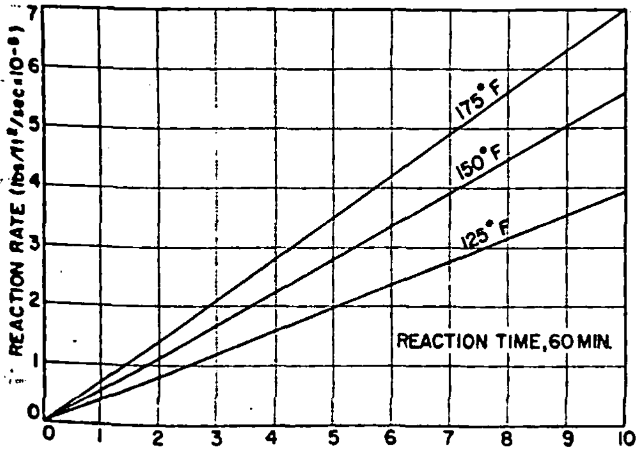

Fig. 3—Reaction Rate of HCl-HF on Glass.

EFFECT OF CONCENTRATION

The effect of concentration on reaction rate is shown in Fig. 4. As the concentration of HF is raised from 2.1 per cent to 4.2 per cent, the increase in reaction rate with glass is approximately double, regardless of temperature.

In Fig. 5, the comparative reaction rate vs time is plotted as 8.4 per cent. HF reacts and is reduced to one half of its original concentration. At half strength, 4.2 per cent HF, it may be compared with the reactivity of fresh 4.2 per cent HF. The reaction rate of the fresh acid of equal concentration is somewhat higher than that of the partially spent HF. This is due to secondary deposition of by-products of the reaction of HF on glass. This phenomenon is likewise noted in the reaction of HF with quartz.

EFFECT OF PRESSURE

The effect of pressure on the reaction rate of HF on glass or quartz is quite surprising. In the analogous reaction of HCl on limestone, the CO_2 maintained in solution slows the reaction. As HF reacts with sandstone, silicon tetrafluoride, normally a gas, is forced into solution

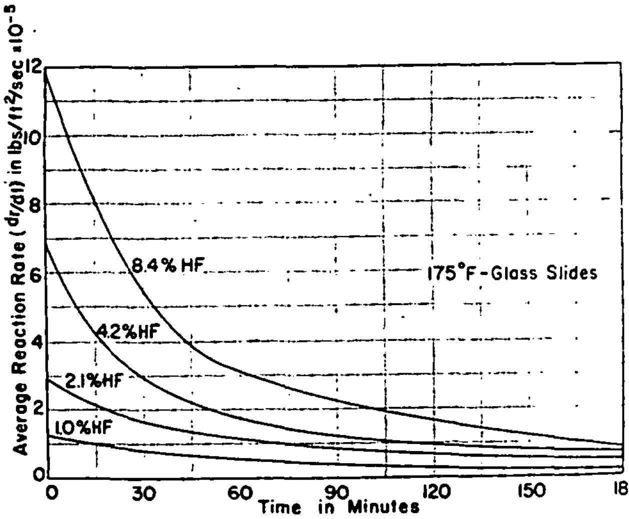

Fig. 4—Effect of Concentration on HF Reaction Rate.

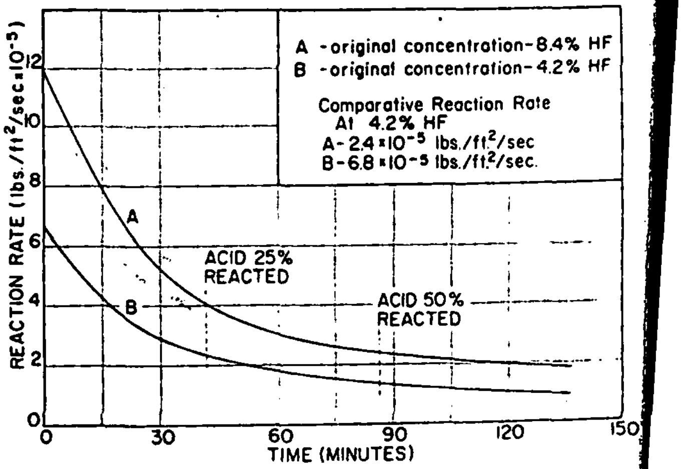

Fig. 5—Effect of By-Products on HF Reaction Rate with Glass.

by the pressure of the reservoir. However, holding the tetrafluoride in solution accelerates the reaction rate as much as 20 per cent in glass and 24 per cent on quartz.

COMPETITIVE REACTIONS

The competition of quartz and clay within a reservoir for reaction with HF may be demonstrated by superimposing the relative reaction rates of the HF-glass reaction on those of HF-quartz reaction at varying acid concentrations. Fig. 6 is a plot of reaction rate vs time. Note the reaction of 8.4 per cent HF on glass and quartz. The faster reaction rate on glass declines quite sharply compared to that of quartz. After 15 minutes reaction, the average rate on glass is approximately 10 times that of quartz; however, after 120 minutes, the reaction rate of glass is only twice that of the reaction on quartz. This preferential reaction with glass would indicate that the reaction with clay in a reservoir takes place at a very fast rate, and indicates that a minimum amount of acid will be spent on the sand grains. However, as discussed earlier, the net area for reaction must be considered. Within a period of three hours, the HF still available reacts at an equal rate on glass and quartz.

The over-all reaction rate measured in sandstone cores may be the basis of predicting over-all spending rates of HF. These data from glass and quartz slides show the possible effect of competition between the sand grains and clay within the reservoir for reaction. No attempt is made, at this point, to determine the effect of area-volume ratio on the acid spending or to apply the data derived from slide tests to conditions in reservoirs. There are many factors which do not lend themselves to direct comparison. Direct application can only come as a result of tests conducted within cores which are representative of given formations.

HF SPENDING IN SANDSTONE CORES

In the discussion of HF spending on glass and quartz, it was mentioned that a more applicable test would come from determining the spending time of HF in core samples from producing reservoirs. Before this could be done, however, it was necessary to develop spending-time relationships within a rock of known chemical composition. Berea sandstone cores were used for this purpose.

Petrographic analysis showed the untreated rock to have the following chemical composition: α-quartz 85.3 per cent; fieldspar 5 per cent; dolomite 4 per cent; and total clay 5.7 per cent.

The clay fraction (5.7 per cent of total formation) may be further subdivided: kaolinite 2.6 per cent; illite 2.4 per cent; and chlorite 0.7 per cent.

This formation exhibits water sensitivity in spite of the absence of montmorillonite in the X-ray analysis. It normally has a permeability to air of 150 to 300 md.

Petrographic analysis gives the following description of Berea sandstone: fine grained, dolomite sandstone composed of angular to subrounded quartz, orthoclase feldspar, twinned plagioclase and irregularly shaped masses of dolomite, feldspars altered partially to kaolinite; isolated, altered muscovite grains present; bedding faint; sorting poor to fair; limonite, hematite and chlorite present in isolated patches; cement is primarily dolomite with some silica present.

EFFECT OF CONCENTRATION

A series of experiments was run to determine the effect of concentration on the amount of acid which will spend within a given length of time. Initial acid concentration for these tests was 4 per cent HF. The results are noted in Fig. 7.

One pore volume of acid was eased into each Berea core, and shut in for a given period of time. It was then displaced with an immiscible solvent. The acid was analyzed to determine the concentration of HF remaining after the given period of spending. At the end of 90 minutes, the concentration of HF recovered was one half of the original concentration. This is termed "the first half-life". During the next 90-minute interval, the concentration was again reduced by one half. Finally, during the third 90 minutes, the concentration was again reduced by one half. The half-life, T, is equal to T_2 which is equal to T_3, each being 90 minutes. By plotting these data, it can be seen that the reaction is first order. This was also noted on the glass slide and quartz slide tests described earlier. Such data should not be construed to mean that HF will spend one half its original concentration in 90 minutes in any reservoir. The effect of flow rates and actual composition of the formation to be treated must be considered in determining acid spending time in a reservoir.

Acid concentration plays a very important role in the permeability increase resulting from HF treatments. Fig. 8 demonstrates the effect of acid concentration when plotted vs spending time. In these tests with one pore volume of acid, the rate of reaction is dependent on acid concentration. At concentration of 8 per cent, HF initially reacts at twice the rate of 4 per cent HF. In turn, 4

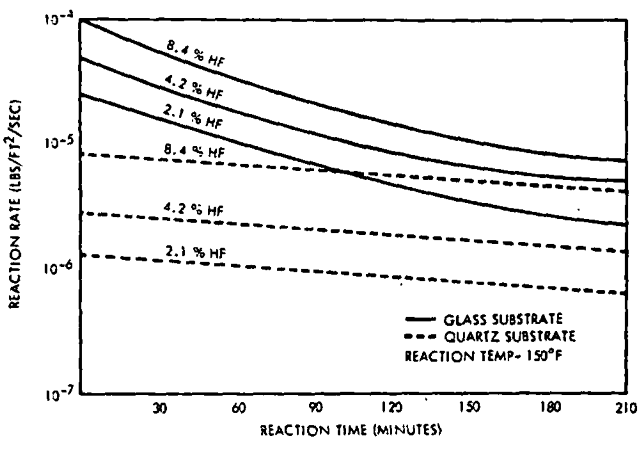

Fig. 6—Reaction Rate of HF on Quartz and Glass.

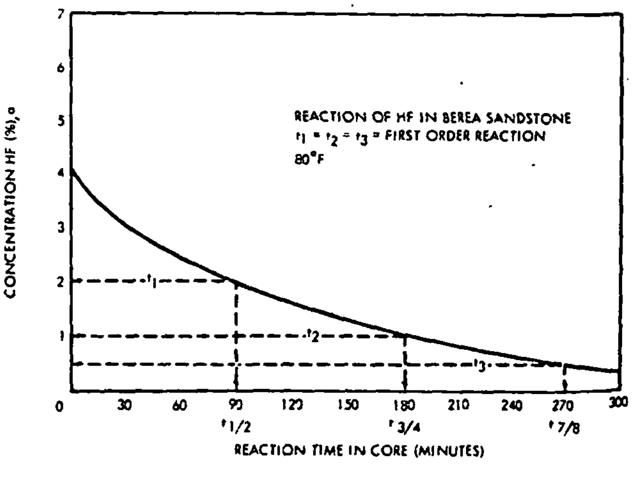

Fig. 7—Kinetic Order of Reaction by Half-Life.

per cent initially possesses twice the reaction rate of 2 per cent. This, again, is in general agreement with the results earlier observed from glass and quartz slide studies. The effect of acid concentration is graphically demonstrated as a function of acid volume in Fig. 9. The more highly concentrated acids give a reduced permeability which is temporary in nature as the acid enters the core. By the time 10 pore volumes penetrate the core, the restriction is apparently removed and the core permeability is increased by the acid treatment. The response is so definite that in some cases the core was reduced to unconsolidated sand by the action of 8 per cent HF. HF of 4 per cent concentration showed the same pattern of temporary reduction in permeability followed by a large increase with partial degradation of the cores. Tests with 13 per cent HCl—2 per cent HF acid mixtures showed less temporary damage, but a slightly larger volume of acid was required to give the over-all desired increase in permeability. Three to four times the acid volume of the 2 per cent HF solution is required to gain the same permeability increase noted by the 8 per cent HF.

EFFECT OF GASEOUS PRODUCTS

As HCl-HF acid mixtures spend, there is a possibility of forming two gaseous by-products, carbon dioxide and silicon tetrafluoride. The effect of confining pressure on these gases is presented in Fig. 10. The permeability increase is measured as a function of acid volume on Berea sandstone at 80F. A back-pressure device was placed on the core test apparatus to maintain a differential pressure of 500 psi, with a driving pressure of 1,500 psi and a back pressure of 1,000. Data from this series of runs are compared to that where a 500-psi drive was applied against atmospheric pressure. The results of these tests show a somewhat increased reactivity when the gases are held in solution by the applied back pressure. This, again, is in agreement with the data mentioned earlier that were obtained from glass and quartz tests. The action of the pressure in holding the silicon tetrafluoride in solution possibly increases reactivity through increasing the number of hydrogen ions available for continued reaction.

EFFECT OF FLOW RATE

HF has a definite spending profile as a function of the rate at which it flows into the reservoir. Fig. 11 graphically illustrates the effect of various flow rates and their spending in Berea sandstone at 80F. At small pore volumes, permeability was reduced. This reduction was overcome as acid volume increased. In these experiments, various acid mixtures were driven through cores measuring 1 in. diameter × 3 in. long at Δp of 50, 100 and 1,000 psi. Fig. 12 is a flow diagram of the fluid-loss cell used in these experiments. In the case of the low rate of flow, $\Delta p = 50$ psi, there was little, if any, temporary damage

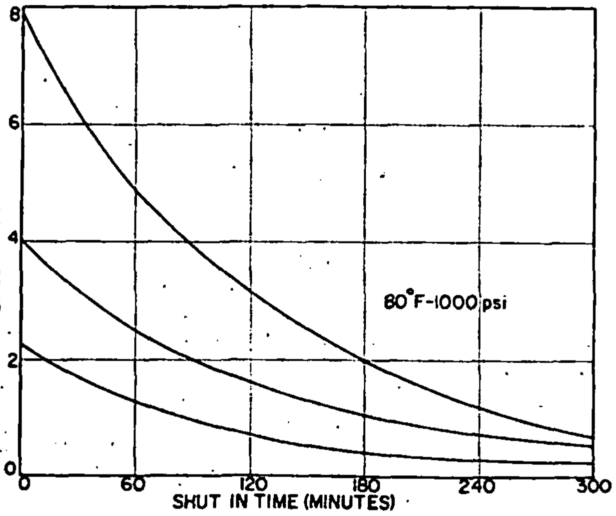

FIG. 8—EFFECT OF HF CONCENTRATION ON SPENDING TIME IN BEREA SANDSTONE.

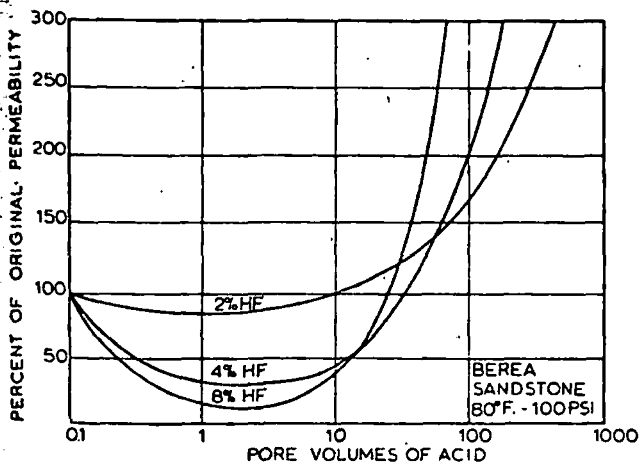

FIG. 9—EFFECT OF HF CONCENTRATION ON PERMEABILITY.

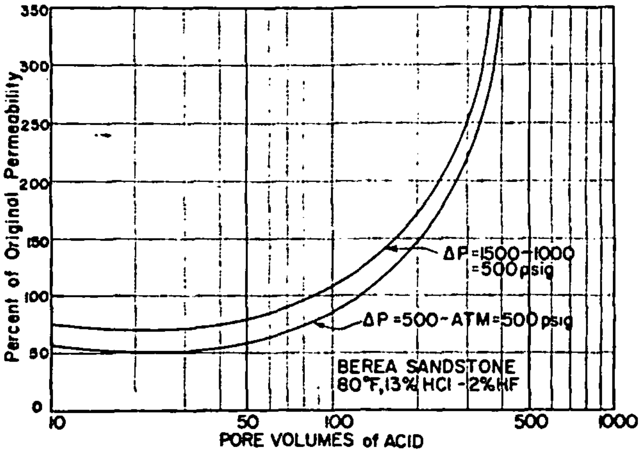

FIG. 10—EFFECT OF GAS EVOLUTION ON PERMEABILITY.

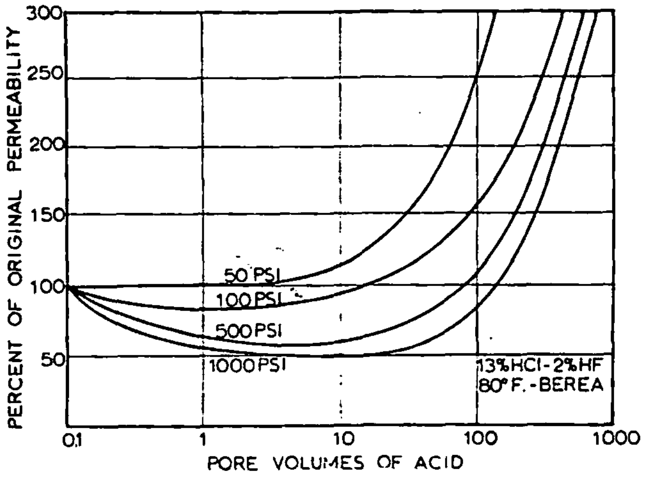

FIG. 11—EFFECT OF ACID FLOW ON PERMEABILITY.

to the permeability when small volumes of acid penetrated the core.

As drive pressure was increased to 100 psi, temporary permeability damage also increased. This was probably due to the increased turbulence at the higher fluid flow rate which stirred fines within the pore structure of the core. These would act as a check valve to fluid attempting to return to the wellbore. This check-valve effect was overcome and initial permeability increased by increasing acid volume to 10 pore volumes or greater.

Further increase of drive pressure from 100 to 1,000 psi once again increased temporary damage, and also reduced over-all effectiveness of the acid treatment. This reduction in effectiveness at the higher flow rates can probably be attributed to insufficient reaction time. In other words, the acid rushed past the reactive materials at such a rate that it was not capable of extensive reaction.

In all the test cores, those with low natural permeability had a more pronounced response as acid penetrated the core. This response is blamed on migration of formation fines, rather than secondary deposition resulting from HF spending, since it occurs immediately on acid entrance into the core and is removed by acid reaction. Deposited by-products of acid spending would not be prone to dissolution by the same acid mixture. A curve showing deposion of this type would be characterized by an initial rise in permeability followed by a decline as the by-product deposition occurred. This was noted only in the case of the test cores which were intentionally plugged by fluosilicate. Migrating fines are of two major types—nonswelling clay minerals and feldspartic materials. Since clay reacts more rapidly with HF, those cores with higher clay content (Fig. 13—Lines A and B) had the blockage removed more quickly than those responding by migration of the less reactive silicious materials (Line C).

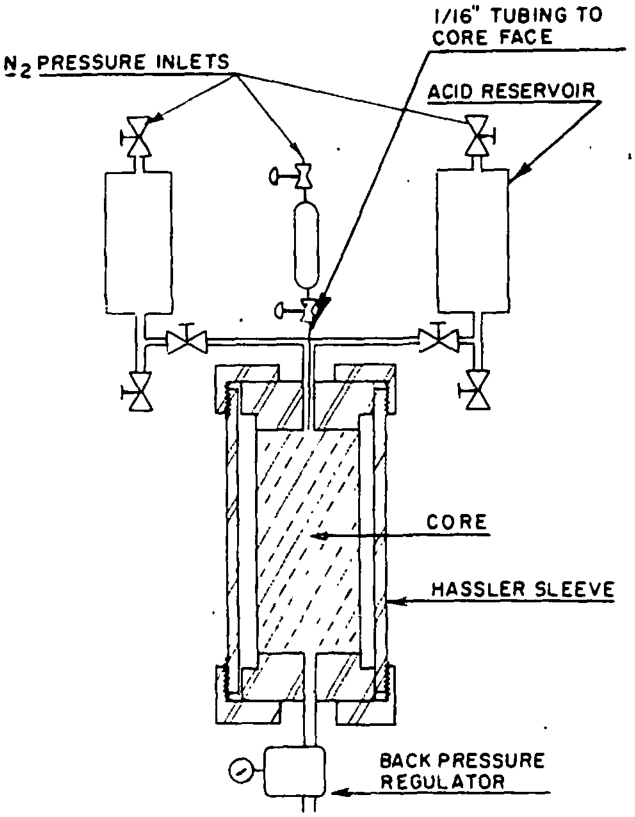

FIG. 12—FLOW TEST CORE CELL.

It appears that a continual flow, followed by an overflush, is a most effective means of applying HF. As flow is reduced to the state of static spending, an over-all reduction in reaction rate is noted. Very long shut-in times give little increase in permeability as compared to the possible damage which could result from secondary deposition of reaction by-products from static spending. The flowing system gives the maximum increase in permeability with a minimum volume of liquid. An overflush with an inert liquid, such as kerosene or treated water, will actually tend to increase the effectiveness of acid treatment by increasing the penetration of the acid before it spends. As the acid is flushed to greater distances from the wellbore, less measurable damage to productivity would exist. This effect on productivity can be seen in the relationships that are shown in Figs. 1 and 2.

By comparison, 15 per cent HCl was used in treating Berea sandstone cores in a manner analogous to those procedures used earlier with HF solutions. HCl showed a small reduction in permeability between 1 and 10 pore volumes, and an increase in permeability was obtained after the addition of 100 pore volumes of acid. The hydrochloric acid gave a total increase in initial permeability of approximately 20 per cent. Equal volumes of HF-HCl mixtures gave a permeability increase of 350 per cent. Berea sandstone, as previously mentioned, contains approximately 6 per cent clay minerals. This clay fraction gives the sandstone a definite water sensitivity. The initial or temporary damage in either HCl-HF treatment of the cores could be attributed to this water sensitivity and resultant clay flaking or swelling prior to significant reaction. The clay can be removed, the calcite can be removed, and some of the quartz will be reacted. These reactions lead to the eventual multiples of increase in permeability.

Several cores from producing formations have been tested to determine their application in the overall presentation of data. Fig. 13 shows the effect of various volumes of mud acid (13 per cent HCl-2 per cent HF) on cores from the Cotton Valley formation, Donovan, and South Texas San Miguel. These data are superimposed on the earlier plot of permeability change vs acid volume for Berea sandstone. There is some scatter in the correlation of the data, but the over-all comparison with Berea sandstone is good. This scatter emphasizes the effect of the difference in the chemical composition of the rock and shows the hazard in applying data from one sandstone to the next.

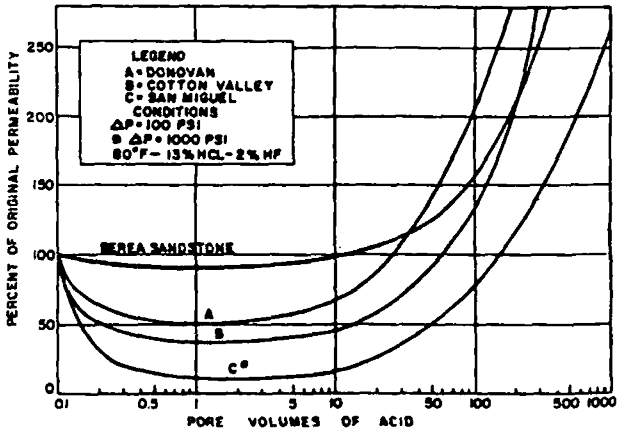

FIG. 13—COMPARISON OF HF BREAKDOWN OF CORES FROM PRODUCING RESERVOIRS.

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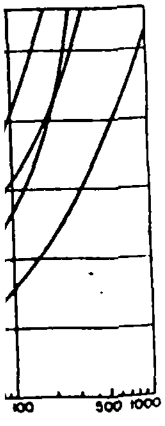

F CORES FROM

EFFECT OF SECONDARY DEPOSITION

As HF spends in a sandstone maxtrix, there are several reactions possible. The primary reaction, previously used as a basis for kinetic interpretation, produces silicon tetrafluoride, SiF_4, which is capable of additional reactions in the rock matrix. In addition, there is some calcite, $CaCO_3$, in most sandstone reservoirs which reacts with HF. Certain metal salts are also present in sandstone in varying quantity and these metals possibly react with the products of the primary reaction to yield insoluble complexes. The exact reactions possible and the extent thereof are a function of reservoir composition and other variables which control chemical kinetics. Since the reaction paths are so varied, no attempt is made to discuss all possibilities, but merely present data concerning some of the more common reactions observed. Many adverse reactions of HF which could be written, simply are not observed in practice.

CALCIUM FLUORIDE

Since the introduction of HF treating in sandstone reservoirs, there has been a great deal said about damage resulting from calcium fluoride deposition. CaF_2 can be easily precipitated in demonstration by adding HF to a calcium chloride solution in a test tube. Based solely on this demonstration, it would be questionable to treat wells where calcite is present. Care must be exercised in the use of HF in calcite-containing reservoirs, but reaction under reservoir conditions is quite different from those encountered in a test tube demonstration.

Two sandstone cores containing 15 per cent calcite were acidized with 2 per cent HF. The effluent was analyzed by X-ray diffraction technique. The CaF_2 content was less than 120 ppm. The core had a net permeability increase in excess of 100 per cent in each case. While CaF_2 definitely formed, it was not sufficient to cause measurable damage. Its concentration was less than that of certain other silicates present in the effluent. CaF_2 particles are very small and discrete. Evidently, particle sizes were sufficiently small to allow migration in flow channels and minimize bridging.

In another test, a series of five Berea cores was saturated with 5 per cent calcium chloride, then acidized with partial pore volumes of 4 per cent HF. The acid was shut in overnight in an attempt to deposit CaF_2. Thin sections were prepared from the cores and X-ray analyses were run. No CaF_2 deposition was observed, although signs of acid attack were readily visible in the thin sections. Analysis showed the presence of 4 per cent acid-soluble carbonate in the cores.

Analysis of return fluid after HF acidizing of another Berea sandstone core gave the following approximate composition: CaF_2—23 per cent; $Ca_3(AlF_6)_2$—66 per cent; $CaSiF_6$—8 per cent; and $AlF_3 \cdot xH_2O$—3 per cent.

These materials represent less than 0.05 per cent of the acid volume and would be considered trace quantities. They were obtained by evaporating the return fluid and determining the composing elements by wet analysis, thus some of these solids were in solution in the effluent acid. Calculations of composition based on this type of elemental analysis are approximate values and are not necessarily indicative of the per cent values shown. X-ray diffraction failed to give any better results, however.

The addition of HCl to HF partially inhibits the formation of CaF_2 and complex silicate salts by maintaining a low pH. Calcium fluoride has an increased solubility in mineral acids, such as HCl. Thee traces of calcium fluoride noted are generally the results of very long shut-in times with resulting rise in pH as the acid is spent. Further reaction in the reservoir could actually inhibit CaF_2 formation by converting it to the more soluble calcium hexafluosilicate. In any case, it is felt that other side reactions are capable of causing more problems than the one leading to the formation of CaF_2. These reactions are discussed below. Maintaining low pH and moderate shut-in time are good insurance against extended CaF_2 deposition.

FLUOSILICATE DEPOSITION

Little consideration has been given to the formation of hexafluosilicates as HF spends in sandstone. The formation of these silicates occurs as follows:

$$SiO_2 + 4\,HF \rightarrow SiF_4 + 2H_2O \quad \text{(Primary Reaction)},$$
$$SiF_4 + 2\,HF \rightarrow H_2SiF_6 \quad \text{(Fluosilicic Acid)}.$$

The fluosilicic acid could partially ionize to give $2H^+ + SiF_6^{-2}$. The hydrogen ions probably contribute to over-all forward progress of the reaction and could account for the increased reactivity of HF when held under pressure. The hexafluosilicate anion, SiF_6^{-2}, is capable of further reaction with common cations present in producing reservoirs. These ions include sodium, calcium and ammonium, among others.

CALCIUM

Calcium fluosilicate is quite soluble (10.6 gm/100 ml) in water, and has increased solubility in acid. No problems are anticipated or observed from formation of this compound. Certain borates can be added to HF and drive the reaction of HF with calcite to forming $CaSiF_6$. Although the fluosilicate would be more desirable than CaF_2, the addition of the borate reduces the HF activity.

AMMONIUM

The ammonium ion is considered since it is present in quantity in mud acid generated from ammonium bifluoride. Ammonium hexafluosilicate is very soluble (18.6 gm/100 ml) and is removed from the formation as the spent acid is returned to the wellbore. The presence of the NH_4^+ ion is considered an asset in mud acid treatment, since it increases the over-all solubility of the resulting products of reaction.

SODIUM AND POTASSIUM

These ions could lead to problems as a result of HF reaction. Sodium and potassium hexafluosilicate are quite insoluble and the precipitant is gelatinous in nature. In a series of tests, three Berea cores with permeability of about 130 md were treated with HF to which 3 per cent sodium chloride had been added. The treatment plugged two of the cores on standing overnight and seriously damaged the third, apparently due to the formation of Na_2SiF_6. This same gelatinous block could result if sodium bifluoride were used to generate the HF. The damage occurred after several hours' shut-in where the reaction products had been subject to static conditions and increasing pH. Mud acid should not be delivered with rock salt added because of this by-product formation. Small amounts of sodium normally present in fresh water are not sufficient to cause problems.

In the displacement of high-sodium brines from cores by HF in a similar test series, no significant plugging occurred. The case where sodium ions were present in the acid before introduction into the reservoir is the only one in which actual damage was recorded. In well treatments, such formation plugging is minimized since there is little mixing of the treating fluid with connate water.

The use of NH_4HF_2 to prepare HF prevents the most serious cause of fluosilicate deposition. When $NaHF_2$ was used to generate HF, fluosilicate problems were quite real and serious as a result of the added Na^+.

OVER-ALL EFFECT OF BY-PRODUCTS

In spite of the possible side reactions, HF materially increases permeability. The amount of increase previously demonstrated in core tests is large in comparison to damage which could result if detrimental by-products formed. The use of HF in matrix treatments where calcite concentration is in excess of 15 per cent is questionable. Such reservoirs are subject to hydrochloric acid treatment which could produce the required permeability increase more economically without danger of side reaction.

SUMMARY

1. The rate of HF spending in sandstone is a function of the chemical and physical composition of the rock, acid volume and the surface area of rock matrix in contact with the acid. This rate may be further affected by acid concentration, formation temperature and pressure and the formation of insoluble or unreactive by-products.

2. The kinetic order of reaction has been experimentally determined using glass and quartz slides as well as sandstone cores. The reaction of HF in sandstone is first order —reaction rate is directly proportional to concentration of the acid and the area-volume ratio. Core tests indicate an acid half-life in Berea sandstone which is 90 minutes or less in duration under static conditions.

3. The effectiveness of HF acidizing is dependent on technique of application as well as the cause and extent of formation damage. Skin damage, or blocking in the vicinity of the wellbore, is most susceptible to matrix acidizing and many folds of production increase may result from damage repair in the first few inches of the reservoir.

4. HF-HCl treatments, as shown by core studies, offer increases in permeability. Most successful treatment results from the reaction of flowing acid. This would indicate that overflush treatments with moderate shut-in times would be preferred to those involving long periods where the acid reacts in a static system.

5. The effect of gaseous products resulting from HF acidizing is apparently not detrimental to the forward progress of reaction. This is in contrast to HCl reaction where the CO_2 formed reduces the rate of the reaction.

6. Laboratory testing, even using core test procedures, is only an approximation of chemical behavior in a formation. The data, such as spending time and reaction rate, can be valuable guidelines in choosing treatment procedures and materials, but cannot be applied indiscriminately to reservoirs.

7. Deposition of calcium fluoride in acidized cores was not extensively observed. Although some CaF_2 was detected, it was not generally considered a major source of damage in cores with low (5 per cent or less) HCl solubility. Tests on cores with 15 per cent solubility in HCl responded to HF-HCl treatment with greatly increased permeability. The physical structure of CaF_2 (i.e. its discrete, particulate crystal lattice) causes less tendency to block flow channels than other gelatinous precipitates such as Na_2SiF_6. Maintenance of acid flow and low pH tend to inhibit secondary deposition. Intentional addition of potassium and sodium compounds of NaF acid should be avoided because of danger of fluosilicate gel formation.

ACKNOWLEDGMENT

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How cyanidation can treat copper ores

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ALTHOUGH CYANIDATION has long been used in the treatment of gold and silver ores, only recently, with the refinement of cyanide regeneration techniques, has it shown promise in the treatment of copper ores.[2] This process has now reached the stage where certain concentrates can be treated to produce metallic or high grade products.

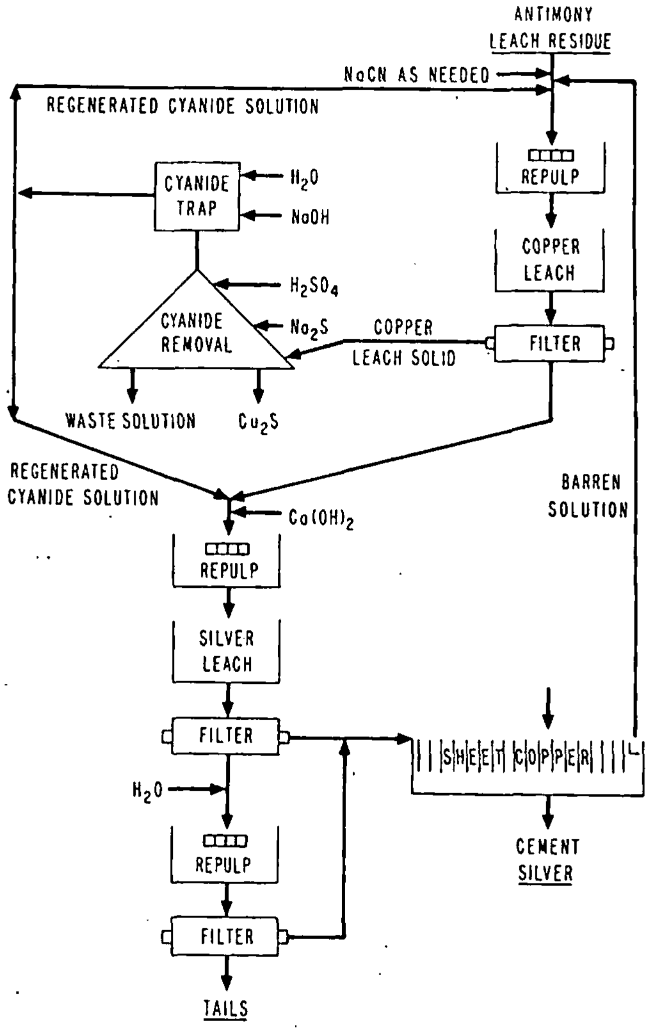
The Sunshine Mining Co., the Idaho silver producer, makes a leach residue well suited to treatment with a concentrated cyanide solution. Cement silver and a high grade copper product can be produced efficiently with a relatively simple circuit.

Sunshine's mill presently processes about 20,000 tons of ore per month. Following grinding and classification to 60% minus 200 mesh, a differential float produces a high-grade silver concentrate consisting largely of argentiferous tetrahedrite and a pyrite concentrate. The silver concentrate is subject to a hot caustic sodium sulphide leach which dissolves the antimony in the form of sodium thioantimonite or sodium thioantimonate. Metallic antimony is deposited from solution by electrolysis. The leach residue, which is largely decomposition products of tetrahedrite, contains about 30% copper and 1,600 oz per ton silver; at present it is being sold to a smelter.

Since substantial custom smelting charges cut deeply into profits, a practical method of producing separate copper and silver products was desirable. Preliminary studies begun at the University of Idaho before the detailed investigation, indicated that cyanidation had good potential.

Cyanidation provides a convenient hydrometallurgical method of treating this complex residue. Based on detailed cyanide regeneration studies conducted by American Cyanamid Co., cyanide recovery would be high, thus giving a differential leach definite economic potential. The silver and copper sulphide products are both of high grade.

Fig. 1: Proposed cyanidation flowsheet



In a proposed flowsheet (above) for the cyanidation treatment of the antimony leach residue, the copper leach would be of two-hour duration whereas the silver leach would require 24 hours. The copper would be precipitated as a high-grade copper sulphide immediately before the cyanide regeneration step. The silver could be precipitated in a tank containing vertically hung copper sheets. As the cement silver built up it would slough off, keeping the copper exposed for good solution contact.

During the investigation, quicklime and cyanide concentrations, oxygen pressure and leach time were the variables studied. Effects of iron and zinc in the residue were also studied. However, since iron proved harmless and the zinc concentrations were low, much of this information was of academic interest only and will not be dealt with.

A two-stage cyanide treatment resulted in a good differential leach. Initial cyanidation dissolved about 90% of the copper in two hours with almost no silver going into solution. At 5% solids, a solution strength of the order of 65 gpl was required which led to the rather startling figure of 2,500 lb of NaCN per ton of residue being treated. The need for efficient cyanide regeneration was obvious. Increasing the quality of sodium cyanide above 3,200 lb per ton resulted in some silver dissolution. At this point, all

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[1] From a thesis for the M.S. (Met.E.) degree at the University of Idaho. Work done in cooperation with the University Research Council and the Sunshine Mining Company.

[2] U.S. Patent No. 3,189,435 by George William Lower, assigned by American Cyanamid Co., Stamford, Conn. Reviewed in *E/MJ*, Aug. 1965, p. 110.

Fig. 2: Copper leach characteristics

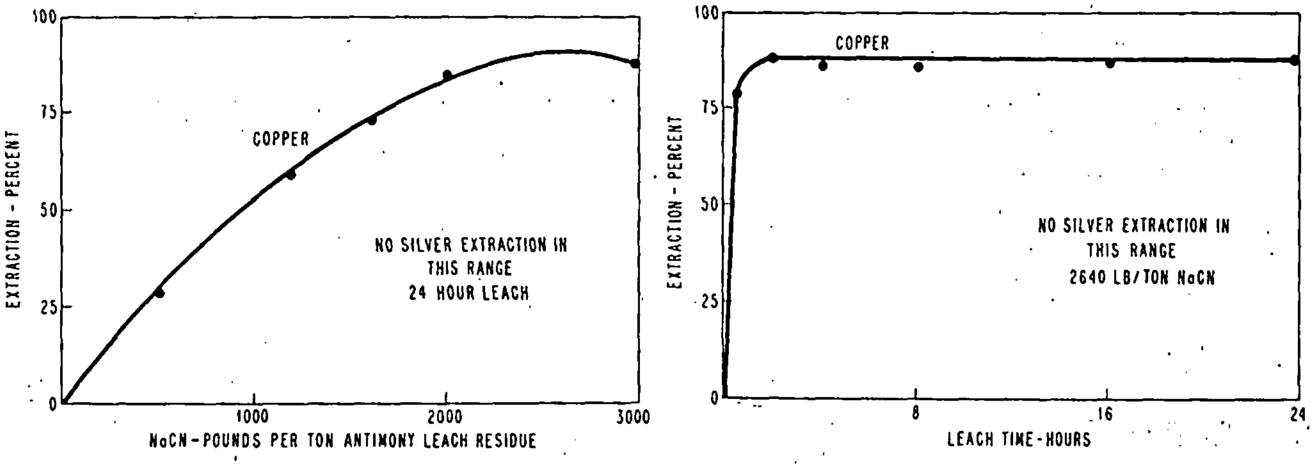
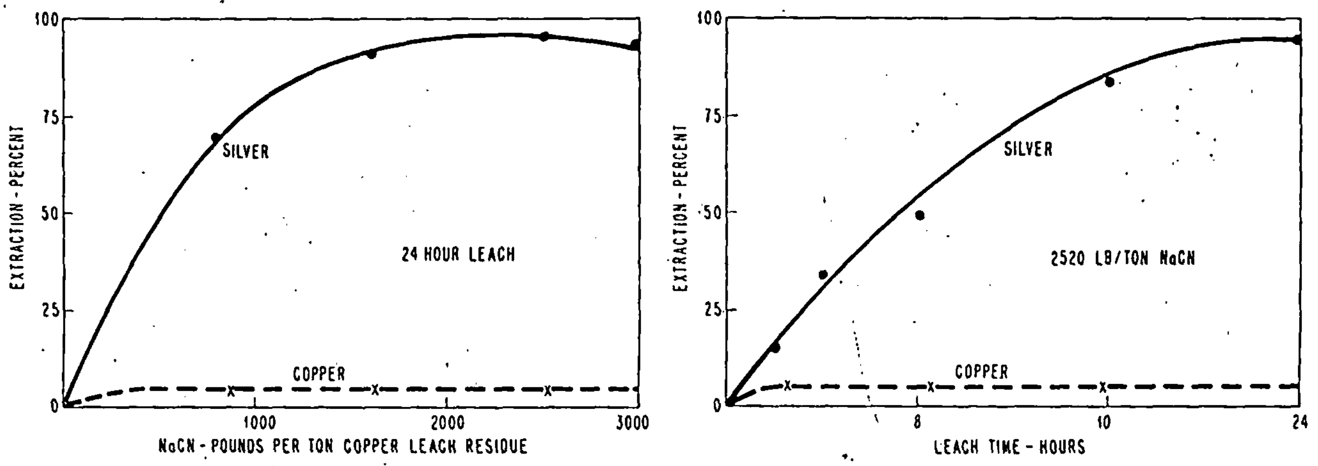


Fig. 3: Silver leach characteristics



soluble copper had been dissolved allowing the excess free cyanide to begin its action upon the silver.

Increased oxygen pressures had little effect upon copper dissolution time, indicating that oxygen did not enter into the dissolution process.

The following reactions predominated:

$$Cu_2S + 6\ NaCN \longrightarrow 2Na_2Cu\ (CN)_3 + Na_2S$$

and

$$2CuS + 8\ NaCN \longrightarrow 2Na_2Cu\ (CN)_3 + 2Na_2S + (CN)_2$$

Quick-lime was found to be of little importance in the copper leach and, since enough alkalinity remained from the antimony leach to give a high pH, it was not needed.

The precipitation of copper from cyanide solutions has been the subject of considerable recent study. Sodium sulphide can be used as a precipitant prior to the regeneration stage:

$$2Na_2Cu\ (CN)_3 + Na_2S + 3H_2SO_4 \longrightarrow Cu_2S + 6\ HCN + 3Na_2SO_4$$

Acidification of the filtered copper leach liquor with H_2SO_4 without sodium sulphide resulted in a precipitate containing 55% copper. This, however, represented a cyanide loss, because insoluble CuCN precipitated.

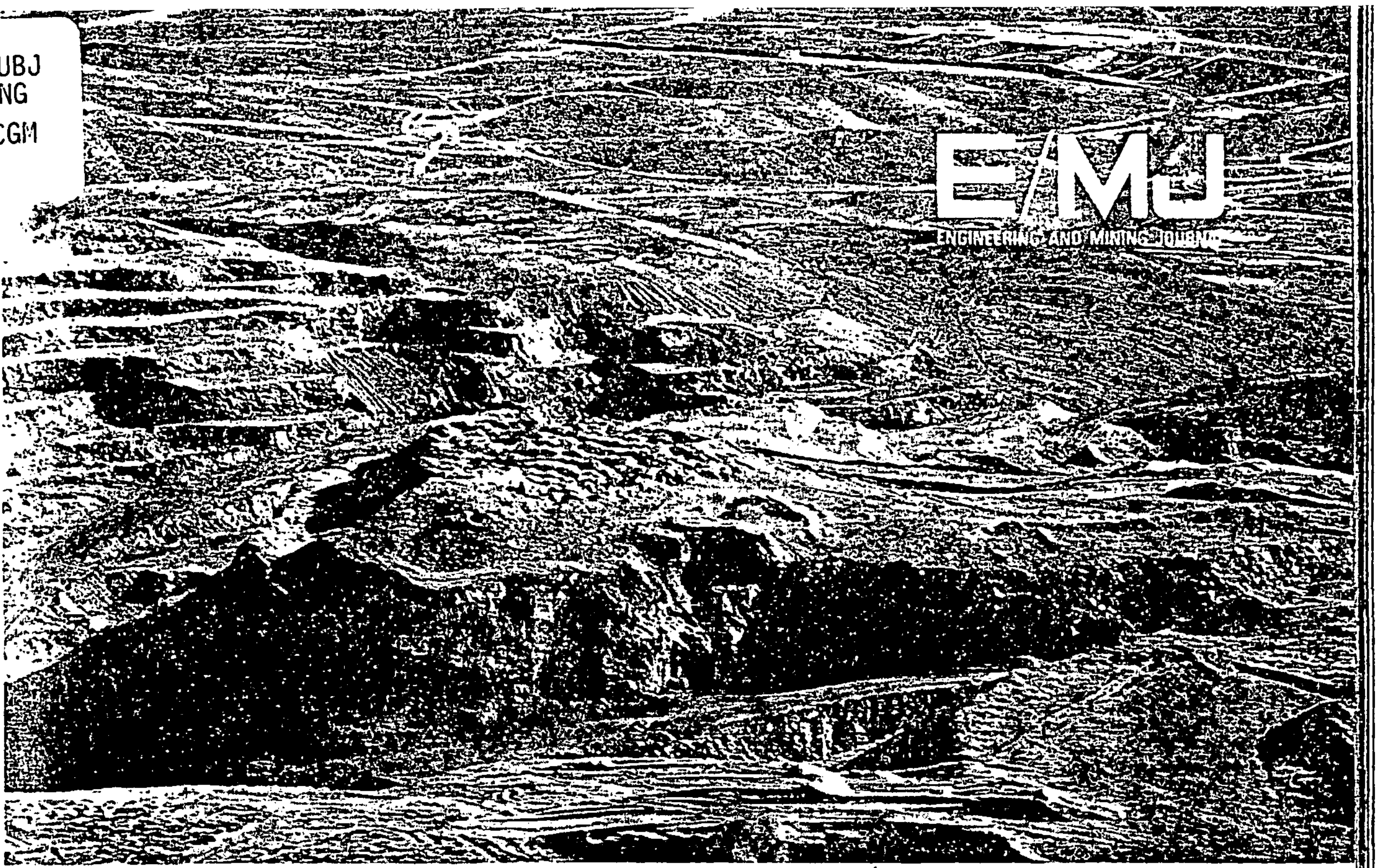
The residue remaining, following the initial copper leach, was again treated with cyanide solution to extract the silver which, upon removal of the copper, had concentrated to about 3,000 oz per ton. Approximately 2,500 lb of NaCN per ton of the copper leach residue or about 1,250 lb per ton of the initial residue was required for the silver leach. (See accompanying curves). Ninety-five percent of silver and about one-half of the remaining copper (5% of the original) dissolved. Twenty-four hours were required for the completion of this reaction; however, increasing the oxygen partial pressure to 20 p.s.i. enabled an end-point to be reached in one-half hour. This substantiated Elsner's equation as being the predominant reaction in the dissolution of the silver.

$$4\ Ag + 8CN^- + O_2\ (Aqueous) + 2H_2O \longrightarrow 4\ Ag\ (CN)_2^- + 4OH^-$$

Quick-lime (or lime) was found to be of marked importance, with approximately 200 lb per ton being needed for good dissolution.

Cement silver, of at least 970 fine, was rapidly and almost completely deposited from the filtered leach liquor on metallic copper. The more soluble copper replaced the silver from solution to give a spongy white silver precipitate. This reaction required less than two hours if the copper surfaces were kept reasonably clean.

With efficient cyanide regeneration this process appears to have definite potential in economically treating other complex concentrates.



The Cortez Gold Acres mine produced feed for the company's conventional mill and low grade ore for heap leaching (background).

How Cortez Gold Mines heap-leached low grade gold ores at two Nevada properties

D. M. Duncan and T. J. Smolik*

FOR 7½ YEARS, Cortez Gold Mines has been successfully operating heap leaching circuits for low grade gold ores in conjunction with a conventional 2,300-tpd milling operation at its Nevada mine sites. A total of 10 million tons of ore has been processed—one-half by heap leaching. Additional ore in the district offers potential for continued production.

Early in the Cortez operation, management recognized that a substantial tonnage of subgrade ore would have to be removed during normal mine operation. In 1969, Cortez started work to develop technology for recovering the gold values in this ore. At the same time, the US Bureau of Mines Salt Lake Research Center was performing small scale heap leaching tests on a number of gold ores.[1] The technique appeared to be a logical choice for Cortez, and the company inaugurated pilot testing at that time. Commercial scale heap leaching of the oxidized limestone ore from the Cortez deposit began in 1971.

Early in 1973, when Cortez reserves were exhausted, properties at Gold Acres, 8 mi from the Cortez plant, were placed in production, extracting a fault breccia ore of ground-up limestone, chert, and shale with a high percentage of clays. Economics again dictated heap leaching of the low grade ore. (See cover photograph.) High grade ore was trucked to the Cortez plant for milling. A carbon recovery circuit was constructed at the Gold Acres site to process pregnant heap-leach liquor. The integrated heap leach and carbon recovery operation remained very profitable as long as Gold Acres was mined. Gold Acres leaching is reviewed in detail here, with a discussion of the similarities and differences of the distinct Cortez and Gold Acres leach circuits.

Mining similar at both sites

Because both the Cortez and Gold Acres ore zones were small, 15-ft benches were required to control ore grade. Blasthole drilling on a 12 x 12-ft pattern was accomplished with three rotary drills—two track-mounted and the third truck-mounted—drilling 6¾-in.-dia holes. A truck-mounted rig dispensed an ANFO mix into the blastholes, and primacord was used for shot detonation. A B-E 5-yd shovel and a B-E 3½-yd shovel were used for digging and loading. Three 988 Cat

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*D. M. Duncan, formerly general manager of Cortez Gold Mines, is currently manager of the Pitch uranium project of Homestake Mining Co. T. J. Smolik, formerly mill superintendent at Cortez Gold mines, is now metallurgical development engineer in the uranium division of Homestake Mining Co.

loaders, four D8 Cat dozers, two motor graders, 12 35-ton Haulpak rear-dump trucks, two 110-ton Euclid bottom-dump haul trucks, and two water trucks completed the list of mine equipment. The machinery was used also to haul leach ore, prepare the leach sites, and haul materials for construction of leach pads.

A truck-mounted portable lab aided in grade control at the digging face. Analysis of grab samples could be obtained within minutes and proved to be an important supplement to conventional blasthole assays. Blasthole assays could be used to locate and flag ore zone locations, but the portable lab assays could pinpoint the ore, especially when blasting caused displacement.

Cortez mill cutoff grades varied with the gold price, haulage distance, and varying royalty agreements. The mill cutoff grade dropped as low as 0.040 oz per ton at Cortez and 0.050 oz per ton at Gold Acres, emphasizing the importance of good control of ore grade.

The portable lab included a hydraulic system to operate the crushing and grinding equipment, while a 7.5-kw generator supplied all electrical requirements. The lab truck also contained chemical dissolution facilities and a Model 1000 Varian-Tectron atomic absorption (AA) unit. Grab sampling during shovel operations—with close cooperation between the shovel operators and the ore grade control technicians—permitted substantial tonnages of mill-grade ore to be salvaged instead of being diluted to leach-grade ore. At a leach cutoff grade of 0.015 oz per ton, the portable lab also allowed salvaging some leach ore that would otherwise have been wasted.

Leach ore was trucked in 35-ton Haulpaks directly from the pits to leach pads prepared on gently sloped valley terrain about 1 mi. away. The terrain at the leach sites graded about 5%, which was considered optimum for adequate heap solution drainage without undue erosion. Preliminary preparation for the leach site included removal of vegetation, grading, and compaction of the base with a vibrating roller compactor. Impervious pad material was then hauled to the site with 110-ton bottom-dump trucks.

Leach pad construction

Pad materials were local clay-silt or slime tailings. The clay-silts used for pad construction were 60% minus 200 mesh and at 90% compaction produced permeabilities of about 0.05 in. per day. Slime tailings used were 80% minus 200 mesh and at 91% compaction produced permeabilities of 0.025 in. per day. Pad material was spread in thin, 2- to 3-in. layers, brought to the required moisture content, and then compacted with a Bros self-propelled, 78-bhp, 14,000-lb vibrating machine. Compaction control was maintained by on-site measurements with a Model A Campbell Pacific Portaprobe. Compaction of all pad materials was maintained above 90%. Successive layers were added and treated until a pad depth of about 15 in. was attained. Required pad thickness was a function of percolation rate and length of leach time.

After the pad was constructed, a 3- to 4-in. layer of coarse gravel was placed over the pad to prevent erosion by leach solution movement and to provide a porous medium through which the effluent solutions could move laterally under the heaps. The gravel also protected the pad from impact damage by large rocks cascading down the face of the heap during dumping. Occasionally, if insufficient gravel was placed, flooding occurred within the heap, causing poor leaching conditions and uncontrolled solution flow from heap faces. Leach solutions normally traversed the length of the heaps through the gravel and collected in a ditch at the front of the heap. The ditch, lined with 30-mil butyl rubber or Hypalon, directed the leach effluent to a central point, where it entered a steel or asbestos-cement pipe for gravity flow to the pregnant solution storage pond.

The ponding areas were constructed in the same manner as the leach pads, being lined with compacted tailings or local clay silts. The ponding areas were large enough to hold two or three days of heap drainage in case of plant operating problems or to retain runoff from a major rainfall. The Gold Acres facility required a pregnant solution storage of 1.6 million gal and a barren solution storage of 1.0 million gal.

Ore heaped 20 ft high at Gold Acres

After experimenting with various heap heights, including 10 ft, 20 ft, and 30 ft, an average height of 20 ft was established at Gold Acres. Ore was dumped in a single lift for the 20-ft heaps, and any area driven on by the trucks was thoroughly ripped before leach solutions were applied. A D8 Cat was used to push ore after truck dumping.

Heap base dimensions on the individual pads varied but were typically 350 ft wide x 450 ft long. With a top slope of 2½%, an average 20-ft heap contained about 170,000 tons of ore. A total of 2.2 million tons of ore was heap-leached at Gold Acres, while 2.8 million tons were heap-leached at the Cortez site.

A D8 Cat with an extended 30-in. ripper worked the tops of the heaps prior to leaching, and during the leaching cycle, the surfaces of the heaps were periodically ripped again to minimize ponding.

Placing additional lifts of ore on top of leached-out heaps was not satisfactory, producing low gold extractions from the Gold Acres ore.

The rocky, competent Cortez limestone ore was leached in both 20-ft and 30-ft lifts. Additional lifts placed over leached-out ore produced better gold extractions than at Gold Acres, but the extractions were not as good on the second lift of ore as on the first. Single 60-ft lifts of Cortez ore produced low gold extractions and were subsequently redistributed in lower lifts for further leaching.

Leach solutions were pumped from the carbon plant through 6-in. steel pipe to the heap surfaces. The 3-in. pumps used were equipped with 60-hp, 3,600-rpm motors. Piping to distribute solution over the heaps was Class 160, 3-in.-dia PVC, spaced 50 ft apart. Armstrong

Spraymatic plastic sprinklers with ⅛-in. nozzles, spaced on 50-ft centers, were used for applying leach solution. Solution flow to a typical heap was maintained at 300 gpm, for a solution application rate of 0.0025 gpm per sq ft. Normally, three areas were available for leaching, with the third area leached intermittently to maintain an average effluent flow of 550 gpm.

With an average yearly water evaporation loss of 30%, maintaining an effluent flow of 550 gpm required an average fresh water make-up of 235 gpm. However, the evaporation rate varied considerably with the seasons, and the peak fresh water requirement ran as high as 550 gpm. The fresh water at Gold Acres was of poor quality and caused severe scaling problems. A large barren pond was used to "condition" the water before introduction into the spraying system.

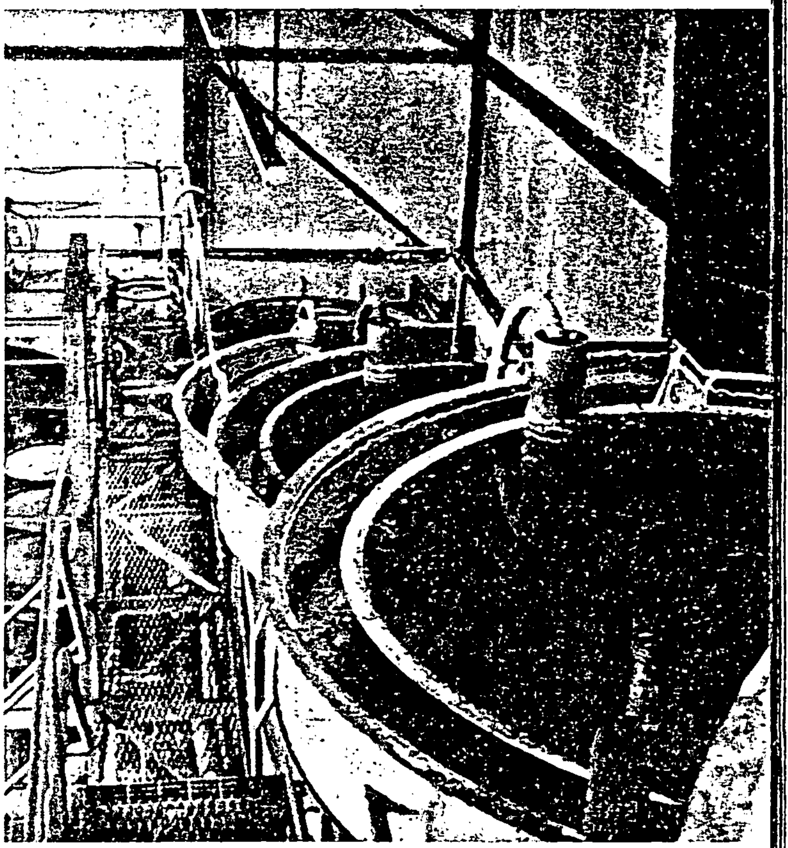
Sodium hydroxide (purchased at a 50% liquid concentration) was metered into the barren pond with fresh water and recycled barren solution. Dissolved solids in the hard water precipitated out in the pond, minimizing scaling problems. With the caustic addition, the pH of the leach solution was maintained at 10.5. Sodium cyanide stock solution (at 15% strength) and an S-35 Baroid water treatment chemical were metered and injected into the pump lines as the leach solution returned through the pumps to the leach heaps. The sodium cyanide concentration of the leach solution was maintained at 0.030%. Reagent consumption for Gold Acres ore averaged 0.45 lb NaCN and 0.41 lb NaOH per ton of ore.

Gold production from the heaps was monitored by sampling, assaying, and measuring each effluent flow. Truck counts during the leach haul and survey measurements of the heaps provided tonnage figures, and blasthole assays and portable lab assays were used to determine the grade of each heap. This information provided enough data to calculate gold recoveries on each heap.

Leach extraction and ore character varied, depending on the area mined. (Typical curves for extraction vs. time are shown in the accompanying graph, including the low leach extraction rate for a second 20-ft lift of ore placed above the original No. 2 heap.) The clayey Gold Acres ore averaged 50% extraction. By contrast, the "blocky" Cortez leach ore averaged 65% extraction.

Carbon adsorption recovery plant

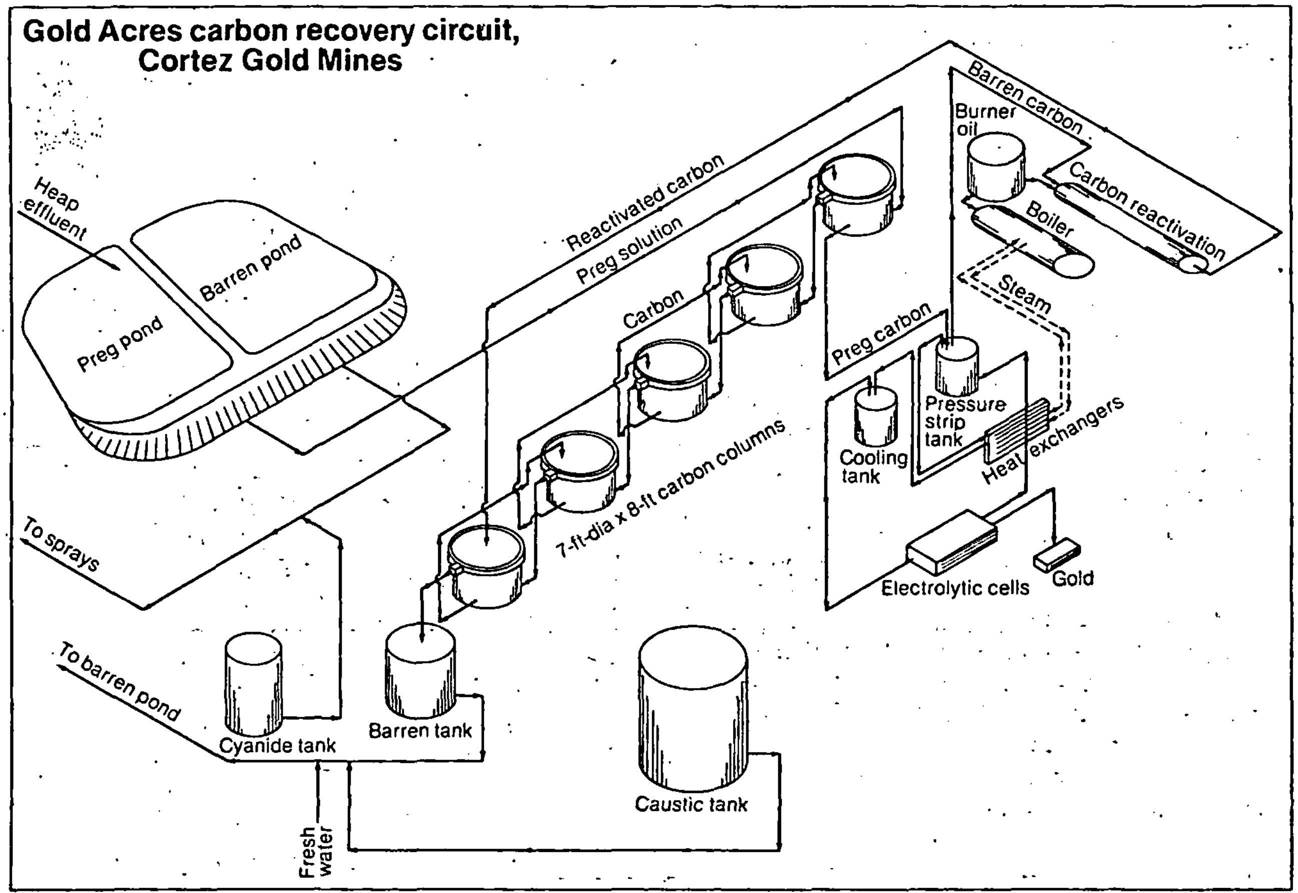
A 75 x 40-ft pre-engineered building housed all spray and process pumps, reagent mixing and distribution facilities, carbon adsorption columns, pressure stripping facilities, carbon reactivation furnace, and all associated electrical instrumentation and controls. A location directly in front of the pregnant and barren storage ponds was chosen to facilitate solution transfer. A 24-ft eaves height was required for gravity flow through the five carbon adsorption columns, such flow requiring a 3-ft differential between columns. An 18,000-gal tank for caustic solution, a 6,000-gal fuel oil tank, and bulk storage for cyanide were located outside the building.



Carbon adsorption columns at Gold Acres are 7 ft in diameter x 8 ft high; each holds 3,000 lb of activated carbon.

Gold-bearing pregnant solution was pumped through the carbon columns at a flow rate of 550 gpm. The tanks each held 3,000 lb of 12 x 30-mesh coconut shell activated carbon. An upward flow rate of 14.3 gpm per sq ft produced a carbon bed expansion of about 35%. As the pregnant solution passed through the carbon bed, the carbon absorbed the soluble gold cyanide complex. The tanks were arranged so that the pregnant solution flowed upward through the first and decanted and then flowed by gravity through each of the remaining carbon columns. A total of 48 solution ports or nozzles evenly spaced about a baffle plate near the bottom of each tank permitted even solution flow through the carbon. Each port had three openings or slots measuring ⅜ x ¾ in. and was constructed to prevent the carbon from dropping into the manifold chamber under the baffle plate. In the countercurrent system, high grade gold solutions contacted the most heavily loaded carbon. (See flowsheet.)

Carbon advanced hydraulically through 2-in. Schutte-Koerting eductors in a direction opposite the pregnant solution flow. High pressure water from the heap spray pumps was used as motive water through the eductors, at a flow rate of 40-50 gpm. About 1,500 lb of carbon (dry weight basis) was periodically advanced from each carbon column. Carbon removed from the No. 1 column was treated in the stripping circuit for gold recovery and then returned to the No. 5 carbon column. Solution overflow from the No. 5 column, depleted in gold values, was pumped to the barren storage pond for reagent make-up and subsequent recycle back to the heaps. The data for April 5, 1976 are typical of an operating day:


Gold Acres carbon recovery circuit, Cortez Gold Mines

- Operating time—24 hr.
- Pregnant solution flow—3,290 tons at 548 gpm.
- Pregnant solution assay—0.021 oz per ton.
- Barren solution assay—0.0005 oz per ton.
- Gold recovery from pregnant solution—97.7%.

At the Cortez mill, where a zinc precipitation circuit was available when the mill was operating, the effluent solutions from Cortez heaps were combined with the mill pregnant solution for gold recovery in the Merrill-Crowe precipitation circuit. When the Cortez mill operation was curtailed, a small four-stage, 5-ft-dia carbon column circuit was installed for gold recovery and performed very satisfactorily. Pregnant carbon from the Cortez circuit was stripped and reactivated in the Gold Acres plant.

Carbon stripping in pressure vessels

There are various known methods of stripping gold-loaded activated carbon, among them atmospheric hot caustic stripping,[2] pressurized hot caustic stripping,[3] and methanol stripping.[4] Each method has merit, and the best approach is a matter of management preference. Atmospheric stripping is slow, typically taking around 48 hr for a carbon strip cycle. Pressure stripping reduces the cycle to 12-20 hr but requires pressurized vessels. Methanol stripping, which can further reduce the stripping time, operates at atmospheric pressures but increases the stripping cost.

Pressurized hot caustic stripping was used at the Gold Acres carbon plant. Between 1,200 and 1,700 lb (dry weight basis) of loaded carbon was introduced into a 42-in.-dia x 10-ft pressure vessel. A 1% sodium hydroxide solution was used for stripping, at a pressure of 60 psi and a temperature of 240°F. A 25-hp steam boiler supplied heat, with fin-tube heat exchangers external to the stripping vessel used to reclaim the heat and preheat incoming strip solution. All facilities were constructed of mild steel.

Stripping solution was pumped at 13 gpm into the bottom of the strip vessel, passed through the loaded carbon, and discharged from the top of the pressure vessel. After passing through the heat exchangers, the strip solution was cooled to 180°F, sent through the electrolytic cells for gold recovery, and then recycled back to the strip vessel. The carbon was usually stripped to 0.5-2.0 oz per ton of gold loading, then washed, reactivated, and recycled back to the carbon columns.

Gold was electrowon from the strip solutions in two rectangular electrolytic tanks, each measuring 3½ ft long x 3 ft wide x 3 ft deep. The electrolytic tanks were constructed of mild steel and lined with neoprene rubber. Anodes were made of perforated, electrolytic grade carbon, while cathodes were constructed of perforated ¼-in. polypropylene sheet and fabricated to hold 2 lb of carbon steel wool. The polypropylene sheet served as an insulating medium between anodes and cathodes. Each tank could hold six cathodes and seven anodes, although fewer cathodes and anodes were normally used, to reduce the quantity of steel wool that would have to be refined. The caustic solution used for carbon stripping served as electrolyte, with spent electrolyte recycled back to the pressure vessel to recover more gold from the loaded carbon. After stripping a batch of carbon, cathodes were removed from the tanks, and the plated steel wool was treated in the refinery for recovery of gold doré bullion.

A 200-amp rectifier was used in the gold electrowinning circuit. Cathodes were connected in parallel so that under normal operating conditions a potential of 2.5 v could generate 22.5 amps per cathode. In this batch electrowinning, gold values were taken to depletion, and the average current efficiency was low. (Data from a typical strip electrowinning log are shown in the accompanying table.)

After completion of the strip cycle, barren carbon was washed with fresh water and educted to the carbon reactivation circuit. A screw feeder delivered the dewatered carbon at a rate of 2.5 dry lb per min to a rotary-type, oil-fired reactivation furnace. The stainless steel tube through which the carbon passed measured 20 in. in diameter x 12 ft long. A temperature of 1,350°F was maintained in the stainless steel chamber during carbon reactivation. After the high temperature treatment, the carbon was quenched and educted back to the No. 5 carbon column for reuse.

Heap leaching: low cost operation

The integrated heap leaching and carbon recovery circuit for gold required a minimum of operating labor. One full-time worker and a part-time helper were required 8 hr per day, seven days per week, to take care of the leaching, carbon column, stripping, and reactivation circuits. The major costs of the operation were power, reagent requirements, pad preparation, and leach haulage. The carbon loss in the Gold Acres circuit was insignificant: an indicated carbon consumption of 0.0025 lb per ton of ore leached. Repair costs were moderate.

Typical strip-electrowinning log at Gold Acres

Date: March 14, 1976.
Carbon identification: CP-4V1.
Strip conditions: reagents—150 lb NaOH, 25 lb NaCN; flow—13 gpm = 2.5 bed volumes per hr; vessel pressure—65 psi; vessel temperature—235°F.
Electrolytic cell: nine cathodes used, 18 lb steel wool; 190 total amps at 2.5 v.

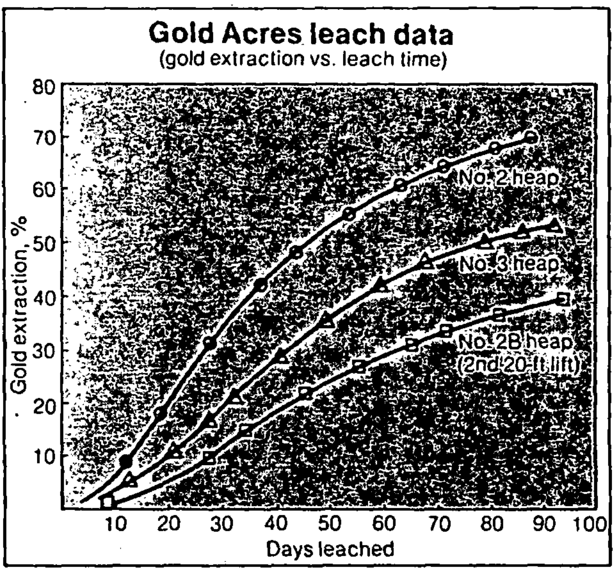
	Solution assays, oz per ton	
Time	Cell feed	Cell discharge
8:00 a.m. (start)	—	—
12:00 a.m. (at temp.)	24.7	18.7
3:00 p.m.	17.5	10.1
7:00 p.m.	5.4	1.0
11:00 p.m.	0.7	0.07
7:00 a.m., March 15	0.06	0.01

Off: carbon washed 1½ hr.

Strip time: 23 hr total. Average current efficiency: 30.3%.

Assay data:

Carbon	Doré bullion
Preg carbon (1,202 lb): 485.4 oz/ton	Weight: 333 oz
Barren carbon (1,202 lb): 0.4 oz/ton	Gold: 859.64 fine
Indicated gold in carbon: 291:5 oz	Silver: 119.58 fine
	Gold recovery: 286.3 oz.


Gold Acres leach data
(gold extraction vs. leach time)

A leaching operation was viable as long as run-of-mine ore produced reasonable gold extractions. Crushing of the Cortez or Gold Acres leach ores could not be economically justified, precluding purchase of expensive crushing equipment and additional operating expense. With different ore grades and/or leaching characteristics, however, the effect of crushing on the rate of gold production and recovery should be evaluated.

With suitable topography and the availability of adequate soils or tailings, construction of a leach pad is relatively inexpensive. In other cases, soil sealers or more expensive permanent pads of concrete or asphalt may be considered.

The leaching characteristics of different ores have a dramatic effect on the economic viability of heap leaching. Percolation problems may be severe with one ore and moderate with another. Reagent consumption can vary drastically with varying percolation rates and varying content of sulphide mineralization in the ore. Each potential leach property must be tested and evaluated individually.

The presence of other metals, such as silver, copper, zinc, and mercury, in the pregnant solution can create special problems with carbon loading capacity and gold bullion quality. Under the right circumstances, however, the simplicity of operation and the low capital and operating costs make carbon adsorption-electrolytic recovery of gold economically superior to conventional zinc precipitation circuits. ☐

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How dry mix explosives can increase costs—even in dry holes

Melvin A. Cook, president, Ireco Chemicals

In the July 1971 issue of E/MJ, *John R. Lansdale, in his article entitled "How Dry Mix Explosives Can Shave Costs," took issue*[1] *with an article by Dr. Melvin A. Cook previously published in* MINING MAGAZINE. *In his reply, Dr. Cook writes:*

"I would like to be able to answer Mr. Lansdale without reference to physical chemical equations but cannot see how this is possible. Still, I have tried to make my write-up clear and concise.

"The problems raised by Mr. Lansdale are vitally important. I think it is therefore proper to have formal scientific answers to them, particularly in the best interests of the mining community."

SUCCESS IN HARD ROCK BLASTING is due either to shock and/or compression waves or to the (pressure-volume) work integral, or to a combination of the two. In any case, the "borehole pressure" (i.e., the maximum pressure developed by the explosive in the borehole) and the thermodynamic maximum available energy of the explosive are of fundamental significance. The pressure is even more important in the shock wave mechanism than in the thermodynamic work mechanism which is illustrated here. That is, in the former, pressure is the main factor. It goes as about the second to third power of the density. In the latter, maximum available energy is the main factor. It also increases with density. In any event, both borehole pressure and maximum available work can be measured and calculated. [2-5]

Useful work in general is given by the work integral

$$A = \int_{v_i}^{v_f} p\,dv = \epsilon Q \qquad (1)$$

where A is the well known "maximum available energy," in other words, *strength*. Here p is the pressure, v is the specific volume, and i and f designate initial and final states, respectively. Also, Q is the *heat* of *explosion* and ϵ the *mechanical efficiency*. This integral can be solved exactly for explosives (thanks to the well established thermohydrodynamic theory of detonation) by using the "inverse method" to derive the equation of state.[2] This has been done, and one can thus determine the parameters of this equation [needed to integrate Equation (1)], namely,

$$P = nRT/a \qquad (2)$$

where n is the mols of gas per unit weight, R the gas constant, T the absolute temperature, and a is the *effective* free volume

$$a = v - \alpha(v) \qquad (3)$$

For instance, from Equation (2) one may plot exactly P against v (for adiabatic expansion) for any given explosive and thus determine A by means of the *area under the curve* between v_i and v_f. (This can also be done analytically, but here the graphical solution shows the real nature of the problem better.) Before discussing this integral, however, let us consider some general principles of importance in evaluating explosives.

Variation of the heat of explosion Q with density ρ

Accurate thermohydrodynamic calculations show clearly—and reliably—that Q *is* itself a *function of the density* ρ_i of the explosive. True, in some cases like ANFO (but not metallized ANFO or slurry) the variation of Q with density is negligible, e.g., less than 20 calories per gram/cc, or no more than 2% per g/cc change of Q with density in ANFO. In an extreme case like TNT, for instance, this change is much greater, e.g. at $\rho_i = 0.5$ g/cc, Q is 770 cal/g, but at $\rho_1 = 1.6$, it is 1140 cal/g, about 50% higher.

It has been asserted that there would be no influence of density on *strength* in aluminized ANFO and slurry. This is definitely not true. It is not even true in general for Q, let alone A. For example, while in 82/18 AN/AL, Q does not change appreciably with loading density, A does. On the other hand, in 76/4/20 AN/FO/AL, for example, or in any other mixture where oxygen balance is far from zero, Q and A, and therefore the weight strength, both depend strongly on density. Moreover, LeChatlier's Principle shows that Q will always increase with density in any case where it is not already at a maximum. "Strength," incidentally, is the conventional usage throughout the explosives industry for the maximum available energy of the explosive. ("Weight strength" is the energy per unit weight and "bulk strength" the energy per unit volume.)

Even if one were to assume that Q does not vary appreciably with density, still A (or weight strength) *will* depend *strongly* on density, particularly in those cases where work can be done only at high pressures, i.e., because of a requirement of a large overpressure to break a particular type rock. The *minimum* influence of density on A occurs when v_f/v_i is a maximum, or since $v = \rho^{-1}$, where ρ_f/ρ_i is a minimum. This corresponds to performing work adiabatically over the entire range of expansion right up to the point where the pressure in the gases is ambient. Even in this (the most favorable case for minimizing the influence of density on A), there remains an appreciable influence of density on weight strength.

Examples of integration of work integral

Fig. 1 refers to the integration of the work integral. Curve A is the adiabatic pressure-volume or p-v curve for one explosive of $Q = 900$ cal/g at 1.4 g/cc, and curve B is the corresponding curve for an explosive of the same Q but at 0.8 g/cc. Consider now three separate examples as follows:

Case 1. Assume that useful work can be done by an explosive only at overpressures (pressures above ambient) greater than 2,000 atm (or 2 kb). Then A (or weight strength) would be the area under the curves down to the point where the pressure equals 2 kb. This is the area bounded by the curve A and $a_1o_1b'_1$ *for* Explosive A and that bounded by curve B and $a_2o_2b'_2$ for Explosive B. As illustrated in Fig. 1, these strengths are 550 and 330 cal/g, respectively. Thus ϵ is 0.61 for Explosive A and 0.37 for Explosive B. The weight strength ratio of Explosive A to Explosive B is thus $0.61/0.37 = 1.65$. Explosive A thus has a weight strength 1.65 times as great as Explosive *B* under this condition. Moreover, the corresponding bulk strength ratio is $\rho_{1A} \bullet A_A / \rho_{1B} \bullet A_B = (1.75)(1.65) = 2.9$. The energy per unit volume of Explosive *A* is, in other words, 2.9 times as great as that of Explosive *B* under this condition.

Case 2. Next, assume that another type of burden requires a minimum overpressure of 1,000 atm (1 kb) to break it. Then Explosive *A* will do work corresponding to the area bounded by curve *A* and $a_1 o_1 b''_1$ while Explosive *B* will have a work integral equal to the area $a_2 o_2 b''_2$. These amount to 610 cal/g and 425 cal/g, respectively, for a weight strength ratio of 1.43 and a bulk strength ratio of 2.5 for Explosive *A* to Explosive *B*. Therefore Explosive *A* is still appreciably stronger than Explosive *B* but not as much as in Case 1.

Case 3. Now assume one requires no overpressure, i.e., that the gases can do work adiabatically all the way from the maximum (borehole) pressure to atmospheric pressure. In this example one finds that Explosive *A* has a weight strength of 890 cal/g, and Explosive *B*, a weight strength of 830 cal/g. Hence, in this most favorable condition, Explosive *A* is now only 7% stronger than Explosive *B* on an equal weight basis.

Thus it is possible for Lansdale's conclusions[1] to be approximately right on weight strength *if* the work integral is unlimited by the "strength" of the burden. Even in this case a slurry has nearly enough advantage over a dry mix to offset the water dilution effect cited by Lansdale.

Most effective utilization of borehole

There is another factor of extreme importance to be considered, namely, the "bulk strength." Even ignoring the obvious variation of weight strength with density (one cannot ignore the influence of density on bulk strength) and the less important variation of heat of explosion with density, there yet remains another factor to be considered, namely, the cost of drilling plus other fixed costs, and their influence on overall blasting costs. When one considers this factor, he will often find that he saves money by using the more expensive explosive. The following simple analysis shows how this can be done:

Suppose it costs *T* dollars to load *N* boreholes each with *W* pounds of explosives at a fixed cost of *D* dollars per hole and explosive cost of *C* dollars per pound of explosive. Then the total cost to blast a given "block" is

$$T = N(D + W \cdot C) \qquad (4)$$

When comparing total costs for two different explosives *A* and *B*, the formula is

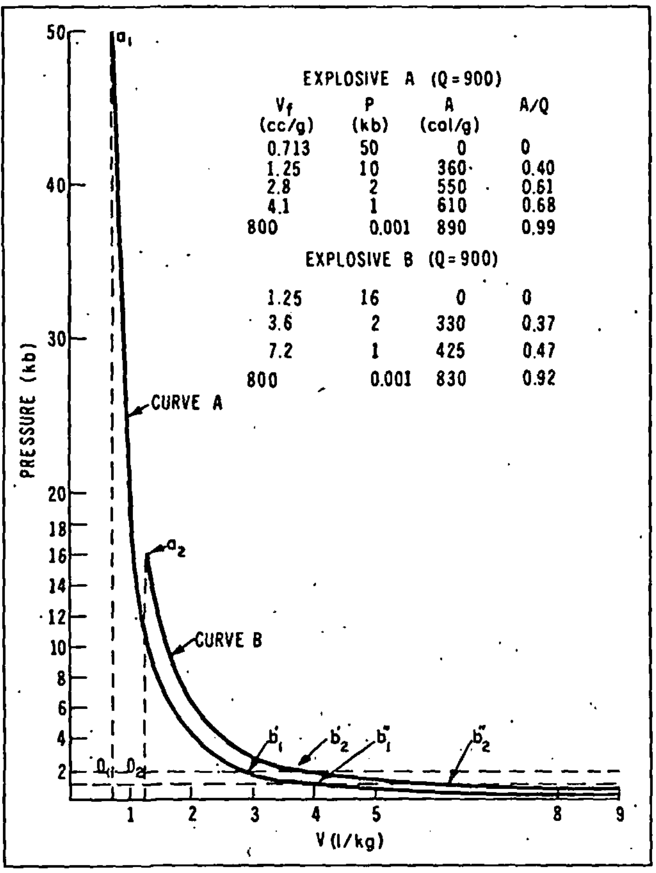
$$T_1 - T_2 = N_1(D + W_1 \cdot C_1) - N_2(D + W_2 \cdot C_2) \qquad (5)$$

Next, assume the number of holes in the block are sensibly adjusted to match the explosive used with the size of the borehole. Then the relative number of boreholes is N_1/N_2 given by the relation

$$\frac{N_1}{N_2} = \frac{A_2 \Delta_2}{A_1 \Delta_1} \qquad (6)$$

Here Δ is the average density of the explosive in the borehole, and the number of boreholes needed is inversely proportional to the bulk strength or to the density multiplied by the weight strength. Also the weight per borehole is proportional to Δ, giving

$$\frac{W_1}{W_2} = \frac{\Delta_1}{\Delta_2} \qquad (7)$$



EXPLOSIVE A (Q=900)

V_f (cc/g)	P (kb)	A (cal/g)	A/Q
0.713	50	0	0
1.25	10	360	0.40
2.8	2	550	0.61
4.1	1	610	0.68
800	0.001	890	0.99

EXPLOSIVE B (Q=900)

V_f (cc/g)	P (kb)	A (cal/g)	A/Q
1.25	16	0	0
3.6	2	330	0.37
7.2	1	425	0.47
800	0.001	830	0.92

Fig. 1. — Adiabatic expansion curves for a high (A) or low (B) density explosive.

Then, solving equations 5, 6, and 7 simultaneously gives

$$\frac{T_1 - T_2}{N_1 W_1 C_1} = \frac{D}{W_1 C_1}\left(1 - \frac{\Delta_1 A_1}{\Delta_2 A_2}\right) + \left(1 - \frac{A_1 C_2}{A_2 C_1}\right) \qquad (8)$$

The criterion for determining which explosive is better for a given job is simply whether the left-hand side of Equation (8) is positive or negative. If it is positive, Explosive *B* is better than Explosive *A*; if it is negative, the reverse is true. Note that there may be a great advantage for a high-density explosive even when $A_1 = A_2$.

Anyone willing to apply this criterion will often find that he can save money by using metallized or nonmetallized slurry rather than metallized or nonmetallized ANFO. He may even find that a high-grade metallized slurry is more economical in the long run than a low-grade one, whether in blasting dry, wet, or water-filled boreholes. This is especially true in very hard rock where A/Q is, in general, appreciably below unity and depends strongly on loading density. It is also true where fixed costs are appreciable relative to explosive costs, i.e., D/W_1C_1 is appreciable, as is most often the case.

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How dry mix explosives can shave costs

John R. Lansdale

SLURRY PRODUCTS are an excellent explosive when mine conditions warrant their use, but in dry blastholes, such slurries can substantially increase mining costs. And the reason is simple. Slurries cost more per volume energy than a dry-mix product, and a greater quantity per foot of borehole must be used to achieve results comparable to those of dry-mix explosives.

A survey recently conducted by the author on a number of open pit copper mines in the Southwest showed that when dry holes are loaded with AN/FO/AL, performance is far better than holes containing low-energy slurries. Today on the Mesabi Range, other companies are involved in developing practical, economical methods of removing water from blastholes, because they, too, have found that under dry conditions, low-cost AN/FO/AL mixes will effectively and economically shoot taconites.

The importance of slurries in wet holes remains unchallenged, but for companies blessed with bone-dry conditions such as those in the southwestern US, Australia, Latin America and Africa, one must wonder about the insistence on using slurries — in effect putting water into these blastholes. The reason, it turns out, is quite simple—the widespread but erroneous belief that density has a direct correlation to energy.

Mining men around the world associate energy with density. In other words, if an explosive or blasting agent is dense, the assumption is that it has to have high energy. However, based on practical evidence, this is a case of fallacious thinking. At one major open pit operation in the West, a study has revealed that the slurries in use contained from 1% to 2% aluminum with a density of 1.3. An analysis of comparative energies indicated that it would take 1.5 lb of the slurry to equal an equivalent energy of 1 lb of prills and oil with a density of 0.88. Fragmentation also indicated this deficiency in energy.

In a recent article[1] slurry was compared to gelatin explosives, a valid comparison since both products have water resistance. But gelatins do not have more equivalent energies than dynamites, nor do slurries have higher equivalent energies than AN/FO/AL dry-mixes. A slurry does have water resistance which a bulk AN/FO/AL mix does not have, which makes slurry explosives so valuable in wet holes. However, under dry conditions, water resistance is a high price to pay for the resulting loss in energy from slurry usage. In the aforementioned article, a new development was cited in DBA slurries, one that contains only 11% water as opposed to the standard 15-20% water. The net result, according to the author, is a 15% gain in energy. This is certainly a step in the right direction, but why not go all the way *when dry conditions prevail*—add no water at all and take full advantage of all the energy available.

Maximum energies in dry mixes are usually generated using from 6% to 15% aluminum, yet to achieve these types of energies in slurry products, 20-30% aluminum must be used. Why is this so? According to the cited article: "A 2% decrease in water content has about the same influence on strength as a 1% increase in aluminum in the zero to 20% range and with the water above about 10%." With the average slurry containing 17% to 20% water and the new 11% formulation, we are in the plus 10% range. It can then be said conversely that for every 1% of water in the formulation, it will take 0.5% of aluminum to offset the loss. For example, if a miner is working with a slurry containing 18% water, it will take 9% aluminum to merely equalize the loss from the water and bring its energy level up to that of plain AN/FO. If this is compared to the high-energy dry NCN mixes available, the comparative energy ranges of the slurries in order to achieve similar energy equivalents would have to run from 15% to 24% aluminum. Aluminum is a costly item, especially when it is used merely to counteract a loss of energy created by the addition of water which was not needed to provide the water resistance in dry holes in the first place.

Many operations exist today with mild water problems — a foot or two of water in a borehole after sitting drilled for a week or more. A serious consideration of a dry-up program could provide the operator with lower costs and increased results, considering that for less money he could use a higher-energy dry AN/FO/AL mix and realize better drill efficiencies and fragmentation.

The low-priced slurries on the market today were introduced to compete with the lower-cost dry NCN mixes, but do these low-energy slurries really compete? The goal in buying an explosive product is to obtain the most energy for the money spent. Does a slurry containing 1% to 2% aluminum and 15% water provide economical energy units compared with other products available? For the open pit mines surveyed by the author, low-energy slurries are a poor energy buy. When poor results are achieved, the supplier usually recommends that higher aluminum content be used—which substantially increases blasting cost.

When a mining operator overseas decides to go with the bulk slurries, it is a total commitment on his part since such a move involves the purchase of high-priced pumpers, tanks, and storage facilities. The same bulk delivering advantages can be achieved with dry NCN mixes formulated to meet the specific energy requirements. Slurry formulations are much more costly to make due to capital equipment requirements and raw materials.

Furthermore, since there are patents covering the formulation of slurries, a license or royalty payment must be paid to the patent holder in order for the mine to mix its own product. In contrast, the AN/FO/AL mixes are not patented and are in no way proprietary. They can be readily and economically mixed at the mine location by setting up a system to utilize the correlation between energy requirements and formulations. The AN/FO/AL mixes can be developed in all ranges of energies and densities, depending upon the grade of ammonium nitrate, the method of processing, and the nature and percentage of metallic ingredients added.

Before deciding on a total commitment to slurries, it is wise to determine whether mine conditions dictate such a procedure: is it the most economical and efficient method? Such an investigation may reveal many profit dollars available through a different approach—and profit dollars are getting mighty hard to find.

About the author

John R. Lansdale is general manager, Australia and Southeast Asia for Marion Power Shovel Co., and a graduate of Michigan Technological University. He resides in Brisbane.

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HYDRAULIC FRACTURING AND OVERCORING STRESS MEASUREMENTS IN A DEEP BOREHOLE AT THE STRIPA TEST MINE, SWEDEN

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compiled by H.H. Einstein

INTRODUCTION

The importance of in situ stress measurements in the prediction of the behavior of underground openings is widely recognized, yet the methods for obtaining reliable values for these stresses have long been the object of controversy. Overcoring methods--besides having generally been limited to holes of tens of meters in length-- have been questioned as to the cause of data scatter, roles of residual stresses, and appropriate scale over which to measure strains. Hydraulic fracturing, the only alternative for deep measurements has gained increased acceptance, yet questions remain particularly in the areas of non-coincidence of the borehole with one of the principal stresses, role of tensile strength in data interpretation, and determination of fracture orientation away from the borehole.

Recently, the Swedish State Power Board has developed a workable method of performing overcoring measurements in holes hundreds of meters in length. With the need to obtain in situ stress values for nuclear waste disposal simulation experiments at the Stripa Mine in central Sweden, we undertook the task of running both the Power Board's Leeman triaxial cell and hydraulic fracturing in the same hole. This paper is a report of the results of the comparative measurements.

The borehole for the stress measurements was located approximately 250m north of the experimental test area at the 348m level of the mine (Figure 1). The borehole and the test facilties are entirely in medium grained granite. The mine had produced iron ore from stratabound layers in leptite (interbedded metasedimentary and metavolcanic rocks of Precambrian age) which had been intruded by the granite. The contact follows the northeast trend of the outcrops in Figure 1, and dips at about forty-five degrees to the southeast. Whereas the iron ore follows the trend of the beds and the contact, the mined out areas are confined roughly to a northeast striking, southeast dipping slab.

The total depth of the stress measurement hole was 381 meters and it was drilled with a 76mm (3 inch) diameter core barrel. Overcoring measurements were carried out in groups of four to five measurements each at roughly one hundred meter intervals in the hole. After completion of most of the drilling, hydraulic fracturing measurements were carried out at approximately 50 meter intervals with additional measurements below 300m at the approximate depth of the test facility.

OVERCORING MEASUREMENTS

The Swedish State Power Board stress measurement system is a modification of the Leeman triaxial cell, which measures the complete state of stress from a single borehole. The procedures used in the overcoring by the Swedish State Power Board at Stripa are the same as those described in Hiltscher and others (1979). As with most overcoring techniques, a pilot bore of a few decimeters in length is drilled at the end of the main borehole. A strain cell consisting of three, three-component strain gage rosettes is cemented to the wall of the pilot hole. After a reading of the strain gage outputs, the strain cell is overcored by a drill with a larger diameter bit. For the Power Board strain cell the pilot bore and main borehole diameters are 38 mm and 76 mm respectively. The

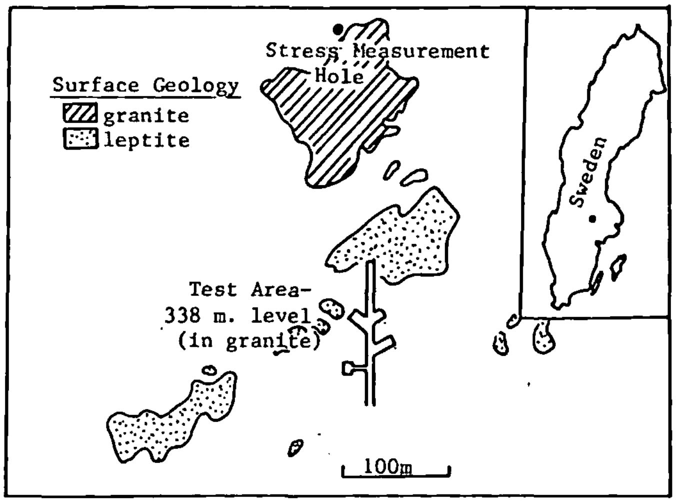

Figure 1. Location of stress measurement hole relative to test area in mine; inset shows location of Stripa Mine.

$$\frac{P_b \text{ at } r_1}{P_b \text{ at } r_2} = \frac{F(L/r_2)}{F(L/r_1)} \qquad (4)$$

Given the average strength of 2355 psi (16 MPa) for the 0.25 inch (7mm) holes, equation 4 gives a strength of 1950 psi (13 MPa) for the 0.5 inch (13mm) holes and 1280 psi (9 MPa) for the 3 inch holes in the field. The calculated strength for the larger laboratory test holes agrees well with the observed strengths. The 3 inch holes strengths are calculated as 54% of the 0.25 inch holes; Rummel and Jung (1975) observed that the ratio in their tests in limestone was about 45%. Whereas the failure should be expected to occur on the largest flaws available rather than the average sized flaw, one might expect tensile strengths in the larger holes to be smaller than those calculated above. Tensile tests on large cores containing 3 inch holes are planned.

The field tensile strength, which has been defined as the difference between the first and second breakdown pressures varied from 350 (2.4 MPa) to 1400 psi (9.7 MPa) and averaging 750 psi (5.2 MPa). The "field" values are considerable lower than the extrapolated laboratory values thus resulting in a lower calculation of σ_{Hmax}. Table 1 gives the data for calculation methods based on both eq. 1 and eq. 2. The laboratory based values are shown as a function of depth in Figure 8.

In comparing the two methods of hydrofracture analysis, it should be noted that the second breakdown technique is only applicable where the ratio of the maximum to minimum horizontal stress is less than two, as for greater stress differences the second breakdown would be less than the shut in pressure. Furthermore, fracture opening pressure depends on the total load on the fracture wall (J. Noorishad, personal communication) and not just the borehole pressure. The opening of the fracture depends on the transient pressure distribution along the fracture wall and may thus reflect pumping rate as well as stress conditions.

Table 1. Hydrofracture Stress Results *

		STRESS, psi (MPa)			
No.	Depth m.	First Breakdown σ_{Hmax}	Second Breakdown σ_{Hmax}	σ_{Hmin}	σ_v
1	28.5	1140 (7.9)	265 (1.8)	240 (1.7)	105 (0.7)
4	52.2	760 (12.1)	960 (6.6)	600 (4.1)	195 (1.3)
5	101.2	2050 (14.1)	1490 (10.3)	890 (6.1)	380 (2.6)
6	153.2	2000 (13.8)	1490 (10.3)	817 (5.6)	570 (3.9)
7	203.8	1370 (9.4)	1300 (9.0)	939 (6.5)	760 (5.2)
19	201.4	2330 (16.1)	1680 (11.6)	1070 (10.4)	750 (5.2)
8	251.6	3230 (22.3)	2730 (18.8)	1790 (12.3)	940 (6.5)
18	279.6	2610 (18.0)	2480 (17.1)	1560 (10.8)	1040(10.1)
17	304.9	1510 (10.4)	1850 (12.8)	1390 (9.6)	1140 (7.8)
9	308.6	2480 (17.1)	1980 (13.7)	1320 (9.1)	1150 (7.9)
10	318.1	2600 (17.9)	2310 (15.9)	1700 (11.7)	1190 (8.1)
16	325.8	3800 (26.2)	3340 (23.0)	1980 (13.7)	1215 (8.4)
11	328.6	3070 (21.2)	2720 (18.8)	1620 (11.2)	1230 (8.5)
13	356.7	3300 (22.8)	2530 (17.4)	1790 (12.3)	1330 (9.1)
14	367.1	2580 (17.8)	2080 (14.4)	1540 (10.6)	1370 (9.4)
15	369.7	3210 (22.1)	2640 (18.2)	1780 (12.3)	1380 (9.5)

* based on T=1100 psi

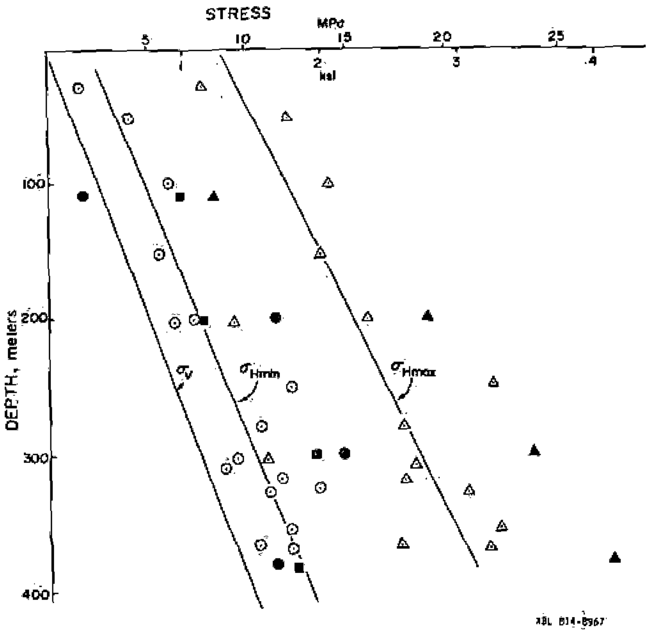

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Figure 8. Variation in horizontal and vertical stress with depth. Hydrofracture values are open, overcoring are solid. Hydrofracture values based on first breakdown. σ_{Hmax}-triangles, σ_{Hmin}-circles, σ_v-squares

RESULTS -- IMPRESSION PACKER WORK

Successful impressions were obtained for only nine of the tests. Although this is as many impressions as have usually been taken in hydrofracture experiments, a larger number of results would have been more satisfying. The failed impressions generally appeared to be the result of uneven inflation of the packer. The problem of the uneven inflation of the impression packer may be solvable by using elements that are both shorter in length and larger in diameter. Although our original aim in designing the wireline impression packer system was to minimize the size to avoid potential problems getting hung up in the hole, our experience with running the wireline system in high quality rock has given us greater confidence in using larger packers.

Despite the lost impressions, the impressions that were successful show a reasonably consistent WNW trend to the fracture strikes. The stereographic projection of the fracture planes in Figure 9 shows a set of fractures with a mean strike of N 65 W, with a standard deviation of 28 degrees.

COMPARISON OF STRESS DATA BY OVERCORING AND HYDRAULIC FRACTURING

Table 2 gives the interpolations of the horizontal and vertical stresses at the depth of the test facility based on the overcoring results and both methods of hydrofracture interpretation. The overcoring results agree well with the hydrofracturing in both the magnitudes of the minimum horizontal stress and in the orientation of the maximum horizontal stress. The overcoring results are higher than those calculated by either breakdown pressure technique (Figure 8). The first breakdown data, being higher, agrees better with the overcoring results. The vertical stress values in excess of the overburden weight may indicate that the overcoring values are too high; however the

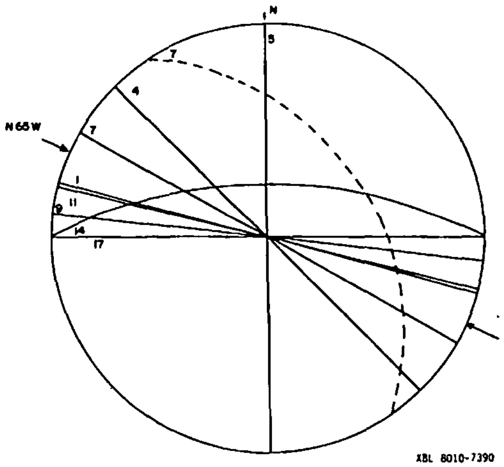

Figure 9. Lower hemisphere stereographic projection of planes of hydrofractures. Numbers refer to tests (see Table 1).

the preliminary calculations of Chan et al (1981) show that the mine openings may cause an increase in vertical stress at the shallow depths where the overcoring results are also the highest.

The area of closest agreement between the stress measurement techniques is in the northwest to east-west orientation of the maximum stress. This direction is consistent with previous data collected by the Power Board (Hiltscher et al, 1979) and N. Hast (1969).

In conclusion, the overcoring and hydraulic fracturing results give comparable data with respect to magnitudes of horizontal stresses and to orientation. In holes where principal stress may not be coincident with borehole axes, the hydraulic frac turing may yield mainly the stresses normal to the hole rather than principal stresses. Although major questions remain both as cause of the scatter in the over coring data and the question of tensile strength in hydrofracture data analysis, the overall agreement of the methods would indicate that both the overcoring and hydraulic fracturing provide data applicable to practical problems in the field.

Table 2. Interpolated <u>In Situ</u> Stress Values at the depth of the Test Facility (310 m in the borehole)

Method	σ_{HMax}	σ_{HMin}	σ_v^*
Overcoring	3670 (25.3)	1650 (11.7)	1750 (12.0)
Hydrofracturing (1st breakdown)	2740 (18.9)	1550 (10.7)	1160 (8.0)
Hydrofracturing (2d breakdown)	2390 (16.5)	1550 (10.7)	1160 (8.0)

*Hydrofracture values calculated based on overburden weight.

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1980

HELIUM...
A GEOCHEMICAL GUIDE FOR URANIUM EXPLORATION

David E. Kahler

ABSTRACT

Helium is produced from alpha particles (helium nuclei) combining with electrons during radioactive decay of uranium and thorium. These helium atoms are non-reactive chemically and due to their light weight and molecular size they tend to escape from their source. This migration takes place through minute fractures and helium will eventually reach the surface, thus producing measurable helium halos. These anomalous concentrations of helium can be measured in subsurface water, soil and soil gas, and provide a useful means of remote detection of radioactive mineral deposits. Sampling equipment to conduct helium geochemical surveys and precision analyses are available from Western Systems, Inc.

INTRODUCTION

From the point of view of uranium geochemistry, the elements of greatest interest are uranium, radium, radon and helium. Gamma-ray detection of the uranium daughter bismuth-214 is also an effective remote sensor of uranium, but this technique falls more into the category of geophysics.

Uranium of course is the most specific geochemical indicator and actually has a fairly long range of dispersion. Radium and radon (which is tied to radium) may move moderate distances by water transport, but these two elements seldom migrate far from the uranium deposit. Helium, conversely, is extremely mobile and since it is nonradioactive with an infinite half-life, it can be detected at great distances from uranium deposits. Helium has the longest range of the uranium geochemical tracers and therefore provides a convenient means of identifying potential uranium deposits.

Gaseous geochemical sampling equipment, leak-free sample storage containers and high sensitivity (± 10 ppb) mass spectrometers have recently been developed and are now available to uranium explorationists. This time and cost effective remote sensing technique provides an added tool for the long range identification of radioactive mineral deposits.

HELIUM USE FOR URANIUM EXPLORATION

It is well known that uranium deposits generate substantial quantities of helium and thus helium halos will be present in water, soil and soil gas surrounding the deposits. While not every helium anomaly will be directly related to a uranium ore deposit, nevertheless the discovery of helium anomalies in areas of high uranium potential can be of significant benefit to exploration programs.

Radon differs considerably from helium as a soil-gas geochemical tracer for uranium and it is necessary to distinguish between these two elements. Radon is severely limited in its use as a distant trace element for uranium, since the half-life of radon-222 is only 3.8 days. Additionally, radon is an extremely dense gas which diffuses slowly. It is likely that most radon soil-gas anomalies related to deeply buried uranium deposits result from the fortuitous migration of radium-226 (radon's immediate parent) and possibly to vertical/near vertical water movement. Radon survey techniques have definite application in remote sensing for shallow uranium deposits, as well as use in ground water sampling for deeper deposits. Radon is essentially a near source indicator, which when present in anomalous concentrations is a valuable trace element for uranium.

Continued

Helium, however, is easily the most stable (infinite half-life) and mobile of the isotopes in the uranium-238 decay series. Helium's extremely small molecular size and light weight make it the ideal trace element for large halo, geochemical exploration for uranium. Helium atoms, from the moment of formation during radioactive decay of uranium and thorium, are in constant motion and are "seeking daylight". Helium in rocks will migrate into the ground water and preferentially into surface-connected faults and fractures. Due to its light weight, helium will migrate through the entire geologic column where it is eventually lost to the atmosphere and escapes to outer space. It is this unrestricted movement of helium that provides the explorationist with a significant geochemical guide to uranium – the ultimate parent of helium.

SAMPLING TECHNIQUES

Atmospheric helium concentrations vary slightly with time and from place-to-place, and average 5.24 ppm at the Earth's surface. Due to rapid mixing of Earth-source helium with air at the surface, atmospheric sampling for helium to locate uranium deposits is not practical.

Commonly used helium sampling methods include water, soil and soil-gas geochemical surveys. The following will briefly review these three techniques:

Water: Water sampling will generally provide the highest anomalies and is an ideal regional reconnaissance technique. The limiting factor of course is the availability of sampling points. Also, since helium readily degasses from water, surface samples from lakes and streams are of little value. Practically speaking, water samples must be collected from non-aerated sources such as springs and wells or below the thermocline in lakes or from near the ocean floor. Ideally it would appear that samples from packer-isolated formations would give the most useful information. However, for regional exploration, well water samples from various depths/formations will define anomalous areas due to helium's freedom of movement between formations in its ascent to the surface.

Soil gas: A hollow steel probe is driven into the ground and a gas sample withdrawn through a rubber septum on top of the probe. By evacuating the probe a gas sample is gathered from an area near the open tip, which will represent soil gas conditions at that point. The sample thus removed is then stored in a small steel tube with a lead seal and later analyzed. This is an extremely rapid sampling technique that can be carried out by one or two persons with light-weight, hand carried equipment.

Soil: Soil surveys, in which an auger soil sample is collected, provide an outstanding helium sampling method. This represents essentially a time-integrated sample, where helium has accumulated in soil moisture and soil micropores. The exact sampling procedure is to obtain soil from a depth of 30 inches (75 cm.) or more, place the sample in a steel container and immediately seal the container. The soil is degassed, reaches equilibrium with air in the container and the gaseous sample is later withdrawn and analyzed in the laboratory. While soil surveys require somewhat more time to conduct, they will provide higher helium anomalies than the soil-gas probe method.

SAMPLE DENSITY AND ANALYSIS

Water, soil or soil-gas samples for uranium exploration can be collected at widely varying densities ranging from one sample per 100 square miles (kms.) to 100 or more samples per square mile (km.). Each project is different and must be evaluated for sample spacing based upon geological, geochemical and geophysical knowledge of the area. A usual spacing of one to five samples per square mile(km.) is quite adequate for regional studies and will provide sufficient data to significantly reduce the area of interest for more detailed surveys.

Followup, detailed surveys are usually at 0.1 mile (km.) to 0.2 mile (km.) grid spacing. Grids are customarily modified to fit elongate trends and line surveys are usually laid out normal to trend projections of known deposits. Grid surveys are preferred to line surveys, however, for ease of interpreting anomalies.

The gaseous samples are analyzed in the laboratory with a modified, helium leak detector mass spectrometer. The modifications result in the removal of active gases from the measurement samples, thus permitting a 100 times larger sample to be injected into the mass spectrometer. Also, highly sensitive temperature and pressure indicators, inlet manifold volume reduction and thermal insulation permit instrument accuracy in the range of ± 10 ppb with reference to atmospheric helium concentration of 5240 ppb.

WESTERN SYSTEMS, INC.

Western Systems has been providing precise helium measurements for the uranium exploration industry since 1978. As a leader in helium geochemical analysis, Western Systems has been active in domestic and international projects in mineral and energy resource evaluation. Western Systems is available to discuss your particular exploration project and to set up a sampling program to fit your requirements.

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The National Uranium Resource Evaluation (NURE) Program includes the systematic collection and analysis of hydrogeochemical samples throughout the United States. Many of these samples have been analyzed for helium and are noted in NURE Data Reports, which have been released by the Department of Energy, Grand Junction, Colorado. Several of these reports are listed below:

NTMS Map Sheet	States Included	Report Number
Walker Lake	California & Nevada	GJBX-107(80)
Elko	Nevada & Utah	GJBX-163(80)
Price	Utah	GJBX-172(80)
McDermitt	Nevada	GJBX-173(80)
Escalante	Utah	GJBX-209(80)
Okanogan	Washington	GJBX-210(80)
Mesa	Arizona	GJBX-216(80)
Salina	Utah	GJBX-218(80)

Heap leaching will produce 85,000 oz/year of doré bullion for Smoky Valley Mining

Lane White, Managing editor

HIGH, dry, and sparsely populated, the Big Smoky Valley stretches for about 100 mi through central Nevada, between the high peaks of the Toquima Mountains of the east and the Toiyabe Mountains on the west—sites of the ghosts of numerous mining camps. At Round Mountain, about 55 mi north of Tonopah on the valley's eastern flank, gold was discovered in 1905, and production from underground mines continued until 1935. Placer operations produced intermittently through the late 1950s, and over the years an estimated total of $8 million in gold was mined in the district.

In 1977, Smoky Valley Mining Co. has revived gold production at Round Mountain, heap leaching low grade ores to produce 85,000 oz per year of doré bullion assaying 67% gold and 33% silver. The company, a subsidiary of Copper Range Co., employs about 100 people. Felmont Oil Corp. and Case-Pomeroy & Co. are partners in Smoky Valley Mining. The processing scheme includes open-pit mining, crushing to 100% minus ½ in., cyanide-lime trickle leaching, carbon adsorption and desorption, electrowinning, and refining.

Smoky Valley Mining works gold deposits in sections 19 and 30 T10N R44E in Nye County, on the western side of Round Mountain, an isolated hill of mineralized welded rhyolite tuff flanked by gold placer deposits of similar eroded materials. The property is remote from its major sources of supplies. Reno is about 240 mi to the northwest and Las Vegas is about 262 mi to the southeast by the shortest highway routes.

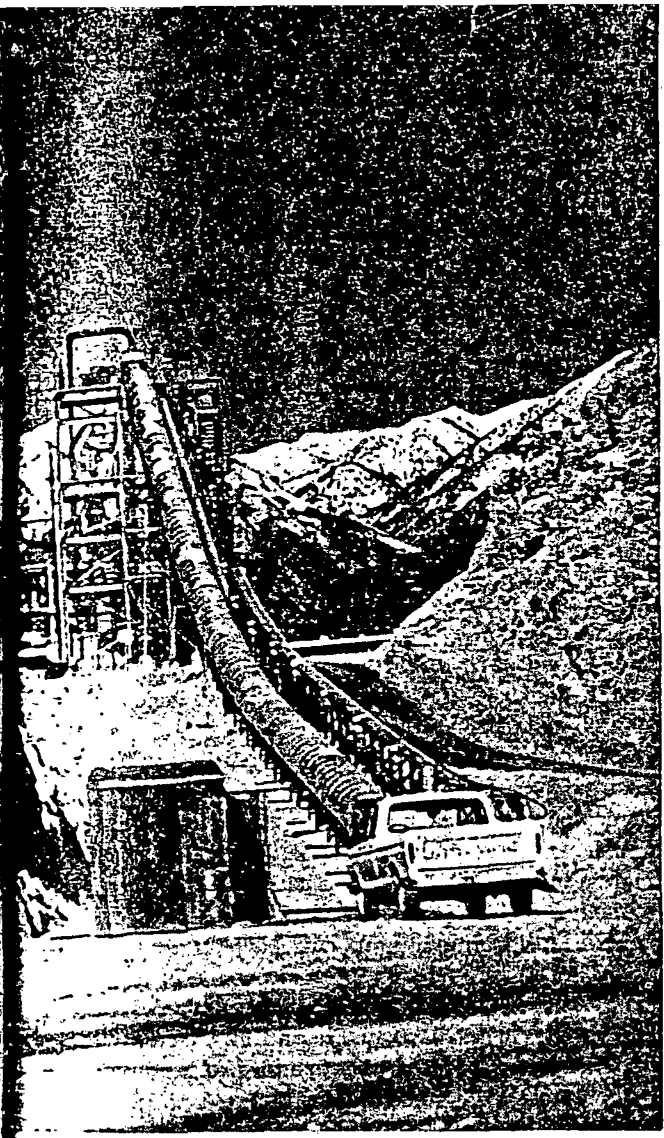
Climatic conditions are extreme in central Nevada. Summers are hot and dry, with temperatures on occasion exceeding 100°F, while winters are windy and cold, with temperatures dropping below zero. The work area elevation on the Smoky Valley Mining property ranges from 6,100 ft to 6,600 ft above sea level. Vegetation consists of sage and desert grasses. Precipitation averages 8 in. per year, and snowfall is minimal. Leaching activity is expected to proceed during 10 months of the year.

Water for Smoky Valley Mining operations is drawn from Jett Canyon in the Toiyabe Mountains and, during periods when Jett Canyon is dry, from wells in the valley bottom. In Jett Canyon, about 8.5 mi west of the plant site at an elevation about 760 ft above the plant, a small concrete stream diverter provides input for a 15-in.-dia water pipeline that first went into operation in 1915. The Smoky Valley Mining plant draws make-up water at the rate of about 400 gpm.

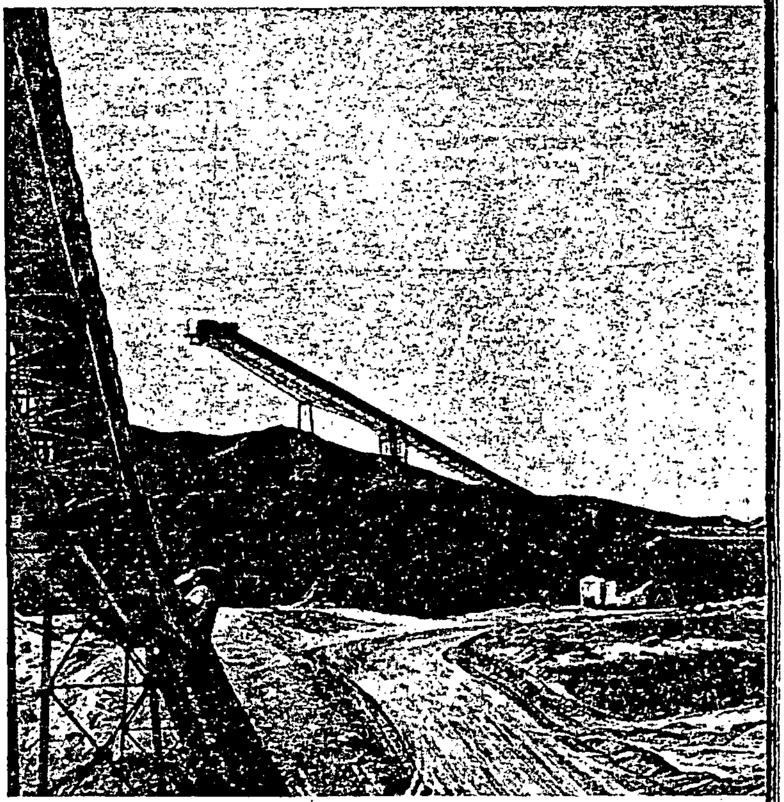
F. E. Girucky is general manager of the operation, D. E. Hayes is executive secretary, R. W. Frailey is assistant general manager, R. M. Jones is mine and maintenance manager, R. J. Leone is manager of ore quality control, R. H. Hattrap is manager of administra-

Each of five 400-ft-long x 250-ft-wide leaching pads holds about 40,000 tons of ore, stacked 10 ft high.

A control panel at the primary crusher monitors and controls ore flow from the crusher through to fine ore storage.



A 761-ft-long conveyor advances ore from the primary crusher to the secondary crusher. The conveyor reaches a height of 52 ft 5 in. (left). Three vibratory feeders beneath the fine ore stockpile pull ore and feed it to a conveyor for transfer to a truck loading bin near the leach pads (below).



tive services, and L. G. Hayes is manager of technical services. At Smoky Valley Mining, operations are divided between two departments—mining and maintenance, and leaching and gold recovery—supported by three service departments: geology, engineering, and administrative services. Buildings on the plant site are six in number: administrative, change house, combination warehouse and plant maintenance shop; adsorption-desorption-refinery; reagent mixing complex; and laboratory. Equipment installations include primary, secondary, and tertiary crushers; surge-stockpile facilities; a truck loading bin; interconnecting conveyors; and permanent asphalt leach pads.

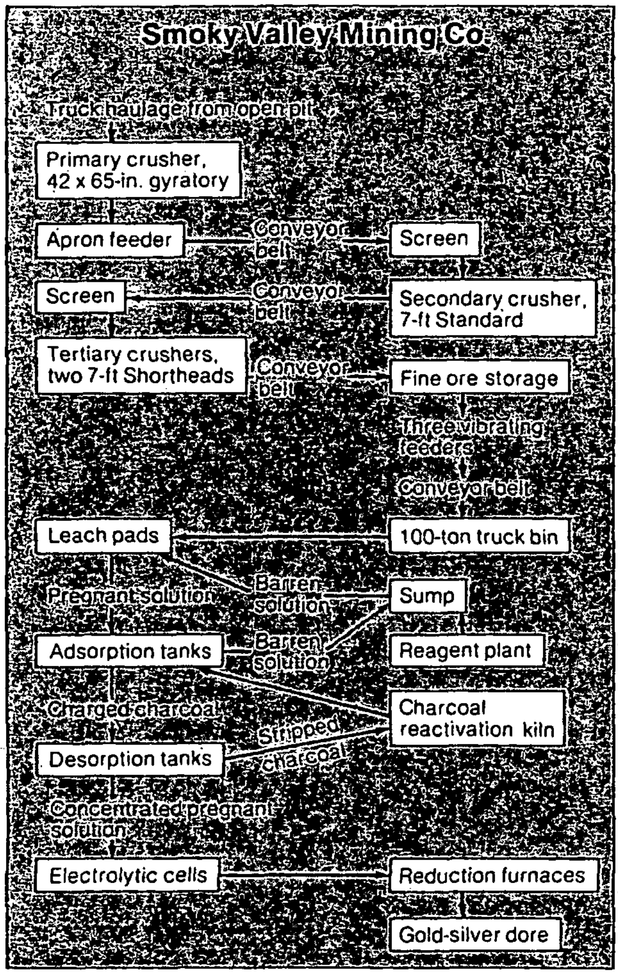
Mountain States Engineers was awarded the design and construction contract.

Mining 8,000 tpd at 1:1 stripping ratio

The Smoky Valley mining and maintenance crews work three shifts per day, seven days per week, providing plant-wide maintenance, stripping 8,000 tpd of waste, and moving 8,000 tpd of broken ore through a crushing and conveying system to a truck bin near the leaching pads.

The welded rhyolite tuff of Round Mountain probably dates to the Miocene, though the age has not been definitely established. Fracturing in the Tertiary permitted intrusion by hydrothermal solutions high in gold, silver, and other trace minerals. Gold-bearing pyrites formed first; oxidation of the pyrite then remobilized the gold. Grade control is difficult because it is difficult to make a visual distinction between ore and waste. Grade control is maintained through drill cuttings and photogeology, with best results gained on drillhole assays. Assaying has been aided by the installation of improved sample collecting devices on the Ingersoll-Rand blasthole drills. Ore at Smoky Valley averages 0.06 oz of gold per ton, and the current cutoff grade is 0.02 oz per ton.

Blastholes are drilled on a 17 x 19-ft pattern, using an Ingersoll-Rand T-4 drill to sink 6¾-in.-dia holes. They are blasted with ANFO, using 50 lb of aluminized ANFO containing 7% aluminum on the bottom. Kinepak primers and Nonel delays are used for detonation. A P&H shovel of 6-cu-yd dipper capacity loads out ore at a 35-ft bench. There are also three Cat 992 front-end loaders on the property, using slicks on the front and regular tires on the back. Other equipment includes nine Euclid R-50 trucks, one Terex 8250, and a Cat D9. The trucks make a short ore haul to an Allis-Chalmers 42 x 65-in. primary gyratory crusher having a design capacity of 550 tph. Primary crushing reduces the Smoky Valley ore to minus 7 in.



A Stephens-Adamson 42 x 20-in apron feeder draws ore from a 75-ton bin under the primary crusher and feeds it to a 36-in.-wide conveyor belt, which moves it 761 ft to the Symons 7-ft Standard secondary crusher for reduction to minus 2 in. Another 36-in. conveyor belt, 182 ft long, advances the ore to two 7-ft Symons Short Head tertiary crushers in parallel, which reduce the ore to 94% minus ⅜ in. x 1½ in. An 1,100-ft-long, 36-in.-wide conveyor belt then advances the material to a 30,000-ton fine ore stockpile that has a 9,000-ton live load. Three vibratory feeders beneath the stockpile pull ore and feed it at a normal capacity of 1,000 tph to a 1,200-ft-long, 36-in.-wide conveyor belt, which transfers it to a 100-ton truck loading bin located near the leach pads. The truck loading bin has automatic bin gates with a manual override and is equipped with a weightometer and a two-stage automatic sampler.

Rear-dump trucks draw ore from the ore bin and transfer it to the five leaching pads, which cover a total area 2,100 ft long x 282 ft wide. The individual pads, which are constructed of high grade asphalt 7 in. thick with a protective membrane 2 in. from the bottom, are separated by haulage roads.

Leach solution, with sodium cyanide added at about 1 lb per ton of ore, is sprinkled at about 400 gpm over each heap by Bagdad wigglers. The leach pads slope at about 3% to a common drainage trench on the western side of the pile. The normal leaching cycle is expected to be 27 days for leach solution sprinkling, two days for washing, and two or three days for drainage, for a total leach pad on-off cycle time of about 35 days. A lime addition maintains the leaching pH between 9.5 and 10.5.

Worthington turbine pumps are used for moving solution to the heaps and from the heaps to the refinery, with flow meters measuring the rate of flow both ways. A 2.5-million-gal solution storage pond provides capacity for holding all solutions in the event of a plant emergency and maximum rainfall, and a well below the leach pads monitors ground water to assure that no cyanide escapes the processing system.

Effluent from the heap leaching pads moves at 1,200 to 1,600 gpm through five countercurrent charcoal adsorption tanks in series. Gold and silver in the pregnant leaching solution precipitate onto activated 12 x 30 mesh coconut carbon, starting at the No. 1 tank. Each of the 8-ft-high x 12-ft-dia adsorption tanks holds about 7,000 lb of carbon.

Loaded carbon advances from the No. 1 tank to three desorption vessels, each of 1-ton capacity, in series, while barren solution from the No. 5 tank receives a sodium cyanide and lime addition and is returned as leaching solution to the asphalt leaching pad.

About 1 ton of gold-loaded charcoal is removed from the No. 1 adsorption tank each day at a chemical analysis of about 250 tr oz of gold per ton of charcoal, and a corresponding amount is advanced at each of the other tanks. Charcoal, treated in an Envirotech reactivation kiln following desorption, is added to the system at the No. 5 tank. Charcoal reactivation takes place under controlled heat (1,100°F) in the absence of air.

In the desorption circuit, caustic-cyanide solution at 190°F redissolves and strips gold and silver values from the loaded charcoal. The pressure vessels are heated by hot water jackets.

The adsorption-desorption system requires a make-up carbon addition of about 1 ton every 24 hr.

Pregnant solution from the desorption circuit flows through electrowinning cells in the refinery at Smoky Valley Mining. Metal values are electrowon from the solution at 60 amps and 2.5 v in three electrolytic cells in parallel, precipitating on steel wool cathodes. Cathodes are usually loaded to 100 oz of metal values per pound of steel wool before they are removed from the electrowinning cells. About 1,000 tr oz of gold and silver are removed from the cells at each reloading.

Barren caustic-cyanide solution returns from the electrolytic cells to the desorption circuit, where chemicals are added to restore it to the original concentration.

Loaded cathodes are smelted in one of three Lindberg crucible reduction furnaces, the steel is slagged off, and the doré metal is poured into bars for marketing.

Laboratory facilities at Smoky Valley Mining include atomic adsorption instruments and conventional wet lab and fire assaying equipment to serve exploration programs, mine planning, pit operations, grade control, leaching and processing control, and quantification of gold-silver in the product to be marketed. ☐

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HEAP LEACHING OF URANIUM - A CASE HISTORY

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INTRODUCTION

Union Carbide began looking seriously at heap leaching in 1971. At that time some 1.6 million tons of mineral averaging 0.040% U_3O_8 were stockpiled at various sites around the Gas Hills, Wyoming, uranium facility. Several alternatives for economically exploiting these reserves were considered and heap leaching seemed the most attractive. At the time, Western Nuclear Inc. was operating a heap leach project nearby in which the low-grade ore was leached with sulfuric acid, the product liquor treated in an on-site solvent extraction circuit, and the stripped product liquor re-acidified and recycled. They were most generous in allowing us to visit their site, answering our questions, and were helpful in discussing the problems associated with heap leaching. They confirmed our belief that it was possible to operate a heap leach profitably on material too low grade for conventional milling.

Based largely on what we had learned from Western Nuclear's experience, a program was set up involving a laboratory study to determine the characteristics of the mineral stockpiles as related to heap leaching and to conduct a pilot heap leach adjoining our Gas Hills mill. Basically, the pilot heap construction and leach procedure were similar to those described in the literature(1,2) with certain modifications to permit detailed monitoring of the operation.

In May, 1972, the decision was made to construct a test heap. The UCC plant at Gas Hills, Wyoming was selected as the most appropriate site for the following reasons:

1. The necessary equipment for heap construction was readily available.
2. Stockpiles of mineral from the various mining sites were on hand.

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(1) Heap Leaching of Low Grade Ore, D. S. Mashbir, Min. Cong. J. Dec. 1964

(2) The Extractive Metallurgy of Uranium, Robert C. Merritt, Copyright 1971 by Colorado School of Mines Res. Inst.

3. Construction of the heap could be made on an abandoned tailings pile minimizing problems associated with environmental approval.
4. Proximity of the mill would allow product streams to be absorbed into existing circuits.
5. Necessary utilities were available.
6. Tailings water from the existing circuit could be used for leaching.

The primary objectives of the pilot heap leach program were:

1. To confirm the data obtained in bench-scale tests particularly on uranium recovery, acid usage, and ore permeability.
2. To evaluate plastic liners used for base preparation.
3. To investigate heap configuration variables.
4. To determine heap leach amenability of the different mineral sources.
5. To establish the economics of heap leaching low-grade ores.

PILOT TEST PROGRAM

Prior to the pilot heap test, samples of the various mineral piles were evaluated in bench-scale testing. The objectives of this study were to determine (1) the acid requirement, (2) permeability of the ore, (3) ultimate U_3O_8 recovery, (4) probable product liquor grade, and (5) an estimate of heap economics. These tests were conducted on small samples, usually 100 grams or less. The laboratory data on these samples indicated that the liquor would flow readily through the ore with an anticipated flow rate of 10-20 gallons per square foot per day (400-800 l/m^2) compared to about 3-6 gallons per square foot (129-240 l/m^2) of pond area observed by Western Nuclear. The tests indicated that 20 pounds of H_2SO_4 per ton of ore (10 kg/t) were required for leaching and that only 100-150 gallons of leaching solution (400-600 l/t) per wetted ton would be required for uranium recoveries of 90% and that the liquor grade could reach as high as 2.0 grams U_3O_8 per liter.

Three test heaps, employing various sources of low-grade mineral, were planned. The stockpiles were essentially unconsolidated sands and required no crushing.

An area large enough for a 68-foot (20.7m) x 124-foot (37.8m) base overlying an old tailings pond was graded for drainage toward the collection launders and the base was covered with a 6-mil polyethylene liner. Ten rows of perforated 4-inch Orangeburg drain pipe placed at 12-foot (3.7m) intervals were covered with drainage rock in tapered piles 4 foot (1.2m) wide mounting to about one foot (.3m) above the pipe.

Heap W-1 construction consisted of piling approximately 730 dry tons (662 t) from the West Gas Hills stockpile to a depth of 8 feet (2.4m) on one end of the base. A second heap, E-1, consisting of 875 tons (794 t) of stockpiled material from East Gas Hills, was constructed 25 feet (7.6m) from Heap W-1 on the opposite end of the base. The third heap, E-2, consisting of 755 tons (685 t) of freshly mined mineral from East Gas Hills, was formed by filling the void between Heaps W-1 and E-1. To isolate this material, polyethylene lining was laid on the interior slopes of Heaps W-1 and E-1. Figure 1 is a sketch showing the final configuration of the three test heaps.

On top of the heaps 2-foot (0.6m) berms were constructed so that each heap could be isolated for leaching. The depth of each berm was about 18 inches (0.5m).

The calculated physical properties of the three heaps as constructed are shown in Table I.

TABLE I

Physical Properties of Heaps

Heap No.	W-1	E-1	E-2
Dry mineral in heap, tons (t)	760 (689)	875 (794)	755 (685)
Calculated bulk density, lb./ft.^{3} (kg/m3)	99 (1587)	107 (1715)	116 (1859)
Calculated porosity, %	39	33	28
U_3O_8 assay, %	0.032	0.015	0.024
Calc. U_3O_8 under ponds, lb. U_3O_8 (kg)	177 (80.3)	105 (47.6)	295 (134)
Calc. U_3O_8 under slopes, lb. U_3O_8 (kg)	309 (140)	158 (71.7)	67 (30.4)

Total U_3O_8 in heaps, lb. U_3O_8 (kg)	486 (220)	263 (119)	362 (164)

Three fixed bed ion exchange (IX) columns, each containing about 20 cubic feet (0.57m^3) of Dowex 21K resin, were installed for uranium extraction of the heap leach liquor. The leaching system was designed to allow flexible operation. The liquor collected from the heaps could either be pumped directly to the plant, to the IX columns or to a surge tank for recycle to the heaps. The leach solution is made up from either tailings pond water or from the recycle surge tank, employing a 2000-gallon wood tank for mixing in the sulfuric acid to the desired solution strength. Normally, leaching was accomplished with a 5% H_2SO_4 solution and the heaps washed with a 1.5 pH solution.

Daily logs were maintained on the amount of acid added to the heaps along with the total gallons pumped to each pond. Careful monitoring was also maintained on each drain for flow rate, % U_3O_8, % Fe, pH, and free acid. To obtain an overall solution balance, the amount of water lost each day by evaporation was estimated from readings obtained from pond evaporation and capillary evaporation gauges. Values derived from these data, together with a knowledge of adsorption of solution by the mineral, resulted in a solution balance of 102%.

Upon completion of the campaign, the leached heaps were sampled by augering 1-1/2 inch diameter by 6 foot long samples on a pattern over the top of the heap. A sample map showing the location of the holes and the assay values appears in Figure 2. In the area bounded by the dotted lines, the sample assays are about three times higher than those of the remaining area. This is the area where trucks drove onto the heap during construction and suggests that the nonuniform packing caused channeling of the leach solution.

In addition to the auger sampling, two trenchs were driven into the heap as shown in Figure 2. A typical set of trench sample analyses are shown in Figure 3. The dotted line, which makes an angle of 58° with the horizontal, Indicated that portion of the slope contacted by the leach liquor.

The metallurgical results of the pilot test campaign are summarized in Table II.

TABLE II

Pilot Test Metallurgical Results

Heap No.	W-1	E-1	E-2
U_3O_8 solubilized, lb. (kg)	269 (122)	64 (29)	209 (95)
U_3O_8 recovered, lb. (kg)	228 (103)	53 (24)	206 (93)
U_3O_8 solubilized under ponds, %	86	46	60
U_3O_8 solubilized under slopes, %	38	10	46
U_3O_8 solubilized total, %	55	24	58
Max. liquor grade g/l U_3O_8	1.10	0.78	0.58
Average liquor grade, g/l U_3O_8	0.48	0.23	0.21
Duration of test, days	59	41	26
H_2SO_4 consumption, lb./ton ore contacted (kg/t)	19 (9.5)	27 (13.5)	15 (7.5)
H_2SO_4 consumption, lb./lb. U_3O_8 solubilized (kg/t)	34 (17)	168 (84)	51 (26.5)
Fluid conductance, gal./day/ft.^{2} (l/day/m^2)	2.3 (94)	2.7 (110)	6.4 (260

The total uranium shipped to the Gas Hills plant was about 55 pounds (25 kg) less than that shown above. This discrepancy is attributed in part to uranium transport to the sides of the heaps by capillary diffusion. Grab samples from the wet line in the slopes, where the capillary action would be maximum, were several times more concentrated in U_3O_8 than the mineral head samples.

A large amount of data was generated during the summer campaign from which the following conclusions were drawn:

1. Small-scale bench tests could be used for acid consumption requirements and ultimate U_3O_8 recovery but had little, if any, value with regard to other characteristics.

2. Solution conductance of Gas Hills mineral is about 2.5 gallons per square foot per day (100 $l/m^2/d$.) The higher conductance of heap E-2 is attributed to the wall effect of the liner covered slopes.
3. Uranium recovery is dependent solely on the mineral wetted by the leach solution, original ore grade, and a constant residue assay of U_3O_8.
4. Heap permeability is effected by heap construction techniques and selective compaction should be avoided.
5. The good solution balance confirmed the satisfactory performance of the polyethylene liner for a base. However, the difficulty of installation, together with the extreme care required to position the rock and gravel over the drains, led us to consider a clay base as a more practical alternative for commercial heaps.
6. The ore wetted by the leach solution extended downward from the berms at an angle of 32° into the heap slopes.
7. Recovery of the uranium to a residue tail of 0.008% U_3O_8 could be achieved with 200-300 gallons of solution per ton of mineral wetted (850-1250 l/t).
8. Soluble uranium in economic concentrations would not appear in the drains until the solution pH reached 4.0 or less.
9. As much as 10% settling within the heap occurred as a result of flooding the ponds.
10. To adequately handle the nonuniform settling due to flooding and leaching, berms between ponds as well as the side berms should be at least four feet across.
11. Once leaching has started on a pond, the operation should continue without interruption to avoid gross changes in the

permeability characteristics of the heap.

In view of these test results and conclusions, heap leaching the mineral stockpiles at the Gas Hills facilities was determined to be economically feasible. With the full cooperation of the Colorado Plateau Operations Department, a program for a full-scale pilot heap was proposed, designed, and in operation by May of 1973. Simultaneously, a laboratory program was initiated whereby large columns were constructed that would more closely simulate heap conditions and allow for a better evaluation technique of heap leach amenability of the various mineral sources available.

LABORATORY AMENABILITY PROGRAM

It was apparent that bench-scale testing of small samples would not provide suitable scale-up data for evaluating the amenability of an ore to heap leaching. Because we anticipated heap heights of 20 feet (6.1m), the decision was made to construct a full-sized column test unit from FRP pipe with a diameter of 2 feet and a full 21 feet in height. The column was filled with 2-1/2 tons of 0.029% U_3O_8 and the auxiliary equipment to conduct and monitor the test was installed. Seven sample ports were installed at 3-foot intervals for periodic sampling of the percolating solution and for residue sampling. Figure No. 4 shows the typical metallurgical results obtained on this unit employing 40 pounds of sulfuric acid per ton of low-grade ore. Essentially 90% of the recoverable uranium is obtained after only 110 gallons of leaching solution per ton of ore (460 l/t) have passed through the column. Essentially all of the recoverable values are obtained after 200 gallons of leaching solution per ton (850 l/t) have been reached.

Bed permeability or fluid conductance appears to be a function of the leaching cycle. A typical flow rate through the column is illustrated in Figure 5. The flow rate remains fairly constant until the acid consuming constituents are removed and the pH of the product liquor approaches 1.0 or less. At this point, the flow rate increases steadily with time. There is evidence suggesting that the flow rate curve is more a function of product liquor pH than of volume through the bed.

Although the 21-foot column seemed to yield relatively reproducible results, it required a large quantity of ore to conduct a single test. For expediency and economy, a smaller 12-foot (3.7m) column was constructed for leach amenability tests. The results obtained from this shorter column were sufficiently close to the data from the larger column that this shorter column has since been used for amenability testing.

The results obtained on the laboratory columns were compared with those of the test heaps. In general, efficiency was greater for the columns. Under field conditions, an additional 200 gallons of leachant per ton (850 l/t) were required to produce recoveries comparable to those achieved with 100 gallons per ton in the columns. Product liquor grades were proportionally lower, fluid conductance somewhat lower, and residue tails slightly higher for the test heaps.

In general, the principal conclusions derived from the column testing were:

1. Uranium and iron move through the bed in distinct fronts.
2. Bed permeability is fairly constant with time until the fronts reach the bottom of the column after which it steadily increased.
3. The leached tails approach a constant uranium content of 0.006-0.008% U_3O_8. This value should be used in conjunction with the head assay to estimate production. The practice of quoting per cent recovery disguises the influence of head analyses.
4. Channeling was observed in the column. It is apparently the major factor in the discrepancies observed in scale-up factors to commercial heaps. The fact that the

channels did not persist throughout the run is encouraging and supports field conclusions.

FULL-SCALE PILOT HEAP OPERATION

In the early spring of 1973, construction of a 225,000-ton (204,000 t) full-scale pilot heap was begun at Gas Hills. The heap base was limited to the area of the old tailing pond and this determined the size of the heap. While leaching operations would start in 1973, the heap construction would not be completed until 1974. This was accomplished by starting the base at one end of the heap area and progressing lengthwise. As soon as the base was laid and compacted, the perforated pipe was laid down with a covering of gravel. This operation was followed by a 5-foot protective covering of ore, and lastly the heap itself was constructed to elevation in a single lift. About 125,000 tons (113,000 t) were placed on the base in 1973 with the remaining 100,000 tons (91,000 t) added in 1974. All the construction operations were carried out simultaneously. Figure 6 is an aerial photo at the time the first pond was flooded showing the heap in various stages of construction.

The construction of the clay base was carried out under the guidance of Dames and Moore. Their field engineers sampled and tested local clays and conducted the laboratory tests to determine the suitability of the available clays. Placement of the 12-inch (0.3m) clay liner was accomplished in two 6-inch (0.15m) lifts compacted with a sheepsfoot roller. The moisture content of the clay was adjusted and each lift was compacted to 85-90% of maximum dry density. Seepage rate through the clay liner was calculated to be less than one foot per year. Two monitor drains, located under the base, showed no seepage throughout the duration of the test. Finally, a 3-foot (0.9m) compacted clay dike was constructed around the perimeter of the base to prevent seepage from the base of the heap.

Heavy duty 4-inch (0.1m) perforated drain pipe, spaced 18 feet (5.5m) apart, was laid from the toe of the clay dike on the north to the toe of the clay dike on the south and covered with a foot of gravel. At the south dike, the perforated pipe was coupled to a solid pipe extending through the dike to the collection launders. A flexible section of pipe was attached to the exterior end of the solid pipe to permit coupling to any of the three collection launders.

The heap dimensions are shown in the cross-section diagram of Figure 7. The larger berm is placed on the south side above the collection launders as an added precaution for sloughing and for access to the various ponds. An additional berm is located down the center of the heap to minimize loss in the event of a washout and to minimize wave action over the ponds. Divider berms between ponds were located such that the flows could be controlled based on an anticipated fluid conductance of 2.3 gallons per square foot (94 l/m^2) of pond. Upon completion of the individual ponds, the ponds were ripped to the full cut of the ripper giving each pond base the appearance of a harrowed field. This "ripple" effect permitted the slimes to settle in the valleys to maintain slime-free ridges for improved percolation.

The operating scheme was to leach the individual ponds in a staged sequence. Two ponds were to be on the leaching cycle while the third was being washed. In effect, 2/3 of the heap production was to be processed for uranium recovery with the low-grade wash liquor on recycle. Figure 8 is a schematic plan of the operating procedure. Upon completion of the 200-gallons-per-ton (840 l/t) leach and the 100-gallon-per-ton (425 l/t) wash, the Stage 3 pond would be shut down and Ponds 4A and 4B would be flooded. Ponds 3A and 3B would continue as Stage 2 leach while Ponds 2A and 2B would be converted to a washing stage. The objective, of course, was to optimize liquor grade to the processing facilities without sacrificing uranium recovery.

Due to weather conditions, the leaching was limited to the months from May to October. The ponds were flooded about May 1 and the operation shut down on October 1. Because 30 days were required to drain the heaps, flooding ceased on September 1.

Certain operational problems did occur during production but for the most part the project ran smoothly. The 5-foot (1.5m) protective covering of ore laid on the base prior to heap construction proved to be a source of seepage around the pile and contributed to several occasions of minor sloughing. Also, in one of the ponds the total acid required for leaching was not completed before winter shutdown. The following spring an unacidified solution was inadvertently added to the pond; this caused precipitation of salts in the heap and reduced the fluid flow to a trickle. After two years of effort, no solution for restoration of permeability has been found. On properly run ponds, an average flow rate of 2.0-2.5 gallons per square foot per day (81-102 $l/m^2/d$) was readily maintained.

During the first three years of operation, 75,800 pounds (34,400 kg) of U_3O_8 were recovered at an average liquor grade of 0.54 grams per liter (4.5 pounds of U_3O_8 per 1000 gallons).

This was very close to our original estimates and on completed ponds the anticipated uranium recovery calculated on a residue analysis of 0.008% U_3O_8 was achieved. Production costs were on target proving that heap leaching is, indeed, an economic method of treating mineral and an alternate process for the economic exploitation of low-grade reserves.

MAYBELL HEAP LEACH EXPERIENCE

As a result of the economic success achieved through heap leaching at Gas Hills, UCC began a review of its other sources of marginal ore reserves. The most obvious target was the abandoned UCC mill and mine site at Maybell, Colorado. Considerable previously mined low-grade mineral reserves were available from several stockpiles and the old mine maps indicated additional reserves in the pits previously abandoned as being uneconomical to mine and process conventionally. A preliminary feasibility study indicated that these reserves could be exploited profitably if a low-cost means was developed for producing a concentrate for shipment to either the Gas Hills, Wyoming mill, 240 miles (386 km) north or to the Uravan, Colorado facility, 270 miles (434 km) to the south.

Construction of the Maybell heap base was started in June 1975. The entire base for the planned 1976 operation was constructed prior to the placing of ore and mineral (average length 670 feet (204 m) and width 485 feet (148m)). Ore and mineral haulage were started the first week in August and completed by the end of November. Base construction was from local clays following the procedures developed at Gas Hills. The entire heap was constructed to 21 feet (6.4 m) in a single lift.

The completed heap was left dormant during the winter months without apparent ill effects. In the spring of 1976, the pond berms were built, the pond bottoms ripped, and construction of the processing plant was begun. The processing plant consisted of three 120-gpm (7.6 l/s) skid-mounted, continuous IX columns and three elution columns with the attendant solution makeup facilities. Yellow cake precipitation tanks with a filter press for recovery of the yellow cake were installed. Rather than install drying facilities, the wet filter cake is packaged in drums for shipment to the UCC Uravan plant for final processing. The processing plant is uncovered and intended to operate in the months of May through November. The entire processing plant was run with a total of 13 men consisting of a plant foreman, one clerk, one analyst, 2 maintenance men, and 8 operators.

The water for leaching was obtained from an abandoned pit, acidified with H_2SO_4 and pumped to the appropriate ponds. Once the operation was underway all solutions were recycled and only the necessary makeup water was required from the pit. Pond size and flooding schedules were designed at levels to provide full flow of product liquor to the IX column and maintain recycle of wash liquor.

Construction of the processing plant was not completed until late summer, allowing for only about two months of operation. The heaps, however, were flooded prior to the completion of the plant, and brought to full flow with the high-grade surge ponds full. All excess product liquor was recirculated to the heaps until treatment capacity was available. Because the most readily available material for the heaps was from the stockpile, the average ore grade of the 1976 operating heap was only 0.03% U_3O_8.

During the period of plant construction and operation, additional base was under construction and mining of heap material continued. By the end of summer the 1977 operating heap was completed for scheduled startup in May.

Uranium production from the 1976 Maybell heaps exceeded the anticipated goals. This was due principally to the initial recycle prior to production which resulted in liquor grades above normal. Production costs were within target and the prospect for future production appears exceedingly bright.

ECONOMIC CONSIDERATIONS OF HEAP LEACHING

In determining the feasibility of a uranium resource to exploitation by heap leaching, the UCC procedure consists of establishing the leaching parameters of the ore or mineral by laboratory evaluation first through small-scale laboratory tests to determine the acid requirement and the ultimate uranium recovery by extended leaching at pH 1.0. Once these parameters are developed, a large-scale column test is conducted and acid requirements and uranium recovery are confirmed. Also, the fluid conductance is determined and the volume requirement is noted for leaching and washing. Appropriate scale-up factors are applied for calculation of probable heap response.

It has been our experience that for heap leaching relatively low-grade ores, a final tail of 0.008% U_3O_8 to 0.01% U_3O_8 (solubilized plus unsolubilized) is achieved in the leach zone. On an average, 80% of the recoverable uranium (heads minus tails) is extracted in 200 gallons per ton (840 l/t) of ore wetted. The remainder, or 20%, is recovered in the final 100 gallons per ton. Because the final 100 gallons per wetted ton (425 l/t) is advanced, the average liquor grade expected during leaching is the recoverable uranium per ton of material contained in 200 gallons of heap product liquor. Thus, with an ore grade of 0.044% U_3O_8 and a final tail of 0.009% WO_3, the average liquor grade can be expected to be (0.044-0.009) 20 pounds per 200 gallons or 0.45 gm/l. Overall pounds of recoverable uranium are calculated to be:

$$\frac{(0.044-0.009)\ 20 \times \text{tons wetted}}{0.044 \times \text{tons in heap}}$$

Optimization of the heap configuration is a rather complex calculation and beyond the scope of this paper. Fundamentally, the larger the heap, the greater the percentage of wetted ore. Also, the shallower the heap, the greater the percentage of wetted ore, but this must be balanced by the higher base costs associated with shallower heaps. Our experience has been that a clay liner base complete with drain pipe and dikes can be constructed for \$0.35 to \$0.40 per square foot (\$3.80-\$4.30/m^2). Frequently, however, these optimizing considerations are influenced significantly by the construction schedule, increased risk of sloughing at the higher heap heights, production scheduling, and base area available.

Ideally, a heap accessible to an under-capacity, existing mill offers the lowest cost potential. When the heap must operate independently, a low-cost liquor processing facility should be considered. UCC has found that a skid-mounted continuous IX column based on the USBM design is quite practical. The skid-mounted units are low cost, readily assembled in the field, and can be economically transported to another project when needed. Upsets to the recovery system are not serious as all liquor is recycled and lost values can be recovered on the next cycle. Solution makeup facilities, precipitation tanks, and filters are skid-mounted and each unit can be operated without covering. Reagents are delivered in tank car quantities, where possible, and serve as their own storage facilities. Offices, laboratories, etc. are trailer units and can be readily moved from site to site. Surge and storage ponds are low cost in-ground, PVC lined ponds and are generally trouble free.

Minimal maintenance of the heap ponds is required and can be handled during day shift only. Adequate pumping capacity is installed so that pond flooding is limited to day shift only. Experience shows that a properly designed plant can be operated with two operators per shift. An auxiliary, gasoline-powered pump is recommended on the heap product liquor pond for solution recycle in the event of an extended power outage. Once a heap is in operation, there is no way of shutting it off, and an emergency means of handling the liquor must be provided.

FUTURE OF URANIUM HEAP LEACHING

As a result of five years of development, heap leaching has shown to be an economic method for recovering uranium from marginal uranium reserves. The principal advantages we found in this technique include:

1. A low initial capital cost method of uranium production
2. A means for economically exploiting marginal ore reserves
3. An environmentally attractive means of processing uranium ore as the process is essentially a closed system
4. Early return of capital due to the short lead time required for production

The major disadvantage of heap leaching is that not all the ore is contacted by the leach solution. Thus, while recovery may be good in the wetted zone, the uranium contained in the unwetted slopes area is lost. For this reason, overall uranium recovery is generally lower than for conventional processing. A second disadvantage is that the technique, as we have applied it, is only applicable to ores that are amenable to percolation leach.

In total, the heap leach program has proved to be highly successful. This application is now a prime consideration within UCC for all uranium projects that are either too small or too low grade to justify conventional processing. Its significance to the uranium producer is becoming ever more important as the demand for uranium increases and the discovery of major uranium deposits dwindles. It is reasonable to assume that the percentage of uranium recovered by solution mining techniques will continue to grow much as it has been the experience in the copper industry.

The fact that this program was continuously successful from its inception through its development can be attributed to the Division-wide cooperation and efforts of the Technology Department, Production Department, the Resource Development Group and the full support of Management. Without their contributions and support this project would most certainly have been less successful and considerably longer in its development.

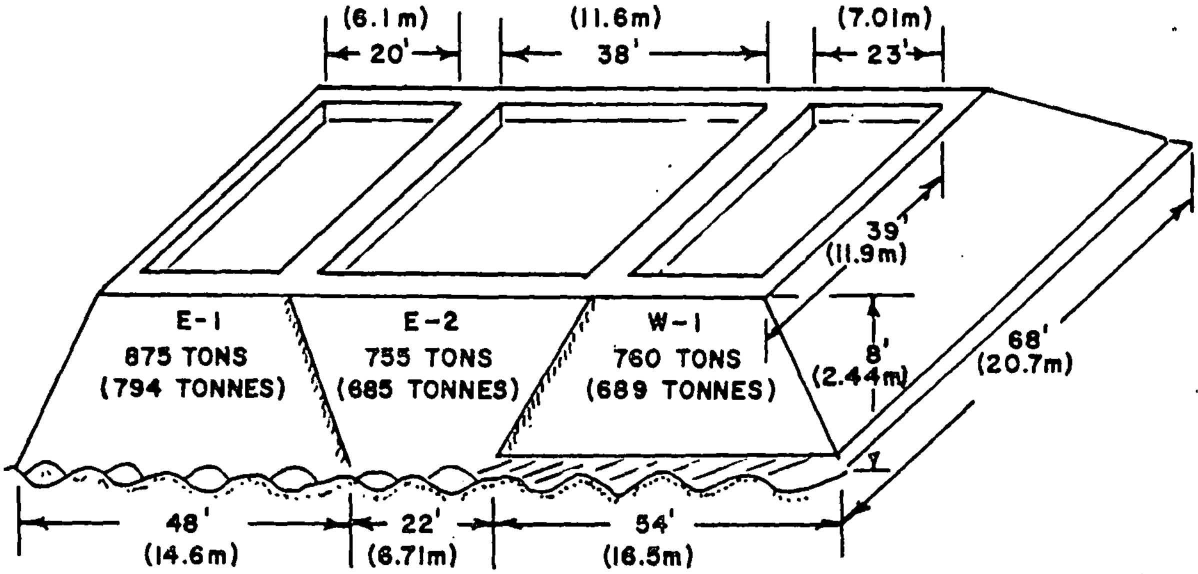


FIG. I
PILOT SCALE HEAP CONFIGURATION

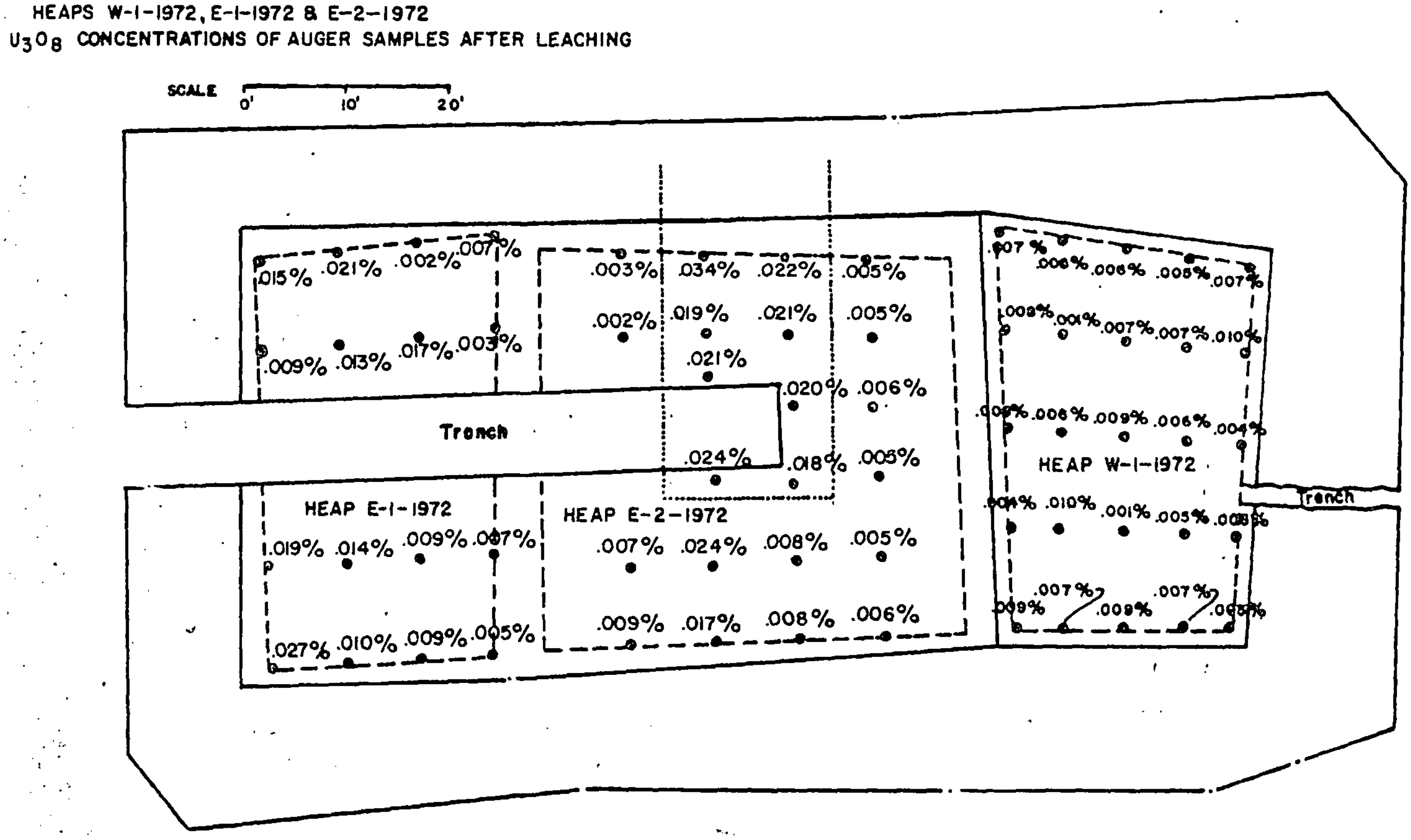


FIG. 2
AUGERING PATTERN AND U_3O_8
ANALYSES OF AUGERED SAMPLES
AFTER LEACHING

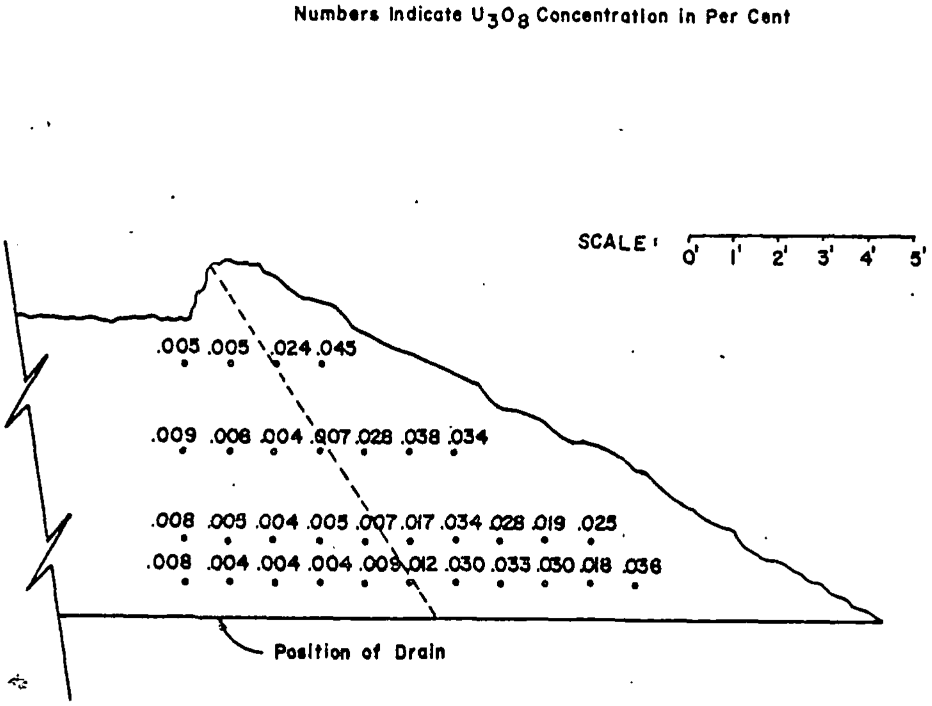


FIG. 3

TRENCH SAMPLES—SLOPE OF HEAP W-1

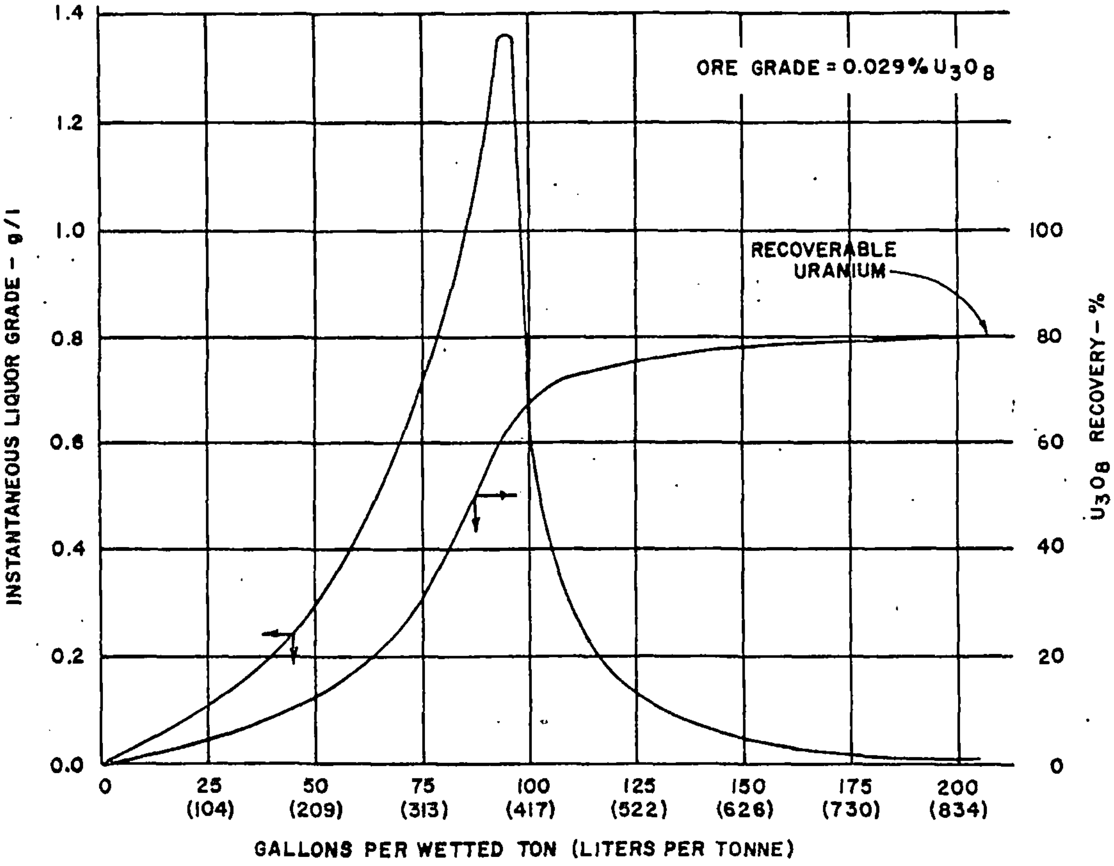


FIG. NO. 4
TYPICAL PERCOLATION DATA 20 X 2 FOOT LABORATORY COLUMN

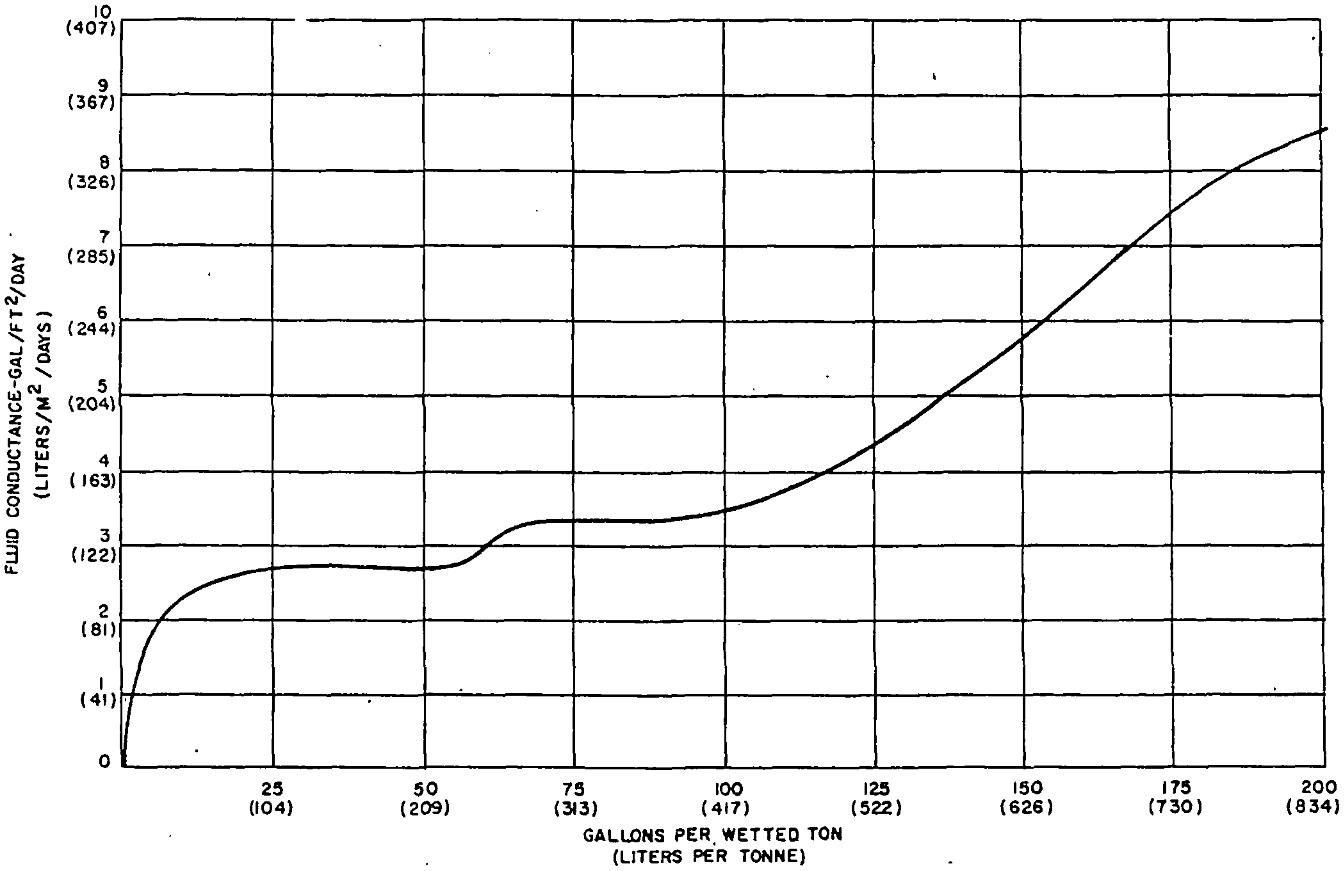


FIG. 5
TYPICAL PERCOLATION DATA
20 X 2 FOOT COLUMN

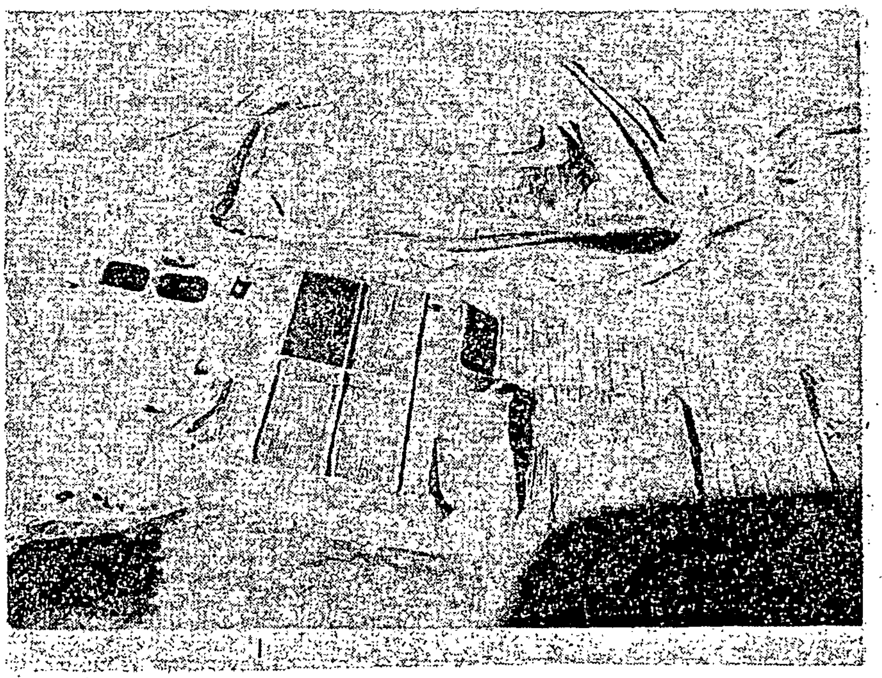


FIGURE 6 - STAGES OF HEAP CONSTRUCTION

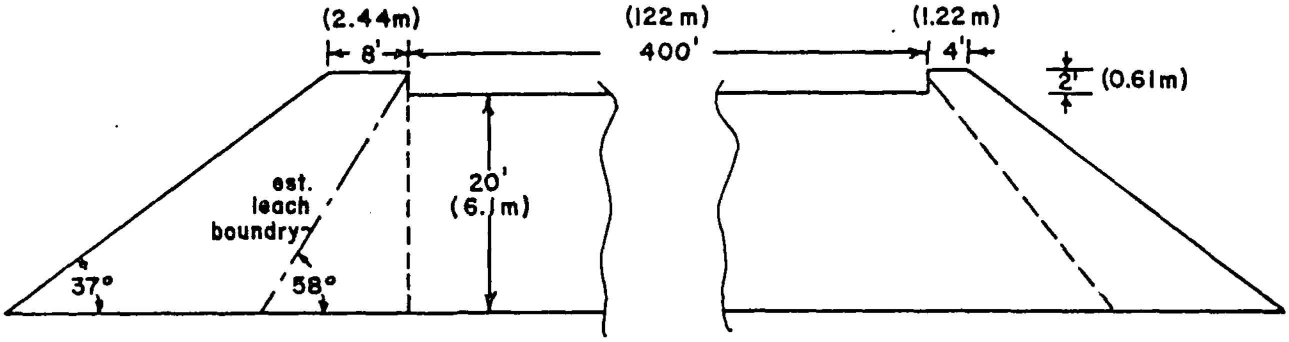
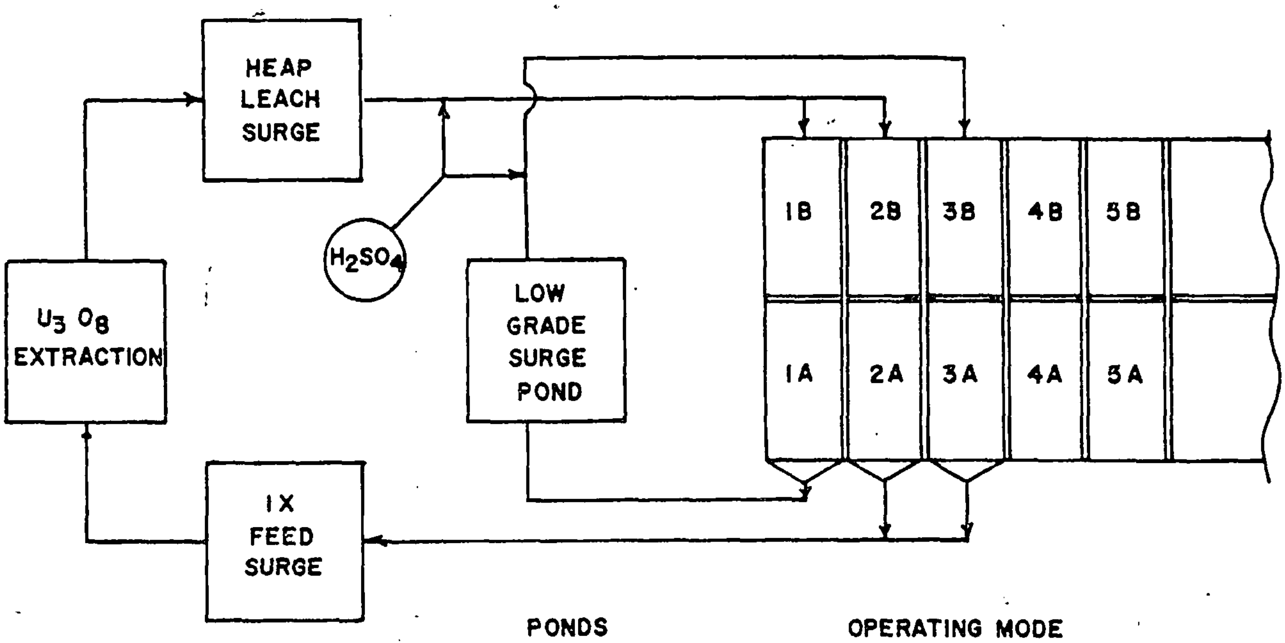


FIG. 7

CROSS SECTION OF GAS HILLS HEAP



PONDS	OPERATING MODE	
1A-1B	STAGE 3	200-300 GALS/TON (WASH) (834-1252 L /TONNE)
2A-2B	STAGE 2	100-200 GALS/TON (LEACH) (417 -834 L /TONNE)
3A-3B	STAGE 1	0-100 GALS/TON (LEACH) (0-417 L /TONNE)

FIG. 8

OPERATING PROCEDURE - GAS HILLS HEAP LEACH

1977 №18 N5

A HEAP LEACHING ROUTINE FOR UNGRADED AURIFEROUS ORES

UDC 669.213.6

G. G. Mineev and G. A. Stroganov

A series of laboratory investigations and pilot-plant tests on a method for heap leaching of gold from ungrades ores from certain deposits in Eastern Siberia has been conducted at the Irkutsk State Rare Metals Industry Research and Design Institute.

The ore samples were from sand-clay weathering crust deposits of pre-Jurassic age mineralized with quartz, pyrite, and iron hydroxides with an ungraded ore gold content ranging from 1.5 to 3.0 g/ton.

The gold was present in finely dispersed form, mostly as -5 μ grains predominantly finely laminated in form or sometimes nodular; powdery ocherous gold occurred in the argillaceous ores. A highly-developed pore and capillary surface and confinement of the gold to the fine ore fractions were features of the material studied. Thus, the -0.3 mm fraction (yield from 30 to 55%) contains from 40 to 60% of the gold in the initial material.

The method in the laboratory investigations was as follows. Cyanide solutions at various concentrations were passed through ore of initial size -100+0 mm and 10-30 kg in mass in polyethylene percolators or filter columns 150 mm in diameter and 2 m high at set linear percolation speeds.

The filtrate was collected and analyzed for gold and residual cyanide.

The investigation results showed that leaching with stronger cyanide solutions was preferable to leaching with weak solutions, because treatment time was reduced and filtrates were obtained which were more highly concentrated in terms of gold. Thus, 81% Au is extracted in 6 and 25 days when 0.1% and 0.025% cyanide solutions respectively are used, with practically equal consumption factors (Fig. 1).

Gold concentration in the filtrate falls sharply at ore spraying rates above 275 liters/(m^2·day).

The maximum gold concentration in the solution at a spraying rate of 275 and 400 liters/(m^2·day) is 9 and 4.5 mg/liter, respectively; the high level of gold extraction into solution of 94% is achieved in these circumstances (Figs. 2 and 3).

However, the $C_{Au}/\Sigma C$ impurities ratio decreases (see Table) when the rate of spraying increases; with a reduced rate of spraying the solvent-ore mass contact time increases, making it possible to use less concentrated solutions. However, this involves a substantial increase in processing time.

The speeds of solvent percolation through the auriferous material are governed by the presence of argillaceous fractions, the depth of the filtering layer, and other factors. An increased clay content not only affects the filtrate flow, but also causes losses of gold which has already dissolved, due to the high residual moisture content of material.

Research on material of various sizes to determine the kinetics of gold dissolution and of gold washing from the ore mass showed that 87% Au is leached out in 5 days even from the coarse class of ore, -120+100 mm (Fig. 4).

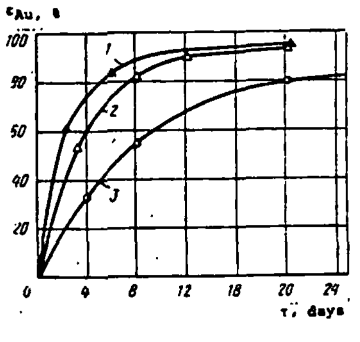


Fig. 1. Au extraction in leaching with solutions with various NaCN contents, %: 1 - 0.1; 2 - 0.05; 3 - 0.025.

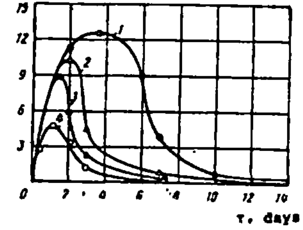


Fig. 2. Changes in the gold concentration (C_{Au}) in outgoing filtrates according to rate of ore spraying, liters/(m.day): 1 - 75; 2 - 125; 3 - 275; 4 - 400.

Up to 95% Au is extracted in a shorter time from the finer ore fractions. Washing out of dissolved gold is bounded by the fine ore fractions (Fig. 5).

Whereas the dissolved metal is washed out practically completely in 8 days from the -120+ +110 mm fraction, a similar stage is reached with the -0.3 mm fraction only in 15-18 days, and this class will govern the total duration of the washing procces.

It was established that solvent filtration deteriorated in time in ores with a substantial clay content; this is mainly due to changes in the pore space during the filtration process due to swelling and mechanical silting-up, which makes argillaceous ores diffi-

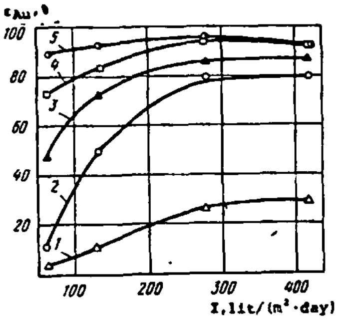


Fig. 3. Au extraction in leaching according to rate of ore spraying with solvent (I) at the following leaching times, days:
1 - 1; 2 - 2; 3 - 3;
4 - 6; 5 - 7.

Ionic Composition of Filtrates According to Rate of Ore Spraying with Solvent

Rate of spraying lit/(m²·day)	Metals concentration, mg/l						Ratio of C_{Au} to ΣC of impurities
	Au	Cu	Zn	Fe	Co	Ni	
75	12.7	3.7	3.45	0.2	0.2	1.35	1:0.7
125	10.5	3.5	4.35	0.3	0.2	1.1	1:0.9
275	9.0	4.5	5.23	0.4	0.15	0.62	1:1.2
400	4.5	2.3	5.62	0.2	0.08	0.8	1:4.0

cult to process by the heap leaching method.

When the ore is leached with recirculating solutions with gold separation onto a sorbent, filtrates with a higher gold concentration are produced after several cycles, although the time required to wash out the dissolved gold increases.

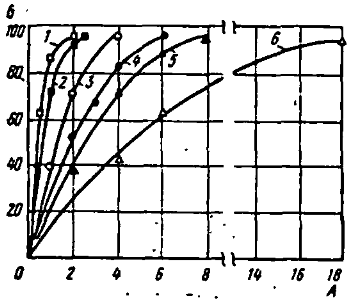


Fig. 5. Patterns of dissolved gold washing from various ore size classes, mm: -1+0.3 (1); -2+1 (2); -10+5 (3); -110+60 (4); -120+110 (5); - 0.3 (6). The time for washing out dissolved gold in days is shown on the A axis, the percentage of gold washed out on the B axis.

Alternate ore spraying with solvent and pauses (1-2 days standing) increase the gold concentration in the outgoing filtrates as a result of increased solution-ore contact time, but does not affect the final process figures substantially.

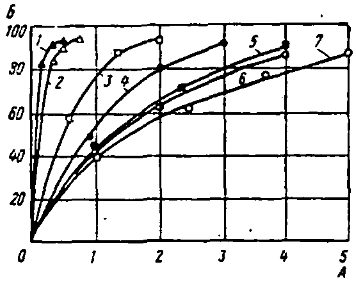


Fig. 4. Kinetics of Au leaching from various ore fractions, mm: -0.3 (1); -1+0.3 (2); -2+1 (3); -10+5 (4); - 60+30 (5); -110+60 (6); -120+110 (7). Au dissolution time in days shown on the axis, the degree of Au dissolution (in %) on the B axis.

Large scale laboratory tests were conducted with the set optimum routine; the results showed that 93% Au is extracted by heap leaching with an initial ore size of -100+0 mm and tailings containing 0.24 g/ton Au are produced (the initial content according to the balance was 3.6 g/ton).

The good leaching figures (Fig. 6) were due firstly to the presence of dispersed gold and the highly developed pore and capillary suface and secondly to the fact that the gold was confined to the fine ore fractions.

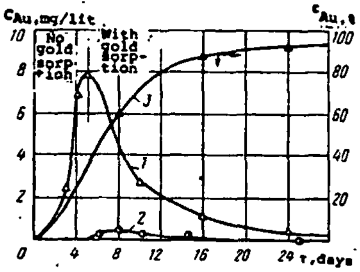
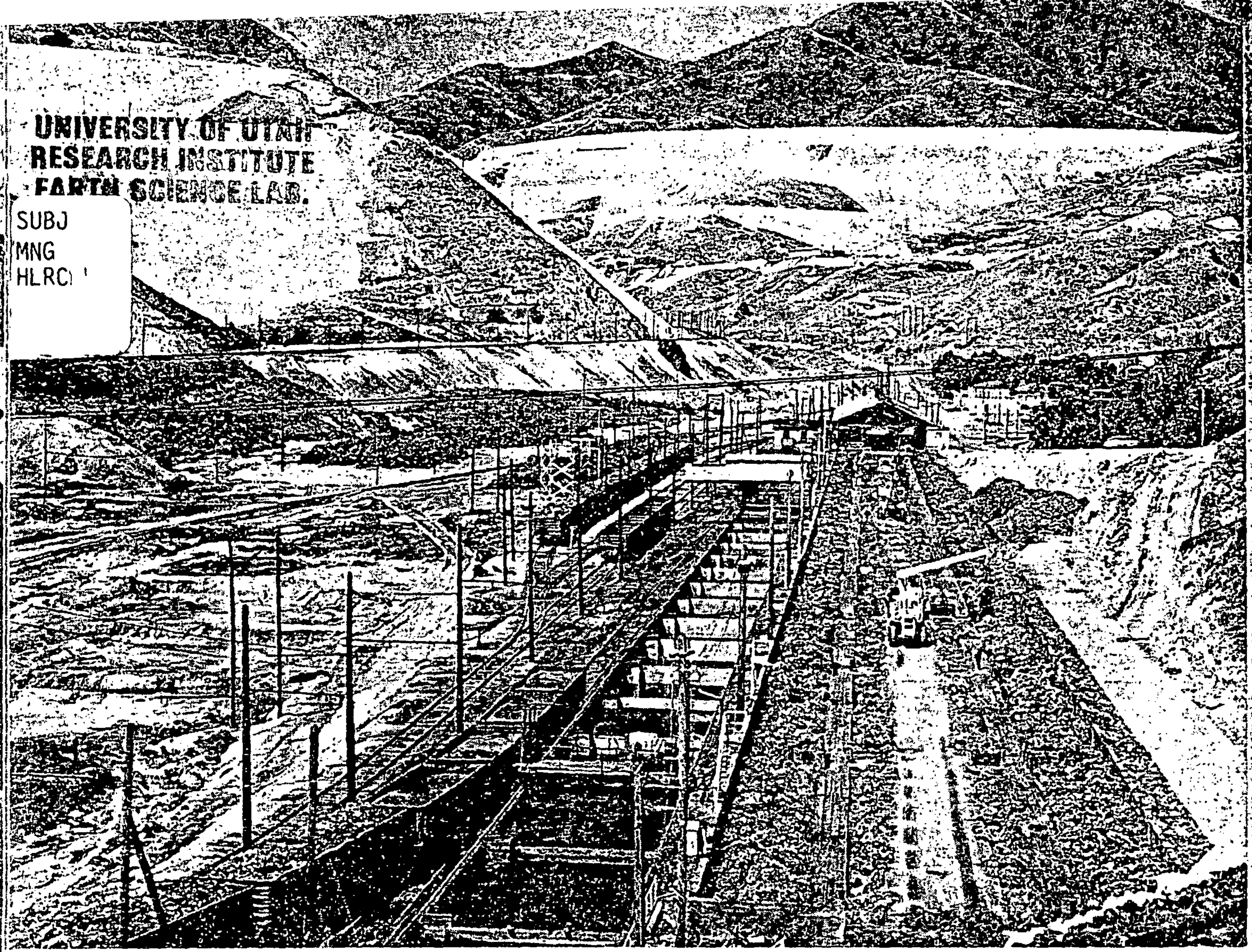


Fig. 6. Patterns of heap leaching of Au with cyanide solutions from ungraded sand-clay ore under large-scale laboratory conditions:
1 and 2 - Au concentration in solution before and after sorption respectively; 3 - extraction of Au into solution.

Thus, the-0.3 mm ore class contains 4.8 and 0.18 g/ton of gold before and after leaching, while the yield of this fraction is 38% and it contain 50% of the gold present in the initial material. The ore was leached with 0.06-0.10% cyanide solutions at a rate of material spraying of 0.1 liters/(kg·day) for a 30 day period. Gold concentration in the filtrate reached 8 mg/liter, and the respective reagent consumptions were 0.94 and 2.0 kg/ton of cyanide and lime.

Gold can be successfully sorbed from heap leaching solutions by the AM-2B anion-exchange resin which is used in the gold-mining industry. The saturated resins contain up to 20 g gold per kg of resin.

In pilot-plant tests, 64.5 and 80% Au was extracted in 30 days from ungraded ore -100 mm in size with an initial gold content of 1.3 and 2.8 g/ton using cyanide solutions; waste tailings containing 0.4-0.6 g/ton Au were obtained.



UTAH COPPER DIVISION'S leading-system from dumps at top to cement copper in railroad cars. Crane at right loads detinned scrap iron into precipitation vats. Cement copper precipitate tanks on left side of plant alongside cars.

How leaching recovers copper from

Please see the October 1963 issue of Mining World for the first part of this article. It covered the five reasons for acceleration in leaching activity, the 11 points to be considered in leaching, chemistry of leaching, control, and iron for copper precipitation.

By George O. Argall, Jr.,

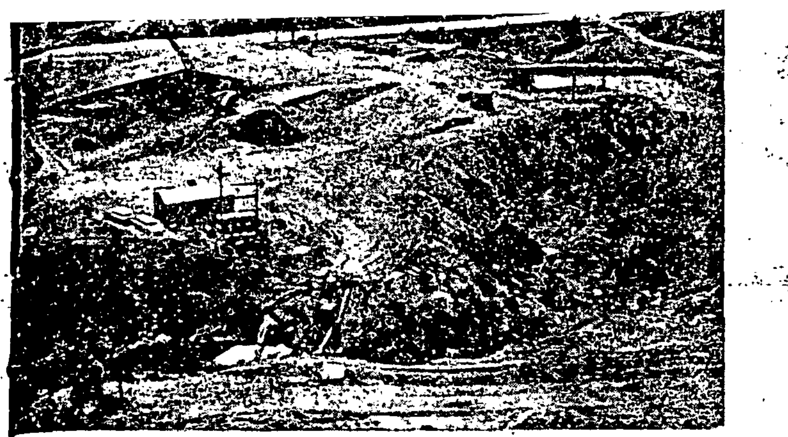
Part II of II

Bagdad Copper Corporation has the most elaborate and complete leaching program of any mine in the Southwest. It is the only mine to have built and operated its own sulphuric acid plant as a key component of its leaching program. Bagdad has long segregated the oxide capping of the ore body into two dumps, one of which is now being leached. Because these dumps are essentially barren of sulphides it is impossible to leach with water alone, as is done at other mines. Therefore a 200-ton per day sulphuric acid plant burning Louisiana native sulphur was the first unit to be built in 1960 for the leaching program. Leaching started at the Alum Creek dump, in 1961, with production of 1,005,616 pounds of copper. Output increased from 235,000 pounds per month the first of 1962 to 900,000 pounds at year's end. The increase in copper was due primarily to sprinkling of solutions on the dump. This resulted in the wider and more uniform application of the solution, and resulted in much slower percolation (about six days) of solution through the dump. This in turn results in the leaching of more copper.

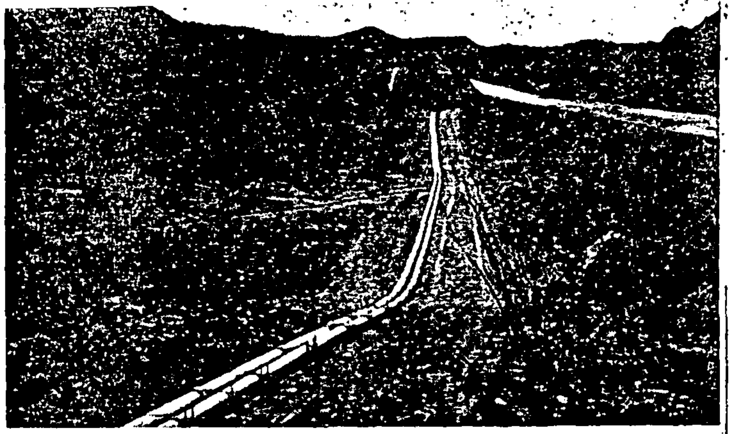
Main solution lines are 14-inch stainless steel, with plastic lining and 10-inch Polyethylene. Distribution lines, through which 3,300 gallons per minute are sprayed are made from four-inch Polyethylene. Lines are shifted manually.

Sulphuric acid is added by flowrator to the "On" flow weir. Consumption is now 4.8 pounds per pound of recovered copper; appreciably lower than the initial consumption of 10 pounds.

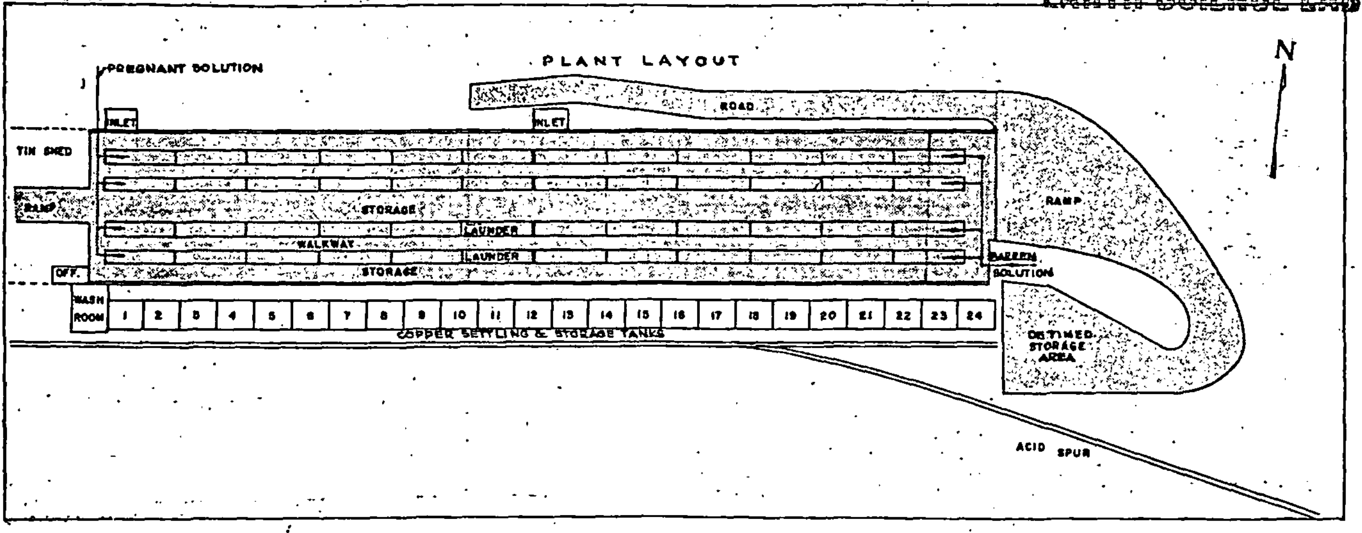
Bagdad's leaching plant has two



SILVER BELL precipitation plant from Oxide mine dump. Pregnant dam at left, barren at right. Precipitation cells behind crane.



TWIN pipe line carries leaching solution and pregnant solution 3.5 miles from El Tiro dump to Silver Bell plant.



COPPERTON precipitation plant layout. Pregnant solution flows from left over newly charged scrap iron. Copper precipitate is washed into 24 storage and settling tanks along south side. Precipitate is loaded directly to railroad cars.

waste and leach dumps in Southwest

important innovations. The first is the pregnant solution storage pond holding 1,400,000 gallons. This 264-foot long, 114-foot wide and 7-foot deep pond is completely lined with an aluminum-coated Koroseal polyvinyl plastic sheet. The eight-mill thick plastic is acid resistant and saved an estimated $24,000 in construction costs.

The second innovation is the semi-automatic tin can charging device to load precipitation cells. The machine moves back and forth lengthwise to the cells. Shredded cans, stored alongside the cells, are picked up by two 48-inch diameter traversing Schrader electromagnets. Each magnet has a load cell which sends information to a totalizing device that keeps a record of the tonnage deposited in individual cells.

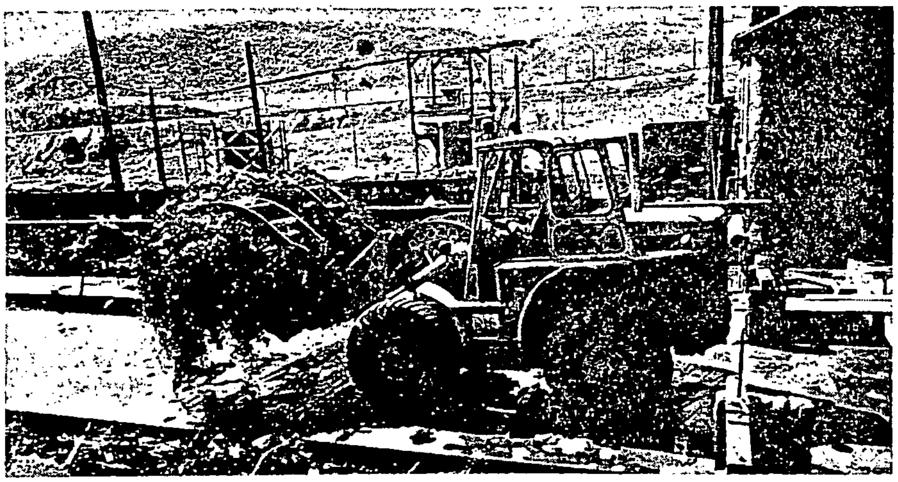
A diagram of the special, deep Bagdad precipitation cells is shown. Cells are cleaned every 48 hours on an average. Drying is by decantation and solar evaporation.

Barren leach solution is returned to the dump by gravity. Remember that most of the other leaching projects pump barren to dumps. The pregnant solution from the dumps is collected behind the dam and pumped about 4,500 feet to the plastic reservoir by two 1,750 gallon per minute capacity pumps against a 700-foot head.

The size of the installation and operation of the acid plant requires a fairly large operating crew. The chief metallurgist and leaching plant superintendent oversee four foremen, six muckers, one crane operator, two mechanics, four leach plant operators, one chemist, and one utility man.

The newest Southwestern dump leaching program was started in 1962 at the Esperanza mine south of Tucson, Arizona, by the **Duval Corporation**. Improvements in leaching practices are expected to increase copper recovery in the future.

Esperanza has been successful in spraying its leach solution on to the top of the dumps. The solution is pumped to the top of the dump in cement-asbestos and PVC pipes, with diameters of 12, 10, and 8 inches, with size depending on distance from solution sources. An Austin-Western crane is used to speed and ease handling of larger pipes. The PVC is installed manually and is used for the spray leads with ¼-inch holes in the two- and three-inch pipe. Holes are spaced from two to eight feet apart to deliver a total of 1,000 gallons of solution per minute, over a large



UTAH COPPER DIVISION uses a front end loader to charge scrap iron to precipitation cells at Copperton plant. Railroad cars loaded with scrap in background.

area. It takes approximately 48 hours for the solution to percolate through the dump.

Duval uses a deep precipitation cell. The concrete vat with 12 4-foot wide by 25-foot long by 4-foot deep (above wood grating) cells are charged with shredded cans by an electromagnet on a rubber-tired, mobile, internal combustion powered crane. Six by 12-inch timbers protect the top of the cell walls. The pregnant solution is directed over, down through, and up through the bed of cans.

Vats are cleaned, as required, by high pressure leaching solution, with precipitate washed into a decant sump. A front end loader is used to transfer cement copper from sump to concrete drying pad, and to load dried precipitate into truck trailer for haulage to railroad.

Barren solution is pumped through a 12-inch line to a concrete sump on top of the dump, in contrast to which most mines pump directly to several types of distribution systems with no sump on the dump proper.

The concentrator supervisory and research personnel devote a minor amount of time to operation of the precipitation plant. Three men are normally assigned to the plant; one equipment operator who charges cells and moves the cement copper, and two laborers who wash cells and clean up. The Bull Gang is used to install leaching solution lines when required.

Dump leaching has long been important at **Kennecott's Chino Mines.** Today Chino circulates one of the largest volume of solution at any of the mines discussed in this report. Dumps were started in 1910 and first cement copper was recovered in 1924. Water was pumped to the dumps for the first time in 1936. Initially, sprays were used. Rubber, wood stave, and steel pipe were all used before the advent of cement-asbestos and stainless steel pipe and pumps. In 1939, Chino built a new precipitation plant patterned after the one in use at Ray. Several additions have been made since that time, and there are now five units of six cells each. Each cell is 40 feet long, 10 feet wide, and six to 10 feet deep with a concrete wall separating the cell longitudinally to double the effective length.

Solution pipe lines now are 10- and 14-inch diameter polyvinyl chloride-lined steel and cement asbestos. Final distribution on the dumps is by ditches. Chino early found that when mill tailing water was used in the leaching circuit, large amounts of iron precipitated on the bottom of the solution ponds. Experimentation proved that this layer could be dried, pushed to the side of the pond by a bulldozer, the bottom of the pond ripped, and the pond again flooded for leaching. It now takes from one day to three weeks for leaching solutions to percolate through dumps and flow to a small collection pond, depending on height of dump and distance from the collection dam.

Chino's leaching operation is supervised by one general foreman and four shift foremen. There are six pumpmen, four crane operators, 12 washers, and one laborer.

Dump leaching produced 4.95 percent (5,174,374 pounds) of 1963 copper production at the **Inspiration Consolidated Copper Company,** Inpiration, Arizona. Leaching of a portion of the Thornton pit dump was started in December 1962 to replace older dumps which were showing signs of exhaustion. A total of 1,083,242 tons of leachable overburden was mined during the year. Sulphuric acid is added to the leaching solution with a flow meter, at the rate of 2.25 pounds per pound of recovered copper, at a weir box at the approach to the dump. Solutions are pumped through 4, 8, 10, 12, and 14-inch diameter transite pipes to the dumps. Leaching solution is piped to 100-by-100-foot dams on top of the dumps, where a depth of three to four inches of solution is maintained. Percolation takes about three days, with the pregnant solution collecting by gravity in pump sumps in the canyon below the dump.

Shredded cans in 60-by-20-by-3-foot concrete vats are used to precipitate copper. Cans are charged with a magnet pick-up on crane. Pregnant solution flow is in series through vats to deposit enough copper to warrant cleaning on a five- to seven-day cycle. Solution water is used to wash precipitate in a trommel with solution being re-used as make up. Inspiration artificially dries precipitate, mixing with flotation concentrate before drying.

Leaching personnel consists of a leaching plant superintendent, one man per shift who takes care of the leaching area, and one crane man per shift who charges cans into vats and unloads precipitate.

Dump leaching has been conducted intermittently at **Kennecott's Nevada Mines Division** since 1940. In 1962, leaching was resumed at the Molly Gibson dump, using automatic controls to insure correct acid content (pH) of the leaching solution pumped to the dump. Sulphuric acid is automatically metered into the leaching solution. So successful has the new leaching program been that the forecast is for three percent of the Division's total copper to be so recovered from this source in the next several years.

Pregnant solution is pumped into a "precipitation cone", which is a wood stave tank about 14 feet in diameter and 20 feet high. Scrap iron is charged into the cone three times a day, and the resultant copper precipitate is periodically flushed into a settling pond from which it is transferred to a drying area by a clam shell.

Asarco's Silver Bell dump leaching program is unique in that three separate dumps are leached by nearly equal volumes of solutions at the same time, and that one dump is about 3.5 miles from the precipitation plant. While this does not entail as long lines and high heads as those necessary to reach the extremities of the Utah leaching dumps, the

Silver Bell system is unique among the smaller mines. The well-designed and engineered system, with first leaching in January 1960, was one of the first to use epoxy lined Transite pipe for solution lines.

The two oxide mine dumps are fairly close to the precipitation cells and barren solution dam. The solution to the El Tiro mine dump, however, must be pumped 3½ miles and the pregnant solution returned a like distance. The blending of the underflows from the three areas affords better control of the grade of copper to the precipitating cells.

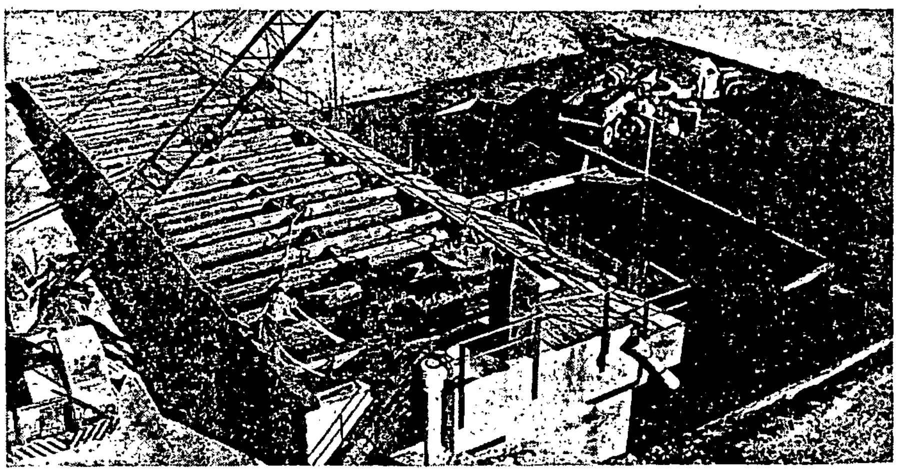
Another factor which is different from many leaching operations, but not unique, is that the only acid added to the circuit is in the feed to the precipitation cells to maintain good precipitating conditions. The acid for the leaching of the ore is generated in the dumps by oxidation of pyrite in the presence of the barren solution.

The solution pipe lines, 10-inch, 8-inch (Epoxy lined), and 6-inch are permanently installed to discharge to head-boxes, ditches, and ponds. They require only rare changes to divert flow to other areas. Solutions are distributed from these central points by pipes, ponds and ditches. Ditches are the most frequent method to direct solution into the 60-foot square ponds on top of the dump, which are filled with solution to depths of from 18 to 24 inches.

Usually, several small ponds are being leached at the same time. As the grade of copper in the underflow tends to fall, a new pond is cut in, and the pond which has been leaching the longest is cut out. The length of time during which a particular pond may be covered by solution varies from a few days to several weeks.

Pregnant solution is collected behind dams across the canyon below the dumps, then diverted by gravity flow or pumps to the main pregnant solution dam, from where it is pumped to precipitation cells. Silver Bell uses 10 cells for precipitation, each with two compartments 8 feet wide, 12 feet long and 5 feet deep. A perforated screen made of 1-inch plywood drilled with ¾-inch holes is placed at a depth of five feet. These screens are supported by stainless steel grids with 2-by-4-inch openings. The grids rest on two 6-by-8-inch timbers keyed into the concrete side walls. See plan and section diagram.

Pregnant solution flow in cells (see diagram) is through cells Nos. 1 and 2 in parallel, then continues in series through the remaining six cells. Cells Nos. 1 and 2 produce about 60 percent of the copper and are washed three times a week. Cells Nos. 3 and 4 produce about 20 percent of production and are washed once a week. Nos. 5 through 10 produce the remaining 20 percent of production. Nos. 5 and 6 are washed twice a month and 7, 8, 9, and 10 once a month.



PRECIPITATION plant at Duval's Esperanza mine. Crane at left is charging scrap iron to cells. Dried precipitate is loaded into truck at right for shipment.

Washing water for precipitates is furnished from the tailing solution sump by a 2½-inch vertical centrifugal pump to two 1½-inch high pressure hoses equipped with shutoff fire nozzles. As the cans are washed clean, the magnet on the crane transfers them to an adjacent launder. Precipitate washes through screen bottoms of cells to settling tanks. Decanted water returns to cells and to tailing solution.

Cement copper is bailed out of the settling tanks once a week with a crane swinging a clam shell bucket. Precipitate is stacked in rows with a front end loader and allowed to dry for one to three weeks before shipment.

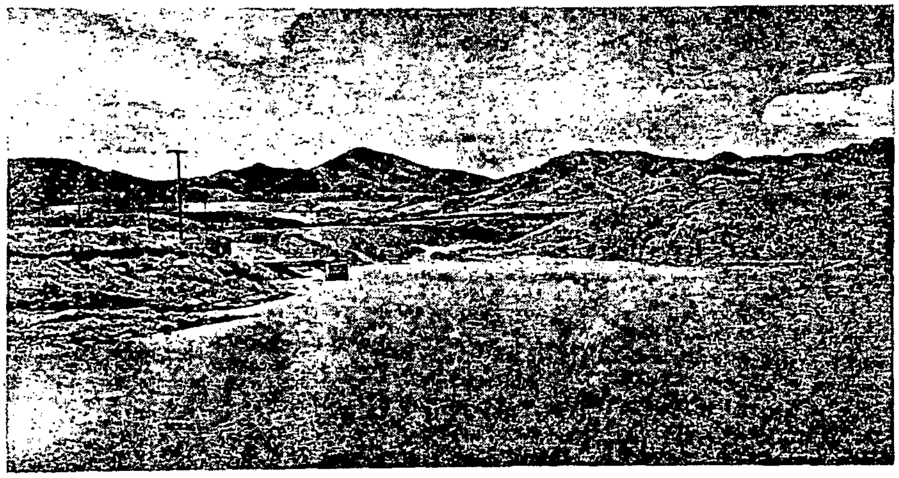
The plant is operated by one metallurgist foreman; one mobile crane operator; and two operators who wash cells, work on solution distribution and ponds, regulate acid to control pH, and take samples for assay.

Ray Mines Division of Kennecott Copper Corporation, in common with other Kennecott divisions, is expanding its dump leaching facilities. A sixth reinforced concrete precipitation unit (see sketch for details) is being added, to efficiently handle increased volume of pregnant solution. A typical unit, 43-foot wide by 71-foot long, consists of six cells. The head two cells in these vats are cleaned every two days; the last cells as infrequently as every two weeks, depending on copper content of the water treated. Copper recovery by individual cells starting at the head unit is 40 percent, 23, 12, 11, 9, and 5 percent, respectively.

Leaching of dumps and caved underground workings at Ray Mines is a closed circuit. All of the stripped solution from the precipitation cells is returned to the dumps or underground workings with sufficient make-up obtained from shallow wells to maintain a fixed gallonage flow through the plant. The caved underground workings provide storage for excess solutions during periods of runoff when additional water is available. All pumps in the leaching circuit are of stainless steel construction and submersible pumps are used in two shafts connected with the underground workings, which are flooded to a maximum vertical depth of about 500 feet.

Leaching of the Nos. 1, 2, 3, and 4 leach dumps and caved underground workings is currently underway. Sulphuric acid is added to the leach water feeding ponds on top of No. 1 dump. In order to obtain a better circulation pattern in the No. 2 dump, 8-inch diameter solution injection holes several ten of feet deep have been drilled from the top of the dump with a rotary blast hole drill.

Stripped solution from the precipitation plant, together with make-up water from wells, is pumped through several 10-inch diameter Transite pipes from the tailwater sump at the precipitation plant to the caved underground workings and to the top of the dumps where water flows in open streams to ponds with a normal size of 50 by 50 feet. Leaching cycle is 24 hours to four days, depending on height of dump. Effluent is analyzed for copper and sulphuric acid. When copper content drops below set limit, sulphuric acid is sometimes added to the leaching solution. If copper content does not



NEW WATER STORAGE DAM below Copperton has a 20,000,000 gallon capacity. Make-up water is pumped to main pumping plant for recirculation to dumps.

increase, the solution is moved to different ponds, seeking a higher copper content. Eventually the solution will be returned to first ponds for other leaching attempts.

Pregnant solution drains normally into dams for collection and gravity delivery to the precipitation plant through Transite pipelines. At times part of this solution is stored in old underground mine workings before being pumped into precipitation cells.

Precipitation cells are washed with high pressure tail-water in manually-held hoses into decant tanks. Wash water is recirculated through iron-filled cells and the precipitates clammed out of the tanks into drying cells. Precipitates are turned to speed drying and when partially dry (25 percent moisture) are shipped to the copper smelter.

A general foreman is in charge of the 11-man leaching crew. There are two operators on "A" shift who operate the clamshell and magnet cranes. One head operator on "B" shift operates the cranes. Two operators on "A" shift flush cells, change grills and gates, and take care of plant cleanup. Two "B" shift operators do the same. Balance of crew are swing men for vacations, days off—on seven-day operation, and to cover absenteeism.

Not surprisingly **Kennecott's Utah Division,** with by far the greatest tonnage of dumps, plus its closeness to Kennecott's Research Center has received the greatest dump leaching attention. It has been the proving ground and management has gladly built several experimental dumps to learn how to recover more copper.

Sponge iron is growing in importance as a source of iron. Ore from many of the mines contains pyrite, which can easily be recovered from the copper tailing and roasted to produce SO_2 gas (which is a basic raw material to make sulphuric acid for leaching) and sponge iron.

Sponge iron has the disadvantage of packing in the precipitation cells. Kennecott's research staff has made two important developments—the automatic cone precipitator, and the rotary furnace production of sponge iron, which will lead to greater use of sponge iron. Ray Mines now makes sponge iron for use in its LPF process.

A 13,000 gallon inverted cone is partially filled with sponge iron and the pregnant solution pumped into the apex (bottom). Rapid precipitation of the copper takes place as the solution rises through the cone. Barren solution overflows the top while the cement copper remains in cone. It takes several hours to consume the iron and when automatic measurement shows that all the copper is not being precipitated the inflow to the cone is shut off and directed to another cone. The precipitated copper is then flushed out of the cone. The cone is recharged with sponge iron, and then is ready for another precipitation cycle. A cone of this size can handle an inflow of about 1,000,000 gallons per day.

Four Kennecott engineers recently patented, with assignment to Kennecott, a method to prevent reoxidation of portions of the metallic iron, as the sponge iron produced in a rotary kiln is discharged into a water-cooled rotating sealed cooling drum. Heretofore, significant reoxidation of the iron occurred at the lip of the kiln and in a conveyor chute. In the new process, the sponge iron is removed intermittently from the bottom of the kiln bed through a door which opens and closes on a programmed cycle. A large mass is discharged so that the incandescent coke fuel in the mass reacts with any air to form a protective layer of carbon-monoxide-carbon dioxide gases to blanket the sponge iron and prevent reoxidation during transfer from kiln to cooler.

First leaching started at Utah in 1923, when the first precipitation plant was built in the bottom of the pit to collect and precipitate copper in meteoric waters within the mine proper. In 1924 a new precipitation plant was built at Copperfield to collect runoff. The present Lead Mine precipitation plant was built in 1929.

Utah uses pipes and ditches to deliver leaching solution to 20-by-400-foot ponds on the top of its dumps. Solution depth is maintained close to 12 inches in the ponds. With the very high dumps it takes six to twelve days for percolation. Collection is behind dams in several canyons and into the new Dry Fork collection adit.

The Nos. 1 and 4 systems are on the East side while Nos. 2 and 3 are on the West side dumps. The new No. 5 system of pumps, pipes, and collection dams and pipes covers the Dry Fork dumps.

The Lead Mine precipitation plant has 12 concrete launders 4-by-4-by-480 feet long, in series. Control gates divide the launders into 80 individual sections. Detinned cans and sheet scrap are charged into vats by front end loaders. A traveling clam shell crane bails the precipitate from vats and loads directly to railroad cars without drying (40 percent moisture). Cement copper is two grades, high which assays about 87 percent copper and is used by paint and brake lining manufacturers, and smelter grade (77 percent) which is all shipped to the Garfield smelter.

Precipitation effluent is recycled by pumps to the dumps. A new 20,000,000 gallon reservoir east of Copperton catches and stores spring runoff for use in leaching.

The Lead Mine plant has a total crew of 31; one general foreman, four plant foremen, one office clerk, four plant operators, four equipment operators, four launder washers, and 13 precipitation plant operators.

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HYDROLOGY OF DUMP LEACHING AND IN-SITU SOLUTION MINING

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INTRODUCTION

Dump leaching and in-situ solution mining have received considerable attention during the past few years due to their apparent economic viability and minimal environmental impact. Solution mining actually dates back to the 17th century when leaching of copper ore was first reported. However, modern day leaching didn't begin on a wide scale until the mid-1900's. In-situ mining for copper, nickel, salts, and oil shale is currently looking more attractive as the technology advances. Presently, about 15 percent of the copper production in the United States is from leaching operations at approximately 14 active sites, the largest of which are the waste dumps near the Bingham Copper Mine, Utah.

To establish a common background, the discussion is centered around state-of-the-art conditions. For dump leaching, complications inherent to the physical conditions and chemical reactions such as channeling, porosity and permeability, sorption, air flow, rock alteration and pH control are discussed. Emphasis is made on those conditions which render solution recovery rates and solution mineral concentrations unpredictable. By illustrating typical and actual field conditions, the generally accepted flow theories for both dump leaching and in-situ solution mining, including rubblization, are presented. For in-situ mining, hydrogeologic techniques such as geophysical well logging, aquifer testing and digital computer modeling are also discussed. The importance of artificial fracturing and well stimulating to solution injection and recovery is made with regard to project development. Finally, the subject of water pollution control techniques and the potential impact of the of the various regulations is discussed. A brief discussion as to the areas where research is being conducted completes the presentation.

HYDROLOGY OF DUMP LEACHING

To assist in understanding the various factors which affect the hydrology of dump leaching, a basic understanding of a typical leaching system should be reached. In general, a dump leaching system used for extraction of copper consists of a mineralized waste dump usually containing rock too low in grade to extract; a leach solution application system suitable to the rock/ore type and dump construction; and a recovery system capable of capturing the maximum solution flow. In addition, a solution storage reservoir, return pumping system, and processing plant is normally included. The dumps are usually deposited near the mine on either high or low angle side slopes or in a confined canyon. Dump construction can be monolithic, multi-level or finger in configuration, usually depending upon the mode of deposition -- haulage truck, rail or conveyor.

The several factors which are known to affect the hydrology of dump leaching can be divided into three main categories as follows:

Physical	Chemical	Others
Stratification	pH Control	Solution Application and Collection
Channeling	Precipitation/ Hydrolysis	Pollution Control Methods
Segregation	Temperature	
Sorption	Alteration	
Foundation	Oxidation	
Permeability	Solution Type	
Construction		

A discussion of these factors with respect to the individual and combined effects on dump hydrology and solution flow is made later in the paper. The potential impact of existing and proposed pollution control regulations could become a major factor in operation of leaching facilities. Figure 1 illustrates a section through a typical waste dump showing the interrelationship and mode of occurrence of features such as runoff entry, bacterial zones, seeps, trapped zones and oxidation through air convection.

Leach Solution Application Techniques

Five main solution application techniques are used through the copper and evaporite industry today. They are:

1. Pond - irrigation
2. Trickle
3. Multi- low pressure spray
4. Single high pressure spray
5. Well injection

The choice made to use a single application or combined technique depends upon the type of dump and its specific physical and chemical characteristics: whereas most dumps are generally suitable for all types of solution application, not all techniques would be successful for special dumps or in cases where leach system conditions have changed with time.

Pond irrigation is the most widely used technique and consists of flooding by irrigating or by a peripheral spigot discharge system. A series of dikes are constructed on the top of the dump to contain the leach solution. To rejuvenate flow within the dump when recoveries begin to decrease, pond surfaces are scraped and ripped with a dozer. Efforts to artificially disturb the dump using liquid or slurry explosives have had variable success but are generally not acceptable due to the high potential for slope failure. Acid and ammonia injection have also had variable success in stimulating the chemical process of mineral extraction. The success of these injected solutions in clearing the void spaces of clays deposited during rock and mineral alteration is variable. The degree of instability resulting from dissolvement of dump particle cementing agents is of high concern but total impact is unknown.

Trickle leach application is a relatively new technique which is used primarily to extract copper sulfides from fresh dumps and those exhibiting high permeabilities. The more gradual application of solutions by the trickle system tends to avoid the quick breakdown of rock and mineral particles, thus enabling the solutions and air to flow through at a more uniform rate. Better coverage of the dump materials is also accomplished in trickle leaching. The method is employed by utilizing an interconnected system of PVC piping arranged and perforated at close intervals. The solution is then forced through the system at high pressure.

Spray solution application techniques have been employed with varying degrees of success. Even though spraying provides a uniform means of material contact, excessive solution losses to evaporation and high maintenance of sprinkler heads are the major problems. In areas where evaporation rates are low and leach solutions closely resemble the mineral contents of normal water, spray techniques are very successful. One problem inherent to both the spray and trickle systems is that of ice formation during winter months where the dump surface and fixtures will clog if allowed to be temporarily dormant.

The practice of injecting leach solutions into dumps using well bore techniques is not generally used in the copper industry. Utilization of injection techniques is, however, used quite extensively in the in-situ uranium, potash and salt industries. Well bore injection in copper leach dumps is sometimes employed to activate a trouble zone or area within the dump unaccessable by gravitational surface flow. Double-stem drilling techniques seem most suitable for this practice.

Dump Channeling and Stratification

Most copper leach dumps exhibit a high initial permeability due to the unconsolidated method of construction and coarse particle size. However, permeability is soon reduced as alteration progresses. *During this period, flow channels develop which control and concentrate* the migrating path of the leach solutions. These channels develop into major water courses as the leaching process advances, since they constitute the path of least resistance to normal gravity flow. Of prime concern is the problem of limited mineral contact due to channeling. Some dumps, uncovered after being pond leached for several years, have shown the dominating effects of channeling where the downward flow path had been almost completely directed to the narrow channels, thus leaving the majority of the dump surface untouched.

Dump stratification is a result of the dumping method. The practice of dumping by truck or rail from one level, continually expanding the dump outward, creates a stratified zone usually near and parallel to the dump face. Stratified zones, like alluvial sand and gravel layers, will tend to control the flow quantity and direction of leach solutions. As the layers become clogged with iron oxides and other altered minerals including clays, the permeability decreases; sometimes resulting in a surface seep or blow-out. Stratified zones also cause pregnant leach solution to become trapped or perched within the dump interior. Some trapped zones, uncovered or released during a dump failure or encountered during a drilling test, are believed to have been dormant for several years due to the high mineral concentration of the contained solutions. When identified, solutions in trapped zones can be recovered using horizontal drilling techniques if it is not detrimental to slope stability.

Dump Flow Factors Affecting Recovery 1/

Permeability - The permeability of a waste dump can be defined as the measure or the ability of liquid or gas to flow through the dump. In order to understand the role of various factors in determining the overall permeability of a dump, the following permeability definitions are presented:

1. Bulk - The permeability of an entire dump, including the flow through cracks and channels, and through interstitial void spaces.
2. Matrix - Matrix permeability is defined as the permeability of a portion or segment of the dump characterized by flow through the interstitial void spaces only.
3. Intrinsic - A measure of permeability which is independent of the viscosity of the fluid in the dump media and is theoretically a function of the media alone. Depends

upon the interstitial void space porosity, tortuosity, particle shape and rock particle diameter. The common unit of measurement is the darcy.

4. Hydraulic Conductivity - A term used to describe the flow in a mass media which is a function of the properties of the fluid as well as the characteristics of the medium. Hydraulic conductivity includes the effect of the unit weight and the dynamic viscosity of the fluid as well as the interstitial void porosity, tortuosity, particle shape and rock particle diameter. A dimension of velocity is used to describe hydraulic conductivity.

When determining dump flow, the permeability of discrete rock particles (less than 10^{-3} darcies) cannot be ignored. Even though rock permeability does not affect waste dump flow, this permeability determines lixiviant penetration, which affects total waste leaching capability.

Also, since in dump leaching, both air and lixiviant flow are important, the bulk, matrix and rock particle permeabilities are usually measured in terms of intrinsic permeability.

The variance in darcy values shown in Figure 2 illustrate the differences in permeabilities throughout the same dump at different depth intervals. Values for both air and water permeability are shown. Values range from a low of near 0.10 to a high of about 10.0 darcies for fluid flow. Air flow values were found to be generally above 10.0 darcies to a maximum beyond 200 darcies.

Air flow - Leaching occurs through the oxidation of sulfide minerals, in a reaction which includes the replacement of copper by ferric iron. The presence of air and the pattern of air flow through the dump is critical to the leaching operation and provides a useful technique for understanding fluid flow in the dump media. The various factors related to air flow are discussed as follows:

1. Temperature - Accelerated temperatures are characteristic within leach dump reaction zones which are caused by exothermic conditions generated by the replacement of copper by ferric iron. The temperature in different zones varies due to heat dissipation by gas convection and generation of water vapors.
2. Heterogeneity/Anisotropy - Normal waste dumping techniques, termed "over-dumping," where dump materials are deposited over previous materials and allowed to mix with the existing slope materials results in a heterogeneous deposit and anisotropic flow conditions. Permeability values are variable since particles are segregated during dumping due to gravity causing the coarser particles to collect at the toe of the slope where permeability values can be quite high. Lower permeabilities are found in the finer-grained materials above the coarser materials.
3. Exothermic Reaction - In the dump interior, air undergoes chemical changes which deplete the oxygen and form water vapor. Several unknowns exist as to the complete role played by air entry and the complex reactions which take place. However, it is known that oxygen in the air is the only significant oxidizing agent.

4. Convection - As air enters the dump along the more permeable base and dump face, temperatures increase and chemical changes occur which affect the buoyant state of the air and cause the air to migrate upward to the cooler dump surface. Air convection within the dump is essential to mineral extraction. Generally, natural convection is dependent upon the proximity of the dump to local air currents and the permeability of the face and dump base. Zones at the back of dumps are generally not affected by convection and remain isolated.

Solution Flow - The most important aspects of the hydrology of dump leaching are the physical and chemical factors influencing solution flow. Those factors are discussed as follows:

1. Application Methods - Leach solution application methods can vary, as explained earlier in the paper, from trickle and spray to pond flooding. The nature of solution flow is therefore a function of the application technique, saturated fluid head and physical and chemical dump conditions. Solution flow should be directly proportional to the fluid head and the dump permeability but the channeling effects on fluid flow discount the normal flow theory.
2. Lixiviant Chemistry - The hydrolysis and precipitation of iron salts reduces the surface permeability of the dumps which causes ponding of leached solutions and leads to channeling. When availability of pyrite and oxygen is not sufficient to produce adequate amounts of acid, then acid addition may be necessary to prevent precipitation of ferric

salts. However, acid attacks the rock particles, decrepitating them into clay minerals which further reduces permeability and enhances channeling, therefore, the pH of leach solutions should be controlled to strike a suitable balance between mineral extraction and void-clogging salts.

3. Sorption - The total effects of adsorption and absorption of rock and mineral particles in the dump media is considered its sorptive capacity. Obviously, sorptive conditions vary due to particle difference and represent one of the major unknowns in the estimation of leach solution loss. A portion of all leach solution is permanently lost to sorption.

4. Foundation Conditions - The characteristics of the underlying dump foundation is important when determining solution loss and dump stability. The foundation, being either unconsolidated soil and/or consolidated rock would have naturally different values of permeability and other hydrologic features. Coarse alluvial soils or heavily fractured rock formations would become "thief zones" to leach solutions migrating along the dump base. These seepage loss zones are usually short-lived, however, since they become filled with iron sulfide and other precipitate deposits including highly absorptive and sealing clays, such as montmorillonite derived from mineral and rock alteration. Artificially sealing a dump to prevent temporary solution loss is usually not economically feasible or practicable due to the threat of slope instability created by the liner which represents a potential slip surface.

5. Channeling - As discussed previously, the effects of channeling can be very significant in controlling solution flow.

The presence of a well established channel flow system within a dump can be difficult to define and overcome since all normal permeability values are masked by the channel flow. The effects of a channel flow system are distinctly shown in Figure 3 where the results of a series of falling head permeability tests are illustrated. The direct influence of the channel is clearly shown in each test in relation to water level depth and percent of total elapsed time.

6. Stratification - Briefly, since the effects of stratification were discussed previously, stratification is a companion to the effects of channeling and sometimes works hand-in-hand to control solution flow. Usually, a particular strata delineation is the start of a channel system. When flow is impeded by clogging, the head pressure will force the flow through stratified zones, expanding the channel system.

Pregnant Solution Recovery Systems

Recovery systems are important to dump hydrology in that a properly constructed leach solution collection dam and ditch or reservoir is the key to water balance determinations. Knowing that a collection facility is properly sealed or lined against seepage loss provides one of the five main factors needed to determine percent of solution recovery. The other factors being: injection rate, evaporation, dump particle sorption and seepage loss to the foundation. With the exception of the injection rate, all other factors present a certain amount of doubt as to exact values represented. Most leach solution collection facilities are satisfactorily lined to prevent product loss and to provide recycle waters after mineral extraction, especially in water-short areas.

Dump Failures Resulting from Flow Problems

Dump failures often occur due to physical conditions within the dump and from surface and foundation conditions accompanying dump construction. A description of the different types of dump failures and their relationship to leach solution flow is as follows:

Blow-Out - A blow-out is a result of a sudden release of water, usually within the upper dump face as a result of a build-up of fluid along a compacted zone or area of pronounced stratification. Typically, a blow-out will occur in a relatively short period of time following the introduction of leach solution to a dump where downward solution flow is impeded by a barrier or is permitted to accumulate by strata patterns or channeling near the dump face. Eventually, the accumulating solutions literally explode outward onto and down the dump face creating a crescent-shaped depression extending above and to the sides of the rupture point. The affected dump materials in the fail zone are carried by the exiting fluid down the dump face creating a flow channel to the toe of the slope. Solution flow will generally continue from the failure for several days after rupture until all dump-stored fluids are released.

Slope Erosion - Seepage - Erosion of dump slopes by natural precipitation runoff can cause dump disfigurement or establish weak points where future failures can occur. Unfortunately, very little can be done to prevent slope erosion from runoff of active dumps and efforts to vegetate or terrace the faces of inactive dumps would fail due to the presence of unsuitable growth factors, highly unconsolidated material, and constantly changing surface conditions.

Seepage onto the dump slope face from internal flow can lead to localized failures typical of the rotational-slip land slide. Control of seepage can be done by relieving the pressure through the use of horizontal drains in the face or by vertical recovery wells on the dump surface. Generally, the lower the seep on the dump slope, the higher the potential for a serious failure.

Foundation Slope Failures - Failures of the foundation are more likely if unconsolidated soils exist beneath the dump. Overtaxing the stress shear point is the most common reason for failure. Compression and movement of silts and clays is another failure cause. The association of groundwater in any of these conditions would greatly increase the potential and magnitude of the failure. Foundation failure of rock is less frequent, but not uncommon. Typical rock foundation failures include bedding plane separation, fracture separation, structure collapse, shale parting and shear. Foundation slope failures are generally of higher magnitude and more difficult to repair or contain.

Overtopping - Failures from overtopping are quite common in dump leaching and are usually the result of inadequate dike construction, poor water management or excessive runoff accumulation -- all of which, if not checked in a short period of time, could cause serious impairment to the dump slope and upper surface.

The importance of all these failure conditions to the hydrologic characteristics of the dump is that almost all failures are due to dump flow problems. By understanding dump flow technology and building dumps to minimize failure problems, a more efficient leaching system will result.

Pollution Control Techniques

Techniques to control pollution depend upon the type of facility involved, the nature of the pollution problem, the requirements of the controlling regulation and economic considerations. A leach solution collection dam and pond or reservoir can be lined with a suitable synthetic, bentonitic, or natural clay liner. The dam should be keyed into bedrock around its perimeter and grouted in place to prevent any seepage loss. A concrete, grout, clay, or synthetic lined collection ditch is adequate to prevent seepage loss. Utilizing a dependable, closed piping system is also practiced as a means of pollution control.

Installation of monitor wells at key locations, especially in drainages below collection dams and at select down-gradient sites, is necessary to determine if solution flow losses are occurring. Properly constructed and installed monitor wells are essential in making accurate water level and quality control measurements to comply with existing and proposed controls.

Environmental Controls

Seepage controls for non-point effluent discharges are being formulated by the Environmental Protection Agency (EPA). No controls other than local state regulations, should they exist, are designed explicitly to control contamination of groundwater from surface seepage. The regulations are being issued under the authority of the National Safe Drinking Water Act of 1974 (SDWA). Currently proposed regulations under the Act pertain to drinking water standards and groundwater contamination from deep well injection. Seepage control regulations should be proposed and/or promulgated within the next year, pending completion of an EPA contractor study. Some states (New Mexico, in particular) have already passed, effective February 18, 1977, their own set of groundwater regulations under authority of the SDWA.

Controls from other proposed and approved legislation such as the Solid Waste Disposal Act, Resource Conservation and Recovery Act of 1976, Hazardous Waste Disposal Act, and the Toxic Substance Control Act, are in the review stage, with various bills pending congressional approval. When fully promulgated and finalized, however, the controls will undoubtedly result in regulations restricting seepage to groundwaters in excess of established parameters. All of the proposed controls contain provisions for seepage control -- some of which will overlap and/or conflict with each other.

Effluent guidelines promulgated in 1975-76 for control of mining, milling, and smelting wastes, are yet to be finalized and pertain only to effluent discharges from point-sources into navigable bodies of water or their tributaries. Senate hearings were conducted in June 1977 on the Federal Water Pollution Control Act. Testimony submitted by various industry and AMC representatives recommended extension of the July 1, 1977 deadline (BPT) and elimination of the July 1, 1983 (BAT) requirements. EPA will consider these and other comments in view of the respective impact on industrial operations and the environment.

HYDROLOGY OF IN-SITU SOLUTION MINING

Although in-situ leaching of copper deposits has been reported as being practiced back in the 15th century, the technique is little used today in comparison to dump leaching or conventional mining methods. However, recent environmental concerns resulting from conventional open pit and underground mining techniques and technology improvements has made in-situ mining more attractive. Recent advancements in technology, some borrowed from the petroleum industry, are making several low-grade or inaccessible mineral deposits more viable. In actuality, in-situ leaching has been occurring naturally since the deposits were formed millions of years ago. Oxidation of the sulfide minerals first occurred when migrating groundwaters made contact.

Despite the history of minimal use, in-situ mining may finally be coming into its own. Starting with the in-situ production of copper from an underground worked-out, block-caved mine by Miami Copper Company, several other companies (Ranchers Development Company, McAlester Fuels, Occidental Petroleum Company, and Kennecott Copper Corporation), have experimented with in-situ mining techniques. Future regular production operations appear feasible for those sites having suitable conditions. In-situ product extraction from uranium, salt, potash and phosphate deposits is currently in full operation at several localities in the Western U.S. Considerable interest and research is being expanded towards the development of feasible in-situ techniques for extraction of the hydrocarbons and mineral salts contained in the vast oil shale and tar sand deposits of Utah, Wyoming and Colorado.

Basically, the technology development essential to the future of in-situ solution mining is centered around the sciences of geology, hydrology, mineralogy, chemistry, and hydraulics. Other factors such as artificial fracturing and stimulation, economic viability and environmental compatibility are also important and must be understood. The successful advancement of in-situ solution mining is dependent upon understanding these factors and other parameters uncovered during long-term mining operations.

A discussion of the major factors which are known to control the success of in-situ leaching operations and their hydrologic importance is presented as follows:

Mining Techniques

Generally, in-situ mining techniques involve the injection of chemically balanced lixiviants or water into the mineralized zone at depths dependent upon the mineralized zone, but usually in excess of 500 feet from the surface. Injection and recovery of the pregnant solution is accomplished by large diameter, deep well methods. The well depths, spacing and number are dependent upon the existing physical and chemical conditions of the site and ore zone. Some of the more common and successful techniques used are discussed as follows:

In-Line Confined Layer - The in-line method is commonly used when the ore zone is known to be contained between confining layers of clay-bearing strata or rocks expressing low permeability values. The method is efficiently used in extraction of evaporite minerals where sedimentary formations tend to contain and trap injected solutions resulting in maximum recoveries. To further expedite recovery, sometimes more than one recovery well is employed.

Horizontal Line-Drive - The horizontal line-drive technique is a system generally utilizing a single injection and recovery well positioned so that the cones of impression and depression overlap, thus enhancing maximum recovery. To be effecitve, the injection well should be higher than the recovery well near the top of the enriched zone. Additional injection or recovery wells can be added as needed to improve operation efficiency. The line-drive technique is most effectively used in shallower disseminated rock zones above the water table where the unsaturated flow is influenced by the attitude of the bedrock and fracture patterns.

5-Spot Line-Drive - Four recovery wells and a single injection well in the center of a "dice" pattern constitute this technique. The method, commonly used in the petroleum industry, is proving effective in recovery of mineral deposits in both sedimentary and disseminated deposits. To be effective, the injection well is terminated above the recovery well drawdown plane so that the cone of impression is superimposed above the cones of depression. Depending upon physical conditions of the strata, the pattern can be reversed (inverted 5-spot) with the recovery well on the inside surrounded by four injection wells to achieve peak efficiency.

Adit/Shaft Injection and Recovery - Abandoned underground workings can either act as a means of solution injection or recovery if properly located. Adit injection is used in areas where low grade or higher grade, but inaccessible ore remains after conventional mining has ceased. Wells can also be installed into the system to further enhance injection or recovery.

Artificial Stimulation

To increase and sustain fracture flow within the ore zone, it is usually necessary to artificially induce fracturing through well bore and/or fracture plane techniques. Three methods being experimented with which seem to have the most reliable results are discussed below:

Hydrofracturing - The injection of water under high pressure through a perforated well casing appears to be the most efficient technique where suitable conditions prevail. See Figure 4. Typical oil well stimulation equipment is used, modified somewhat for use in the shallower wells and disseminated rock strata which fracture differently than sedimentary formations. Propagation of the newly-created or expanded fractures is necessary to prevent closure. The fracturing is begun at the bottom of the well or enrichment zone and repeated at regular intervals proceeding upward to the top of the zone. Injection pressure depends upon the depth and fracture resistance to expansion or rock density. Observation wells are usually installed around the test well to determine the extent of fracturing. Special well bore packers are used above and below the injection zone to prevent formation bypass. Slurry concrete is pumped into the annulus between the casing wall and the borehole to prevent solution entry during high pressure injections. Sometimes repeat fracturing is necessary to reopen or increase the fracture pattern.

Oxyfracturing [2/] - Liquid oxygen injected into the previously hydraulically fractured zone serves to accomplish three main purposes: (1) increase the fracture pattern due to the expansion as a result of the change from a liquid to a gaseous state; (2) increase the availability of water soluble copper salts; and (3) increase the solution acidity by the oxidation of sulfides in the formation. Several tons of the liquid injected under pressure are necessary to provide sufficient results. Due to the presence of naturally contained agents, it is usually not necessary to follow up with a propping agent when using liquid oxygen.

Slurry/Liquid Explosives - Explosives are utilized for somewhat the same purposes as the hydrofracturing technique. Even though fracturing generally occurs, the patterns are not as easy to control or define. Also, since detonation is usually complete, the well casing and bore may be damaged or clogged, necessitating additional installations for injection and recovery. Propagation is also difficult due to the highly irregular fracture pattern. Explosives, however, are effective in creating a rubble zone for mass leaching. However, void sealing due to fines generated by rock shattering can occur on the outer periphery of the impact zone.

Ammonia/Acid Additives - The application of chemical additives into an in-situ leaching zone can stimulate mineral alteration and increase recovery rates due to release of void-filling clays and iron salt precipitates.

Fracture Patterns [2/]

Fracture patterns resulting from artificial fracturing techniques are generally oriented in two directions -- horizontal and vertical -- although cross-directional patterns are also common. Figure 4 illustrates a typical fracture pattern set showing both the horizontal and vertical interconnecting and isolated fractures. Horizontal fractures are more commonly generated through hydrofracturing, sometimes resulting in a "pancake" configuration completely around the well bore. Vertically interconnecting fractures tend to result in better sweep-efficiency since the injection and recovery rates are increased more quickly than by isolated horizontal fractures.

Fracture Propagation

The tendency for expanded fractures to collapse or become filled is the single largest factor to overcome when developing a fracture pattern set. Since collapse or filling occurs shortly after expansion, a propping agent must be injected into the opened fractures immediately. Suitable materials for propagation are silica sand, glass beads, and chemical gels, which revert to the same viscosity as water upon contact with leach solutions. Figure 4 illustrates the general propagation technique

Hydrogeologic Studies

Critical to the success of any in-situ mining operation is understanding of hydrogeological conditions inherent to the project site. Many subsurface factors affect the flow of injected leach solutions. They are:

Geology	Hydrology	Others
Faults	Groundwater Level & Gradient	Solution Type & Application Techniques
Fractures/Joints	Perched Zones	Mineral Alteration
Bedding Planes	Saturation/Porosity	Evapotranspiration
Strata Attitude	Permeability	Recovery Method
Alteration Zones	Hydraulic Conductivity	Fracture Filling
Rock Types - Clay Content	Sorption	

Many tools are available to the hydrogeologist to make the necessary determinations as to subsurface flow conditions, both natural and imposed. Some of the more important techniques are:

Pumping Tests - Pumping test data at key locations and depths are invaluable in establishing hydraulic conductivity parameters such as transmissivity, storage coefficient, static and dynamic drawdown water levels, intrinsic permeability and recharge capability. An understanding of these factors, coupled with a knowledge of interstitial rock void space porosity and permeability can enable adequate predictions to be made as to expected flow conditions for injected solutions.

Geophysical Well Logging - Well logging methods could prove to be very useful to in-situ mining technique development. Well logging is used to determine and/or verify visual core logging and pumping test evaluations. It is also useful in verifying general geologic conditons. The various well logging techniques are listed below as to data determination capability:

- Gamma-Ray and Neutron (lithology and porosity)
- Temperature (oxidation zones and water origin)
- Caliper (bore hole configuration)
- Density (grain density of rock)
- Resistivity (lithology, conductivity)
- Velocity (porosity, strata correlation)

A significant problem in evaluation of well log data is delineating an area of permeability from a zone of mineralization, especially when Gamma and Neutron are used.

Digital Flow Models - Another useful tool in determining subsurface flow patterns and travel times are mathematical flow models. Digital models such as finite element and finite difference are used to simulate subsurface flow conditions in two- or three-dimensional form. Models are extremely useful in establishing equipotential lines so that fluid flow can be predicted. Model application is useful in controlling and predicting the coverage of injected solutions above the natural groundwater piezometric surface. Data essential to model development are strata permeabilities, lithification and fluid inflow sources - artificial and natural. Boundary conditions such as the groundwater level, lake or river, major fault zone, mountain range, or distinct change in strata, are also essential to model development

Another important use of flow models is their ability to graphically portray through the construction of an isopotential flow map, the impact of injected solutions on groundwater flow. The effect of water quality, as predicted by a model, can also be verified provided suitable data from properly placed monitor wells is available. Water quality contour maps can also be developed for comparison of solution migration times and direction. Not to be overlooked is the value of the computer model for storing important data in an immediate recall program.

<u>Recovery Flow Patterns</u>

The flow patterns of solutions being recovered by pumping wells influence is essential to the prediction of system efficiency and design of future or improvement of existing in-situ leaching systems. To determine the recovery flow pattern, theoretical values are used based on hydrologic data and well hydraulics. Figure 5 [3] illustrates the flow lines and equipotentials for a line-drive pattern where a single injection and recovery well is employed without the benefit of induced fracturing. Figure 6 shows the same wells, but with the injection well having been vertically fractured. Note the effect on the flow pattern which illustrates a pronounced effect on the pressure profile throughout the entire formation which generates the increase in flow rates. Flow rates would increase even more if the recovery well were also fractured. Flow rate through a well system can be increased many times by well stimulation -- as much as three to five fold.

Figure 7 [3] shows how the flow patterns are developed on an inverted five-spot with the recovery well in the center. Flow line uniformity is dependent upon the homogeneity of the rock and the uniformity of solution injection at the four corner wells. The heavy lines show the position of the fluid front at the time of breakthrough.

Environmental Controls

Federal regulations for control of groundwater contamination from deep well injection were initially proposed under the authority of the Safe Drinking Water Act (SDWA) on August 21, 1976. The controls call for identification of lixiviant chemistry, maps of the project site showing all surface facilities, identification of local private water wells and gas/oil wells, in-situ well hydraulics, aquifer(s) definition, mineral resource description, geologic and hydrologic data, potentiometric maps, volume rate and injection pressure of the fluids and several additional facts concerning physical features of the site, both surface and subsurface. A water quality monitoring plan must also be formulated and the current groundwater quality identified so that potential impact of injected solutions, should they become lost, can be determined. Corrective actions depend upon the magnitude of contamination or the potential degree for contamination. Protective barriers such as grout curtains air/water hydrologic barriers, and injection of chemical neutralizing agents or clean water are some of the proposed corrective measures.

State control regulations vary with geographic locale and are generally not specific as to deep well injection. However, the states now have the authority of the SDWA to set groundwater enforcement laws and are instructed to do so under the law. The state of New Mexico has already formulated and passed a ground water control law which became effective February 18, 1977. Other western states such as Texas and Arizona are in the process of finalizing more explicit groundwater control regulations.

Pollution Control Techniques

Besides the flow barriers mentioned in the previous section, other studies and corrective measures to prevent surface and groundwater contamination from in-situ leaching operations could be:

- lined surface storage basins and ditches
- sealed well casings
- berm protected pregnant solution storage tanks
- exclusive use of multi-spot patterns for maximum recovery
- complete aquifer definition, including flow modeling
- water balance and maximum recycle plans
- monitor well installation at select locations and depths
- incorporation of a continuous water level and water quality programs.

Other Related In-Situ Solution Mining Techniques

Open Pit Wall Leaching - The extraction of low-grade or higher grade zones of minerals remaining in the walls of abandoned open pit mines via solution mining could be a viable technique where proper physical and mineralogical conditions exist. A typical condition suitable[4] for leaching includes a pit face where the upper leached zone (capping), middle leaching zone (supergene) and the lower enrichment zone (primary) are still intact. Completing the system is a pit bottom collection pond to capture those solutions emitting from the pit wall or bottom.

Factors limiting the success of pit wall leaching which should be understood prior to solution application are similar to those for in-situ mining and include geology, hydrology, mineralogy, well hydraulics, and chemistry. Other factors which would be employed and must be evaluated as potential assets to the system are artificial fracturing and chemical stimulation. Environmental impact and economic feasibility must also be defined. The configuration of the resultant groundwater table, altered during mining operations, is of prime importance to injected solution flow. Studies have shown that, due to the effects of evapotranspiration, chemical sealing of the pit face mineral zones, reduction in hydrologic head and disturbance of hydrologic continuity results in an extensively altered groundwater piezometric surface. Figure 8 illustrates a typical open pit groundwater "halo." Note the effect of fault zones acting as water courses or barriers. Fracture zones are also shown as to their impact on flow resulting in flow impoundment due to fracture filling or as seeps onto the pit wall.

Leach solution application techniques include pit perimeter pond injection and/or well injection. Artificial fracturing is employed to increase the fluid contact potential and enhance recovery of pregnant solutions. Hydraulic, oxygen and explosive techniques could be used depending upon desired results. Contact of migrating solution with the pit face is common in pit wall leaching, causing oxidation of iron salts which tend to seal the surface areas of the face where head pressures are minimal. Otherwise, high head pressure zones readily flow or seep out onto the pit face causing erosional flow channels and eventually terminating in the pit bottom collection pond. Better control of solution travel is experienced using well injection and recovery methods similar to those practiced in in-situ solution mining.

Additional pregnant solution recovery techniques, besides pit bottom collection, are adit and shaft collection and installation of horizontal drains into the pit face at key locations and depths.

Rubblization - In-situ leaching of rubblized orebodies can be a practicable method of mineral extraction depending again upon the physical and chemical characteristics. The role of hydrogeologic and mineralogic features is important to the success of the technique. Interest created by the availability of nuclear explosives for fracturing and creating rubblized chimneys in deep-seated sulfide orebodies has decreased to the point of unsuitability, due to non compatibility with environmental concerns and due to the high development cost and risk factors involved. An example of the fate of such a project was Project SLOOP, a joint venture in the 1960's between the Atomic Energy Commission, the U.S. Bureau of Mines, and Kennecott Copper Corporation on a deep-seated copper deposit near Safford, Arizona. The project was delayed indefinitely due to a combination of the factors, as listed. Figure 9 shows the typical configurations of the deep and shallow detonation zones characteristic to rubble leaching.

An example of a successful rubblized leaching operation is that of the Miami Copper Company at Miami, Arizona [5/]. At Miami, leach solutions are sprayed over the surface of a block-caved area and allowed to percolate downward to an underground collection system -- through some 600 feet (183 m) of fractured rock. It is reported that from 3 - 4 weeks are required for leach solutions to emerge in the collection system under gravitational flow. The solution application rate is near 2500 gpm (158 ls).

Other in-situ rubblized leaching operations which have been attempted with varying degrees of success are the McAlester Fuel's Zonia project near Kirkland, Arizona where 4.1 million pounds of explosives were used in 1973 in what is believed to be the largest non nuclear blast ever detonated in the United States. Ranchers Development Corporation detonated 4.0 million pounds of explosives at the Old Reliable Mine near Mammoth, Arizona in 1972 and 1.6 million pounds of explosives at the Big Mike Mine near Battle Mountain in 1974. All three of these projects were closed after efforts to extract significant percentages of copper were limited to lower recoveries of 15 - 18 percent. In all cases, the prime reason for closure was the inability to overcome the pronounced effects of channeling. Other problems encountered, included fracture zone perimeter sealing due to the production of fines from rock shattering during detonation and recovery losses.

Major factors previously discussed as affecting flow in in-situ leaching operations generally apply to injection and recovery techniques of pit wall and rubblized leaching zones also.

Research

As is evidenced by the foregoing discussion, considerable research and development is needed on many aspects of dump leaching and in-situ solution mining techniques to develop future viable solution mining operations. Key areas of concern currently under research are:

Dump Leaching

- Flow testing - air and water
- Lixivant testing
- Construction design
- Environmental compatibility

In-Situ Solution Mining

- Well hydraulics
- Lixivant testing
- Hydrogeologic studies
- Environmental impact

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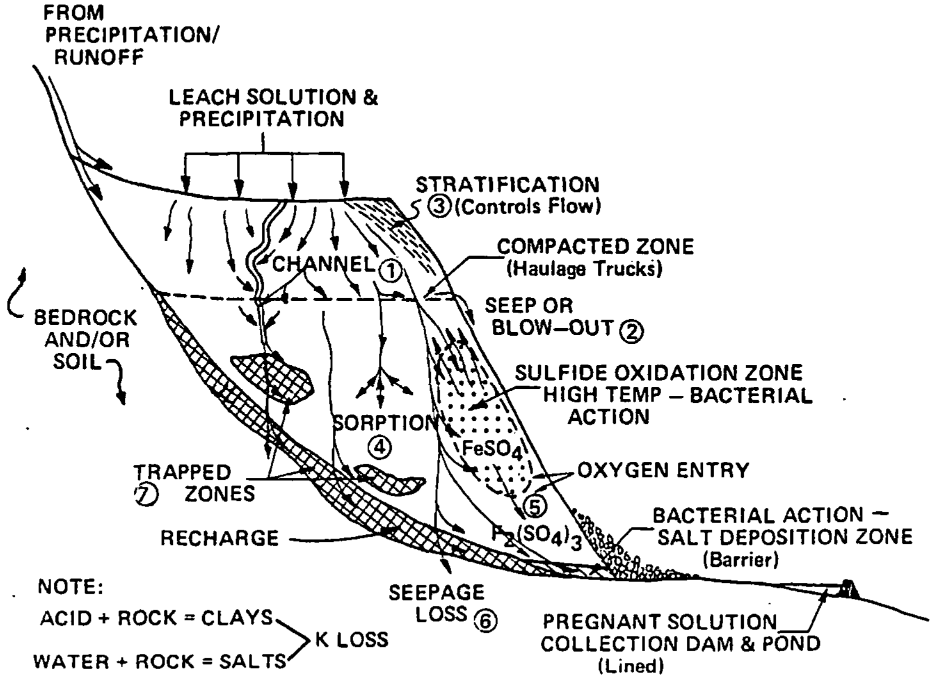
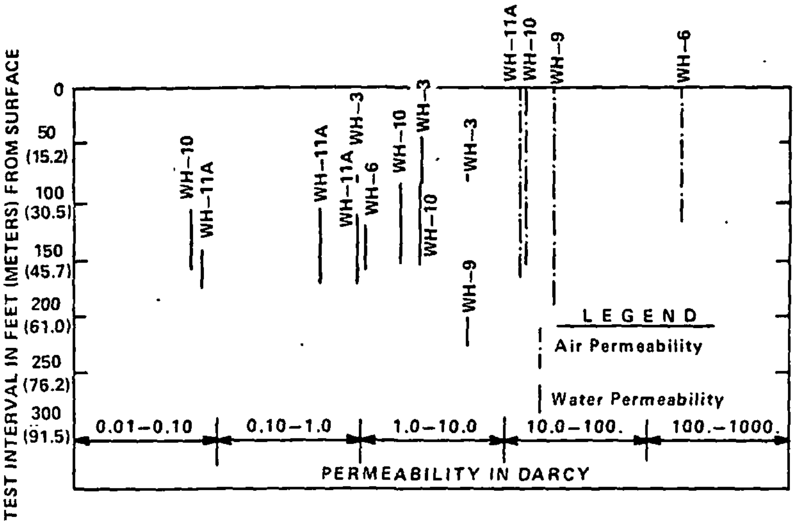


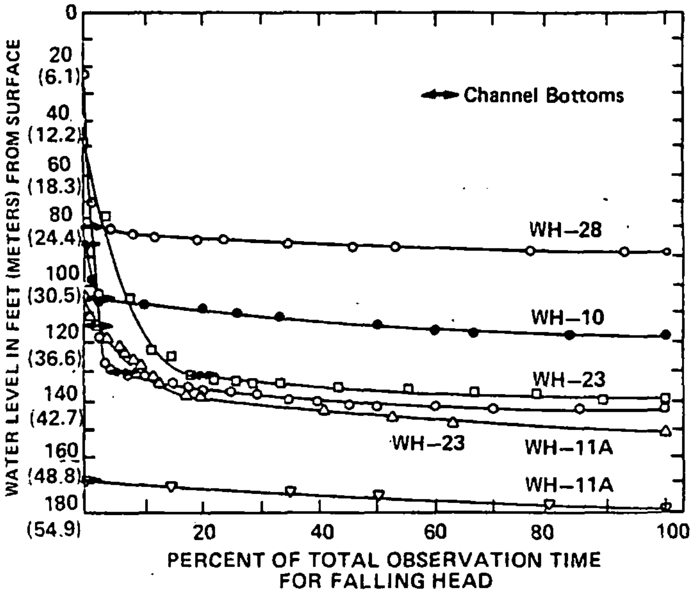
TYPICAL WASTE DUMP SECTION

FIGURE 1



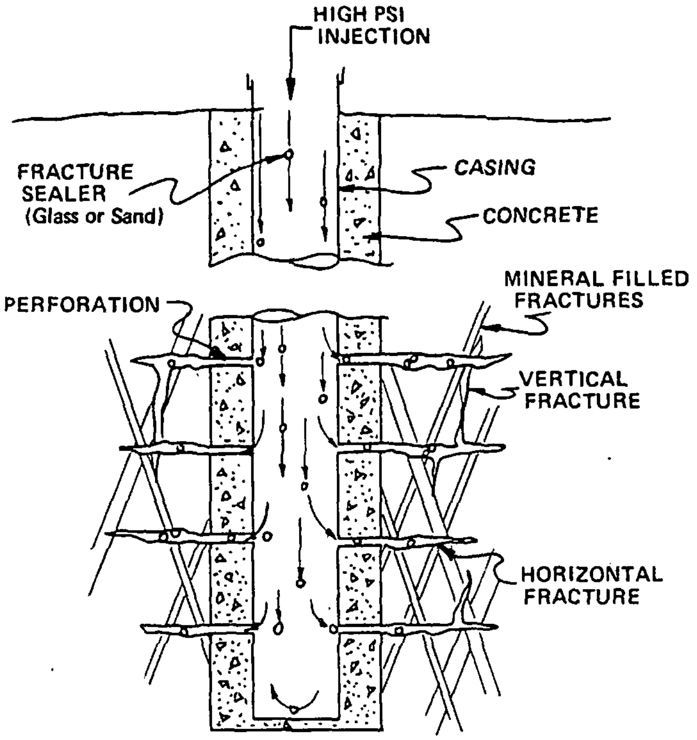
DUMP PERMEABILITY VALUES

FIGURE 2



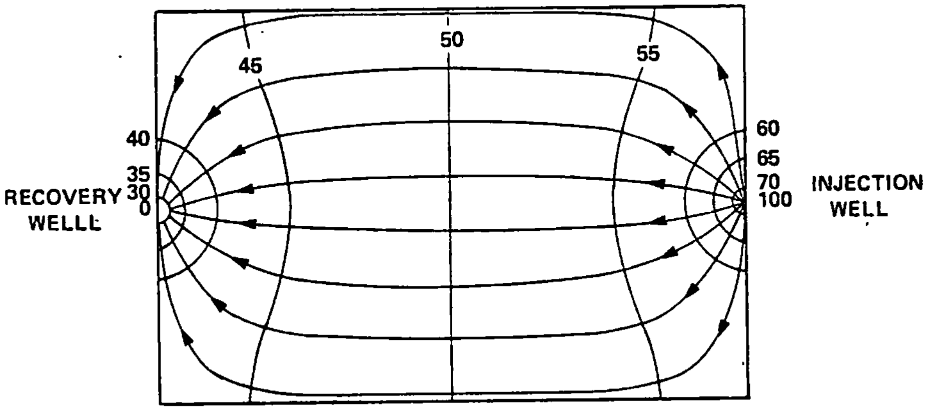
CHANNEL FLOW DATA

FIGURE 3



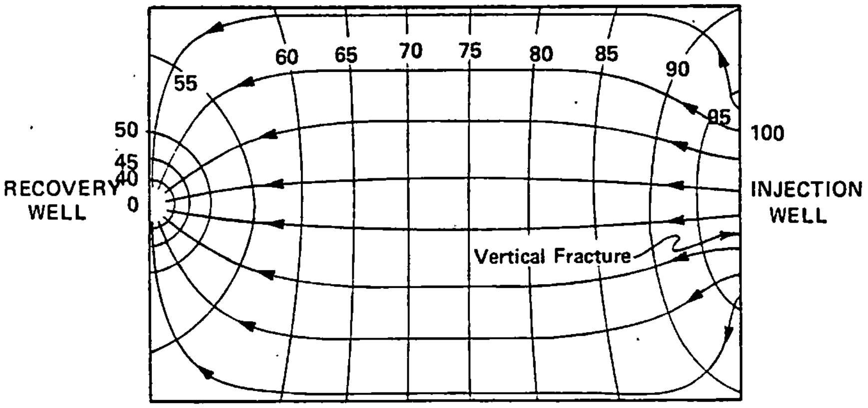
IN–SITU SOLUTION MINING FRACTURE PATTERN

FIGURE 4



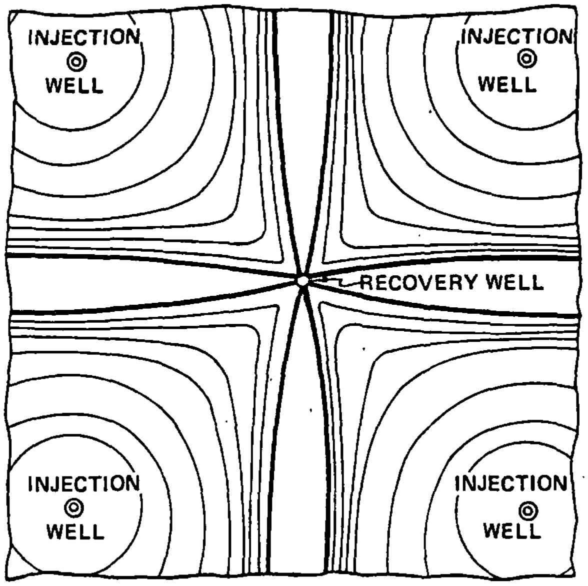
FLOW LINES AND ISOPOTENTIALS FOR LINE–DRIVE PATTERN

FIGURE 5



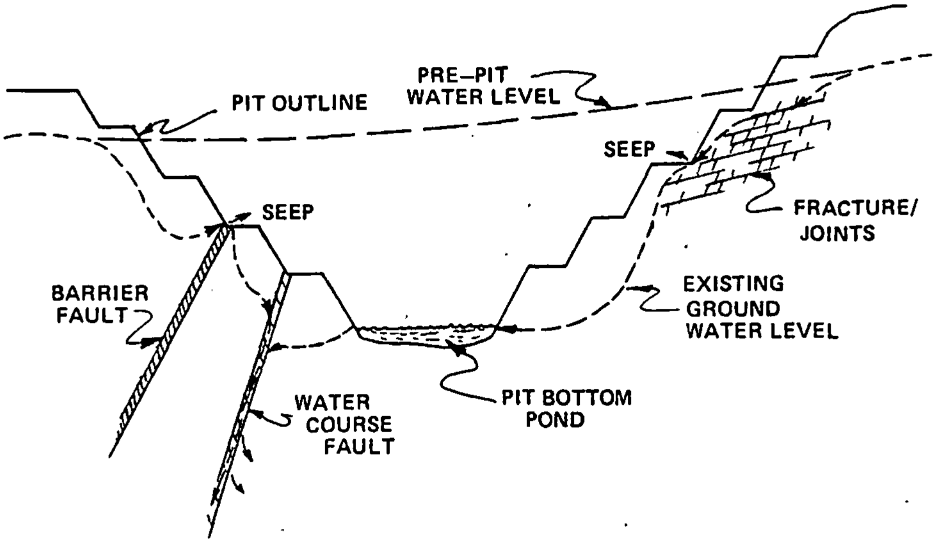
FLOW LINES AND ISOPOTENTIALS FOR LINE–DRIVE PATTERN WITH VERTICAL FRACTURE

FIGURE 6



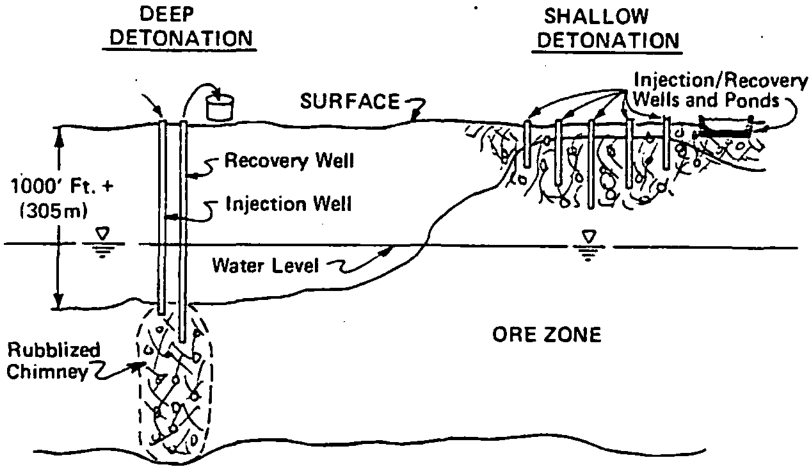
TYPICAL FLUID FRONT OF A5 – SPOT PATTERN

FIGURE 7



OPEN PIT GROUNDWATER HALO

FIGURE 8



IN–SITU SOLUTION MINING
RUBBLIZATION

FIGURE 9

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HYDROMETALLURGY OF ZINC

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The zinc industry of the USSR has used the hydroelectrometallurgical method of producing zinc from its earliest days. The journal "Tsvetnye Metally" has remarked upon the potential of this method when informing its readers about the first research in the laboratories of the Gintsvetmet and Tsvetmetzoloto and about the work of the experimental zinc plant at Leninogorsk.

Coverage given in the journal to problems in zinc production theory and practice has helped in choosing ways to improve processes and make design improvements for apparatus and equipment.

Zinc production developed rapidly in the Soviet Union after the Second World War, in the 1950's and 1960's. Technical progress has extended to all the stages in zinc hydrometallurgy. The accelerated development of science and technology made a considerable contribution to increases in the quantity of zinc production and its quality. The zinc industry was radically transformed and received a stimulus to further improvements in its technical standards and in the quality of output.

The distinguishing features of present-day hydrometallurgical zinc production are a closed production circuit with maximum mechanization of production processes and automation of a number of technological operations. Mechanized raw materials stockpiles are available at all plants, and containerized shipment of concentrates has been adopted. Zinc concentrates are roasted in high-output fluidized-bed furnaces which have replaced the multiple-hearth roasters. Separate processing of calcine and zinc sublimates from Waelz kiln processing of cake, slags, and other metalliferous materials has been organized.

Leaching processes with preliminary wet and dry classification of calcine and the equipment and apparatus for leaching have changed radically. Zinc sulfate solutions are efficiently and thoroughly purified in two or three stages, removing associated metals and harmful impurities. High-capacity filters with mechanized clamps and automated vacuum filters of various types have been installed at all plants instead of filter presses with manual clamps and a filtration surface of 40 m^2.

Zinc electrolysis has been greatly intensified: the high standard of solution purification has made electrolysis at a current density of over 600-680 A/m^2 possible, and current efficiency has increased appreciably. Vacuum-evaporation cooling of electrolyte has been adopted at many plants. The cathode zinc is melted in induction furnaces, and the casting and storing of zinc ingots is completely mechanized and automated. Only stripping of the cathode zinc has not been perfected, but important research is in progress in this direction.

Large shops for the integrated utilization of raw materials operating at high levels of technical and economic efficiency have been set up at the plants to extract all the valuable constituents in the material being processed.

Natural gas and an oxygen-enriched blast are widely used, in roasting zinc concentrates in fluidized-bed furnaces, in Waelz-kiln processing, and in slag sublimation.

A number of measures have been implemented to protect water resources and the atmosphere from pollution.

Automatic monitoring and automation of individual processes and production operation have been extensively introduced at all stages of zinc production and are still being introduced.

The Ust'-Kamenogorsk Lead-Zinc Combine and the Chelyabinsk Zinc Plant are the leaders of the lead-zinc industry; their results in many areas are superior to those of the leading foreign plants.

The journal, "Tsvetnye Metally" has been an important factor in these achievements. In 1946, the journal published papers by B. V. Gromov vital to the theory and practice of zinc production, on cobalt removal from zinc solutions using xanthate, and on the importance of the pH value in the processes of leaching and precipitation of impurities from solutions. This contribution was the result of many years of creative work by the author at the Chelyabinsk Zinc Plant and helped to improve leaching processes.

A paper by S. I. Pol'kin on the integrated utilization of raw material, proposing the construction of Waelz kiln installations at all zinc plants (1946), was aimed at mobilizing specialists in the institutes and the managers of plants. In the 1950's all the zinc plants were finally equipped with Waelz kiln installations.

A paper by Z. I. Trotskaya entitled "The Principles of Calculating Prime Cost in the Integrated Utilization of Raw Materials" (1948) was of vital importance in developing the integrated utilization of raw materials.

During this period, the metallurgists increased their efforts to find ways of increasing zinc production at operational plants.

A paper by A. P. Snurnikov (1953) provided an analysis of trends in increasing the productivity of zinc electrolysis shops and advanced the arguments in favor of the most important ways of intensifying the electrolysis process and increasing plant productivity: increased current density, provided that the zinc sulfate solutions are carefully purified to eliminate harmful impurities.

The next review by A. P. Snurnikov (1957) examined the main trends in intensifying processes in zinc hydrometallurgy, which formed the basis of subsequent improvements in zinc production.

Interesting reviews were submitted by L. S. Getskin (1966, No. 12; 1974, No. 10) and A. F. Nikiforov (1975, No. 4).

Papers on a variety of problems in zinc production theory and practice which have been of great importance in solving many technical and economic problems have been published in the journal. Progress in the by-product extraction of cadmium became the first stage in extending the utilization of zinc raw material. Papers by O. A. Khan and G. N. Sosnovskii and co-workers (1961-1966, 7 papers) described ways of intensifying cadmium electrolysis and methods of obtaining high-quality metal.

Subsequently, as the problem of thorough purification of electrolyte was solved, all the associated metals began to be extracted more completely. The best results were obtained by using a solvent extraction-sorption technology, described in papers by V. N. Startsev, V. I. Mal'tsev, V. P. Pimenov, and L. S. Getskin (1974, No. 10 and 11).

A paper by G. N. Pakhomova and L. M. Marenkova described the use of a two-stage scheme of removing impurities from solutions by cementation with zinc dust in apparatus with a fluidized bed (1974, No. 12). G. N. Pakhomova often published papers on research in the electrodeposition of zinc and its intensification (1963, 1964, No. 3), corrosion phenomena in deposited zinc, and on reactions on insoluble anodes (1966).

Difficulties in stripping cathode zinc often occurred in electrolysis shops. Specialists from the research institutes and the zinc plants studied the reasons for difficult stripping and engineering measures were introduced to eliminate this phenomenon.

In 1954, G. M. Shteingart published a very valuable paper in the journal, written at a high scientific level, on the principles and practical application of a method for complete elimination of difficulties in cathode zinc stripping by additions of antimony salt to the electrolyte. In recent years there has generally been no difficulty in stripping during zinc electrolysis practice.

N. I. Ful'man, G. A. Iskandarova (1969), V. I. Ogorodnichuk (1974, No. 10), N. A. Pilipchuk, G. S. Kir'yakov, and others (1975, No. 8) published papers in the journal on ways to increase the service life of anodes. A quaternary anode composition which proved resistant when adopted at the Chelyabinsk Plant is recommended in the latter paper.

A. A. Salin and his co-workers described the methods used at the Chelyabinsk Plant to improve zinc electrolysis (1961, 1962, 1965) and in particular research on factors effecting current efficiency in zinc production.

I wish to remind the present-day readers of the journal of the great practical importance of the review paper (1952) on the use of the first anti-corrosion material in the Soviet Union (viniplast) for lining electrolytic cells and for the manufacture of pipes at non-ferrous metallurgy plants.

A revolution occurred during the 1950's in the hydrometallurgical production of zinc due to the creation and adoption of a process for roasting zinc concentrates in the fluidized bed.

The creative and active participation of V. N. Kostin, specialists from the institutes and plants, and the author of this paper in developing fluidized-bed furnace designs, coordination of research, design, and project work, and in the practical implementation of multiple-hearth furnace conversion to fluidized-bed furnaces helped to complete all of the work on the adoption of concentrate roasting in fluidized-bed furnaces at all electrolytic zinc plants in 1955-1957.

A detailed account of the stages of adoption of fluidized-bed furnaces in the USSR is given in papers by G. M. Shteingart and others. The following papers were published in the journal during 1961-1970: by A. M. Vartanyan, V. D. Ponomarev, and T. Kh. Tserekov on roasting zinc concentrates with an oxygen-enriched blast at the Ust'-Kamenogorsk Lead-Zinc Combine; by M. P. Smirnov, on mechanization and automation of a zinc melting and casting line; by P. N. Alentov on the adoption of cast and rolled anodes at the Chelyabinsk Zinc Plant, by G. M. Gordon on problems of dust trapping; by K. A. Tiksne and B. K. Plastinkin on the startup of the Leninogorsk Zinc Plant; and by M. A. Bogdanov on the adoption of semiconductor rectifiers at the plants in place of mercury rectifiers. L. I. Zelenskaya and O. A. Khan published a review paper on methods of cooling solutions at electrolytic plants.

A. A. Salin and his co-workers correlated methods of operating the vacuum evaporation installation at the Leninogorsk Zinc Plant and produced initial data for calculation and for the installation operating schedule.

Bulgarian specialists A. M. Aleskandrov, I. D. Enchev, and D. D. Gochev published a paper on methods of oooling electrolyte in electrolytic cells in carbon coils.

Papers by L. S. Getskin (1964, No. 1), A. P. Snurnikov (1966, No. 3; 1968, No. 1; 1969, No. 6), and A. S. Yaroslavtsev (1974, No. 12) set out the results of development and adoption in collaboration with specialists from the Ust'-Kamenogorsk Lead-Zinc Combine of a processing technology for lead-production dusts, by sulfatization with strong sulfuric acid in a fluidized bed.

Papers on processing zinc cakes, slags, dusts, and other zinc-bearing materials have often been published in the journal. The steady increase in the extent to which these materials have been processed has greatly increased the proportion of zinc sublimates in the total zinc materials balance and of the materials of a more complex composition.

The problem of sublimate utilization was of great importance to the Almalyk Plant. A paper by N. N. Ushakov, O. A. Khan, and others describes the pilot-plant testing of a sublimate leaching process at a constant pH value, resulting in increased extraction of zinc and cadmium and solutions with a lower impurities content when processing Waelz kiln oxides and slag sublimates.

The hydrometallurgical zinc cake processing scheme, and also the single-stage leaching scheme with continuous counterflow cake washing, have helped to improve zinc production. It has been brought in on an industrial scale at the the Leninogorsk and Almalyk Zinc Plants and is being brought in at the Ust'-Kamenogorsk Lead-Zinc Combine and the Chelyabinsk Plant. The new technology increases metal extraction and makes the Waelz kiln shop capacity available for slag processing. The zinc cake counterflow was ing scheme at the Almalyk Plant has been described in detail in a paper by L. S. Gusar, I. M. Pen, and N. N. Ushakov.

The zinc industry has reached high levels in the production of sulfuric acid from zinc concentrate roaster gases. The degree of sulfur recovery from raw material at the leading plants has exceeded 90%, and the highest technical standard of organization in sulfuric acid production is found at the Chelyabinsk Plant. A group of specialists from that plant has informed the readers of the journal about the assimilation in the USSR of a method of producing sulfuric acid by double contact with intermediate absorption (DC/DA).

Beginning in 1972, the journal has regularly published papers devoted to the implementation of the Decree of the Central Committee of the Soviet Communist Party on the work of Party organizations at the Ust'-Kamenogorsk Lead-Zinc Combine and the Balkhash Mining and Metallurgical Combine on increasing the degree of raw material utilization. Specialists from the Ust'-Kamenogorsk Lead-Zinc Combine, the Chelyabinsk Electrolytic Zinc Plant, the Leninogorsk Polymetallic Combine, the Chimkent Lead Plant, and other plants and organizations have published material on this problem.

It is impossible in a short paper to give a complete description of the many aspects of specialist work in the field of zinc hydrometallurgy and of the active part played by the journal "Tsvetnye Metally" over a period of 50 years,

Workers in the zinc industry, like those employed in other branches of the national economy, are faced with great and difficult problems in the light of the resolutions of the 25th Soviet Communist Party Congress. In the future, "Tsvetnye Metally" will give active and creative assistance to those working in the industry to obtain successful solutions to problems in the technical develolment and re-equipping of plants in the 10th five-year plan.

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THE JOURNAL AND THE DEVELOPMENT OF NICKEL PRODUCTION IN THE USSR

UDC 669.24

S. D. Sheremet'ev

The nickel industry in the Soviet Union has now become a leading branch of the national economy, meeting the demands of the country for nickel, extracting up to fourteen elements as commercial products from the raw material, and reaching a technical standard which is as good as that produced in leading foreign plants.

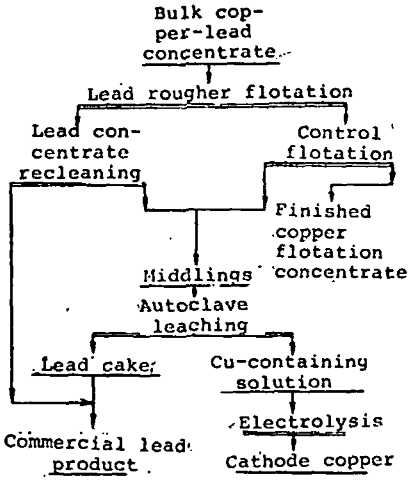
This was not always the case. During the pre-war years, the Soviet Union had insufficient experience in nickel and cobalt production. It was necessary for us to find our own industrial and scientific personnel capable of maintaining the growth and development of this vital branch of production, without which the comprehensive development of the national economy was impossible and the capacity of the country to defend itself could not be increased. The scientific and technical journal "Tsvetnye Metally" played a vital

N6, 1975

HYDROMETALLURGICAL PROCESSING OF COPPER-LEAD MIDDLINGS

V. V. Belikov, V. A. Kuchaev, and L. I. Grosman

In processing the complex copper-lead ores of the Dzhezkazgan deposit, the extraction of copper and lead into the bulk concentrate is 94-95% and 88-90% respectively; however, losses of lead in the copper concentrate and losses of copper in the lead concentrate are considerable when the bulk concentrate is separated.



Combined processing scheme for bulk copper-lead concentrate.

Slime particles - 0.044 mm in size of the minerals to be separated are the principal source of copper and lead losses in the different concentrates; this is due both to the specific characteristics of the inital raw material (a high content of secondary copper minerals with a tendency to overgrinding) and to physicochemical behavior in the flotation process. These factors lead to a situation in which the finely dispersed and separation-resistant copper and lead minerals accumulate in the middlings from the bulk concentrate selection cycle and circulate in the lead rougher flotation and rough concentrate recleaning operations.

The present investigations, the subject of which was the middlings produced in the process of concentration by the scheme shown in the Figure, were devoted to finding and checking a hydrometallurgical middlings processing technology.

The scheme provides for the flotation separation of bulk concentrate to produce a rich lead concentrate with a lead extraction of 50-60% (from the ore), a copper concentrate containing 18-20% Cu and 1-1.5% Pb, and middlings (tailings from rough lead concentrate recleaning and control flotation concentrate).

Composition of middlings, %

29.38 Cu	3.90 Fe	23.46 SiO_2	1.33 Al_2O_3
13.22 Pb	15.0 S_{tot}	0.96 MgO	
2.32 Zn	14.81 S_s	1.32 CaO	

The copper in the middlings is represented by chalcocite and (in part) by bornite, the lead by galena, and the zinc by sphalerite.

It is known that secondary copper minerals oxidize comparatively easily during autoclave leaching in the presence of oxygen or compressed air. In these circumstances the copper and zinc pass into solution, whereas the lead and the elementary sulfur which forms pass into the insoluble residue.[1] The process must be carried out at a temperature below the melting point of elementary sulfur (112° C) in the presence of sulfuric acid.

Table 1
Distribution of Sulfuric Acid in the Autoclave Leaching-Electrolysis Process

Operation	kg/t	%
H_2SO_4 consumed in leaching	545	76.6
Free (unreacted) acid in autoclave solution	165	23.4
Total . . .	710	100.0
H_2SO_4 regenerated in electrolysis	620	87.2
Fresh H_2SO_4 added to process (acid consumption per ton of product)	90	12.8
Total . . .	710	100.0

The effect of acid consumption, leaching time, and oxygen partial pressure was studied. The following optimum leaching characteristics were found: time 4 hr, H_2SO_4 feed 700 kg per ton of middlings, oxygen partial pressure 6-10 atm, temperature 100-110° C. Under these conditions, extraction of copper and zinc into solution reaches 98% and 90% respectively.

The yield of insoluble residue (cake) is 60-65%, containing 20-22% lead and ~ 15% elementary sulfur. The lead cake can be added to lead concentrates.

Leaching yielded solutions of the following composition, g/liter: 30-34 Cu, 3.0 Zn, 1-3 Fe, and 10 H_2SO_4.

Electrolysis should be used in processing the solutions obtained by leaching, as is shown by numerous investigations and foreign practice. In the process of electrolysis, metallic copper is produced on the cathode by reduction and sulfuric acid is regenerated at the same time:

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[1] I. N. Maslenitskii, V. V. Dolivo-Dobrovol'skii, G. N. Dobrokhotov, et al., Autoclave Processes in Non-Ferrous Metallurgy, Moscow, Metallurgiya, 1969, 349 pages, illustrated.

$$CuSO_4 + H_2O + 2e = Cu^\circ + 1/2\,O_2 + H_2SO_4.$$

Reduction of 1 g of copper regenerates 1.54 g H_2SO_4. Electrolysis is carried out at a current density of 200 A/m^2, voltage 2.5 V, without electrolyte circulation. Power consumption is these circumstances is 3700 kW-hr per ton of cathode copper and current efficiency is 55-60%. Dense lustrous copper deposits are produced. The basic impurities content was in accordance with foreign plant data for electrolysis of copper with insoluble electrodes. The data on consumption of sulfuric acid throughout the process (autoclave leaching-electrolysis with sulfuric acid regeneration) are of considerable interest.

Table 2
Approximate Copper and Lead Extraction Values

Flotation scheme			Combined scheme		
product	extraction, %		product	extraction, %	
	Cu	Pb		Cu	Pb
Lead concentrate	8	68—70	Lead flotation concentrate	4	60
Copper concentrate	85—87	20	Copper flotation concentrate	83	10—12
			Cathode copper . .	6—8	—
Bulk concentrate	93—95	88—90	Lead leach cake . .	—	18
			Bulk concentrate .	93—95	88—90

Sulfuric acid at the rate of 90 kg/ton is required to offset losses in dissolving acid-soluble gangue constituents and in breaking down sphalerite (Table 1).

The zinc content of the solutions rises in proportion to the extent of their circulation, and when a high concentration is reached the zinc should be extracted by one of the generally known methods (precipitation with lime or sodium sulfide or solvent extraction). Iron does not accumulate in the solutions.

Thus the investigations have demonstrated the possibility of processing copper-lead middlings by a technology which includes sulfuric acid oxidizing autoclave leaching with subsequent electrolysis of the autoclave solutions, yielding copper as cathode copper and regenerating the sulfuric acid, which is returned to the leaching operation with the recirculating solution.

Lead and elementary sulfur pass into the autoclave leach cake, which should be added to the lead concentrate and processed with it.

It is apparent from Table 2 that separation of the middlings and processing them by the proposed technology will increase the overall extraction of copper and lead.

How to Predict Explosive Stimulation Results

by Charles G. Laspe, *Research Director*
Talley-Frac Corp., Mesa, Ariz.

A new technique of explosively stimulating oil and gas well production involves hydraulic or pneumatic displacement of a powerful slurried explosive far back within the fracture system of the pay zone. Upon detonation, which propagates through fissures as small as 1/64-in. in width, high energy shock waves are initiated. These waves cause extensive rubblizing and secondary fracture generation at considerable distances from the original fissure. In addition, the large quantity of product gases generated by the explosion result in lengthening of the primary fracture system. The rubblized fragments, some of which are in the typical frac sand particle size range, are blown into the newly formed fractures to provide an autogenerated proppant.

The mathematical basis for determining the effects of explosive well stimulation is still in its infancy. However, testing and development programs of the Talley-Frac Corp. have resulted in considerable insight into the basic phenomena at work. This information, coupled with existing theories of rock mechanics, the studies of shock waves in solids, and the excellent work done by the Bureau of Mines on rock breakage by explosives, has provided the foundation for this model study.

The T/F explosive fracturing reservoir model consists of the following essential parts:

- Determination of the extent of the pulverized and rubblized zone.
- Determination of the permeability of the above zone.
- Determination of the extent of the secondary fracture zone.
- Determination of the permeability of the secondary fracture zone.

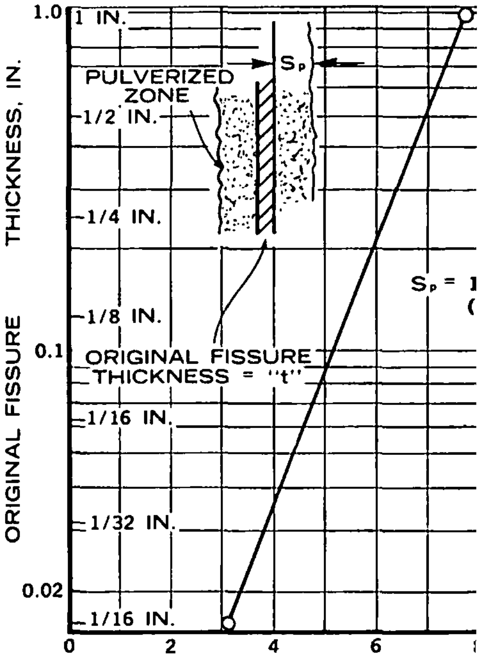
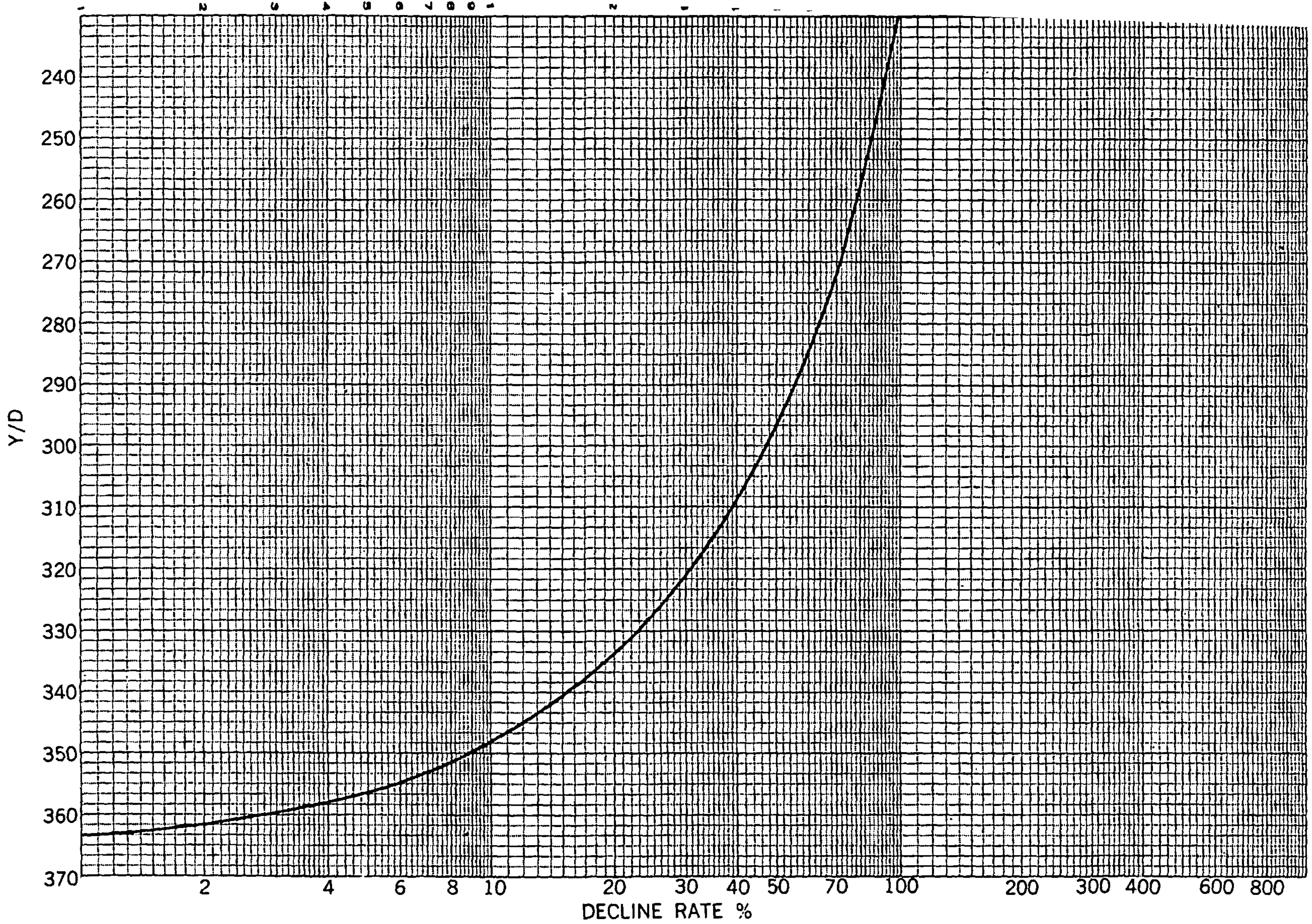


Fig. 1. Theoretical pulverization distance i

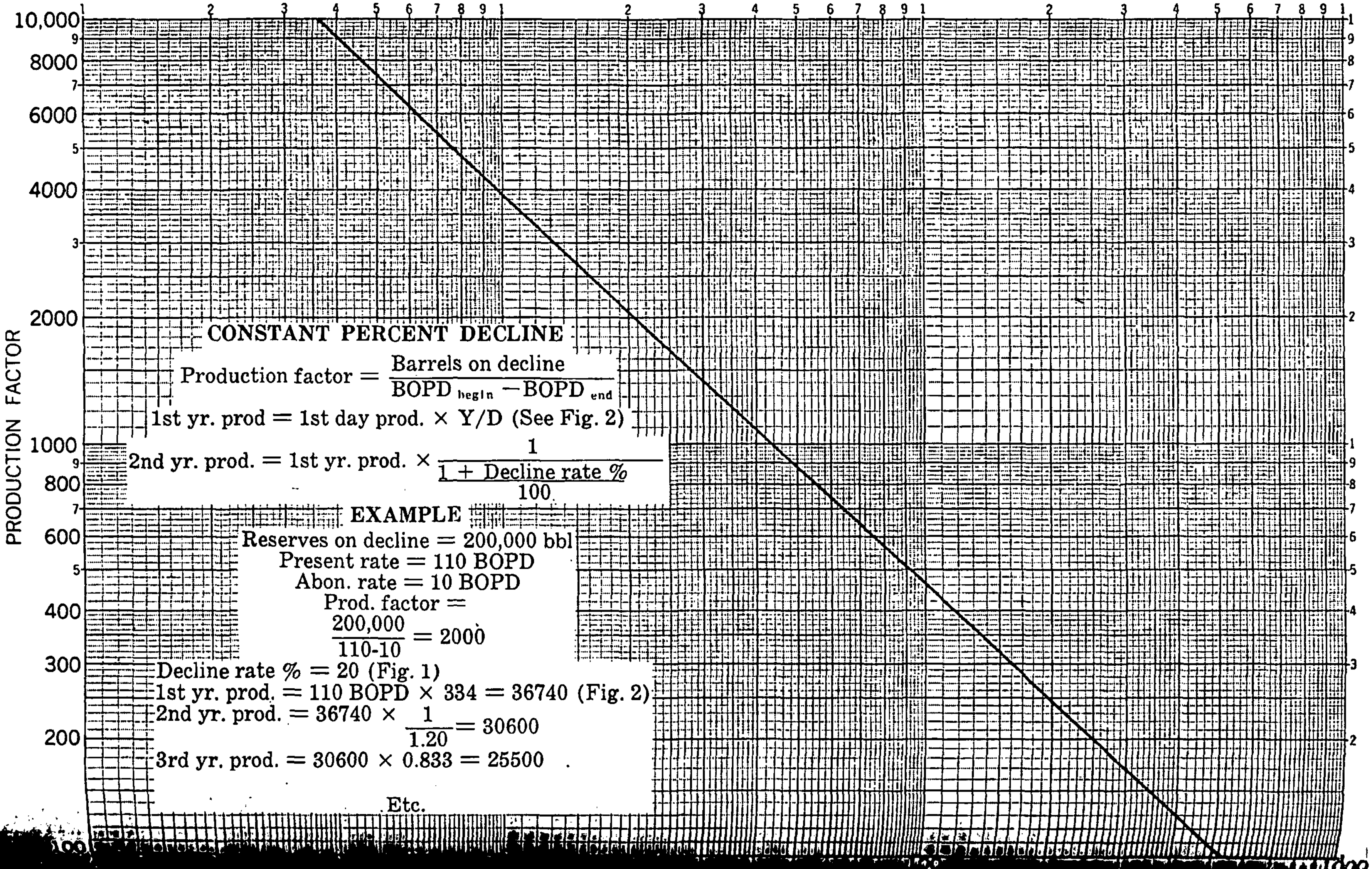
- Use of the above information to
productivity increases.

The Pulverized/Rubblized Z

Assuming that the initial shock w
explosion is mainly responsible for the
tion of rock in the immediate vicinit
1005C loaded in a fissure, the extent of
tion and resultant permeability may be
if the energy absorbed as a function
is known or can be estimated. If in s
rocks, we assume that there is a statis
bution of bonding strength in the partic
ed together, the exponential functio
defensible. Beer's law for the absorptio
traversing an energy absorbing medi


Y/D
240
250
260
270
280
290
300
310
320
330
340
350
360
370
2
4
6
8
10
20
30
40
50
70
100
200
300
400
600
800
DECLINE RATE %

Yearly Production on Constant Percentage Decline



CONSTANT PERCENT DECLINE

$$\text{Production factor} = \frac{\text{Barrels on decline}}{\text{BOPD}_{\text{begin}} - \text{BOPD}_{\text{end}}}$$

1st yr. prod = 1st day prod. × Y/D (See Fig. 2)

$$\text{2nd yr. prod.} = \text{1st yr. prod.} \times \frac{1}{1 + \frac{\text{Decline rate \%}}{100}}$$

EXAMPLE

Reserves on decline = 200,000 bbl
Present rate = 110 BOPD
Abon. rate = 10 BOPD
Prod. factor =

$$\frac{200{,}000}{110\text{-}10} = 2000$$

Decline rate % = 20 (Fig. 1)
1st yr. prod. = 110 BOPD × 334 = 36740 (Fig. 2)

$$\text{2nd yr. prod.} = 36740 \times \frac{1}{1.20} = 30600$$

3rd yr. prod. = 30600 × 0.833 = 25500

Etc.

$I_T = I_o e^{-KX}$ . . . . . . Eq. 1

Where:

I_T = transmitted energy

I_o = incident energy

K = absorption coefficient

X = length of absorption path

ing the above equation, one may calculate nergy absorbed per rock unit volume at any fied distance from the face of the original ·e. Secondly, knowing a value of the rock's ce energy, the surface area generated per volume can be calculated. Then assuming the rized particles to be spherical in shape, the alent particle size can be estimated.

the zone in which the diam of the particles is than the basic or intrinsic grain size, we safely assume that extensive grain fracture pulverization occurs. This fine powdery ma- l will normally be washed from the fissure formation fluids are produced into the well For particles whose diam is equal to or er than the intrinsic average grain size, it is able that their environment is more com- it even though fractured. Using this basic ise, we may estimate the character of the s in the immediate proximity of the original re.

For,

(1) $d_p < d_{sand}$

Zone is pulverized.

(2) $d_p > d_{sand}$

Zone is fractured and competent.

Using the above criterion, with the following assumption:

- Intrinsic average grain size of 50 mesh.
- Surface energy, 1×10^3 ergs/cm^2
- Vertical planar fissure

The pulverization distance can be expressed by:

$S_p = 1.104 \ln (1095t)$ . . . . Eq. 2

This equation is graphically presented in Fig. 1.

Pulverized/Rubblized Zone Permeability

Using the calculated particle size distribution as a function of distance from the center of detonation, the equivalent permeability may be estimated. Obviously, for this calculation something must be known of the packing characteristics of the pulverized material. For the T/F model we have assumed that the particle geometry and compaction pressure response would be equivalent or typical frac sand. As a further simplification we have found that the overall conductivity of the pulverized and rubblized zone is approximately equivalent to a zone of the following charac-

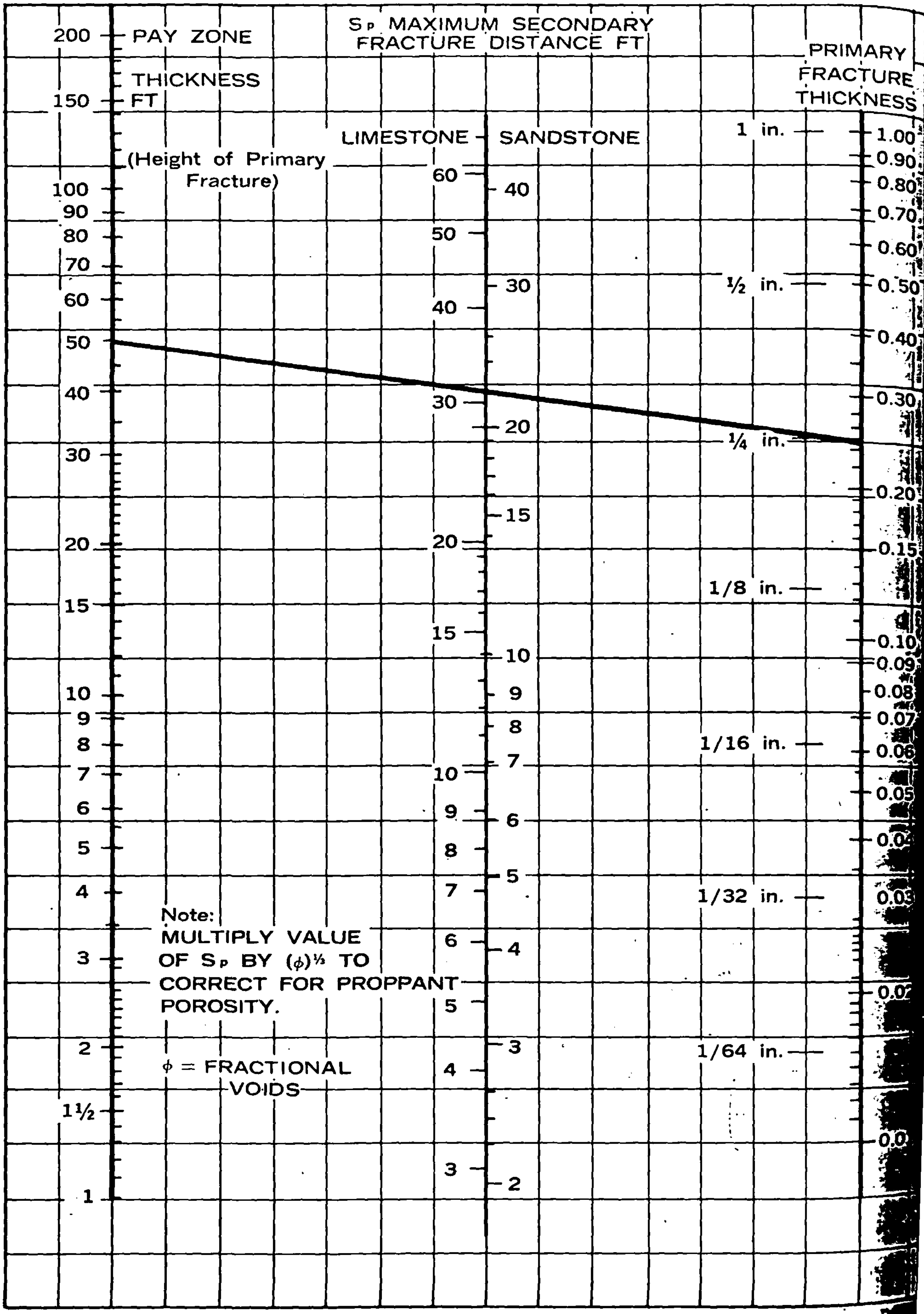


Fig. 2. Monograph to estimate secondary fracture lengths per Eq. 6.

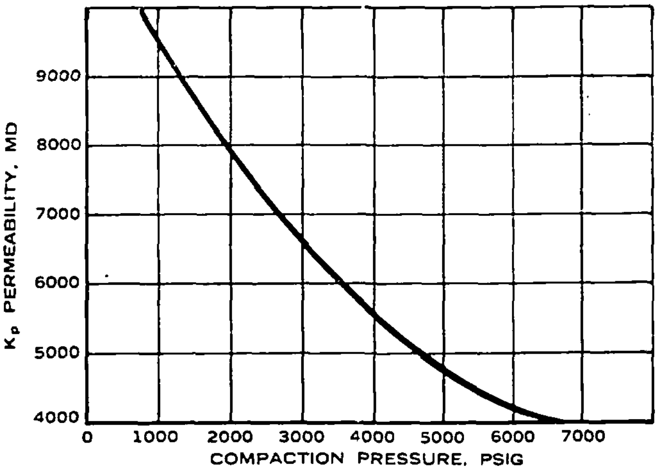


Fig. 3. Permeability of rubblized zone vs compaction pressure (*for dp = 300 micron, 50 mesh*).

teristics:

- Width = 2 S_p + t
- Permeability = same as a frac sand with diam equal to average grain size, e.g. 50 mesh.

Secondary Fracture Generation

Dysart[1] presents a formula for estimating the radius of a rock zone fractured from downhole explosions. All his data are derived from well bore shots which present a different explosion geometry than that experienced in the application of Talley-Frac technology. The two different total volume of damage-affected rocks are assum to be equivalent.

Dysart's equation states:

$r = K(W)_E^{1/3}$ = radius in ft . . Eq. 3

Where:

K = factor based on rock properties

K = 5 for sandstone

K = 7 for limestone

W_E = explosive weight in lb

Since these data were obtained from shallo downhole experiments a cylindrical geomet blasting effect may be assumed. Thus the volum of damage rock per ft of well bore can be computed from:

$V_c = \pi (KW_E^{1/3})^2$ . . . . . Eq. 4

However, for the T/F planar fissure situatio the volume of affected rock per ft of fissure are depends upon the attitude and thickness of th fracture. For vertical fissures, assuming they e tend from the top to the bottom of the pay zon interval, would result in the following volume o affected rock.

$V_P = \pi \, \varepsilon \, S_2^2$ . . . . Eq. 5

Where ε = an eccentricity factor

S_2 = secondary fracture extension, ft.

Equating 4 and 5 and substituting the app

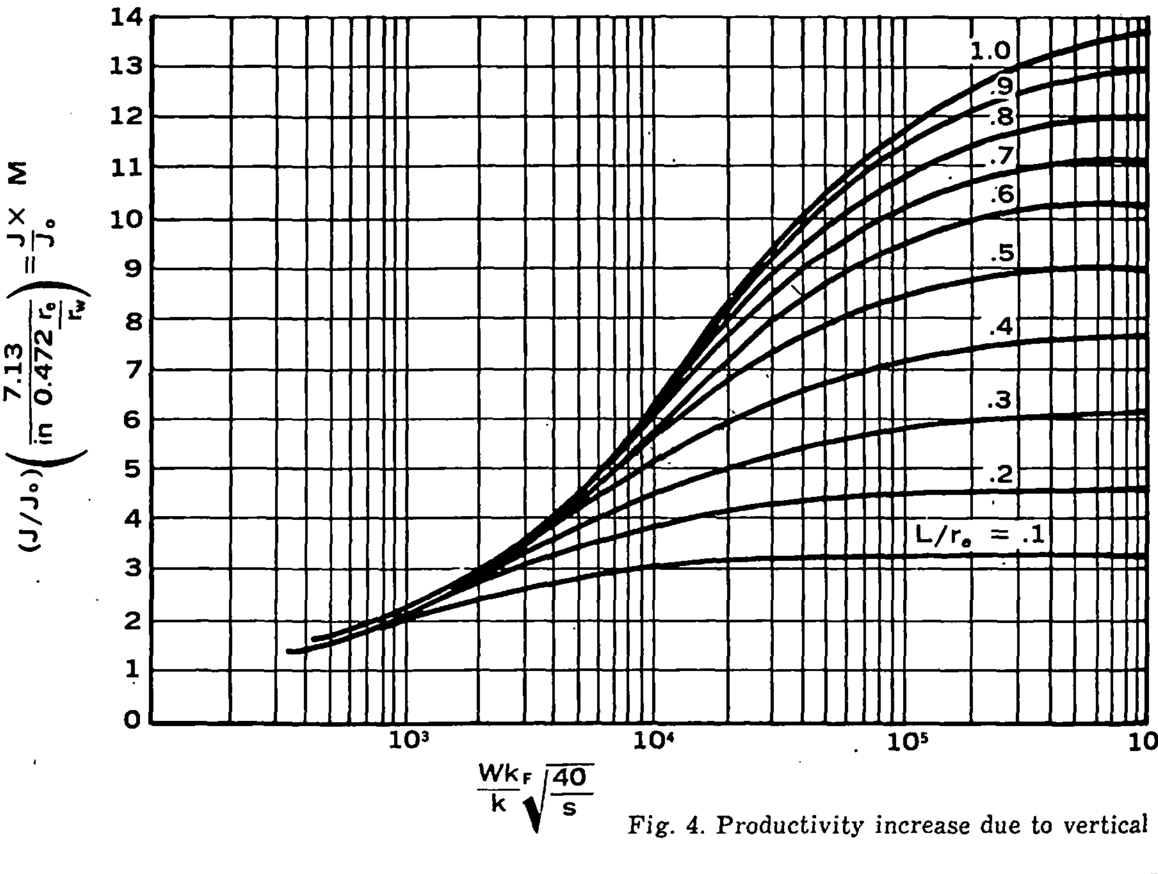


Fig. 4. Productivity increase due to vertical frac

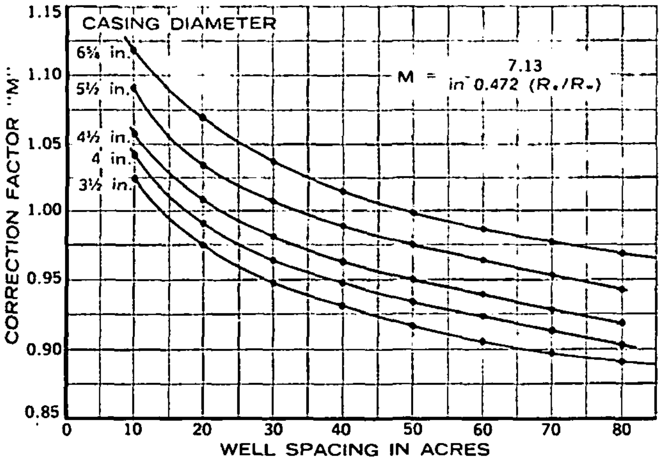


Fig. 5. Correction factor for well spacing, casing diam.

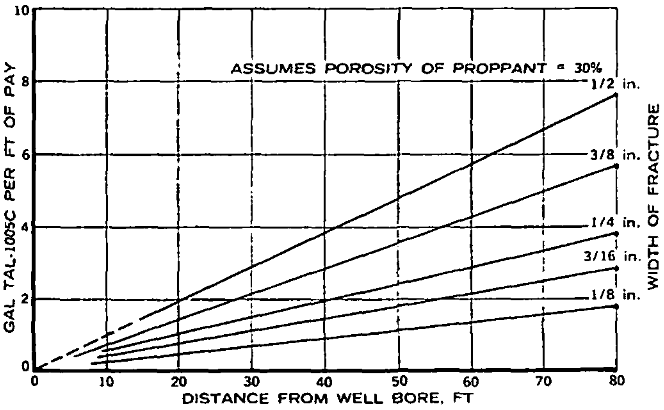
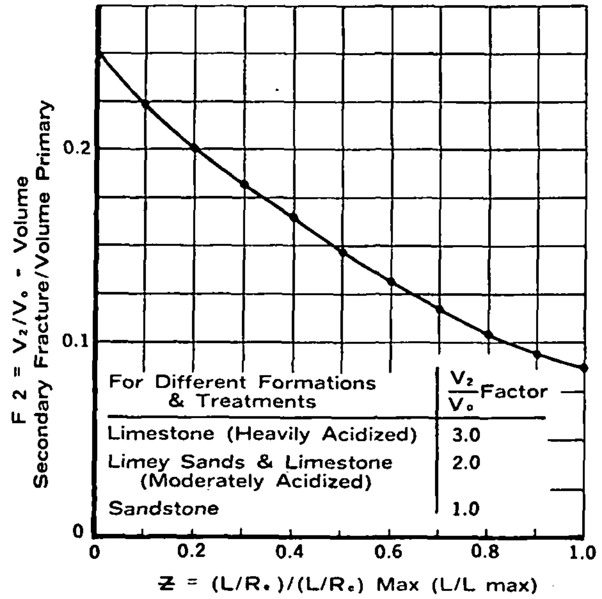


Fig. 6. Volume of vertical fractures in gal/ft of pay.



For Different Formations & Treatments	$\frac{V_2}{V_0}$ Factor
Limestone (Heavily Acidized)	3.0
Limey Sands & Limestone (Moderately Acidized)	2.0
Sandstone	1.0

Fig. 7. Estimation of secondary fracture and solution channel volume as fraction of primary fracture volume.

priate constants results in:

$$S_2 = 1.92K\ (\phi th)^{1/3} \quad . \quad . \quad . \quad . \quad . \quad \text{Eq. 6}$$

The above equation appears in Fig. 2 in non graphic form. However, in using the figure, t computed value of S_2 must be multiplied by $\phi^{1/3}$ t correct for the porosity of the frac sand originally in place.

Secondary Fracture Zone Permeability

Permeability of the secondary fracture can be calculated on the basis of the follow three quantities:

- Permeability at the boundary nearest the detonation is assumed to be equivalent to the permeability, K_p, of the pulverized/ rubblized zone.
- Permeability at the far boundary will be equal to that of the unfractured formation as measured by core analysis.
- Change with distance will be governed by the exponential decrease as implied by Eq. 1.

Algebraic manipulation of the above three sumptions leads to:

$$K_S = \frac{0.25\ K_p}{\ln\left(\frac{0.25K_p}{K_F}\right)} \quad . \quad . \quad . \quad . \quad . \quad \text{Eq. 7}$$

The permeability of the rubblized zone, K be read from Fig. 3.

How to Use Model

Table 1 contains the pertinent data necessary order to use the T/F model in predicting the sults from an explosive stimulation job.

Table 1.

A. Well
  - 40-acre spacing (R_e = 660 ft)
  - 3800 psi bottomhole compaction pre sure
  - 4½-in. — 11.6 lb/ft casing
  - 50 ft pay zone (h)

B. Formation
  - 12% porosity
  - 1.0 md permeability (K_f)

C. Existing Fracture Geometry
  - Length, 400 ft each side of bore (L)
  - 0.25-in. width (t)

D. Current Production
  - 10 b/d
  - 50 Mcfd

Procedures

1. Calculate the maximum (L/R_e).

$(L) = 400/600 = 0.606$
(R_e) max

2. Width of rubblized zone.
   $S_p = 1.104 \ln (1095t) = 6.24$ in.
3. Width of secondary fracture zone.
   $S_2 = 1.92\ K\ (\phi th)^{1/3}$
   if $K = 60$ (sandstone) and $\phi = 0.30$
   $S_2 = 178.6$ in.
4. Conductivity factor for rubblized zone from Fig. 3 for 3800 psig.
   $K_p = 5600$ md
   then
   $$F_p = \frac{K_p}{K_F}(2.5\ S_p - t) = 8.89 \times 10^4$$
5. Conductivity factor — secondary fracture.
   $$F_s = \frac{0.5\ K_p\ S_2}{\ln\left(\frac{0.25\ K_p}{K_f}\right)} = 6.91 \times 10^4$$
6. Combined effective conductivity.
   $$\frac{(WK)_p}{K_f} = F_p + F_s = 15.8 \times 10^4$$
7. Calculate improvement ratio.
   Fig. 4 is the McGuire-Sikora (14) correlation for vertical fractures for,
   $$\frac{(WK)_p}{K_f} = \sqrt{\frac{40}{S}} = 15.8 \times 10^4.$$
   Read off values of $\frac{M(J)}{(JO)}$ for the desired penetration ratios, $\frac{(L)}{(R_e)}$. In this example, we chose $\frac{L}{R_e} = 0.1, 0.2, 0.3$ and 0.4. The correction factor "M" can be read off Fig. 5.

   The resulting calculations give:

L/R_e	J/J_o
0.1	3.22
0.2	4.68
0.3	5.97
0.4	7.44

8. Calculate volume of explosive slurry required for:

L/R_e	0.1	0.2	0.3	0.4
L	66	132	198	264
(L/L_{max})	0.165	0.330	0.495	0.660
V_2/V_o	0.208	0.176	0.147	0.120
(from Fig. 6)				

T/F slurry gal

Primary (Fig. 7)	310	620	930	1240
Secondary	64	109	137	149
Casing	33	33	33	33
Total gal @ 10.8 lb/gal	407	762	1100	1423
Total lb	4386	8200	1183	15305

T/F costs

Slurry	\$6590	\$12300	\$17765	\$2301
Service	550	550	550	55
Total T/F charges	\$7140	\$12850	\$18315	\$2356

9. Calculate stimulation response.

Estimated stimulation response and benefi

for L/R_e	0.1	0.2	0.3	0.4
J/J_o	3.22	4.68	5.97	7.4

Incremental production increase

Oil (b/d)	22.2	36.8	49.7	64.
Gas (Mcfd)	111.0	184.0	298.0	322.0

Increased revenue*

\$/day	\$ 77.60	\$128.80	\$174.00	\$225.00
\$/year	\$28,400	\$47,000	\$63,500	\$82,100

Payout on T/F Charges

(days)	99	104	109	107

*Based on \$2.50/bbl of oil and 20¢ Mcf of gas.

T/F Explosive Stimulation Model

Nomenclature

d_p = Average formation particle grain size.
F_p = Conductivity factor for primary rubblized zo
F_s = Conductivity factor for secondary fractu zone.
h = Vertical height of pay zone, ft.
J/J_o = Production improvement ratio. $\frac{\text{production after stimulation}}{\text{production before stimulation}}$
K = Rock constant = 60 for sandstone (Dysart's equation). = 84 for limestone.
K_f = Permeability of formation, mds.
L = Length of primary fracture from well bore,
M = Correction for well bore diam in improveme ratio calculation (see Fig. 5).
P_c = Compaction pressure, psi.
P_{BD} = Formation breakdown pressure, psi.
R_e = Drainage radius of well, ft.
R_w = Well bore radius, ft.
S_p = Length of rubblized zone, in.
S_2 = Length of secondary fracture zone, in.
t = Primary fracture width, in.
TD = Total depth of well, ft.
V_o = Volume of primary fracture system, cu ft (be fore explosive stimulation).
V_2 = Volume of secondary fracture system, cu (before explosive stimulation).
W_s = Weight of proppant sand, lb. used in origi hydrofrac treatment.
W_e = Weight of explosive slurry, lb.
(W_pK_p) = Effective permeability of explosively stimula zone.
$\frac{(W_pK_p)}{(K_f)}$ = Effective conductivity factor (to use with F 4).
ϕ_s = Porosity of proppant sand at given compact pressure, (expressed as a fraction).
P_s = Crystal density of sand, lb/ft.^{3}
P_e = Density of explosive slurry, lb/ft.^{3}

References

1 Dysart, G. R. et al: Blast Fracturing, presented at spring meeting of the American Petroleum Instit Mid-Continent District, Hot Springs, Ark., April 1969.

1976 v.17 N/10

HYDROMETALLURGICAL PROCESSING OF PYRRHOTITE-BEARING COPPER-NICKEL MATERIAL

UDC 669.243+669.33

A. B. Voronov, A. S. Ladygo, and V. N. Fedorov

The complexity of the mineralogical composition of Noril'sk copper-nickel ores and the similarity in the sulfide mineral physical properties limit the possibilities of separating them by flotation. The concentration scheme for these ores provides for the production of copper, nickel, pyrrhotite, and magnetite concentrates, but the level of selection will be low. Thus the pyrrhotite concentrate will contain 1.8-2.4% Ni and the nickel concentrate will contain up to 45% pyrrhotite.

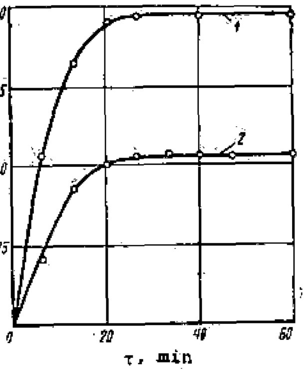


Fig. 1. Relationship of degree of pyrrhotite decomposition η to leaching time: 1 - with addition of NaCl (1% of weight of solids); 2 - without addition.

Processing the pyrrhotite material by pyrometallurgical methods is inefficient [1], because it entails high consumption of silica flux, heavy losses of cobalt, and difficulties in the extraction of sulfur into a commercial product.

A scheme for oxidizing leaching of pyrrhotite concentrates in autoclaves was developed in 1969-1970 and tested on a pilot-plant scale in 1971-1974 [2].

The difficulty of the assignment and the lack of time for a wide-ranging scientific investigation made it impossible to solve all the problems involved in efficient processing of the material. As a result the scheme in [2], developed for the first phase of the Nadezhda Metallurgical Plant of the Noril'sk Combine, proved to have some serious disadvantages.

1. Leaching time was considerable (~5 hr), due to slow oxidation of monoclinic pyrrhotite.
2. The capacity of the equipment was low, because there were contradictory operations in the scheme: boiling down-pulping, and bulk dissolution-precipitation of non-ferrous metals.
3. Reagent consumption was high: 2 tons of sponge iron per ton of nickel (in the solution from leaching) and 0.1 tons of sodium sulfide per ton of commercial sulfur.
4. The end-product nickel content was relatively low (10-12%).
5. The quality of the final sulfide concentrate and the process figures were closely dependent upon the composition of the initial material (its monoclinic pyrrhotite and gangue content).
6. There were unavoidable losses of valuable constituents, especially cobalt (up to 40%) and a proportion of the platinum group metals, in the subsequent pyrometallurgical processing of the sulfide concentrate.

The autoclave leaching process can be intensified by increasing the partial pressure of oxygen, improving mass transfer conditions for the reacting substances, and raising the temperature.

Maintaining the first two conditions on an industrial scale entails increases in capital and running expenditure. Thus, according to calculations by the Chemical Machine Building Research Institute, 300-400 kW of power will be required to reach a sulfide number K_s = 3-4 in an industrial autoclave with an effective chamber volume of 20 m^3.

Raising the leaching temperature is more effective, but this cannot be done without using special methods because the elementary sulfur which is formed in the process will melt, occluding the sulfides, and will prevent the access of oxygen to the reaction zone (Fig. 1, curve 2). A method [3] was therefore developed and tested for oxidizing autoclave leaching of sulfide materials at temperatures in excess of the melting point of sulfur, with prior addition of halogen-bearing compounds to the pulp.

All the halogen compounds tested (NaCl, NaBr, NaI, KI, HCl) have the same beneficial effect upon this process and permit the practically complete decomposition of all the pyrrhotite in 45-60 min (Fig. 1, curve 1) and passage into the liquid phase of 96-98% Ni, 92-95% Co, 70-80% Cu (Fig. 2), and of 65-70% S into elementary sulfur.

The optimum characteristics of exidizing autoclave leaching for nickel-pyrrhotite concentrates were worked out on a laboratory scale:

Temperature, °C	150-160
Oxygen partial pressure, gauge atmospheres	10-12
Solid-to-liquid ratio	1 : 1
NaCl consumption, % of weight of solids	0.5-1%

Pilot-plant tests in an autoclave of 1.75 m^3 capacity in a continuous routine entirely confirmed the results of the laboratory investigations; leaching time under these conditions was 2.5-3 hr.

An improved hydrometallurgical scheme for processing nickel material (pyrrhotite and pentlandite concentrates) producing rich selective non-ferrous products (Fig. 3) has been proposed, based upon the high-temperature autoclave leaching process which has been developed. The distribution of valuable constituents among these products is shown in the Table.

The new technology provides for the following operations. Oxidizing autoclave leaching of pyrrhotite concentrate at 110° C with an oxygen partial pressure of 10 gauge atmospheres is designed to obtain the maximum possible oxidation of hexagonal pyrrhotite and the minimum passage of nickel into solution (20%).

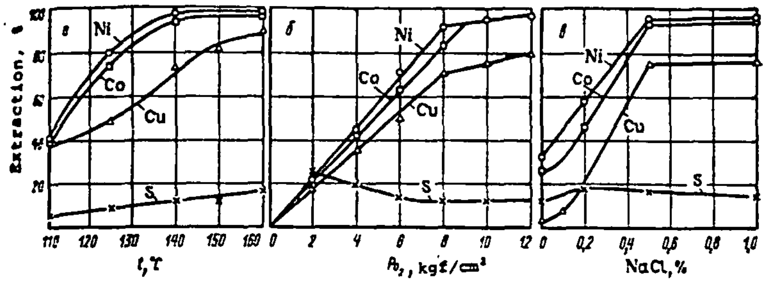


Fig. 2. Extraction of metals and sulfur into solution according to temperature (a), oxygen partial pressure (b), and NaCl consumption (c).

The leached pulp is subjected to sulfur-sulfide flotation to separate the sulfides undecomposed by leaching and the elementary sulfur formed from the hydrated iron oxides. The yield of sulfur-sulfide concentrate is not more than 50%.

The non-ferrous metals are extracted from the flotation tailings liquid phase by sorption, followed by sulfuric acid regeneration and the production of a concentrated eluate (up to 40 g/liter Ni).[1] The pulp is discharged to the tailings reservoir after neutralization and thickening.

The sulfur-sulfide concentrate, together with the pentlandite concentrate, is subjected to high-temperature leaching at a pressure of 10 gauge atmospheres at 150° C, with addition of sodium chloride to the pulp at the rate of 0.5% of initial concentrate weight. In 3 hr, not less than 95% Ni, 70% Cu, and 92% Co is extracted into the solution. The liquid phase iron content does not exceed 8 g/liter.

Sulfur granules are formed in the autoclave, because the process temperature is above the melting point of sulfur; these granules collect non-ferrous and platinum metals related to relatively insoluble natural compounds.

Distribution of Valuable Constituents Among the Principal Products

Products	Yield, %	Content, %, g/l						Extraction, %					
		Ni	Cu	Co	Fe	S_{tot}	S_{el}	Ni	Cu	Co	Fe	S_{tot}	S_{el}
Pyrrhotite concentrate......	50.0	2.80	1.20	0.17	51.00	30.0	—	23.73	21.05	44.95	52.04	47.62	—
Pentlandite concentrate...	50.0	9.00	4.50	0.20	47.00	33.00	—	76.27	78.95	54.05	47.96	52.38	—
Strong solution	—	45.0	17.0	1.80	1.50	28.00	—	78.37	68.97	77.09	0.83	14.16	—
Flotation concentrate after fluidizing....	9.19	10.0	6.37	0.26	35.0	39.0	2.5	14.10	20.53	12.76	6.56	11.40	0.73
Waste tailings.	92.0	0.32	0.22	0.016	49.2	2.0	0.5	5.0	7.0	8.0	92.38	5.6	1.4
Cu concentrate.	3.97	3.76	52.0	0.10	13.0	30.0	2.0	2.53	72.47	2.15	1.05	3.78	0.06
Cobalt concentrate.........	0.324	3.0	—	44.0	1.5	—	—	0.16	—	77.09	0.01	—	—
Nickel solution	—	45.0	0.05	0.01	0.05	26.0	—	78.21	—	—	—	13.22	—
Elemental S....	20.79	—	—	—	—	—	100	—	—	—	—	—	66.0

The granules, which contain 85-95% S, are separated out and washed in a classifier and sent for melting out of the sulfur.

After classification, the pulp is sent for countercurrent decantation to separate the solution from the iron residue. It is recommended that this operation should be carried out in 4 stages in radial thickeners; in these circumstances non-ferrous metal extraction into the strong solution is 85-90%. The upper discharge from countercurrent decantation is combined with the sorption regenerate and processed to obtain high-grade selective products containing copper, cobalt, and nickel.

It is suggested that copper should be precipitated with sulfur dioxide and sulfur; tailings from the autoclave extraction of sulfur from the sulfur granules may be used as the sulfur-bearing product. The elementary sulfur content of this product varies from 10 to 40%, the remainder being copper and nickel sulfides. It is important with the sulfur in the tailings is activated during melting out of the sulfur

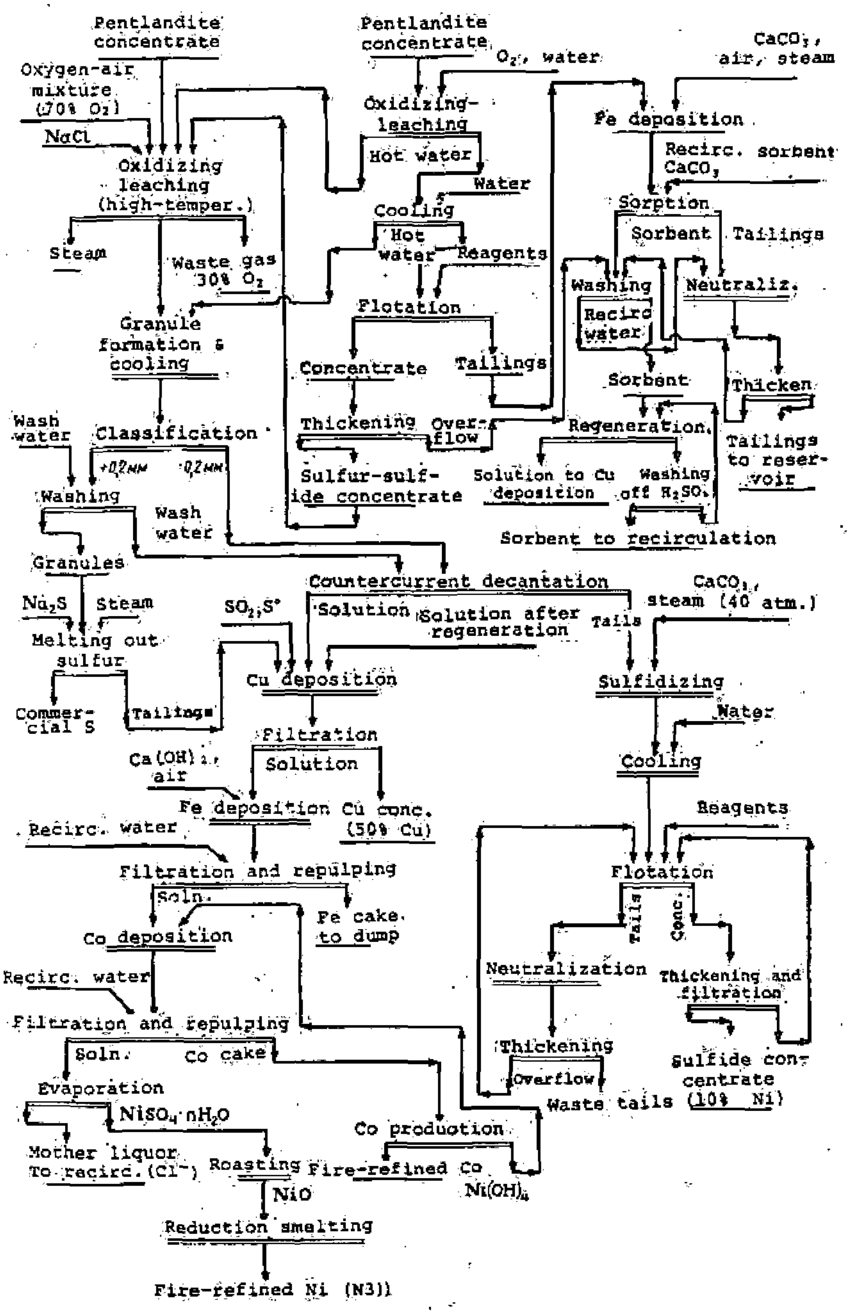


Fig. 3. Proposed improved scheme for hydrometallurgical processing of nickel material at the Noril'sk Combine.

with sodium sulfide. Copper extraction from the solution is practically 100%, and the copper content of the copper cake is 45-50% (according to the quality of the tailings).

Cobalt can be precipitated with coarse nickel hydrates; it is suggested that these should be obtained from nickel sulfate solutions by precipitation with a mixture of hypochlorite and soda. Nickel in the necessary amounts will come into the shop with the cobalt cake.

It is proposed that the nickel solution should be proceeeded to N3 grade-refined nickel by evaporation, crystallization, roasting, and reduction smelting.

The lower discharge from the countercurrent decantation thickener should be sent for sulfidizing by S. I. Sobol's method [4] in a weakly alkaline medium at 230° C for final extraction of the valuable constituents. The non-ferrous metals present in the pulp liquid phase hydrolyze in the alkaline medium to form the corresponding hydroxides and are then sulfidized. Limestone is recommended as the neutralizing reagent, and the sulfidizer is elementary sulfur which has not been incorporated into the granules. The sulfidized pulp is subjected to flotation separation to produce a 10% (nickel) sulfide concentrate and waste tailings.

Sulfidizing [5] may be used both in the proposed scheme and to replace precipitation of non-ferrous metals with sponge iron as adopted in the design for the first phase of the Nadezhda Plant.

The autoclave-hydrometallurgical processing scheme which has been developed for nickel-pyrrhotite concentrates is certainly not the final solution, especially as regards the processing of liquors. However, the proposed technology provides a solution to the basic problem: selection is assured in the separation of non-ferrous metals and iron, with fairly high extraction of valuable constituents.

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The Editorial Board notes the value and originality of the research by the authors of this paper, in that the subject is a vital technical problem for the national economy.

The Board anticipates replies from readers of the Journal to the points raised in this paper.

United States Patent [19] [11] **4,214,901**

Michal et al. [45] **Jul. 29, 1980**

[54] **HYDROMETALLURGICAL REFINING OF NICKELIFEROUS SULFIDES**

[75] Inventors: Eugene J. Michal, Golden; Simon O. Fekete, Arvada, both of Colo.; H. Jan Roorda, Ryswyk, Netherlands

[73] Assignee: Amax Inc., Greenwich, Conn.

[21] Appl. No.: 12,774

[22] Filed: Feb. 16, 1979

[51] Int. Cl.^{2} C22B 23/02; C22B 23/04; C22B 15/00

[52] U.S. Cl. .... 75/119; 75/82; 75/101 R; 75/101 BE; 75/117; 75/121; 423/139; 423/148; 423/153

[58] Field of Search .... 75/119, 117, 101 R, 75/101 BE, 82; 423/139, 148, 153

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Primary Examiner—G. Ozaki
Attorney, Agent, or Firm—Michael A. Ciomek

[57] **ABSTRACT**

Nickeliferous sulfidic materials containing at least one other metal selected from the group consisting of cobalt, copper and iron are leached with an at least 3 N hydrochloric acid solution to produce a pregnant nickel chloride solution. The pregnant nickel chloride solution is treated with a liquid organic extractant to extract the other metals. The nickel chloride raffinate is concentrated with respect to nickel chloride, and the concentrated nickel chloride solution is heated to at least about 750° C. to hydrolyze the nickel chloride to a refined nickel oxide product and a hydrogen chloride-containing gaseous effluent which is recycled to the concentration step and then through water to regenerate the leaching solution.

36 Claims, 4 Drawing Figures

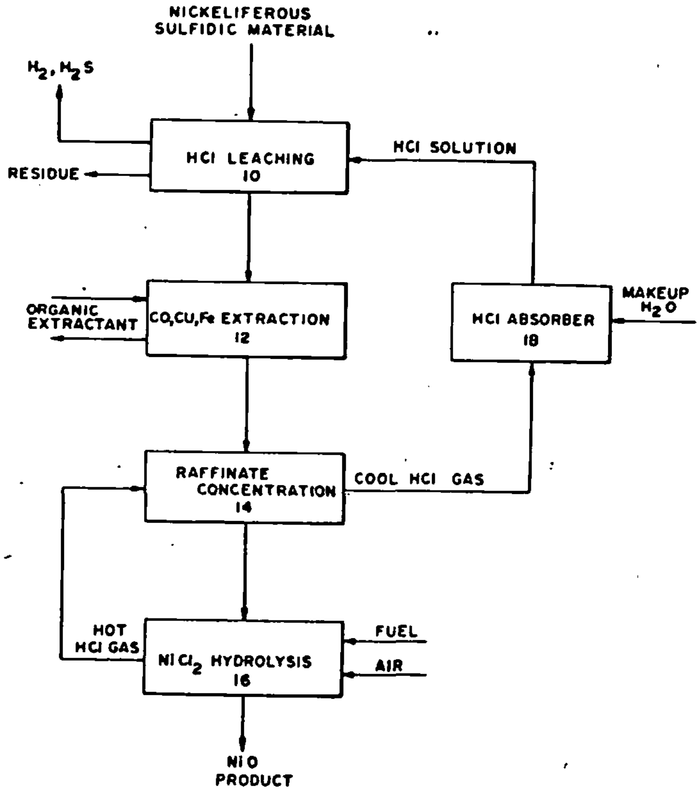
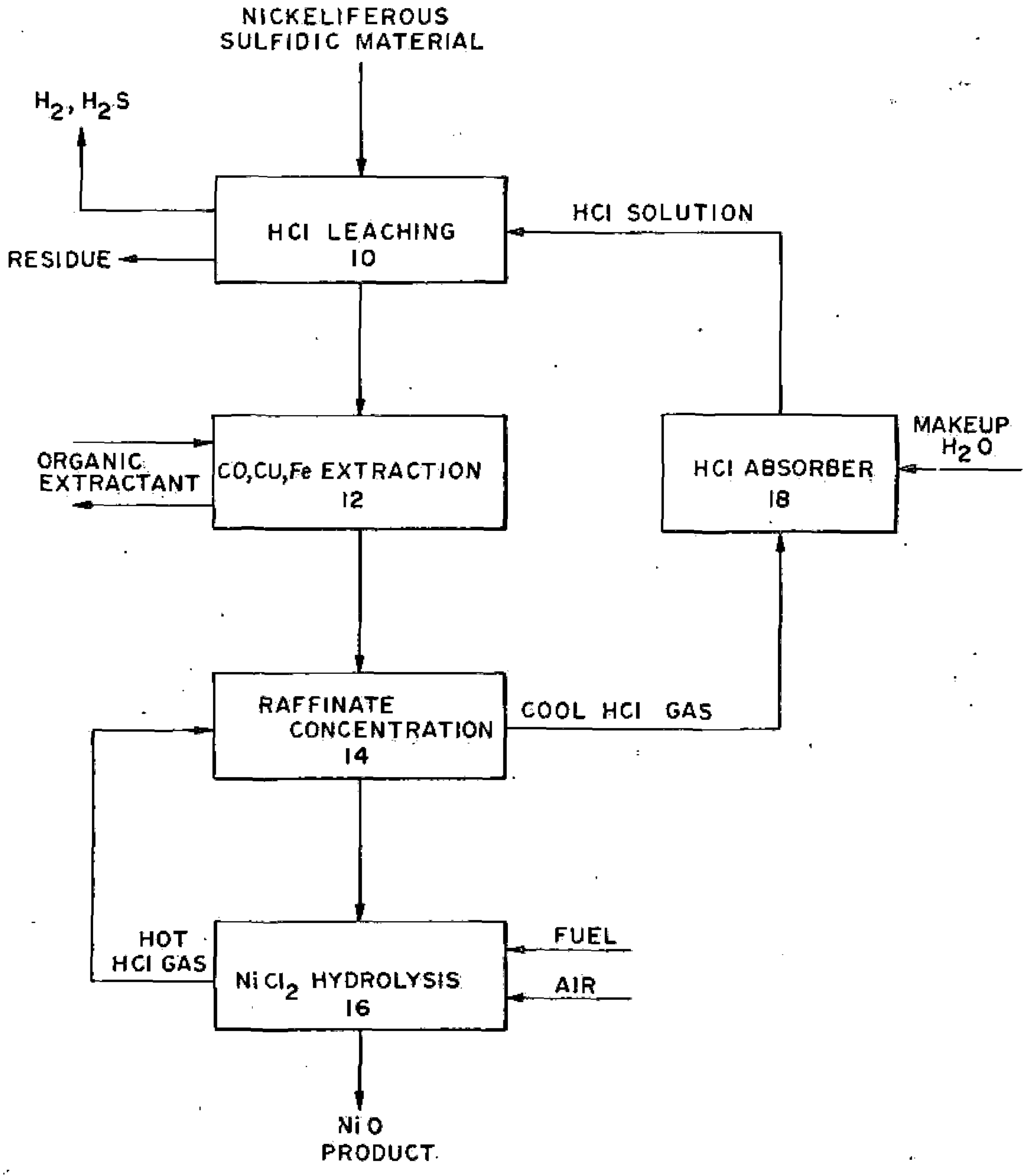


FIG. 1


NICKELIFEROUS SULFIDIC MATERIAL
H2, H2S
HCl LEACHING 10
RESIDUE
HCl SOLUTION
ORGANIC EXTRACTANT
CO,CU,Fe EXTRACTION 12
HCl ABSORBER 18
MAKEUP H2O
RAFFINATE CONCENTRATION 14
COOL HCl GAS
HOT HCl GAS
NiCl2 HYDROLYSIS 16
FUEL
AIR
NiO PRODUCT

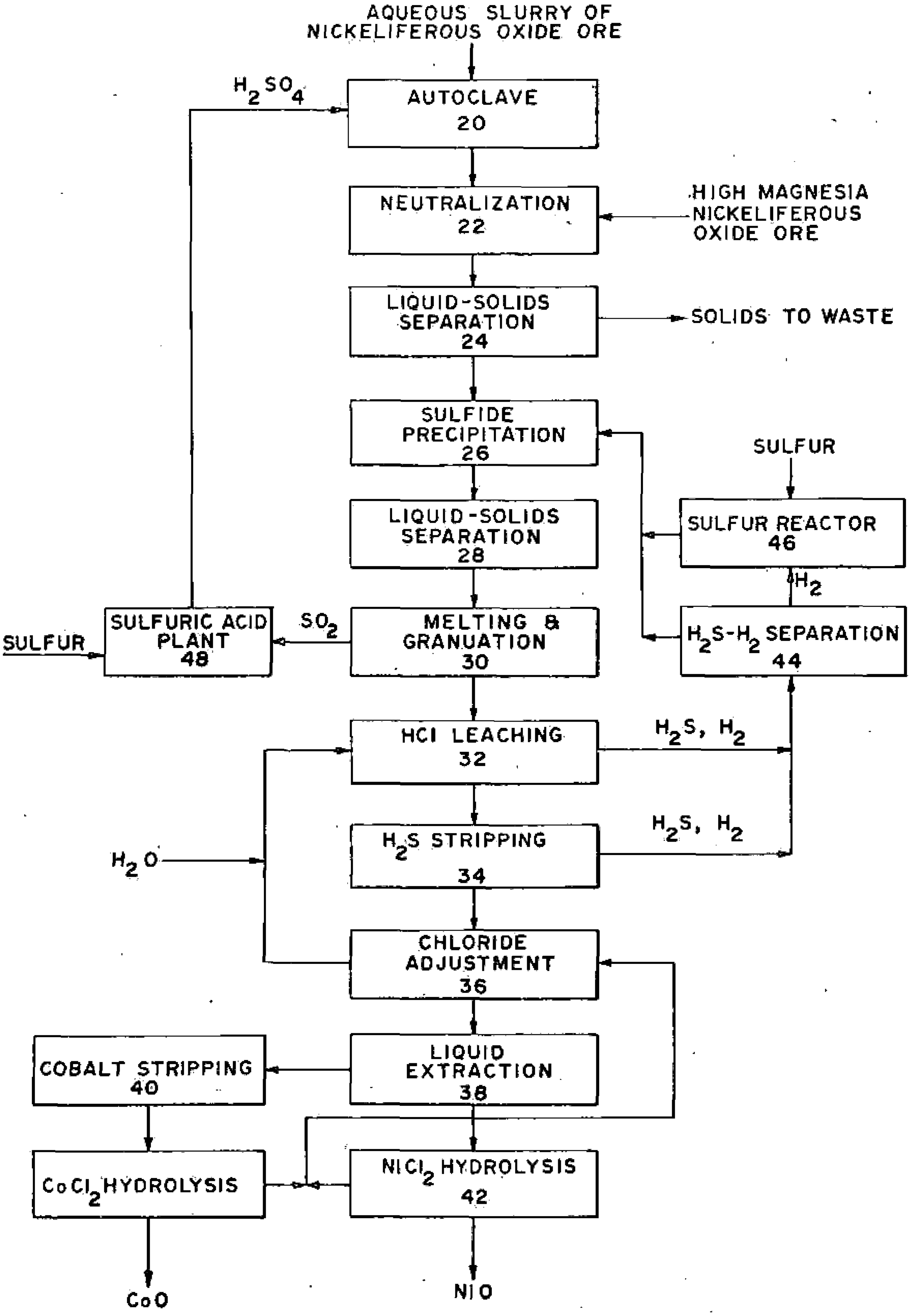

AQUEOUS SLURRY OF NICKELIFEROUS OXIDE ORE
H_2SO_4
AUTOCLAVE 20
NEUTRALIZATION 22
HIGH MAGNESIA NICKELIFEROUS OXIDE ORE
LIQUID-SOLIDS SEPARATION 24
SOLIDS TO WASTE
SULFIDE PRECIPITATION 26
SULFUR
LIQUID-SOLIDS SEPARATION 28
SULFUR REACTOR 46
H_2
SULFUR
SULFURIC ACID PLANT 48
SO_2
MELTING & GRANUATION 30
H_2S-H_2 SEPARATION 44
HCl LEACHING 32
H_2S, H_2
H_2S STRIPPING 34
H_2S, H_2
H_2O
CHLORIDE ADJUSTMENT 36
COBALT STRIPPING 40
LIQUID EXTRACTION 38
$CoCl_2$ HYDROLYSIS
$NiCl_2$ HYDROLYSIS 42
CoO
NiO

FIG. 2

FIG. 3

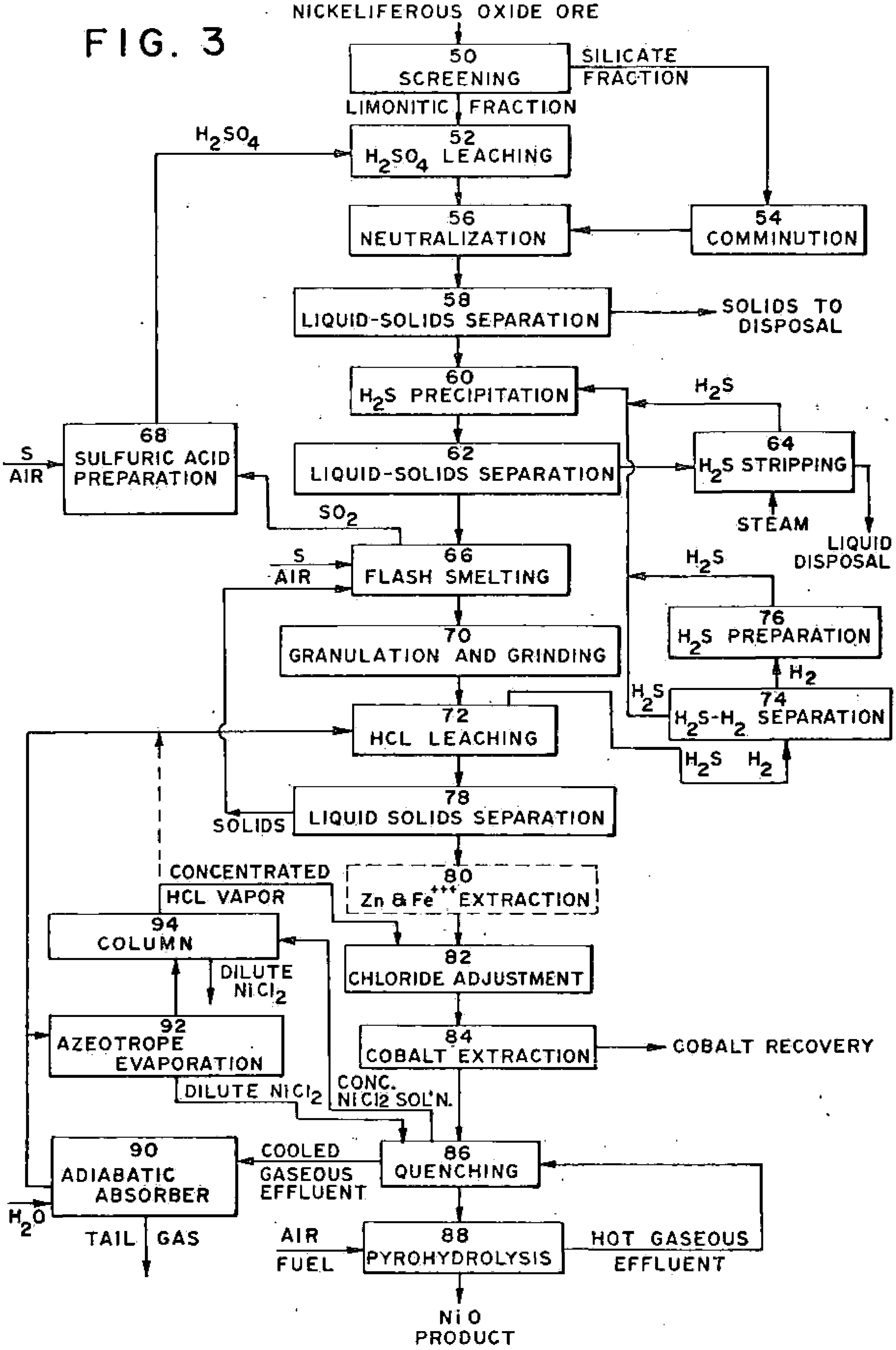
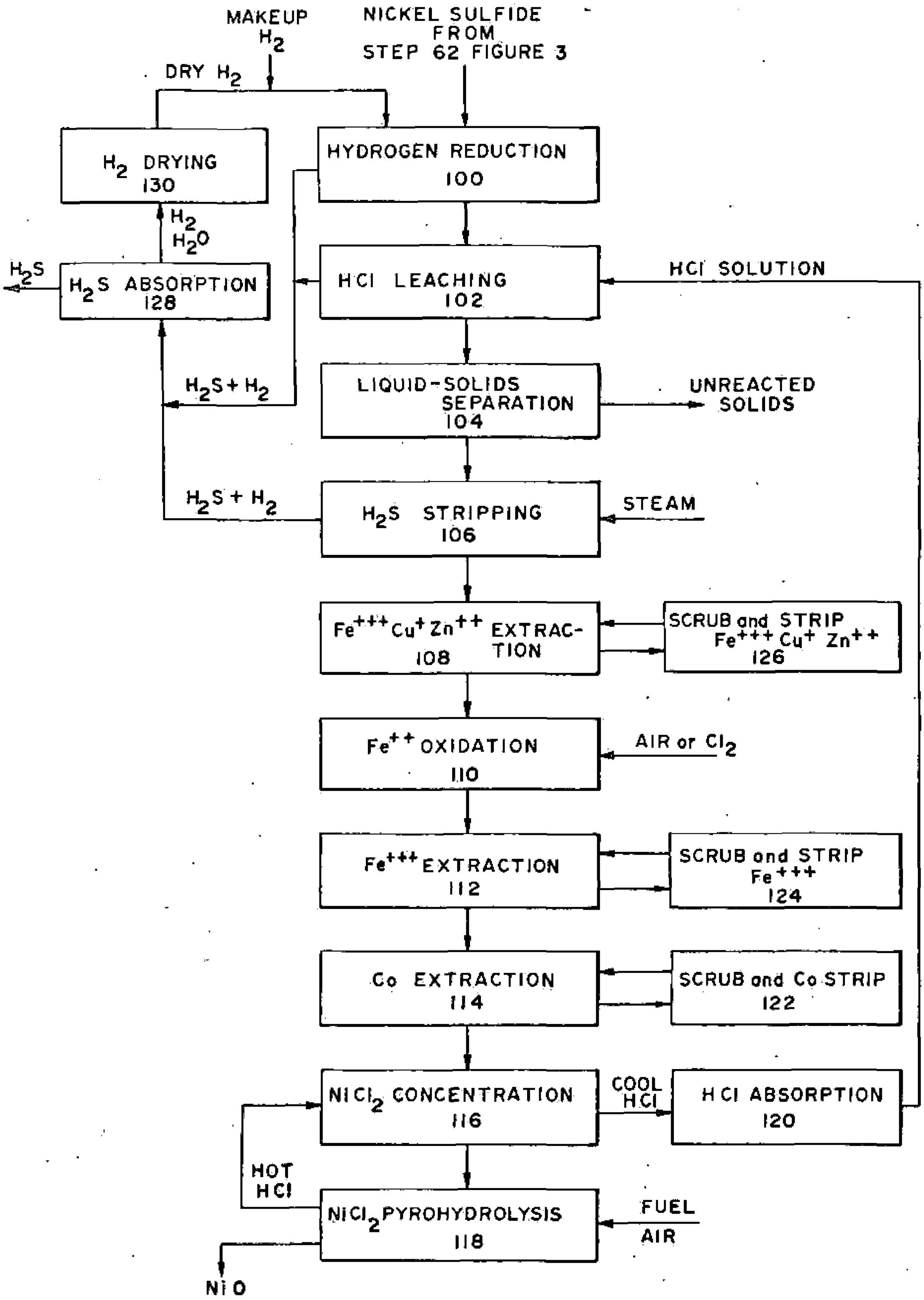

NICKELIFEROUS OXIDE ORE
50 SCREENING
SILICATE FRACTION
LIMONITIC FRACTION
H_2SO_4
52 H_2SO_4 LEACHING
56 NEUTRALIZATION
54 COMMINUTION
58 LIQUID-SOLIDS SEPARATION
SOLIDS TO DISPOSAL
60 H_2S PRECIPITATION
H_2S
68 SULFURIC ACID PREPARATION
S
AIR
62 LIQUID-SOLIDS SEPARATION
64 H_2S STRIPPING
STEAM
LIQUID DISPOSAL
SO_2
S
AIR
66 FLASH SMELTING
H_2S
76 H_2S PREPARATION
H_2
70 GRANULATION AND GRINDING
H_2S
74 H_2S-H_2 SEPARATION
72 HCL LEACHING
H_2S H_2
78 LIQUID SOLIDS SEPARATION
SOLIDS
CONCENTRATED HCL VAPOR
80 Zn & Fe^{+++} EXTRACTION
94 COLUMN
82 CHLORIDE ADJUSTMENT
DILUTE $NiCl_2$
92 AZEOTROPE EVAPORATION
84 COBALT EXTRACTION
COBALT RECOVERY
DILUTE $NiCl_2$
CONC. $NiCl_2$ SOL'N.
90 ADIABATIC ABSORBER
COOLED GASEOUS EFFLUENT
86 QUENCHING
H_2O
TAIL GAS
AIR
FUEL
88 PYROHYDROLYSIS
HOT GASEOUS EFFLUENT
NiO PRODUCT

FIG. 4


MAKEUP H_2
NICKEL SULFIDE FROM STEP 62 FIGURE 3
DRY H_2
H_2 DRYING 130
HYDROGEN REDUCTION 100
H_2
H_2O
H_2S
H_2S ABSORPTION 128
HCl LEACHING 102
HCl SOLUTION
H_2S+H_2
LIQUID-SOLIDS SEPARATION 104
UNREACTED SOLIDS
H_2S+H_2
H_2S STRIPPING 106
STEAM
$Fe^{+++}Cu^{+}Zn^{++}$ EXTRACTION 108
SCRUB and STRIP $Fe^{+++}Cu^{+}Zn^{++}$ 126
Fe^{++} OXIDATION 110
AIR or Cl_2
Fe^{+++} EXTRACTION 112
SCRUB and STRIP Fe^{+++} 124
Co EXTRACTION 114
SCRUB and Co STRIP 122
$NiCl_2$ CONCENTRATION 116
COOL HCl
HCl ABSORPTION 120
HOT HCl
$NiCl_2$ PYROHYDROLYSIS 118
FUEL
AIR
NiO

HYDROMETALLURGICAL REFINING OF NICKELIFEROUS SULFIDES

FIELD OF THE INVENTION

The present invention relates to hydrometallurgy and, more particularly, to the hydrometallurgical treatment of nickeliferous and cobaltiferous sulfides to recover separately the nickel and cobalt values.

BACKGROUND OF THE INVENTION

Wells in U.S. Pat. No. 940,292 discloses a process for treating nickel-copper mattes to recover nickel separately from the matte. This process involves leaching finely divided matte with hydrochloric acid solutions containing not more than about 25% hydrogen chloride to selectively dissolve the nickel values contained in the matte. Any copper dissolved is removed by fresh matte or by hydrogen sulfide which is a by-product of leaching. Nickel in a commercially acceptable form is recovered from the chloride solution by crystallization followed by hydrogen reduction or by precipitation of nickel ammine sulfate.

In U.S. Pat. No. 3,085,054 to Thornhill, there is disclosed a process for treating a nickel copper matte to recover metallic nickel and copper sulfide. The process involves the selective dissolution of the nickel values with a concentrated hydrochloric acid solution while leaving most of the copper values undissolved. After separation of the nickel chloride solution from the copper sulfide, the pregnant nickel chloride solution is oxidized with air or chlorine while adding further amounts of hydrogen chloride to oxidize ferrous iron to ferric iron and to form anionic chloride complexes of the various impurities. The thus treated pregnant solution is contacted with an anion exchange resin or a liquid extractant to extract those metals which form anionic chloride complexes. Additional amounts of hydrogen chloride are added to the purified nickel chloride solution to crystallize nickel chloride therefrom. Metallic nickel is recovered from the crystallized nickel chloride by electrolysis or by hydrogen reduction. When electrolysis is used to recover metallic nickel, gaseous chlorine is generated at the anode. In a separate operation, the gaseous chlorine is reacted with hydrogen and hydrogen sulfide generated during the dissolution of the matte to form hydrogen chloride which is recycled to both the dissolution and the nickel chloride crystallization steps. The liquor remaining after the nickel chloride crystallization step is treated to strip a portion of the hydrogen chloride therefrom and is then treated to remove lead. The lead-free liquor containing substantial amounts of nickel, e.g. more than 25 grams per liter, is heated and recycled to the matte leaching operation. When metallic nickel is recovered by hydrogen reduction the same general flowsheet is employed except that upon reduction of the nickel chloride with hydrogen a gaseous effluent containing hydrogen and hydrogen chloride is obtained which effluent must be treated to scrub the hydrogen chloride therefrom.

Although the process described by Thornhill is useful in producing a highly refined nickel product, there are certain inherent disadvantages. For example, as the process relies on the crystallization of nickel chloride for the ultimate recovery of nickel, it is necessary to recycle the mother liquor from which nickel chloride has been crystallized. Thus, substantial amounts of nickel are inventoried in the circulating mother liquor adding to the capital and operating costs. Another disadvantage of the process disclosed by Thornhill involves the recovery of metallic nickel. Whether metallic nickel is recovered by electrolysis or by hydrogen reduction, recovery of hydrogen chloride is complicated either by the fact that electrolysis generates gaseous chlorine which must be converted to hydrogen chloride, or in the reduction of nickel chloride with hydrogen both the hydrogen and hydrogen chloride must be recovered which entails not only an absorbing process for recovering hydrogen chloride but also a process for drying the hydrogen stream from which the hydrogen chloride has been absorbed. The conversion of gaseous chlorine to hydrogen chloride and the drying of the hydrogen stream from which hydrogen chloride has been removed entail additional capital and operating costs. Another disadvantage is the high cost of hydrogen.

Van Weert in U.S. Pat. No. 3,642,441 describes a process for hydrolyzing chlorides in fluidized beds and specifically refers to nickel chloride derived from the Thornhill process described above. Van Weert describes the hydrolysis of hydrated nickel chloride crystals, although he states that solutions can be similarly hydrolyzed. Although van Weert suggests his process may be capable of hydrolyzing metal chloride solutions, there is no suggestion that hydrochloric acid solution approaching its azeotropic composition and containing metal chlorides could be hydrolyzed by his process. Moreover, the van Weert process does not provide 100% hydrolysis of the metal chlorides and is silent on the recovery of the unconverted metal chlorides. Hydrolysis of nickel chloride crystals, besides presenting materials-handling problems, also presents control problems because the combustion of fuel must be carefully regulated to insure substantially complete combustion without generating an atmosphere containing such excesses of free oxygen which oxidize generated hydrogen chloride to gaseous chlorine which must be recovered with difficulty and with added cost. The presence of gaseous chlorine also creates severe corrosion problems.

SUMMARY OF THE INVENTION

The present invention relates generally to a process for recovering nickel from a sulfidic material containing at least one other metal selected from the group consisting of cobalt, copper and iron. The sulfidic material is leached with an at least 3 normal (N) hydrochloric acid solution to provide a pregnant nickel chloride solution. The pregnant nickel chloride solution is contacted with a liquid organic extractant to extract the other metal. Nickel chloride raffinate is first concentrated and is then fed to a high temperature hydrolysis unit where nickel chloride is oxidized to a substantially pure nickel oxide product and hydrogen chloride. The hot gaseous effluent from the hydrolysis unit is first passed through the nickel chloride raffinate to heat the solution and to evaporate water therefrom. After passing through the nickel chloride solution, the gaseous effluent is passed through a water absorber to generate hydrochloric acid for leaching fresh sulfidic material.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flowsheet of the process in accordance with the present invention;

FIG. 2 is an overall flowsheet depicting the use of the present invention in conjunction with an acid leaching process for recovering nickel and cobalt from oxidic ores; and

FIG. 3 discloses an advantageous flowsheet depicting the use of the process in accordance with the present invention; and

FIG. 4 is a particularly advantageous flowsheet incorporating the process in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves a novel combination of steps for treating nickeliferous sulfidic materials containing at least one other metal selected from the group consisting of cobalt, copper and iron for the separate recovery of nickel and the other metal. The novel combination of steps includes leaching the sulfidic material with hydrochloric acid to form a pregnant nickel chloride solution, extracting the other metal from the nickel chloride solution with at least one liquid organic extractant, concentrating the raffinate from the liquid organic extraction step, and feeding the concentrated nickel chloride raffinate to a pyrohydrolysis step to oxidize the nickel chloride raffinate to a refined nickel oxide product and a hot gaseous effluent containing hydrogen chloride which is passed through the nickel chloride raffinate to concentrate the nickel and to recover heat from the hot gaseous effluent and the cooled gaseous effluent is then passed through a water absorber to generate a hydrochloric acid solution for leaching fresh nickeliferous sulfidic material.

The process in accordance with the present invention is advantageously used to refine nickel sulfide precipitates produced by precipitating nickel and cobalt contained in pregnant leach solutions derived by leaching oxidic ores with sulfuric acid. The combination of sulfuric acid leaching and chloride refining provides numerous advantages. Sulfuric acid leaching at elevated temperatures and sulfide precipitation provides an initial separation of nickel and cobalt from the bulk of the iron that is invariably present in nickeliferous oxide ores. Chloride refining separates nickel and cobalt and provides gaseous streams at various stages for recycling throughout the overall process. The combination of chemical extraction and chemical refining steps provides a highly integrated process which minimizes the consumption of the major reagents while producing a highly refined nickel-containing product and a highly refined cobalt-containing product.

Referring to FIG. 1 there is depicted a flowsheet of the present process. Nickeliferous sulfidic material containing at least one other metal selected from the group consisting of cobalt, copper and iron is leached at stage **10** with hydrochloric acid to produce a pregnant nickel chloride solution which is treated for nickel recovery and a gaseous stream which is treated to recover hydrogen sulfide and any hydrogen generated during leaching. The pregnant solution is treated with an organic extractant in stage **12** to extract the other metal. The raffinate from stage **12** is concentrated at stage **14**. The concentrated raffinate is fed to a bed of nickel oxide in a fuel-fired reactor at stage **16** to hydrolyze the nickel chloride to a marketable nickel oxide and a hot gaseous effluent containing hydrogen chloride which is passed through the raffinate in stage **14** to concentrate the raffinate and then through water at stage **18** to absorb hydrogen chloride to regenerate the leaching solution.

The process in accordance with the present invention can be used to refine nickeliferous sulfidic materials from any source. Thus, nickel sulfide concentrates, nickel mattes, nickel-copper mattes, nickel sulfide precipitates and any other nickeliferous sulfidic metallurgical intermediates can be treated to recover separately nickel and cobalt or copper. However, the sulfur content of the nickeliferous sulfidic material is advantageously lower than that required to satisfy the stoichiometry of nickel monosulfide.

Most nickeliferous materials can be leached without any pretreatment. However, the rate and the extent of dissolution of nickel sulfide precipitates can be significantly improved by activation. Nickeliferous sulfide precipitates can be activated in an number of ways. The sulfide precipitates can be smelted and granulated to a particle size of at least about 100% minus 60 Tyler Screen Size (TSS) or granulated and then ground to a particle size of at least about 100% minus 60 mesh, TSS. Activation can also be accomplished by heating the sulfidic material in a hydrogen atmosphere to lower the sulfur content. Activation by hydrogen reduction is advantageously conducted at temperatures between about 250° C. and about 700° C. and most advantageously between about 300° C. and 600° C. in a hydrogen atmosphere with the off-gases being treated to separate the hydrogen and the hydrogen sulfide which are both recycled to the process. When activating the sulfidic material by smelting or hydrogen reduction only a portion of the sulfidic material need be so activated. The portion that is thermally activated is selected so that the overall sulfur content of the entire feed is less than that required to satisfy the sulfur stoichiometry of all the metals present in the feed. Other means of activating the sulfidic material include the addition of acid soluble metals, such as cobalt, copper, iron and preferably, nickel to the aqueous leach, or by heat treating mixtures of finely ground sulfidic materials and metals, preferably nickel to provide an excess of metal atoms (Me) over the stoichiometric residue.

The nickeliferous sulfidic material, whether activated or not, is leached with a hydrochloric acid solution having a hydrochloric acid concentration from at least about 3 normal (N), advantageously the acid concentration is between about 3 N and about 9 N. Hydrochloric acid concentrations of at least about 3 N insure commercially attractive rates of dissolution and extraction and minimize the volume of liquor that must be handled. Hydrochloric acid concentrations above the azeotrope (about 6 N) provide high rates of dissolution and extraction but present problems in materials handling and require special techniques for regenerating such highly concentrated solutions. Advantageously, hydrochloric acid concentrations between about 4 N and about 6 N are employed to provide acceptable rates of dissolution and extraction while minimizing the problems associated with acid concentrations above the azeotrope. Any loss in the rate of dissolution attributed to the use of azeotropic or lower acid concentrations is regained by the ability to use higher leaching temperatures without resort to the use of pressure vessels. Another advantage of using acid concentrations between about 4 N and about 6 N is that the pregnant solution can be more effectively treated for removal of certain impurities, such as zinc and ferric iron. Substantially all the nickel and cobalt in the matte are dissolved producing a pregnant solution and a gaseous effluent containing by-products of hydrogen and hydrogen sulfide.

Leaching is terminated before the free hydrogen chloride concentration of the leach liquor falls to below about 1 N, advantageously leaching is terminated at acid concentrations between about 1 N and about 3 N. Although leaching can be continued until more acid is consumed, at acid concentrations below about 1 N the rate of leaching slows down to commercially unattractive rates. The pregnant solution derived from leaching sulfide precipitates from laterite leach solutions usually contains between about 50 grams per liter (gpl) and about 300 gpl nickel, cobalt in amounts between about 1 gpl and about 50 gpl, small amounts of copper and having a free hydrochloric acid concentration between about 1 N and 3 N.

Hydrochloric acid leaching of the nickeliferous sulfide material can be conducted at ambient or elevated temperatures. However, it is preferred to leach at temperatures between about 50° C. and about 110° C. Although leaching can be conducted at ambient temperatures, lower rates of dissolution and lower nickel concentrations in the pregnant solution are encountered. Higher temperatures increase the rate of dissolution and the extent of the leaching reactions and nickel concentrations in the pregnant solutions but at temperatures in excess of the boiling temperature the incremental costs involved for autoclaves outweigh any benefits so gained. The process for leaching the nickeliferous sulfidic materials with hydrochloric acid is described in greater detail in U.S. Patent Application Ser. No. 12,781 filed on even date herewith in the name of Gustavo A. Meyer and entitled "Dissolution of Nickeliferous Sulfide Material" which is incorporated herein by reference.

Leaching is advantageously conducted in closed stirred vessels. Agitation insures good liquid-solid contact and thus increases the rate and extent of leaching. The leaching vessel is advantageously closed to avoid oxidation of the hydrogen sulfide evolved during the dissolution of the sulfidic material and to allow the recovery thereof for recycling.

When leaching nickel-copper mattes, leaching is conducted to maximize dissolution of nickel. Small amounts of copper will inevitably be dissolved. Most of the dissolved copper can be removed from the pregnant solution by treatment with fresh matte to cement the copper. Alternatively, the pregnant solution can be treated with hydrogen sulfide generated during the earlier leaching stages to precipitate copper sulfide.

After leaching is completed, the pregnant solution is passed through a filter or other liquid-solid separator to remove any undissolved solids. The undissolved solids, depending upon their nature, can be recycled for retreatment or sent to waste. The pregnant solution is then stripped of its hydrogen and/or hydrogen sulfide by passage through a stripping tower in which the pregnant solution is heated with steam to expel dissolved gases. Stripping hydrogen and hydrogen sulfide with steam is an advantageous feature of the present invention. Stripping with steam minimizes oxidation of the dissolved hydrogen and hydrogen sulfide thereby making possible their recovery in useful form. The stripped gases and the gases evolved during leaching are combined for purification and recycling, as described hereinafter.

After the stripping hydrogen and hydrogen sulfide from the pregnant nickel chloride solution the stripped solution can be treated with one or more liquid organic extractants to extract metals such as cobalt, copper, iron and zinc from the chloride solution. Advantageously, the pregnant nickel chloride solution is first contacted with tributylphosphate dissolved in an organic solvent to extract ferric iron, zinc and copper and the raffinate from this first extraction is then contacted with a water-insoluble amine dissolved in a water-immiscible organic solvent to extract cobalt. The pregnant nickel chloride solution will generally contain copper ions and ferrous and ferric iron in which case the pregnant solution is first contacted with a tributylphosphate solution to extract the copper, ferric iron and any zinc; and then the unextracted ferrous iron is oxidized to ferric iron by bubbling air or chlorine through the solution from which ferric iron is then extracted with a second tributylphosphate solution. Alternatively, as described hereinafter, the chloride concentration of the pregnant solution can be increased and the other metals can be extracted by various organic extractants. Cobalt, copper, iron, and zinc can be extracted from the pregnant solution by a variety of organic extractants. For example, cobalt chloride complexes can be extracted by higher alcohols, such as capryl alcohol, or by other suitable solvents. Complexed cobalt values can also be extracted from the pregnant solution with an organic extractant of water-insoluble amines, quarternary ammonium compounds, or organo-phosphorus compounds dissolved in a water-immiscible organic solvent.

Examples of suitable amines include x-heptalamines, x-dodecylamines, didodecylamine, tri-x-propylamine, tri-x-butylamines, tri(2-ethylhexyl) amine, triisooctylamine, tertiary amines which are derivatives of styrene oxide such as di(2-hydroxy-2-phenylethyl) ethylamine and tertiary amines which are polyglycolamines, such as tripropyleneglycolamine. The use of x hereinabove as in the term "x-heptyl-amines" is intended to refer to any structural isomers, as 1-n-heptylamine, 2-n-heptylamine, etc.

Two classes of quarternary ammonium compounds are found particularly advantageous for complexed metal extraction. These are Aliquat 336 reagent, hereinafter referred to as Aliquat chloride, a monomethyl quarternary ammonium chloride in which the alkyl chains each contain eight to ten carbon atoms, supplied by General Mills, Inc., and Arquad 2C reagent, hereinafter referred to as Arquad chloride, a dialkyl dimethyl ammonium in which the two alkyl groups each have a carbon chain length varying from eight to eighteen and averaging about twelve supplied by the Armour Industrial Chemical Company. However, other classes of water-insoluble quarternary ammonium compounds or their chlorides may be utilized.

When amines or quarternary ammonium compounds are used to extract cobalt or other metals, the amines or quarternary ammonium compounds are initially treated with hydrochloric acid to form the hydrogen chloride salts thereof. This acidification treatment has at least two benefits. Initial acidification minimizes loss of acid from the leach solution and the hydrogen chloride salts in the extractant promote the formation of the chloride complexes that are extracted by the amines or quarternary ammonium compounds.

The organo-phosphorus compounds that can be used are exemplified by alkyl-substituted phosphorus acids, alkyl substituted phosphates and alkyl-substituted phosphine oxides. Examples of generic groups include heptadecyl phosphoric acid, tributylphosphate and tri-n-octyl phosphine oxide.

The amines, quarternary ammonium compounds or organo-phosphorus compounds are advantageously dissolved in water-immiscible non-polar solvents. Suitable solvents include kerosene, naphtha, gasoline, xylene, methyl isobutyl ketone, water-insoluble alcohols and mixtures of aromatic hydrocarbon solvents. The concentration of the amines, quarternary ammonium compounds, or their chloride salts in the organic solvent can vary from about 5% to about 50%, by volume, and advantageously between about 10% and about 20%.

A particularly advantageous embodiment of the present invention is the use of tributylphosphate, heptadecyl phosphoric acid and tri-n-octyl phosphine oxide dissolved in a water-immiscible organic solvent to extract the metal values commonly associated with nickeliferous oxide ores. The use of tributylphosphate is particularly useful when the ore contains small but significant amounts of zinc, which is quite deleterious to the final nickel product when the nickel is used as an alloying constituent for stainless steels or high temperature alloys. The reasons for using an organic extractant containing tributylphosphate when zinc is present is that zinc forms highly stable complexes with most other organic extractants and is very difficult to strip therefrom. In fact, zinc forms such stable complexes with most other extractants that the extractants become so loaded with zinc that the extractant loses its capacity for extracting other metals and must ultimately be replaced with fresh extractant.

When treating nickel chloride solution containing zinc, it has been found advantageous to extract the zinc when the chloride concentration of the nickel solution is between about 5 N and 7 N (approximately the chloride concentration of the pregnant leach liquor) with an organic extractant containing between about 15% and about 70%, by weight, tributylphosphate dissolved in a water-immiscible organic solvent. Any ferric iron present in the aqueous phase will also be removed at this stage.

After removing zinc, copper and any ferric iron from the nickel chloride solution, the nickel chloride solution can then be treated for cobalt extraction. Cobalt can be extracted without significantly increasing the chloride concentration with one or more of the amines described hereinbefore. Cobalt can also be extracted from the nickel chloride solution, after chloride adjustment, with an organic extractant of between about 15% and about 70% tributylphosphate dissolved in a water-immiscible organic solvent. The chloride concentration of the nickel chloride solution can be adjusted by quenching the off-gases from the high temperature hydrolysis unit or by sparging the chloride solution with concentrated hydrogen chloride vapors produced as described hereinafter. A method of purifying the pregnant nickel chloride solution is described in greater detail in U.S. Patent Application, Ser. No. 12,782, filed on even date herewith in the name of Gustavo A. Meyer and entitled "Purification of Nickel Chloride Solutions", which is incorporated herein by reference.

Cobalt, copper, iron and zinc can all be extracted from the pregnant nickel chloride solution with tributylphosphate by increasing the chloride concentration of the pregnant solution and the concentration of tributylphosphate in the organic extractant. The chloride and nickel concentrations of the stripped pregnant solution can be increased by evaporating water therefrom and by passing hydrogen chloride therethrough. This operation can be accomplished by using the stripped pregnant solution to quench the gaseous effluent from the pyrohydrolysis unit. Alternatively, the chloride concentration of the stripped solution can be increased by passing concentrated hydrogen chloride therethrough. Sufficient water is evaporated from the stripped pregnant solution to increase the nickel content to between about 150 gpl to about 300 gpl while at the same time the chloride concentration is increased to between about 7 N and about 11 N.

Concentration of the chloride contents in the pregnant solution by using the pregnant solution to cool gaseous effluent from high temperature hydrolysis has numerous advantages. Use of the hot gaseous effluent from the high temperature hydrolysis unit recovers a substantial portion of the sensible heat thereby lowering the overall energy requirements. Another important advantage is that by increasing the chloride concentration in the stripped pregnant solution the efficiency of the organic extraction process in extracting metal values, such as cobalt, can be increased significantly. Although use of the nickel chloride solution to quench the gaseous effluent from the pyrohydrolysis step prior to purification has advantages, one disadvantage is that some nickel oxide may be suspended in the gaseous effluent and the suspended nickel oxide may interfere with the organic extraction processes. This problem can be avoided by using purified nickel chloride solution to quench the effluent from pyrohydrolysis and to generate a gas stream having high hydrogen chloride concentrations for use in the chloride adjustment step and for other purposes. Any suspended nickel oxide in the gaseous effluent becomes suspended in the purified nickel chloride solution which in turn is fed to the pyrohydrolysis unit where the suspended nickel oxide presents no problem.

As organic extraction processes are based on mass action principles, the higher concentrations of most metal values in the pregnant solution allow smaller quantities of organic extractants to remove the same quantity of metal values as contained in more dilute solutions. The combination of high nickel and chloride concentrations has the further advantage of providing high chloride concentrations, which promote the formation of chloride anionic complexes of cobalt and of other metal values such as iron and copper without resorting to unduly high hydrogen chloride concentrations which can have adverse effects on the stripping of the metal values in the organic extractant.

The chloride anionic complexes are removed from the pregnant solution with an organic extractant in one or more stages using one or more organic extractants. The organic extractant can be in the form of a water-insoluble ion exchange resin or in the form of a water-immiscible organic liquid that has a greater dissolving potential for the chloride anionic complexes or has dissolved therein an organic anion exchange constituent.

Extractant of the cobalt, copper, iron and zinc is achieved by employing countercurrent principles in a series of reactors in which nearly exhausted extractant contacts fresh pregnant solution. The loaded extractant is stripped of the complexed metals which regenerates the extractant for use in recovering additional amounts of the complexed metals. The raffinate, purified nickel chloride solution, is then sent to a hydrolysis unit to recover refined nickel oxide and hydrogen chloride.

Hydrolysis of the purified nickel chloride solution is conducted in a direct-fired reactor. Pyrohydrolysis can be conducted in any type reactor that provides good liquid-gas contact between the nickel chloride solution and the products of combustion. Thus, pyrohydrolysis of the nickel chloride solution can be effected in a suspension type furnace or in a fluid bed reactor. The fluidized bed consists substantially of nickel oxide heated to a temperature above about 750° C., advantageously between about 800° C. and about 950° C. The particulate nickel oxide is maintained in the fluidized state and at temperatures by introducing fuel, advantageously a liquid or gaseous hydrocarbon, and air directly into the fluidized bed. The ratio of fuel to air is such that the products of combustion are nonreducing to nickel oxide and nickel chloride and nonoxidizing to hydrogen chloride. When hydrolyzing nickel chloride solution within the foregoing temperature range, the oxidizing nature of the atmosphere within the fluidized bed can be controlled by adjusting the air to fuel ratio to provide substantially complete combustion of the fuel while maintaining the free oxygen content of the off-gas at less than about 2%, by volume, e.g. preferably less than about 1%. Nickel chlorideis fed to the fluidized bed where the nickel chloride reacts with water to form nickel oxide and hydrogen chloride. Refined nickel oxide is withdrawn from the bed at a molar rate substantially equivalent to the rate at which nickel chloride is introduced into the bed. The gaseous effluent is treated to recover hydrogen chloride and heat.

The gaseous effluent from the fluid bed is first passed through a cyclone separator to remove most of the suspended nickel oxide, which is returned to the fluid bed reactor, and a substantially solids-free gaseous effluent. The gaseous effluent is treated to recover its sensible heat and hydrogen chloride. The gaseous effluent can be passed through a quench tower which uses the stripped pregnant solution as the coolant and then through an adiabatic absorber to provide an azeotropic solution of hydrogen chloride, a portion of which can be recycled to the leaching step. From the foregoing, it is apparent that the chloride refining process is closed with respect to hydrogen chloride except for the chlorides that accompany the impurities during the stripping of the organic extractant. Even the chloride removed by the stripping operation can be recovered by hydrolyzing the stripped values, e.g. cobalt.

In another embodiment of the present invention, purified nickel chloride solution is employed to quench the gaseous effluent from the pyrohydrolysis to recover sensible heat from the gaseous effluent, to concentrate the nickel chloride solution and to recover any suspended nickel oxide. The embodiment is advantageously employed when the pregnant nickel chloride solution is purified by one or more treatments with tributylphosphate to extract copper, iron and zinc and by treatment with an amine or a quarternary ammonium compound to extract cobalt, beacuse this purification scheme does not require high chloride concentrations for effective extraction of cobalt, copper, iron and zinc.

When a series of tributylphosphate treatments are used to extract cobalt as well as all of the other metals, purified nickel chloride solution is used to quench the gaseous effluent from the pyrohydrolysis unit to produce a concentrated nickel chloride solution which is split into two portions. A portion of the concentrated nickel chloride solution is fed to the pyrohydrolysis unit. A second portion of the concentrated nickel chloride solution is fed to a tower to generate concentrated hydrogen chloride gases. The cooled gaseous effluent from the quench tower is sent to a adiabatic absorber to recover the residual hydrogen chloride vapors to produce a hydrochloric acid solution approaching the azeotropic composition. A portion of the azeotrope is fed to the leaching step to dissolve further amounts of nickel sulfide. Another portion of the azeotrope from the adiabatic absorber is fed to a heat exchanger to form an azeotropic vapor phase which is fed to the same tower to which the concentrated solution from the quench tower is fed. As the azeotropic vapor phase passes through the column the water content thereof is absorbed by the concentrated nickel chloride solution thereby producing a gas having a high hydrogen chloride concentration which can be utilized for adjusting the chloride concentration of the stripped pregnant solution to facilitate recovery of metal values by organic extraction. A portion of the gas phase having high hydrogen chloride concentrations can also be used to adjust the acid concentration of the leach liquor. The concentrated nickel chloride solution now diluted with water from the azeotropic gas is fed to the column and is recycled to the quench tower. In order to provide gas streams having sufficiently high hydrogen chloride concentrations for adjusting the chloride concentration of the stripped pregnant nickel chloride solution, the concentrated nickel chloride solution from the quench tower should have a nickel concentration between about 250 gpl and about 330 gpl nickel, advantageously between about 300 gpl and about 330 gpl nickel.

An advantageous embodiment of the present invention is the use of the process in conjunction with an acid leaching process for recovering nickel and cobalt from oxidic ores. Cobalt is present in most oxidic ores (even in sea nodules) in far higher quantities than in sulfidic ores so that the nickel to cobalt ratio is about 30:1 or less. These comparatively low nickel to cobalt ratios present problems in the separation of the two metals. Pyrometallurgical and electrolytic processes generally used in commercial practice are economical in separating cobalt from nickel but as the nickel to cobalt ratio approaches 10:1 the costs of cobalt separation per unit of nickel produced become excessive. However, the process in accordance with the present invention provides an economically attractive alternative for treating intermediate products of these ores to recover separately the nickel and cobalt values.

Referring now to FIG. 2 there is depicted a flowsheet illustrating the advantageous embodiment of acid leaching nickeliferous oxide ores and treating precipitates obtained from the leach solution by the process of the present invention. An aqueous slurry of nickeliferous oxide ore is fed to autoclave 20 to which sulfuric acid in amounts sufficient to react with the acid soluble constituents is added. The acidified slurry is heated to a temperature between about 230° C. and about 300° C. to dissolve the nickel and cobalt values. Advantageously, this leaching operation is conducted on a continuous basis.

The pregnant solution, after discharge from the autoclave, is neutralized in step 22. Neutralization of the pregnant solution is required to facilitate subsequent sulfide precipitation. In order to minimize reagent costs and to improve overall recovery the pregnant solution is neutralized with fresh ore, particularly ore having comparatively high concentrations of basic constituents, such as magnesia. Neutralization with ore is preferred as any nickel or cobalt contained in the ore will dissolve and report in the pregnant solution, but other common neutralizers can be used. The neutralization slurry is then subjected to a liquid-solid separation treatment at stage **24**. The separated solids are sent to waste and the pregnant solution is treated for ultimate nickel and cobalt recovery.

Nickel and cobalt are precipitated from the neutralized pregnant solution as sulfide at sulfide precipitation stage **26**. The actual precipitation conditions form no part of the present invention but the conditions are selected to provide a readily filterable and easily handled precipitate. Hydrogen sulfide is advantageously used to precipitate the nickel and cobalt values. The nickel and cobalt sulfides are separated from the barren solution in liquid-solids separation stage **28**.

The sulfides of nickel and cobalt precipitated as described above are not chemically reactive and dissolve slowly, if at all, in hydrochloric acid. Therefore, the sulfide precipitate can be melted and granulated at stage **30** to activate the metal values for the hydrochloric acid leaching operation. When nickel sulfide is heated to elevated temperatures, a portion of the sulfur is vaporized and the composition of the nickel sulfide approaches Ni_3S_2. Continued heating melts the sulfide which is then granulated. Such heating and melting can be conducted in an electric arc furnace which minimizes gas flows and therefore eases the problems associated with sulfur recovery. The sulfide precipitate can also be flash smelted with extraneous fuel requirements being met with elemental sulfur in order to produce off-gases rich in sulfur dioxide (e.g. 8% or more) which off-gases can be readily converted to sulfuric acid for recycle for leaching the oxide ore. Processes for flash smelting are adequately described in U.S. Pat. Nos. 3,754,891 and 2,668,107 which are incorporated herein by reference. Smelting is controlled to produce a nickel matte containing not less than about 20% sulfur and not more than about 33% sulfur. Although sulfur deficient mattes, particularly those having sulfur contents below about 20%, are highly reactive and dissolve very readily in hydrochloric acid solutions, such mattes react with the hydrochloric acid to generate increasing amounts of hydrogen and decreasing amounts of hydrogen sulfide as the sulfur content of the matte decreases. Hydrogen sulfide is a useful reagent in the process and can be costly to prepare, and the presence of such large quantites of hydrogen in an industrial setting can be hazardous. By controlling the sulfur content to between about 25% and about 27% during smelting, a reactive matte product is obtained while at the same time the amount of hydrogen sulfide generated for recycle is maximized.

The granulated sulfides are then leached with hydrochloric acid at stage **32**, as described hereinbefore. Hydrochloric acid leaching of the granulated sulfides produces a pregnant solution containing between about 50 gpl and about 300 gpl nickel and a gaseous effluent containing hydrogen and hydrogen sulfide. The pregnant chloride solution is then stripped of any dissolved hydrogen sulfide at stage **34**. Stripping is accomplished by heating and passing a gas, such as steam, air or nitrogen, through the pregnant solution.

The nickel concentration of the stripped pregnant solution is adjusted to between about 150 gpl and about 300 gpl by evaporation in stage **36** during which treatment the chloride concentration also increases forming anionic chloride complexes of cobalt, iron and other metal impurities. The nickel concentration is adjusted by passing the hot effluent from high temperature hydrolysis through the stripped pregnant solution.

The complexed metal values are extracted from the concentrated solution at stage **38**, which may include two or more sequential steps using different extractants. For example, complexed iron can be extracted with tributylphosphate dissolved in a suitable organic solvent. Thereafter, the other complexed metals can be extracted with water-insoluble amines or quarternary ammonium compounds dissolved in water-immiscible solvents. The loaded organic extractants are stripped, e.g. cobalt is stripped from the amine extractant at stage **40**, with the regenerated amine extractant being recycled to stage **38**. It will be appreciated by those skilled in the art that other processes and/or reagents can easily be employed for separating the metals from the concentrated metal chloride solution.

The purified nickel chloride solution is then hydrolyzed in a fluid bed reactor to form nickel oxide and hydrogen chloride at stage **42**, as described hereinbefore.

An important feature of this embodiment is the recycling of the gaseous effluents to the various stages of the overall process. The gaseous effluent from hydrolysis stage **42** is passed through the stripped pregnant solution to concentrate the solution with respect to nickel and chloride ions prior to liquid organic extraction and then through water to recover the remainder of the gaseous hydrogen chloride to produce the hydrochloric acid for leaching the granulated sulfides. Hydrogen sulfide generated from hydrochloric acid leaching stage **32** and from stripping stage **34** is used to precipitate nickel and cobalt sulfides in stage **28**. The gaseous effluents from stages **32** and **34** are advantageously passed through a solution of organic absorber, e.g. citric acid or monoethanolamine, at stage **44** to separate the hydrogen sulfide from the hydrogen, and the hydrogen sulfide is regenerated from the solution by conventional techniques for reuse. The separated hydrogen, after drying, is reacted with sulfur at **46** to form additional amounts of hydrogen sulfide for use in precipitating nickel and cobalt at stage **28**. The sulfur containing gases generated at melting stage **30** are cycled through acid plant **48** to produce acid for leaching stage **20**. Thus, except for unavoidable losses, the preferred embodiment provides a closed cycle for all of the reagents and only make-up amounts must be added at the various stages.

Referring now to FIG. **3** which is a block flowdiagram of a preferred embodiment of the present invention, nickeliferous oxide ore having limonitic and silicate (high magnesia) fractions is pretreated by screening at stage **50**. The fine limonitic fraction is pulped with water, preheated to a leaching temperature between about 260° C. and about 300° C. and fed to autoclave **52**. Sulfuric acid in an amount between about 0.15 and 0.25 by weight of the dry ore is incrementally added to the autoclave to leach at least about 90% of the nickel contained in the ore and a like amount of any cobalt. The leaching operation is described in greater detail in U.S. Pat. No. 4,098,870 to Fekete et al. which is incorporated herein by reference. The silicate fraction is comminuted to a particle size of at least about 95% minus 65 mesh USS at **54**. The leach pulp from autoclave **52** and the ground ore from **54** are fed to neutralization stage **56** to neutralize any free sulfuric acid in the leach liquor. The neutralized pulp is sent to liquid-solids separation **58** from which the solids are sent to disposal and the pregnant solution is sent to hydrogen sulfide precipitation **60**. Nickel, cobalt and other metal values whose sulfides are insoluble in sulfate solutions having a pH value greater than about 1 are precipitated with gaseous hydrogen sulfide. Precipitation of the nickel and cobalt sulfides is conducted at ambient pressures and at temperatures of about 85° C. or more with substantial recirculation of the precipitated sulfides. The hydrogen sulfide precipitation process is described in greater detail in U.S. Pat. No. 4,110,400 to Jha et al, filed Aug. 1, 1977, which is incorporated herein by reference. The slurry from hydrogen sulfide precipitation **60** is fed to liquid-solids separation **62** where the liquid is separated and sent to hydrogen sulfide stripping **64**. Steam is passed through the liquid from liquid-solids separation **62** to sparge hydrogen sulfide therefrom, which hydrogen sulfide is recycled to hydrogen sulfide precipitation **60** and the stripped liquid is sent to disposal.

The sulfide precipitate from liquid-solids separator **62** is dried and sent to flash smelter **66** where additional extraneous heat is generated by burning elemental sulfur and air. The flash smelting separating is conducted to provide a nickel matte having sulfur content between about 25% and about 27%. Sulfur dioxide generated during flash smelting is transferred to sulfuric acid plant **68** to produce sulfuric acid which is recycled to autoclave **52** for leaching additional amounts of nickeliferous oxide ore.

Molten nickel matte from flash smelter **66** is granulated in water and, if necessary, ground to a particle size of at least about 100% minus 100 mesh USS at **70**. Granulated and ground matte from **70** is sent to hydrochloric acid leaching **72** where the ground matte is leached with hydrochloric acid having a hydrogen chloride concentration between about 3 N up to the azeotropic composition. Hydrochloric acid reacts with the nickel matte to form hydrogen sulfide and hydrogen which is conveyed to hydrogen sulfide separator **74**. The separated hydrogen sulfide from separator **74** is recycled to hydrogen sulfide precipitation **60** and the hydrogen is sent to hydrogen sulfide preparation **76** from where the prepared hydrogen sulfide is sent to hydrogen sulfide precipitation **60**.

The pulp from hydrochloric acid leaching **72** is sent to liquid-solids separation **78** from which the underflow is returned to **72** and the overflow is treated for nickel and cobalt recovery.

If the overflow from **78** contains significant amounts of zinc and iron these metals can be extracted at **80** from the chloride solution with an organic extractant comprising tributylphosphate dissolved in a suitable organic solvent. As shown in FIG. 3, this step is optional and will be used only if the nickel chloride solution contains significant amounts of zinc. The chloride raffinate from **80** is treated in chloride adjustment **82** with concentrated hydrogen chloride vapor to increase the chloride concentration of the solution to between about 8 N and about 10 N. The chloride solution from **82** is sent to a cobalt extraction **84** where cobalt and other metal values forming complex chloride anions are extracted with an organic extractant comprised of tributylphosphate dissolved in an organic solvent, preferably the organic extractant contains between about 30% and 50% tributylphosphate by weight.

The loaded organic extractant is treated for cobalt recovery with the stripped organic extractant being recycled to **84**. The raffinate from **84** is conveyed to quench tower **86** where the raffinate is concentrated and heated to near its boiling point. A portion of the concentrated nickel chloride solution from **87** is fed to the pyrohydrolysis unit **88** which comprises a fuel-fired fluidized bed of nickel oxide granules. The concentrated nickel chloride solution fed to **88** is oxidized to nickel oxide and produces a hot gaseous effluent containing hydrogen chloride. The hot gaseous effluent from **88** is fed to quench tower **86** where nickel chloride solution is concentrated. The cooled gaseous effluent from **86** is sent to adiabatic absorber **90** where the hydrogen chloride contained in the cooled gaseous effluent is absorbed. A portion of the azeotrope from adiabatic absorber **90** is recycled to leaching stage **72** and another portion is sent to azeotrope evaporator **92**. Azeotropic vapor from **92** is fed to column **94** where it reacts with a portion of the concentrated nickel chloride solution from **86** to produce a vapor concentrated in hydrogen chloride which can be recycled to chlorine adjustment stage **82** an if recycled to leaching stage **72**, the concentrated nickel chloride solution from **86** picks up water from the azeotrope vapor in **92** in column **94** to produce a dilute nickel chloride solution from **86** to produce a vapor concentrated in hydrogen chloride which can be recycled to chlorine adjustment stage **82** and if recycled to leaching stage **72**, the concentrated nickel chlolride solution from **86** picks up water from the azeotrope vapor in **92** in in column **94** to produce a dilute nickel chloride solution which is fed through azeotrope evaporator **92** and then to quench **86**.

It is evident from the description of the flowsheet in FIG. 3 that the process in accordance with the present invention provides a unique combination of steps in which various reagents such as sulfur, hydrogen sulfide and hydrogen chloride are recycled in such a manner as to minimize the amount of fresh reagents required in the overall process.

A particularly advantageous variation of the process in accordance with the present invention is depicted in FIG. 4. The sulfide precipitate from step **62** in FIG. **3** is reduced at **100** with hydrogen at a temperature between about 250° C. and about 700° C., advantageously between about 300° C. and about 600° C., to lower the sulfur content of the sulfide precipitate so that the reduced material corresponds roughly to Ni_7S_6. This reduction can be conducted in any reactor that provides good gas-solid contact, e.g., an indirectly-heated rotary kiln or a fluid bed reactor which is either indirectly-heated or employs gaseous hydrogen preheated to the reduction temperature. The off-gas from **100** containing hydrogen and hydrogen sulfide is sent to **128** which is an absorber containing monoethanolamine in which hydrogen sulfide is absorbed providing a gaseous effluent containing water vapor and hydrogen which gaseous effluent is dried at **130** and the resulting hydrogen is recycled to **100**.

The reduced sulfide precipitate is fed to **102** where it is leached with a hydrochloric acid solution having a concentration between about 3 N and the azeotropic composition at a temperature between about 50° C. and about 110° C. to produce a pregnant nickel chloride solution containing between about 50 gpl and about 300 gpl nickel. Hydrochloric acid leaching produces a gaseous effluent containing hydrogen and hydrogen sulfide which is sent to **128** for hydrogen sulfide and hydrogen recovery. When leaching is completed the slurry is sent to **104** for liquid-solids separation where the unreacted solids are recovered for further treatment and the pregnant nickel chloride solution is recovered. The pregnant nickel chloride solution is sent to **106** where hydrogen sulfide is stripped from the nickel chloride solution by passing steam therethrough. The gaseous effluent from the stripping operation containing hydrogen sulfide, hydrogen and steam is sent to **128** to recover further amounts of hydrogen sulfide and hydrogen.

The stripped pregnant nickel chloride solution is sent to **108** where it is treated with a liquid organic extractant comprising between about 5% and about 35%, by weight, tributylphosphate and the balance essentially a non polar, water-immiscible organic solvent. Treatment with this tributylphosphate solution extracts ferric iron, zinc and copper producing a loaded organic extractant and a nickel chloride raffinate. The loaded organic extractant is sent to **126** where it is scrubbed with water to recover nickel chloride which is returned to **108** and, after scrubbing, is stripped with weak (about 4 N) hydrochloric acid solution to regenerate the extractant for recycling to **108**. The nickel chloride raffinate is sent to **110** where ferrous iron is oxidized to the ferric state. Oxidation of ferrous iron to ferric iron is accomplished by sparging the nickel chloride raffinate with air, chlorine or mixtures thereof. The nickel chloride raffinate containing additional amounts of ferric iron is sent to **112** where it is treated with an organic extractant containing between about 5% and about 35% tributylphosphate dissolved in a water-insoluble, non polar, organic solvent which extracts ferric iron. This loaded organic extractant is sent to **124** where it is scrubbed with water which scrub solution contains nickel chloride and is sent to **112** and then is stripped with a weak hydrochloric acid solution to regenerate the extractant which is recycled to **112**.

The raffinate from **112** is sent to **114** for cobalt extraction. The cobalt is extracted by contacting the nickel chloride solution with hydrogen chloride salt of an amine or a quaternary ammonium compound. The amine or quaternary ammonium compound is dissolved in a non polar, water-immiscible organic solvent in amounts between about 10% and about 20%. The organic extractant containing cobalt is sent to **122** where it is scrubbed with water to recover nickel chloride which is recycled to **114** and is then contacted with additional amounts of water to strip the cobalt therefrom and to regenerate the organic extractant for recycling to **114**.

The purified nickel chloride solution from **114** is sent to **116** for concentration. The concentrated nickel chloride solution is then sent to **118** where the concentrated nickel chloride solution is hydrolyzed at elevated temperatures. Advantageously, the concentrated nickel chloride solution is fed to a fluidized bed of nickel oxide heated to a temperature above about 750° C., advantageously between about 800° C. and about 950° C. The fluidized bed is maintained at temperature by combusting a hydrocarbon fuel and air with the amounts of air and fuel being controlled to provide an atmosphere that is nonreducing to nickel oxide and nickel chloride and nonoxidizing to hydrogen chloride. High temperature hydrolysis produced a marketable nickel oxide product and a hot gaseous effluent containing hydrogen chloride and suspended nickel oxide. The hot gaseous effluent is passed through a cyclone separator to recover a preponderant part of the suspended nickel oxide and is then fed to **116** where the hot gaseous effluent is quenched with purified nickel chloride solution from **114**. The cooled gaseous effluent from **116** is sent to absorption column **120** where hydrogen chloride contained in the cooled gaseous effluent is absorbed in water to produce a hydrochloric acid solution having a concentration between about 3 N and the azeotropic composition. The hydrochloric acid solution from **120** is recycled to **102** to leach additional amounts of reduced nickel sulfide.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative example is given:

EXAMPLE 1

A nickeliferous oxide ore containing 2.00% nickel, 0.08% cobalt, 32.4% iron and about 18.3% silica was leached with sulfuric acid at 270° C. under 56 atmospheres. The resulting slurry was neutralized with a high magnesia nickeliferous silicate ore. The dissolved nickel and cobalt values were precipitated as sulfides from the solution with hydrogen sulfide. Analysis of the precipitate showed that it contained 60% nickel, 2.4% cobalt and the remainder substantially sulfur and minor impurities such as zinc, copper and iron.

The sulfide precipitate was smelted in an electric arc furnace and the resulting melt was granulated in water and then ground to an average particle size of 50 microns. The ground material contained 67.0% nickel, 2.7% cobalt and 27% sulfur. The off-gases from the electric furnace were suitable for subsequent treatment to produce sulfuric acid.

The granulated matte was leached with 6 N hydrochloric acid at the boiling point to produce a pregnant solution containing 110 gpl nickel, 4.4 gpl cobalt, 2 gpl iron and 75 gpl free hydrochloric acid. Hydrogen and hydrogen sulfide generated during leaching were recovered for recycling to the earlier stages of the process. Hydrochloric acid leaching dissolved substantially all of the nickel contained in the granulated matte. Solids from liquid-solids separation were washed and recycled to the melting furnace.

Live steam was passed through the pregnant solution to strip it of any dissolved hydrogen or hydrogen sulfide, and the loaded stripping gas was combined with the gases generated during leaching for use in the earlier stages of the process. After being stripped the pregnant solution was concentrated with respect to nickel and chloride ions by evaporation using the off-gases from the high temperature hydrolysis unit. Evaporation increased the nickel content to 230 gpl, the cobalt content to 9.2 gpl, the iron content to 4.2 gpl and the chloride content to 360 gpl.

The concentrated solution was contacted with tributylphosphate dissolved in an aromatic diluent. An organic to aqueous ratio of 5:1 was used. This treatment lowered the cobalt content to 0.05 gpl and the iron content to 0.01 gpl. The raffinate substantially free of chloride-complex-forming impurities was ready to be treated for nickel recovery.

The nickel raffinate was fed to a fluidized bed of nickel oxide heated to 850° C. The fluidized bed was maintained at temperature by combusting light fuel oil with an excess of air so that the off-gas contained 1.0% free oxygen, i.e. the atmosphere within the fluidized bed was non-reducing to nickel chloride and nickel oxide. Nickel oxide was withdrawn from the bed at a rate that approximated the amount of nickel contained in the raffinate.

The off-gas from the fluid bed reactor was passed through a cyclone precipitator with the solids being returned to the fluid bed reactor and the cleaned gas was passed through the pregnant solution to evaporate the solution and to redissolve part of the hydrogen chloride contained in the gas. Any unreacted nickel chloride or unprecipitated nickel oxide contained in the cleaned off-gas were also recovered at this point. After passing through the pregnant solution the gas was then passed through a water absorber to recover the remaining hydrogen chloride for recycling to leaching.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. For example, ion exchange resins can be employed to extract various impurities from nickel solutions, particularly when such impurities as zinc are present in small amounts. When zinc is present in small amounts, carboxylic resins can be used to extract the zinc from the nickel chloride solution. Another example is the use of activated carbon to extract small amounts of metallic impurities or gaseous impurities, such as hydrogen sulfide. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for recovering nickel from a nickeliferous sulfidic material containing at least one other metal selected from the group consisting of cobalt, copper and iron which comprises leaching the sulfidic material with an at least about 3 N hydrochloric acid solution to provide a pregnant nickel chloride solution; contacting the pregnant nickel chloride solution with an organic extractant to extract the other metal and to provide a nickel chloride raffinate; concentrating the nickel chloride raffinate; feeding the concentrated nickel chloride raffinate to a high temperature hydrolysis unit wherein the concentrated nickel chloride raffinate is oxidized to a nickel oxide product and a hot gaseous effluent containing hydrogen chloride; recycling the hot gaseous effluent from the high temperature hydrolysis unit through the nickel chloride raffinate to concentrate the raffinate and to produce a cooled gaseous effluent containing hydrogen chloride; and passing the cooled gaseous effluent through a water absorber to generate hydrochloric acid for leaching fresh nickeliferous sulfidic material.

2. The process as described in claim 1 wherein the leach solution has a hydrochloric acid concentration of between about 3 N and 9 N.

3. The process as described in claim 2 wherein the leach solution has a hydrochloric acid concentration of between about 3 N and the azeotropic composition.

4. The process as described in claim 3 wherein the leach solution has a hydrochloric acid concentration of between about 4 N and about 6 N.

5. The process as described in claim 4 wherein the nickeliferous sulfidic material is leached at a temperature between about 50° C. and about 100° C.

6. The process as described in claim 1 wherein the nickeliferous sulfidic material is a sulfide precipitate obtained by precipitating nickel from acidic leach solutions.

7. The process as described in claim 6 wherein the nickel sulfide precipitate is thermally activated to increase both the rate and extent of nickel leaching.

8. The process as described in claim 7 wherein the nickeliferous sulfide precipitate is smelted to provide a nickeliferous sulfidic material having a composition approaching Ni_3S_2.

9. The process as described in claim 7 wherein the nickeliferous sulfide precipitate is activated by heating the nickeliferous sulfide precipitate to a temperature between about 250° C. and about 700° C. in a hydrogen containing atmosphere whereby the hydrogen reacts with sulfur contained in the nickeliferous sulfide precipitate to produce hydrogen sulfide and a nickeliferous sulfidic material having a sulfur content less than that required to satisfy the stoichiometry of all the metals present in the nickeliferous sulfide precipitate.

10. The process as described in claim 1 wherein the high temperature hydrolysis unit is a fluidized bed of nickel oxide particles heated to a temperature of at least about 750° C.

11. The process as described in claim 10 wherein the fluidized bed is maintained at a temperature of at least about 750° C. by combusting a hydrocarbon fuel and air in the fluidized bed with the composition being controlled such that the products of combustion are nonreducing to nickel oxide and nickel chloride and nonoxidizing to hydrogen chloride.

12. The process as described in claim 11 wherein the combustion is controlled so that the off gas from the fluidized bed has a free oxygen content of less than about 2%, by volume.

13. The process as described in claim 10 wherein the temperature of the fluidized bed is maintained between about 800° C. and about 950° C.

14. The process as described in claim 1 wherein the liquid organic extractant is tributylphosphate dissolved in a water-immiscible organic solvent with the tributyl phosphate being present in the organic solvent in amounts between about 15% and 70%, be weight.

15. The process as described in claim 1 wherein the pregnant nickel chloride solution is first contacted with a liquid organic extractant containing tributylphosphate dissolved in a water-immiscible organic solvent to extract any ferric iron and then the pregnant nickel chloride solution is contacted with a second liquid organic extractant containing a water-insoluble amine or a quarternary ammonium compound dissolved in a water-immiscible organic extractant to extract cobalt and copper from the pregnant nickel chloride solution.

16. The process as described in claim 1 wherein the nickeliferous sulfidic material also contains zinc and the pregnant nickel chloride solution is first contacted with a liquid organic extractant containing tributylphosphate dissolved in a water-immiscible solvent to extract any ferric iron and zinc and then the nickel chloride solution is contacted with a second liquid organic extractant containing a water-immiscible compound dissolved in a water-immiscible organic solvent to extract cobalt from the pregnant nickel chloride solution.

17. The process for recovering nickel and cobalt from nickeliferous oxide ores which comprises leaching the oxide ore with sulfuric acid at a temperature between about 230° C. and about 300° C. in an autoclave to produce a pregnant sulfate solution containing nickel and cobalt; treating the pregnant sulfate solution with hydrogen sulfide to precipitate the nickel and cobalt values as sulfides; leaching the sulfide precipitate with a

hydrochloric acid solution having an acid concentration of at least about 3 N to product a pregnant nickel chloride solution and hydrogen sulfide; recycling the hydrogen sulfide to the sulfide precipitation step; contacting the pregnant nickel chloride solution with a liquid organic extractant to extract the other metal and to provide a nickel chloride raffinate; concentrating the nickel chloride raffinate; feeding the concentrated nickel chloride raffinate to a high temperature hydrolysis unit wherein the concentrated nickel chloride raffinate is oxidized to a nickel oxide product and a hot gaseous effluent containing hydrogen chloride is produced; recycling the hot gaseous effluent from the high temperature hydrolysis unit through the nickel chloride raffinate to concentrate and to produce a cooled gaseous effluent containing hydrogen chloride; and passing the cooled gaseous effluent through a water absorber to generate hydrochloric acid for leaching fresh nickeliferous sulfidic material.

18. The process as described in claim 17 wherein the leach solution has a hydrochloric acid concentration of between about 3 N and 9 N.

19. The process as described in claim 18 wherein the leach solution has a hydrochloric acid concentration of between about 3 N and the azeotropic composition.

20. The process as described in claim 19 wherein leach solution has a hydrochloric acid concentration of between about 4 N and about 6 N.

21. A process for separately recovering nickel and cobalt from a sulfidic material which comprises leaching the sulfidic material with an aqueous solution of hydrochloric acid having a concentration at least about 3 N to dissolve substantially all of the sulfidic material and to produce a pregnant nickel chloride solution, increasing the nickel and the chloride concentrations of the pregnant nickel chloride solution by evaporation and by adding hydrogen chloride thereto to form anionic chloride cobalt complexes, contacting the concentrated nickel chloride solution having the anionic cobalt chloride complexes with an organic extractant to extract the anionic cobalt chloride complexes and to produce a nickel chloride raffinate, hydrolyzing the nickel chloride raffinate at a temperature above about 750° C. to produce a refined nickel oxide product and a hot gaseous effluent containing hydrogen chloride which is first passed through the pregnant nickel chloride solution to increase the nickel and chloride concentrations thereof and to form anionic cobalt chloride complexes and then through water to form a hydrochloric acid solution which is recycled for leaching additional amounts of the nickeliferous sulfidic material.

22. The process as described in claim 21 wherein leaching is conducted at a temperature between about 50° C. and about 110° C.

23. The process as described in claim 21 wherein the organic extractant is at least one member selected from the group consisting of water-insoluble amines, quaternary ammonium compounds and organic-phosphorus compounds dissolved in a water-immiscible solvent.

24. The process as described in claim 21 wherein the hydrolysis is conducted in fluid bed reactor maintained at a temperature between about 800° C. and about 950° C.

25. The process as described in claim 24 wherein the off-gas from the fluid bed reactor contains free oxygen in an amount less than about 1% by volume.

26. A process for recovering nickel and cobalt from nickeliferous oxide ores which comprises leaching the oxide ores with sulfuric acid at a temperature between about 230° C. and about 300° C. in an autoclave to produce a pregnant sulfate solution containing the nickel and cobalt values; treating the pregnant sulfate solution with hydrogen sulfide to precipitate the nickel and cobalt values as sulfides, leaching the sulfide precipitate with up to 6 normal hydrochloric acid to produce a pregnant nickel chloride solution, increasing the nickel and the chloride concentrations of the pregnant nickel chloride solution by evaporation and by adding hydrogen chloride thereto to form anionic chloride cobalt complexes, contacting the concentrated nickel chloride cobalt complexes, contacting the concentrated nickel chloride solution having the anionic cobalt chloride complexes with a liquid organic extractant to extract the anionic cobalt chloride complexes and to produce a nickel chloride raffinate, hydrolyzing the nickel chloride raffinate at a temperature above about 750° C. to produce a refined nickel oxide product and a hot gaseous effluent containing hydrogen chloride which is first passed through the pregnant nickel chloride solution to increase the nickel and chloride concentrations thereof and to form anionic cobalt chloride complexes and then through water to form a hydrochloric acid solution which is recycled for leaching additional amounts of the nickeliferous sulfidic material.

27. The process as described in claim 26 wherein leaching with hydrochloric acid is conducted at a temperature between about 50° C. and about 110° C.

28. The process as described in claim 26 wherein the organic extractant is at least one member selected from the group consisting of water-insoluble amines, quaternary ammonium compounds and organic-phosphorus compounds dissolved in a water-immiscible solvent.

29. The process as described in claim 26 wherein the hydrolysis is conducted in fluid bed reactor maintained at a temperature between about 800° C. and about 950° C.

30. The process as described in claim 29 wherein the offgas from the fluid bed reactor contains free oxygen in an amount less than about 1%, by volume.

31. The process as described in claim 26 wherein hydrogen and hydrogen sulfide generated during leaching with hydrochloric acid are recovered for recycling to the sulfide precipitation stage.

32. The process as described in claim 26 wherein the pregnant nickel chloride solution is stripped of dissolved hydrogen and hydrogen sulfide which are combined with the hydrogen and hydrogen sulfide recovered during leaching.

33. The process as described in claim 32 wherein the hydrogen sulfide in the combined stream is separated from the hydrogen by an organic absorber and the hydrogen is reacted with elemental sulfur to generate hydrogen sulfide for the sulfide precipitation step.

34. The process as described in claim 26 wherein the sulfide precipitate is melted to a matte in an electric arc furnace to adjust the sulfur content of the precipitate to less than about 30% and the matte is granulated or ground for leaching with hydrochloric acid.

35. The process as described in claim 34 wherein the sulfur-containing gases generated in the electric arc furnace are recovered and converted to sulfuric acid for use in leaching the nickeliferous oxide ore.

36. A process for recovering nickel from a nickelcopper matte which comprises leaching the nickel copper matte with at least about 3 N hydrochloric solution to provide a pregnant nickel chloride solution and a cop-

per sulfide residue; separating the copper sulfide residue from the pregnant nickel chloride solution for subsequent treatment to recover copper; contacting the pregnant nickel chloride solution with a recycled organic extractant to extract any copper remaining in the nickel chloride solution and to provide a nickel chloride raffinate; concentrating the nickel chloride raffinate; feeding the concentrated nickel chloride raffinate to a high temperature hydrolysis unit wherein the concentrated nickel chloride raffinate is oxidized to a nickel oxide product and a hot gaseous effluent containing hydrogen chloride; recycling the hot gaseous effluent from the high temperature hydrolysis unit through the nickel chloride raffinate to concentrate the raffinate and to produce a cooled gaseous effluent containing hydrogen chloride; and passing the cooled gaseous effluent through a water absorber to generate hydrochloric acid for leaching fresh nickel copper matte.

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HYDROLOGIC SITE CHARACTERIZATION FOR IN-SITU COAL GASIFICATION

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Note: Same methods are used for in-situ uranium
mining

ABSTRACT

Recent experience at Hoe Creek and Hanna underscores the importance of the hydrological properties of the coal seam and adjacent confining layers to the gasification process. Permeability of the confining layers governs water influx and therefore gas quality. Directional permeability and the ratio of horizontal to vertical permeability and vertical stratification will control linking and the orderly progress of forward gasification. Practical hydrologic testing methods are outlined for obtaining directional permeability, the ratio of horizontal to vertical permeability, permeability of confining layers, along with compressibility, well efficiency and the in-situ fracture distribution. Vertical stratification is obtained using a new downhole flow tool sensitive to flow rates as Low as .1 gpm. Field examples are given to illustrate the required instrumentation and derived parameters.

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1.0 INTRODUCTION

In-situ mining is different from other forms of mining in that the reactor vessel is located underground and therefore removed from direct observation. "Out of sight, out of mind" is a saying which is especially applicable to the subsurface portion of in-situ projects. As a result we often direct our attention to the surface facilities and neglect proper utilization of information and characterization of the hydrologic properties of the deposit to determine if linking, gasification and containment can be properly effected. It is now recognized that more thorough site characterization and selection must be exercised to insure successful results.

It is the purpose of this paper to briefly state the factors important to characterizing a site with respect to hydrology and reservoir engineering and then present techniques for their measurement. Recent tests at Hoe Creek[1,2], and in Texas[3] have demonstrated the importance of hydrologic factors in site selection. At these sites water influx due to leakage and the presence of overlying high permeability aquifers were detrimental to gas quality and flame front propagation. Other factors affecting linking and gasification are directional permeability, and the ratio of horizontal to vertical permeability. If directional permeability is present, then failure to align injection and production wells parallel to the major direction of permeability can result in erratic linking paths. This was evidently the case for the recent Hanna IV test.[4] The ratio of horizontal to vertical permeability is as important or more so than the areal directional permeability. A high ratio of horizontal to vertical permeability ensures confinement of linking and gasification to the bottom of the coal seam. When this ratio is less than one then override conditions are favored as at Hoe Creek where the ratio was approximately 0.5. On a more basic level permeability itself of both the coal seam and confining layers determines the rate of linking and water influx from the surrounding groundwater.

Since permeability, and particularly directional permeability, is so important to in-situ coal gasification, it is appropriate to discuss the procedures we have found useful for its measurement. To provide background we first review previous hydrologic studies conducted at in-situ coal gasification sites. We then present a general approach for hydrologic site characterization beginning with basic aquifer definition which is accomplished using core data together with logs. Instrumentation and procedures are recommended for obtaining accurate hydrologic test results. This is followed by the three phases of hydrologic testing. The first phase is designed to provide criteria as to whether the lease should be kept for further development or rejected. The second phase entails broadening of the hydrologic data base to aid in delineating coal amenable gasification from that which is not, as well as acquiring more precise data for design purposes. Lastly we concentrate on methods for intensive pattern evaluation to obtain detailed engineering information for pilot and commercial operation.

The methods we present for hydrologic site characterization have been tested on several hundred wells used in evaluating properties for in-situ recovery. Some of the solutions we present have not been previously published in the literature.

The techniques we present account for the combined effects of aquifer thickness, partially penetrating wells, directional permeability, leakage, the ratio of horizontal to vertical permeability, and compressibility.

Our solutions embody the main features we are concerned with in in-situ processes. While some are complex three-dimensional solutions, we will demonstrate that they are economical to implement in the field and practical to analyze.

2.0 PREVIOUS STUDIES

2.1 Hydrologic Studies on UCG Sites

Four previous coal gasification tests have been conducted with reported hydrologic tests. These include those conducted at Hoe Creek[1, 2,5,6,7,8], Hanna III, IV[9,10,11], by Texas A & M[3], the Alberta Research Council[12,13] and Arco's Rocky Hill Test.

A number of aquifer tests were performed at Hoe Creek by Stone and Snoeberger[7,8] to evaluate the characteristics of the Felix No. 2 seam and adjacent layers. The tests were based on analytic solutions appropriate to saturated homogeneous porous media. The methods used included Hantush's method for fully penetrating wells in isotropic leaky aquifers, Week's method for partially penetrating wells in isotropic non-leaky aquifers, Papadopulos' method for anisotropic non-leaky aquifers with fully penetrating wells, Neuman and Witherspoon's ratio method for measuring the properties of the semi-confining layer. A single well slug injection test was also used. The test work was thorough and professional. The wide variety of tests and methods employed was due to the fact that no single method in existence at the time could include the combined effects of areal anisotropy, the ratio of horizontal to vertical permeability leakage and partial penetration. The method we present in a subsequent section includes all of these effects simultaneously.

The major horizontal hydraulic conductivity was 0.3 m/day (432 md) while the minor was 0.15 m/day (216 md). The vertical permeability was estimated to be approximately 2 times the horizontal geometric mean permeability of 305 md. Permeability for the lower confining layer was reported at 10^{-3} m/day (1.4 md). Permeability of the upper confining layer ranged from 22 md - 432 md. The permeability in millidarcies was computed using a water temperature of 12.5°C. It was concluded that the Felix No. 2 was a leaky to very leaky aquifer. From our previous work on aquifers being considered for in-situ uranium mining we would classify the Felix No. 2 as an extremely leaky aquifer. Based on the high leakage and the low ratio of horizontal to vertical permeability both of which can lend to override conditions, this site should have been abandoned on the basis of hydrologic characterization alone.

Hutchinson et al[10] evaluated the areal anisotropy of Hanna III coal gasification site by performing a multi-well pump test. The drawdown data was analyzed by the Papadopulos method. The average permeability for the seam was found to be 9.2 md and the calculated axis of major permeability in the Hanna III site lies in a direction which is 51° east of north. These values are corrected[14] from those in the original paper and are now within 12° of the major fracture direction of Hanna. The major and minor transmissivities are respectively 0.108 m^2/day (17 md) and 0.032 m^2/day (5 md).

Again the test pattern for linking and gasification was selected prior to the hydrologic information. The hydrologic information was not used in selecting the orientation of wells. However, the major fracture direction was used as a guide in orientation. The ratio of horizontal to vertical permeability was not measured.

In test IV the wells were not aligned with the major permeability direction. As a result the linking took a longer path in line with the direction of major permeability as shown in Figure 1, thereby demonstrating that directional permeability is an important factor.

Strickland and Jennings[3] conducted hydrologic testing at the Texas A & M gasification site. Conventional straight line (Jacob, Horner) and type curve matching techniques were employed. Anisotropy was presumably inferred from drawdown contours. An overlying high permeability of the lignite was determined from cores. All wells responded as if they were in communication with the high permeability sand. Leaky type curve analysis was not used. However, it appears from the high permeability values and negative skins reported that both the lignite and overlying sand were in communication with one another. They

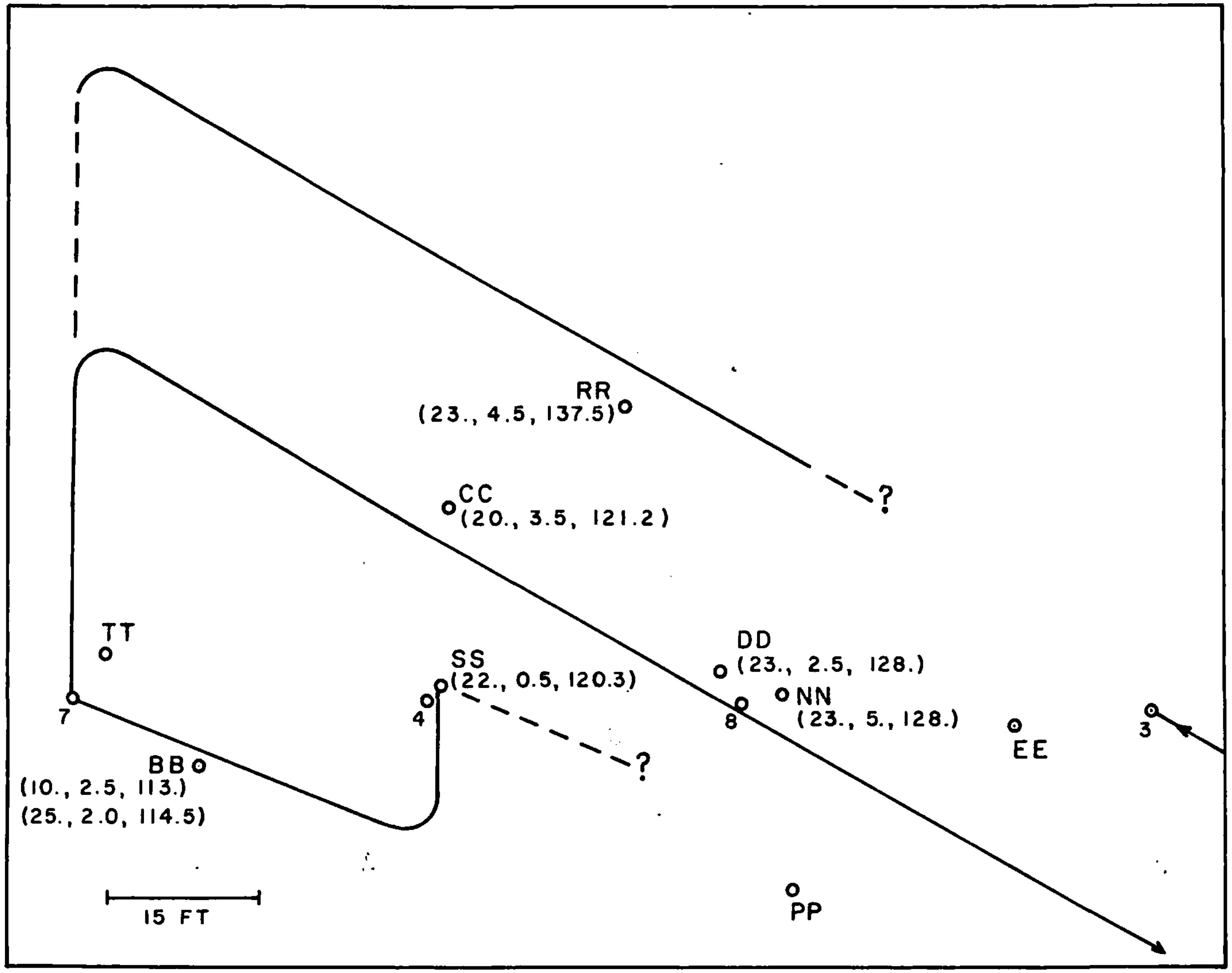


Figure 1. Estimated Hanna IV-B linkage paths. Instrument well data give height above floor in 30 ft. seam, distance from well to zone of reverse combustion, Julian day of passage nearest each well. The test ignited on 110.5. The lines depict the longer path lengths taken during linking as a result of following the natural fracture system. Had the wells been aligned with the major permeability direction the linkage is anticipated to have been along the lines linking wells 7,4,8, and 3.

concluded that the hydrologic conditions of the site prevented successful gasification.

Vogwill[13] performed a thorough series of hydrologic tests on a site near Forestburg Alberta for the Alberta Research Council. Both Jacob's method and Papadopulos' method were used to establish aquifer parameters. The major cleat direction was approximately 50° east of north. Pre-gasification hydrologic tests yielded the local major direction of permeability as 20° east of north--a difference of 30° from the major cleat direction. The geometric mean pre-gasification hydraulic conductivity was 0.57 m/day (1020 md). The ratio of maximum to minimum permeability was 1.55. A post-gasification (test 3) pump test using the same pumped well as before yielded the same ratio. The ratio was determined by ourselves using Hantush's contour method.[15,16] The average hydraulic conductivity in observation wells was approximately 50% higher. A different pumped well was used in test 4 and the results are not directly comparable to the previous tests.

Linking and gasification were performed along the assumed minor cleat direction. However the path did not coincide with the measured directional permeability. Vogwill[13] states "there is some evidence to suggest that preferential movement of air took place along the two directions of maximum anisotropy as determined from aquifer testing." There is no indication that the hydrologic tests were used as a basis to design the gasification tests.

During 1977 and 1978 ARCO conducted extensive hydrologic tests at their Rocky Hill site.[17] Single-well water injection, pumping-recovery, and multi-well pump tests were performed to determine transmissivity and directional permeability. Borehole tracer, spinner, and packer tests were also conducted to investigate vertical permeability and fracture zones.

The hydrologic testing program identified that permeability existed in the lower part of the coal seam supporting the potential for linking in the zone. Values were not reported. However this test is significant in that the hydrologic data were used as a basis for test design.

Overall we conclude that hydrologic studies have been previously unrelated to the process design. We believe this is now recognized by the scientific and engineering community. In the future the trend will be to use the hydrologic information to design the relative spacing and position of the process wells.

2.2 Previous Hydrologic Techniques for Analysis of Coal Aquifers

Here we wish to briefly describe some of the hydrologic techniques which are currently available for evaluating coal aquifers. In subsequent sections we extend these methods to encompass the parameters we wish to measure for process design. We will not discuss the environmental aspects of the hydrologic evaluation. Suffice to state that a good hydrologic evaluation for the process design can be successfully combined with an environmental evaluation. In the following sub-sections we list these methods and critical comments.

2.2.1 Single Well Tests

Pumping or injecting given volumes or flow rates using only one well and measuring the transient response in the same well is termed a single well test. The tests used in hydrologic studies above generally include the slug test,[18] and straight line methods for drawdown[19] and recovery.[20] From the tests the transmissivity and storage coefficient can be determined. The basic problem with these methods as recognized by Stone and Snoeberger,[7] is that they generally yield lower values of transmissivity due to wellbore losses. A method to correct this defficiency will be given in Section 3.

2.2.2 Two Well Tests

Two well tests consist of one well being used for either pumping or injecting, while the second well is observed for its transient response. The major reason for doubling the cost with an additional well is that an observation well is usually unaffected by wellbore losses thereby yielding a truer value of transmissivity and storage coefficient. Furthermore, leakage of confining layers can be measured.

The methods which have been used include the Theis type curve method,[20] the straight line method[19] and Hantush's method for leaky aquifers. Both are applied to wells which are completed over the entire aquifer thickness (fully penetrating wells). The Theis method allows determination of both the storage coefficient and transmissivity. Hantush's method allows in addition the measurement of the degree of confining layer leakage. The straight line method yields values of transmissivity and storage coefficient. However it is less desirable since many phenomena can lead to straight line behavior in some portion of the transient response history. The type curve methods of Theis and Hantush are therefore preferable over the straight line technique.

2.2.3 Multi-Well Tests

We reserve the term multi-well for those tests employing ~~3~~ 4 or more wells including the pumped well. Multi-well tests are resorted to when it is desired to measure directional permeability. For this purpose a minimum of one pumping or injection well together with three observation wells are required. The method employed to date has been that of Papadopulos.[22] It is valid for fully penetrating wells in non-leaky aquifers. We will treat it and its extension in greater depth in a subsequent section.

2.3 Discussion

A number of available solutions from hydrology have been utilized to evaluate coal aquifers for in-situ processing. However none of these has been suited to the simultaneous measurement of anisotropy, leakage and vertical permeability. Furthermore little has been done to assess vertical stratification. Instead the tendency has been to use a number of solutions to attempt to obtain accurate aquifer data. For example Stone and Snoeberger encountered a very complex situation at Hoe Creek involving anisotropy (vertical and areal), leaky aquifers, and partially penetrating wells. They used Papadopulos' solution for directional permeability which is only valid for fully penetrating wells with no leakage. Weeks' method for measuring ratio of horizontal to vertical permeability was also employed. However it was only valid for a non-leaky aquifer and a ratio of horizontal to vertical permeability less than one. Neither assumption was valid. We might add that they were fully aware of these limitations. Our intent in the following sections will be to introduce solutions which are particularly appropriate to evaluating the complex hydrology normally encountered in characterizing sites for in-situ processing. In-situ mining involves technology appropriate to both hydrology and petroleum engineering. To be successful both disciplines must be used together with geologic information.

3.0 SITE CHARACTERIZATION

After the deposit has been identified as worth pursuing for in-situ processing a logical step in evaluation proceeds beginning with lithologic definition as to permeability of various units. Permeability is assessed using core inspection and permeabilities together with logs. Care must be exercised since exploration drill holes are often left unplugged. Hard or more brittle confining layers with little or no vertical hydraulic gradient across them will generally exhibit leakage from unplugged drill holes. This type of leakage can only be found from aquifer tests.

Once the lithology has been assessed, overlying and underlying aquifers should now be delineated in relation to the coal seam. This knowledge provides a basis for designing the hydrologic testing program. Such a program consists of at least three phases. The use of logs in delineating lithology and the hydrologic tests are described below.

The interested reader is also referred to Bartel,[23] for discussions of surface and borehole geophysical techniques for site characterization.

3.1 Lithologic Definition

Logging techniques are basic to determining a definition of the coal seam and adjacent aquifers prior to drilling wells and hydrologic testing. Logs performed for mineral exploration are normally uncalibrated. This means that lithology must be inferred from qualitative changes in curve shapes rather than quantitatively as in the petroleum industry. This is because of costs and the orientation of the industry toward conventional mining. Historically the confinement aspects important to in-situ mining and proximity of aquifers detrimental to gasification were not normally the objective of log investigations. Furthermore mineral companies are reluctant to spend the money required to obtain good logs. This can be readily appreciated since wells in the petroleum industry cost several hundred thousand to several million dollars as compared to a few hundred to thousand dollars for mineral logging holes. The quality of the equipment is accordingly lower in the mineral industry. For example focussed logs to minimize borehole effects are not generally employed. Nevertheless with proper selection of logs, core comparison, drilling fluids, and operational supervision, acceptable results can be obtained.

The logs which are normally available are the caliper, natural gamma, density, neutron, resistivity and the spontaneous potential. The caliper log is a mechanical measurement of hole diameter as a function of depth. The primary reason for running the caliper log is to separate the effects of changes in readings of other logs due to lithology from changes due to hole diameter. All the logs we have mentioned with the exception of the SP are affected by hole diameter. Normally a two arm caliper is run. However if vertical fractures are present the boreholes may tend to be elliptical. For this reason a three-arm caliper should be used where available to compensate for the effect.

A primary lithologic tool is the natural gamma ray log. It measures the natural radioactivity of the formation due primarily to potassium which is normally associated with clays and shales. Hence it is useful in delineating sand-shale sequences. However trace amounts of radioactive daughters of uranium and other elements can substantially effect this log. Comparison with core is therefore important.

The density log directly measures electron density. The principle elements in sedimentary sequences possess a ratio of electron number to atomic weight of approximately .5. Therefore the measurement of electron density correlates directly with mass density. This log readily distinguishes coal from surrounding sand-shale sequences. Furthermore it aids in delineating shaly sands from high porosity sands. This log must be analyzed in conjunction with the caliper log since enlarged hole sections may give spurious low density readings.

The neutron log is primarily a hydrogen finder. Essentially all of the hydrogen in a lithologic sequence would be contained in the formation fluid and in coal beds. Shales and clays have a high porosity and therefore high fluid content. Coal will be indicated as a high porosity material. In general clean sand will exhibit a lower porosity.

The resistivity log measures the voltage difference between a reference ground and a point downhole required to maintain a constant current. Resistivity is affected by formation fluid and matrix surface area. If total dissolved solids (TDS) exceed 10000 ppm then the effect of surface area can be neglected. However in general TDS is less than 5000 ppm in shallow sedimentary formations. In Wyoming, water quality of many aquifers is generally excellent. The combined effect of surface area and formation fluid makes the interpretation of this log difficult. Coal will exhibit a high resistivity. However a high porosity coarse grained aquifer and a low porosity fine grained siltstone can give a similar response on a resistivity log. For this reason the resistivity log should be used in conjunction with cores and other logs for proper interpretation.

The spontaneous potential log is the only log that responds primarily to permeability. However, it is not a quantitative indicator of permeability. This log's response is a combination of electrochemical and electrokinetic effects. In general the electrochemical portion is dominant. However if the well is artesian (flowing) or an exchange of fluid is occurring in the corehole between adjacent strata then the electrokinetic effect can be important. The best response is obtained using a sodium-bentonite mud (minimum 5-10 lbs/ barrel) as the borehole fluid. To properly interpret the log the ionic composition of major components in the formation and drilling fluid is essential to an accurate interpretation of the SP log. The interpretation of this log is especially difficult in shallow fresh water formations and should be left to an experienced log analyst.

From the logs and cores, cross-section which delineate aquifers, aquitards, and confining layers in relation to the coal beds can be constructed. The number of holes logged and cross-sections constructed are a function of the complexity of the lithology and must be determined for each site.

Since permeability cannot be inferred quantitatively from logs, it is usually estimated from porosity relationships. However shale yields a high porosity response on all logs except the density log. Furthermore siltstone also gives a high response on resistivity logs due to the high surface area. It is therefore mandatory to run a combination of several logs to adequately define aquifers and confining layers.

Coal also presents problems. Its low gamma ray response and high resistivity makes it appear similar to sandstone or limestone. It may or may not display an SP response due to natural oxidation-reduction potentials. Furthermore SP response for subbituminous coals is similar to sandstones further complicating interpretations.

The lithologic and log combinations which result in similar responses are too numerous to be discussed in this paper. Each case should be considered individually. However, a minimum logging program should include a gamma ray, resistivity and density logs together with an SP log on selected holes drilled with a good bentonitic mud.

3.2 Hydrologic Characterization

3.2.1 Test Preparation, Instrumentation and Procedures

The design of a pump test consists of the selection of appropriate locations and open intervals of pumped and observation wells and the determination of appropriate pumping rate and duration of the test. All available information should be compiled and examined before pumping.

The location of wells should be chosen in view of both distribution of coal to be gasified and the requirements for analysis of the data which will be discussed later.

All the wells should be developed at least one week prior to the collection of baseline level data and aquifer testing. Water level measurements with 0.01 foot accuracy are required for the baseline water level data. These measurements along with the well collar elevation survey records (±0.01 foot) are used to draw a local piezometric surface map. From this the local groundwater gradient and flow can be computed.

Water level change measuring devices, such as pressure transducers, with an accuracy of ±0.01 psi are best used to record water level changes during the aquifer test.

Virtually all analytic solutions for aquifer test analysis require constant flow rate to yield accurate values. To achieve constant flow rate conditions, a flow regulator is recommended. Flow rate can be measured using a flow meter and/or a totalizer. A tank filter ahead of the devices used is desirable to remove solids from the flow stream to prevent malfunctions.

The water being discharged must be disposed of in such a manner that it cannot return to the water-bearing formation. Also, the water should be conveyed away from the area of work to provide safe and comfortable working conditions. In some cases, a pipeline several hundred feet long is required.

Since the water levels are dropping fast during the initial stage of the test, water level readings must be taken at short time intervals. The time between readings may increase gradually as pumping continues.

The question as to how long the well should be pumped continuously is difficult to answer because the period of pumping depends on the properties of the aquifer to be tested, the degree of accuracy desired in establishing the hydraulic properties and the radius of influence. Economizing on the period of pumping is not recommended because the costs of pumping a few extra hours are low compared with the total costs of the test, particularly when the wells have been specially constructed for test purposes.

It is recommended that a drawdown data analysis on selected wells be made in the field. The preliminary analysis provides the basis for determining the radius of influence, the possible existence of hydraulic boundaries and the duration of the pump test. If the onset of leakage or boundary effects are detected, the test should be continued for a sufficient length of time to establish a definite trend on the field plot.

Recovery data should be collected until water levels have recovered to within 10% of the static water levels prior to the test.

The data obtained during recovery permit the calculations of transmissivity and permeability, thus giving a check on the results of the analysis of the data obtained during the pumping period. Moreover, the recovery method has the advantage that drawdown variations resulting from slight differences in the rate of discharge during pumping do not occur during recovery. Owing to well loss effects the recovery method works best in observation wells and under non-leaky conditions.

3.2.2 Preliminary Hydrologic Evaluation--Phase I

Having delineated the lithology and aquifers, we proceed to the first phase of hydrologic testing. From the coal owners' point of view, after establishing that a resource exists, his next question is, "What is the minimum amount of hydrologic work to perform in order to determine whether this lease should be rejected or kept for further development?" The answer to this question must be given in the context of the process to be utilized. In our paper we assume that the linked vertical well process will be selected over alternatives such as directional drilling since it appears to be the most economical one at present. One of the criteria recommended by the Soviets is that permeabilities be above 15 md. The lowest permeability successfully gasified in the U.S. was Hanna III having an approximate geometric mean permeability of 10 md. It would appear that a comfortable lower bound for permeability should be in the range of 10-20 md. For a 30 ft thick coal seam such as Hanna, a permeability of 15 md yields a transmissivity of 0.1 m^2/day as a safe lower bound. The transmissivity of overlying aquifers (and underlying if the process is to use less than hydrostatic pressure) should also be measured to assess potential water influx problems. The most cost effective way to accomplish the measurement of permeability is with single well tests. If open hole completion is used over the entire coal seam then a vertical permeability profile can also be obtained using downhole flow logs or tracers.

Single Well Tests

As previously discussed, conventional single well tests in hydrology generally yield lower values for transmissivity due primarily to excluding the skin effect and to a lesser extent wellbore storage effects. We have used the method of Agarwal, Al-Hussainy, and Ramey[22] which includes wellbore storage, the skin effect or well efficiency, and transient response. If the skin factor is close to zero then conventional straight line methods or slug tests may be used. Through use of their solution the effect of wellbore damage can be separated from true formation transmissivity. An example of the technique is given in Figure 2 from a well in the Red Desert Area of Wyoming. The skin is a measure of the extent of damage around the well. In other terms the value of 13 for the skin factor translates into a 60% well efficiency. Since the well was cemented and then perforated the lowered efficiency is presumably the result of cement invasion. To compare the accuracy of the single well method this same well was used as an observation well in a multi-well pump test. The result is given in Figure 3. The transmissivity from the two methods is very close. In general we have found good agreement between single well and observation well results for transmissivity in both fractured and semi-consolidated formation. However the storage coefficient with this method is only accurate to within an order of magnitude. Our confidence in accuracy of the method for transmissivity has been justified in numerous tests.

It is difficult to state categorically the number of wells required in this phase. Each site is unique and the number of wells will be dictated by geology and available funds. However as a general guide, properties we have evaluated for in-situ mining have employed approximately 10-12 wells in this phase. Seven to eight wells would be completed open hole through the entire coal seam while two to three wells would be paired with selected wells in the coal seam. The latter wells would be used to check for vertical leakage and test the transmissivity of the overlying aquifer. One to two wells would be used in conjunction with the coal seam - overlying aquifer pairs of wells to check the single well results and measure leakage if present.

Vertical Permeability Stratification

Vertical permeability is most conveniently and economically assessed using downhole flow logging with formation fluid. The logs

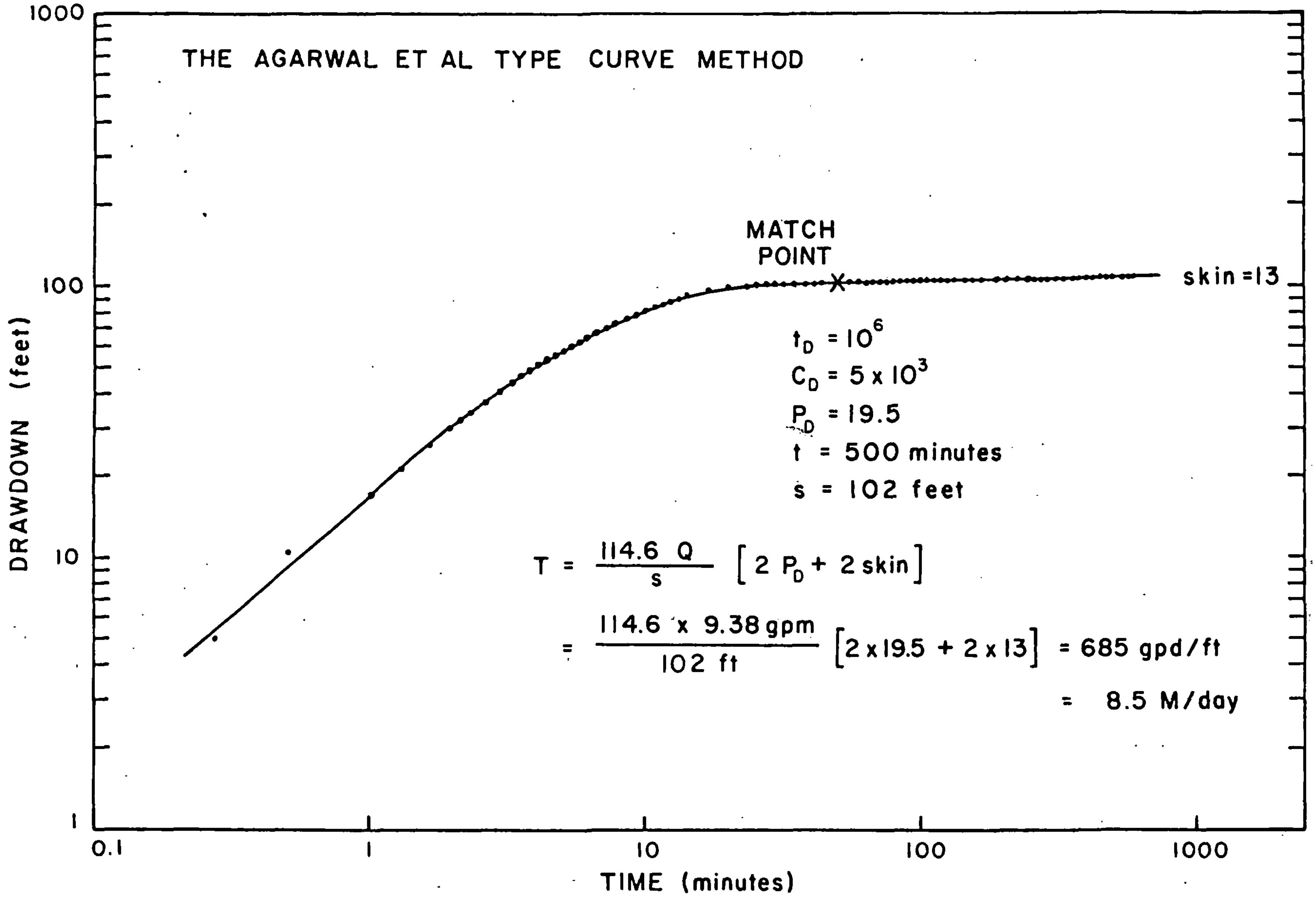


FIGURE 2 SINGLE WELL TEST ON AN AQUIFER IN THE RED DESERT ORE OF WYOMING. BOTH WELLBORE STORAGE AND SKIN EFFECTS ARE INCLUDED THEREBY OBTAINING IMPROVED VALUES OF FORMATION TRANSMISSIVITY

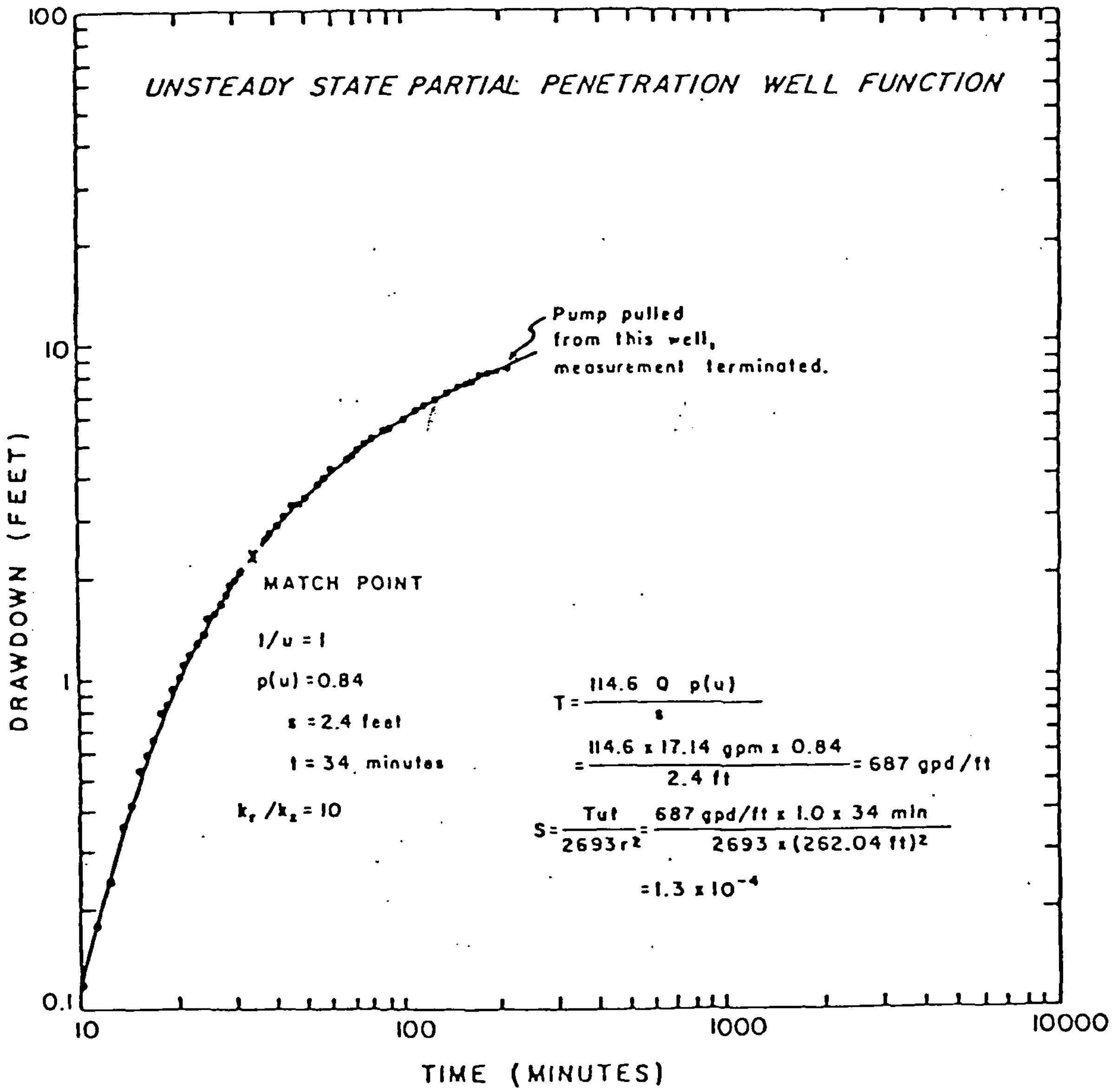


FIGURE 3 PUMPED WELL OF PREVIOUS FIGURE USED AS AN OBSERVATION WELL TO ASSESS SINGLE WELL PUMP TEST RESULTS. AGREEMENT BETWEEN THE TWO METHODS IS EXCELLENT.

are obtained utilizing the single wells in the coal seam which are completed as open holes and described in the previous section. A water truck containing formation water serves as the water supply. Accurate flow logging, in common with other hydrologic tests requires precise control over the injection rate to achieve reliable data. Its interpretation must be performed in conjection with a caliper log.

Conventional spinner tools require a minimum of 20-30 gpm in a 5 in borehole to respond and approximately 40 gpm to obtain reliable results. If injection is used then for typical depth to water in Wyoming (100 ft), and injection head of 50 psi a 30 ft coal seam must have a minimum permeability in the range of 1-2 darcies ($10^{-12} m^2$). Since this is unusual to find permeabilities this high in coal we have developed a solid state downhole flow meter* (Figure 4) based on a thermal principle. Its minimum and maximum accurate response is 0.2-11.0 gpm in a 5 inch well. For the same coal aquifer thickness and injection head its lower range of permeability is approximately 15 md. The only method we know at present to operate in this range is to use radioactive tracers which must be licensed or hole to hole air flow tests. The results of air injection are often inconclusive due to two phase flow.[23]

Figures 5 and 6 illustrate two very different downhole flow profiles determined by using the new thermal downhole flow tool. These were taken on sedimentary formations in the Powder River Basin of Wyoming. Maximum flow is observed at the top of the aquifer where the open hole begins. As flow rate declines uniformly it implies that permeability is approximately the same throughout the entire thickness of the aquifer. On the other hand a sharp decline in flow indicates larger fluid acceptance of the adjacent zone and therefore higher permeability.

Figure 5 displays a flow log indicating the highest permeability

*Proprietary Tool with In-Situ Consulting Developed by C. B. McKee

FIGURE 4 DOWNHOLE FLOW TOOL BEING CENTERED OVER WELL PRIOR TO LOGGING

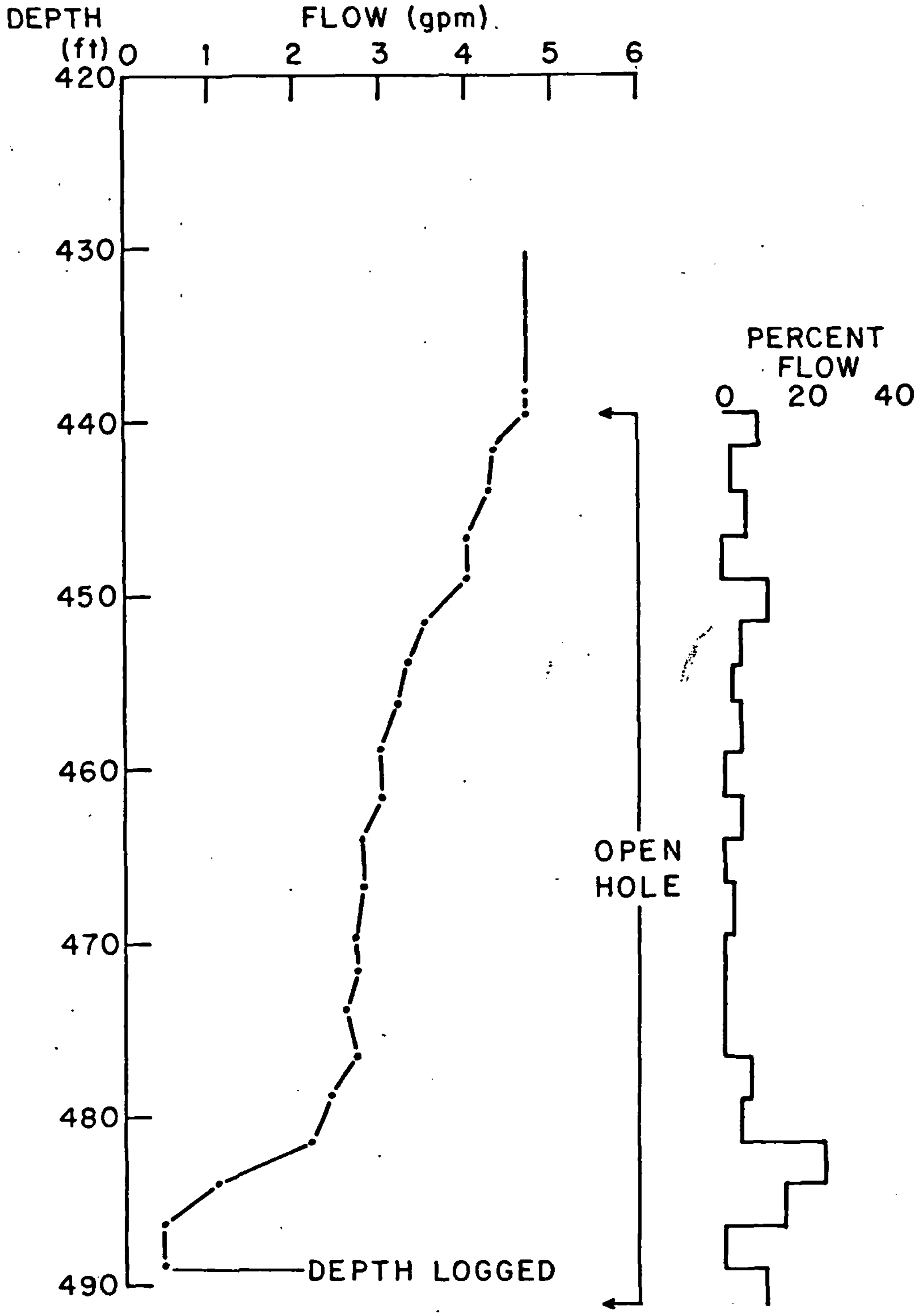


FIGURE 5 DOWNHOLE FLOW LOG EXHIBITING HIGHEST PERMEABILITY AT THE BOTTOM OF THE AQUIFER. THIS CONDITION IS FAVORED FOR SUCCESSFUL LINKING AND FORWARD GASIFICATION.

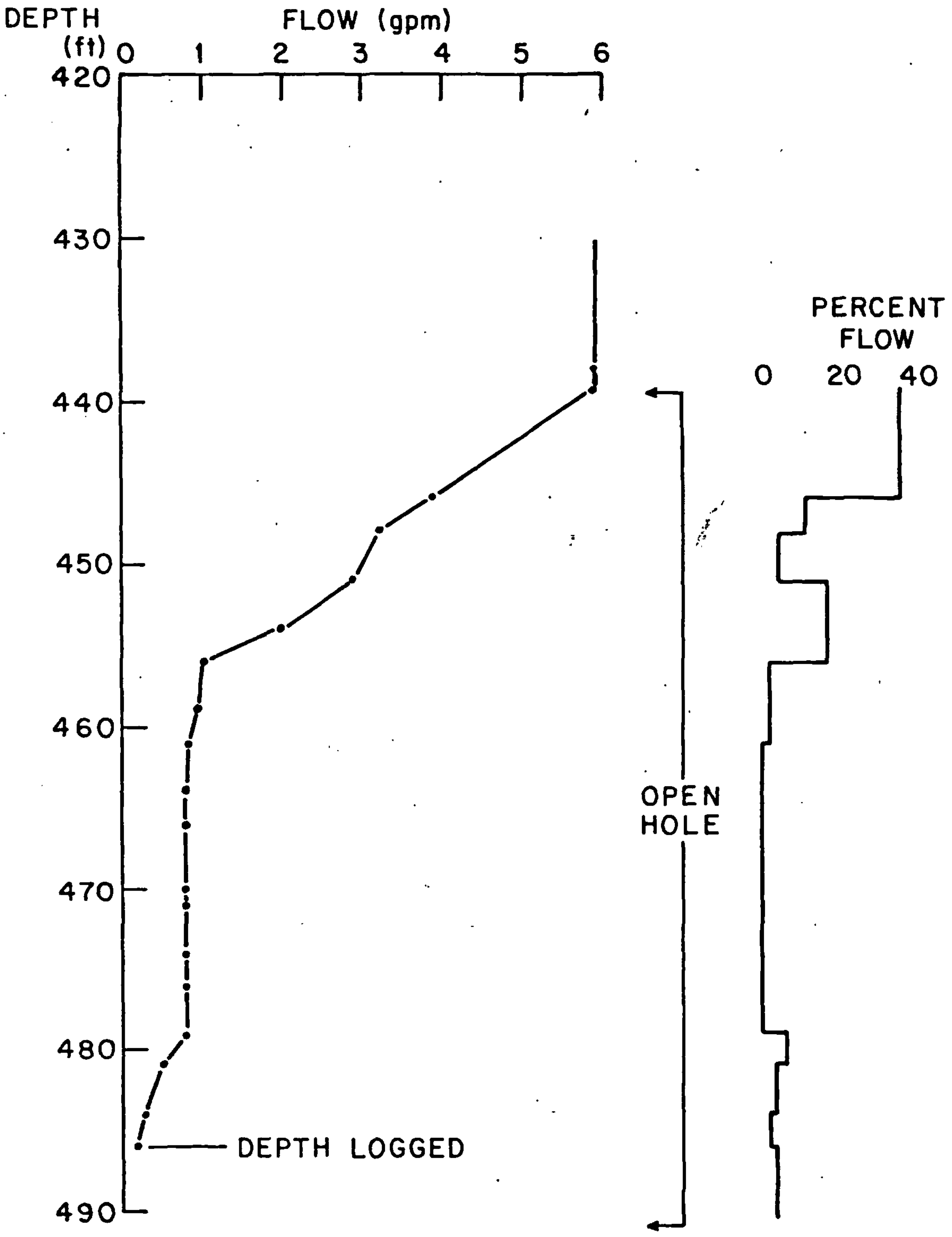


FIGURE 6 DOWNHOLE FLOW LOG EXHIBITING HIGHEST PERMEABILITY AT THE TOP OF THE AQUIFER. THIS SITUATION IS UNFAVORABLE TO GASIFICATION SINCE IT TENDS TO PRODUCE OVERRIDE CONDITIONS AND BYPASSING OF THE BULK OF THE COAL.

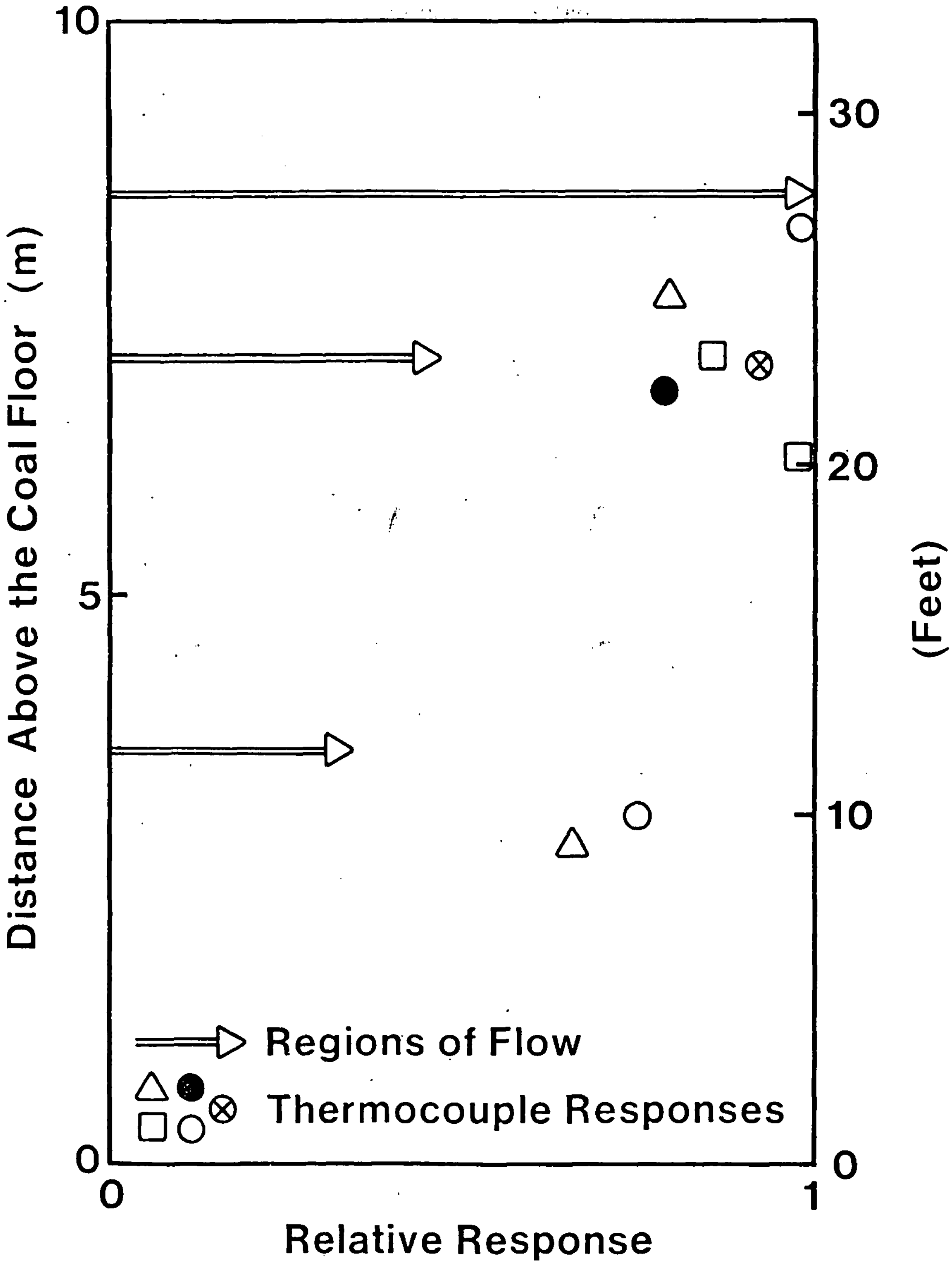


FIGURE 7 VERTICAL FLOW PROFILE AT HANNA IV. FLOW IS HIGHER AT TOP OF SEAM FAVORING COMBUSTION OVERRIDE AS VERIFIED BY THERMOCOUPLE RESPONSE.

at the bottom of the aquifer. Combined with a high ratio of horizontal to vertical permeability this situation is ideal for reverse combustion linking and forward gasification since the flow would be confined to the lower part of the seam. Conversely, the aquifer in Figure 6 is unfavorable for gasification since the permeability is highest in the upper portions of the aquifer. This situation tends to produce override conditions and hence incomplete gasification. However, if the ratio of horizontal to vertical permeability is favorable and well spacing is restricted then successful gasification may still occur. (The precise spacing would have to be obtained from a flow model together with other hydrologic data.) Figure 7 shows a flow profile for Hanna IV. As previously discussed this situation favors override and incomplete gasification. Thermal response indicates that this was indeed the case. The override was at first thought to be due to prior cementing in well completion.[11] However, reworking the wells using a cement squeezing technique produced little improvement.[25] Well completion is obviously important to in-situ processes. The simplest explanation for the override appears to lie in the spacing of wells and the vertical permeability profile. As in many natural phenomenon, the path of least resistance prevails over the seemingly shortest route. As recognized by Bartel[23] downhole flow logging is an essential element in evaluating a site for in-situ gasification.

Discussion

Based on the results of this phase, a preliminary assessment of the hydrology is obtained. If the permeability is too low then the lease may be rejected. If the overlying sand possesses high transmissivity and leakage or major water influx is anticipated as a result of monitoring adjacent aquifers during pump tests, again the lease may be rejected. If the coal seam possesses high permeability at the top as determined from flow log analysis and seam thickness does not economically warrant the close spacing required to prevent override, then the lease may be rejected. Any of the three hydrologic criteria-permeability, leakage, unfavorable permeability stratification may cause the lease to be rejected.

However, if results are favorable in all or a substantial fraction of the tests, then the data base may be expanded to confirm or provide better definition of the suitable areas as well as additional data for engineering and economic evaluation. This is the purpose of phase II hydrologic testing.

3.2.3 Hydrologic Evaluation Phase II--Expansion of Data Base

From phase I, a preliminary impression of the variability in hydrology is obtained. A simple geologic model is helpful to understand the reasons for the variability. It is also valuable as an aid in planning phase II well locations and their design. A conceptual diagram[26] of sedimentary deposition and coal bed formation is shown in Figure 8. While the model is made in Fort Union coal it is thought to be widely applicable to coals in other formations.[27] In this model, coal is found in the poorly drained swampy regions between stream channels. A typical paleo channel is shown in the figure together with adjacent material on either side. In the Powder River Basin the distance between channels varies from five miles to tens of miles.[27] For the Hanna Basin the distance between channels is on the order of miles.[27] The coarsest material is found nearest the stream channels and grades into finer silts and clays and shales at the midpoint between them. Permeability is therefore highest near the channel and least at the midpoint. The thinnest coal is found in the channel area and separated from permeable aquifers by leaky layers exhibiting poor confinement. Water influx in this zone has a high probability of being detrimental to successful gasification. Coal nearest the channel, area termed well drained swamp in Figure 8, may have to be deleted from underground coal gasification (UCG) reserve. The coal at Lawrence Livermore Laboratory's Hoe Creek site was evidently in this category.[27]

As we proceed toward the area between the channels, coal thickness and sediments exhibit progressively lower permeability. Water influx problems tend to be minimized due to more effective confinement and isolation of coal seams. Also the surrounding material is less capable of transmitting significant quantities of water.

While the above model is qualitative, it does strongly indicate

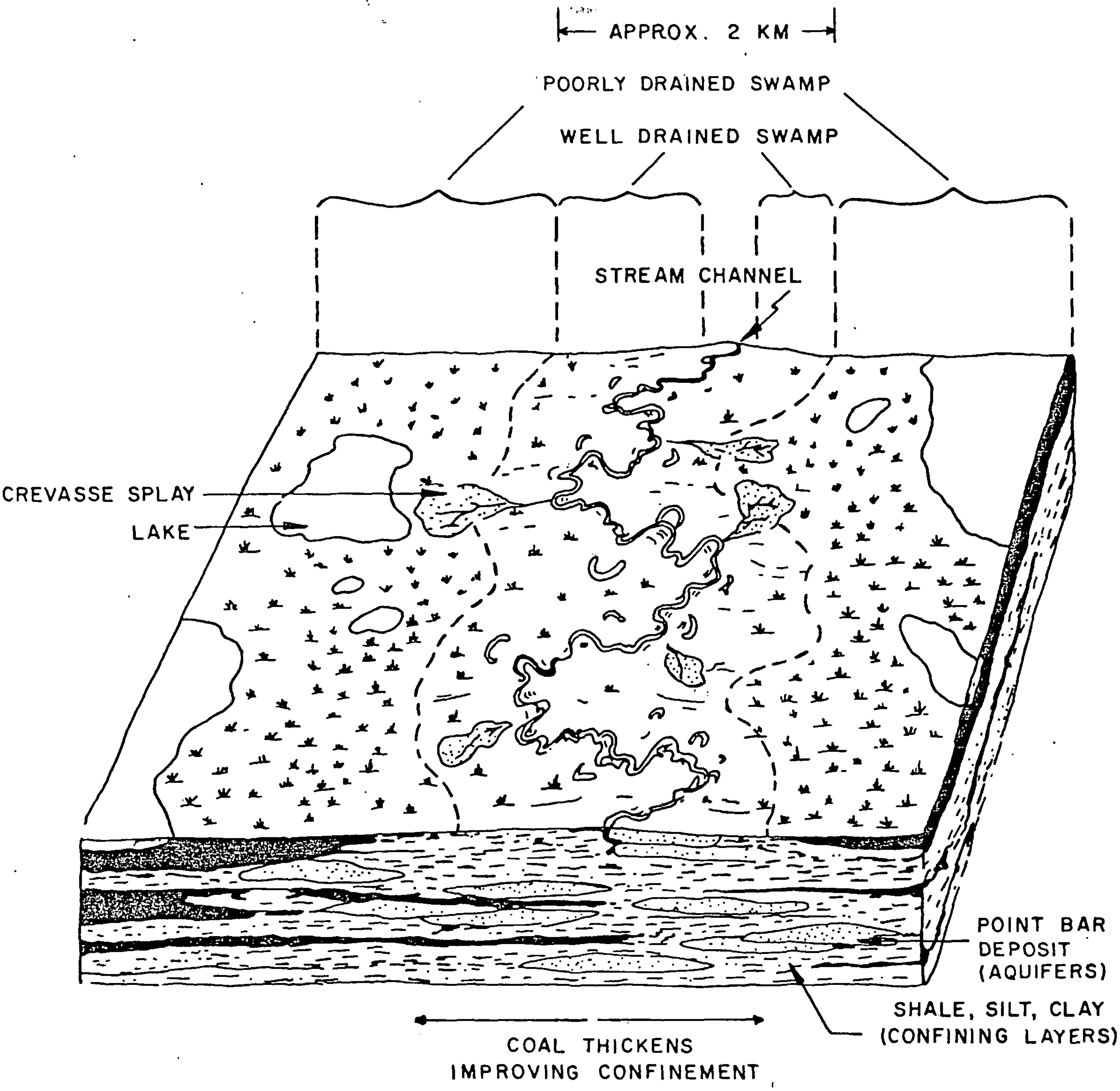


FIGURE 8 TYPICAL PALEO CHANNEL ILLUSTRATING PATTERNS OF SEDIMENTATION AND COAL FORMATION. IN GENERAL THICKER COAL AND BETTER CONFINING CONDITIONS FOR UCG ARE FOUND AWAY FROM THE CHANNEL. (AFTER BEAUMONT[26])

that the most favorable sites for UCG are found in the areas between the paleo channels.

The above discussion underscores the important role of geology in understanding the hydrology of the site. The two disciplines must work together to produce a clearer picture of the complex hydrology involved. Using the results of phase I hydrology the lithologic description can be improved. Phase I hydrology wells are more in the nature of exploration wells. If the hydrology emerging appears unfavorable we may desire to confirm the results with a few additional wells before finally rejecting the lease.

Having decided that the lease merits further evaluation, the work in phase II proceeds in two stages. Stage 1 is for the purpose of defining coal areas within the lease boundary which are most likely to be amenable to underground coal gasification. Stage 2 involves placement of additional wells to gather more precise hydrologic data in favorable areas for preliminary engineering design of well spacing and economic evaluation.

Stage 1

If substantial areas of the lease appear favorable while others do not, additional wells are required to delineate coal reserves for UCG. The remaining coal must remain a resource, awaiting some as yet undiscovered process for its utilization. The number of wells required to accomplish the definition of coal reserves is a question which must be answered in the context of site specific cases. The available hydrologic data should be used in conjunction with geology to form a model of the area along the lines we have previously discussed. This model will serve as a guide in placement of wells and be undated as new information arrives. The wells used in this stage would be similar to those in phase I. Depending on the problem (low permeability, leakage and water influx, or unfavorable permeability stratification), wells would be designed accordingly to investigate the problem.

Stage 2

In those areas deemed favorable for in-situ coal gasification we now place additional wells to obtain improved data for engineering design and economic evaluation purposes. These wells would be completed as partially penetrating wells. They would be open only in the bottom portion of the formation similar in design to linking and gasification wells. The spacing between the wells would be such that the ratio of horizontal to vertical permeability could be adequately determined.

Pairs of partially penetrating wells are useful for simultaneously measuring transmissivity,storage coefficient, leakage, the ratio of vertical to horizontal permeability and true aquifer thickness which to now has been inferred from logs.

Based on the Theis or Hantush's type curve method the data is fitted to obtain approximate ranges for the dimensionless variables involved. Equation A-23 from the Appendix is then used to generate type curves to match the data. In a properly conducted test the data should lie on nearly the entire type curve except very early in time where a deviation is commonly observed due to wellbore storage effects in the pumped well.

Two examples are given in Figures 9 and 10 from wells in Wyoming which were used to evaluate a property for in-situ recovery. All parameters are determined by a best fit type curve to the data. Figure 9 shows a match illustrating the parametric effect of thickness. This well is open to the aquifer in the bottom 20 ft. and is interesting since geologists anticipated from logs and core that the aquifer thickness would be only 60 ft. The impermeable nature of the upper confining layer, its thickness and continuity strongly suggest the smaller thickness. The fact that the effective thickness is 245 ft. was substantiated by the excellent match to the type curve and response

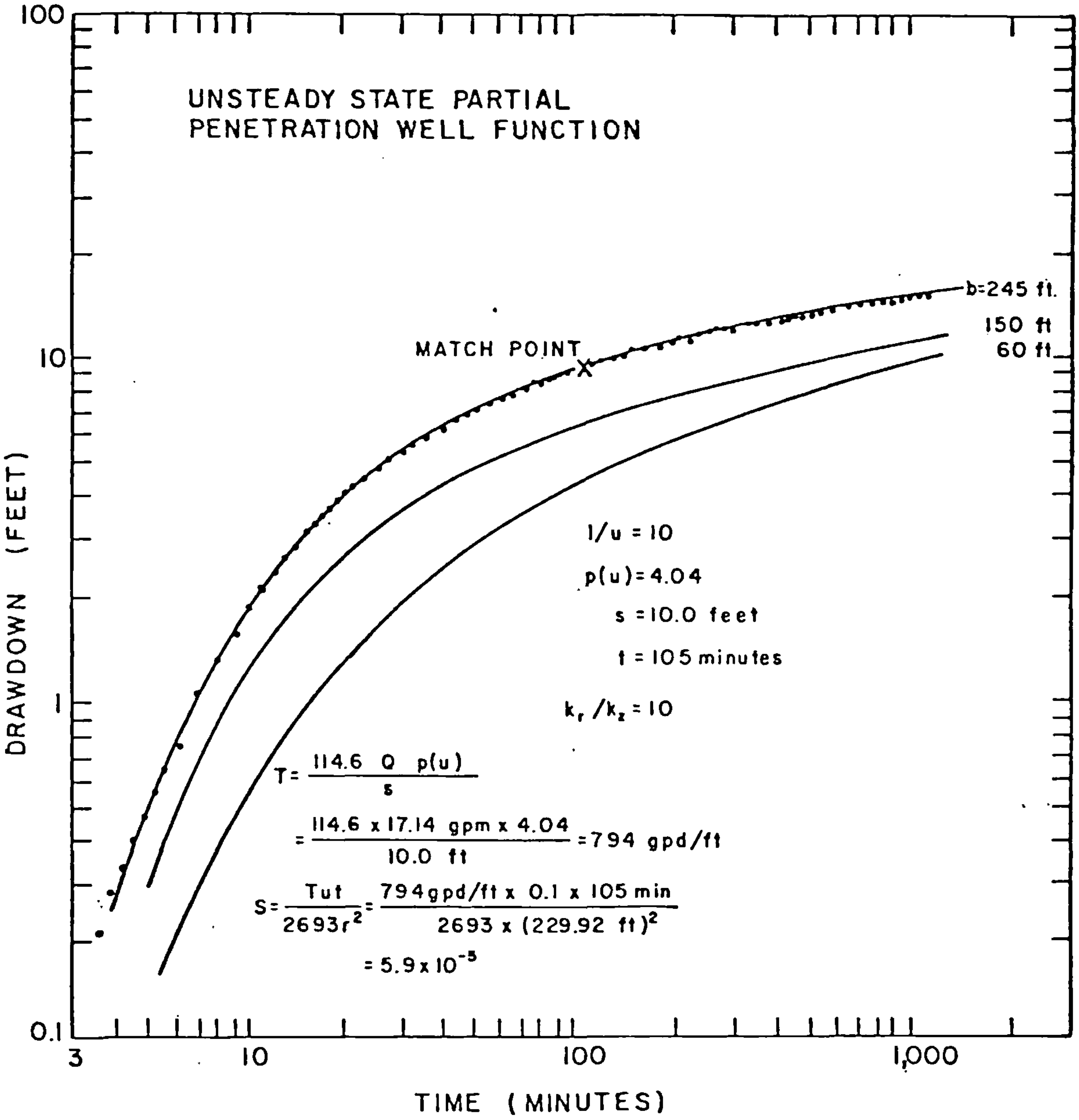


FIGURE 9 HISTORY MATCH OF PUMP TEST DATA TO THREE-DIMENSIONAL TYPE CURVE (SPECIAL CASE OF RADIAL AND AXIAL SYMMETRY) ILLUSTRATING THE PARAMETRIC EFFECT OF VARYING THICKNESS.

of a well in the upper layers during the test. In this instance we believe that unplugged drill holes were responsible. The confining layer is totally ineffective. From the point of view of water influx this situation would be highly detrimental to underground coal gasification. If the confining layer is partially effective in limiting water influx then the data would match a type curve indicating reduced aquifer thickness and leakage. Unplugged drill holes can occur from previous mineral exploration or from a lack of adequate supervision during intensive coring and logging of a given pilot site.

Figure 10 shows a type curve match showing the effect of varying the ratio of horizontal to vertical permeability. The high ratio of 10 in this case would be excellent for UCG.

Discussion

The phase II hydrologic study has been divided into two stages. In the first stage leases, which are on the order of square miles, are further evaluated to delineate reserves amenable to underground coal gasification. Stage II was concerned with gathering further data using two well pairs for engineering and economic evaluation. This data would be used in flow models to determine factors such as optimum flow rate.

Anisotropy or directional permeability has not yet been addressed and has an effect at this stage. The two well tests measure the true geometric mean transmissivity (T_r in the Appendix) and ratio of horizontal to vertical permeability. Leakage and storage coefficient are to some extent affected by directional permeability. Aquifer thickness is only slightly affected. These errors due to anisotropy fall within the fluctuations in values normally encountered owing to random heterogeneities.

Assuming the property has passed phase I and II testing and justifies commercialization, the next logical step is to use intensive multi-well tests on a few selected sites which are candidates for

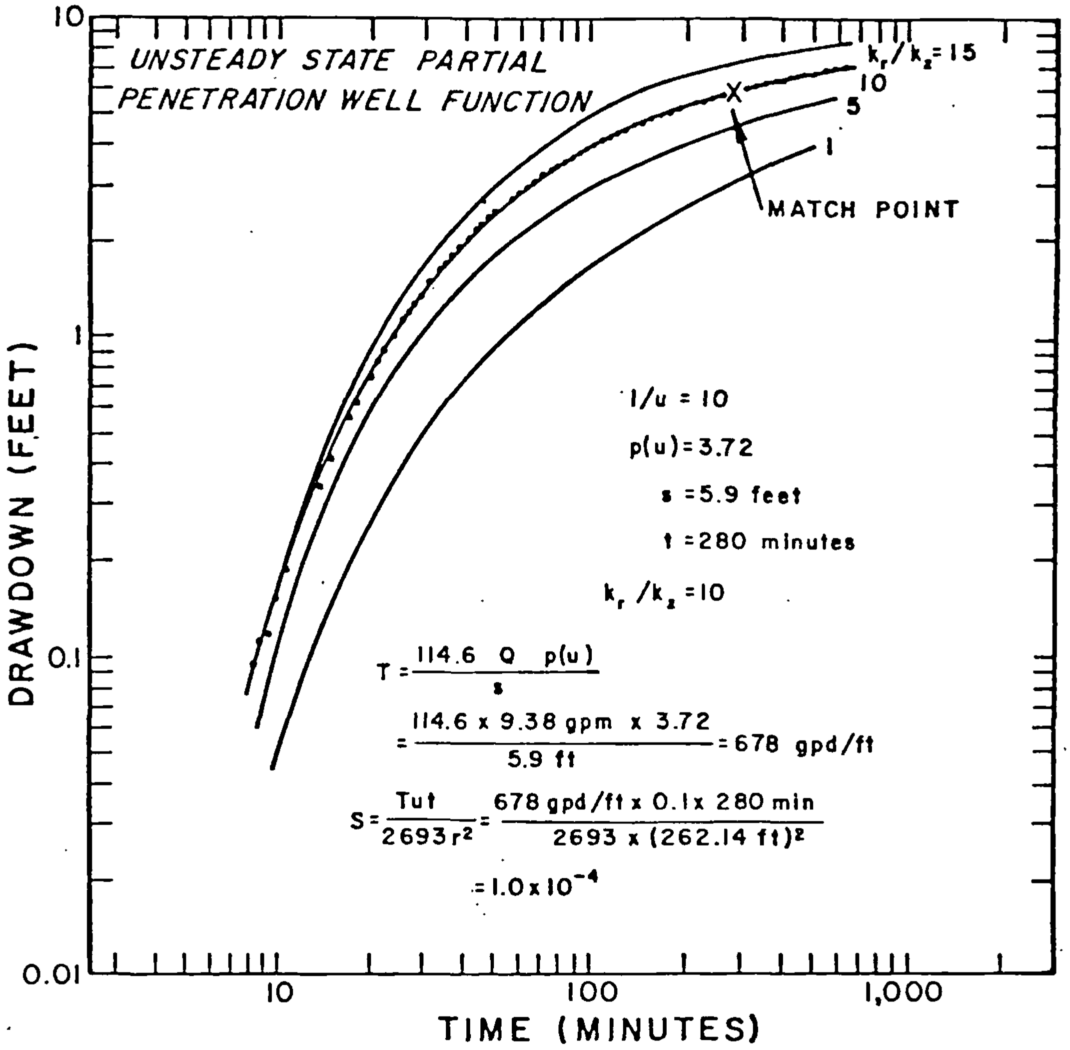


FIGURE 10 HISTORY MATCH OF PUMP TEST DATA TO THREE-DIMENSIONAL TYPE CURVE (SPECIAL CASE OF RADIAL AND AXIAL SYMMETRY) ILLUSTRATING THE PARAMETRIC EFFECT OF VARYING RATIO OF HORIZONTAL TO VERTICAL PERMEABILITY

pilot testing. This will obtain more precise data and more importantly directional permeability which will be used to orient injection and production wells for gasification.

3.2.4 Hydrologic Evaluation Phase III--Pilot Site Evaluation

At this point one should have a good appreciation of the hydrology of the site. In addition to the factors we have mentioned we assume that maps have been made of the piezometric surface, transmissivity, leakage, and other parameters in relation to the coal isopach map. This information should be sufficient to identify several potential sites for pilot testing. There, sites would be the subject of more intensive hydrologic studies. The results would be used to plan the wellfield, interpretation of pilot operation, and environmental purposes. The pilot sites would be located near previously drilled wells to reduce costs and take advantage of hydrologic data already acquired.

The theory we use combines the partially penetrating leaky formula of Hantush[21] with that of Papadopulos[22], which only treats non-leaky fully penetrating well conditions. Our approach is given in the Appendix.[28] Equation A.23 is the result and includes the three-dimensional components of permeability (k_x, k_y, k_z). To find the components of permeability a minimum of 4 wells (1 pumping or injecting and 3 observation) are required. The pumped well and at least 1 observation well must be partially penetrating. All observation wells must lie in three different directions about the pumped well. Our method of finding the areal components of transmissivity (T_x, T_y) and hence permeability is identical to that of Papadopulos. The complete matching technique is listed in the Appendix.

If the formation were homogeneous and isotropic then only three wells would be required to solve for both areal and vertical permeabilities. However most formations are both heterogeneous and anisotropic. In coal the primary anisotropy is due to fractures with smaller effects attributable to the pattern of sedimentation. Depending on the spacing and angular distribution of these features in relation to the wells, various three-well combination can yield dramatically different results. Different results can be obtained due to some wells being near high permeability fractures while others are not. Virtually every site we have examined has displayed this phenomenon. Even though spatial variability in permeability is a fact of life, acceptable engineering data can still be obtained.

We illustrate our approach using the example of Figure 11. In this case the coal-shale sequence under the lower sand formed an impermeable lower boundary. We were interested in the directional permeability of the lower sand and vertical permeability of coal layer separating the upper sand from the lower. From the outcrop the lower sand was expected to display fractured permeability.

A pump test was performed using OB-1 as the pumped well. The computed directional transmissivities, with different well combinations are shown in Table 1. The discrepancy resulting from different well combinations is a clear indication that the formation is not homogeneous. As mentioned previously the heterogeneities and therefore variations in orientation are attributed to the presence of fractures. Adopting this hypothesis, a directional frequency diagram may be constructed by plotting the major direction of permeability for each workable three-well combination on a frequency diagram as 1 unit. By doing so an interesting result is obtained as displayed in Figure 12. The direction of highest frequency is in good agreement with the observed orientation of the predominant fracture in the outcrop area. The frequency diagram indicates the presence of several minor sets of fractures, some of which are also in agreement with the outcrop observations.

To obtain an average directional permeability all observation wells were used in a computer program to obtain:

T_{major} = 1402 gpd/ft (2.3 darcies)

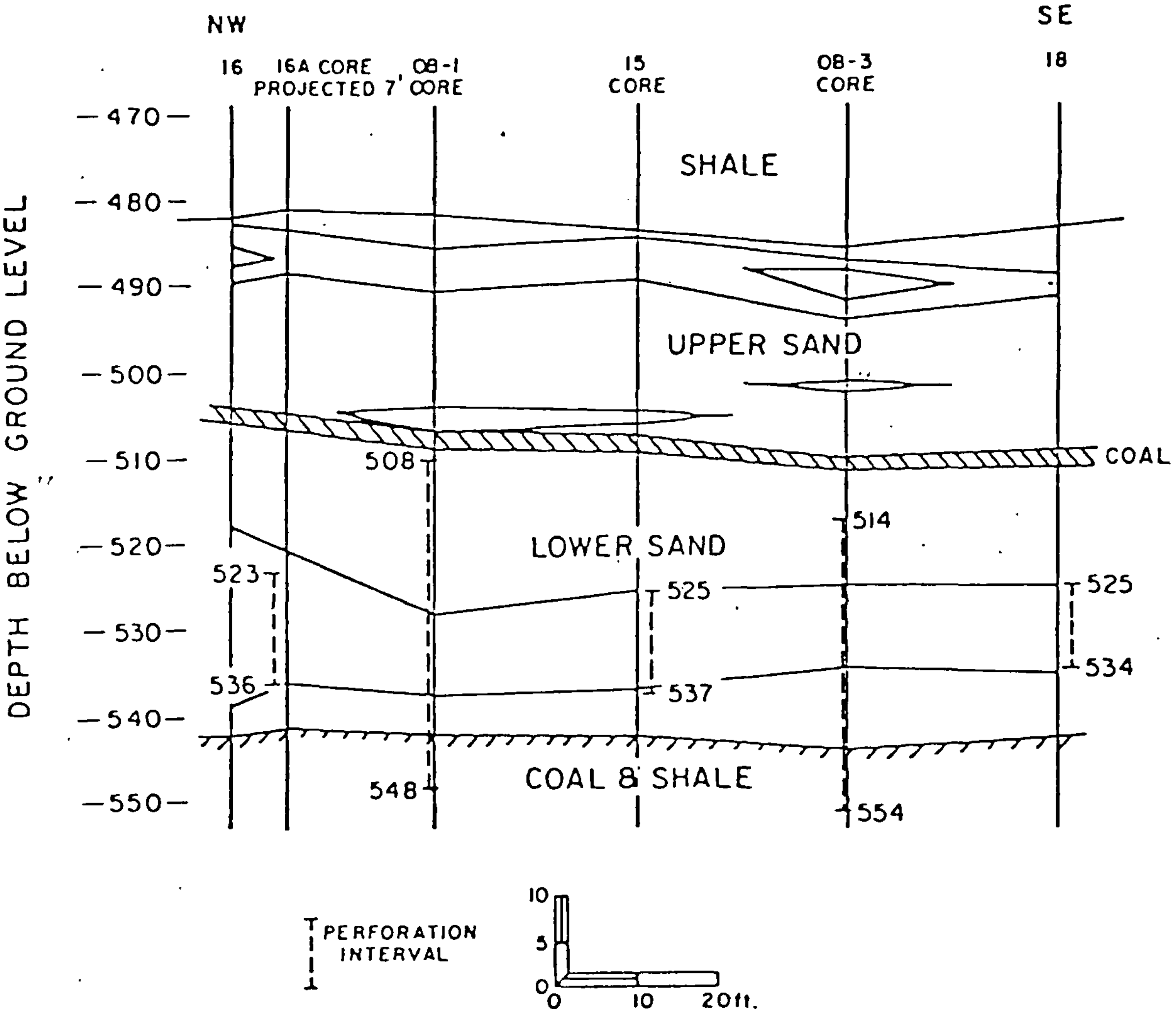


FIGURE 11 NORTHWEST-SOUTHEAST CROSS SECTION THROUGH A PILOT PATTERN IN WYOMING. THE LOWER SAND BETWEEN COAL LAYERS WAS EVALUATED TO PRIMARILY ASSESS DIRECTIONAL PERMEABILITY

TABLE 1 DIRECTIONAL TRANSMISSIVITIES FOR VARIOUS THREE-WELL COMBINATIONS CORRESPONDING TO FIGURE 12

WELL NOS.	TRANSMISSIVITY (gpd/ft)			DIRECTOR OF MAJOR TRANSMISSIVITY	STORAGE COEFFICIENT
	MAJOR	MINOR	MEAN		
082, 083, 19	963	432	645	N 79° E	1.9×10^{-4}
082, 18, 19	1013	439	667	N 45° W	1.9×10^{-4}
082, 20, 23	1815	598	1042	N 15° W	1.2×10^{-4}
083, 17, 19	766	274	458	N 75° E	1.2×10^{-4}
11, 17, 23	1980	410	901	N 39° W	7.2×10^{-5}
11, 20, 23	2196	487	1034	N 42° W	8.6×10^{-5}
15, 17, 19	1344	156	458	N 47° E	1.2×10^{-4}
17, 18, 19	850	271	480	N 44° E	1.2×10^{-4}
17, 19, 23	1205	390	686	N 63° E	2.0×10^{-4}
17, 20, 22	1203	411	703	N 32° W	6.9×10^{-5}
17, 20, 23	1724	424	855	N 40° W	7.5×10^{-5}
18, 20, 23	2127	346	857	N 2° E	9.4×10^{-5}
20, 22, 23	1611	515	911	N 31° W	9.2×10^{-5}
ALL WELLS EXCEPT I-11	1252	333	645	N 14° W	7.2×10^{-5}
ALL WELLS	1402	332	682	N 37° W	6.9×10^{-5}

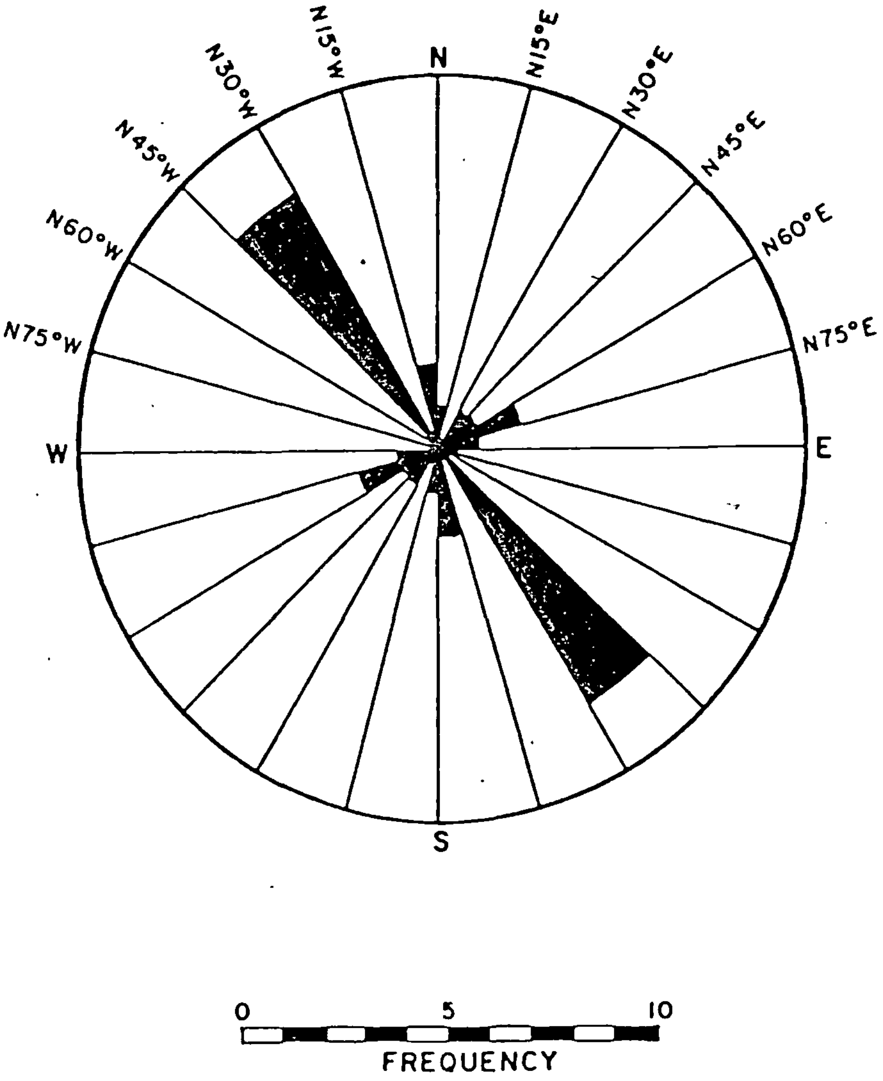


FIGURE 12 FRACTURE FREQUENCY DIAGRAM AS DETERMINED FROM HYDROLOGIC TESTING

T_{minor} = 332 gpd/ft (.5 darcies)

Geometric Mean = 682 gpd/ft (1.1 darcies)

Direction of Major Transmissivity = N 37° W

The major and minor directions are in excellent agreement with the drawdown contour map given in Figure 13. The geometric mean permeability is also in good agreement with the mean value of measurements from single well analysis.

Using the above average values for directional permeability and the permeability of the upper shale-lignite confining layer was calculated to be .6 md. Results indicate that the coal zone separating aquifers acts as a semipermeable layer.

A second pump test using the partially penetrating well no. 15 resulted in a ratio of horizontal to vertical permeability of one which would be expected of pervasive vertical fractures.

We have obtained many frequency diagrams over the past several years. To date the resulting frequency plots have been in very good agreement which the geology. In sedimentary deposits the frequency diagram represents the direction of paleo currents or small stream channels largely parallel to the direction of sedimentation. A frequency diagram together with the drawdown contours are given in Figures 14 and 15. Again both types of plots are in excellent agreement.

To obtain results representative of the geology, care should be exercised in the selection of the pump test well pattern. Figure 16 shows one arrangement of wells we have found satisfaction. All wells were in different directions producing a maximum of 20 unique three-well combinations. Three are selected close to the pumped well to provide sufficient sensitivity to determine the ratio of horizontal to vertical permeability. Wells furthest removed from the pattern together with interior wells provide a larger scale average of directional permeability. These wells can also serve as monitor

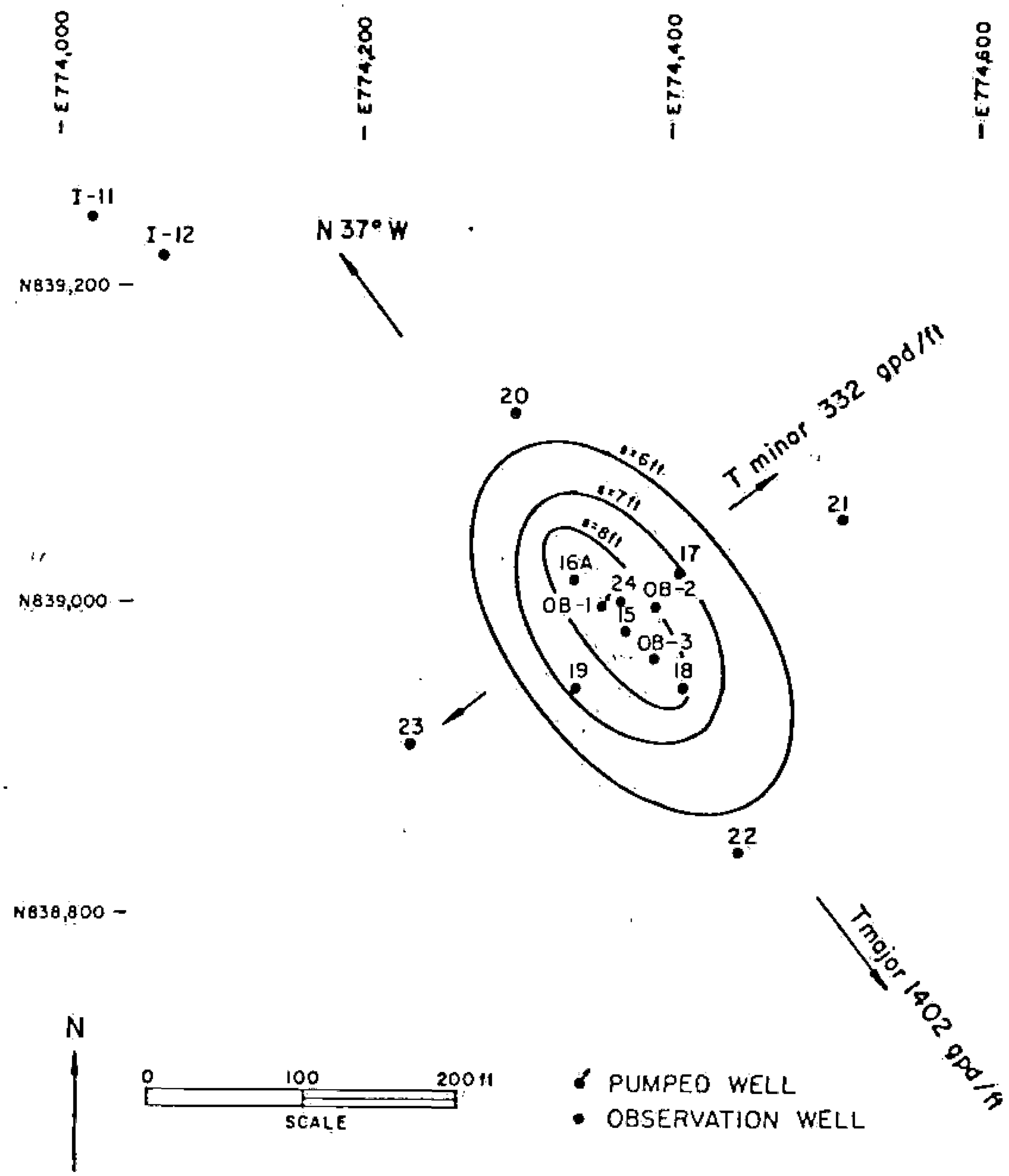


FIGURE 13 DRAWDOWN CONTOUR MAP DISPLAYING MAJOR AND MINOR DIRECTIONS OF TRANSMISSIVITY. THE CONTOURS ARE IN EXCELLENT AGREEMENT WITH THE FREQUENCY DIAGRAM OF THE PREVIOUS FIGURE.

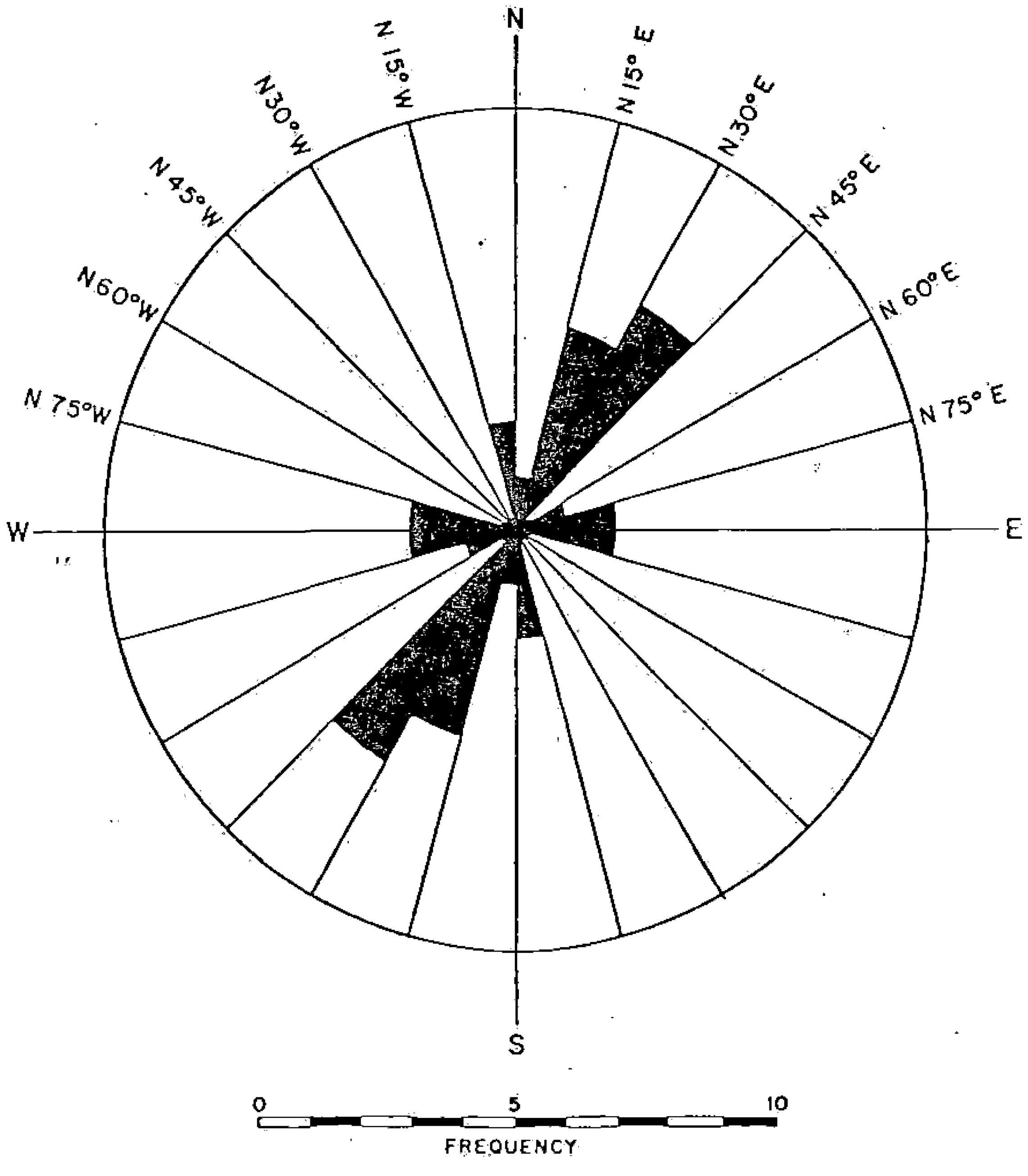


FIGURE 14 FREQUENCY MAP OF MAJOR COMPONENT OF DIRECTIONAL TRANSMISSIVITY REFLECTING THE ORIENTATION OF PALEO CURRENTS IN A SEDIMENTARY DEPOSIT AS DETERMINED FROM HYDROLOGIC TESTING

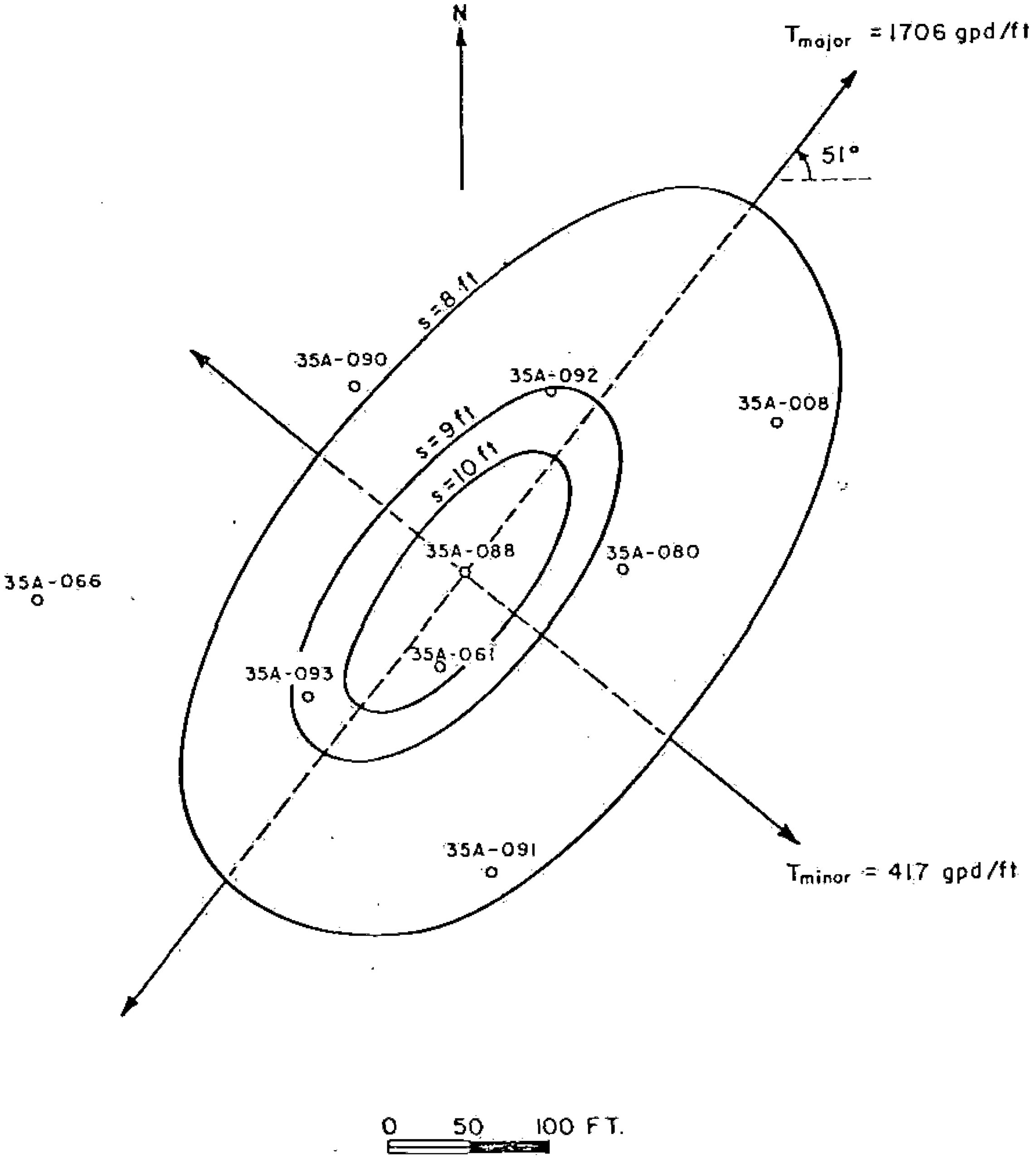


FIGURE 15 DRAWDOWN CONTOUR MAP SHOWING THE MAJOR AND MINOR DIRECTIONS OF TRANSMISSIVITY. THE MAJOR DIRECTION OF PERMEABILITY CORRESPONDS CLOSELY TO THE PALEO CURRENT FREQUENCY DIAGRAM OF THE PREVIOUS FIGURE.

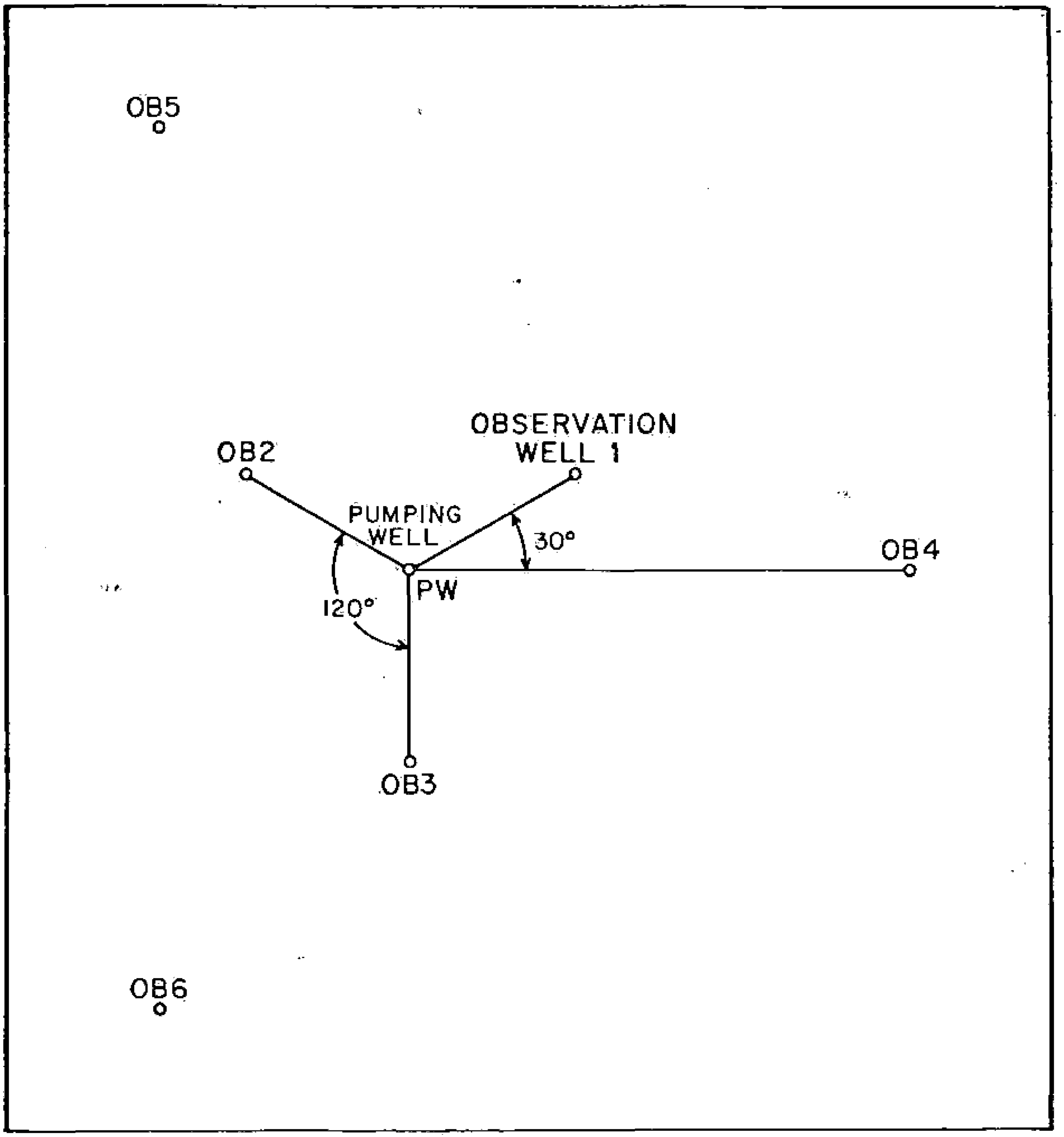


FIGURE 16 RECOMMENDED PUMPING AND OBSERVATION WELL LAYOUT FOR PILOT SITE PUMP TESTING

for environmental purposes during the pilot test.

Discussion

Using the measured directional permeability, wells can be spaced and oriented properly for air acceptance and pilot testing. The well pattern we suggest using is no more costly and in some instances less costly than others used in previous hydrologic evaluation of sites for in-situ coal gasification. The analytical techniques are more tedious to apply. However they are more complete in the sense that more parameters are accounted for simultaneously thereby increasing the accuracy of the analysis.

SUMMARY AND CONCLUSIONS

The reactor vessel for underground coal gasification will be formed underground and therefore removed from direct observation. To insure proper formation of the reaction zone and flow paths as well as prevent undesirable leakage certain general criteria must be met. These include the absence of major aquifers, good confining layers exhibiting little or no leakage, adequate permeability to allow sufficient injection of gases to produce reasonable linkage rates, a favorable ratio of horizontal to vertical permeability, favorable stratification in permeability, and a knowledge of directional permeability to properly align injection and production wells. The limiting values in each case must be decided using flow models and economic criteria for each property.

New formulations have been introduced for interpreting pump test data. These are more naturally suited to evaluating deposits for in-situ recovery. Also a highly sensitive downhole flow logging tool has been developed to aid in measuring vertical variations in permeability.

We have outlined a phased approach to site or property evaluation having several decision points. By following this procedure a property can be evaluated as to whether it should be retained for further development or abandoned. Using this approach, expenditures of evaluating and selecting sites for UCG should be minimized.

The methods we outline involve more analytical effort in data analysis, especially for characterizing a pilot site. However they do not entail additional cost in wells or field time over previously used techniques.

A review of in-situ coal gasification to date reveals that hydrologic site characterization has either not been performed prior to testing, or not been utilized in site selection and test design. The disappointing results obtained at Hanna IV and Hoe Creek fall into the former and latter categories respectively. Problems with Hanna IV were also further compounded by well completion difficulties.

The task of site characterization is a search for the proper underground conditions for the process in relation to coal seam depth, thickness, composition, and economic factors.

Every site is not amenable to underground coal gasification. Some properties such as Hoe Creek, for example, should not have been gasified. It is pointless to perform detailed site characterization if we are committed to gasification regardless of the results. Site characterization is a two-edged sword. If we perform it, we must be prepared to abandon the property site for another if the results are unfavorable.

In selecting sites for in-situ gasification, care must be taken that the site is located in areas which are the most likely targets for UCG. Very little attention has been devoted to this aspect of site selection. Based on available data and a widely accepted model of coal formation we believe that a site such as Hoe Creek was not typical of the coal and confining conditions constituting bulk of UCG reserves in the Powder River Basin.

APPENDIX - THEORY FOR THREE-DIMENSIONAL PERMEABILITY DETERMINATION

A.1 Theory

In terms of drawdown(s), the differential equation for flow in a homogeneous, anisotropic (3-D), leaky aquifer can be expressed as follows (Figure A-1):

$$S_s \frac{\partial s}{\partial t} = K_{xx} \frac{\partial^2 s}{\partial x^2} + 2K_{xy} \frac{\partial^2 s}{\partial x \partial y} + K_{yy} \frac{\partial^2 s}{\partial y^2} + K_{zz} \frac{\partial^2 s}{\partial z^2} - \frac{K'}{b'} \frac{s}{b} \qquad (A.1)$$

where K_{xx}, K_{yy} and K_{xy} are the components of hydraulic conductivity tensor of the aquifer, S_s is the storage coefficient per unit thickness, b is aquifer thickness, K' is the hydraulic conductivity of the semi-confining layer and b' is the thickness of the semi-confining layer. Multiplying equation (A.1) by b gives

$$S \frac{\partial s}{\partial t} = T_{xx} \frac{\partial^2 s}{\partial x^2} + 2T_{xy} \frac{\partial^2 s}{\partial x \partial y} + T_{xy} \frac{\partial^2 s}{\partial y^2} + T_{zz} \frac{\partial^2 s}{\partial z^2} - \frac{K'}{b'} s \qquad (A.2)$$

where T_{xx}, T_{xy}, and T_{yy} are components of the transmissivity tensor of the main aquifer and S is the storage coefficient and

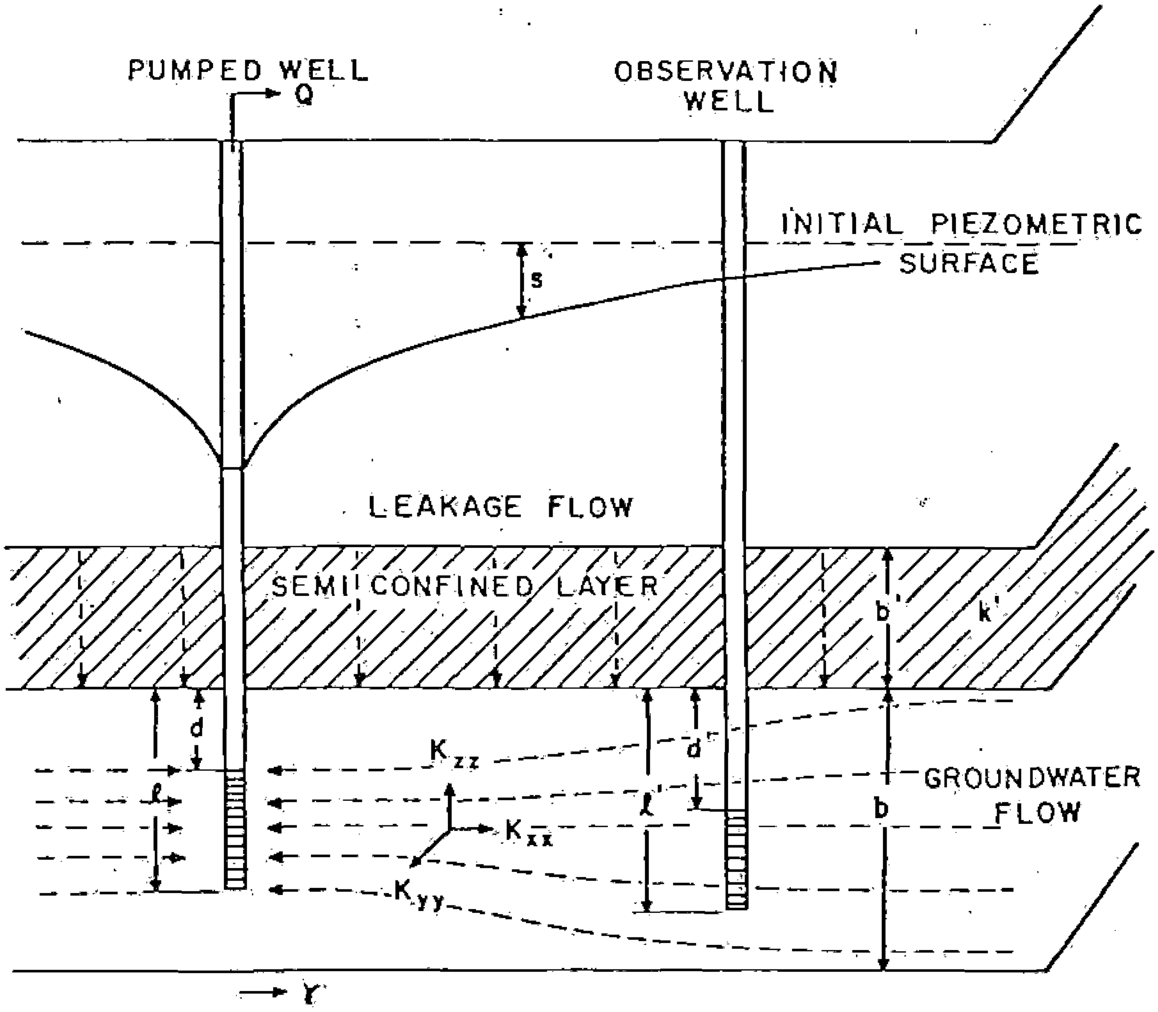
$$T_{zz} = K_{zz} b \qquad (A.3)$$

Define a new coordinate

$$r = \frac{1}{T_r^{1/2}} (T_{xx} y^2 + T_{yy} x^2 - 2T_{xy} xy)^{1/2} \qquad (A.4)$$

with

$$T_r = (T_{xx} T_{yy} - T_{xy})^{1/2} = (T_X T_Y)^{1/2} \qquad (A.5)$$



Diagrammatic Representation of Partially Penetrating Wells in a Leaky Artesian Aquifer

Figure A-1

where T_X and T_Y are the principle transmissivities and T_r is the geometric mean transmissivity and is invariant to change in coordinates. Equation (A.1) therefore can be reduced to

$$S \frac{\partial s}{\partial t} = T_r \left(\frac{\partial^2 s}{\partial r^2} + \frac{1}{r} \frac{\partial s}{\partial r}\right) + T_{zz} \frac{\partial^2 s}{\partial z^2} - \frac{K'}{b'} s \qquad (A.6)$$

Dividing by T_r to obtain

$$\frac{1}{\nu} \frac{\partial s}{\partial t} = \frac{\partial^2 s}{\partial r^2} + \frac{1}{r} \frac{\partial s}{\partial r} + \frac{T_{zz}}{T_r} \frac{\partial^2 s}{\partial z^2} - \frac{K'}{b'} \frac{s}{T_r} \qquad (A.7)$$

where

$$\nu = T_r/S \qquad (A.8)$$

Define the

$$B_r^{\ 2} = T_r/(K'/b') \qquad (A.9)$$

and let

$$z = z'(T_{zz}/T_r)^{\frac{1}{2}} = z'(K_{zz}/K_r)^{\frac{1}{2}} = z'(k_{zz}/k_r)^{\frac{1}{2}} = \alpha z' \qquad (A.10)$$

where k_{zz} is the vertical permeability and k_r is the geometric mean permeability

$$K_r = (K_{xx}K_{yy} - K_{xy})^{\frac{1}{2}} = (K_X K_Y)^{\frac{1}{2}} \qquad (A.11)$$

K_r is called the geometric mean hydraulic conductivity. K_X amd K_Y are the major and minor hydraulic conductivities.

$$k_r = (k_X k_Y)^{\frac{1}{2}} \qquad (A.12)$$

k_X and k_Y are the major and minor permeability and

$$\alpha = (k_{zz}/k_r)^{\frac{1}{2}} \tag{A.13}$$

Therefore, we obtain

$$\frac{1}{\nu}\frac{\partial s}{\partial t} = \frac{\partial^2 s}{\partial r^2} + \frac{1}{r}\frac{\partial s}{\partial r} + \frac{\partial^2 s}{\partial z'^2} - \frac{s}{B_r^{\,2}} \tag{A.14}$$

The equation is now identical to the one used by Hantush[21] in example 9.

From an examination of the boundary conditions (Figure A-1), we have

$$s(r,z,o) = 0 \tag{A.15}$$

$$s(\infty,z,t) = 0 \tag{A.16}$$

$$\frac{\partial s(r,o,t)}{\partial z} = \frac{\partial s(r,b,t)}{\partial z} = 0 \tag{A.17}$$

$$\lim_{r\to 0}\left\{(\ell-d)\,2\pi r K_r \frac{\partial s}{\partial r}\right\} = 0 \qquad 0<z'<d/\alpha \tag{A.18}$$

$$= -Q \qquad d/\alpha<z'<\ell/\alpha \tag{A.19}$$

$$= 0 \qquad \ell/\alpha<z'<b/\alpha \tag{A.20}$$

where ℓ and d are the distances from the top of the aquifer to the bottom and to the top of the well screen in the pumped well.

The solution is the same as given by Hantush[21] namely

$$s = \frac{Q}{4\pi T_r}\left\{W(u_{xy}, r/B_r) + \frac{2b}{\pi(\ell-d)}\sum_{n=1}^{\infty} R_n \cdot W\left(u_{xy}, \sqrt{(r/B_r)^2+(n\pi\alpha r/b)^2}\right)\right\} \tag{A.21}$$

with

$$R_n = \frac{1}{n} \{\sin(n\pi\ell/b) - \sin(n\pi d/b)\} \cos(n\pi Z/b) \tag{A.22}$$

where

$W(u_{xy}, r/B_r)$ is the well function for leaky artesian aquifers.

Since the average drawdown in the observation well must be used, equation (A.21) must be integrated over $d' < z < \ell'$ to give

$$s = \frac{Q}{4\pi T_r} P(u_{xy}, r/B_r) \tag{A.23}$$

with

$$P(u_{xy}, r/B_r) = W(u_{xy}, r/B_r) + \frac{2b}{\pi(\ell - d)} \sum_{n=1}^{\infty} R'_n \cdot$$

$$W(u_{xy}, \sqrt{(r/B_r)^2 + (n\pi\alpha r/b)^2}) \tag{A.24}$$

$$R'_n = \frac{b}{(\ell' - d')n^2\pi} \{\sin(n\pi\ell/b) - \sin(n\pi d/b)\} \cdot$$

$$\{\sin(n\pi\ell'/b) - \sin(n\pi d'/b)\} \tag{A.25}$$

where ℓ' and d' are the distances from the top of the aquifer to the bottom and to the top of the well screen in the observation well.

$P(u_{xy}, r/B_r)$ can be called a "three-dimensional partial penetration well function", where

$$u_{xy} = \frac{S}{4tT_r} (T_{xx} y^2 + T_{yy} x^2 - 2T_{xy} xy) \tag{A.26}$$

A.2 Procedure for Calculating Three-Dimensional Formation Permeability Using Partial Penetration Well Function

The use of $P(u_{xy}, r/B_r)$ to determine three-dimensional permeability from aquifer test data is outlined below:

(1) A minimum of three observation wells located at difference directions to the pumped well are required. Observation wells should be within a distance of 1.5 times the aquifer thickness to the pumped well. Partial penetration effect on drawdown diminishes rapidly beyond this distance. All wells have to be partially penetrating.

(2) With variation on r/B_r and k_r/k_{zz}, values of $P(u_{xy}, r/B_r)$ can be calculated from equation (A.24) by computer and plotted against values of $1/u_{xy}$ on logarithmic paper and families of type curves are constructed.

(3) For each observation well, values of drawdown, s, against time, t, are plotted on logarithmic paper of the same scale as the type curves.

(4) For each observation well, superpose the time drawdown plot on the type curves, keeping the coordinate axes of the two plots parallel, and obtain the best fit of the data on one of the type curves. Choose a match point for each well and record the dual coordinates $P(u_{xy}, r/B_r)$, u_{xy}, s, t, and values of r/B_r and k_r/k_{zz}.

(5) The best fit type curve gives the value of the ratio of horizontal to vertical permeability (k_r/k_{zz}) and the value of r/B_r. Knowing the distance between the pumped and observation wells (r), B_r can be calculated.

(6) Substitute the values of $P(u_{xy}, r/B_r)$ and s from each match point into equation (A.23) and solve for T_r. All match points should yield the same, or approximately the same, value for T_r.

(7) Substitute the values of u_{xy} and t from each match point and use Papadopulos' method to calculate S, k_{xx}, k_{yy} and k_r.

(8) The value of k_{zz} can then be calculated from equation (A.13).

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High-Speed Cinematography of Production Blasting Operations

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High-Speed Cinematography of Production Blasting Operations

Blasting is generally regarded as being the most efficient means of reducing a rock face to fragments of a size that can be efficiently handled by mechanical crushers and grinders. The blasting operation is critical to the smooth functioning of the overall extraction process. Two factors can be considered to be of primary importance in the success of the blasting operation: 1) fragmentation, which herein means the size distribution of the fragments produced, and 2) muck digability, which refers to the amount of time taken to remove the fragmented rock to the next level of processing.

Despite considerable work over the past 25 years, the basic details of the blasting operation remain poorly defined. These include the mechanism(s) of fragmentation of the rock and the fundamental factors by which delay initiation functions to improve (or deteriorate) the results of a production blast. For the past three years, we have been engaged in research aimed at answering some of the questions raised in these two areas.

Quantitative analysis of a production blast, and its results, is difficult. The typical production blast lasts, on the average, between 0.5 and 1.5 seconds. The event can be broken down into parts with durations ranging from a few hundred microseconds (the passage of explosively induced stress waves through the rock), through several tens of milliseconds (the detonation of individual boreholes through use of delay initiators), to a few seconds (the distribution of the resulting fragments into the muckpile). To assess the results of a production blast, it is necessary to obtain quantitative information on the size distribution of the fragments in the muckpile and on the rate at which the muckpile can be processed. We have developed the technique of high-speed cinematography used first to monitor underground test explosions[1] and used later by the Bureau of Mines and others[2–6] to observe bench blasting operations. This allows us to obtain quantitative data on fragmentation, detonation times, rock motion and flyrock velocities.[7, 8] Our technique for monitoring production blasting operations is described in Ref. 8.

Two schools of thought on fragmentation

In general, there have been two schools of thought relating to the mechanisms of rock fragmentation by explosives since research began in this area. The first group believes that the prime mechanism of fragmentation involves propagation of a "strain pulse" through the rock to a free face, whereupon it is reflected, generating a tensile pulse (e.g., Refs. 9, 10). Because rock is weaker in tension than compression (under static loading), it fails in tension. When this type of failure takes place at a free surface, it is often called reflection breakage, or spalling. The second group thinks that the primary mechanism of failure is due to propagation of radial cracks outward from the borehole by pressure generated by gaseous explosion products[11, 12] or by some combination of this process and others.[13]

In 1971, Kutter and Fairhurst published a paper attempting to synthesize the views of both schools into one.[14] In studying the mechanisms of fragmentation, both groups used either homogeneous acrylic resin plastic models or homogeneous rock models of small size to illustrate the various effects of detonating a charge in a cylindrical hole near a free face.

While pressurized radial cracks adequately describe the presplit blasting process, neither set of theories adequately describes the fragmentation process in production blasting. As formulated by Duvall and Atchison, the strain pulse model alone does not explain the disintegration of an entire face, as is evident from high-speed cinematography and model studies and from calculations of strain energy at the free face in a production blast. Likewise, radial crack development cannot explain the degree of fragmentation observed, because, typically, only 8-12 radial cracks propagate any distance from the borehole,[15] and thus much larger (and fewer) fragments would be expected.

Small rock models inadequate for needs

Recently, we and University of Maryland's mechanical engineering department jointly undertook studies aimed at clarifying difficulties encountered with the models currently in existence. The principal difficulty with earlier studies is that the models used did not adequately reflect the rock structure that is usually found in production blasting situations. All larger volumes of rock contain a variety of pre-existing flaws, ranging in size from less than 1 mm to hundreds of meters in length.

The small rock models previously used by researchers generally contained only the smallest flaws (grain-boundary flaws or small discontinuous cracks), and, in fact, were usually chosen for this reason. Larger volumes of rock contain joints, faults, bedding planes and other large penetrative flaws that are continuous over distances comparable to the bench height or length.

Our investigations seek to define the effects of these discontinuities as well as smaller flaws on the fragmentation process. To this end, we have undertaken experiments in brittle birefringent polymers with small and large flaws[16, 17] to identify the mechanisms of crack nucleation and growth, and in large blocks of well characterized limestone to ascertain which (if any) of the mechanisms identified in the polymeric models operate in rock. The results of the experiments in large limestone blocks and their application in production blasting situations are reported here.

Experiments simulated production blasts

The block experiments were designed to approximate, as closely as possible, a production blasting operation while keeping the total yield small enough to screen the entire muck. The diameter of the blasting agent used is the determining factor in the design of the experimental pattern, as we wished to use explosives that approximated commercial explosives used in production blasting operations.

The most commonly used commercial explosive is ANFO (ammonium nitrate/fuel oil), with a density range from 0.8 to 0.95 g per cu cm (depending on the method of loading) and a detonation velocity ranging from 2438 to 4572 m/s (depending on the size of the borehole). The theoretical maximum detonation pressure at the CJ (Chapman-Jouget) plane for ANFO is 71 kb (kilobars), but actual measurements indicate pressures ranging from 24 to 36 kb.[18]

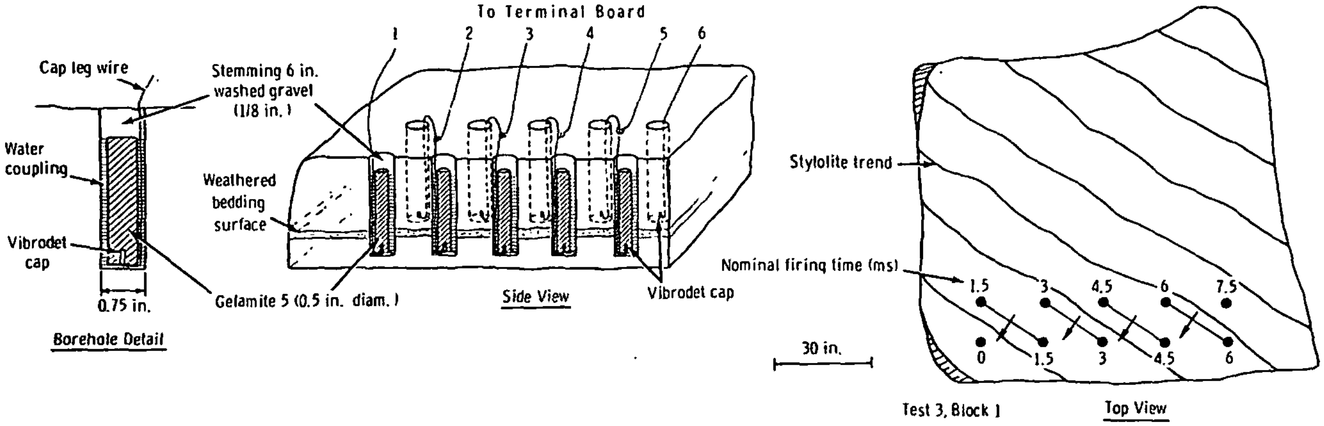


Fig. 1. Schematic diagram, drawn to scale, of a typical block blast configuration along with the loading and firing sequence

To approximate the explosive characteristics of ANFO with an explosive that will detonate in boreholes with small enough diameters to make the experiment practical, we used a commercial product called Gelamite 5. The product comes in 1.25-in. diam cartridges, with a density of 0.95 g per cu cm and a detonation velocity of 2723 m/s. On an energy-equivalent basis, it is 91 percent ANFO by weight and 111 percent by volume. These figures are given for comparison only, as little relationship between energy and fragmentation has been found.[19] Detonation pressure is not available for the Gelamite. Detonation pressure is, however, a function of velocity, density and the amount of explosive reacted at the CJ plane; thus, by comparing density and velocity, we can indicate qualitatively how the two explosives would perform.

The density of Gelamite 5 is 0.95 g per cu cm. We used 0.5-in. diam cartridges, 30 in. long, varying in weight from 102 to 124 g. The variation in detonation velocity, at this diameter, is 2177 (101-g stick) to 2368 (126-g stick) m/s. Although the density is somewhat higher, the detonation velocity is somewhat lower than ANFO in its smallest usable diameter. We expect, therefore, that the detonation pressures and the performance of the two explosives would not be radically different.

Limestone blocks weighed up to 25 tons

We used limestone blocks weighing up to 25 tons. These blocks were obtained from the lower Ordovician Chambersburg formation, a dense fine-grained limestone comprising the uppermost of the two units quarried at Pinesburg, Md.[20] The Chambersburg is made up of relatively thin beds (average thickness is less than 1 ft) recemented by later metamorphism to produce massive layers 2 to 6 ft thick. These layers form large blocks bounded by the two principal joint sets at Pinesburg.

We chose 11 blocks ranging in dimension from 4 × 6 ft × 40 in. to 7 × 11 ft × 42 in. They were large enough to contain flaws representative of those present in the quarry itself. Of the 11 blocks initially chosen, four were used in tests. The experiment was set up as follows: The flaws present in each block were mapped in detail and photomosaics were made of the active face, the top surface of the block and the sides up to 1 ft behind the last row of boreholes. These photomosaics were later used to determine the crack length per unit area and also for comparison with high-speed films of the disintegration of the block face.

All blocks had similar orientations with respect to structure, because they were defined by bedding, joint planes and other random failure surfaces. The top and bottom surface of each block is a bedding plane, and the structural trends of the stylolites and joints can be seen on the top and side surfaces of the block (see Ref. 20 for structural details of the Pinesburg quarry).

The borehole diameter used for the limestone block tests was 0.75 in. Each hole was loaded with a continuous cartridge of explosive 0.5 in. in diameter and up to 30 in. long. The explosive diameter and column length determines, using the formula (B) ft = $\sqrt{dL}$, where d is in in., L is in ft, that the burden is 13.4 in. Because of the uncertainties in using a calculation of this sort, we compared our values to those obtained by the Bureau of Mines[21] for their experiment in limestone benches; and, due to the lower values of density and velocity for our explosive vs the high density dynamite used by the Bureau of Mines, we reduced our burden to 12 in. A two-row pattern with a burden of 12 in. and a spacing of 18 in. was used (fig. 1). All boreholes were drilled with a small diamond coring drill with a 0.75-in. OD, recovering a 0.5-in. core. Recovered cores were used to provide a three dimensional assessment of the flaw density and distribution in each block.

Each hole was loaded in a similar manner. A single Vibrodet (Hercules) cap was placed in a well at one end of the dynamite cartridge. This end was placed in the hole first, then the hole was filled with water to help couple the charge. Six in. of $^1/_8$-in. washed gravel was used for stemming.

Two delay intervals used on test shots

All patterns were fired in an echelon opening at one end of the block (fig. 1). This echelon was always oriented roughly parallel to the stylolite trend on the block surface, again to minimize structural variation. Two delay intervals were used: 450 μs and 1.5 ms between echelons. Timing was achieved by using a 450-volt, programmable blasting machine capable of obtaining intervals from 100 μs to 999 ms, with an error of 10 percent (relative) at 100 μs and less than 1 percent relative at 999 ms. At 450 volts, the Vibrodet cap will detonate at about 21 μs, with a small scatter.

Blasting machine output was checked on an oscilloscope for voltage and timing. Voltage varied by under 10 percent between capacitors, while timing was within the limits stated above. Errors in timing were found during analysis of the two tests that used 1.5 ms between echelons. These errors were caused by bleedover inside the machine, which allowed the delay interval to be bypassed when the longer interval was used, and thus, comparison of fragmentation with delay interval could not be made.

Tests monitored with motion picture cameras

Blocks to be blasted were placed in a log enclosure in a special test arena located at Martin Marietta Aerospace, Orlando, Fla. (fig. 2). For the first test, the block was left with all sides free; however, recoil was considerable, and the block fragmented behind the last row of holes. To more closely simulate a bench configuration, the remaining tests were done with the block banked on three sides with sand. This gives the block more apparent mass and contains the recoil, but the impedance mismatch at the faces is still considerable.

All tests were monitored with three high-speed, 16-mm motion picture cameras that were generally set along three mutually perpendicular axes (fig. 3). Two Wollensak WF-4 Fastax cameras and one Redlake Hycam, with a half-frame head were used. The Fastax cameras were run at approximately 8500 frames/second for each test, while the Hycam ran between 5500 and 7100 frames/second, depending on the test, resulting in 11,000 to 14,200 images per second. The Fastax cameras were equipped with externally driven, crystal-oscillator-controlled timing lights accurate to 50 ppm for establishing framing rate; the Hycam was equipped with an internally driven 1000-cycle timing light accurate to within ± 1 percent.

At these speeds, artificial lighting had to be used to obtain a clear image. This was accomplished by using three to five banks of nine Sylvania S-2 Photoflash bulbs mounted 5 ft from the front (active) face and 5 ft from the top of the block. Illumination was checked prior to shooting by running actual footage at the site. Each bulb has a rise time to peak illumination of approximately 13 ms (measured on test films) and a duration at peak brightness of another 12 to 17 ms. To keep the face lit for the duration of the event, the bulbs had to be synchronized and fired in order. This was accomplished by wiring one bulb from each bank together and to one terminal of a Research Energy of Ohio (REO) sequential blasting machine. In all, nine bulbs on each bank were wired to nine terminals and had a 17-ms interval between terminals. This means that a set of bulbs is fired just as the previous set reaches peak brightness. The overall effect is an even intensity persisting for about 150 ms.

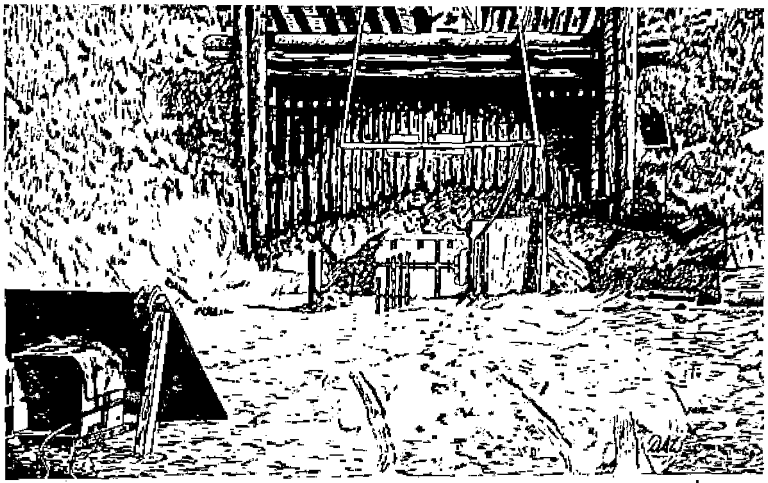
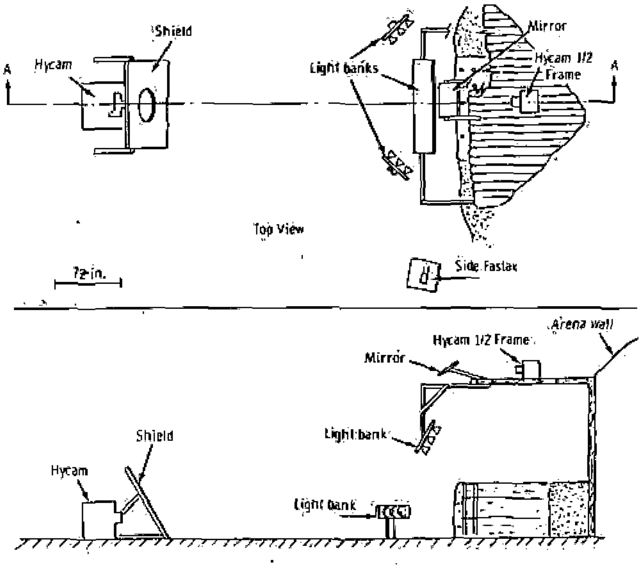


Fig. 2. Block test in place. Scale sticks are placed 1 ft apart in front of the block, and a scale target is painted on the face itself. Both make possible the quantification of fragment size and velocities

Event sequencing was accomplished by using a closure from the high-speed cameras to trigger the REO blasting machine, which has an undetermined lag (generally under 200 ms) between the time when the signal to fire is received and when the firing sequence begins. To assure that the event was properly synchronized, the first terminal of the REO machine was used to trigger the programmable blasting machine controlling the event. The programmable machine was set to an interval of 40 ms between terminal 1 and 2, to allow the flashbulbs to

Fig. 3. Camera orientations (drawn to scale) for a typical block test



come to full brightness, then the first borehole was initiated from terminal 2, followed by the remainder, using the chosen interval of either 450 μs or 1.5 ms. Kodak VNF film (ASA 400) was used to record the event.

Fragment sizes measured on film

Four shots were carried out. As the intent of the experiments was twofold (to identify fragmentation mechanisms and to assess the effects of delay interval on fragmentation), all rock fragmented by the shot was collected and screened using a portable test screen. This gives fragment size distribution by weight, which can be compared with the three-dimensional structural model of the block. In addition to bulk fragmentation, fragmentation of the active face was obtained using a Model 110 photo-optical digitizer. Measurements of fragment size (longest and shortest dimension) and area were made from the high-speed films shortly after detonation of all the holes and then again, 5 to 20 ms after the burden was well in motion. A unit thickness equal to the smaller of the two surficial dimensions of each fragment was assumed, and the weight of each fragment was calculated from the volume and the measured density of the Chambersburg limestone. This assumption of thickness, while not exact, is a reasonably close approximation, since the two shortest dimensions (width and thickness) of the fragments examined after the blast are within a factor of two.

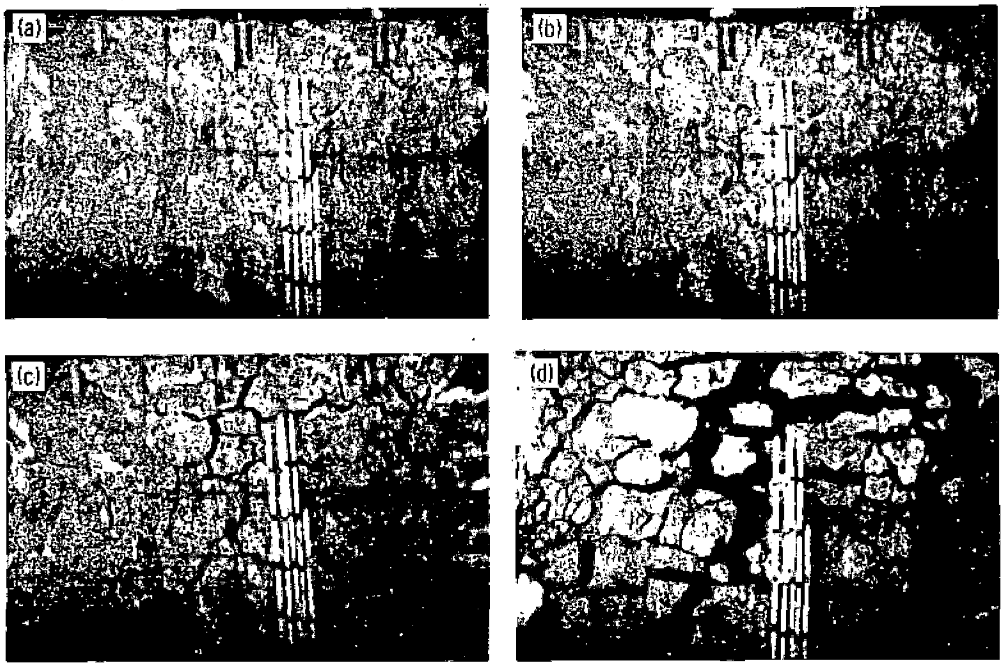
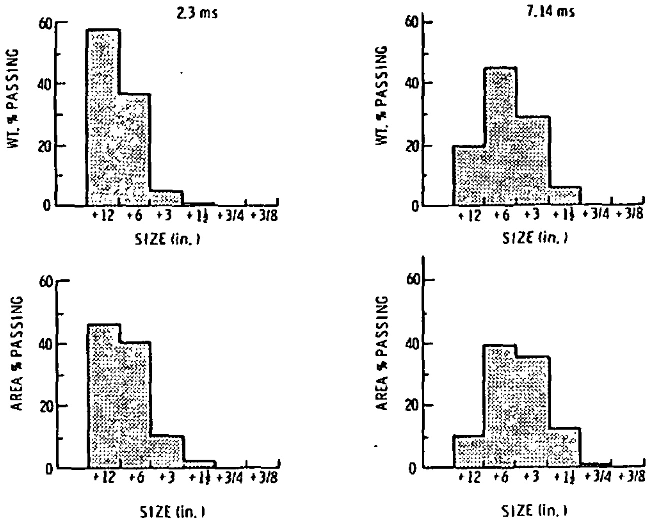


Fig. 4. Single frames taken from a high-speed film of block test 4. Framing rate is 8500/s (a) taken at detonation of the first borehole, (b) taken 120 μs later, (c) taken 1.5 ms into the event, just prior to detonation of the third borehole [No gas venting can be seen from earlier opening cracks, but some can be seen at far right.], (d) taken 2.9 ms into the event [All holes have fired.]. Block is 40 in. thick

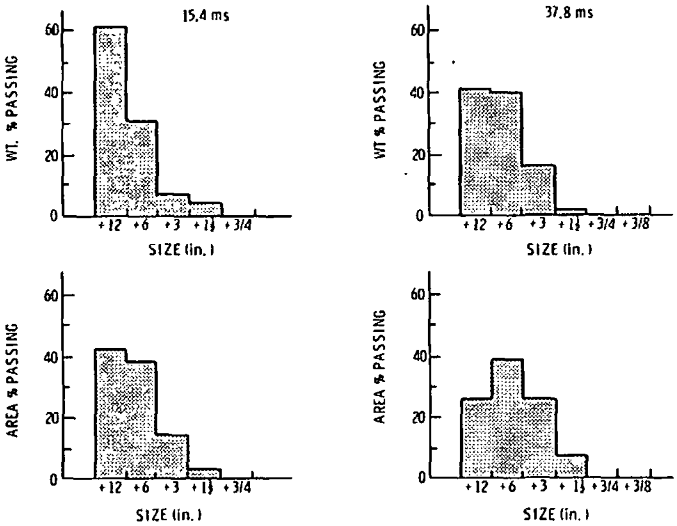
Fig. 4 shows four frames taken from the fourth block test. All blocks show the same sequence of disintegration, thus the frames shown here are representative of blasts using either 450 μs or 1.5 ms delays. The first photograph was taken after detonation of the first hole, the second 120 μs later, when cracks can be seen opening in the face, both in front of the first hole and well along the face to the right of the second hole to fire. It takes between 365 and 397 μs for each explosive column to detonate from bottom to top (from measured detonation velocities), so the P and S waves from the bottom of the charge would have had sufficient time to reach the free face [based on a measured propagation velocity of 0.399 to 0.457 cm/μs (P) and 0.254 to 0.264 cm/μs (S) given by Holloway, pers. commun. 1979]. However, even the fastest radial crack would not have had time to reach the face (based on a crack propagation velocity equal to 1/3 of the P wave velocity). At 120 μs following the first indication of stemming vent from the first hole, cracks were opening beyond the second hole in the first row. It would require at least 550 μs for any crack to propagate from the borehole to this location; thus it is reasonable to assume that the opening of these cracks is associated with arrival of the stress waves rather than with any crack propagating from the borehole.

Another piece of evidence supporting the idea that stress waves play a role in fracturing the blocks is the absence of gas venting through the early opening cracks. The next two photographs in fig. 4 show numerous fractures opening in the face, but no gas venting. The third photo, taken about 1.5 ms after detonation of the first hole shows some gas venting through opening bedding planes (lower left) and through a few cracks opened at the right in front of borehole 3 (note that #3 has not yet fired). The fact that no gas is seen venting through any of the early opening fractures indicates that they cannot be due to pressurized radial cracks propagating outward from the borehole.

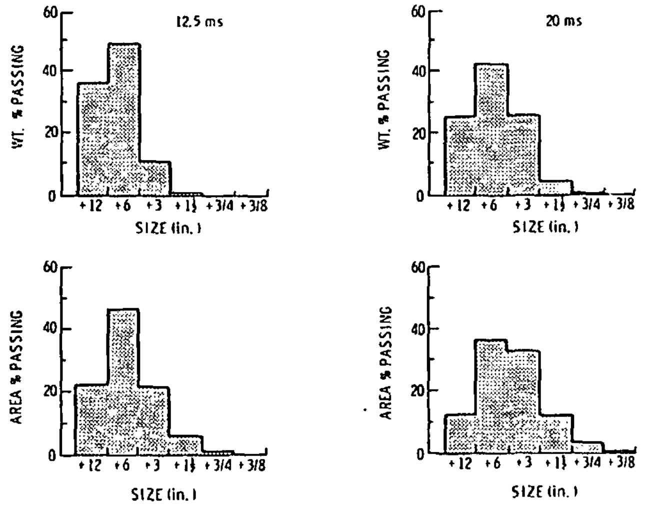
Close observation of the disintegration of the face reveals other important details relating to the fragmentation mechanism. First, many of the cracks that opened during the event existed prior to the detonation of the explosives. The primary cracks involved were large-scale penetrative discontinuities such as joints (those cracks which go from the top of the block to the bottom, as, for example, the first major vertical crack to open); bedding planes (those cracks that are parallel to the top and bottom surfaces of the blocks); and smaller, vertical cracks between open bedding planes. Second, as fragmentation of the face progresses, opened bedding plane cracks were joined by cracks perpendicular to the bedding. Many of these cracks appeared to be new, in the sense that no previous crack was discernable prior to opening. The bedding plane cracks are usually the first to vent gases (apart from the column itself). This is likely due to the fact that the bedding planes form the



Test 2 Block B Nominal Delay Interval - 300μs/ft,
No. of Holes - 6, Burden - 12 in., Spacing - 18 in.,
Hole size - 3/4 in., Explosive diameter - 1/2 in.



Test 3 Block 1 Nominal Delay Interval - 1.0 ms/ft,
No. of Holes - 10, Burden - 12 in., Spacing - 18 in.,
Hole size - 3/4 in., Explosive diameter - 1/2 in.



Test 4 Block A Nominal Delay Interval-1.0 ms/ft,
No. of Holes - 6, Burden - 12 in., Spacing - 18 in.,
Hole size - 3/4 in., Explosive diameter - 1/2 in.

Fig. 5. Histogram plot of time-dependent size distribution for block test 2, 3 and 4

most penetrative of all discontinuities present in the Chambersburg and that they are often deeply weathered and weakened. Where these weathered bedding planes intersect the borehole, they are a ready conduit through which gaseous products of the detonation of explosives can vent.

Changes in fragment size and distribution with time following detonation of the explosives have been quantified by deriving size distributions using the photo-optical digitizer. The results are presented as histograms in fig. 5. Two observations can be made from the histograms. Most important, the fragment size distribution changes with time. Each figure represents an observation taken as soon after detonation as the fragmentation is evident and then a further observation 5 to 18 ms later. The burden velocity is 20.5 m/s for all shots, so this amount of time represents 10 to 35.6 cm of movement of the burden away from the face. It is obvious from all three tests that the mean fragment size decreases with time and that this occurs rather rapidly. The decrease in fragment size results from the continued disintegration of fragments, especially the larger ones, following their initial movement off the face. Observation of the progress of the fragments on the high-speed films indicates that these disintegrating fragments are no longer in contact with any part of the block, or with other fragments. Second, the overall size distribution for all four tests is nearly the same. This is also reflected in the results derived from screening the muck. No further discussion can be made of the meaning of this observation until tests with better control on delay at longer times are made.

New fragmentation mechanisms identified

The data presented provides strong evidence regarding the importance of stress-waves in fragmenting rock loaded with commercial explosives. As stated, previous stress-wave theories have concentrated on the reflected tensile pulse resulting from the reflection of the P wave off the free face.

Recent work by Barker et al[16] and Fourney et al,[17] using Homalite models with induced flaws or with layers simulating joints and bedding planes, has identified new fragmentation mechanisms applicable to the data derived from the block tests. In layered Homalite (a clear, high-temperature resistant plastic) models, the outgoing P wave, upon intersecting and traversing a penetrative discontinuity, such as a joint or bedding plane, causes shear stresses to build up until a sufficient magnitude is reached to initiate and propagate cracks. These cracks initiate at about 70° to the plane of the discontinuity. This type of failure is found in the Homalite models at planes removed from the borehole layer as well as at the planes bounding the borehole itself. This fracture process is further aided by the arrival of the S wave at these planes. Later crack extension occurs when the tensile wave resulting from the reflection of the P wave off the free face passes back through the model. These tests also showed that separation occurred along the bonded interfaces between the strips of Homalite and that crack propagation continued within the strip even after separation from the main mass of the model.

Block fragmentation continued after detachment

We can, with suitable caveats, apply the results of these model tests to the observations from the block tests. Since the stress waves propagating in the blocks cannot be seen, we cannot ascribe fracture of the block to one stress wave or another by direct observation of the stress waves as was done with the models. We can only do this by examination of the results. We observed the cracks begin to open and that fragments begin to move within 100 to 200 μs following detonation of the explosive and that cracks opening at the face do not vent gases. These observations are consistent with the fragmentation mechanism identified by Fourney et al[17] in layered Homalite models.

We further observed continued fragmentation of blocks after detachment from the face. This is consistent with what occurred in the models when cracks continued to propagate by trapped stress waves within separated strips of Homalite 100. The motion of rock fragments off the face prior to gas venting through bedding planes or open cracks suggests that gas pressure is not primarily responsible for the initiation of rock motion.

Rinehart,[22] in chapter 10 of his book, identifies mechanisms for transfer of momentum by stress waves reflected from free faces. Because the incidence of stress waves in the rock mass will vary from 90° to zero, the proportion of the total energy transferred as momentum imparted to the fragment will be difficult to model quantitatively and will not be attempted here. The observation of motion in the models and in the blocks, coincident with the arrival and reflection of stress waves, is considered to be at least qualitatively consistent with the mechanisms outlined by Rinehart.

Examination of fragments resulting from the block test reveals crack patterns consistent with the failure mechanisms discussed above. Fig. 6 shows a portion of the face from one of the blocks. The fragment is bounded on two sides by failure surfaces originally present as semiopen cracks (black marker lines on upper surface and right-hand side). Other cracks which were present before explosive loading (black marker lines perpendicular to the failure surface shown above) have not participated either by generating new cracks or by failing themselves. Fig. 7 shows several types of cracks observed in the remaining "face" of a block after a test, as well as the borehole, with a heavily cracked and crushed zone at the immediate wall. The light colored surface extending 6 to 8 in. to the right and 4 to 6 in. to the left in the upper massive block is a radial crack which angles back toward the block and terminates at a joint on the right and a dipping fracture surface to the left. Further to the right are fractures perpendicular to the bedding planes (defining the long horizontal failure surfaces), and fractures perpendicular to the joints (the short horizontal fractures to the right).

Fig. 6. Fragment from the face area after a test: Dark lines mark the location of fractures existing prior to blasting. The failure surface beginning above the scale occurred along a pre-existing crack. Another such surface is at the far left end. Pre-existing cracks not activated by the blast cut across the fragment

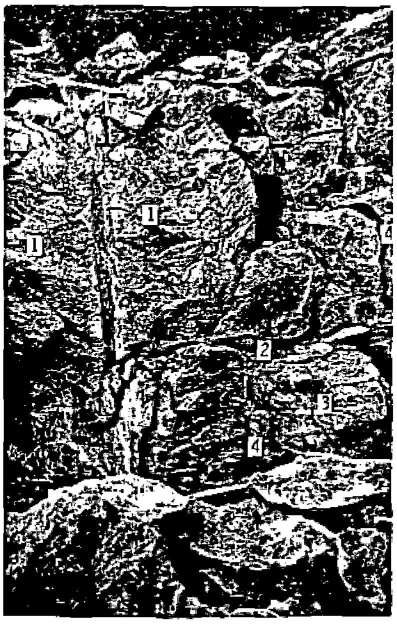


Fig. 7. "Face" remaining after a test. Severe cracking and crushing is evident at the borehole wall. Light surface to either side of the borehole is a radical crack (1). Evident are: a failure along the begging plane (2), cracks originating from pre-existing cracks (3), and new cracks formed perpendicular to the bedding (4). Scale divisions are 6 in. apart

Intense stress pulse starts fragmentation

The data derived from studies of fragmentation mechanisms in Homalite models with simulated joints and bedding planes, and from high-speed motion pictures of fragmentation of large blocks with explosives whose properties closely simulate commonly used blasting agents, allow a reasonably consistent model of the fragmentation of rock to be made. The data strongly supports the concept of fragmentation dominated by explosively induced stress waves rather than gas-pressurized radial cracks.

Fragmentation begins with transmission of an intense stress pulse consisting of a compressive wave (the P wave) with its tensile tail followed by the S wave propagating at about half the P-wave velocity. Both elastic waves quickly outrun the initial radial crack network formed at or near the borehole wall. As soon as the P wave encounters a planar discontinuity with sufficient contrast in density, or sufficient surface roughness (such as a semi-open joint which will have both), a resultant shear stress builds up and initiates cracks at the planar discontinuity. If sufficient contrast is present, the P wave will reflect and generate a family of stress waves (PP, PS, etc.), which propagate back toward the original disturbance. Part of the energy of the original P wave will be transmitted, if the discontinuity is not too open, to continue to the next discontinuity.

Energy transformed into motion at discontinuities

The S wave, upon interacting with the discontinuity, will also initiate and propagate cracks and will itself be reflected, or it will be partly or completely transmitted, depending on the nature of the discontinuity. At each discontinuity, some energy will be transformed into motion such that ultimately the fragments, defined by failed joint or bedding plane surfaces and/or new cracks, will be set into motion. All of these processes act within several hundred microseconds of the initial detonation of the explosive column. Further elongation of radial cracks must occur, since radial fractures can be observed which have propagated up to a foot from the borehole.

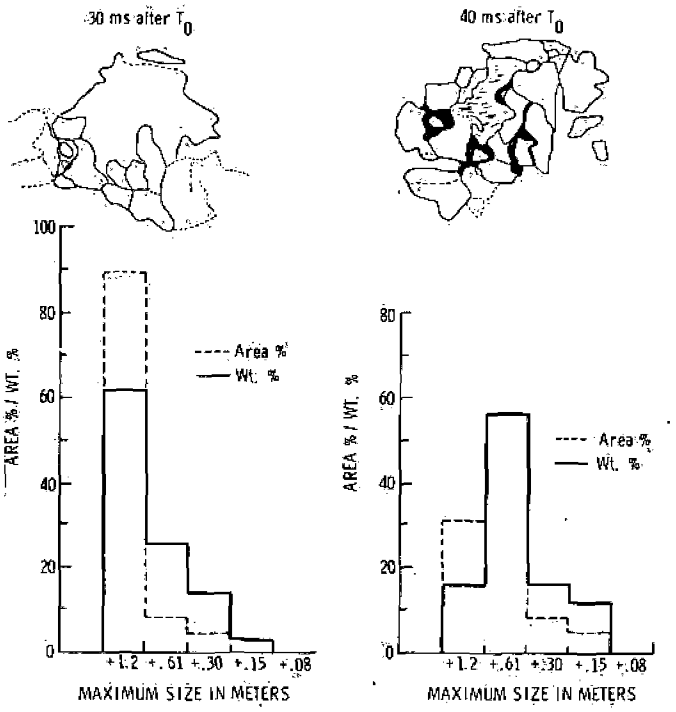


Fig. 8. Time-sequence derived from a high-speed film of a production blast in granite. Each drawing shows continuing fragmentation of a block following ejection of the mass from the face

The cracks may or may not be gas pressurized. If they are, the time lag for gas venting suggests that radial crack development is completed several hundred microseconds to several milliseconds after initial disintegration of the face. In three of the four tests, the face fragmentation is defined prior to the detonation of the last borehole in the sequence. This is further evidence for stress wave mechanisms, as the extremes of the block are 2 to 3 ft from the second to the last borehole, and no evidence exists that any radial crack propagates this far. Also included, but less well documented, is the mechanism of reflection breakage (spalling) caused by reflection of the P wave as a tensile pulse causing failure on a fracture surface parallel to the free face. As the burden moves off the free face, a separation can be seen between the larger fragments that are 6 to 8 in. thick and the remainder of the bulk of the fragments. This pattern is consistent with tensile failure behind the free face, but it could also be due to shear failure perpendicular to the joint planes parallel to the active face and could be due to separation along those planes.

Role of gas pressure in moving rock obscure

The mechanisms described above all occur within the first 300 to 500 μs of the event. The energy entrapped in detached fragments appears to remain high enough to continue the fragmentation process by stress wave extension of cracks for several tens of milliseconds; however the data from tests two and four suggests that most of the fragmentation is complete 7 to 12 ms after the initial event.

The role of gas pressure in moving the rock is obscure. Initial motion is apparently imparted through momentum transferred from reflected stress waves, and the fragments are well detached before gas is seen venting from the face. The role of gas pressure may be partly a function of delays, as the fourth test shows more gas leakage within the portion of the burden set in motion $1^1/_2$ ms after the detonation of the first borehole. This shot differs from the other three in that there is much more angular motion imparted to the fragments, and pieces rotate several milliseconds after the blast. To provide a full explanation, we need further work with delays, wherein full control of the delay time is retained.

Longer delay times in blasting suggested by films

The use of high-speed cinematography in the analysis of production blasting operations and for control of the major parameters of a production blast has now been well established.[7, 8, 23] In 1978,[24] we reported on the irregularity of current commercial pyrotechnic delays, and in 1979,[8] we established quantitative relationships between firing times and burden motion, flyrock velocity and production of backbreak and oversize.

Detailed examination of high-speed films to analyze face fragmentation and examination of fragments and resulting bench faces following production blasting operations reveal the same operating mechanisms as were found during the block tests (fig. 8). Comparison of the evolution of a production blast and of blasts in the blocks reveals one major difference which is of singular importance in designing a successful shot. The block tests clearly reveal that the major character of the fragmentation is defined within the first few hundred microseconds after detonation of the explosive charges. This evidence alone would suggest that relatively short delay times, on the order of a few hundred microseconds per foot of burden, would be adequate to produce good fragmentation.

Quantitative analysis of high-speed films reveals that much longer times than this are needed to reduce flyrock and backbreak and to obtain more easily dug muck.[8] Fig. 9 is a plot of flyrock or stemming vent velocity against relief, measured in ms/ft between adjacent holes, for a sequential timer shot made in Kansas on a 20-ft limestone bench. Burden is 11 ft, spacing 13 ft and the timer interval is 58 ms. Ten rows of holes were used. The nominal relief in this shot is 1.9 ms per ft between holes and 5.7 ms per ft on the theoretical echelon. Because of the irregularity in firing times of the pyrotechnic delays used, the actual relief varies considerably from hole to hole and along the developing echelon. This variability, which can be accurately measured on the films, provides the data plotted in fig. 9. This data suggests that, to achieve zero flyrock velocity (assuming proper stemming) about 3.4 ms/ft of relief is required between holes and about 8.6 ms/ft is required along the echelon.

More than size affected by delay interval

The results suggest that more than just the size distribution of the material may be affected by the delay interval, and it will take quantitative measurement of the

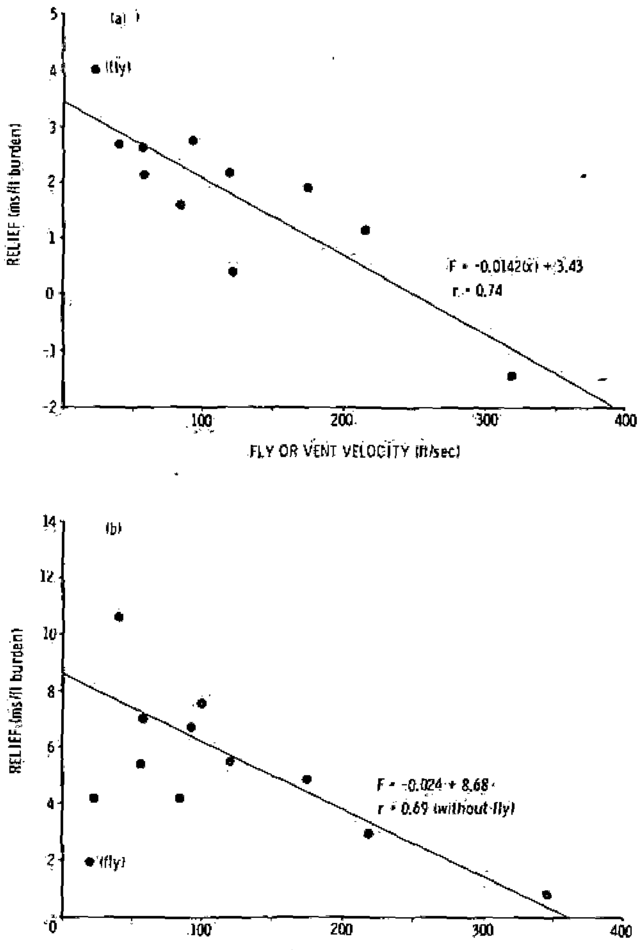


Fig. 9. Relief measured between adjacent holes plotted against vent or flyrock velocity (top) and between echelons plotted against vent or flyrock velocity (bottom)

fragment size distribution of muck from production blasting operations to separate the fragmentation factor from other important factors such as handling properties (digability), backbreak and flyrock.

The difference between the data from the blocks and the data from the production blasting operations suggest that beyond a certain point, delay intervals function principally to influence rock motion or physical distribution rather than fragment size. This is quite important because significant cost savings are realized when the time necessary to complete the muckout operation is reduced. There can be a considerable difference in the muck handling operation even when the fragment size is not radically different.

Joints control production of oversize on free face

Another important aspect of the use of high-speed cinematography is in the identification and *quantification* of the importance of the structure in influencing the results of a blast. The fact that structure plays a part in the success or failure of a blasting operation has been qualitatively known for some time.[13, 25] The real significance of structural discontinuities like joints and bedding planes has gone unnoticed until now. Examination of high-speed films reveals that joints, either opened by previous blasting or by tectonic activity, exert dominant control over the production of oversize from the free face.[7] Examination of remaining benches and of fragments in the muck confirms that fragmentation in the general size ranges found is controlled by joints and bedding planes.

Joints and bedding planes act as attenuators of stress waves induced into the rock by explosive loading. This means that the placement of boreholes with respect to jointing can have a considerable effect on the results. In Pinesburg, there are two principal joint sets and prominent bedding planes 3 to 7 ft apart. The bedding dips from 15° to 78° within the pit but is usually closer to the first figure. One of the joint sets closely parallels the face, while the other cuts into it at a steep angle (fig. 10).

The pattern used at Pinesburg consists of a single row of $6^1/_8$-in. boreholes drilled on an 18-ft burden and 16-ft spacing. At this burden, at least two major and several minor joint planes are crossed between the borehole and the free face. Examination of high-speed films from Pinesburg reveals the fact that oversize blocks are produced by a combination of the effect of attenuation of stress waves by joint planes and failure initiated at contacting joints and bedding planes.

Fig. 11 illustrates (drawn from high-speed films and data from model studies) the sequence of events leading to the production of oversize at Pinesburg. Fig. 11a shows the bench, with the borehole position and the loading, and the bedding planes. Detonation of the boreholes induces stress waves into the system, which cross successive joint planes both outward toward the free face and along the row between holes. Cracks will form and propagate perpendicular to all joint sets (fig. 11b), as well as perpendicular to the bedding planes (these cracks are visible in fig. 10). Because the stress wave is attenuated, fewer cracks will nucleate and propagate as the wave approaches the free face. This sets up the condition for the production of oversize blocks (fig. 11c).

Structure all important in blasting

These mechanisms operate in all blasting situations, both open pit and underground. This data, obtained from high-speed cinematography, provides information which can be used in several crucial areas of blasting. It indicates that structure is perhaps the most critical factor defining the initial fragment size distribution which will result from a blasting operation with a given spacing and burden. The orientation, spacing and physical aspects (openness, weathering, recementing, etc.) of joints and bedding planes control the attenuation of stress waves, provide sites for initiation of new cracks, and provide primary failure surfaces themselves. The location of boreholes does exert considerable influence over

Fig. 10. Resulting face after a production blast at Pinesburg quarry. The light-colored portion of the face is an open joint, along which failure has taken place. Bedding planes dip to the right. Note cracks perpendicular to bedding planes. Bench height is 44 ft

the ultimate fragmentation because of the influence of joints and bedding planes.

In general, the fewer open joints between the free face and the boreholes, the lower the probability of producing oversize fragments from this region. In quarries where the dominant joint set runs parallel to the face, burdens need to be reduced, but spacings can be increased with overall improvement in fragmentation. Care must be taken to assure adequate relief, because, in many cases, the wall will be defined by a joint plane (as in fig. 10), but insufficient relief causes separation along joint planes behind the free face (a type of backbreak). When the dominant joint set is perpendicular to the face, too wide a spacing will result in unbroken rock between the boreholes, leaving a sawtooth pattern in the wall.

Design blasting pattern in advance of opening pit

The best time to make decisions on pattern design is prior to opening the pit. Structural input to the blasting plan is of primary importance at this stage because it is easier to begin the pit in the proper orientation for optimum blasting results than to try and reorient it later or live with less than optimum results. At present, further work is needed to derive a quantitative formulation of the effect of different types of penetrative discontinuities on stress waves so that more specific calculations can be made on site.

The other area benefiting from detailed study using high-speed cinematography is the development of delay patterns which can give optimum results for specific configurations of spacing, burden, number of rows and bench height. Data presented in fig. 9 indicates that for this type of pattern, in order to reduce backbreak and flyrock, increased relief [in ms delay per foot of spacing between holes and on the active burden (echelon) between rows] is needed. Data from the block tests also suggests that fragment size is a function of delay time only at much shorter delay intervals; however, further work is needed to quantify the delay effect in the blocks.

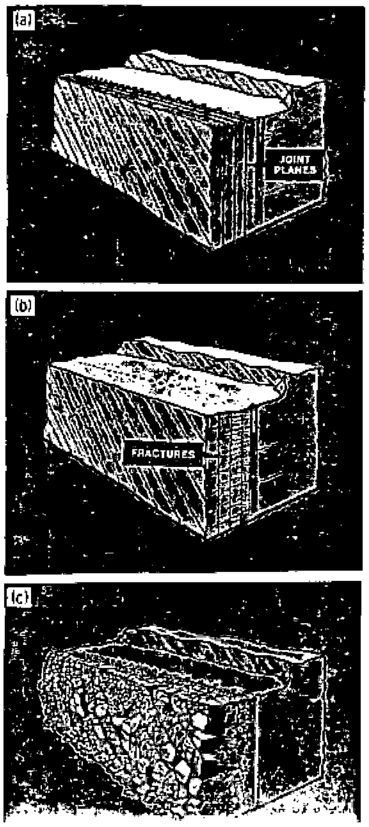


Fig. 11 (a) Structural schematic of a bench in Pinesburg quarry. Bedding planes are shown as dipping lines across the face. A second set of joint planes cuts into the face at a high angle. (b) Schematic diagram of fractures formed perpendicular to joints parallel to the face. (c) Schematic diagram (drawn from high-speed motion pictures) of the fragmentation of the Pinesburg bench. Oversize was formed between the face and the last open joint plane

Work by Bergmann[26] indicates little change in fragmentation beyond about 0.6 ms/ft of burden. Should these trends be borne out by further work, they would indicate that longer delay times primarily influence muck digability, backbreak and flyrock production—factors which are significant from the point of view of increased production. Significant cost benefits have been realized by optimizing the blasting pattern with respect to structure and by improving relief using the data derived by high-speed cinematography of production blasting operations and block and model testing. The technique holds promise for further, quantitative and cost-effective solutions to production blasting problems. ◆

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How Silver-Gold Ores Respond To Salt Roasting, Cyanidation

R. J. MELLEN

Mr. Mellen, now retired and doing consulting work from El Paso, is a graduate of the Massachusetts Institute of Technology. He joined Asarco after working at various properties and began 38 years service with that company. In 1942 he was named chief metallurgist in the Mexican Mining Dept. and 11 years ago was named chief metallurgist for the entire mining department.

THE MINERA KILDUN Y ANNEXAS gold-silver operation, which American Smelting & Refining Co. operated from January 1937 to April 1944 at Matehuala, Mexico, amply demonstrated that the salt roasting and cyanidation procedure is entirely workable—and practical for silver manganese ores that do not give satisfactory recovery by other means, even though treatment costs may be high. With current interest in precious metals increasing, there is also renewed interest in such operations—particularly in one which made profitable recoveries when the New York price for silver stayed below 45¢ per oz.

The 300-mtpd operation treated an oxide ore averaging about 2g of gold, 500g silver per metric ton, and containing 4% to 5% manganese. The ore was roasted with a 5% salt (96% NaCl), raising the calcine to a temperature of 810° at the discharge of the kilns.

Cyanidation of the ore without roasting indicated about an 86% gold recovery, but only about 20% possible recovery of silver. In preliminary laboratory roasting tests, a slightly better gold recovery and a leap in silver recovery to 88% was found obtainable by crushing to minus-4 mesh, roasting with the 5% salt, raising the temperature of the charge to 810° C over a period of 30 to 60 minutes and maintaining peak temperature for five minutes before cooling, then grinding the calcine to 50% minus-200 mesh and cyaniding. Some "play" was found in use of the salt, with slight lowering of values if the salt content dropped to 4%, but the temperature requirements were found to be extremely rigid, with disastrously lower recoveries occurring when the temperature was allowed to go below 800° C.

This figure, of course, corresponded to the melting point of the NaCl, which could always be determined by the adhesive qualities of the charge. Final pilot plant tests made with a 2x20-ft kiln at the University of Utah substantiated the laboratory results but showed feed rates and temperatures to be somewhat less critical.

The mill which was designed (see flowsheet) proved adequate in all respects with the exception of the cooling section. Several weeks delay was needed to revise the conveyor and cooling systems, largely involving the building of a concrete submergence basin around the cooler to the height of the trunnions so that the cooler would be at least one-third completely covered with water, and in increasing the size of pipelines and providing baffles so the cooler could be completely flooded with water.

Even with those steps, the calcine was found too hot to discharge directly onto conveyor belts available at that time, so the material was discharged into a covered launder and carried directly to the classifier with a ratio of mill solution to calcine of 4:1.

"Forcing" Penalties

A loss of efficiency existed for the first year, even after introduction of the additional cooling techniques, mostly due to the need for "forcing" the discharge temperatures of the roasters to the maximum to obtain desired recovery on the 300-ton basis. With forcing, the kilns clinkered up quite badly, and the roasters had to be shut down several times a day to bar the clinker off the walls of the kiln. In spite of that difficulty, for the remainder of the year a 300-ton milling rate was maintained, but with only a little better than 82% Ag recovery.

Early in the following year a mechanism was designed and installed which permitted cutting out the clinker without a shutdown. Operations improved throughout; and for the year 1938 there was a slight tonnage increase, and silver recovery raised to 85.5%.

Another change from pilot plant experience to obtain optimum results was dictated for the ore size. While there had been no difficulty in roasting the ore with minus-4 crushing in the 2x20-ft kiln, studies indicated finer crushing for feed to the 6x90-ft units. The shipping ore bin was converted to a surge bin for Symons and roll crushing on a three-shift basis, which did not interfere with hoisting and coarse crushing on a two-shift routine. Eight-mesh screens were introduced in closed circuit with the roll crushers and throughput rose to 400 tpd, with the plus-20 fraction reduced from 63% of the total roaster feed to only 23%. With that innovation in early 1939, the rate was continually held at 400 tpd; and silver recovery raised to 87% Ag for the rest of the life of the installation.

The greatest single cost item in the Minera Kildun y Annexas operation was the cost of salt. Original plans called for the building of evaporation "pilas" for salt recovery, but poorly consolidated ground proved unable to hold this solution. One or two concrete ponds were built, but even these permitted major solution losses due to cracking. After these unsuccessful attempts, steam-heated and direct-fired steel evaporation pans were introduced; salt recovery went from 24% in 1940 with one pan working and to 69% in 1942 with three pans in operation. As salt recovery increased, the amount of fresh water usable on the filters also increased, providing slightly lower soluble loss and less cyanide loss. Grade of salt increased, too, with all three pans working, from 83% NaCl to 90%.

Apparently, the amount of soluble salts introduced from the ore was more or less constant and resulted in a lower grade recovered salt when only a small amount of salt was recovered, with better returns when distribution was greater. It is believed that recovery could have been increased even more with additional evaporation pans, but a cutoff point had to be established in relation to the cost of recovery per unit of salt saved. Through the life of the operation, volatilization loss was held below 1%, and the over-all rate settled out at 0.5%.

Because of the volume of Cottrell fume produced at the plant, the original plan to ship that product to the smelter or refinery was altered; the Cottrell was simply sluiced out, and the product pumped back to the primary thickeners.

Repair and maintenance costs were high at Kildun y Annexas, and became particularly troublesome in the fourth year, primarily due to the 15%

19. Merrill Precipitation Co. equipment and solution pumps
20. Two Butchart thickeners, 10x40 ft
21. Mill sol tank, 30x12 ft
22. Two Dorr drum filters, 11 ft 6 in. x 12 ft

Normal solution strengths
NaCN ...... 1.0 to 1.5 lb
CaO .... 0.2 lb
NaCl ......12% to 20%

Measured Contact Angles Under 'Standard' Conditions

System	Determination number	Measured Angle			Overall average	Literature value
		Left side	Right side	Average		
Galena-potassium amyl xanthate	1	85°	90°	88°	84°	86° (a)
	2	80°	85°	83°		
	3	80°	85°	83°		
Chalcocite-sodium diethyldithiophosphate	1	60°	60°	60°	58°	59°
	2	60°	55°	58°		
		60°	55°	58°		

(a) Value given for iso-amyl xanthate.

relative lateral motion of the protractor and bubble. Such operation introduces an error of less than 2° in contact-angle measurement because of the relative rotation of protractor and bubble which accompanies the lateral motion.

Results of Experiments

To establish the accuracy and reproducibility of contact-angle measurements with the instrument described, a series of measurements was made in systems for which the contact angle is known. These systems were:

1. Galena in contact with an acqueous solution of 50 mg of potassium amyl xanthate per liter.

2. Chalcocite in contact with an acqueous solution of sodium diethyldithiophosphate (35 mgpl).

Measurements were made of the angles on both sides of three different bubbles placed on three different spots on each mineral. Results of these measurements and values from the literature are given in the accompanying table.

The table shows a difference of 5° between the measurements made on the two sides of the bubble. This was undoubtedly due to failure to align the bases of the bubble and protractor absolutely parallel. However, agreement of the average of a number of measurements with the accepted value was quite good.

Reliability of this instrument has been amply demonstrated in our laboratory. It is believed that the simplicity of its construction and of its operation will be useful to others—in particular, laboratories of mining companies investigating more effective flotation reagents and newly developed techniques.

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Salt Roasting *(Continued)*

improvement at all in recovery if exposed at any time to an oxidizing atmosphere about 500°C.

It would seem that the chemistry involved in the salt roasting procedure might be that the higher oxide of manganese breaks down into the lower oxide even in an oxidizing atmosphere at temperatures above 760°, but is protected against reconverting to the higher oxides upon cooling solely by the solidified NaCl coating of every ore particle, which forms a barrier against oxidation and reformation of the refractory silver. If such is the case, the function of the salt is purely physical in action but protects against oxidation just as effectively as the maintaining of a reducing atmosphere. Such a premise is largely based on the following conditions:

1. If a charge of ore is roasted in the normal manner at 800°C with 5% salt, cooled, washed well and filtered to remove the salt, and then reheated to 200°C, it begins to become refractory. If reheated to 600° it may become more refractory than it was originally. Under these conditions, the salt originally added to the roast has certainly made no permanent change in the nature of the ore or its behavior upon heating.

2. If a charge of ore containing 5% salt is heated to 800°C or higher, and maintained at this temperature until one-half or more of the salt has volatilized, and then cooled and treated in the normal manner, the recovery of silver will be far below what it would have been if held at 800°C for only five minutes, showing that results depend more upon the amount of salt left in the ore during cooling than they do upon the amount of salt available at the maximum temperature used.

3. If the roast is made with any chloride which melts at below 700°C, the results are poor even when such chloride was used in excessive amounts and the temperature raised to 800°C, indicating that the chloride must have a melting point close to 800°C.

4. During the period of operation when the ore was being crushed to only minus 4 mesh and the coarse particles were not being heated to 800°C and giving poor results, it was found that such coarse material contained very little salt, while the fines contained a much higher proportion of the total than they should have. It may be difficult to see why the molten salt was not absorbed by the cooler material but certainly not difficult to see the effect on results.

Major Copper Mine Is Begun in Poland

THE FIRST TON of development ore was brought to the surface from one of three shafts in the vicinity of Lubin, in Poland's "western territories." The copper ore marked the beginning of development of an estimated $1-billion project in the Silesian fields, between the towns of Lubin and Glogow, from which 100,000 tpy of refined metal is expected to be produced. The complete project, including three properties, concentrating plants, two smelters, subsidiary buildings, roads and a townsite, is not due for completion until 1972.

The ore reportedly averages "at least" 2% Cu, with some higher grade veins, even as high as 10% to 12%, located by geologists.

The deposits, located some 1500 ft below surface, will begin producing on a regular basis in 1966 or 1967. A new 50,000-ton smelter is to be built near Glogow, and an existing plant at nearby Legnica will be expanded to equal size.

Although the full extent of the deposits was not known until 1957, the Germans, who controlled the area before World War II, made an attempt during the war to exploit them. Those efforts were defeated by the existence of water saturated sands about 1000 ft thick above the orebody.

The Poles employed a freezing technique to create a 30-ft wall around the shaft which first tapped the orebody. It was in celebration of that event that the first ton was mined and shipped for analysis and development of a flowsheet for the concentrator.

The Polish government looks to the development of the Silesian fields as a benchmark in the development of a number of industrial projects undertaken by the Communist Gomulka regime to make the nation self-sufficient in critical materials.

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Hydrometallurgy—Today and Tomorrow

By *FRANK M. STEPHENS, JR.,*
Vice President & Technical Director
and
L. F. ENGLE,
Assistant Technical Director
Parsons-Jurden Corp.

BEFORE starting any discussion of the role of hydrometallurgy in the minerals industries, it seems proper to define the subject. It would be perhaps easiest, in this case, to explain what hydrometallurgy isn't, rather than what it is. To start with, if the primary separation is physical and does not involve extensive chemical reaction, then it is not hydrometallurgy. This would, of course, eliminate such techniques as gravity separation and flotation procedures, even though they operate in aqueous media. To narrow the field still further, those separation techniques which involve the use of sufficient heat to melt or volatilize one or more constituents from a mixture of minerals, can also be eliminated. This, in turn, would remove smelting procedures and fused salt electrolysis from our list, even though they deal with the chemistry of solutions.

To continue this method of elimination, a point is reached where it could be said that, by definition, "all else is hydrometallurgy." It seems more germane to meet the issue head on, and to define hydrometallurgy as the science or art of selectively dissolving and/or separating metals, or their compounds, from solutions which are primarily aqueous in nature.

Using this definition, we can then include the following techniques in this discussion of hydrometallurgy:

- *Dissolution*
- *Precipitation*
- *Ion exchange*
- *Solvent extraction*
- *Electrolysis*

Many metals use hydrometallurgical process

Historically, hydrometallurgy is perhaps the youngest of the established metallurgical practices, being predated by the physical separation of native metals such as gold, silver and copper, and also predated by smelting techniques for the recovery of tin, copper and iron. Nevertheless, the roots of hydrometallurgy are as old as written history, and even the earliest chemistry texts contain ground rules for hydrometallurgical treatments. Generally, any wet chemical analysis procedure for metals constitutes a feasible, though

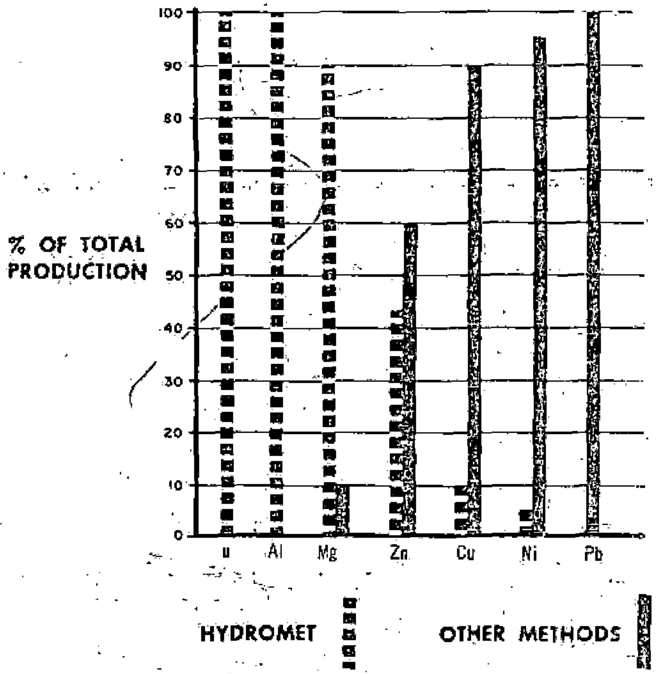

Fig. 1. Major metals which are produced by hydrometallurgical methods

Frank M. Stephens Jr. holds a metallurgical engineering degree from Colorado School of Mines. Prior to his appointment as vice president and technical director of Parsons-Jurden Corp. he was with Battelle Memorial Institute for 23 years. At Battelle, he served as chief of the extractive metallurgy division, director of research planning for the chemical engineering department, and senior technical advisor. He has published many technical papers and has been credited with five patents.

Lester F. Engle, formerly director of research and development for the Calumet division of Calumet & Hecla, Inc., is now assistant technical director for Parsons-Jurden Corp. He has a background of 20 years in engineering, research and development, and operation experience in the minerals, metals, and chemical industries. A graduate of Carnegie Institute of Technology in metallurgical engineering, Engle holds four domestic and foreign patents for metal base fungicides and he has authored several papers.

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not necessarily economic, hydrometallurgical procedure.

Where does hydrometallurgy stand today? A partial answer to this question is shown in figure 1. All of the uranium and aluminum produced in this country depends on hydrometallurgical steps for their production. Ninety percent of the magnesium production involves hydrometallurgy, as does 42 percent of the zinc production, ten percent of the copper production and five percent of the nickel production. Only lead, of the major non-ferrous metals, has resisted the hydrometallurgical approach.

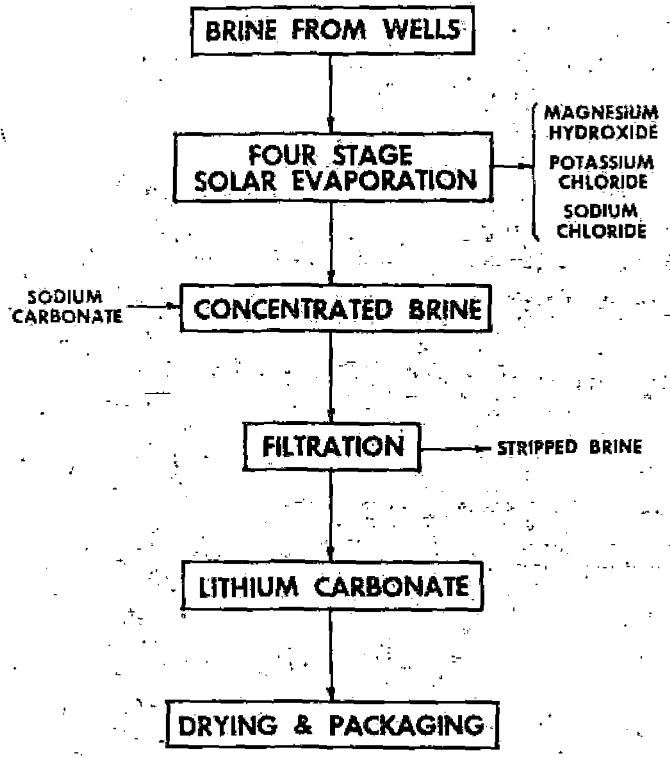

Fig. 2. Lithium recovery from brine

The following are some examples of relatively new hydrometallurgical systems which are in commercial production today:

LITHIUM: In June of 1966, Foote Mineral Co. began commercial shipment of lithium carbonate from its new plant in Silver Peak, Nev. This plant, which has a rated capacity of ten million lb of lithium carbonate per year, uses brines pumped from wells in a dry lake bed as a raw material source. Through the use of solar energy, the brine is concentrated in four stages of evaporation (figure 2), which selectively precipitate the magnesium as hydroxide and the bulk of the sodium and potassium as chlorides. The final brine from the solar evaporation ponds contains six percent lithium chloride. Processing is accomplished in an adjacent plant, where sodium carbonate is used to precipitate lithium carbonate, which is filtered, washed, dried and shipped. Future plans call for expansion of the plant and for production of potassium and possibly magnesium chemicals.

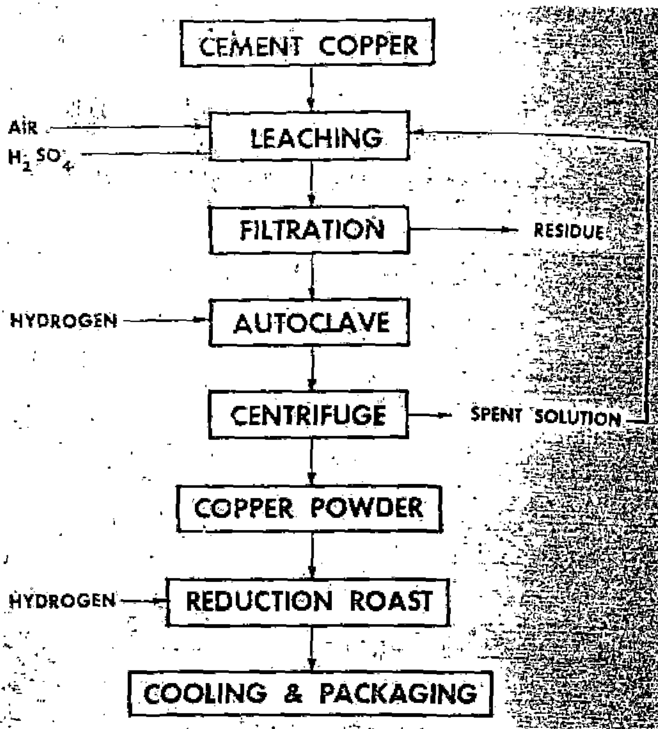

Fig. 3. Acid leach system for production of copper powder from cement copper

COPPER POWDER: One new plant was completed in 1966, and another existing plant was modified to convert low grade cement copper to high grade copper powder, using hydrometallurgical techniques.

In the new 25-tpd plant at Bagdad, Ariz., Arizona Chemcopper Co. uses a buffered sulphuric acid leach system to dissolve cement copper (figure 3). Leaching in the presence of air takes place at 180° F and yields a solution containing approximately 90 grams per liter of copper. This solution is filtered to remove excess

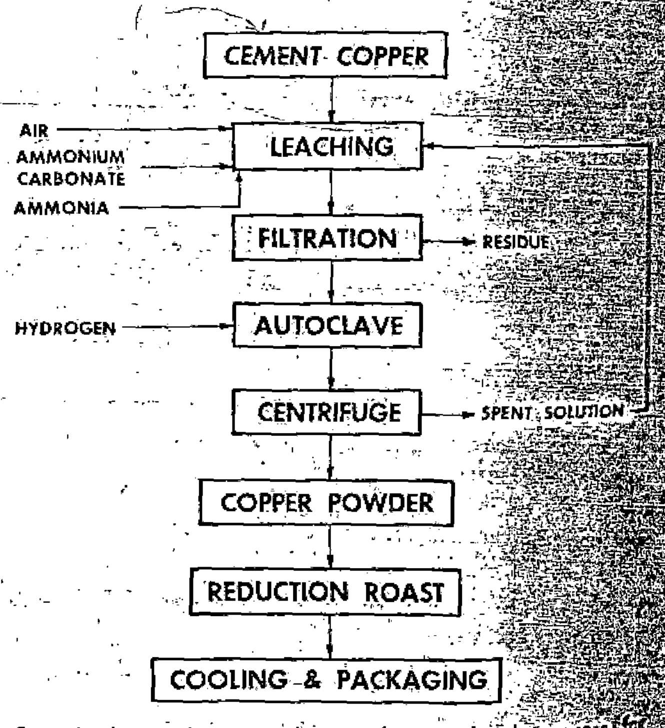

Fig. 4. Ammonia-ammonium carbonate leach process for recovering copper powder from cement copper

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suspended solids and then sent to an autoclave operating at 425 psig and 300° F. Hydrogen gas is then introduced into the solution to produce a controlled precipitation of finely divided high grade copper powder. The slurry from the autoclave is centrifuged to recover the copper powder which is washed, dried and given a final treatment with hydrogen at 1400° F, before being cooled and packaged for shipment.

In the modified 10-tpd plant of Universal Metals Corp., at Kansas City, Mo., the cement copper is leached in an ammonia-ammonium carbonate solution to yield a solution containing 120 grams per liter of copper (figure 4). After filtering to remove solids, this solution is treated with hydrogen in an autoclave at 1000 psig and 320° F to precipitate copper powder, which is finished in the same manner as that used at the Arizona Chemcopper plant.

MOLYBDENUM: Two years ago, Climax Molybdenum Co. started up its new plant for the hydrometallurgical treatment of molybdenum oxide ores. The production of three million lb per year of molybdenum, in this facility, represents the first commercial production of molybdenum by a hydrometallurgical process.

In the process, (see figure 5), molybdenum oxide is dissolved from the ore using a sulphuric acid-sulphurous acid leach. The dissolved molybdenum is separated from the leach solution by absorption on activated charcoal. The molybdenum is then stripped from the charcoal with ammonia and water. After purification with magnesium sulphate to remove phosphate, the pregnant liquor is sent to evaporation and crystallization where molybdic acid and ammonium paramolybdate crystals are removed. These crystals are then calcined to produce the final molybdenum trioxide product.

EUROPIUM AND RHENIUM: Also recently placed on stream are the hydrometallurgical plants at Molybdenum Corp. of America in Colorado for the recovery of rare earth oxides such as europium, and the hydrometallurgical plant of Kennecott Copper Corp. in Utah for the recovery of rhenium in an ion exchange circuit.

The following processes are under development and should be ready for commercial production in the next five years:

COPPER: Continental Copper and Steel Corp. is completing pilot plant studies on a radically new electrolytic copper cell which appears capable of producing high grade cathode copper directly from relatively weak and impure copper leach solutions. In addition, this cell shows promise of being able to handle normal purified tank house solutions at current levels that are at least twice those now used in the industry, without loss of current efficiency or product quality.

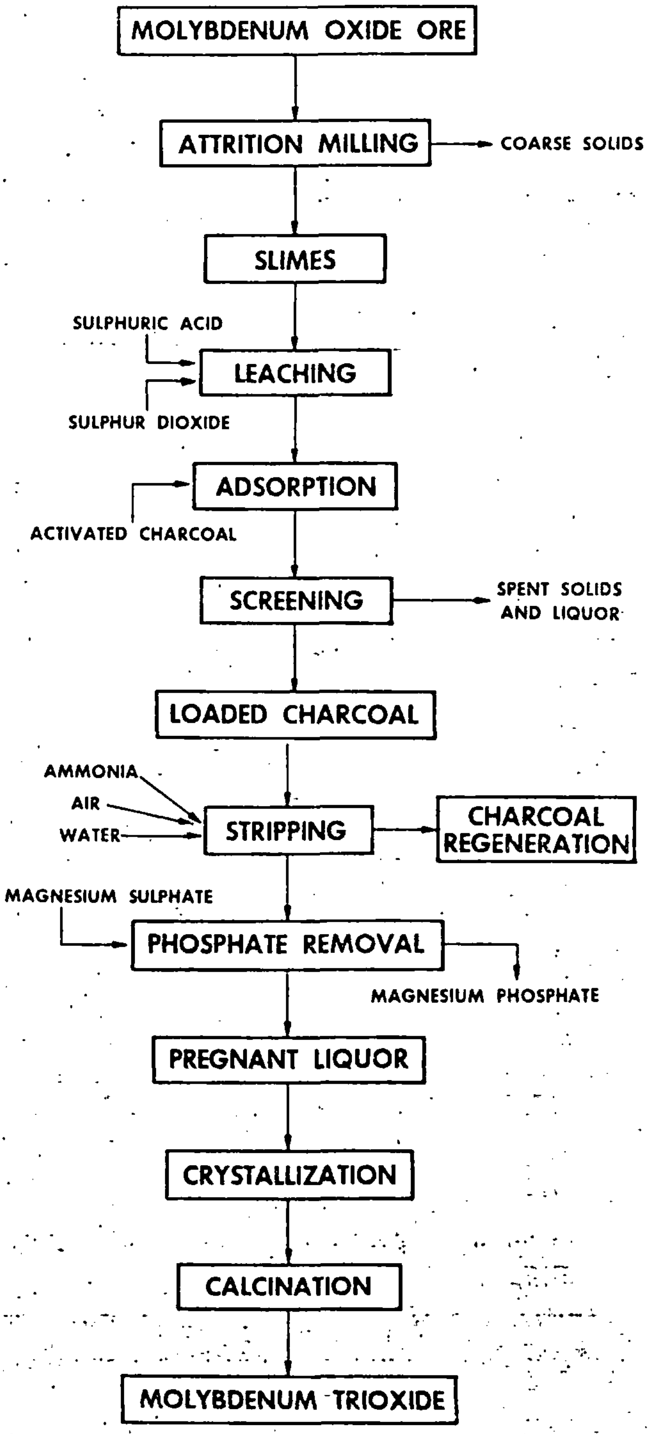

Fig. 5. Oxide molybdenum flowsheet

LEAD AND ZINC: Pilot tests are now underway by Bunker Hill Co. to produce lead and zinc directly from sulphide ores, following the high pressure leaching system developed by Dr. Frank Forward and Sherritt Gordon Mines Ltd. If successful, this will represent the first commercial production of lead by a hydrometallurgical process.

MAGNESIUM: At least two companies have recently announced plans for producing magnesium from the Great Salt Lake Brines. Presumably, this will be done through solar evaporation concentration followed by purification, dehydration and electrolysis of the molten salt.

Future looks promising

By adding together the predictions and statistics from the economists, sociologists and geologists, we can develop an interesting picture.

- Half of all the people who have ever lived are alive today.
- The population is still increasing.
- Per capital consumption of metals is increasing.
- Reserves of metallic ore are decreasing in grade and increasing in complexity.

This means that in the next 10 to 20 years, the mining industry will be called upon to double or triple the current output; and this increased production will come predominately from lower grade raw materials. This, in turn, offers a promising future for hydrometallurgy.

Basically, the inherent advantages of hydrometallurgical treatment are: (1) A high degree of automation can be achieved with resulting low per-ton labor costs; (2) Complex ores can be treated even if physical liberation cannot be obtained; and (3) Lower grade materials can be processed economically.

Possibilities of metals recovery

What are some of the developments which one might expect to see during the next 20 years?

Firstly, as the search for raw materials continues, the newer sources are apt to be more remote from civilization. This means that transportation will become an important cost item. And certainly, pipeline transport of slurries, and the use of pipelines as processing plants, will be considered.

For example, silica might be removed from iron ore slurries by adding caustic to the system, thus upgrading the product while transporting it to market. Similarly, pyrite sulphur might be removed from coal during pipeline transport.

Secondly, as decreasing grades of ore continue to be worked, mining costs will become even more important in the future. Because of this, the industry will seriously investigate the possibilities of leaching ore in place.

Such practice is currently used in the sulphur industry and is beginning to be used in the solution mining of potash ores. With the use of atomic devices to shatter large orebodies underground—a procedure already demonstrated in the Atomic Energy Commission's Operation Plowshare—leaching shattered ores in place and pumping only the solutions to the metals recovery plant, is another possibility.

Lastly, what about the world's largest low-grade mineral deposit—seawater. It could be that the increased use of atomic energy power plants for production of freshwater from seawater will spawn a secondary industry to recover minerals from concentrated brine wastes. Pure fantasy?—not at all. Remember that much of our magnesium and bromine already comes from this source.

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l pilot, the new Arco plant at George West, inerals' active development program, and de's interest in entering the in-situ development activity all point to future growth of uranium production by in-situ leaching in south Texas. This prospect is strengthened, of course, by recent improvement in yellowcake prices—now topping $20 per lb and expected to go still higher. ☐

~~How to extract uranium from refractory ores~~

Professor Alcidos Caldas, director of engineering chemistry, Federal University of Rio de Janeiro

A SOLID-PHASE TECHNIQUE of oxidizing-sintering has been developed for recovery of uranium from essentially insoluble ores, at lower temperatures than conventional methods, with minimum use of an oxidant.

A number of uraniferous minerals lock uranium in the tetravalent form, but U^{+4} is essentially insoluble in sulphuric acid, or in a solution of alkaline carbonate, when oxidizing agents are absent. To dissolve uranium, U^{+4} must first be oxidized to U^{+6} by means of topological reactions that take place on the surface of the solid particles of the ore. The usual method is to treat ground ore with a hot dilute solution of sulphuric acid and then add a suitable oxidizing agent.

In the new method, the oxidizing agent may be added to ore during grinding. The mixture is then heated to an appropriate temperature determined by the nature of the oxidizing agent, so that an oxidizing sinter occurs in a solid state reaction. The presence of V_2O_5—either occurring naturally in certain uranium ores or added prior to calcination—improves the subsequent extraction of uranium.[1]

Even though the new method utilizes ordinary oxidizing agents, it differs from the conventional method in that oxidation is done prior to lixiviation instead of simultaneously. This technique offers better conditions for efficient oxidation and dissolution of uranium, while using less acid and dissolving fewer of the other constituents of the ore. Compared with current methods, the new process uses milder conditions of temperature with less corrosion of the equipment, shorter residence time, and a better extractive yield of uranium.

Without considering economics, some oxidizing reagents are well suited to this type of reaction, as they produce a dry oxidation.

Manganese dioxide (either the natural or the artificial product) is a highly insoluble and infusible material. Its efficiency, and consequently the reproducibility of the results, are very much dependent on the surface conditions of the particles, since this is really a reaction in the solid state, between insoluble and infusible reagents. MnO_2 is low in cost and can be recovered either by chemical precipitation or by an electrolytic process. The "formation of salt by sintering" reactions do not occur in a wet way between MnO_2 and WO_3 or MoO_3, nor with natural sulphides such as FeS_2. They can be realized very easily by sintering.[2]

Sodium nitrate, $NaNO^3$, is a very mild oxidizing reagent (except in the presence of a strong reducing agent), and a very soluble compound, allowing easy penetration into the pores of the ore. It also has a relatively low melting temperature (310°C), and by decomposition at a high temperature (400°C) it furnishes the correspondent nitrite, $NaNO_2$, which is both an oxidant and a solvent for the metallo-acid elements.[3] However, sodium nitrate cannot be recovered.

Chromium trioxide, CrO_3, is an extremely strong and easily soluble oxidizing agent whose oxidizing power increases with decreasing water content of the solvent.[3] It is the anhydride of chromic acid, H_2CrO_4, which in acid media forms higher condensed acids such as $H_2Cr_2O_7$.

The use of $Cr_2O_7^{-2}$ as an oxidizing agent in dilute acid (usually sulphuric) is well known:

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightleftarrows 2Cr^{+3} + 7H_2O$$

This is a reaction between ions in solution. In the presence of insoluble iron mineral products, the corresponding oxidation does not take place easily unless Fe^{+2} is first put into solution. In hot concentrated sulphuric acid, the following reaction occurs:

$$2H_2Cr_2O_7 + 5H_2SO_4 \rightleftarrows 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

On the other hand, the CrO_3 decomposes above its melting point (197°C) according to the reaction:

$$4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$$

Under these conditions, the oxidizing reaction would occur because the gaseous O_2 formed is not very soluble and not very efficient for the reaction with the insoluble minerals of U^{+4}.

The use of CrO_3, obtained by evaporation (105° to 110°C) of H_2CrO_4 solution added to the ore, is especially efficient since the solid that is formed does not decompose at this temperature and acts directly on the reducing agent:

$$3UO_2 + 2CrO_3 \rightarrow 3UO_3 + Cr_2O_3$$

In this way U^{+4} passes to U^{+6} and becomes easily soluble, requiring a minimum of acid for its extraction.[5]

The acid solution thus obtained, containing U^{+6} and Cr^{+3} sulphates, can be treated by conventional processes in the same way as the solution obtained when dichromate is used as the oxidizing agent. In this way the U^{+6} can be extracted by appropriate organic solvents, and the chromic and sulphuric acids can be recovered from the aqueous layer by electrolytic oxidation, according to the overall equation:

$$Cr_2(SO_4)_3 + 5H_2O + 1\tfrac{1}{2}O_2 \rightarrow 2H_2CrO_4 + 3H_2SO_4$$

The new process has been tested with good results for the extraction of uranium from low grade refractory uranium ores, such as uraniferous zirconium ores, and from pyrochlore concentrates. ☐

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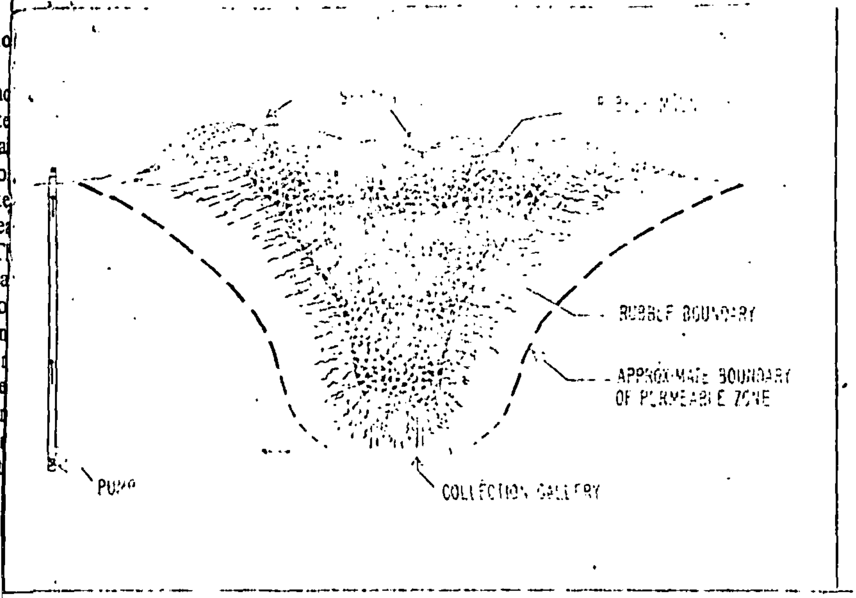
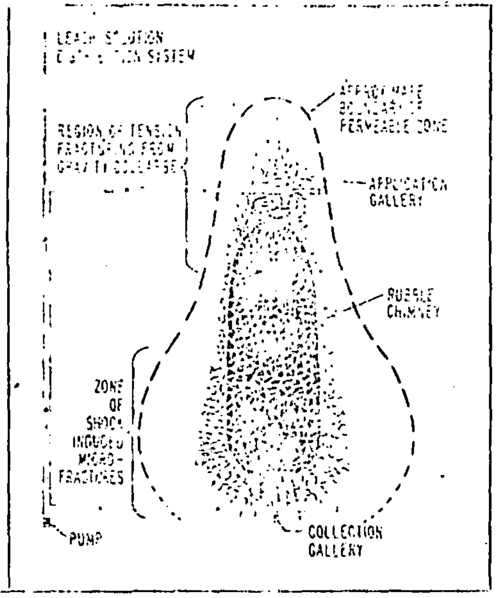


In-situ leaching system for shallow, underground nuclear blasts. The gallery collects the pregnant solution and this liquid is pumped to surface.



Leaching system for a deeper nuclear shot whereby pear-shaped zone forms.

How to make ore from marginal deposits

Teaming nuclear explosives with in-situ leaching of the broken rubble has a potential of increasing total reserves by turning what is now considered marginal deposits into ore

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Consolidated Oil & Gas Inc.
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Alan R. Jager, staff engineer, Occidental Minerals Corp.
(Now consulting for the Lawrence Radiation Laboratory)

WINNING MINERALS by leaching from what was once conidered submarginal deposits is a growing factor today n total U.S. metal production, with about 175,000 tpy f copper, or roughly 12% of domestic production, deived in this manner. In 1963, leaching accounted for nly 8% of total copper, but at its present rate of growth expected to increase to 20% of total output in 1975. urrently, Kennecott Copper Corp. at Bingham Canyon capable of recovering about 25% of its copper metal y this method. In addition, hydrometallurgical techniques ow under development by a number of companies are pected to open up the exploitation of ores other than pper and uranium in the near future.

In-place leaching from ore broken by buried nuclear plosions (*Nuclex* environment) is now under developent, and it represents a potential for exploiting what e now submarginal deposits. A better grasp of the pontial of this technique can be appreciated by considering e work done so far and the hardware used.

Fission explosives and thermonuclear explosives (using a sion trigger mechanism) have been tested for in-situ ching. Both designs release some radioactivity, hower, thermonuclear explosives emit substantially fewer sion products but do give off tritium, a radioactive isope of hydrogen.

The charges for thermonuclear explosives have been reased by the Atomic Energy Commission, and are shown table form as follows:

Cost of a possible nuclear in-situ operation

Conditions and assumptions

1. 50-Kt yield nuclear explosion at 1,000 ft depth of burst.
2. Grade .5% copper (10 lb per ton)
3. 4-million tons of fragmented rock contained in the chimney. Assume 75% recovery of contained copper, or 30-million lb.
4. 6-million tons of rock in the permeable envelope. Assume 50% recovery of contained copper or 30-million lb.
5. Leaching life—10 years.
6. Production rate of 6-million lb per year of copper (20,000 lb per day). Total copper recovery 60-million lb.

Total capital costs — $25-million including:

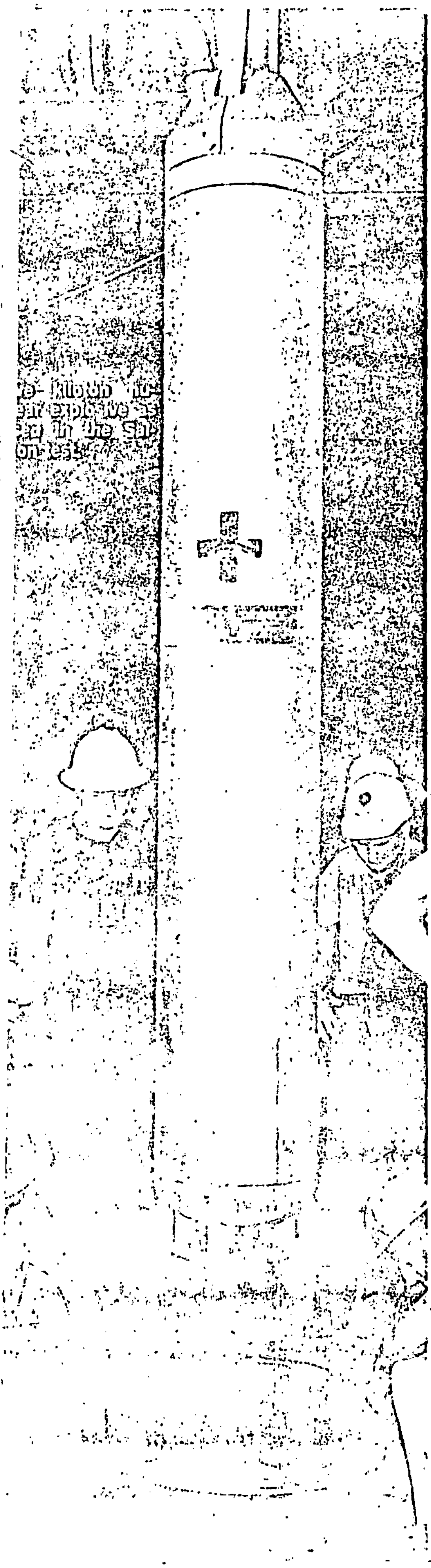
1. Charge for nuclear explosive.
2. Emplacement and related costs.*
3. Underground development of galleries to apply and recover leach solutions.
4. Pumps and piping.
5. Precipitation plan (10 tpd copper output).

Total operating costs—20¢ per lb including:

Assuming a 10 lb per 1,000 gal copper concentration, with 2-million gpd. of solution circulated and treated including:
1. General operation.
2. Interest and amortization.
3. Costs of smelting, sales, etc.

Such an operation would be potentially profitable.

*Safety and outside property damage costs are not included since they vary widely depending on locality and other factors. In the opinion of the authors, indirect safety costs such as long range meteorological and ground water studies should properly be borne by the Public Health Service or some other tax-supported Government agency.



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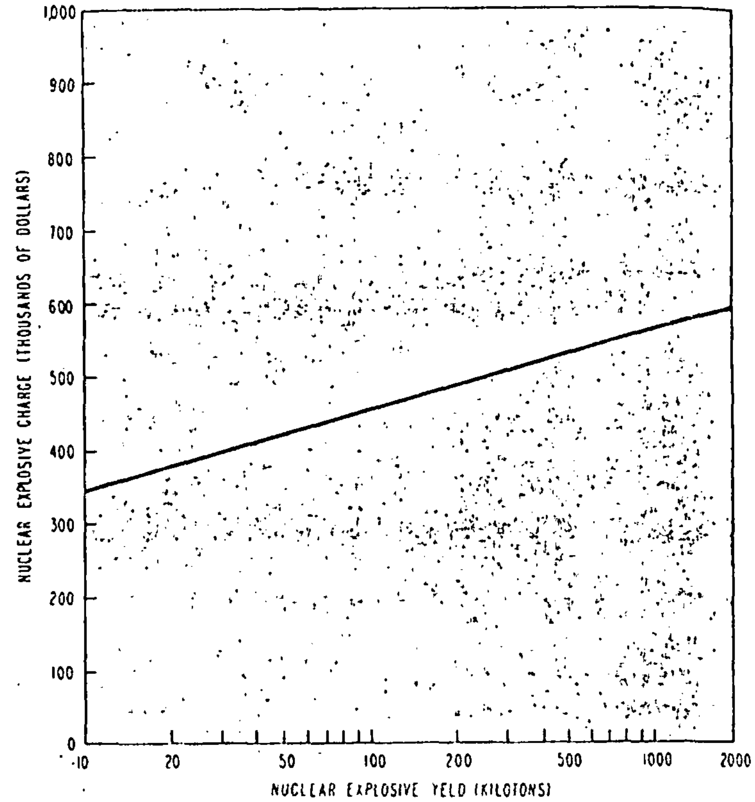
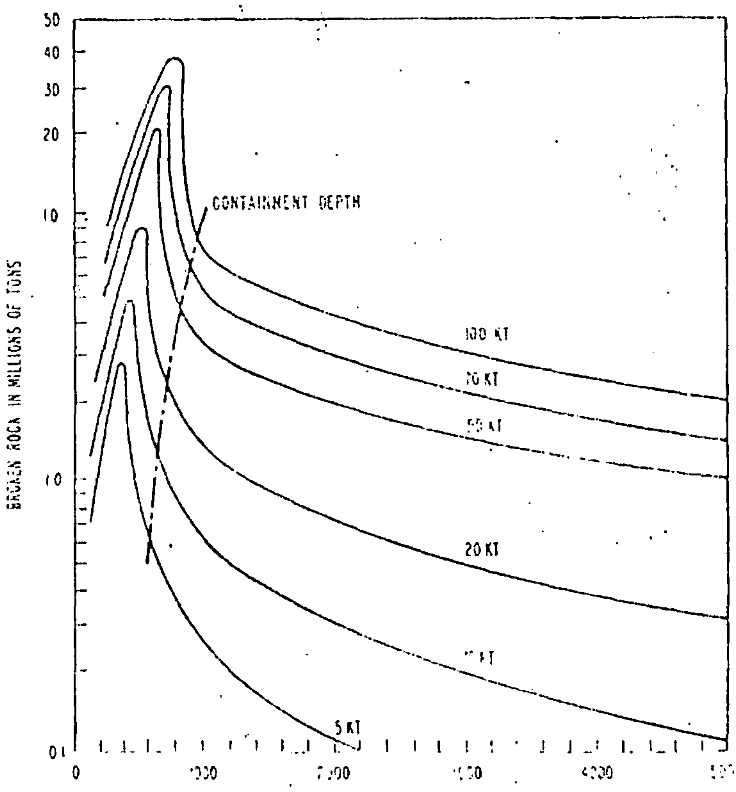
Cost for nuclear explosive including arming and firing



Tons of rock broken by underground nuclear explosion



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Summarizing the cost of nuclear explosives to industrial users varies accordingly:

- Larger explosive yields produce the lowest energy cost per unit.
- Present charges are probably maximums for thermonuclear explosives with standard characteristics.
- Special explosive designs (including minimum diameters and those to be used under unusual temperature or pressure conditions) will probably be higher in cost than standard thermonuclear devices.
- Fission explosives are priced higher because fission fuel (enriched uranium and plutonium) is scarcer and more costly than thermonuclear fuel.
- Quantity purchases of several explosives for use in one locality will probably cost less.
- Widespread industrial use should result in production economies and lower charges.
- Nuclear explosive technology will continue to improve.

Sizes of nuclear explosives available

Nuclear explosives have not been designed specifically for underground engineering applications, although some existing devices are suitable for this use, and when conditions warrant, special designs can be undertaken. Yields of 100 kilotons can be obtained in a cannister with an outside diameter of 11 in., but unusually high pressures, temperatures, and special requirements may require larger diameters.

Under some circumstances, leaching in the *Nuclex* environment can have advantages over deep pitting or block caving operations because nuclear explosions produce extensive permeable zones suitable for leach recovery at relatively low cost.

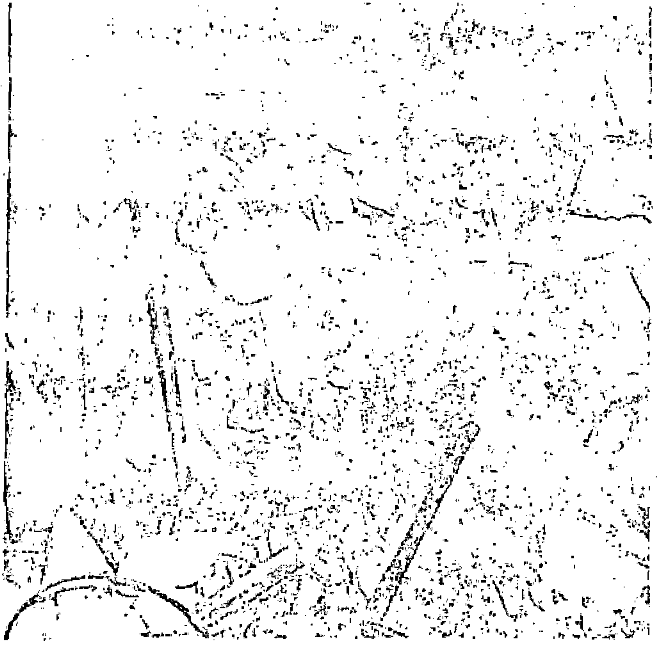
Technology for breaking rock with nuclear explosives and the methods for solution recovery have progressed to the point that commercial in-place leaching operations in the *Nuclex* can now be designed. In-place leaching of nuclear fractured rock closely resembles dump leaching, but the Nuclex environment has important advantages: For example, high residual temperatures may promote solubilization of refractory ores in autoclave like conditions. In addition, shock-induced fracturing along mineralized joints or throughout the groundmass will provide access for leach solutions enhancing metal recovery. Leaching methods also have inherent capital and operating cost advantages for some mineral deposits over alternate routes.

Controlling leach solutions may be a problem

Difficulties will, no doubt, be encountered in controlling the course of solutions, and the formation of undesirable reaction products. These factors may seal off the leach area, stopping production. Supplemental oxygen might be required, and bacterial activity might be restricted to near surface environments where temperatures promote bacterial growth. The radiation and seismic hazards must be considered, but it is felt that they can be reasonably dealt with in most applications. Detailed reports on these subjects are available from the Lawrence Radiation Laboratory.

Charges for thermonuclear devices, though somewhat arbitrary at the present time, show cost advantages for higher explosive yields when compared to conventional chemical explosives. The physical dimensions of the present nuclear devices allow for rapid, low-cost emplacement in drill holes, and it appears that many different ore deposits can be exploited by in-situ leaching in the *Nuclex*, as explained later.

During the past 10 years, experience has been gained with the detonation of several dozen underground nuclear explosions at the Nevada Test Site and elsewhere. These hard rock experiments have been fired in granite, granodiorite, basalt, andesite, trachyte, rhyolite, dolomite and volcanic tuff.



Rubble inside the chimney at the Piledriver test site. Note the mixture between large and small fragments.

The post explosion environment consists of a central rubble zone of fragmented rock surrounded by a permeable envelope of rock fractured by the explosion. Detailed examinations of test sites provide the quantity and characteristics of the broken rock, nature of the permeable envelope, as well as temperature and radioactive distribution in the fractured area.

Cavity radius, rubble chimney height, tonnage of rock broken, and dimensions of the permeable zone can be predicted within limits of 10% for deeply buried explosives. Results from subsequent nuclear explosions having the same yield range and in the same rock and area can be predicted within 5%. Curves representing the results obtained at a particular site can be prepared only after experience has been gained in that locality, since specific rock characteristics are a factor. The portion of a curve which represents the maximum amount of rock broken for a given yield, lies between containment and crater formation. A mound of rubble (retarc) forms as the broken rock falls back and overfills the hole from which it was ejected by the explosive force. The tonnage broken under these conditions is two to five times that produced with deeper burial (where a chimney is produced), and greater also than shallower burial (where a large percentage of the explosive energy is used in excavating a crater).

Rubble size distribution produced in basalt and granodiorite during several nuclear blasts at the Nevada Test Site (NTS) is shown on page 78. The size distribution depends primarily on characteristics and frequency of natural fractures, and the rock's crushing and shearing strength. Size distribution is not uniform throughout because proximity of the explosion and impact breakage from the downward fall of fragments have an affect. Smaller fragments and lower permeability can be expected near the base of the chimney.

Void space produced in hard rocks by nuclear shots results predominantly from rubble bulking and it usually varies between 15% and 30%. Typical values are 18% for craters and retarcs in basalt; 23% to 26% for chim-

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Mound of rubble (retarc) resulting from the Sulky nuclear experiment. The retarc measures 158 ft across and the cavity radius, rubble chimney height, tonnage of rock broken and permeable zone dimensions can be predicted within 10% limits.

neys in granitic rock; 27% for chimneys in dolomite; 16% to 20% for chimneys in rhyolite, and 5% to 15% for chimneys in various volcanic tuffs. The rubble bulking factor is important since, in most cases, the chimney grows upward until the bulking volume equals the original explosion cavity volume, with the rubble partially supporting the upward arch. For explosions in granite rock, the chimney height has been about four and a half times the cavity radius. At NTS, relatively low bulking factors in tuff and vesicular rhyolites resulted in several very tall and elongated chimneys with heights eight or more times the cavity radius. Rock tonnage in the rubble chimney is inversely dependent on bulking factor, since a low bulking rock will produce a taller chimney containing a greater tonnage. Retarc rubble tonnage is independent of bulking factor, but it does depend on the absolute value of the nuclear yield and the relationship between this and the depth of burst. A lower bulking factor produces a smaller rubble mound but the same tonnage of broken rock.

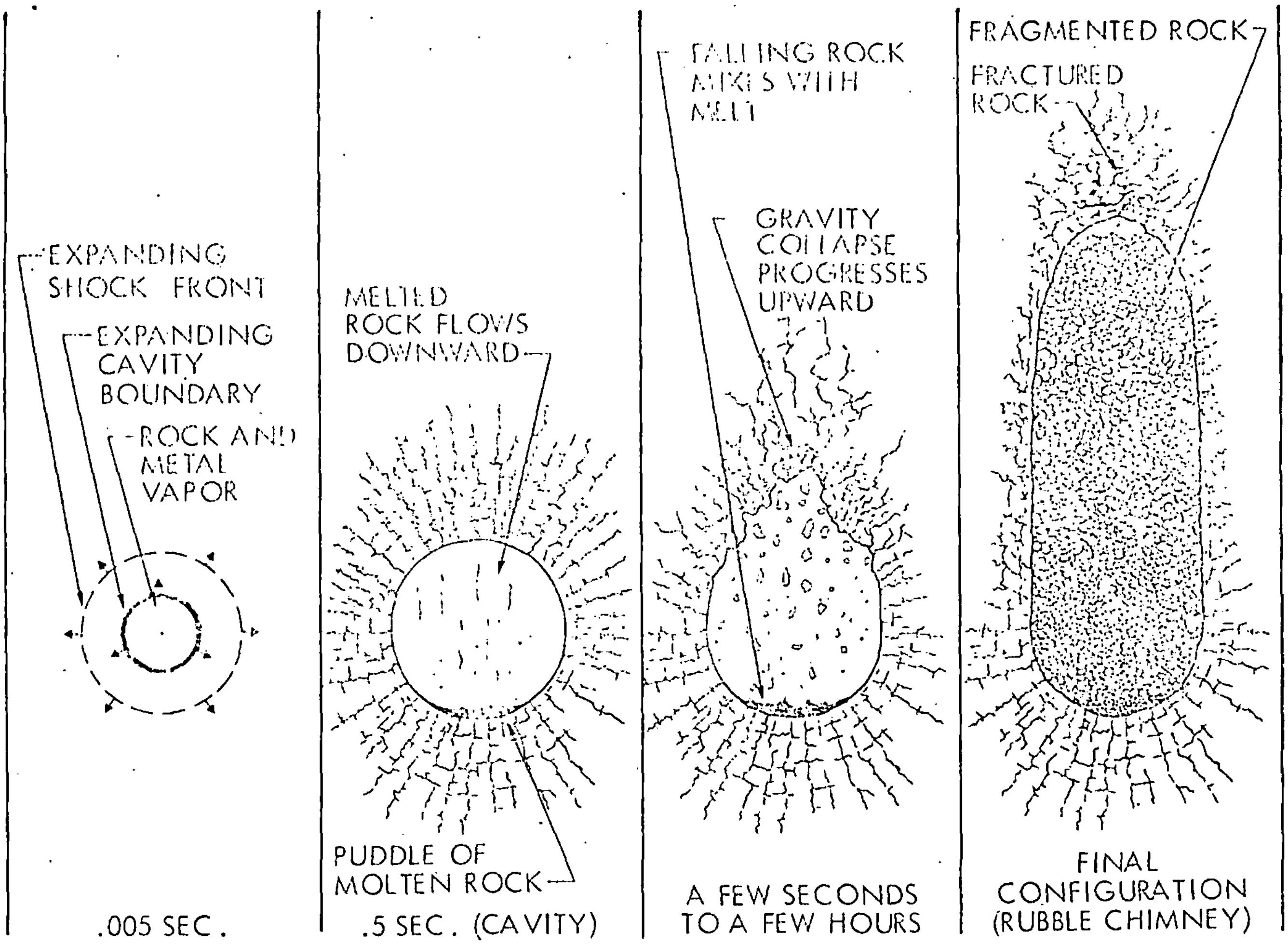
The best documented change in fracture permeability from a nuclear explosion is in the region outside the rubble chimney of the *Hardhat*[1A] test. A number of drill holes from 50 to 75 ft in length were drilled and pressurized with air to measure permeability variations by rate of pressure drop.[2] A regular decrease in permeability was measured outwardly from the explosion center. Permeability levels near the chimney boundary were up to 1,000 times greater than pre-shot recordings. At approximately 4 cavity radii from the explosion center (the outermost pressurized drill hole) permeability was still greater than pre-shot measurements. An increase in total number of visible fractures, and an increase in the size of pre-explosion fissures were observed in mine openings reentered after the explosion. Similar trends in visible fracture distribution were observed in the *Piledriver* experiment.

Physical properties of grandiorite samples obtained both pre-shot and post-shot from the vicinity of the *Hardhat* experiment were studied.[3] It was noted that very extensive changes in the physical properties of these rocks had occurred in the postshot samples. Bulk density, permeability, porosity, sonic velocity, crushing strength, and

Size distribution analysis of rock broken by a nuclear device*

Sieve size	Percent passing
6 ft	100
5 ft	96
4 ft	90
3 ft	80
2 ft	65
1 ft	45
6 in.	35
4 in.	30
2 in.	24
1½ in.	18
1 in.	16
¾ in.	14
½ in.	12
⅜ in.	9
#4 (0.127 in.)	6

*[illegible] the [illegible] in [illegible] site.



Sequence of events that unfold immediately after initiating a nuclear explosion underground to form fragmented rock.

Young's modulus were measured. Direct correlation was shown between all properties and distance from the explosion center. Porosity and permeability decreased in magnitude while the other properties all increased. In most cases, the properties measured were within a few percent of the pre-shot values at a distance of 3 cavity radii from the explosion center.

The *Handcar*[4] test was fired in highly fractured bedded dolomite. Air pressure tests[5] in the permeable zone surrounding the chimney indicated that increased permeability was evident up to five times the cavity radius from the explosion center. Void volume measurements suggest that the sum of the void space produced by explosion fracturing surrounding the chimney is approximately equivalent to the void space available between the rubble fragments in the chimney.

Migration of leach liquors is enhanced by fractures

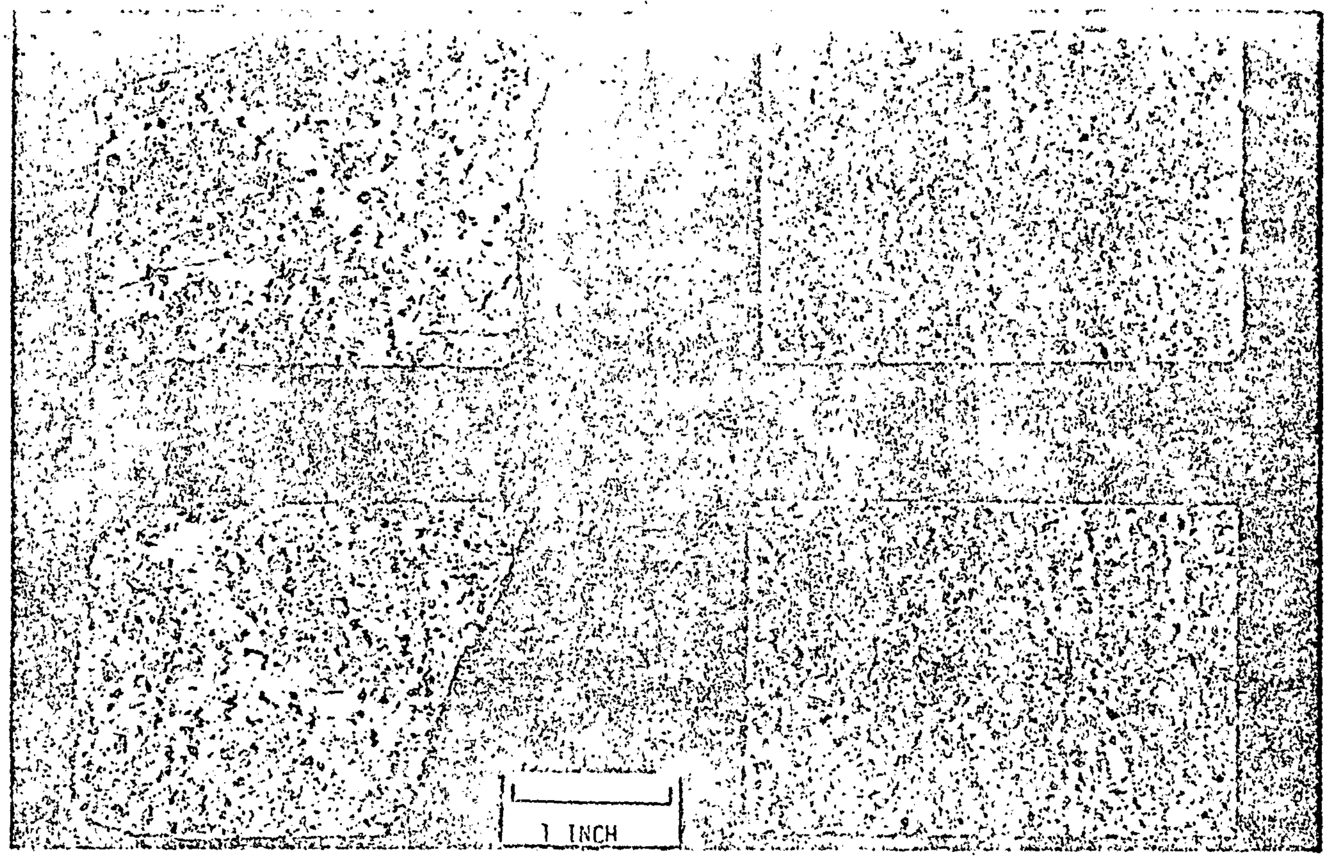
A study of microfractures in rocks exposed to nuclear explosive shock has been carried out with a petrographic microscope on specimens from several experiments.[6] A reproducible fracture index was defined and found to vary as a function of distance from the explosion center. This systematic change in number of microfractures was documented outward to 4 cavity radii from the explosion center.

Tests on more than 100 samples of granodiorite from the fracture-permeable envelopes surrounding the *Hardhat* and *Piledriver*[7] sites demonstrate that rock from this zone can be more easily penetrated by aqueous leach solutions than can rock broken by other means. Specimens of controlled size and shape were immersed in solutions containing Zyglo-22 (a dye that fluoresces in ultraviolet light). The samples were subsequently cut to determine the extent of penetration. It was noted that the penetration was significantly more rapid and complete in the rocks subjected to nuclear shock. Where ore minerals tend to be concentrated along fracture planes (even those which are recemented) an advantage will be gained since planes of weakness tend to be focal points for shock stress relief by dislocation.

Microfractures can be expected to increase the rate and completeness of penetration of solutions into and out of mineral grains and also increase the rate of chemical decomposition of the rock. This may be detrimental where minerals present have a tendency to form clays and cause plugging. Leaching operations frequently are a race between recovery of metal values and plugging of host rock permeability by alteration. Microfractures from nuclear shock tend to accelerate both processes, but by degrees that are not necessarily equal.

50% of generated heat retained in ground

Approximately 50% of the energy released by a nuclear explosion remains in the nearby vicinity as heat. In general terms, it has been established that 4 x 10^9 Btu's of heat energy are deposited in the shot environment for each kiloton of yield. Because rocks conduct heat slowly, temperatures in the explosion chimney and adjacent rock remain relatively high for many months or years, depending upon local conditions. Heat retention data are available from several experiments. Rock temperatures about 1½ cavity radii outside the *Hardhat* explosion center were approximately 135°F six months after the explosion.



Microfractures in rock within 1 cavity radius from the chimney boundary (left) are greater than at 4 cavity radii (right).

The temperature of the *Shoal*[8] chimney rubble was 160°F about three months after the shot. *Handcar* rubble temperature six months following the shot was 150°F at the chimney edge.

Oxidation of sulphide minerals (an exothermic reaction) will add heat to the explosion environment depending on the rate of oxidation and the quantities of sulphide minerals present. Temperatures in the 160°F range are frequently encountered in copper sulphide bearing dumps at depths in the 25-ft range from sulphide oxidation.

Temperature changes the rates of both chemical and bacterial reactions. Temperatures between 160° to 200°F significantly increase the rate of leach recovery, particularly in the case of the more refractory sulphide minerals. Since the optimum temperature for bacterial action is approximately 95°F, or slightly above, and the pasteurization temperature is about 160°F,[9] it is to be expected that little bacterial action will take place underground in the early stages after a shot because of the high temperatures involved. The lack of bacterial action at the higher temperatures is probably more than compensated for by the increase in chemical reaction rates. In the beginning it may be desirable to utilize bacterial action for oxidizing ferrous sulphate to ferric sulphate in specially designed holding ponds or tanks at the surface. After the temperature drops below 140°F or so, bacterial action underground may then become important.

Characteristics of a Nuclex environment

The *Nuclex* leaching environment of a contained explosion consists of three regimes of widely differing permeability. These are: (1) The leach environment in the rubble chimney; (2) the permeable envelope (roughly pear shaped); and (3) the unchanged surrounding rock. In the case of a retarc, the shapes of the rubble mound, permeable envelope and surrounding rock are different, but the characteristics are similar.

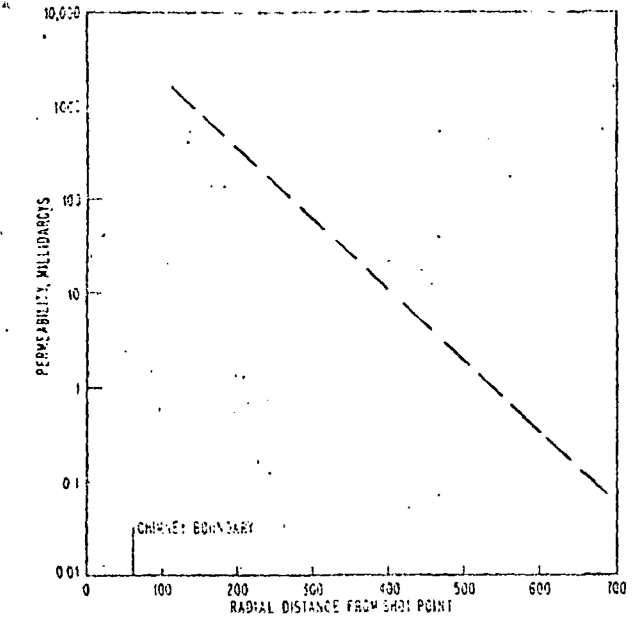
The physical characteristic of the chimney rubble approximates a pile of unsorted crushed rock which has passed through a large jaw crusher. The permeability of the chimney is typically greater than 1,000 darcys, with 15% to 30% void space. The chimney walls are abrupt and sharply defined. This permeable envelope has two subzones. They are: A spherical-shaped shock-fractured zone extending 3 to 4 cavity radii around the explosion center, and a zone of increased permeability surrounding the upper chimney and overlying its top. This zone forms from tension fractures related to the upward growth of the chimney by gravity collapse.

The total permeable envelope is composed of these two sub-zones which merge together to form an elongated and pear-shaped configuration outside the rubble chimney. The zones differ primarily by virtue of their different mechanisms of formation, and the reduced importance of shock microfracturing adjacent to the upper chimney. For granite, the typical permeability is from 100 millidarcys to 10 darcys at the inner portion of the zone, decreasing gradually farther out.

Outside the permeable envelope, the undisturbed rock retains its original pre-shot permeability. For comparison with the above zones, the *Hardhat* and *Piledriver* values were measured in tenths to a few millidarcys. Increased density around and beneath the explosion center, due to compaction and injection of molten rock into fractures, has provided a "barrier" to the downward loss of fluids. Shock-produced fractures, however, may penetrate this zone and cause difficult solution recovery problems.

Controlling leach solution may be a problem

The permeable regions described above can be expecte to pose rather unique problems of solution circulatio and recovery. Because of the extremely high permeabili of the "rubble chimney core," there is little tendency o the part of a fluid to penetrate the adjacent permeab envelope using percolation methods. Even though this e velope has substantially greater permeability than unfr



Rock permeability varies with the distance from the shot.

tured rock, it is 100 or more times less permeable than the chimney. The circulation of leach liquor into this envelope is important to the overall economics of any operation, since potentially two to ten times (depending on lower permeability cut-off limit) as much leachable rock exists in this section as in the chimney itself.

Periodic flooding of the "rubble chimney core" is suggested as offering the greatest hope of moving leach liquor in and out of the permeable envelope. The widest part of the envelope surrounds the explosion center, which will also be the locality of greatest hydrostatic pressure and fluid penetration. Subsequent pumping will permit flow of pregnant solutions into the "rubble chimney core" for complete removal. This technique promotes reversed capillarity, which carries dissolved values from the center of an ore fragment to the surface through microfractures. Subsequent reflooding of the ore column dissolves the surface salts from the ore.

Autoclave environment enhances chemical reactions

A high-temperature, high-pressure autoclave like environment might be produced from the controlled oxidation of contained sulphide minerals in a deeply buried rubble chimney. Elevated temperatures would result from the residual heat of the explosion (which would initially increase average rock temperatures in the chimney 60° to 80°F), and heat generated by the exothermic reaction of sulphide oxidation. The rate of heat generation in the "bedrock autoclave" subsequent to the explosion would depend on:

- The availability of oxygen to combine with the sul-sulphides to form sulphates, as $2H_2O + 4FeS_2 + 15O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 + \text{Heat}$.
- The reaction rate for the sulphide minerals under the temperature and pressure conditions present.
- The quantity of sulphide minerals available for reaction.
- Circulation of fluids in the environment.

Liquid oxygen has been used experimentally to initiate and maintain the sulphide-sulphate reactions in-situ, which might also promote internal circulation of solutions. The temperature of the "autoclave" will be a function of reaction rate and heat loss (by conduction through surrounding rock and from pregnant liquor removed). Optimum operating temperatures would be a compromise between a number of factors, including reaction rates of sulphide oxidation and rates of alteration to clay. The operating temperatures might be from 300° to 450°F. Pressures could approach the hydrostatic equivalent.

Ni, Zn, Co and Cr may be amenable to leaching

An operation of this nature may offer promise for the exploitation of low-grade, deeply buried, sulphide mineral deposits.[10] The reactions would not be dependent on bacterial action, or the relative low oxidation rate of sulphides at surface temperature and pressure. Also, potential applicability includes metals not ordinarily considered leachable, but those which have soluble sulphates: nickel, zinc, cobalt and chromium.

The retarc rubble mound consists of tumbled, angular fragments of poorly assorted broken rock with very high permeability. The characteristics of permeability and fluid flow are similar to the rubble chimney formed by contained explosions. The boundary between the fallback rubble and the surrounding fractured zone is gradational and can be distinguished only with difficulty. The extent of fracturing decreases outward until, at a distance equal to about 2 to 3 true cavity radii, it approaches that of pre-explosion rock.

Present information is not adequate to define the limits of effective permeability for leaching purposes since no permeability tests have been conducted in the area outside of retarcs. Available data, however, indicate the zone has approximately the shape shown in the accompanying diagram, and extends outward from the lower portion of the true crater 2 cavity radii or more.

Some advantages of nuclear blasting, then leaching

When conditions permit, several advantages can be realized if retarc configurations are used for in-situ leaching. These include:

- Maximum tonnage of rock is broken for any particular explosion yield, giving the lowest price per ton of rock broken for any nuclear explosion use.
- Expense of nuclear device emplacement is reduced because of the decreased depth.
- Leach solutions can be applied at minimum cost since the rubble is exposed at the surface.
- Development work for solution application galleries is eliminated. Underground collection galleries will be at minimum depths.

Conditions permitting retarc configuration are: The ore zone must be at or near the surface, the area must be some distance from populated areas to protect people from air blast and the escape of small amounts of radioactive fission products.

References

[1] Inquiries are sent to Technical Information Section, University of California, Lawrence Radiation Laboratory, P. O. Box 808, Livermore, Calif.

[1A] Hardhat was a 4.9-kiloton nuclear explosion fired on Sept. 15, 1962, in granodiorite at a depth of 939 ft. Dimensions of the rubble chimney were 63 ft in radius and 281 ft in height.

[2] Boardman, C. R. and Skrove, J., "Distribution in fracture permeability of a granitic rock mass following a nuclear explosion," pp 619-623, May 1966, JOURNAL OF PETROLEUM TECHNOLOGY.

[3] Mehta, M. M., Gupta, V. S., Somerton, W. H., "Changes in physical properties of rocks in he vicinity of an underground nuclear explosion," February 1964, unpublished report of University of California's Rock Physics Laboratory.

[5] Boardman, C. R., Meyer, G. L., Rabb, D. D., "Microdeformation resulting from the Handcar event," Lawrence Radiation Laboratory, UCRL-50149, 1967.

[4] Handcar was a 12-kiloton nuclear explosion fired on Nov. 5, 1964, in dolomite at a depth of 1,320 ft. Dimensions of the rubble chimney were 70 ft in radius and 223 ft in height.

[6] Short, N. M., "Effects of shock pressure from a nuclear explosion on optical and mechanical properties of granodiorite," September 1964, Lawrence Radiation Laboratory, UCRL-7949.

[7] Piledriver was a 61-kiloton nuclear explosion fired on June 2, 1966, in granodiorite at a depth of 1,502 ft. Dimensions of the chimney rubble were 160 ft in radius and 890 ft in height.

[8] Shoal was a 12.5-kiloton nuclear explosion fired in granite at a depth of 1,205 ft. Dimensions of the chimney rubble were 84 ft in radius and 356 ft in height. The chimney contained 750,000 tons of broken rock.

[9] Trussell, P. C., "Recent advances in the microbiological leaching of sulphides," February 1966, AIME reprint 66B21.

[10] Johnson, P. H., "The underground autoclave and its applications to hydrometallurgy," February 1965, paper presented at annual AIME meeting in Chicago.