tion and recleaning operations (g/ton): 230 potassium permanganate, 450 lead acetate, 25 aerofloat.

The results from an experiment on the separation of the collective concentrate, realised in a continuous process from five samples with recycling of the intermediate products, are given in table 2.

The antimony concentrate contained 5.7%Pb with extraction of about 74% of the lead into it. The pyrite concentrate contained 38-40%S and 20 g/ton of gold. More than 70% Sb was extracted from it into solution during leaching with sodium sulphide.

Table 2: Results from selection of the collective concentrate

Product	Yield %	Content %			Extraction %		
		Sb	Fe	As	Sb	Fe	As
1st Sb concentrate	13.6	44.71	9.52	0.31	52.6	4.6	3.5
2nd Sb concentrate of intermediate cycle	11.4	26.58	15.76	1.18	26.1	6.6	10.9
Total Sb concentrate	25.0	36.6	12.2	0.71	78.7	11.2	14.4
Pyrite concentrate	75.0	3.32	32.5	1.41	21.5	88.8	85.6
Collective concentrate	100.0	11.6	27.25	1.24	100.0	100.0	100.0

Conclusions

In the separation of collective concentrates containing antimonite, pyrite, and arsenopyrite chlorinated lime and potassium permanganate can be used for depression of the pyrite and arsenopyrite.

UDC 622.7

Concentration of lead-baryte ore of the Chachu-Kulack deposit

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Summary

The article gives the results from tests on the concentration of a technological sample of ore from the Chachu-Kulack deposit. The ore investigated can be assigned to the type of sulphide-oxide lead-baryte ore with a high lead content.

The best results in the concentration of the ore during the laboratory investigation were obtained by a scheme involving preliminary concentration of the ore in a heavy suspension with particle size -30+3mm and flotation of the concentrate mixture from concentration in heavy suspension with the -3+0mm class. The tailings from concentration in heavy suspension (with a yield of 34.14% on the initial ore) contained 0.089% Pb and 2.41% of baryte.

Good technical results were obtained during joint flotation of sulphide and oxidised lead minerals and also during baryte flotation from the concentrate mixture from concentration in a heavy suspension with the -3+0mm class. A lead concentrate was obtained with up to 76% Pb, and a baryte concentrate was obtained with 87-89% $BaSO_4$. With allowance for the de-assignment of the intermediate products the lead extraction can be brought to 85-87% and the baryte extraction to 80%.

The kinetics of the flotation in any cycle (sulphide, oxide, baryte flotation) obey the equation $\varepsilon = kt^{1-m}$. Specific kinetic equations are given for each form of flotation.

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UDC 669.71

Intensification of autoclave processes in alumina production

N I Eremin, Yu A Lainer and V V Medvedev

Autoclave processes find use in alumina production during the leaching of bauxites by the Bayer process: in the desiliconising section for the production of alumina from high-silicon bauxites and nephelines: in the chemical concentration of nepheline syenites: and in the treatment of low-grade aluminium raw material by alkaline and acid methods at the stages of its decomposition and the isolation of aluminium compounds by hydroylsis etc[1-4]).

In the USSR and abroad the leaching of bauxites is realised in batteries of autoclave battery is a complex continuously operating plant, involving heaters, autoclaves and steam separators (fig. 1). Thus, at the Martinswerk plant (Federal Republic of Germany) each autoclave battery intended for the leaching of boehmite and hydrargillite bauxites comprises ten heaters (heat exchangers), four autoclaves (leachers) and nine separators.

Two types of autoclaves are used: 1) autoclaves with a blade mixer and heating coil; 2) autoclaves without mixers and heating coils and with live steam heating (figs. 2 and 3). For the first type the autoclaves used at the alumina plants have a heating surface up to 200m² with p = 40atm. and capacities between 50 and 100m³: for the second they have diameters between 1.6 and 2.5m, heights between 9.8 and 15m, and capacities between 24 and 70m³ [5]). The most powerful autoclaves with diameter of 3.0m, heights up to 21m in the cylindrical part, and total capacities up to 150m³ have been established in the Federal Republic of Germany[6]).

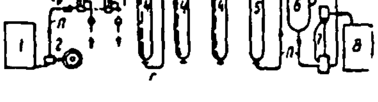
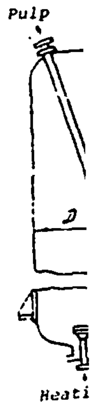


Fig.1 Diagram of the contin autoclave plant for the lea of bauxite: 1 - mixer; 2 - p 3 - heater; 4 - autoclaves; 5 - step I separator; 6 - step II separator; 7 - mixer; 8 - mi for dilution; C live steam f B-1 secondary steam of step I; B the same for step II.



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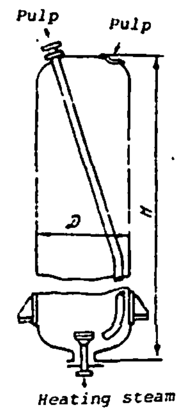

Fig.2 Autoclave with live steam heating

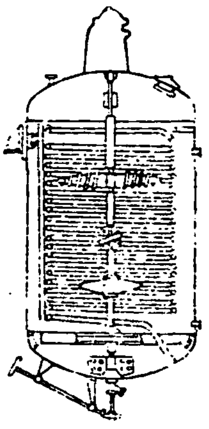

Fig.3 Autoclave with mixer and heating coil.

A great achievement in autoclave technology was the transition to a continuous process, and this secured an increase in productivity, a reduction of operating costs, and more complete utilisation of the heat content of the leached pulp. In respect of equipment continuous leaching of bauxites differs in two main directions.

The first is characterised by the use of autoclaves with blade mixers and built-in heating elements. Batteries of such autoclaves, which act simultaneously as heaters and reactors, are used for the treatment of boehmite bauxites at, for example, alumina plants in France (Gardanne, la Barasse), in Hungary (Aika) and in Yugoslavia. Asa result of the large capacity of the system, which is structurally necessary for the location of the heating surface, and the easy disintegration of such bauxites complete or almost complete leaching can be achieved.

The second direction differs in the use of shell-tubular heat exchangers as heaters and elongated hollow autoclaves without mixers and heated with live steam as reactors, and this is based on ideal displacement conditions. Such batteries are used for the treatment of various types of bauxites in the USSR and the Federal Republic of Germany.

Both types of autoclave batteries are characterised by specific advantages and disadvantages.
1. The presence of mixers in the large-capacity autoslaves required to secure the flow of the pulp around the heating elements, creates conditions close to ideal mixing. Heat transfer takes place at the final temperature difference for a given degree with a heat transfer coefficient of 300-350kcal/m^2.h.deg. In tubular heaters the average heat transfer coefficient amounts to 600-700, since the heat is transmitted with a temperature difference which decreases from the initial to the final value. Therefore, the establishment of large-capacity autoclaves for the production of an equal technical heat effect requires twice the heating surface and four to five times the weight of equipment as with the use of shell-tubular heaters.
2. The presence of drives and rapidly wearing components (packings, bearings etc.) in large-capacity autoclaves creates difficulties in operation. When any mechanical component or apparatus falls out of service for cleaning the heating surface it is necessary to undertake a bypassing operation on the autoclaves for a single shut off, and this requires the establishment of particularly reliable locking devices.
3. Heating of the pulp with live steam, while considerably simplifying the active heating operation, has a substantial disadvantage in the increased steam requirement both for leaching and for evaporation.
4. An advantage of autoclaves with mixers and heating coils in their lower rate of build up and the easier cleaning of the heating surface.

At the present time there are no data for direct comparison of the operation of the first and second types of autoslave batteries on pulps in Soviet plants and in the choice of one or the other type of autoclave in designs for new plants and factories it is necessary to take the properties of the bauxites and slime suspensions, which can be obtained on experimental plants, carefully into account.

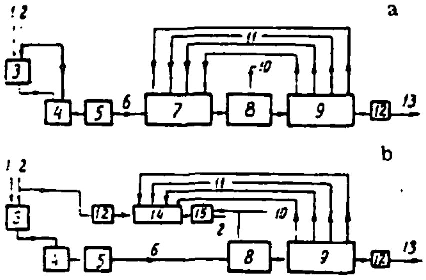

Fig.4 Diagram of the single-flow (a) and two-flow (b) processes: 1) bauxite; 2) strong solution; 3) wet grinding; 4) collecting tank; 5) pump; 6) pulp; 7) heaters; 8) leachers; 9) separation of pulp; 10) high-pressure steam; 11) separator steam; 12) centrifugal pump; 13) to dilution; 14) group of heaters; 15) heat exchanger.

In the continuous leaching of bauxites in autoclaves[7]) it is possible to distinguish two methods, i.e. single-flow and dual-flow (fig. 4). In the single-flow method the pulp, consisting of ground bauxite and strong solution, passes through a series of heaters where the heating is realised by separator steam and then through leachers, where the required bauxite digestion temperature is achieved through the use of live steam. The majority of autoclave batteries in alumina production operate by the single-flow scheme.

In the dual-flow method the material flow is divided into two inequal parts. The main part (80-85% of the total flow) of the strong solution is gradually heated in tubular heat exchangers with the use of separator steam. Heating of the pure solution in the heat exchangers requires a smaller heating surface, and the build up of deposits here must be less. The remainder of the strong solution is withdrawn for wet grinding of bauxite. Both flows (the recycled sodium aluminate solution heated with separator steam and the bauxite pulp with a high solid phase content) are mixed for leaching. Heating to the required temperature is realised by a contact method.

Thus, the difficulties associated with the heating of the bauxite pulps are considerably smaller in this method. The dual-flow method is practised at the plants in Martinswerk[7]). At the same time a considerable improvement was observed in the sedimentation characteristics of the red mud, and this led to improvement in its settling behaviour and the filtration of the pulp. The dual-flow method of autoclave treatment was adopted in the plan of the Razdan Mining-Chemical Combine for chemical concentration of nepheline syenites. In this case there were indications against self-evaporation, and the heat of the autoclave pulp was used by direct heat exchange with the heated solutions. A special design of shell-tubular heat exchange, securing counterflow of two media with equal rates, was developed for this purpose at the All-Union Aluminium and Magnesium Institute.

Temperature is the most important factor in the acceleration of the leaching of bauxites. With increase in temperature the dissolution rate of the alumina increases (fig. 5), and the required leaching time can consequently be reduced with retention of the same degree of extraction[8]).

As far back as 1934 Hiller[9]) proposed to leach bauxites in tubular leachers at 280-290 °C. In more recent years there has been a clear tendency throughout the world to increase the leaching temperature of bauxites. The problems of semi-industrial trials and industrial implementation of high-temperature leaching of bauxites in tubular reactors have been resolved (fig. 6). Thus, a semi-industrial high-temperature (up to 290°C) leaching plant, where bauxite from various deposits of the USSR and abroad were tested, has been in operation at the Dneprovsk Aluminium Works for several years. An industrial plant for the high-temperature leaching of bauxites is in operation at the Nabwerk plant in Germany[10]). In 1969 the same plant, with a productive capacity of 60 000 tons of alumina a year, was introduced at the Lippewerk Works[11]). The time required to leach the bauxites at a temperature of ~300°C amounts to 1-2 min. The maintenance of such a plant is extremely simple and is realised by a small number of workers.

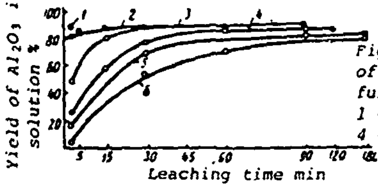

Fig.5 Kinetics of the leaching of North-Urals Bauxites as a function of temperature °C: 1 - 280, 2 - 260; 3 - 240; 4 - 225; 5 - 215; 6 - 205.

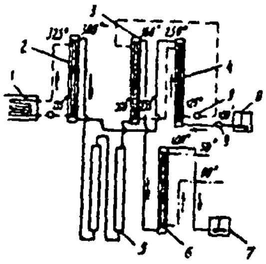

Fig.6 Diagram of the leaching of bauxites at high pressures on one of the experimental plants: 1) heat generator; 2) final heat exchanger; 3) and 4) intermediate heater exchangers; 5) reactors; 6) pulp cooler; 7) and 8) mixers; 9) pumps; --- pulp, diphenyl mixture; -.- water

The flow-type leaching of bauxites at temperatures above 350°C and pressures of 270 atm. in a tubular reactor 14m long, calculated for a continuous process, has been investigated in Hungary. Trials showed that under these conditions the alumina dissolves in 2 min, and the extraction in the solution is higher than the calculated value.

During comparison of ordinary autoclaves with the tubular reactors it should be noted that the former can only operate up to temperatures of 240-245°C, while the tubular reactors can operate up to 300°C or higher[12]). The specific volume of a tubular reactor ($1m^3$ of reaction volume for 1 ton of aluminium oxide produced) is considerably smaller than in the case of a series of autoclaves. The cost of the tubular plant amounts to about two thirds of the cost of an autoclave plant with the same productive capacity. A necessary condition for the operation of the tubular reactors is the existence of pumps suitable for transferring large amounts of pulp at counterpressures of 100-200atm. As heat carrier it is possible to use high-temperature high-pressure steam and also high-temperature organic heat carriers or molten salts.

A great advantage of the high-temperature leaching of bauxites is the fact that the leaching can be realised with dilute recycled solutions and the load on the evaporating batteries can be greatly reduced. The caustic ratio of the solutions after leaching can be at a level of 1.30-1.35, and this leads to their more rapid decomposition at the decomposition section. In order to prevent the separation of finely dispersed aluminium hydroxide it is recommended that a low caustic ratio in the solution be coupled with an increased decomposition temperature. In such a combination centrifuging takes place at a higher rate, and coarsely crystalline aluminium hydroxide is isolated.

A high leaching temperature (>280°C) also leads to an improvement in the sedimentation of the red mud, and this is due to the formation of well crystallised cancrinites and also the complete dehydration of the geothite at this temperature. Complete dehydration of limonite requires a somewhat higher leaching temperature of 320-360°C[10]). In the high-temperature leaching of diaspore bauxites the need to add lime is retained, but its amount can be reduced.

Improvement of schemes for regeneration of the heat of the autoclave pulp is extremely important in the autoclave leaching of bauxites. Such regeneration can be realised either by direct heat exchange from the leaching pulp to the pulp passing on for leaching or by stepwise self-evaporation of the aluminate solution. Thus, the first variant can be more promising for the high-temperature technology of the treatment of low-silicon diaspore bauxites[13]).

An advantage of multi-step evaporation is the combination of the effective utilisation of the heat of the autoclave pulp with the removal of water from it, which is important for the heat scheme of the Bayer process as a whole. A multi-step system for ordinary large-capacity separators requires reliably operating devices for automatic control of the pulp level in each separator.

The main difficulties in the practical utilisation of autoclave processes in the production of alumina are associated with specific characteristics of the bauxite suspensions, including the crystallisation of difficulty soluble compounds which form deposits on the walls of the apparatus. In mineralogical composition these deposits can be divided into three main groups. The first (with a pulp temperature below 160°C) is composed of sodium aluminosilicate of the nosean, haematite and boehmite type; the second (above 160°C) is composed of perovskite, sodium aluminosilicate of the cancrinite type, haematite and a small amount of boehmite and magnetite; the third (above 230°C) is composed of hydroxyapatite and haematite. The deposits are zonal.

The mechanism of the incrustation of the heater during digestion of bauxite can be represented as follows: passage of silicon, titanium, phosphorus, calcium and iron compounds and impurity components into solution; supersaturation of the solution with these components and the formation of precipitates. By forming a compact film the precipitates greatly reduce the heat transfer coefficient, and this leads to an increase in the steam consumption and a decrease in the productivity of the apparatus. On an experimental plant at the Dneprovsk Aluminium Works relationships were obtained between the heat transfer coefficient and the thickness of the deposit on the pulp heater tubes for various leaching temperatures (fig. 7). Decrease in the calculated heat transfer coefficient gives rise to the need for an increase in the number of self-evaporation steps in order to retain the specified heating temperature in the raw pulp in the heat exchangers, as follows from fig. 7, and this leads accordingly to an increase in the capital costs of construction.

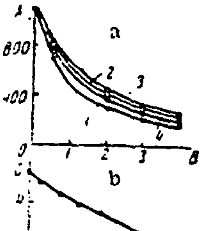

Fig.7 a) Dependence of the heat transfer coefficient (a kcal/m²·deg) on the thickness of the deposit (B mm) on the pulp heater tubes: 1 - 100-160°C, 0.80 kcal/kg·°C; 2) 160-200°C; 3) 200-235°C, 1.40kcal/kg°C; 4 - 235-275°C, 1.10kcal/kg°C; b) Effect of the heat transfer coefficient (A) on the number of self-evaporation steps (C).

The investigations showed that the intensity of the encrustation of the heaters, which is determined by the heating temperature and the composition of the raw material, can be substantially reduced. For this purpose it is necessary to secure the minimum temperature difference between the steam and the pulp and to adopt special measures eliminating supersaturation of the solution primarily in TiO_2 and SiO_2. They include brief holding of the pulps at one or two critical temperature points and also additions of calcium oxide within appropriate limits.

Of other methods for reduction of deposits magnetic and electric treatment of the solutions and pulps is promising. With magnetic treatment of a solution saturated with silicic acid an appreciable decrease in deposit formation was observed at the All-Union Aluminium and Magnesium Institute Heat Exchange Plant. Industrial trials at DAZ on the effect of magnetic treatment on the encrustation of pipelines were successfully completed. Continuing industrial trials on the electric treatment of aluminate solutions subjected to evaporation are giving stable positive results. Analogous trials on the protection of the bauxite pulp heating surface will be carried out at DAZ. If the problem is successfully developed, magnetic and electric treatments will be the least energy-consuming and the simplest methods of protection. Thus, intensification of the bauxite leaching process in the production of alumina will take place in the coming years as a result of improvement in the design of the equipment of the autoclave battery, increase in the bauxite digestion temperature, more extensive regeneration of heat (reduction of steam consumption), and the search for effective methods of fighting against encrustation.

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Some physicochemical characteristics of diaphragms in the electrodialysis of ammonium molybdate solutions

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Summary

Electrodialysis with ion-exchange membranes is a promising method for the extraction, purification, and concentration of solutions containing compounds of various metals. The effectiveness of the method depends on the characteristics of the memberanes. The article gives the results from investigation into the physico-chemical characteristics of membranes in contact with ammonium molybdate solutions, including diffusion coefficients, transport numbers, mobility of MoO_4^{2-} ions, electrical conductivity, and polarisation effects at the membrane-solution boundary. These are the most important characteristics which determine the selectivity of the membranes and the energy expenditures in the electrodialysis process.

Some of the membranes possess high electrochemical characteristics and considerable diffusion coefficients for MoO_4^{2-} ions. They are recommended for use where the attainment of a high degree of concentration is not required during extraction of molybdenum by electrodialysis i.e., where the effect of reverse diffusion flow is small.

Another membrane occupies an intermediate position and has lower diffusion permeability. This makes it possible to use it for the electrodialysis of concentrated solutions of ammonium molybdate.

UDC 669.2

Some relationships in the distribution of the components between the separating phases in the Cu_2S-FeS-FeO-SiO_2 system

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Treatment of the experimental results from investigation of the region of separation in the FeS-FeO-SiO_2 and Cu_2S-FeS-FeO-SiO_2 systems[1,2]) made it possible to obtain relationships describing the mutual solubility of the components between the two equilibrium phases at 1473°K. These relationships were represented in a rectangular system of co-ordinates (some of them were described analytically) and can be used to solve various practical problems. It is difficult to use the phase diagram of the Cu_2S-FeS-FeO-SiO_2 system directly for this purpose on account of the impossibility of constructing isocomposition sections suitable for practical use.

In the present report the relationships obtained are discussed as applied to the processes of fusion of sulphide copper raw material and the converter treatment of copper mattes.

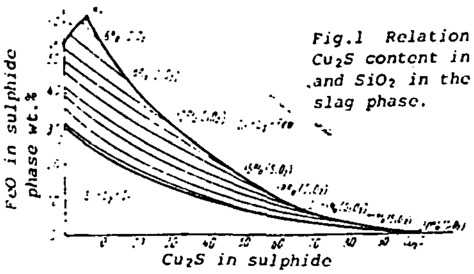

Fig.1 Relation between FeO and Cu_2S content in the matte phase and SiO_2 in the equilibrium slag phase.

Fig 1 shows the relation between the contents of FeO and Cu_2S in the sulphide phase (matte) and SiO_2 in the slag phase in equilibrium with it: $[FeO] = f[Cu_2S](SiO_2)$. (Here and subsequently square brackets are used to indicate that the gas-collection hood, and the variation in the composition of the outgoing anode gas was monitored at the same time. It was established that the length of the transitional process along the gas channel (12 min) depends on the state of the region below the hood. From the presented characteristics it follows that the length of the transitional process along the gas channel is not limited by the gas route.

Conclusions

1. Representative gas sampling points were found where the error from the nonrepresentativeness is comparable with the instrumental error. Consequently, the error of the chromatographic equipment does not limit the accuracy of the analysis.
2. The variation and character of the gas pressure under the gas-collection hood was investigated. On this basis conclus were reached about the gas delivery points.
3. The dynamic characterisitics of the gas channel were investigated.
4. It was established that the largest component of the erro in the determination of the productivity of the electrolytic cell is the disturbance caused by the inflow of air, and the algorithm for control of the productivity must consequently eliminate this error as much as possible.

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Investigation of the behaviour of gold in cyanide solutions.

A N Lebedev V V Gubailovskii and I A Kakovskii (Urals Polytechnical Institute and Lower-Tagil State Pedagogical Institute).

Investigation of the reaction of gold with cyanide solutions is of interest both for the theory of the electro-chemical dissolution of metals in solutions of complex electrolytes and for practice in certain technological processes and, in paeticular, the cyanide method for the treatment of gold-containing ores 1). Previous researches 1-3) have shown that the phase or adsorption layers formed on the surface of gold in the reaction have a considerable effect on the rate of dissolution of gold in cyanide solutions.

In this connection it seemed expedient to study the behaviour of gold in cyanide solutions by the potentiostatic method of recording the anodic polarisation curves. The electrode, made from ZL99.99 gold, was polarised by means of a P-5827 potentiostat. The potentials were measured with reference to a silver chloride reference electrode and converted to a hydrogen electrode. The experiments were carried out in a thermostated cell at 25 and 35°C. The concentration in the solution varied from 4.3 to 14. 4. 10^{3} M. Potassium hydroxide was added to the solution (pH = 11. 6) to reduce the hydrolysis of the cyanide.

Fig. 1a shows the anodic potentiostatic curves for gold with various concentrations of potassium cyanide in the solution. On these curves sections corresponding to active dissolution of gold can be distinguished in the region of potentials between -0. 50 and +0. 75 V. Under these conditions the anodic current depends on the concentration of cyanide in the solution. A similar effect of anions on the electrochemical dissolution rate of metals was demonstrated earlier in work by Kolotyrkin 4), which made it possible for the author to conclude that the anions take part in the electrochemical stage of the ionisation of the metal. The anodic reaction of the dissolution of gold in cyanide solutions can be represented as a two-stage process:

$$\mathrm{Au + CN^- = AuCN + e} \qquad \text{(a)}$$

$$\underline{\mathrm{AuCN + CN^- = Au(CN)_2^-}} \qquad \text{(b)}$$

$$\mathrm{Au + 2CN^- = Au(CN)_2^- + e,} \qquad (1)$$

$$\varphi_0 = -0.543\mathrm{B}\ [5]$$

When $\varphi > -0.10$ V the anodic overpotential of this reaction increases abruptly, and the anodic current, reaching its maximum value, remains practically unchanged over a fairly wide range of potentials ±0. 00-0. 75 V (fig. 1a). Such a "diffuse" maximum on the potentiostatic curves is typical of some metals 6).

It can be supposed that the considerable increase in the anodic overpotential at $\varphi > -0.10$ V is due to the formation of a salt film of AuCN on the surface of the gold in accordance with stage (a) of reaction (1). In this case the shift of the potential results from a fall of the potential in the film, as observed, for example, in the anodic dissolution of copper in sodium chloride solution 6).

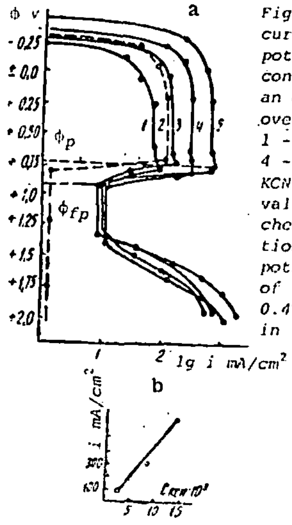

Fig.1. a) Anodic potentiostatic curves for gold in solutions of potassium cyanide with various concentrations (M) at 25°C with an oxygen pressure of 0.21atm over the solution at pH 7.6. 1 - $4.3\cdot10^{-3}$; 2,3 - $2.64\cdot10^{-3}$; 4 - $3.42\cdot10^{-3}$; 5 - $14.4\cdot10^{-3}$ KCN. (In curve 2 the current values were calculated from chemical analysis of the solution for the given electrode potential). b) The dependence of the anodic current at ϕ = 0.4V on the cyanide concentration in the solution (pH = 11.6, 25°C).

However, an electron diffraction analysis confirms the presence of cyanides in the phase film on other metals and, in particular, on copper and silver, but it was not possible to detect them on gold 7). This is evidently explained by the extremely strong affinity of gold to cyanide. In fact, the equilibrium constants of the reactions $\mathrm{AgCN + CN^- = Ag(CN)_2^-}$ and $\mathrm{CuCN + CN^- = Cu(CN)_2^-}$ are almost three orders of magnitude lower than that of the reaction $\mathrm{AuCN + CN^- = Au(CN)_2^-}$ ($5.0.10^4$, 3.10^4, and $1.6.10^7$ respectively 8)).

The limiting value for the anodic current at potentials of ±0. 00-0. 75 V is probably due to diffusion limitations. This is demonstrated, first, by the linear dependence of the anodic current on the cyanide concentration in the solution (fig. 1b) and, second, by the comparatively weak dependence on temperature (fig. 2, curves 1 and 3). The experimental activation energy of the anodic process for φ = 0. 40 V is about 5. 0 kcal/mole, whereas the value for conditions when the ionisation of the metal is the controlling stage it reaches values of 9. 8-14. 1 kcal/mole 1).

The potential corresponding to the beginning of passivation of gold φ_p in cyanide solutions is practically independent of the concentration of cyanide in the solution and is equal to about 0.75 V (fig. 1a). The value of this potential for gold determined by Vetter 9) from the charging curves in potassium sulphate solution differs from our value and is about 0.5 V. This may be explained by the effect of the complexing agent potassium cyanide.

If it is assumed that the transition to the passive state is due to the formation of oxygen compounds on the surface of the gold, the reactions giving rise to this passivation in alkaline cyanide solutions can be written as follows:

$$2Au + {}^{3}\!/_{2}O_2 = Au_2O_3 + 6e\,, \qquad \varphi_0 = 0.532\ [10] \qquad (2)$$

$$Au + 3OH^- = Au(OH)_3 + 3e\,, \qquad \varphi_0 = 0.590\ [11] \qquad (3)$$

Under the conditions of our experiment at pH = 11.6 the thermodynamically calculated equilibrium potentials of these reactions are $\varphi_2 = 0.61$ and $\varphi_3 = 0.73$ V respectively. They are fairly close to the experimentally obtained potential corresponding to the beginning of passivation of gold φ_p. = 0.75 V (fig. 1a), and this confirms the possibility of passivation of gold by its oxygen compounds. Electron-diffraction analysis of the phase film on the surface of gold also shows that it consists of the oxide or hydroxide of trivalent gold 7).

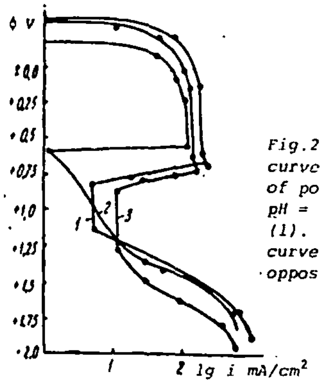

Fig.2 Anodic potentiostatic curves for gold in a solution of potassium cyanide ($4.21 \cdot 10^{-3}$M, pH = 11.6) at 25°C (3) and 35°C (1). Oxygen pressure 0.21 atm; curve 2 was recorded in the opposite direction at 25°C.

At the full passivation potential $\varphi_{fp} = 0.9$ V (fig. 1a) the gold acquires a stable passive state, which is retained at extremely positive potentials (up to 2V). The increase in the anodic current at potentials of more than 1.35 V is due to the anodic reaction of oxygen evolution, and this is confirmed conclusively by comparison of curves 2 and 1, 3-5 (fig. 1a). On curve 2 the values of the anodic current were calculated from the amount of gold passing into solution at a given potential, determined by chemical analysis, and at $\varphi > 1.35$ V no increase in current is found. Curves 2 and 3, obtained from the data from chemical analysis and electrochemical measurements of the anodic current under the same conditions, are fairly close. Only the values of the current in the passive region differ, and this is clearly explained by the difficulty in the chemical determination of gold in a solution with extremely small degree of dissolution.

The passivation of gold is accompanied by the formation of fairly stable layers on the surface, since a hysteresis loop is observed when the potentiostatic curves are recorded in the forward and reverse directions (fig. 2, curves 2 and 3). A feature of the behaviour of gold in the passive state is the nondependence of the anodic current on the cyanide concentration, whereas a clearly defined effect of the cyanide ion on the value of the current is observed, on the other hand, at the active dissolution potentials (fig. 1a, b). This is evidently explained by the fact that the oxide compounds of trivalent gold react little with cyanides. Consequently, the active dissolution reaction of gold (1) takes place mainly on the surface free from oxide layers, while reactions (2) and (3), which give rise to passivation of the gold, greatly reduce the rate of its passage into solution. It is interesting that the passivating effect of reactions (2) and (3) increases with increase in temperature, since the current in the passive state (i_{fp}) is higher at 25°C than at 35 C (curves 1 and 3 in fig. 2). This contradicts the known ideas, according to which increase in temperature usually impedes passivation and increases i_{fp} 8). However, the possibility of intensification of the passivating effect with increase in temperature becomes understandable if the facts that the formed oxide compounds of trivalent gold are pratically insoluble in the cyanide solutions and that the rate of reactions (2) and (3) increases with increase in temperature are taken into account.

Thus, on the basis of the investigations it is possible to distingiush two charatceristic regions of potentials (-0.5 to +0.75 V and 0.75-2.0 V) where the gold dissolves with different kinetic relationships. In the first the ionisation rate of gold increases with increase in temperature and in the cyanide content of the solution. In the second (the region of the passive state), on the other hand, it decreases with increase in temperature and is practically independent of the concentration of the cyanide solution.

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UDC 537.311.1:546.221'86'56-143

The nature of charge transfer in melts of the Sb_2S_3-Cu_2S System

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In the liquid state the sulphides of heavy metals have mixed ionic/non-ionic conductivity. Here, whereas the ionic contribution predominates for the Sb_2S_3 melt 1)2) near the melting point, carriers of nonionic character have the predominating effect on the formation of the character of conductivity in copper sulphide in the liquid state 1).

It seemed of interest to study the effect of continuous cation exchange in the above-mentioned sulphides on the nature of the conductivity of the melts. Melts of the Sb_2S_3-Cu_2S system have previously been investigated by conductivity and thermo emf methods 3) and were interpreted as liquid semiconductors, and this (as will be shown below) simplifies the actual pattern

N12, 1975

INCREASING THE DIRECT EXTRACTION OF ZINC IN HYDROMETALLURGICAL PROCESSING OF TIN-BEARING DUSTS[1]

UDC 669.536.221:669.648

E. Ya. Ben'yash, G. A. Motornaya, and T. M. Sukhorukova

The sublimates produced in converting copper mattes, processing secondary copper material, and fuming certain slags are concentrated by neutral leaching and by final acid leaching of the residue. After removal of impurities, the solution which is formed is used for zinc sulfate production and the lead-tin cake is used for production of lead-tin alloys by electric smelting.

Percentage Composition of Sublimates and Lead-Tin Cakes Processed

Elements and compounds	Fuming sublimates*	Electric-furnace sublimates	Copper plant sublimates	Lead-tin cake	
				existing technology	new approach
Total zinc	23,5	45,3	63,5	12,4	4,5
Including:					
oxide+sulfate	17,5	39,9	62,8	5,08	3,45
metal	0,09	0,11	0,38	—	—
sulfide	0,25	0,85	0,23	0,90	0,57
stannate	5,60	4,37	0,09	6,42	0,52
Copper	0,45	0,20	1,47	1,00	0,73
Tin	12,2	7,15	0,36	12,3	13,7
Lead	25,3	11,8	3,78	19,1	21,6

*The composition of solids from wet dust-catcher pulp is given.

The high zinc content of the cake (see Table) causes the technical and economic results of electric smelting to deteriorate and leads to losses of tin and zinc.

It is apparent from the Table that 60% of the zinc in the lead-tin cake is present in the form of relatively insoluble compounds (stannate and sulfide).

Zinc stannate is decomposed by concentrated sulfuric and hydrochloric acids and in the process of acid autoclave leaching. In practice, however, it proved impossible to increase acidity over 5-7 g/liter because the filterability of the pulp was substantially reduced.

The following sequence of leaching operations was adopted: first the fuming sublimates and electric smelting sublimates were leached at increased residual acidity, then lime was fed in to precipitate fluorine and sublimates with a low content of relatively insoluble forms of zinc (copper enterprise sublimates and the like) to neutralize the acid. The excess of these was leached out with sulfuric acid at a pulp pH of not less than 4.7 ("reverse leaching").

After standing, the upper discharge was decanted and the lower was filtered. The filtrate was combined with the upper discharge and the cake was subjected to acid washing by repulping at a liquid-to-solid ratio of 4 : 1.

Study of the effect of residual acidity in leaching fuming and electric furnace sublimates and of pulp acidity in cake washing upon the lead-tin cake zinc content and filtration speed revealed the following:

1. Zinc extraction increases in proportion to a rise in residual acidity up to 50 g/liter. A further rise in acidity gives practically no increase in extraction.
2. Increasing acidity in cake washing to pH 1.0-2.0 reduces the zinc content to 3.5-4.5%. The speed of filtration of pulp from acid cake washing does not alter significantly in the 0.9-3.8 pH range, amounting to ~ 0.3 $m^3/m^2 \cdot hr$.
3. The sublimate leaching routine breaks down the zinc stannate and 50% of the zinc sulfide and increases the direct extraction of zinc into solution by 7-9%.
4. The cake yield decreases by 10-15% by comparison with the existing technology and its lead and tin content increase from 19 to 22 and from 12 to 14% respectively.
5. The speed of filtration of the lower discharge under the recommended conditions (0.22-0.25 $m^3/m^2 \cdot hr$) is 2-3 times higher than in the routine with final acid leaching (0.07-0.09 $m^3/m^2 \cdot hr$); this makes it possible to mechanize the cake filtration process by replacing the filterpresses used in the existing technology by drum- or disk-type vacuum filters.

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[1] Zh. V. Solntseva assisted in the work.

table 3.
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atmospheric influences the frost resistance of the tailings was determined. *For this purpose each particle size class* was immersed in a solution of sodium sulfate for 20h and then dried at 110°C. The investigations showed that the frost resistance of the tailings corresponds to Mrz-25.

Table 4: Screen and chemical analyses of tailings

Analytical data		Tailings mm				
		+40-80	+25-40	-12-25	+16-12	Total
Yield %	Part	34.5	22.7	18.5	24.3	100
	Total	34.5	57.2	75.7	100	-
Content %	Pb	0.05	0.05	0.05	0.07	0.055
	Zn	0.19	0.24	0.27	0.34	0.25
	Cu	0.06	0.028	0.023	0.03	0.038
	Fe_3O_4	3.43	2.25	2.2	2.37	2.68
	CaO	1.78	1.75	1.65	1.97	1.8
	MgO	0.97	0.90	0.92	0.96	0.94
	Al_2O_3	11.28	9.65	9.11	8.80	9.90
	SiO_2	73.19	75.24	76.90	76.21	75.1
	S_{tot}	0.71	0.44	0.45	0.62	0.58
	$S_{Sulphate}$	0.025	0.007	0.01	0.009	0.014

The data in table 4 *show that most of the sulphur in the* light fraction (tailings) is present in sulphide form. With full oxidation of the sulphides and conversion to the sulphate form the SO_3 content of the tailings will amount 1.54%. Since the State Standard GOST-8267-64 does not permit the presence of more than 1% of sulphur compounds (converted to SO_3) in reinforced concrete constructions, the use of the *tailings in concrete and the reinforced constructions is* contraindicated. To determine the suitability of the tailings in concrete constructions special samples were prepared and tested for compression and frost resistance. The compressive strength of samples prepared from various particle size classes, with steam treatment and with natural ageing. varies between $10.2 \cdot 10^3$ and $23.9 \cdot 10^3$ N/m².

The results from investigation of the physical and mechanical characteristics of the tailings and of concrete made from them show that the concentration tailings obtained during concentration of the mixture of ores from the Sadon mine management in heavy suspensions correspond to the State Standards GOST-10260-62 and GOST-8267-64 and may find wide practical use for road construction, as a foundation under concrete floors, as a ground sealing material, as rubble footings under foundations, in drainage systems as a draining bed, as ballast for railways, as foundations for underground workings, *and as a coarse filler for asphalt*, concrete, and concrete in nonreinforced constructions.

Conclusions

1. Laboratory and pilot plant trials on the concentration of lead-zinc ores on the Kholstin, Sadon, Arkhonskaya and Zgidsk deposits, in ratios of 1.0:2,15:2,35:2.5, showed that with a tailings output of 30-40% the lead and zinc content does not exceed 0.06 and 0.3% respectively. It was established that concentration can conveniently be carried out with control separation, and the density must be kept at 2.7 in the *main operation and 2.65 t/m³ in the control operation.* Increase of the density in the main operation to 2.75 t/m³ leads to a considerable decrease in the extraction of the useful minerals into the heavy fraction. Comparatively cor *material (up to 80 mm) can be concentrated.*
2. Investigation of the physical and mechanical charac of the tailings from concentration in a heavy suspensi firmed the suitability of the tailings for many road ar building constructions, excluding the manufacture of forced concrete and reinforced structures.

UDC 622.765.41

The state of molybdenite surface during flotation

A A Abramov, E M Dzugkoeva and V M Avdokhin (Moscow Institute of Steel and Alloys. Department of the Concentration of Nonferrous and Rare Metal Ores.)

Summary

To understand the mechanism of the reaction of flotation reagents with the surface of molybdenite it is necessary to know which compounds of molybdenum are present at the surface under various conditions. The results are given from thermodynamic and electrochemical investigation of the state of the molybdenite surface as a function of the pH and the oxidation-reduction potential of the solution.

The thermodynamic calculations showed that the main product from oxidation of molybdenite is $MoO_3 \cdot H_2O$, while the formation of elemental sulphur at the surface of molybdenite is only possible in an acidic reducing medium. The results from the thermodynamic calculations were confirmed by the results from the electrochemical investigations.

The results can be used to analyse the mechanism of the action of the reagents on the surface of molybdenite, to create a physical and chemical model, and to improve the processes involved in the selective flotation of molybdenite-containing collective concentrates.

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UDC 669.053.4

Intensification and development of leaching processes in hydro-metallurgy

A N Zelikman and L V Zverev (Moscow Institute of Steel and Alloys. All-Union Institute of Mineral Raw Material)

Summary

The development of hydrometallurgical processes for the treatment of ores is briefly reviewed. The increased use of hydrometallurgical processes is attributed to recent developments in processes, the increasing need to use low-grade ores, and the avoidance of atmospheric contamination. Processes mentioned include fluidised bed, flow-type processes, sonic and ultrasonic treatment, sorption and extraction processes, and autoclave treatment (for various metals). Heap leaching and underground leaching (uranium, copper) are discussed. The role of micro-organisms and the bacterial leaching of copper are mentioned.

Attention is drawn to the need to develop scientific investi-

gations in the following directions: The thermodynamics of aqueous solutions of inorganic substances and the development of methods for calculation of activity coefficients in complex solutions; improvement and development of new physical and other methods for determination of the form in which metals are present in aqueous solutions; further theoretical consideration and experimental investigation of the kinetics and mechanism of the chemical dissolution of minerals; the search for new reagents, including organic reagents, for selective dissolution of metals and, in particular, non-toxic solvents for gold.

UDC 541.48

Investigation of the equilibrium between magnesium and its chloride dissolved in potassium chloride

P V Polyakov, G A Kotel'nikova and A N Tatakin (Krasnoyarsk Institute of Nonferrous Metals. Department of the Metallurgy of Light and Rare Metals)

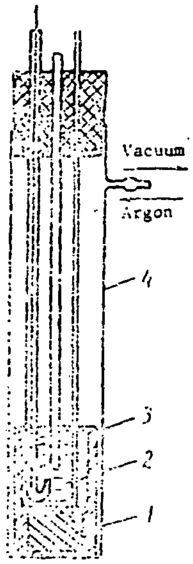

Fig.1 Construction of cell 1) magnesium; 2) melt; 3) tantalum container; 4) quartz beaker

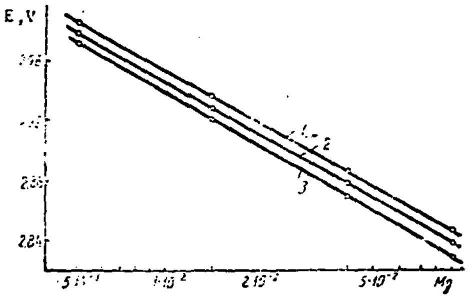

Fig.3 Isotherms of the equilibrium emfs of the magnesium electrode at various temperatures, T°K: 1 - 1063; 2 - 1083; 3 - 1100.

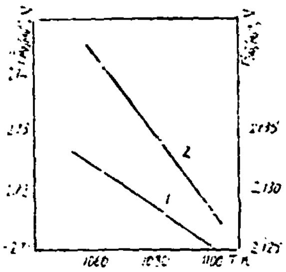

Fig.4 Temperature dependence of the apparent standard electrode potentials of magnesium $E^{0}_{Mg/Mg^{+}}$ (1) and $E^{0}_{Mg/Mg^{2+}}$

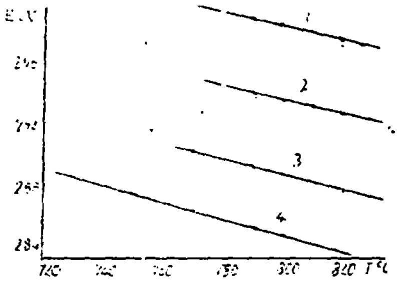

Fig.2 Temperature dependence of the emf $MgCl_2$: 1 - 0.649; 2 - 1.8; 3 - 5.36; 4 - 11.45 wt.%. The points correspond to the emf values obtained in the tantalum cell.

Table 1: Empirical equations for the temperature dependence of the emf

Ion-fraction conc. of Mg	Equations
$0.506 \cdot 10^{-2}$	$E = 3.4514 - 0.439 \cdot 10^{-3}\,T \pm 0.005$, V
$1.42 \cdot 10^{-2}$	$E = 3.452 - 0.480 \cdot 10^{-3}\,T \pm 0.0005$, V
$4.04 \cdot 10^{-2}$	$E = 3.454 - 0.53 \cdot 10^{-3}\,T \pm 0.0005$, V
$9.2 \cdot 10^{-2}$	$E = 3.49 - 0.6 \cdot 10^{-3}\,T \pm 0.0005$, V

Table 2: Average valences, solubilities, and standard electrode potentials of magnesium in the melts

T,K	$\frac{X_2}{X_1}$	X_1	X_2	E^0_1	E^0_2	Solubility at. fraction 10^4				Average valence
						1	2	3	4	
1063	4.09	0.0042	0.0172	2.8495	2.9865	3.37	2.37	1.445	0.931	1.970
1083	4.081	0.00549	0.0224	2.8393	2.8795	5.06	3.16	1.84	1.220	1.964
1100	4.072	0.0758	0.0317	2.8306	2.9494	6.96	3.98	2.241	1.61	1.941

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$\sigma_{1,2}$ and ϵ_{Me} in the coalescence of the mechanical suspension of the metal in the slag. The experiment was carried out as follows.

An artificially prepared suspension of copper in iron-free slag was agitated with the extracting phase by means of argon. As extracting phase we used grade MO copper, copper + 1.33% Cu_2O, and copper + 1.5% S. Copper with 1.5% S, like lead with 1.5% S[3]), is negatively charged in the slag. The results from the experiments are given in fig. 3. They show that for the metal with charge having identical sign the difference in the $\sigma_{1,2}$ value is largely significant for coalescence (curves 1 and 3 in fig. 3). For relatively comparable $\sigma_{1,2}$ values (in the Cu-1.5%S alloy $\sigma_{1,2}$ = 220mJ/m^2, see curves 2 and 3 in fig. 3) the principal role is played by the difference in the sign of the charge in the extracting (the surface of the Cu-S alloy with 1.5% S is negatively charged) and the extracted phases (the surface of drops of grade MO copper in the suspension is positively charged).

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UDC 541.138.2:669.13

Investigation of the dissolution of lower cobalt sulphide in cobalt sulphate solution

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In the leaching of sulphides, in addition to their purely chemical dissolution, an important part is played by electrochemical processes[1]), investigation of which assists the development and improvement of methods for hydrometallurgical treatment of sulphide materials. Some of the progressive methods for investigation of oxidation-reduction reactions occurring at the interface are electrochemical[2]). Whereas extensive researches have been devoted to investigation of electrode processes at copper and nickel sulphides[3,4]), there are hardly any papers on the oxidation-reduction reactions in the dissolution of cobalt sulphides.

In the present work an attempt was made to determine certain relationships governing the leaching of lower cobalt sulphide Co_4S_3 from the standpoint of the laws of electrochemistry by investigation of the electrode potentials of the sulphide in a solution of cobalt sulphate as a function of such parameters of the process as the activity of the metal ions in the solution, the nature and partial pressure of the gas phase, the temperature, and the length of dissolution of the materials. The electrode potentials of the sulphides under normal and autoclave conditions were investigated by the previously described method[5]).

One of the characteristic features of metals of the iron group under normal conditions is the considerable irreversibility of the metal-solution system, as a result of which the steady-state potentials of these electrodes differ substantially from the equilibrium potentials calculated on the basis of thermodynamic data. The latter may be due to the passive state of the electrode surface in the solution[6]), and it was not therefore possible to evaluate the activity of the cobalt ions directly under the experimental conditions.

The activity of the ions in an aqueous solution of the metal sulphate was determined as the product of the activity coefficient ($\gamma_{Me^{2+}}$) by the molal concentration of the ion in the solution. In turn, the activity coefficient of the ion in the solution was determined from the expression:

$$\gamma_{Me^{2+}} = \frac{(\gamma\pm)^2}{\gamma_{SO_4^{2-}}} \qquad (1)$$

where:

$\gamma\pm$ = the average ionic activity coefficient of the electrolyte according to published data[7]);
$\gamma_{SO_4^{2-}}$ = the average activity coefficient of the SO_4^{2-} ions and was obtained from the experimental dependence of the latter on the ionic strength of the solution[8]).

The values observed for the electrode potentials of Co_4S_3 in solutions of cobalt sulphate with various concentrations are given in fig. 1 in the form of their dependence on the calculated activities of the cobalt ions in the solution. The gradient of the line connecting the points plotted on the graph agrees well with the value calculated by means of the equation:

$$\varphi = \varphi_0 + \frac{RT}{2F} \ln \alpha_{Co^{2+}} \qquad (2)$$

and amounts to 0.050V for unit increase in the logarithm of the activity of the cobalt ions. By extrapolation of the potentials to a cobalt ion activity equal to unity it is possible to obtain a value of -0.1V. This shows that the dissolution of Co_4S_3 is accompanied by passage of Co^{2+} ions into solution, while the electrode process is described by the equation:

$$Co_4S_3 \rightleftarrows 3CoS + Co^{2+} + 2e \qquad (3)$$

The experiments were carried out in a neutral atmosphere Replacement of the neutral gas phase (argon) by an oxidising phase (oxygen) leads to an sharp shift of the electrode potential towards the positive side (to 0.5V, fig. 2). The higher the pressure of the gas phase, the more appreciable is the shift of the potential. The value of the electrode potential (0.5V in a 0.5M solution of cobalt sulphate) corresponds fairly satisfactorily to the calculated value (0.42V) for the process:

$$CoS \rightleftarrows Co^{2+} + S + 2e \qquad (4)$$

which indicates the formation of a film with a different cobalt-sulphur ratio (close in composition to CoS) on the Co_4S_3 surface.

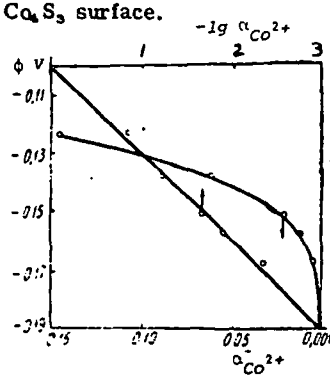

Fig.1 Dependence of the electrode potential of Co_4S_3 on the activity of cobalt ions in the solution.

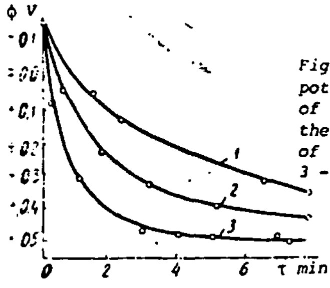

Fig.2 Dependence of the electrode potential of Co_4S_3 on the length of dissolution of the sulphide at the following partial pressures: of oxygen (atm): 1 - 2; 2 - 3; 3 - 12.

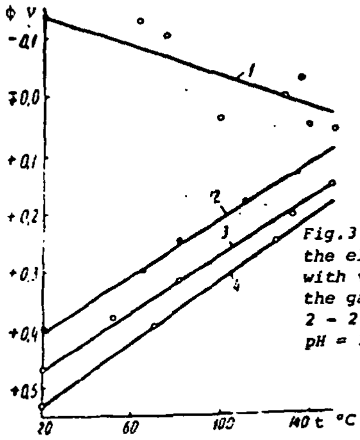

Fig. 3 Temperature dependence of the electrode potential of Co_4S_3 with various partial pressures of the gas phase (atm): 1 - 5, argon; 2 - 2, oxygen; 3 - 3; 4 - 12; pH = 2.

From the temperature dependence of the potential of Co_4S_3 (fig. 3) it follows that in a neutral atmosphere the potential of cobalt sulphide is shifted towards the positive region with increase in temperature (curve 1), reaching a value of +0.03V, and this corresponds in character to the variation of the electrode potential of the sulphide, the dissolution of which is determined by reaction (3). With increase in the temperature in the presence of oxygen the electrode potential of Co_4S_3 is shifted towards the negative side, and it here approaches the value for the potential of the sulphide electrode (Co_4S_3) in a solution of cobalt sulphate in the neutral gas phase (fig. 3).

On the basis of the experimental data the following mechanism can be proposed for the dissolution of Co_4S_3 in a sulphuric acid solution of cobalt sulphate.

1. In a neutral gas phase the electrode potential in the solution corresponds to reaction (3), which determines the process.
2. Under oxidising conditions a sulphide film, approaching CoS in composition, is formed on the surface of the material. Reaction (4) is determining in the process. Increase in temperature evidently leads to an increase in the dissolution rate of the boundary layer, the thickness of which decreases, and the electrode potential begins to be determined by dissolution of the initial sulphide.

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UDC 669.71.046.44

Precipitation of roasted and reduced alunite dust in counterflow systems

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Essentially the method for collection of dust in counterflow apparatus involves the hydrodynamic retardation of two colliding axisymmetrical dust-laden streams of gas, into which a wetting liquid has been sprayed by means of a nozzle before the zone in which they merge. Together with the dust particles the wetting liquid performs a reciprocating motion in the region where the streams collide. In this zone coagulation and enlargement of the particles occurs as a result of interaction of dust particles with the drops of liquid. The coagulated particles, having attained critical dimensions, separate from the collision zone under the influence of gravitational forces and are collected in the precipitation chamber. Any liquid which is lyophilic towards the particles of dust being collected can be used as wetting liquid. In the majority of cases this liquid can be water.

In the present work the motion of the particles and the variation of the concentration of the particles in the zone where the gas streams meet were investigated [1]). The effectiveness of the collection of finely dispersed alunite dust in counterflow systems and the effect of the principal process parameters on it were studied on the previously described apparatus [2,3]). With increase in the specific consumption rate of the wetting liquid (water) per unit weight of dispersed material the degree of collection of the dust at first increases and then remains practically unchanged at a value >0.3 ml/g. On the basis of the experimental data the optimum constructional parameters for the dust collector were determined. The effect of the concentration of the dust and the velocity of the gas stream on the effectiveness of the collection of the dust was investigated. It was established that the degree of collection of the dust increases with increase in the dust content of the stream over the whole range of investigated gas velocities (10-25 m/sec).

The effect of the gas velocity on the degree of collection of alunite dust (η) is extremely significant; with low gas velocities (10-14 m/sec) increase in the velocity of the gas leads to a decrease in the degree of collection of the dust, and with a velocity >14 m/sec, i.e., under conditions where the motion of the particles in the counterflow is more intensive, increase in the gas velocity leads to an increase in the effectiveness of collection. With bilateral delivery of the stream at a velocity of 23.2 m/sec and with a dust content of 350 g/m³ the degree of collection amounted to 98.5%.

With increase in the temperature of the gas and with an unchanged specific consumption of the wetting liquid the degree of collection decreases somewhat, and to increase the degree of collection it is therefore necessary to increase the delivery of water into the spraying system. At temperatures of 250 and 480°C the amounts of water required to secure the maximum degree of collection (88-91%) were 0.33 and 0.37 ml/g respectively, but the obtained granules were dry. This is explained by the fact that evaporation of the water takes place after coagulation of the particles, since the collision of the water drop with the dust particles and between the particles takes place instantaneously.

Table

Particle size mm	Content of dust from apparatus %	
	Roasting	Reducing
+0.104	0.4	0.2
+0.063	1.0	0.5
-0.063	98.6	99.7

The experiments were carried out with roasted and reduced alunite dust from the Kirovabad aluminium works, the granulometric composition of which is given in the table. In

ION-EXCHANGE EXTRACTION OF ALUMINUM

UDC 669.7:66.074.7

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The efficiency of sorption processes increases as more raw material is used with lesser amounts of useful components or raw material with complex substantive compositions. From this point of view, ion exchange has some interest even for the aluminum indusrry.

Today, in order to produce alumina, raw material is used with silicon contents no higher than 20% [1]. Use of alkaline methods to recover aluminum from raw material with higher silica contents is uneconomic because of the laboriousness of the flowsheets, their high energy consumption, and the requirement of many laborious technological operations. Therefore, to process high-silica aluminum raw material, attempts are being made to use various acids [2] or sulfur dioxide [3] for leaching. These methods of processing the aluminum raw material have still to find industrial acceptance, due to the complexities involved in the conversion of aluminum salts to hydroxides and the removal of anions from them.

The variety of ionic forms, formed by aluminum in solutions [3-12], makes it possible to suggest that various grades of ionites can be used for its sorption extraction from solutions.

Among the data published in the literature, the most interesting are the indications about the sorption of aluminum from various solutions to sulfo- and carboxyl cationites [13-17], phosphoryl-treated FB cellulose [18], as well as its absorption by the anionites of various classes [19-21].

Use of sorption processes when acid exposure is performed for aluminum raw material can be effective only in that instance where aluminum would be directly removed from the pulp and it was converted to aluminate or the hydroxide would shift with the desorption process and ionite regeneration. We performed such research on alunite, nephelite, and on a series of sulfate solutions obtained after leaching aluminosilicate ores.

Ion-Exchange Treatment of Calcined Alunite

In the research, use was made of alunite concentrate from the Zagliksk deposit, treated at the Kirovabad Alumina Plant.

Content of basic components in sample, %

9.0 Al; 2.5 Fe; 0.035 V; 0.075 P; 23.2 $SO_4^{=}$;
25.9 lost during calcination (700°C)

Alunite doesn't dissolve in acids at room temperature and is dissolved only when concentrated sulfuric acid is used during heating. After thermal treatment, part of the aluminum, in the form of sulfate, is leached with water [22].

This work uses alunite concentrate, calcined at 550°C for 3 hours. Its aluminum content is 11.98%. Aluminum from the calcined alunite is leached with diluted H_2SO_4 (2N) by 20-25% in cold; when heated to 80°C, leached by 95-97%. This makes it possible to suggest the possibility of effecting an ionite leaching of aluminum from calcined alunite with a strongly acid cationite in an H-form.

Added to the aqueous pulp of ground (to 100 mesh) alunite concentrate was cationite KU-2 in a swollen state, from a calculation of cationite:water:alunite = 50 ml::110 ml:10 g. After a 1.5-hour mixing of the pulp for 1.5 hours, the cationite was separated on a screen; a new portion of cationite in an H-form was added to the remaining pulp and the treatment was repeated. The ionite dissolution cycle was completed after the third treatment; 97% of the aluminum was removed from the concentrate.

The desribed schedule included 6 cycles of coutercurrent three-stage extraction of aluminum from the calcined alunite; 6 portions of saturated cationite and discard pulp were obtained. From an analysis of the solid residue of the discard pulp, the mean aluminum recovery during ionite leaching was 95.7% with the aluminum capacity at 34.8 kg/g cationite.

Al recovery from concentrate by means of ionite dissolution from calcined alunite in a countercurrent system of six sorption cycles was as follows. %:
1 - 96.9%; 2 - 94.8%; 3 - 96%; 4 - 95.5%; 5 - 96%; 6 - 94.9%

Analysis of saturated cationite showed that V is not sorbed during the process of ionite dissolution of alunite; the content of other impurities was also low, the g/g aluminum in the cationite being 0.192 K; 0.145 Na; 0.055 Ca, and 0.009 Mg.

Solutions of sodium hydroxide and soda were used for regeneration of aluminum-saturated cationite. Desorption of aluminum with sodium hydroxide does not cause substanial difficulty and can be conducted in a static schedule for three stages with the commercial regenerate yield at 1 vol/vol sorbent (Table).

When using soda to regenerate aluminum-saturated sorbent, the desorption stage coincides with precipitation of alumina. The process of regenerating the aluminum-saturated KU-2 with soda is completed with the total yield of regenerators at 5-6 vol/vol sorbent:

Yield of eluate, vol/vol sorbent........	1	2	3	4	5	6
Desorbed aluminum, %.	61.5	75.3	78.2	83.7	90.4	100

Finally, to treat calcined alunite concentrate, it is possible to recommend two flowsheets with the use of ion-exchange processes, characterized by a method calling for desorbing aluminum with saturated cationite KU-2. In order to achieve the minimum losses of cationite in the pulp process one should use cationite with an increased mechanical strength, for example cationite KU-2u or KU-23.

Efficiency of Aluminum Desorption with Sodium Hydroxide

Indices	Indices of process in fractions of the obtained concentrate		
	1	2	3
Regenerate yield, vol/vol cationite	1	2	3
Aluminum content in regenerate, g/lit . . .	7,2	2,96	0,2
Residual Al capacity of cationite mg/g of sorbent .	7,6	2,1	Undetermined
Aluminum desorption, %	78,25	93,86	100

Ion-Exchange Treatment of Nephelites

Tests on nephelite dissolution were made on a mineral specimen with 15.8% aluminum. Despite the fact that nephelite decomposes comparatively readily with diluted acids [22], it was not possible to extract aluminum from the mineral directly with cationite in the H-form. Therefore, nephelite was leached with a stoichiometric amount of diluted sulfuric acid with subsequent sorption extraction of aluminum from the formed pulp by cationite in a sodium form.

It was experimentally shown that when leaching was conducted with sulfuric acid (2N), from the nephelite there is an extraction of 99.5% aluminum which is quantitatively sorbed by cationite KU-2 in a sodium form during three sorption stages. The process overall occurred similarly to the process of aluminum sorption from calcined alunite concentrate and provided an almost complete separation of aluminum from silical and the sulfate ion. Following recovery of the aluminum, the discard pulp can be used to produce silica gel, the amount of which is about 1 t/t of alumina. The existing systems of producing silica gel satisfactorily coincide with preceding processes of cation-exchange extraction of aluminum [23]. Sodium sulfate solutions, obtained during the process of sorption processing for nephelintes, can be converted -- by electrodialysis -- to sulfuric acid, and sodium hydroxide for their reuse in the process [24, 25].

Regeneration of aluminum-saturated cationite does not differ from the described process with respect to the treatment of alunite concentrate.

Use of Carboxyl Cationites for Sorption Extraction of Aluminum

As shown by research on the use of sulfocationite KU-2 for sorption of aluminum, its aluminum capacity in neutral and weak-acid solutions corresponds to a complete volumetric capacity, i.e., about 4 mg-equiv/g. Evidently, under these aluminum sorption conditions it boils down to a simple equivalent ion exchange, and the capacity achieved in the described experiments is the maximum for the given conditions and the class of cationites.

It is possible to increase the aluminum capacity by using carboxyl cationites in a salt form, the complete volumetric capacity of which reaches 10 mg-equiv/g ionite. For example, in solutions with the pH = 4, the cationite SG-1 has an aluminum capacity of about 100 mg/g ionite, which corresponds to its complete volumetric capacity [25].

Regeneration of aluminum with type KB carboxyl cationites can be effected with sodium hydroxide or soda solutions, as was described for cationite KU-2. Due to the low stability of cationite SG-1 in alkaline media, its regeneration should be effected with acid; there should be a corresponding use of cationite SG-1 in those instances where one must obtain aluminum salts (sulfate, alum) as the final product.

Ion-exchange processes can be used to treat high-silicon aluminum raw material when using acid methods of exposure.

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UDC 669.712

Increasing the efficiency of leaching and desiliconising operations in the treatment of high-silica bauxites

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It is known that the decomposition rate of gibbsite bauxites depends on their silica content[1]). During the leaching of high-silica bauxites the maximum contents of alumina and silica in the solution are achieved later than in the treatment of low-silica forms. This is explained by the large content of kaolinite in the first case.

The decomposition rate of kaolinite is also affected significantly by its structural characteristics. Thus, kaolinite taken from the interlayers of Krasnooktyabr'skii bauxites are fully decomposed in the course of 1h[2]), but when we studied rocky iron-containing bauxites, in which the kaolinite is present in a well crystallised poorly soluble form, it was observed to be present in the slime of the washing system. This is one of the reasons for the formation of encrustations in the settling equipment. By decomposing in a medium where there is a comparatively low liquid-solid ratio, the kaolinite considerably reduces the caustic ratio of the liquid phase, and this gives rise to the crystallisation of aluminium hydroxide. This is confirmed by the presence of secondary gibbsite, detected during analysis of the deposits in thickeners. It is therefore of interest to study the kinetics of the decomposition of kaolinite in high-silica iron-containing bauxites. Application of the results from this investigation will make it possible to recommend ways of increasing the effectiveness of the leaching and desiliconising operations in the processing of such raw materials. The investigation was carried out by an IR spectroscopic method. An initial material in the form of the kaolinite from the investigated ore, obtained by washing, and the products from its treatment with an alkaline-aluminate solution (260g/l $Na_2O_{caustic}$, $\alpha_{caustic}$ = 3.3) at 105°C for 2 and 5h was submitted to analysis (fig. 1). The spectra were recorded on a UR-20 spectrometer. The standard spectra of sodium hydroaluminosilicates of various types were used for identification[3]).

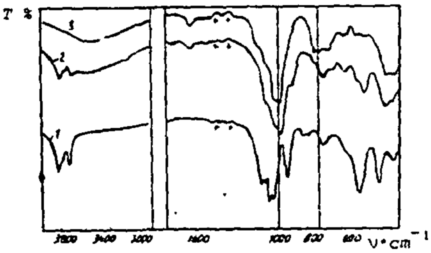

Fig.1 The IR spectra of the initial kaolinite (1) and of the kaolinite treated with the aluminate solution at 105°C for 2h (2) and 5h (3).

In the spectrum of the product obtained by treatment of the kaolinite for 2h there were changes in the form and relative intensity of the bands. For example, the intensity of the bands of kaolinite at 3702 and 3626cm^{-1}, corresponding to the OH stretching vibrations, decreases by a factor of 2-3, and the Si-O stretching band of kaolinite at 1110, 1033 and 1010cm^{-1} merges with the band at 938 and 910cm^{-1}, corresponding to the H-O-Al bond, and is observed with two "shoulders" at 1110 and 930cm^{-1} (fig. 1, curve 2).

The intensity of the bands of kaolinite at 540cm^{-1}, corresponding to the Si-O-Al vibrations, decreases by almost a half after its treatment with the solution, and the bands of kaolinite at 470 and 432cm^{-1}, corresponding to the Si-O bond, merge into a single band, not fully resolved, in the region of 470-440cm^{-1}. After treatment the characteristic bands of kaolinite with low intensity at 800 and 760cm^{-1}, corresponding to the Si-O-Al(IV) bond, disappear completely and the band at 700cm^{-1} (the Si-O bond) decreases in intensity.

All the changes described in the spectrum of the kaolinite can be explained by its partial decomposition and by the formation of sodium hydroaluminosilicate, since the absorption bands of the latter lie in approximately the same regions as the bands of kaolinite. In the spectrum of the product obtained after treatment of the kaolinite with the aluminate solution for 5h (fig. 1, curve 3) the bands of the initial kaolinite are not observed, and there is a set of bands characteristic of sodium hydroaluminosilicate of the nosean type (440, 470, 560, 630, 690, 1000cm^{-1}).

In the leaching of gibbsite bauxites the sodium hydroaluminosilicate is usually of the sodalite type [e.g. [2])[4])], but in this case the leaching of the iron-containing sideritised bauxites leads to the formation of nosean. Here an interesting fact was discovered. The slimes after leaching, desiliconising, and thickening contain a considerable amount of carbon dioxide, although the siderite is completely decomposed after 15-30 min. It is logical to suppose that the carbon dioxide is sorbed at active sites on the surfaces of finely dispersed products, which may be iron hydroxide and sodium hydroaluminosilicates.

During the chemisorption of carbon dioxide on such surfaces mono and bidentate carbonate complexes are formed. The monodentate complex is characterised by a doublet band at 1490 and 1420cm^{-1}, which is present in the IR spectrum of sodium hydroaluminosilicate of the nosean type (fig. 2). The spectra of the iron hydroxides do not change after the action of carbon dioxide on them. In the present case the presence of a large amount of carbon dioxide in the process leads to the formation of sodium hydroaluminosilicate of the nosean type, since either CO_2 or sulphate ions are required for this purpose.

Fig.2

The IR spectrum of the monodentate complex formed on the surface of nosean.

Thus, reaction of kaolinite with the aluminate solution for 5h leads to the formation of sodium hydroaluminosilicate of the nosean type, on which the carbon dioxide is sorbed in the form of a monodentate carbonate complex. Treatment of the kaolinite for 2h results from investigation of the decomposition. Analysis of the results from investigation of the decomposition kinetics of the kaolinite demonstrated the expediency of investigating the time relationships governing the leaching of gibbsite bauxites, which contain a considerable amount of kaolinite in the poorly soluble form.

The experiments were carried out under conditions similar to those for the decomposition of bauxite in the non-autoclave Bayer process. The effect of the holding time of the raw pulp, of the bauxite leaching operation, and of the aluminate solution desiliconising operation on the technological characteristics of the whole process were studied. The temperature conditions for the operations were as follows °C: holding of raw pulp 80; leaching 105; desiliconising 98; thickening 95.

Fig. 3 shows the dependence of the extraction of aluminium oxide on the holding time of the raw pulp. Analysis of the obtained data shows that the average extraction of alumina increases with increase in the holding time. The maximum on the kinetic curve corresponds to 1h.

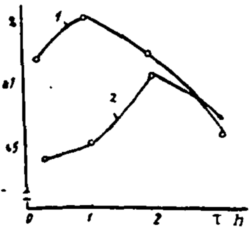

Fig.3 The effect of the length of holding of the raw pulp on the Bayer extraction of Al_2O_3 (1) and SiO_2 (2) into solution.

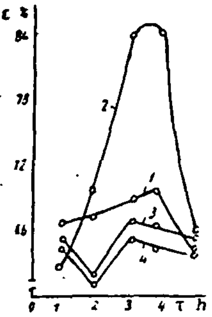

Fig.4 The effect of leaching time on the extraction of alumina by the Bayer method. Holding time of raw pulp h: 1 - 0.25, 2 - 1, 3 - 2, 4 - 3.

The extraction of silica into solution is also characterised by an extremal relationship; it increases with increase in the holding time of the raw pulp to 2h and then decreases. Consequently, after holding for 1h sodium hydroaluminosilicate begins to form in the raw pulp, but dissolution of the kaolinite and the gibbsite continued to be the predominating process. Under these conditions the particles of the sodium hydroaluminosilicate which forms are fine and poorly crystallised. Such a material does not assist effective deposition of the red mud. A holding time of 1h for the raw pulp must therefore be considered optimum to avoid crystallisation of sodium hydroaluminosilicate.

After holding the raw pulp was leached. The results are shown in fig. 4. The maximum extraction of aluminium oxide is achieved with a holding time of 1h for the raw pulp and a leaching time of 4h. With leaching for 5h there is a sharp decrease in the extraction of aluminium oxide on account of the beginning of intensive crystallisation of sodium hydroaluminosilicate. During leaching (105°C, concentrated alkaline solution) coarse readily deposited crystals of this compound are formed. Conditions are created for a high degree of desiliconising of the solutions, and whereas the pulp which has been treated for 2h requires 4-5h for desiliconising in order to obtain a silica ratio of 250 in the aluminate solution, after leaching for 5h a higher silica ratio (~350) is obtained when the diluted pulp is held for 1h.

After desiliconising the pulp is passed on for thickening. Experiments showed that the thickening rate is determined by the size and degree of crystallinity of the sodium hydroaluminosilicate particles. The optimum conditions for the production of a well thickened deposit are obtained with a silica ratio of 230-300, and this corresponds to the maximum thickening rate of 0.14m/h.

The experiments showed that the length of the technological operations of the non-autoclave Bayer process significantly depends largely on the form and amount of the kaolinite present in the bauxite. The factor which determines the holding time of the raw pulp, the leaching time of the bauxite, and the desiliconising time of the aluminate solution is the decomposition rate of the kaolinite. The relation between the lengths of these operations must secure full decomposition of the kaolinite and gibbsite at the leaching stage and prevent the crystallisation of finely dispersed sodium hydroaluminosilicate under unfavourable temperature conditions (the raw pulp holding operation).

However, it is not only full decomposition of the kaolinite and gibbsite at the leaching stage which secures successful realisation of the subsequent operations in the desiliconising of the aluminate solution and the thickening of the red mud. An essential condition for this purpose is realisation of the main purification of the aluminate solution from silica with an alkaline-aluminate solution having a high concentration and at an elevated temperature (105°C). This is achieved by increasing the length of the leaching operation to 5h. This secures a higher degree of desiliconising of the aluminate solutions, while the production of coarse crystals of sodium hydroaluminate intensifies the thickening of the red mud.

Conclusion

To increase the effectiveness of the decomposition of high-silica iron-containing gibbsite bauxites containing the poorly soluble forms of kaolinite it is recommended that the following sequence of operations should be maintained: holding of the raw pulp for 1h, leaching of the bauxite for 5h, desiliconising of the alkaline-aluminate solution for 1h.

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The velocity fields in the electrolyte in aluminium electrolytic reduction cells

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The state of the heat and mass-exchange processes and the technical and economic effectiveness of electrolysis are determined to a significant degree by the hydrodynamics of the electrolyte, due to the movement of gaseous inclusions. The measurements of the velocities of the electrolyte in industrial cells, which relate to the zone of free convection and were described in the literature[1-4]), do not present information sufficient for the construction of a quantitative velocity field. This also holds for the single publications on the hydrodynamics of the interelectrode gap, which were also realised from the results of measurements on industrial cells[5-7]). The results from work on physical modelling obtained at the All-Union Aluminium and Magnesium Institute (G V Forsblom, A I Kulakov et alia) and in the report[8]), reflect the overall pattern of the hydrodynamic circumstances in the electrolysis cell but also do not make it possible to construct detailed vector velocity fields on account of procedural peculiarities.

In our work we used a plastic planar model 30mm thick, in which the release of the anode gases was simulated by blowing air through a graphite plate. The model represented the central cross-section of the electrolysis cell in relation to the electrolyte with an anode width of 800mm. The

Ion exchange recovery of copper promising

General Mills' LIX-64 prompts Bagdad Copper and Duval to set up pilot-plant trials

Major changes may be in the offing for one of the standard practices of the copper industry—recovery of the metal from dump leach liquors. Several companies are taking a close look at a liquid ion exchange process that General Mills' chemical division (Kankakee, Ill.) has been pushing since 1965. The results so far, these companies say, are encouraging, but some problems still remain.

Selective reagent. The industry's interest stems from the introduction of General Mills' LIX-64, a reagent that is highly selective in taking copper out of acid solutions, with only slight affinity for iron. It wasn't until last year, however, that anyone got to the pilot-plant stage. Now, two companies, Bagdad Copper and Duval Corp., have installations that can process about 80 gallons per minute of leach solution. Others are operating small laboratory units.

To copper producers, dump leach liquors are much more important than the term may imply. They obtain the solutions by spraying dilute sulfuric acid on piles of tailings and low-grade ore hundreds of feet high.

The acid may take months to trickle through a dump, dissolving copper as it goes and ending in a natural catch basin. Although the dilute acid may then contain only 0.7 to 2 grams of copper per liter, it is a major economic resource to many producers. Last year, for example, Bagdad Copper produced about a third of its total production of 40 million pounds from leach liquors; Duval got about 10% of its 98 million pounds from that source.

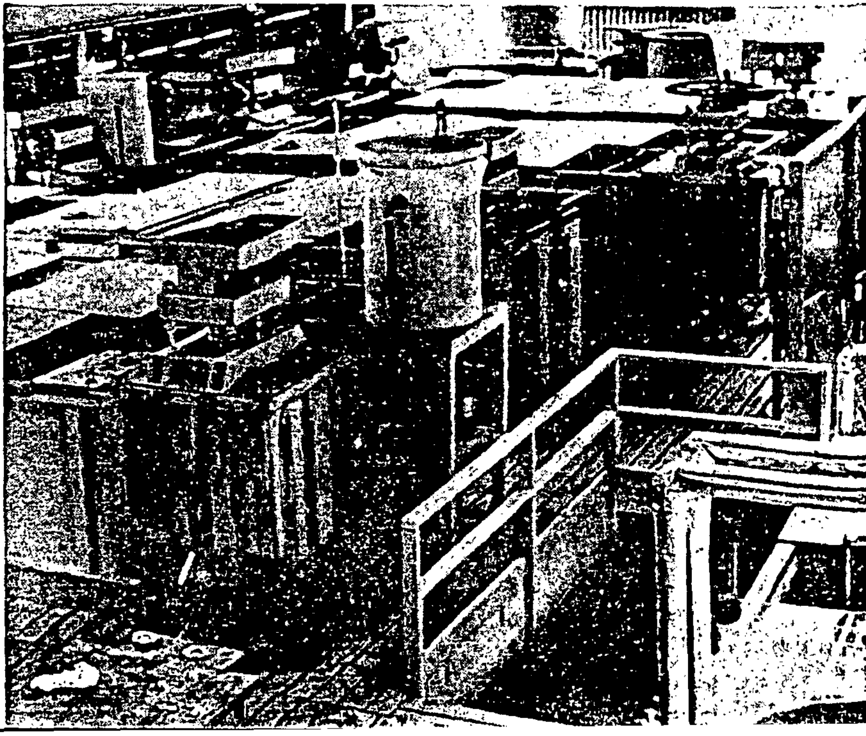
The standard method of processing leach liquors is to precipitate the copper with iron, usually in the form of detinned cans, sponge, or other scrap. The resulting cement copper, containing 75 to 85% copper, goes to a smelter and then to electrolysis for refining. The high cost of this conventional treatment seems to be the major driving force in the work on the ion exchange process.

In the process, as it's operated now, the acidic leach liquors are fed into a series of mixer-settler tanks, while LIX-64 dissolved in kerosine goes through in the opposite direction, exchanging its hydrogen ions for copper ions. The loaded organic phase goes on to the stripper tanks, and the acid raffinate goes back to the leach dump for re-use.

Stripper section. The stripper section consists of another series of mixer-settler tanks, where dilute sulfuric acid extracts the copper from the organic solution. The organic phase is recirculated to the extraction units, and the acid, now containing the copper, is sent to a copper recovery system.

Thus, the process is much like many commercial liquid-liquid extractions. The only differences are the feed and the reagent, which must separate copper not only from iron, the major contaminant, but also from the multitude of other ions present in dump leach

MIXER-SETTLER. R. C. Bogart of Bagdad Copper peers into mixer-settler tank, in which dilute sulfuric acid extracts copper from organic solution



PILOT PLANT. This pilot plant of Bagdad Copper's processes about 80 gallons per minute of leach solution with copper recovery of better than 97%

liquors. According to all reports, LIX-64 does this very well.

General Mills has never disclosed publicly what is in its product. It initially worked with a mixture of two compounds, 2-hydroxy-5-dodecylbenzophenone oxime and 5,8-diethyl-7-hydroxy-6-dodecanone oxime. But these compounds no longer represent the composition of LIX-64, General Mills says.

The development price for the product is $2.50 per pound, and there is no indication as yet how much less it might cost in large quantities. As it now stands, there is little doubt that success of the process hinges heavily on whether losses or degradation of the reagent can be kept low enough.

Bagdad Copper's pilot plant at Bagdad, Ariz., uses a leach liquor that contains from 0.7 to 1.0 gram per liter of copper. The organic phase is kerosine with 6% of LIX-64. The stripping acid, which goes in with 200 grams per liter of sulfuric acid, comes out with 50 grams per liter acid and 90 to 100 grams per liter of copper.

Early last month, Bagdad completed a stabilized two-week run at an average leach liquor feed of 80.1 gallons per minute for a total of more than 1.6 million gallons. Copper recovery was better than 97%. Organic solution losses averaged 0.139 gallon per 1000 gallons of leach solution fed to the system, which works out to about 1.7 cents per pound of copper. Much of this loss is due to Bagdads' heating the stripping solution to about 50°C.

Acceptable loss. The company once figured that an organic loss amounting to 2 cents per pound of copper would be acceptable. Now, according to Bagdad vice president R. C. Bogart, it believes that losses must be much less than that. The reason is that Bagdad estimates that capital costs of a full-sized plant might be twice the $300 per gallon per minute of feed estimated by General Mills and Denver Equipment before the pilot plants came into being. A full-sized plant for Bagdad would have to handle 3300 gallons per minute of leach liquor.

The whole matter of organic losses is clouded by the lack of a simple analytical method for the active components of LIX-64. It's a simple matter to determine how much of the organic solution is disappearing, but far more important is the fate of the expensive reagent. How much of that is lost by entrainment in the raffinate? Is its copper loading capacity changing? Do the active compounds degrade on long use? Frustrated by their inability to get answers quickly during pilot operations and unable themselves to launch analytical research projects, some companies are turning to outside help for a good test.

Duval's pilot plant, at the company's Esperanza mine near Tucson, has a design capacity of 75 gallons per minute of leach liquor, which contains about 1.5 grams per liter of copper. Using 7% LIX in kerosine, the company is getting 95% extraction of copper. They can do much better than this, but other problems are a greater concern at the moment.

Organic loss is less than 0.1 gallon per 1000 gallons of acid feed, and this loss may be mostly kerosine. One method that Duval is using to cut down on entrainment of reagent is a kerosine wash of the acid raffinate before it is sent back to the leach dump. The company is also having some success with ways to separate organic and aqueous phases more completely, but it won't say much about these.

Duval seems to be much further along than Bagdad in solving the loss problem, but Dr. Roger Nelson, research engineer, is still concerned about the reagent's loading capacity. It usually drops off during use but sometimes rises unexpectedly. This behavior may reflect an analytical error, he says, as there is no standardized test to determine loading.

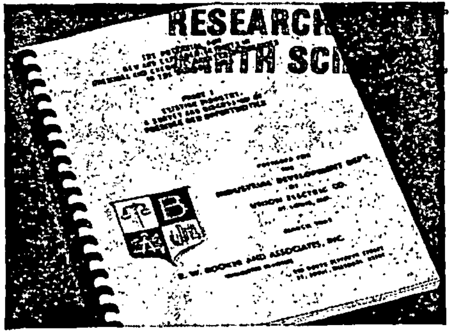
Duval's pilot plant includes a four-cell electrolysis installation. The solution this company uses to strip the copper from the organic phase is not dilute sulfuric acid alone, but acid with about 45 grams per liter of copper. The stripping solution gets enriched to 50 grams per liter, then goes to the cells where only 10% of the copper is plated out, then back to the stripping section in a closed loop.

If Duval decides on a large extraction plant, an electrolysis plant will be part of the setup, and Duval will enter another part of the copper business. Late last month, Duval made its first shipment of 40 tons of cathode copper from its pilot plant.

Bagdad Copper, if it goes ahead, will use the copper-acid solution from the extraction plant to make copper powder by hydrogenation in a plant built last year as a joint venture with Chemetals Corp. The company says that it has six to eight months more work to do before making a decision on the LIX plant.

Six months. Duval's work is budgeted for another six months but will probably go on for a good while after that. A new aspect of its project, now under way, will take one to two years to evaluate. The company is building two ore dumps; each will hold 1 million tons and be as identical to the other as possible.

One will be sprayed with acid as usual, the other with acid raffinate from the LIX pilot plant. The purpose is to find out if the small amounts of



organics entrained in the raffinate will impair or destroy the dump's productivity. Ore dumps that contain copper sulfide, such as Duval's does, depend on bacteria that oxidize the sulfide so the copper can be leached. If these bacteria are destroyed, the dump would be useless.

Both Duval and Bagdad Copper are also involved with some of the more mundane problems of pilot-plant work, such as impeller configurations and equipment sizing and types. Duval's Dr. Nelson is not convinced that the standard mixer-settler tanks are the best units for the LIX process. This thought is echoed by Phil Allen of Metcon Laboratories, a consulting firm in Warren, Ariz. One possibility mentioned by both men is the centrifugal separator.

Elsewhere in Arizona, Inspiration Consolidated Copper (27.7% owned by Anaconda) is operating a 5 gallon-per-minute pilot plant that produces a 50 gram-per-liter solution from a leach liquor containing 1.5 grams per liter of copper. This unit has been operating only since December, says research director William Mitchell, and the company doesn't have enough experience yet to determine organic losses. He expects to operate the pilot unit for another six to eight months before deciding whether to go to a full-sized plant. Inspiration, which already has an electrolysis plant, will use its extracted copper to make cathode copper, just as Duval is doing.

Another Arizona producer is running a laboratory pilot unit at about 80 ml. per minute. This project is less than two months old, however, and the company has nothing to report on it.

Kennecott Copper has been studying the LIX process at its research center at Salt Lake City but doesn't have a pilot plant. In the view of H. R. Spedden, research director, reagents now available have a low loading factor and would require large capital expenditures for plants of the size now being built. A small plant, especially one that doesn't have a nearby, low-cost source of scrap iron, would be a logical step, he says. General Mills is currently working on development of other copper-extracting reagents that have higher loading factors than LIX-64.

Indeed, smaller copper producers are much more fascinated by the prospects of LIX than are the giants. For some of them, the opportunity to turn out higher-priced finished product instead of cement copper is almost irresistible. Work with LIX-64 is also going on overseas and results are encouraging, says General Mills' Joseph House.

Not even the most aloof companies, though, are unaware of the work now going on, and all are watching the progress of the various projects. The mining industry is not as secretive as the chemical industry. Dr. Nelson says that he has shown many a group through Duval's pilot plant. Even wire manufacturers are intrigued by the process and its potential for recovering copper from scrap.

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INITIATOR FIRING TIMES AND THEIR RELATIONSHIP TO BLASTING PERFORMANCE

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ABSTRACT

Commercially produced electric and non-electric ms delay initiators, period 0-19 (0-1000 ms), from the four principal U.S. manufacturers were tested to determine mean and standard deviations of firing times Deviations from nominal firing times given by the manufacturer were noted for all manufacturers' initiators. A predictive statistical model has been developed to describe the behavior of these initiators in actual practice. Application of this model to the test data reveals that, at present, the probabilities of successful shots (no sequencing errors and separation of adjacent periods by 5 ms or more) are low. Observations of production blasting operations in several aggregates quarries, using high-speed cinematography, confirm the results of the test and the statistical model in field practice, and relationships between deviations from nominal firing time and problems with relief, fragmentation, flyrock, and backbreak were established. In addition, data from the high-speed films suggest that currently used timing guidelines for designing properly relieved shots (1 ms/ft of burden) are too short, and that delay times up to 3.5 ms/ft are needed. The low probabilities of success predicted by the model potentially affect vibration and airblast control.

INTRODUCTION

From the time fuse-type delay blasting caps were introduced by Smith in 1895 (1), explosives users have realized that better fragmentation could be attained by using delay initiation instead of instantaneous shotfiring. The introduction of vented delay initiators in the 1920's, ventless delay initiators in the 1930's, and concurrent developments in non-electric delay initiators and relay connectors improved the operation of the earlier fuse-type initiators substantially. Short delay (millisecond) initiators were introduced in 1946, and the design of delay initiators used today varies little from those introduced more than 30 years ago (1).

Millisecond delay initiators provide control of fragmentation and muck distribution, as well as, increasingly, of vibration and airblast noise. Much has been written about which delay sequences achieve optimum fragmentation; however, most of these tend to be empirical in nature (2-4). Many patterns presently used follow the delay design criteria developed by Bergmann et al. (5). These criteria, developed from tests in large blocks of rock, established a minimum delay interval between holes of ~1 ms/ft of burden for optimum fragmentation. Although these authors attempted to relate the optimum delay time to some more fundamental mechanism of fragmentation such as radial borehole crack development, in general, optimum delay times obtained empirically tend to be longer than expected if reasonable crack propagation velocities are used (cf. ref. 6).

Most current approaches to blasting design discuss initiation in terms of its effect on "active burden" or the development of new, internal free faces to which successive boreholes break (cf. refs. 2, 4). All such approaches rely heavily on the assumption that currently available ms delay initiators fire reasonably close to their nominal firing times (in fact, most patterns are presented in terms of the nominal firing times).

Blasting patterns for vibration reduction are generally designed to follow Bureau of Mines guidelines based on the relationship between peak particle velocity and the damage threshold of structures (7). In the study which led to the guidelines, peak particle velocities were found to decrease with reduction in charge weight per delay, providing the delay was at least 9 milliseconds. From these relationships, a scaled distance function was developed which is now used to design blasts to meet peak particle velocity requirements.

Blasting operations produce complaints when peak particle velocities are far below the damage range. This problem is perhaps one of the most serious in the crushed stone industry, where producers must be close to their markets (population centers) if their prices are to be competitive. Aside from the sensitivity of humans to detect small vibrations, part of the reason for complaints at low peak par-

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References and illustrations at end of paper.

ticle velocities lies in the frequencies of the vibrations produced (8, 9). Open pit mining operations generate vibrations with frequencies as low as 10 Hz, and these low-frequency vibrations lie within the resonant frequencies of residential structures. The relationship between frequency and blast parameters (timing, burden, spacing, explosive type and load, etc.) is far less well understood than the relationship between charge weight and peak particle velocity. It is highly likely, however, that the frequency of ground vibration is strongly dependent on the timing of a production blast, as is the total charge weight per delay.

Because of the importance of delay initiation, design, and timing to both production parameters (fragmentation, muck handling, flyrock production, and backbreak) and environmental concerns (vibration and airblast), we have undertaken a joint program with the University of Maryland Mechanical Engineering Department, to study delay blasting. This study is sponsored by the National Science Foundation. Earlier work, sponsored by Martin Marietta Aggregates, in which high-speed cinematography was used to monitor production blasting operations, indicated considerable variation in the timing of borehole detonations in standard production blasting operations. Because of the complexity of the system, unambiguous interpretation of these irregularities was not possible. To separate variables, and because of the potential importance of timing in the production blasting operation, a test was set up to determine the firing times of currently available ms delay initiators manufactured in the United States. The results of this study and corroborating field evidence are presented in this paper.

EXPERIMENTAL METHODS

1. Field Methods

During the past three years, we have developed a method for high-speed cinematographic analysis of open pit production blasting operations (10). This development follows the original high-speed cinematographic work by the Bureau of Mines (11, 12) and others (13-16), but extends it to allow derivation of timing, in situ fragmentation, vent and flyrock velocities, and burden motion. The previous researchers generally used only one camera, and observed only the face in an open pit blasting operation. Their data were principally related to burden motion, although Frantti (15) observed and remarked on the firing times of non-electric relay connectors used in his experimental work.

In contrast, we use four high-speed cameras, and carefully choose both location and framing rate to maximize the return of information from our observations. Camera location and framing rate are critical. Cameras located on the front of a bench cannot provide reliable data on firing times of individual boreholes other than those on the first row, and then only if the sun is at a high angle to the bench. However, the front cameras are needed to derive in situ fragmentation of the face and the effect of structure on fragmentation. The answer to this problem is to use an array of cameras, all linked to a common starting pulse, to observe the blast.

Framing rate is important because, at the higher framing rates needed for optimum timing of events and derivation of rock velocities, the spatial resolution may be insufficient to determine the initial location of an event; for this, low framing rate cameras are needed. The higher framing rate cameras used, either a Wollensak WF-4 Fastax or a Redlakes Hycam, were run at a framing rate between 2000 and 4000 frames/s depending on the lighting conditions, lens used, and camera type. The Fastax is preferred, as the optics allow higher framing rates to be used under low-light conditions. The other camera used is either a Redlakes Milliken or a Locam, with maximum framing rates of 500/s. One set of cameras (one Fastax and one Milliken) is located behind the last row of holes to give data on initiation times, stemming vent velocities, and flyrock velocities. The other set is located in front of the bench, usually at some angle to the face. This set may be split so that the Fastax camera is located with its optic axis parallel to the face, with the Locam or Milliken at a higher angle to the face. These cameras give data on burden motion, in situ face fragmentation, front row flyrock, and front row timing. Stemming vent velocities can also be determined from these cameras if they are located higher than the bench. Film types used are Kodak EF, with a daylight ASA of 160, and, more recently, Kodak VNF, with a tungsten ASA of 400 and daylight ASA of 320 using a filter.

All camera positions are surveyed in relation to positions on the bench to be blasted, and bench locations are marked by ~3-ft piles of rock, sprayed with high visibility paint so that they can be seen on the high-speed films. In addition, each hole is marked with high visibility paint. These markers provide scale and, along with known camera locations, distances to the bench, and horizontal and vertical angles, can be used to make quantitative measurements of moving objects by triangulation or by location of the event in a plane surface normal to the axis of the lens.

2. Determination of Initiator Firing Times

The test of initiator firing times was designed to approximate, as closely as possible, their use in field practice (17). To arrive at a statistically valid data base, 30 initiators of each delay period 0-19 from Atlas, DuPont, and Hercules ms delay electric series, and of each delay period 1-14 of the Ensign/Bickford Primadet non-electric ms delay series were tested. The initiators tested were purchased from distributors in the Southeastern U.S., and box numbers and dates of manufacture recorded. The test apparatus consisted of a 1/4 in. thick steel plate to which were welded 60 3/4 in. ID pipes, each about 2 in. long in six rows of 10 pipes each. The pipes were 10 in. apart. The initiators were placed in the pipes to protect them from schrapnel generated by earlier-detonating initiators. A 1/4 in. hole was drilled through the plate at each pipe location, so that the flash caused by detonation of the initiator could be recorded by the high-speed camera. Electric caps were rigged in one or two series (depending on resistance) and initiated by means of an REO BM 125 sequential blasting machine using either the first set of terminals or the first and second set, depending on the number of series used in the test. Zero time was obtained using a flashbulb rigged to a separate circuit, and both the blasting machine and the flashbulb were triggered by closure from a single Redlakes Hycam used to monitor the test.

Non-electric initiators were rigged somewhat differently, but again as close to field use as possible. Three 10-ft strands of primacord were used to initiate the primaline leg lines of the primadet caps. All three trunklines were initiated instantaneously by a common primacord line passed through one of the pipes to provide zero time. All leg lines were measured, as was their position on the primacord, so that initiator firing times could be corrected for the primacord and primaline detonation times. Temperatures for each test were recorded. The framing rate used for the high-speed camera was 2000/s.

Errors in determination of firing times stem from three areas in the test as initially designed. The resolution, based on a framing rate of 2000/s is 0.5 ms and is the smallest contributor to overall error. The principal errors were with determination of zero time for electric caps. The REO BM 125 uses a free-running oscillator to achieve timing between each of its 10 circuits. When the signal to fire is given, the machine will wait until the end of a cycle to initiate the firing sequence. As a 10 ms interval was used, an error of up to 9 ms is possible in zero time. Another, smaller source of error lies in the cycle time of the flashbulb, which can be as much as 5 ms. It should be noted that the zero time error does not affect the interval between caps in a circuit. To minimize the zero time error, all caps were normalized to the firing time of the instant cap in the series. This decreases the zero time error to about ±1.5 ms for Atlas and DuPont caps and ±4 ms for Hercules caps.

RESULTS

1. Initiator Firing Times

Firing times using forced data for all manufacturers are listed in Table 1; unforced data are contained in (17). These data show that each manufacturer experiences deviations of the mean firing time obtained in this test from the nominal firing time of that particular delay period. Furthermore, the 1σ standard deviation increases sharply as the delay time increases. These two factors affect the success of a blasting operation by increasing the chances of overlap between adjacent period initiators, a situation that will manifest itself either as crowding (adjacent caps firing at shorter than desired intervals) or outright sequencing error where a lower and higher period initiator fire in the reverse order. As will be discussed further on in this paper and as discussed in earlier work (10), such problems have considerable effect on production blasting operations. The probability of an occurrence such as those described above can be evaluated statistically using the data generated by the test.

From the above discussion, it is clear that the time at which any cap will explode is not exactly a predetermined quantity, but acts as if it were a random (stochastic) variable. Therefore, even if we excluded the experimental inaccuracies in determining the firing times, we would still not have a deterministic system. Therefore we must discuss the probability of a sequencing error or crowding problem rather than state that one will occur.

This immediately implies that not only must the nominal (or mean) firing times be known, but the probability distribution of the firing time for each cap as well. Even the determinants of some statistical properties of the distribution (for example, the second moment, or "standard deviation") are really not sufficient to evaluate the probability distribution. Furthermore, the distribution of firing times of a cap at both extremes (very large and very small firing times) must also be known, which makes the determination of the firing time distribution even more difficult than if it only had to be known in the region of the most frequent firing times.

To evaluate the probability of success, one must specify the criteria for "success" in a concrete, unambiguous manner. Clearly, this specification may depend only upon a description of the sequence of events (such as when which cap fired) and must be explicit in detailing the necessary and sufficient conditions for "success." For instance, all period 1 must fire before period 2, and all period 2 before period 3, etc.

To calculate the probabilities of not encountering a sequencing error (i.e., the probability of success), two general approaches can be used. These are:

(1) We can (on a computer) simulate the firing times for all the caps by suitably randomizing the firing times (Monte Carlo approach). For each set of firing times thus computed, we use the appropriate criterion to tell whether or not "success" was achieved.

(2) We can analytically solve for the probabilities of success. Even though the resulting formulas may be difficult to evaluate, they can, in principle, be written and, with the aid of computers, numerically evaluated.

The first method (Monte Carlo) is the preferred approach if the criteria for success are involved, or if the probability distributions for the firing times for each cap are sufficiently complex (incorporating, for example, the firing times of other caps in hybrid non-electric systems). The second approach, which is preferred since it is much simpler to gain insight into the dominating features, is the one which was used for this evaluation.

Let us assume the following:

(1) The configuration consists of N sets of caps (where each set $i = 1 \ldots N$). Each set consists of some number of blasting caps ($K_i = 1, 2, \ldots$). There is a common initiation time for all caps.

(2) The necessary and sufficient criteria for success are that for all sets $i = 2, \ldots N$, the earliest cap of set i goes off no earlier than $\tau_i (\tau_i \geq 0)$ after the last cap of set i-1 has gone off; and that all caps go off.

(3) In each set, the probability that a given cap explodes before time t is given by

$$\int_{-\infty}^{t} P_i(\xi)d\xi \qquad (1)$$

(i.e., $P_i(t)$ is the probability density of the firing times for a given cap in set i, and the cumulative distribution is continuous), and all caps in the same set have the same probability density. Note that this assumption excludes the possibility that a mistake was made in the selection of one of the caps.

(4) The probability of any cap going off in a time interval is independent of when other caps have fired or will fire (i.e., the caps are statistically independent).

The first assumption describes the configuration. The second represents the criteria of success; the third is basically the definition of the probability densities, and the statement that in each set the caps are (statistically) the same. The fourth states that the knowledge of the firing times of other caps has no bearing on the exact time when another cap will fire or has fired.

The first problem is to determine a mathematical expression for the probability of success. Let $P_i^*(T)$ be the probability density that success has been obtained for all sets up to i, and that the last cap (of the set i) goes off at time t (i.e., the probability of success up to and including set N is

$$\int_{-\infty}^{+\infty} P_N^*(t)dt. \qquad (2)$$

The event as defined above can occur only in the following manner for $i > 1$: the elements of the ith set go off between time $\zeta + \tau_i$ and t (with the last cap of the i^{th} set going off at time t), and success has been achieved for set i-1 with the last cap of set i-1 going off at time ζ. The time ζ can be any time up to $t - \tau_i$.

The probability that all of the K_i items go off between time t_1 and t_2 ($t_1 < t_2$) is given by

$$\int_{t_1}^{t_2} P_i[(\phi)d\phi]^{K_i}. \qquad (3)$$

Therefore, the probability density that all go off between t_1 and t_2, and that the last one goes off at t_2, is

$$K_i P_i(t_2)\left[\int_{t_1}^{t_2} P_i(\phi)d\phi\right]^{K_i-1}. \qquad (4)$$

Therefore, we have to evaluate the following functions

$$P_i^*(t) = K_i P_i(t)\int_{-\infty}^{t-\tau_i}\left[\int_{\zeta+\tau_i}^{t} P_i(\phi)d\phi\right]^{K_i-1} P_{i-1}^*(\zeta)d\zeta \qquad (5)$$

$$i = 2, 3 \ldots N$$

where

$$P_1^*(t) = K_1 P_1(t)\int_{-\infty}^{t} P_1(\phi)d\phi^{K_1-1}.$$

Success, for all N sets, is given by

$$Z_N = \int_{-\infty}^{+\infty} P_N^*(t)dt. \qquad (6)$$

The above equations can be numerically evaluated. For the particular case where there is only one cap in set i

$$P_i^*(t) = P_i(t)\int_{-\infty}^{t-\tau_i} P_{i-1}^*(\zeta)d\zeta,$$

$$i = 2 \ldots N$$

with

$$P_1^*(t) = P_1(t).$$

The probability that we will have success for the set i, given that we have been successful up to and including the set i-1, is given by

$$R_i = \frac{\int_{-\infty}^{+\infty} P_i^*(t)dt}{\int_{-\infty}^{+\infty} P_{i-1}^*(t)dt} \qquad (7)$$

and the a posteriori probability density for the last cap of set i is given by $P_i^*(t)/Z_i$.

Equation 6 can be analytically evaluated for only a few situations. Such a set case is described below.

Assume that $\tau_1 = \tau_2 \ldots \tau_N = 0$, and that $P_1(t) = P_2(t) \ldots = P_N(t)$. Let $p = \int_{-\infty}^{+\infty} P_1(t)dt$ (i.e., the probability that any cap will fire at some time). Then, from eqs. 5 and 6, we can show that

$$Z_i = \frac{K_1!K_2! \ldots K_i!}{(K_1 + K_2 \ldots K_i)!}(p)^{(K_1 + K_2 \ldots + K_i)}. \qquad (8)$$

This result can also be obtained by other means. We also have

$$P_i^*(t) = Z_i^* X^{(K_1 + K_2 \ldots K_i)} * (K_1 + K_2 \ldots K_i)P_1(t) \qquad (9)$$

where

X is $\int_{-\infty}^{t} P(\phi)d\phi$.

For this simple case, we can readily calculate the probability of success (Z_i), for various K_i's. In this case, where all the probability distributions are the same, the rapidity with which the probability of success goes to zero as the number of caps is increased is evident. Furthermore, this simple example illustrates that the event "the earliest i occurs after the last i-1," and the event "the earliest i+1 occurs after the last i" are <u>not</u> statistically independent.

The last comment applies also to the general case (eq. 5), as can be reasoned from the following: if success up to the ith set is confirmed, then it is likely that no items of the ith set went off very early. This condition implies that the probability of the last cap going off late (among the caps in set i) has been enhanced. Consequently, there is a slightly lower chance of success for the i+1 set.

It is suspected, however, that if $R_i = 1$, then there is only a small error introduced by assuming statistical independence between adjacent sets instead of performing the (correct) calculations using eq. 5. In practice, it is only such cases in which we are really interested. If the calculations show the probability of success to be low, then the question as to exactly how low is academic.

This discussion of the lack of statistical independence of the probability of success between sets of caps is important since eq. 5 is occasionally difficult to evaluate numerically.* Consequently, we have devised a slightly simplified method of evaluating the probability of success. That method is to evaluate the probability of success for sets 1 and 2, then only for sets 2 and 3, then only for sets 3 and 4, etc. The total probability of success is then the product of these results. This method implicitly assumes that the (pair-wise) results are statistically independent of each other. As the above discussion indicates, this is reasonably correct only for the interesting cases with fairly high chances of success.

For the case of two sets, one can show that

$$Z_2 = K_1\int_{-\infty}^{+\infty} P_1(t)\left[\int_{-\infty}^{t} P_1(\phi)d\phi\right]^{K_1-1}\left[\int_{t+\tau_2}^{\infty} P_2(\phi)d\phi\right]^{K_2}dt$$

$$= K_2\int_{-\infty}^{\infty} P_2(t)\left[\int_{-\infty}^{t-\tau_2} P_1(\phi)d\phi\right]^{K_1}\left[\int_{t}^{\infty} P_2(\phi)d\phi\right]^{K_2-1}dt \tag{10}$$

which, for 2 sets, is a more convenient form than eqs. 5 and 6. Except for the case $\tau_2 = 0$ and $P_1 = P_2$, the value of this expression may depend upon the functional form of P_1 and P_2.

Let us now assume the $P_i(t)$'s have a Gaussian distribution with mean values t_i and standard deviations σ_i. This assumption is reasonable when one examines the firing times. We then have

$$Z_2 = \frac{K_1}{\sqrt{2\pi}\sigma_1}\int_{-\infty}^{\infty} \exp\left[\frac{-(t-t_1)^2}{2\sigma_1^2}\right]\left[\mathrm{erf}\left(\frac{t-t_1}{\sigma_1}\right)\right]^{K_2-1} *$$

$$* \left[1-\mathrm{erf}\left(\frac{t+\tau_2-t_2}{\sigma_2}\right)\right]^{K_2}dt \tag{11}$$

where

$$\mathrm{erf}(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{t} \exp\left[\frac{-\phi^2}{2}\right]d\phi.$$

Therefore, Z_2 is a function of K_1, K_2, $\frac{\sigma_2}{\sigma_1}$, and $\left(\frac{t_2-\tau_2-t_1}{\sigma_1}\right)$. For the case where $K_1 = K_2 = 1$, we have

$$Z_2 = \mathrm{erf}\left(\frac{t_2-t_1-\tau_2}{\sqrt{\sigma_1^2+\sigma_2^2}}\right). \tag{12}$$

Equation 5 was evaluated for some assumed forms of $P_1 \ldots P_N$, and the results were compared to those determined by successive application of eq. 10. We assumed (for the Gaussian distribution) that $t_i = i *$ constant (i.e., constant difference), $\tau_i = 0$, and $\sigma_i = v \cdot t_i$, where v is a small constant. We also assumed $K_1 = K_2 \ldots = 1$. Except for numerical inaccuracies (for $Z_i \approx 1$), the simplified (pair-wise) calculations slightly overpredicted the probability of success. For reasonable probabilities of success (i.e., not low), there are only minor differences between the two methods of computation. We therefore believe that the much simpler pair-wise method of calculation is appropriate for the evaluations.* Calculated values of Z_2, for several values of $\frac{\sigma_2}{\sigma_1}$, $\left(\frac{t_2-\tau_2-t_1}{\sigma_1}\right)$, and K_1 and K_2, are presented in Fig. 1. For very large values of $\frac{\sigma_2}{\sigma_1}$,

$$\lim_{\frac{\sigma_2}{\sigma_1}\to\infty} Z_2 \to \left(\frac{1}{2}\right)^{K_2} \tag{13}$$

while, for small values of $\frac{\sigma_2}{\sigma_1}$,

$$Z_2 \to \left[\mathrm{erf}\left(\frac{t_2-\tau_2-t_1}{\sigma_1}\right)\right]^{K_1}. \tag{14}$$

If $\frac{\sigma_2}{\sigma_1} = 1$, then

$$Z_2\left(K_1, K_2, 1, \frac{t_2-\tau_2-t_1}{\sigma_1}\right) = Z_2\left(K_2, K_1, 1, \frac{t_2-\tau_2-t_1}{\sigma_1}\right). \tag{15}$$

---

*The assumption that the cap firing times are statistically independent still holds.

*Note: Comparisons were also made with the Monte Carlo simulations. The results agreed within reasonable limits.

In fact,

$$z_2\left(K_1,\ K_2,\ \frac{\sigma_2}{\sigma_1},\ \frac{t_2-\tau_2-t_1}{\sigma_1}\right) = z_2\left(K_2,\ K_1,\ \frac{\sigma_1}{\sigma_2},\ \frac{t_2-\tau_2-t_1}{\sigma_2}\right).$$

It is clear from the above equations that the critical parameter is $\frac{t_2-t_1-\tau_2}{\sigma}$ (i.e., the non-dimensionalized difference in the mean time minus the minimum delay). If this difference is small (or less than zero), the chances of success -- for any pair -- are rather dim, and this dimness gets worse as the number of caps in each set is increased. For a reasonable number of caps and sets, we should like to have

$$\frac{t_2-t_1-\tau_2}{\sqrt{\sigma_1^{2}+\sigma_2^{2}}} \gtrsim 3$$

for each adjacent pair.

The approach developed above can be applied to various general configurations of delays in production shots and to the calculation of probabilities of success for them. As an example, Table 2 shows calculated probabilities of success for a shot of 24 holes, using 3 caps of each period 1-8 (25-200 ms). This type of shot, typical of some aggregates quarries in the southeast, uses 3 rows of holes, 8 holes per row, shot on a 35-40 ft granite bench, initiated in a V or offset V (opening from near one end) pattern (see Table 3, Atlas shot). The calculated probabilities of success range from 5% to 70% (no reversals) and 0.2% to 19% (adjacent periods separated by at least 8 ms).

2. Results of Production Tests

Using the high-speed cinematographic technique described earlier, we monitored 37 production blasts in several aggregates quarries, using several different patterns and delay sequences on benches of differing heights and rock types. Analysis of these films provided data on timing of borehole detonations in the field, flyrock velocities, burden motion, and in situ fragmentation of the face.

The previous sections of this paper have discussed the statistical treatment of test data for commercial initiators, and developed a predictive statistical model with which analysis of potential problems arising from shot design using these initiators can be made. Table 3 gives mean and standard deviations of firing times for initiators from three manufacturers, obtained by analysis of high-speed films of production blasts. The error in determination of the firing time of a given initiator in field use was somewhat higher than that for the board tests because the detonation of the explosive column and the number of frames needed to establish visually the disturbance caused by the detonation varied with conditions of exposure (10). This error was generally ±2 ms depending on bench height.

Examination of Table 3 indicates generally good agreement with the results of the board tests even though the initiators used in the field were from different batches, different suppliers, and had different production dates than those used in the board tests. Given this agreement, two conclusions can be made: first, the sample size used for the test is reasonably representative of the population of initiators used, at least in the southeastern and midwestern United States. Second, the irregularities in firing times observed in all of our production shots can be attributed to deviations in initiator firing times, as opposed to other factors such as shock damage from the detonation of adjacent boreholes, primer location, variation in column detonation velocity, etc.

Firing time variations can be correlated with blast parameters that affect production. Fig. 2 represents firing times and vent or flyrock velocities derived from a production blast in Kansas. This shot used a sequential blasting machine (REO SBM 125) and period 3-8 ms delay EB caps to achieve a flat V pattern. Hole diameter was 4.5 in., bench height was 20 ft, and 56 in. of crushed stone was used for stemming. The nominal firing times are the middle values, while uppermost values are the actual times determined from the cameras. Flyrock or vent velocities are recorded as the lowermost values.

As designed, this shot had a between-hole relief of 1.9 ms/ft of burden, and a relief on the echelon of 5 ms/ft of burden. The echelon relief is a formalism, where the holes between rows firing 8 ms apart are joined, and the next hole fires into this echelon. The burden as measured in the test would be 5 ft, the timing, 25 ms, for a relief of 5 ms/ft (see Fig. 2). The actual relief is a function of the actual firing time of the initiators used in the shot. In this shot, the hole-to-hole side (adjacent holes) relief varied from -1.4 ms/ft to 4.02 ms/ft (negative numbers reflect out-of-sequence firing), and the on-echelon relief varied from 0.83 ms/ft to 10.65 ms/ft. It is obvious from Fig. 2 that the development of this shot proceeded quite differently from the way in which it was intended. To determine whether the amount of relief in any way correlates with vent or flyrock velocity, the relief, as defined above, was plotted against vent or flyrock velocities measured for this shot (Figs. 3 and 4). It is clear that both show a correlation, suggesting that increasing relief in this configuration will decrease the vent or flyrock velocity. In addition, carrying the correlation back to the zero flyrock intercept gives a relief of 3.4 ms/ft measured against adjacent holes and 8.7 ms/ft measured on the echelon. These extrapolations imply that, with this pattern, this bench, and the amount of stemming used, more relief is needed to attain zero flyrock or vent velocities perpendicular to the top of the face. These numbers are substantially higher than those derived by Bergmann et al. (5).

Analysis of high-speed films to date has allowed us to correlate between timing problems, such as sequencing errors or crowding, and production of oversize blocks, backbreak, and tight muck. It now appears that correlation can also be made with relief, which is essentially controlled by the timing and the drilled spacing and burden. Since, at present, timing can be more readily varied in the blasting pattern (because drilled pattern is essentially fixed within certain limits by drill size or bench height), work should be concentrated in this area. The problem is not simple, however, because timing is not the only variable. Similar patterns to the one discussed above, when fired on low (6-8 ft) benches, produce poor correlations between relief and vent or flyrock velocity. This is at least partly due to the geometry of the shot: short explosive columns, at similar spacings and burdens used on higher benches, produce conditions that promote cratering. In these situations, vent and flyrock velocities are very high (up to 1400 ft/sec), and virtually all holes vent. The timing correlations can be expected to hold only where borehole diameter and drilled spacing and burden are matched to the bench height to be blasted. At present, the data are insufficient to establish all parameters quantitatively.

CONCLUSIONS

Tests of currently available ms delay blasting caps, both electric and non-electric, indicate considerable deviation from the nominal firing times given by the manufacturer and an increase in scatter around the mean firing time with increase in delay period. These results have been confirmed by observations of actual production blasting operations with high-speed motion picture cameras. Statistical treatment of the data derived from the tests suggests minimum separations necessary to insure success (Fig. 1), and indicate that a high probability of sequencing and crowding errors exists with presently available initiators.

Sequencing and crowding errors are important because they affect the relief in a shot as it develops. Insufficient relief correlates with high vent or flyrock velocities, as well as with production of oversize, backbreak, and tight muck, all of which are detrimental to production or vibration control. From relationships between peak particle velocity vs pounds explosive/delay developed by the Bureau of Mines (7), crowding can be expected to adversely affect particle velocities generated by production blasting, and to increase the difficulty in meeting federal or state regulations. It is also clear that, even if these problems are corrected, not enough is known about the manner through which delay initiation works to improve fragmentation to design optimum delay patterns. For this reason, further work on delay initiation in production blasting must be done.

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TABLE 1

FIRING TIMES OF MS DELAY BLASTING CAPS*

	DuPont 0=5 ms			Hercules 0=12 ms			Atlas 0=1 ms			Ensign/Bickford Primadets		
Period	Rated T(ms)	$\bar{X}(21)$	1σ	Rated T	$\bar{X}(21)$	1σ	Rated T	$\bar{X}(30)$	1σ	Rated T	$\bar{X}(31)$	1σ
0	5	5	NA	12	12	NA	1	1	NA	---	---	---
1	25	27.9	4.4	25	28.6	4.0	8	5.7	1.4	25	38.8	1.8
2	50	51.1	6.2	50	50.8	5.9	25	25.3	4.4	50	59.5	9.4
3	75	86.2	4.2	75	62.7	4.9	50	48.6	5.3	75	81.9	1.4
4	100	111.7	5.6	100	98.5	7.1	75	73.0	11.8	100	110.3	3.2
5	125	140.4	7.8	130	138.7	4.5	100	100.1	5.1	125	135.8	2.9
6	150	173.4	6.0	170	178.5	9.4	125	135.8	6.2	150	168.5	5.7
7	175	185.1	5.9	205	202.5	6.1	150	154.5	5.7	175	168.9	7.8
8	200	183.4	9.6	240	253.9	19.6	175	186.3	7.5	200	234.3	5.8
9	250	279.2	9.6	280	326.9	22.3	200	217.4	7.5	250	255.1	3.9
10	300	307.0	11.7	320	324.3	18.0	250	272.0	12.5	300	486.5	23.8
11	350	362.4	34.4	360	382.9	55.9	300	318.5	12.5	350	356.0	4.7
12	400	428.1	19.8	400	401.5	34.2	350	382.1	20.1	400	403.5	6.4
13	450	440.8	18.9	450	496.8	21.2	400	441.6	17.1	450	466.7	12.1
14	500	523.7	24.0	500	506.9	25.5	450	452.1	17.9	500	506.6	7.6
15	600	649.0	51.8	550	697.8	50.1	500	556.4	22.3			
16	700	735.3	46.3	600	797.8	48.0	550	569.7	17.9			
17	800	913.0	56.1	700	1144.6	73.6	650	708.5	29.5			
18	900	992.3	65.1	900	1050.8	101.4	750	813.2	36.2			
19	1000	1166.0	60.7	1200	1366.1	112.1	875	911.1	36.6			

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*This table presents normalized data for electric caps. See text for details.

TABLE 2

PROBABILITY OF SUCCESS FOR MULTIPLE CAPS
PERIODS 1-8, 3 CAPS EACH

	No Sequencing Error	8 ms Separation
Atlas Forced to 0 = 1 ms	.70	.19
DuPont Forced to 0 = 5 ms	.02	.0002
Hercules Forced to 0 = 12 ms	.60	.09
Ensign/Bickford Primadets	.06	.003

TABLE 3

FIRING TIMES OF MS DELAY CAPS IN PRODUCTION BLASTING*

	DuPont Shot 1				DuPont Shot 2				Atlas				Ensign/Bickford			
Period	N	Rated T(ms)	$\bar{X}$	1σ	N	Rated T	$\bar{X}$	1σ	N	Rated T	$\bar{X}$	1σ	N	Rated T	$\bar{X}$	1σ
0	10	5	2.2	1.9									13	17	16.9	0.6
1	9	25	21.8	5.9					2	8	13.0	4.2				
2	7	50	54.1	2.7					4	25	31.0	10.1				
3	12	75	74.5	3.8	5	75	79.6	5.6	4	50	56.5	11.0		75	78.3	11.5
4	14	100	92.4	5.5	8	100	109.5	10.7	4	75	81.0	2.6		100	83.5	15.4
5	13	125	138.9	5.8	7	125	144.9	8.2	5	100	97.6	19.8				
6	6	150	177.6	7.7	6	150	178.3	12.5	4	125	123.0	36.8				
7	10	175	187.9	7.6	6	175	188.9	23.4	2	150	160.0	5.7				
8	13	200	216.5	8.0	6	200	197.0	26.1	2	175	180.0	11.3				

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*All electric cap firing times are from shots using bottom hole initiation; thus, temperatures should be comparable. Caps are set in cast primers for the DuPont and Ensign/Bickford shots, in dynamite for the Atlas shot.

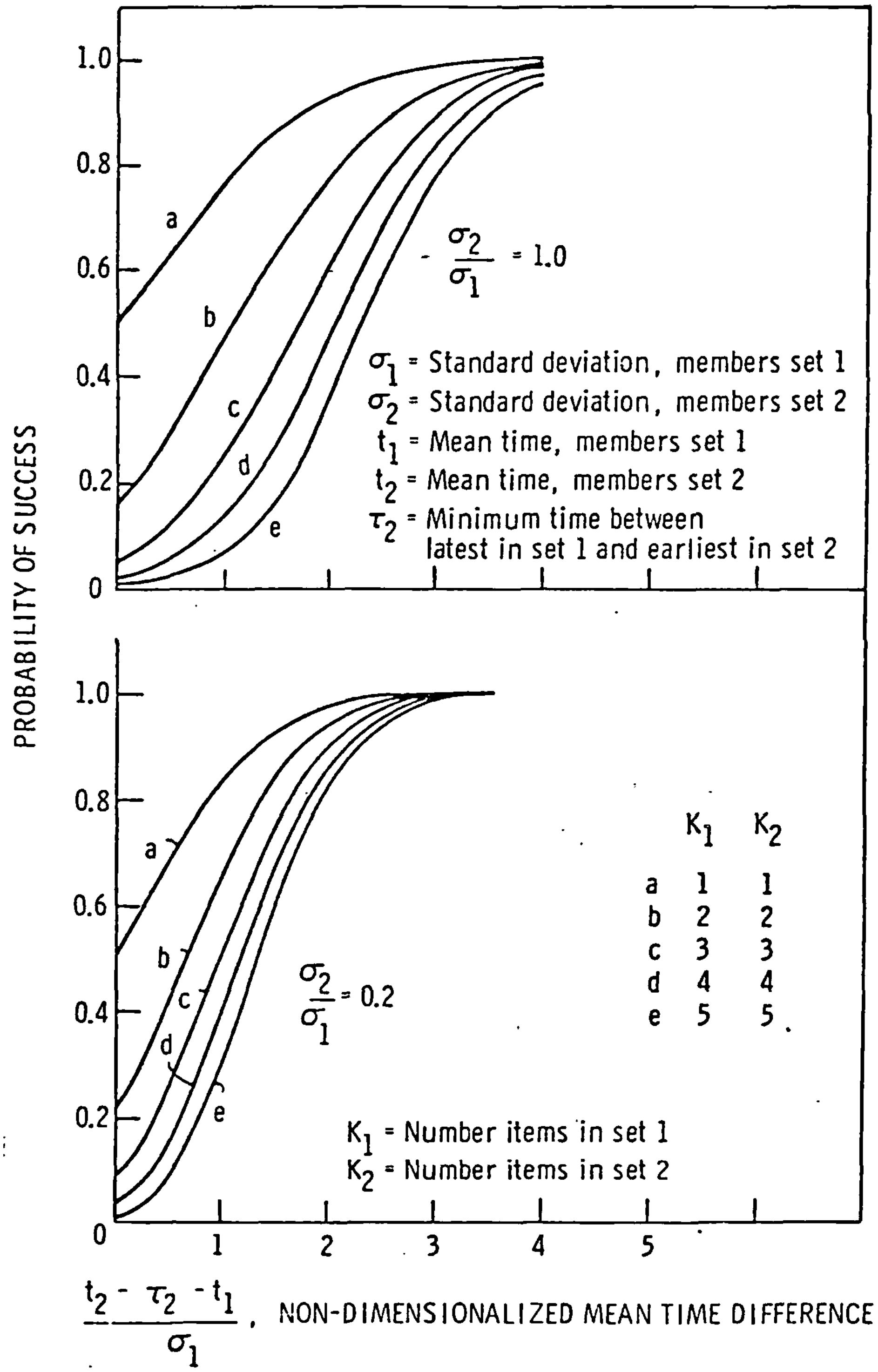

Figure 1. Probability of success, calculated using equation 10 versus non-dimensionalized mean time difference.

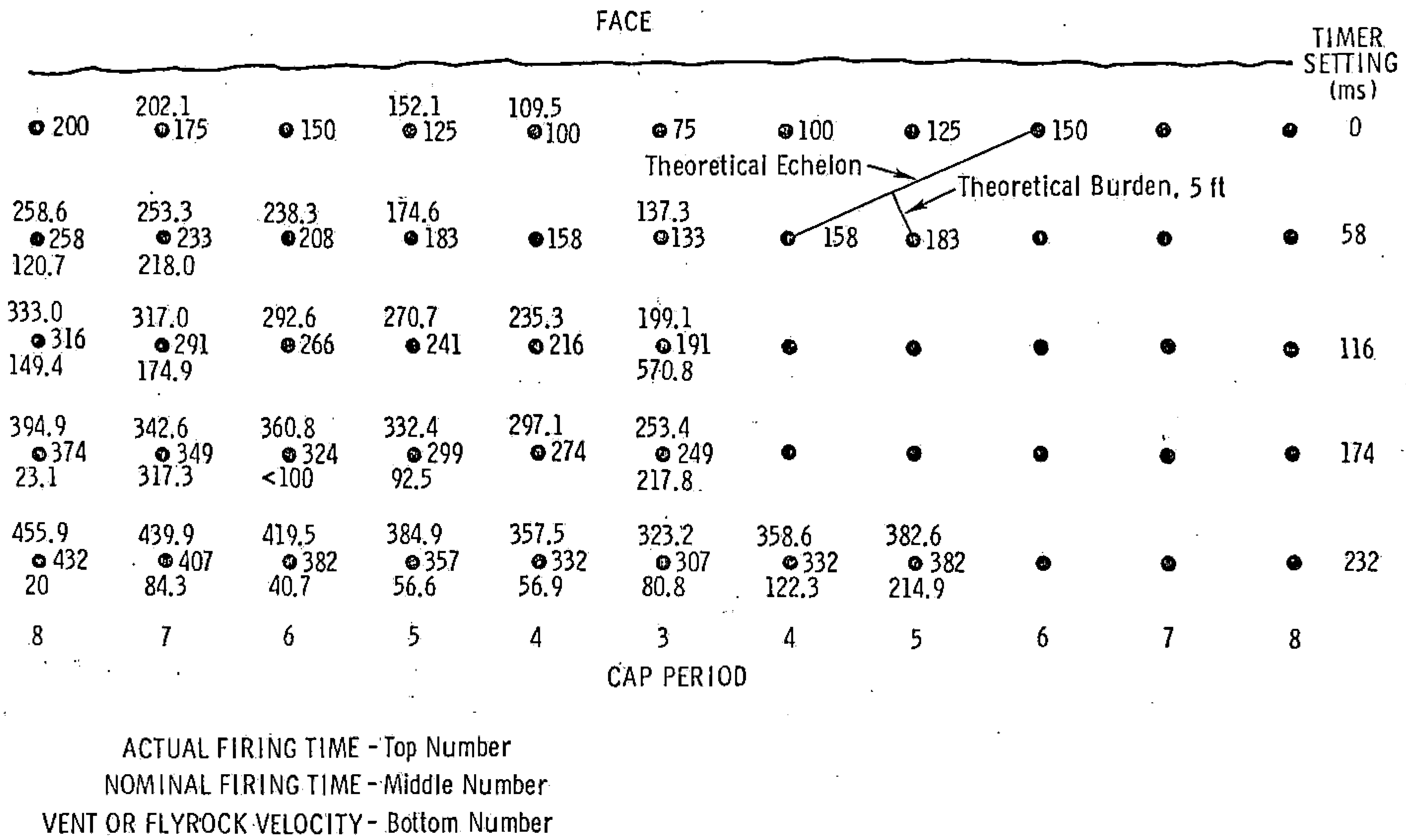

Figure 2. T-26 blasting pattern showing nominal and actual firing times and stemming vent or flyrock velocities. The method of calculating the echelon relief is shown in the upper right portion of the figure.

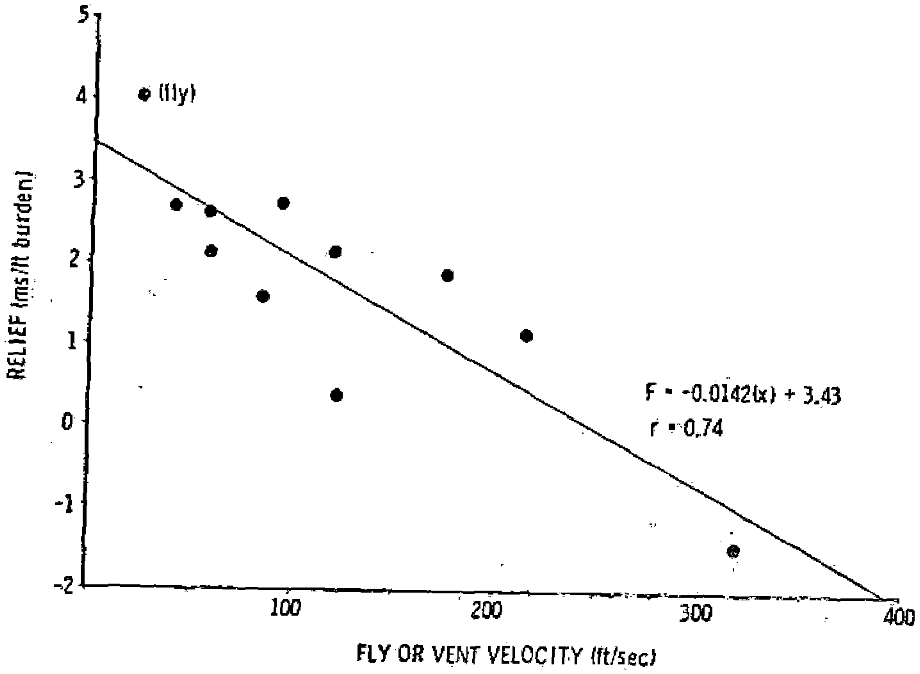

Figure 3. Relief, measured in ms/ft of burden between adjacent holes plotted against flyrock or vent velocity (ft/sec) for the T-26 shot shown in Fig 2. Data obtained from high-speed motion pictures.

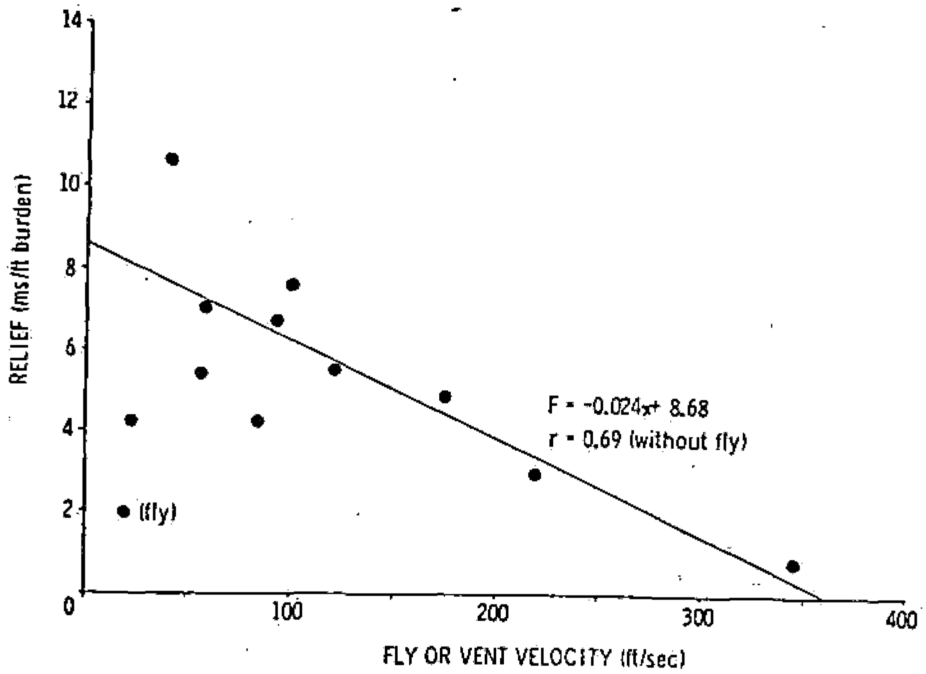

Figure 4. Relief, measured in ms/ft of burden on the echelon plotted against flyrock or vent velocity for the T-26 shot shown in Fig. 2. Data obtained from high-speed motion pictures.

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Investigation of the hydrolytic deposition of iron in the form of jarosites from sulphate solutions

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Hydrolytic purification of solutions from iron is widely used in chemical technology and hydrometallurgy and, in particular, in the hydrometallurgy of zinc. A disadvantage of the process is the poor settling and filtering characteristics of the obtained precipitates [1]).

Ryazanov [2]) noticed that a readily settling precipitate of a compound analogous with the natural mineral jarosite is formed during the hydrolysis of iron in the presence of K^+ ion . This served as the basis for the development simultaneously in Norway [3]) and Australia [4]) of the "jarosite process", which is most promising for the leaching of high-iron zinc raw material (e.g., zinc cakes). Even from iron-rich solutions (during high-temperature sulphuric acid leaching of zinc cakes the iron content of the solution amounts to 40% and its increase during jarosite precipitation of iron from the solution is of interest) it is possible to obtain readily settling precipitates of jarosite and an acidic solution ($pH < 1.0$) with a low Fe^{+++} content, which is treated by standard methods separately or in the cycle of the neutral leaching of zinc calcines.

It is known [5]) that jarosites $R^+Fe_3(OH)_6(SO_4)_2$ can contain the ions of various monovalent elements and groups $R^+ = Na^+$, K^+, Ag^+, H_3O^+, and NH_4^+. Data on reduction of the time for the formation of hydrolytic deposits of iron in the $Fe_2(SO_4)_3$-$ZnSO_4$-ZnO-H_2O system with additions of K^+, Na^+, Rb^+, and NH_4^+ are contained in the literature [6]). However, these data are insufficient for optimum realisation of the "jarosite process".

In the present work we studied the hydrolytic precipitation of iron in the $Fe_2(SO_4)_3$-$ZnSO_4$-ZnO-H_2O system with and without the presence of K^+, Na^+, and NH_4^+ ions under various concentration conditions and also the effect of additions of the crystalline hydrolysis products as seeds. Reagents of analytical and chemically pure grades were used. The method used for the investigation was as follows. A solution of ferric sulphate or a mixture of ferric sulphate and zinc sulphate in a closed flask was placed in a water thermostat at 90 ± 0.5°C. The stopper of the flask contained a mechanical stirrer and a tube for the delivery of an aqueous suspension of zinc oxide with and without various additions and also for the removal of samples at specific intervals of time.

The volume of the suspension and its ZnO content were calculated for a total volume of 1 litre, for initial iron concentrations of 66, 50, or 12 g/l, and for the required molar ratio $m = ZnO/Fe_2(SO_4)_3$ (where m is the specific consumption of the neutraliser in moles per mole of $Fe_2(SO_4)_3$). The solution was separated from the samples of pulp by filtration, the Fe^{+++} concentration was determined by complexometric titration (EDTA), and the pH value was measured (with an accuracy of ± 0.05 at room temperature). The K^+, Na^+, and NH_4^+ ions were added in the form of sulphates. The results are presented graphically in figs. 1-5.

The addition of zinc oxide to a solution of ferric sulphate leads to a sharp rise in the pH value of the solution (fig. 1b) as a result of neutralisation of the acid:

$$2H_3O^+ + ZnO = Zn^{2+} + 3H_2O$$

This displaces the system from hydrolysis equilibrium and thereby accelerates the hydrolysis reaction. The dissolution of zinc oxide by reaction(1) is complete on the attainment of the maximum pH. The pH then gradually decreases as a result of slowly occurring hydrolysis (hydrolysis of Fe^{3+} can lead to the formation of various hydroxo complexes (7)) by the reaction:

$$Fe(H_2O)_6^{3+} + 2H_2O \rightleftarrows FeOH(H_2O)_5^{2+} + H_3O^+$$

Additions of monovalent cations stimulate the crystallisation stage of the formation of a precipitate (fig. 1a, curves 2 and 3), i.e., the removal of the hydroxo complexes of iron from the solution, and this accelerates the hydrolysis reaction (the more rapid decrease of the pH, curves 2 and 3 in fig. 1b). This shows that crystallisation is the controlling stage of the process under the investigated conditions.

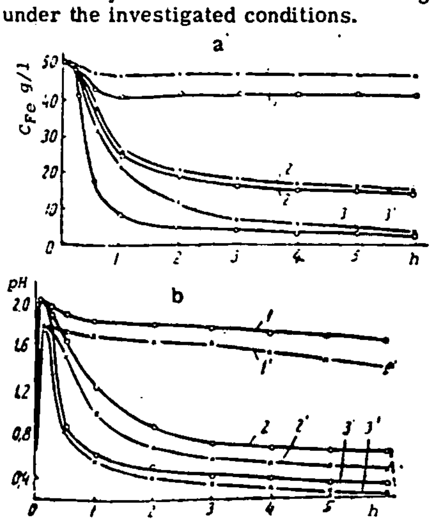

Fig.1 Effect of additions of alkali-metal ions on the hydrolytic precipitation of iron from a concentrated sulphate (C_{Fe}^0 = 50 g/l) with $m = ZnO/Fe_2(SO_4)_3$ = 1.0 at 90°C on the iron concentration (a) and the pH value (b) of the solution. 1 - without additions, 2 - with additions of Na_2SO_4; 3 - with additions of K_2SO_4; C_{Zn}^0 = 0; 1',2',3' - the same for C_{Zn}^0 - 100g l; addition in stoichiometric amounts for the formation of jarosite.

Comparison of curves 1, 2, 3 and 1', 2', and 3' in figs. 1a, b shows that the presence of even considerable inital amounts of $ZnSO_4$ in the solution has little effect on the formation of the hydrolytic precipitates of iron; the degree of precipitation of iron decreases slightly, and the pH of the solutions decreases a little. If the initial concentration of iron in the solution is not 50 (fig. 1) but 12 g/l, the effect of the same amounts of $ZnSO_4$ in the solution hardly shows up at all in the rates of formation of the precipitate and decrease of the pH value. (The presence of considerable amounts of zinc sulphate in the solution increases the degree of dispersion of the jarosite precipitates and the viscosity of the solution, and this substantially impairs the settling characteristics of the precipitates.)

Fig.2 Effect jarosite-forming additions on the hydrolytic precipitation of iron by zinc oxide from a solution of ferric sulphate (C_{Fe}^0 = 12g/l) for m = 1.0 at 90°C. 1 - without addition; 2 - with additions of sodium sulphate; 3 - ammonium sulphate; 4 - potassium sulphate; Amounts of additions - 300% of the stoichiometric.

Comparison of curves 1 (fig. 1a, fig. 2, fig. 3) and 3 (fig. 4) shows that, with the same specific consumption of the neutraliser m and with other conditions equal, the degree of precipitation of iron decreases with increase in its initial concentration: 95.8% with C_{Fe}^0 = 12g/l and 77.6% with C_{Fe}^0 = 66 g/l. This is explained by the fact that a larger initial content of Fe^{3+} in the solution corresponds to a larger inital content of Fe^{3+} in the solution corresponds to a larger initial content of the hydrolysis acid. This destroys the proportional relationship between the initial and final contents of iron in the solution for equal m values. Consequently, the higher the Fe^{3+} content of the solution, the higher the specific consumption of the neutraliser m and with other conditions equal, the degree of precipitation of iron decreases with increase in its initial concentration: 95.8% with C^0_{Fe} = 12 g/l and 77.6% with C^0_{Fe} = 66 g/l. This is explained by the fact that a larger initial content of Fe^{3+} in the solution corresponds to a larger initial content of the hydrolysis acid. This destroys the proportional relationship between the inital and final contents of iron in the solution for equal m values. Consequently, the higher the Fe^{3+} content of the solution, the higher the specific consumption rate of neutraliser required for a given degree of precipitation. Thus, an identical degree of precipitation of iron of ~96% is obtained with m = 1.5 for C^0_{Fe} = 66 g/l (curve 2 in fig. 3) and with m = 1.0 for C^0_{Fe} = 12 g/l (curve 3 in fig. 4).

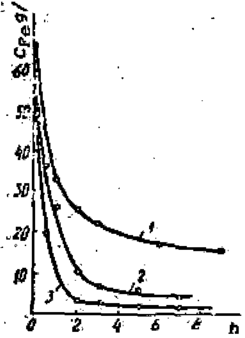

Fig.3 The effect of the zinc oxide consumption on the hydrolytic precipitation of iron from sulphate solution (C^0_{Fe} = 66g/l and C^0_{Zn} = 100g/l) in the presence of the stoichiometric amount of potassium sulphate at 90°C. - m = 1.0; 2 - 1.5; 3 - 2.0.

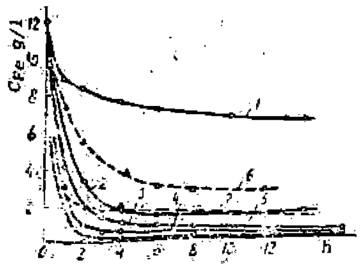

Fig.4 Effect of the amount of additions of K^+ (1-5) and NH_4^+ (6 7) on the hydrolytic precipitation of iron from a solution of ferric sulphate (C^0_{Fe} = 12g/l) by zinc oxide for m = 1.0 at 90°C without additions (1) and with additions of K_2SO_4 (% of stoichiometric): 75(2), 100(3), 230(4) and 300(5); with additions of $(NH_4)_2SO_4$: 100 (6) and 200 (7).

The effect of the consumption of jarosite-forming additions on the hydrolytic precipitation of iron is shown in Fig. 4. Increase in the consumption of such an effective additive as potassium has little effect on the precipitation rate. Increase in the consumption of a less effective additive (ammonium) considerably accelerates the precipitation. Consequently, the lower effectiveness of the additive can be compensated to some degree by increase in its consumption rate.

The effect of a seed as accelerator of the crystallisation stage on the rate of the hydrolytic precipitation of iron is shown in fig. 5. Since goethite α-FeOOH is the stable form of iron in the hydrolytic precipitate under the selected conditions without the jarosite-forming addition, it was used as seed, and it has little effect on the precipitation rate (fig. 5, curves 1 and 2). Clearly, the crystallisation rate of goethite is determined by the linear crystallisation rate and not by the formation rate of crystallisation centres.

Jarosite as a seed under the influence of the less effectiv jarosite-forming addition (sodium) substantially accelera the precipitation of iron (curves 3 and 4 in fig. 5). A similar pattern is found in the precipitation of NH_4 jaros but the seed gives a smaller effect for K jarosite. The accelerating effect of the seeds in the precipitation of the jarosites can be explained by the fact that in this case the crystallisation rate is limited by the formation of crystallisation centres and not by the linear growth of the crystals. Therefore, jarosite precipitates are more coarsely crystalline than goethite precipitates.

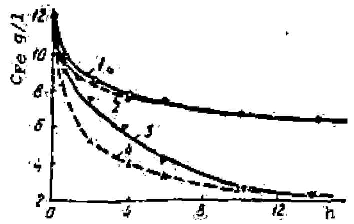

Fig.5 Effect of a seed on the hydrolytic precipitation of with zinc oxide from a solution of ferric sulphate (C^0_{Fe} = 12g/l) for m = 1.0 at 90°C; 1 - without additions and without seed; 2 - without addition and with goethite seed; 3 - with addition of sodium sulphate and without seed; 4 - with addition of sodium sulphate and with jarosite seed (additions in stoich metric amounts).

Conclusions

1. The effectiveness of the acceleration of the hydrolytic precipiation of iron from sulphate solutions by jarosite-forming additions decreases in the order K > NH_4 > Na.
2. The presence of considerable amounts of $ZnSO_4$ in the solution has little effect on the rate of hydrolysis and formation of the precipitate with high contents of iron in the solutions (~ 50 g/l), and with moderate contents (~12 g/l) the effect is not detected. However, a consider content of $ZnSO_4$ in the solution (100 g/l Zn) increases th viscosity of the solution and the degree of dispersion of th jarosite precipitates, and this impairs their settling characterisitics.
3. The specific consumption of the neutraliser for a give degree of precipitation of iron is greater, the higher the initial concentration of iron in the solution.
4. An excess of the jarosite- forming addition over the stoichiometric value slightly accelerates the hydrolytic precipitation if the addition is highly effective (potassium and considerably accelerates it if the addition is less effective (ammonium).
5. A seed of jarosite accelerates the precipitation of iro in the form of jarosite particularly in the case of the precipitation of NH_4 -Na jarosite. A seed of goethite har accelerates the precipitation of iron in the form of goethi at all.

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is greater than unity. An increase in X is observed with increase in temperature and with increase in the oxygen pressure; thus, in the range of 60-140°C it increased from 1.15 to 1.8 (for P_{O_2} = 4 atm) and from 1.4 to 1.88 (P_{O_2} = 8 atm). In order to explain the observed preferential dissolution of copper experiments were carried out on the reaction of alloy 2 with a solution containing 1g/l Cu and 0.1 mole/l H_2SO_4 at 80-180°C in a neutral atmosphere. At 80°C the rate of transfer of zinc into solution amounted to $0.6 \cdot 10^{-8}$ and that for copper amounted to $0.77 \cdot 10^{-8}$ g-atom/cm²·sec; at 180°C these values increased to $1.31 \cdot 10^{-8}$ and $2.93 \cdot 10^{-8}$ g-atom/cm²·sec respectively, i.e. with increase in temperature the ionisation of copper atoms is preferred to the ionisation of zinc atoms under the influence of the copper ions present in the solution. Metallic copper was found in the surface films. Its formation is possible both on account of cementation-type deposition of copper (the concentration of copper in the solution at t < 100°C decreases) and as a result of disproportionation of the copper ions which form (the copper content of the solution increases at t > 120°C). The development of these processes is promoted by the observed increase in the electrochemical activity of the alloy with increase in temperature and also by increase in its zinc content. The dispersed copper which forms dissolves much more quickly in the oxygen atmosphere than the copper (zinc) from the alloy, and this gives rise to the observed preferential dissolution of the copper, which results from the side processes. We therefore classify it as "pseudoselective". For alloy 2, in addition to dissolution in sulphuric acid, we investigated its behaviour in an ammoniacal medium.

We used a solution containing 2.0 mole/l of NH_3 and 0.5 mole of $(NH_4)_2SO_4$. The ratio of ammonia and ammonium sulphate was chosen in relation to the composition of the solvent used in practice³). Most attention was paid to the effect of temperature and oxygen pressure (the most effective technological parameters). The dissolution of copper increases in direct proportion to the oxygen pressure ($V = K \cdot P_{O_2}$), and this indicates that oxygen plays a definite part in the mechanism of the process (fig. b). With other conditions equal the dissolution rate of pure copper in the ammoniacal medium is 1.75 times higher than the dissolution rate of copper from alloy 2. It is clear that during the ammoniacal leaching of the alloys an impermeable film is formed from the oxidation products of tin, lead and iron present in the alloys, and this complicates the diffusion of oxygen. For alloy 2 the K value (g-atom/cm²·sec·atm) amounts to $0.217 \cdot 10^{-7}$ for dissolution in ammonia and $0.2 \cdot 10^{-7}$ (for alloy 1 at 100°C, $K = 0.25 \cdot 10^{-7}$) for dissolution in sulphuric acid, i.e. the oxygen deficiency is more clearly defined in ammonia solutions and increase in the oxygen pressure has a more significant effect on the dissolution rate of copper than in sulphuric acid solutions. With identical oxygen pressures the dissolution rates of copper from the polymetallic alloy in sulphuric acid and ammonia solutions differ by obly 6-10%. For solvents with appreciably differing action this can be explained by the different nature and by the permeability of the films which form. For dissolution in ammonia at 40-95°C (for pure copper) and 40-70°C (for the alloys) the experimental activation energies amount to 2.13 and 0.98 kcal/mole respectively, which is consistent with published data⁴). When t → 70-95°C, the E_a values for the dissolution of pure copper and of copper from alloy 2 increase to 4.3 ± 0.2 kcal/mole. The temperature dependence and the data from microscopic and X-ray analyses of the films make it possible to consider that more permeable films, which facilitate the diffusion of oxygen, are formed on the surface of the alloy at elevated temperatures. In addition, with increase in temperature the role of the oxidative capacity of the divalent copper ions increases, and this leads to additional ionisation of copper atoms⁵). In the range of 40-70°C the dissolution rate of copper (alloy 2) is higher in the ammoniacal medium than in sulphuric acid; at 80-90°C it is comparable for both media, while at 100-120°C the dissolution rate of copper increases by 1.84 times in sulphuric acid and by 1.32 times in the ammonia solution. Thus, at t → 100°C an increase in temperature is more justified kinetically for sulphuric acid dissolution than for ammoniacal dissolution.

Conclusions

1. The dissolution rate of copper (or zinc) from the alloys is controlled by the diffusion of oxygen. The latter is complicated by a screening film of insoluble alloy components. The films formed in ammonia solutions are less permeable.
2. In order to intensify the leaching of the alloys it is advisable to improve the mass exchange of oxygen in the system. The use of elevated temperatures (above 90-100°C) is justified kinetically for dissolution in sulphuric acid.
3. Compared with pure copper the dissolution of copper from the alloys occurs at a higher rate in the sulphuric acid medium than in the ammoniacal medium. Alloys with the minium contents of tin, lead, iron and other insoluble components are therefore better for ammoniacal dissolution.

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Investigation of the hydrolytic precipitation of iron(III) from zinc sulphate solutions in the presence of monovalent cations

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It is known¹⁻³) that the hydrolytic precipitation of Fe(III) from acidic sulphate solutions in the presence of monovalent cations gives jarosites, and this has found wide use in zinc hydrometallurgy⁴). Specific characteristics must be expected in the hydrolytic precipitation of iron from zinc sulphate solutions in the presence of a monovalent cation both with respect to the process in purely iron solutions⁵⁻⁷) and with respect to the process in zinc solutions without the monovalent cation⁸). These specific characteristics can manifest themselves both in the concentration conditions for the formation of the various solid phases and in the kinetics of hydrolysis and precipitation of Fe(III). In the absence of the monovalent cation the primary product from hydrolytic precipitation of Fe(III) from zinc sulphate solutions when $C_{Fe} > 0.1$ g/l is the amorphous basic sulphate $2Fe_2O_3 \cdot SO_3 \cdot xH_2O$, which begins to form at $pH \geqslant pH_{in}$, where $pH_{in} = f_1(C_{Fe}, t)$⁹). In the presence of R^+ jarosite $(R, H_3O)Fe_3(OH)_6(SO_4)_2$ is formed when $pH < pH_{aj}$, and the amorphous basic sulphate is formed when $pH > pH_{aj}$, where $pH_{aj} = f_2(C_{Fe}, t)$[10]).

In order to investigate these specific characteristics in the present work we studied the phase composition of the precipitates and the relative changes in the rate of hydrolytic precipitation of iron in the $Fe_2(SO_4)_3$-$ZnSO_4$-K_2SO_4-ZnO-H_2O system at 50-90°C with C_{0Zn} = 100g/l. For R⁺ we used K^+ as the most effective jarosite-forming cation [11]). (Potassium sulphate was added to the solution in the amount calculated for the combination of all the iron into jarosite). In addition, we studied the rate of conversion of the amorphous sulphate into jarosite. (This transformation occurs during the hydrolytic precipitation of Fe(III) in the presence of K^+ [5]).

The method used to investigate the mechanism and kinetics of the process was similar to that described before [6]). To study the conversion of the amorphous basic sulphate into jarosite we used the freshly precipitated amorphous basic sulphate, which had been washed by decantation and filtered on a vacuum filter, in an amount corresponding to 5g.of iron. The precipitate was repulped in a solution with specific concentrations of iron and zinc sulphates and specific pH values. The pulp was agitated in thermostated flasks. To monitor the degree of conversion samples of the pulp were taken periodically and filtered. The iron content and pH value of the solution and the potassium and iron contents of the precipitate were determined. This made it possible to determine the content of jarosite and amorphous sulphate in the precipitate. The method used for the determination of pH_{aj} was similar to that described in the literature[10]). The determined pH_{aj} values are the average values in the range of pH where the lower limit of the range is the upper limit for the appearance of pure jarosite and the upper limit is the lower limit for the appearance of the amorphous impurity in the jarosite. This pH range amounted to not more than 0.10-0.15pH unit, i.e. the accuracy of determination was ±0.08.

The results from the investigation reduce to the following: data on the phase composition of the precipitate (by the IR spectroscopic method) confirm that the mechanism of the process is similar to that described in the literature [5]). The kinetics of the hydrolytic precipitation of iron are characterised by the variations of C_{Fe} and pH with time (e.g. for C_{0Fe} = 12g/l in figs. 1 and 2). It was established that the pH_{aj} values with the presence of zinc sulphate in the solution (C_{0Zn} = 100g/l) are 0.2-0.3 pH unit lower than under the same conditions but without zinc sulphate in the solution[5]). For example, at 90°C for C_{0Zn} = 100g/l and C_{0Fe} = 2.12 and 25g/l the experimental pH_{aj} values are 1.65, 1.80 and 1.90 respectively. With allowance for published data[10]) the pH_{aj} value for solutions with C_{0Zn} = 100g/l in the presence of K^+ is determined by the equation

$$pH_{aj} = 0.21 \lg C_{Fe} = 0.067t + 2.41 \qquad (1)$$

where: C_{Fe} is in g/l and t is in °C.

The results from the precipitation of iron from zinc sulphate solutions with and without the presence of potassium under identical temperature and concentration conditions are compared in table 1. The hydrolysis rates were determined by conversion of pH to $C_{H_3O^+}$, the $C_{H_3O^+}$-τ curve was plotted from these data, and v_{hydr} was determined on the linear part of the curve having the steepest slope. Such a method for determination of v_{hydr} involves errors, since variations in the activity coefficients are not taken into account. For one and the same system, however, the activity coefficients can be taken as identical and relative assessments can be made of the effect of m within the limits of one system on the hydrolysis rates. Data on the conversion of amorphous basic sulphate into jarosite are given in table 2.

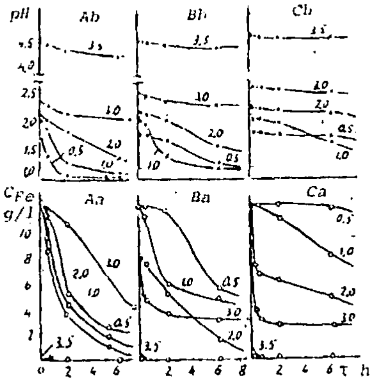

Fig.1 The variation of C_{Fe} (a) and pH (b) in solutions of the $Fe_2(SO_4)_3$-$ZnSO_4$-K_2SO_4-ZnO-H_2O system with time at temperatures °C: A - 90; B - 70; C - 50. The numbers on the curves correspond to the molar ratios m = $ZnO/Fe_2(SO_4)_3$. C_{0Zn} = 100g/l.

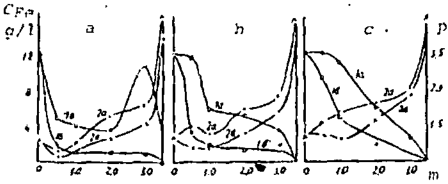

Fig.2 The values of C_{Fe} (1) and pH (2) in solutions of the $Fe_2(SO_4)_3$-$ZnSO_4$-K_2SO_4-ZnO-H_2O system as a function of m = $ZnO/Fe_2(SO_4)_3$ at temperatures °C: a) 90, b) 70, c) 50. C_{0Zn} = 100g/l. Curves 1 and 2 with the letters a and b relate to holding times of 2 and 24h respectively.

Table 1: Comparison of the results from hydrolytic precipitation of iron from solutions of various systems at C_{0Fe} = 12g/l

t °C	m	$Fe_2(SO_4)_3$-$ZnSO_4$-ZnO-H_2O					$Fe_2(SO_4)_3$-$ZnSO_4$-K_2SO_4-ZnO-H_2O				
		pH	C g/l after		Rate		pH	C g/l after		Rate	
			2h	6h	hydrol. g-ion/l min⁻¹ $v_{max}\cdot10$	precip. g-ion/l min⁻¹ $v'_{max}\cdot10$		2h	6h	hydrol. g-ion/l min⁻¹ $v_{max}\cdot10$	precip. g-ion/l min⁻¹ $v'_{max}\cdot10$
90	0.5	1.54	11.9	11.5	0.0067	0.05	1.60	5.0	2.0	0.119	0.64
	1.0	1.95	9.9	8.2	0.0180	0.29	1.93	4.2	1.7	0.160	0.71
	2.0	2.08	8.1	4.6	0.016	7.15	2.08	3.6	0.5	0.080	5.35
	3.0	2.35	10.3	3.7	0.0052	3.21	2.33	10.6	4.0	0.048	36.8
	3.5	4.10	0.1	0.1	0.0002	42.8	4.45	0.1	0.1	0.0001	42.8
70	0.5	1.60	12.0	12.0	0.0051	-	1.65	11.6	5.5	0.0075	0.25
	1.0	2.00	11.3	10.9	0.0096	0.10	1.95	5.9	4.8	0.051	0.54
	2.0	2.15	7.4	7.1	0.0052	12.5	2.10	5.2	1.5	0.0064	13.9
	3.0	2.39	3.7	3.1	0.0020	23.2	2.47	3.6	3.1	0.0028	24.6
	3.5	4.23	0.1	0.1	0.0001	42.8	4.45	0.1	0.1	0.0001	42.8
50	0.5	1.65	12.0	12.0	0.0024	-	1.68	12.0	11.8	0.0036	0.04
	1.0	2.05	11.9	11.6	0.0040	0.02	1.95	10.9	6.0	0.0036	0.21
	2.0	2.20	7.5	7.0	0.0036	14.7	2.15	6.1	4.0	0.0020	16.8
	3.0	2.45	3.5	2.6	0.0036	28.2	2.55	2.6	2.5	0.0004	29.3
	3.5	4.00	0.2	0.1	-	42.8	4.58	0.1	0.1	0.0001	42.8

Note: v_{max} g-ion H_3O^+ l⁻¹ min⁻¹ is the hydrolysis rate of iron, and v'_{max} g-ion Fe^{3+} l⁻¹ min⁻¹ is the precipitation rate of iron.

The observed pH = $f_1(\tau)$ relation for various m values (fig. 1b, table 1) is due to the contribution from concentration and temperature factors to the rate of the hydrolysis reactions proper. The concentration factor in turn is determined by the degree of deviation of the initial (after heating and addition of neutraliser) hydrolysis state of Fe(III) in the solution from the equilibrium state (this is the intensive concentration factor) and also by the amount of Fe(III) in the solution, which is capable of taking part in the hydrolysis reactions proper after the occurrence of the exchange hydrolytic reactions with the hydroxide neutraliser (this is the extensive concentration factor)[6-9]).

For a given temperature the initial degree of non-equilibrium increases with increase in m, while the amount of hydrolysed iron decreases. The hydrolysis rate therefore varies extremally with increase in m at a given temperature and has a maximum (fig. 1b, table 1). The initial degree of non-equilibrium is fairly large over the whole range

Table 2: Data on the conversion of the amorphous basic sulphate into potassium jarosite at 90°C, C_{0Fe} = 100g/l and pH_c = 1.5

Conditions	Time h	pH	C_{Fe} g/l	Content of jarosite in precipitate %	Degree of conversion %
Without $ZnSO_4$	1/12	1.85	11.7		
	1/6	1.80	11.5		
	1/2	1.46	7.05		
	1	1.04	1.14	82.5	40
	5	1.10	0.14	87.5	66
	24	1.07	0.10	96.7	86
	48	1.03	0.10	103.0	100
C_{0Zn} = 100g/l in the form of $ZnSO_4$	1	1.62	13.6	81.5	22
	5	1.15	1.79	87.0	46
	24	1.05	0.56	92.0	78
	48	1.00	0.41	96.5	90
	96	-	0.10	102.0	100

of given m values, the pH = $f_1(\tau)$ curves for the selected temperature increase regularly with increase in m (fig. 1, Ab); otherwise the curves intersect at small m values (e.g. the curves 0.5 and 1.0 in fig. 1Bb and 1Cb).

The hydrolytic precipitation of iron includes two stages: 1) the formation of hydroxo complexes of Fe(III) in the solution (by fast exchange reactions and slow hydrolysis reactions); 2) the formation of jarosite as a result of the participation of hydroxo complexes of Fe(III) in crystallisation or the formation of the amorphous sulphate as a result of polycondensation of the hydroxo complexes[6-7]). The rate of formation of jarosite in the initial period of precipitation is limited by the rate of formation of the crystallisation centres[11]), but acceleration of the process with increase in pH then appears, i.e. the chemical stages become limiting. The precipitation of iron in the form of jarosite and amorphous sulphate has fast and slow stages. The fast stage corresponds to the formation of hydroxo complexes in double decomposition reactions, and the slow stage corresponds to hydrolysis reactions. In figs. 1 and 2 the precipitation of Fe(III) as jarosite corresponds to the condition m $\leqslant$ 2.0, and precipitation as the amorphous sulphate, and the jarosite begins to be precipitated after the pH value has fallen below pH_{aj}.)

From table 1 it is seen that the rate of precipitation of iron from zinc sulphate solutions in the form of jarosite is considerably higher than the rate of precipitation of iron from the same solutions but without potassium in the form of the amorphous sulphate. This difference in the precipitation rates increases with decrease in temperature. Thus, the ratio of the maximum precipitation rates of iron in the form of jarosite (v'_{Jmax}) and in the form of the amorphous sulphate (v'_{Amax}) when m = $ZnO/Fe_2(SO_4)_3$ = 1, i.e. v_{Jmax}/v'_{Amax} is 2.45 for 90°C, 5.40 for 70°C, and 10.5 for 50°C. The presence of potassium increases the precipitation of jarosite even more when there is no zinc sulphate in the solution[6]).

The pH_{aj} value is determined by the equality $v_J = v_A$ [10]), and v_J/v_A increases with decrease in temperature. Consequently, pH_{aj} must increase, and this corresponds to equation (1).

It is characteristic that the slow stage of the precipitation of jarosite has a higher rate than the slow stage of the precipitation of the amorphous sulphate (fig. 1a) as a result of the preponderance of the extensive concentration factor under the conditions for the precipitation of jarosite. At 70 and 50°C, therefore, the flat sections of the 2.0 curves are steeper than those of the 3.0 curves.

In zinc solutions when pH < pH_{aj} the presence of potassium accelerates the hydrolysis of iron, as seen from the rate of decrease of pH, i.e. from v_{max} (table 1). In zinc solutions with pH > pH_{aj}, however, the presence of potassium does not affect the rate of hydrolysis and precipitation of iron (table 1), whereas in a solution not containing zinc sulphate the precipitation rate of iron in the presence of potassium is higher[6]) than without potassium[8]). The stabilising action of zinc sulphate on the colloidally dispersed iron in the solution[5]) evidently compensates for the strengthening second-sphere effect of potassium on the hydroxo complexes of iron[7]), i.e. compensates the accelerating effect of potassium on the precipitation of the amorphous sulphate.

At 90°C when m = 3 (fig. 1, Aa and fig. 2a) anomalously slow precipitation of iron is observed, as in zinc solutions without potassium[8]), and this is due to the formation of a hydrogel of iron at 90°C, pH = 2-4, and $C_{Fe} \geqslant 7.5$g/l.

The decrease of pH_{aj} in zinc solutions compared with pH_{aj} in purely iron solutions[6]) results from the manifestation of the stabilising action of $ZnSO_4$ on the colloidally dispersed iron in the solution, which leads to extension of the concentration region for the formation of the amorphous sulphate. Stabilisation of the colloidally dispersed iron leads to an increase in the fraction of the colloidal form of iron in the solution compared with the fraction of the ionic form. This gives rise to an increase in the rate of formation of the amorphous sulphate v_A compared with the rate of formation of jarosite v_J at a given pH value. From the equality $v_J = v_A$ at pH_{aj} it follows that the pH_{aj} value must decrease, in the presence of considerable amounts of zinc sulphate in the solution, and this is consistent with the experimental data.

The data in table 2 show that the conversion of the amorphous sulphate into jarosite occurs comparatively slowly and is realised by dissolution of the amorphous sulphate (in the initial period $C_{Fe} > C_{0Fe}$) and that the presence of zinc sulphate in the solution retards this transformation.

Conclusions

1. The mechanism of the hydrolytic precipitation of iron from zinc sulphate solutions containing a monovalent cation is similar to the previously established mechanism for purely iron solutions containing a monovalent cation. The limiting pH_{aj} values, separating the regions for the formation of jarosite and the amorphous basic sulphate in zinc solutions (C_{0Zn} = 100g/l), can be determined from equation (1). These pH_{aj} values are 0.2-0.3pH unit lower than pH_{aj} in the purely iron solutions.
2. In the presence of the monovalent cation in the region where pH < pH_{aj} the precipitation of iron in the form of jarosite occurs much more quickly (2.5-10 times, depending on the temperature), and in the region where pH > pH_{aj} it occurs at the same rate as from zinc sulphate solutions without the monovalent cation.

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Innovations in Gold Metallurgy

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A conventional plant for processing lode gold ores containing finely disseminated gold usually embraces fine grinding and agitation leaching in cyanide solution, countercurrent decantation in thickeners for liquid-solid separation and residue washing, clarification of the pregnant solution by filtering, deaeration by application of a vacuum and precipitation of the gold by reacting the solution with zinc-powder. Many known domestic gold deposits are low in grade, of limited reserves, or contain troublesome clays or other components that make treatment by conventional procedures impractical. Recent Bureau of Mines research has been focused, therefore, on developing low capital, low operating cost methods suitable for such ores. This report describes two such methods, namely, cyanide heap leaching and the carbon-in-pulp process. Granular activated carbon may be used to advantage in the heap leaching process, as well as in the carbon-in-pulp method, for recovering the dissolved gold from solution.

Basic information on heap leaching and carbon-in-pulp has been reported by the Bureau of Mines.[1-3] Gold heap leaching has some features in common with copper dump leaching and gold cyanide vat leaching. A fluidized-bed carbon column proposed for use in recovering gold from heap leaching solution was adapted from the Bureau's expanded-bed, ion-exchange column.[4, 5]

The carbon-in-pulp process as formerly used at the Carlton mill of Golden Cycle Corp., Cripple Creek, Co., was described in an article by Seeton in 1961.[6] Development of procedures for removing gold from the activated carbon by stripping with hot caustic cyanide solution in conjunction with electrolysis was reported by the Bureau of Mines in 1952.[7] More recently, a technique for accelerated removal of gold by pressure stripping the loaded carbon has been developed.[8] An improved electrowinning cell for recovering the gold from the recycling strip solution is herein described.

A new technique for pretreatment of ores containing natural organic carbon that absorbs gold from cyanide solutions and thus causes loss of gold in the tailings is used by Carlin Gold Mining Co., Carlin, Nv. Chlorine gas, a strong oxidant, is added to an aqueous slurry of ground ore. The ore pulp is subsequently cyanided in an agitation leach-countercurrent decantation process. Recent laboratory work at the Salt Lake City Center indicates that pretreatment with chlorine water is effective also for certain refractory sulfide ores. An alternative to the direct addition of chlorine to ore slurries is the preparation of hypochlorite in situ by an electrolytic oxidation process.[9]

Heap leaching uses lime-cyanide solution

The heap leaching process (see fig. 1) consists of piling coarse, treatable ore on an impervious pad and percolating it with small amounts of dilute lime-cyanide solution. Unclarified gold-bearing solution draining from the heap is passed through the Bureau's expanded-bed, multiple-compartment activated carbon column to recover nearly all of the gold and is then returned to the leaching step. Loaded carbon is stripped of its gold content in a new Bureau-developed pressure system, reactivated and returned to the column. Gold is electrowon from the stripping solution.

To be treatable by heap leaching, gold bearing rock should be competent, porous, relatively cyanicide-free and contain fine-sized, clean-gold particles. Clay content must be low enough that the ore heap remains permeable to percolating solutions during leaching.

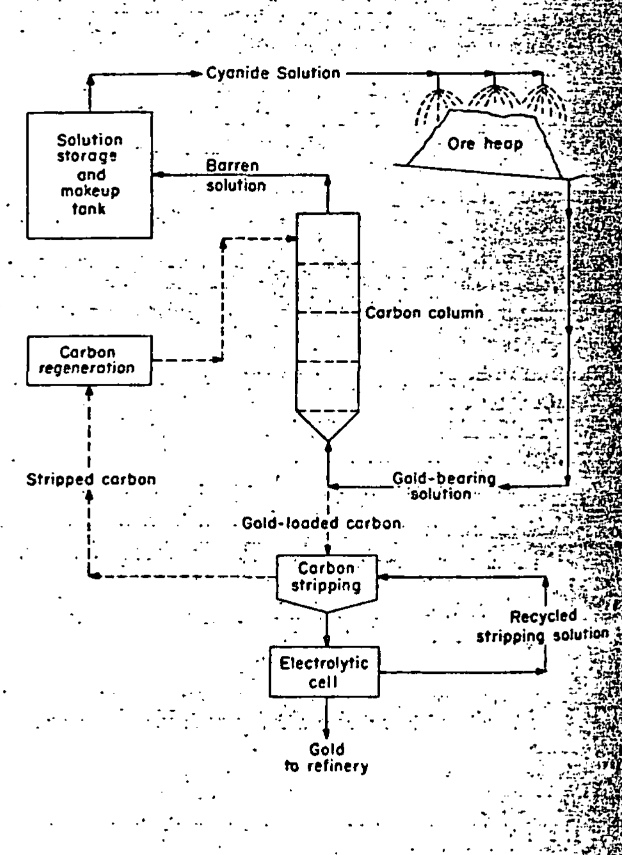

Fig. 1. Gold heap leaching flowsheet

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In commercial applications, the leaching pads have been made of asphalt or other impervious material, or earth-lined with clay as at some copper leaching operations. Ore sizes have ranged from mine run to about 1/2 in., depending upon solution penetrability of the rock. The depth of the heap has been 6 to 20 ft or more, and additional "lifts" have been added for further leaching. Solution strengths have ranged from 0.02 to 0.1 percent NaCN depending on ore requirements and the pH has been maintained at about 10.5 with lime. The rate of solution application by sprays has ranged from 5 to 25 gal per square foot per 24 hours. Adequate storage has been provided for pregnant solution between the leaching heap and the gold recovery step that follows.

Potential for pollution is low

A five- to eight-stage countercurrent column using minus 10 plus 20-mesh activated carbon for gold recovery from the leach liquor would be expected to produce a 0.0002 oz barren solution from 0.10 to 0.20 oz pregnant solution and to load the carbon to at least 400 oz per ton, while flowing at the rate of 15 to 20 gpm per square foot of column cross section. From an ecological standpoint, heap leaching has a low potential for pollution. The residues are coarse and nearly dust-free, no gases are emitted and all solutions are recycled.

Heap leaching results based on laboratory and pilot tests of amenable ores are given in table 1. Gold recoveries of 67 to 95 percent were obtained with consumption of 0.4 to 1.0 lb NaCN per ton of ore and 0.3 to 5.6 lb of lime. Leaching time varied roughly with the rock size from 4 days at 1/2 in. to 42 days at 4-in. size. However, individual ore amenability may be a more important factor in leaching response than rock size.

Sample	Ore size, in.	Gold assay, oz/ton		Gold recovery, pct	Leaching time, days	Reagent consumption, lb/ton ore	
		Head	Tail			NaCN	CaO
1	1/2	0.63	0.03	95	4	0.7	2.7
2	1	.022	.002	91	6	.5	.3
3	1	.068	.015	86	6	.4	.5
4	1-1/4	.08	.02	76	21	.7	3.5
5	2	.20	.03	84	36	1.0	4.3
6	2	.09	.03	67	23	1.0	5.6
7	4	.25	.04	83	42	1.0	4.9

Table 1. Results of percolation leaching of gold ores and stripping waste

Heap leaching is now being used successfully at several commercial operations, principally in Nevada. Although individual metallurgical data and operational information has not been released, recoveries and other factors are similar to laboratory results.

Carbon-in-pulp process suited to slimy ores

The carbon-in-pulp process (fig. 2) comprises cyanide agitation leaching of minus 35-mesh or finer ore in a thick slurry of about 45 percent solids. Protective alkalinity is

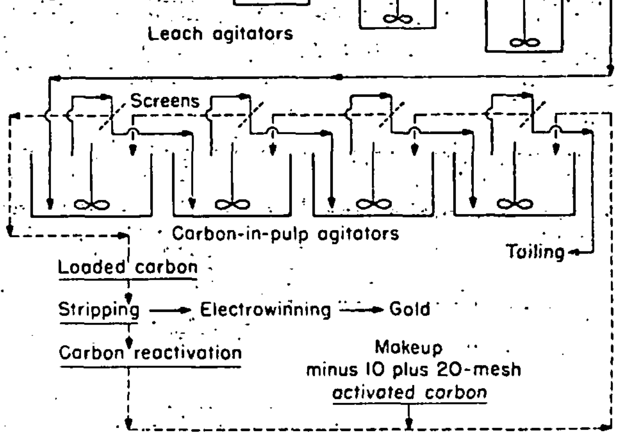

Fig. 2. Flowsheet for carbon-in-pulp process

maintained by adding lime, and the pulp is vigorously aerated during leaching to speed gold dissolution. Gold is removed from the pulp without a prior liquid-solid separation by contacting with activated carbon in a multiple stage-countercurrent system of agitators and screens. Granular carbon, minus 10, plus 20-mesh size is the preferred absorbent. The process is particularly suitable for treating very slimy ores. Silver is also recovered from amenable ores, although recovery is lower than for gold.

As an example of the application of the carbon-in-pulp process, Bureau of Mines and Homestake Mining Co. engineers worked cooperatively on a pilot unit treating 200 lb per hour of gold ore slimes from the Lead, S.D., mill. At the Lead pilot plant the slime ore pulp was leached at about 45 percent solids with 0.04 percent cyanide and lime for about 20 hours in a Pachuca-type agitator. Then the leached pulp was processed in a four-stage countercurrent carbon-in-pulp unit containing 8 grams carbon per liter of pulp and providing 1 hour pulp-carbon contact per stage. Carbon was advanced at a rate of 1/2 gram per minute. Barren solutions of about 0.0002 oz per ton of solution were made, and carbon loadings of at least 400 oz per ton of carbon were readily attained. Carbon was stripped, the gold was electrowon from stripping solution and the carbon was reactivated and returned to use.

Homestake subsequently designed, built and placed in operation in April 1973 a 2,350 tpd carbon-in-pulp unit to replace an existing slime plant. General features of the new plant have been described by Howell, Homestake staff metallurgist.[10]

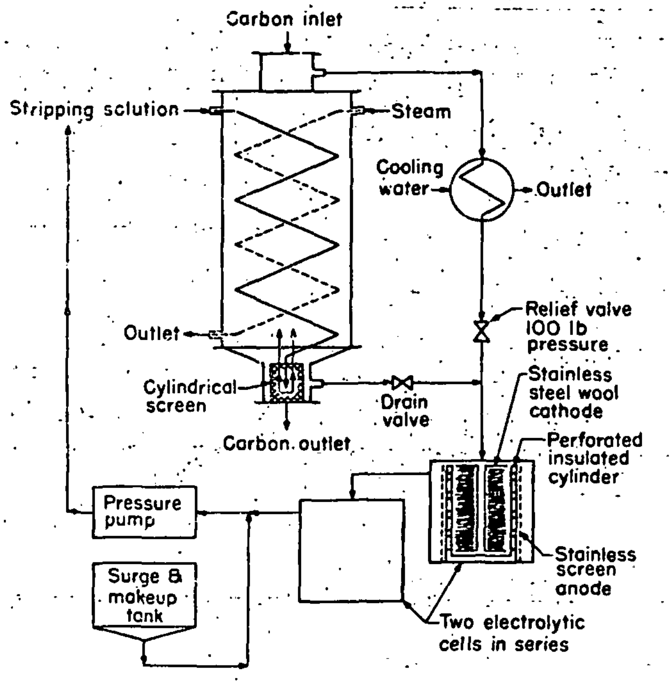

Fig. 3. Schematic of pressure system to strip gold from activated carbon

Pressure stripping is preferred over burning

Activated carbon may be loaded with gold in either the heap leaching or carbon-in-pulp processes and burned to recover the gold, but it is preferably stripped, reactivated and returned to the loading circuit for reasons of process economy. The stripping of gold (and silver) from loaded carbon with hot (93°C) 1 percent caustic-0.1 percent cyanide solution has been described by Zadra[7] who reported that 6 hours of processing under laboratory conditions would reduce gold loadings of 200 to 400 oz per ton down to about 10 oz. However, former practice at the Carlton mill, current practice at Homestake and pilot tests at our laboratory indicated that 24 to 48 hours was needed to satisfactorily strip carbon under plant conditions. Reagent requirements for stripping with hot solution at atmospheric pressure are about 40 lb of NaOH and 5 lb of NaCN per ton of carbon.

Development work is being done at Salt Lake City on a novel pressure stripping method (fig. 3) that greatly reduces process time and reagent consumption. The unit provides for stripping with 0.4 percent NaOH solution at about 150°C and 52 psi. Cyanide is not ordinarily required. The elution flow rate is about 100 milliliter per minute per 1,000 milliliter of wet carbon (about 470 grams of dry carbon). Minus 10, plus 20-mesh carbon loaded to 500 oz of gold can be stripped to less than 5 oz in 2 to 6 hours with about 12 bed volumes of solution. Consumption of NaOH is 13 to 20 lb per ton of carbon.

Eluate solutions assay as much as 100 oz gold per ton at the start of stripping. These solutions are cooled in a condenser to about 90°C before discharge from the stripping unit. Gold is then recovered in a three-stage electrolytic unit using stainless steel mesh anodes and stainless-steel wool cathodes. Solution from electrolysis preferably assaying less than 0.03 oz gold is recycled to stripping. The gold-bearing steel wool is melted with a standard refining flux.

Stripped carbon may be reused for three or four loading cycles without great loss of efficiency before reactivation. However, because carbon returned to columns or agitators loses its identity with carbon already in circuit, reactivation of all stripped carbon before use is advisable. The reactivation step consists of heating the initially damp carbon in a continuously operated, indirectly heated kiln, nearly closed to the atmosphere, for at least 20 minutes at 600° to 900°C depending on the condition of the carbon. Alternatively, the carbon may be heated in a batch retort.

Improved electrowinning cell built

The cylindrical electrowinning cell, used to date in pilot and commercial applications for recovering gold from carbon stripping solutions, is basically a cylindrical shell containing a central stainless steel reel wound with stainless steel wool as the cathode, a concentric perforated plastic cylinder for insulation and a cylindrical stainless steel mesh anode. Careful attention in assembly is required to obtain

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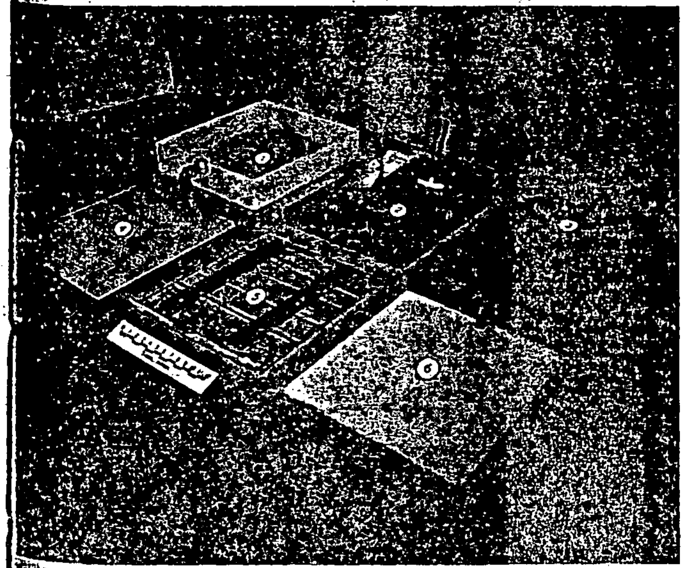
iform electrical contact and gold plating. Despite such re, some areas of poor plating caused by inadequate elec- al contact or solution short circuiting is found from time time in operating cells. Therefore, an improved cell was signed, built and tested (see fig. 4).

Initial operations of the new cell indicate that replace- t of the steel wool cathode is much easier and faster with the cylindrical unit. The weighted assembly in- s uniform electrical contact throughout the cathode el wool and results in a heavier gold deposit and better d removal from solution than when using the cylindrical . Barren solutions of less than 0.03 oz were obtained us- three of the flat cells in series, starting with 60-oz strip- g solution. Operating voltage is 2.5 and the current den- y, based on the rectangular dimensions of the cathode ket, is 3.5 amp per square foot.

ap leaching cheapest of three processes

A preliminary estimate of the capital and operating costs he heap leaching, carbon-in-pulp and countercurrent de- tation cyanidation processes was made at the Salt Lake y Metallurgy Research Center. Relative cost factors of three processes are below:

	Cost factor	
Process	Capital	Operation
ountercurrent decantation	1.00	1.00
arbon-in-pulp	.68	.77
ap leaching	.23	.30 to 44



g. 4. Improved electrowinning cell. 1) Tank with outlet pipe. 2) ainless steel cathode tray and solution feed pipe. 3) Steel wool thode. 4) Perforated plastic divider. 5) Stainless steel mesh anode eighted with steel bars), and 6) lid.

Amenable ore responding to the heap leaching process when crushed to 2 to 3-in. size is assumed in the above. Based on mid-1973 costs, a countercurrent decantation plant to treat 2,500 tpd of amenable ore is assumed to have a capital cost equivalent to $3,100 per daily ton capacity and direct operating costs not including return on investment of $2.25 per ton.

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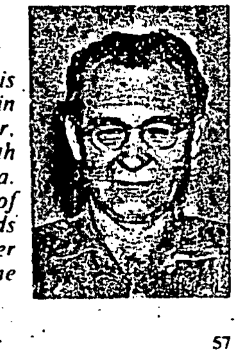
George M. Potter, for six years prior to joining the U.S. Bureau of Mines in 1941, was connected with gold, tin, copper, tungsten and antimony operations in Arizona, California and South America. Following 13 years with the Bureau in extractive metallurgy research, Potter was metallurgical advisor for the U.S. State Department and the Mexican Mines Bureau in the period from 1954 to 1962. He is currently research supervisor at the Salt Lake City Metallurgy Research Center, where he is primarily concerned with copper, gold, silver, flotation and tailings stabilization.



Harris B. Salisbury has spent most of his professional career, which started in 1935, in gold and silver technology as an assayer, operator and superintendent at mines in South Dakota, Colorado, California and Nevada. Having been employed by the U.S. Bureau of Mines since 1958, Salisbury presently holds the title of project leader for gold and silver laboratory and pilot research activities at the Salt Lake City Metallurgy Research Center.

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Investigation of the kinetics of the dissolution of silver in aqueous solutions of thiourea

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In view of the prospects for the utilisation of acidic solutions of thiourea as a solvent for gold ore it was necessary to evaluate the behaviour of silver in this process. The kinetics of the dissolution of silver was studied by the rotating disc method, the details of which as applied to heterogeneous processes have been set out in a series of articles[1]).

In acidified thiourea solutions silver becomes a fairly base metal (the standard potential of the process $Ag + 3T - e = AgT_3^+$ is 0.023 V), and this demonstrates the thermodynamic possibility of its passage into solution even in the presence of relatively weak oxidising agents.

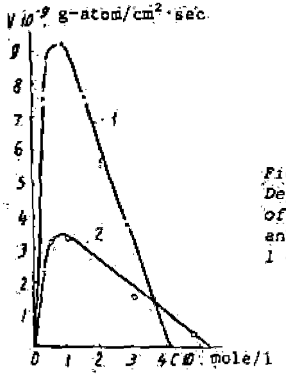

Fig.1
Dependence of the dissolution of silver on the concentration and nature of oxidising agents: 1 - $KBrO_3$; 2 - $K_2Cr_2O_7$.

The effect of certain oxidising agents was studied under the following conditions: Urea concentration 0.195 mole/l; sulphuric acid 0.051 mole/l; temperature 25°C; disc rotation rate 0.67 rps (fig.1). The observed dissolution rate of silver depends on the individual characteristics of the oxidising agent; in the presence of $KBrO_3$ silver dissolves more quickly than with $K_2Cr_2O_7$, and this is explained by the formation of a compact film on the surface of the disc when the latter is used. The results from microspectral analysis on a Cameca instrument showed the presence of dark and light sections in this film, where silver and sulphur were found; chromium was was detected at individual points in the sections. The lowest rate was observed when air was blown through the solution ($0.9 \cdot 10^{-9}$ g-atom/cm^2·sec), which is explained by the low concentration of oxygen in the solution ($2.5 \cdot 10^{-4}$ mole/l), although the experimental rate constant is equal to about 45% of the theoretical.

Since it is known[2]) that in an acidic medium thiourea is capable of being oxidised to formamidine disulphide $(SCNH_2NH)_2$, it was suggested that the latter behaves as an "internal" oxidising agent and electron carrier. To check this suggestion a thermodynamic calculation was made of the possibility of the occurrence of the corresponding reaction, and a series of experiments were set up on the dissolution of silver in mixtures of thiourea and its disulphide. (The formamidine disulphide was prepared by the method of Preisler[3]).

$$(SCNH_2NH)_2 + 2H^+ + 2e = 2SC(NH_2)_2;\ E_0 = -0.42B;\ \Delta G^0 = -19.37\,\text{kcal}$$

$$2Ag + 6SC(NH_2)_2 - 2e = 2Ag\ SC(NH_2)_3^+;\ E_0 = +0.023B;\ \Delta G^0 = +1.06\,\text{kcal}$$

$$2Ag + (SCNH_2NH)_2 + 4SC(NH_2)_2 + 2H^+ = 2Ag\ SC(NH_2)_3^+;$$

$$\Delta G^0 = -18.31\,\text{kcal}$$

The experiments confirmed the thermodynamic calculation; the maximum dissolution rate was observed with a molar ratio of 4:1 between urea and its disulphide. With other ratios there was an insufficiency of one of the reagents, and the dissolution rate decreased (fig.2).

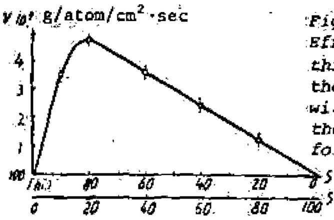

Fig.2
Effect of the concentration of thiourea and its disulphide on the dissolution rate of silver with overall concentration of the reagents 0.13 mole/l at 25°C for n = 0.67 rps.

Unlike the majority of oxidising agents. ferric sulphate hardly oxidises thiourea at all although, to judge from the redox potential of the $Fe^{3+} + e = Fe^{2+}$ system (-0.7698 V), this process is thermodynamically possible. The reason for this clearly lies in the formation of complexes of the FeT_2^{3+} and $FeTSO_4^+$ type[4]). For this reason the dissolution rate of silver in the experiments. the results from which are given in fig.1, decreased sharply with an excess of the oxidising agent. This was confirmed by analysis by (polarography on an instrument designed by the IFKhIMS Institute) of solutions containing 0.065 and 0.158 mole/l of thiourea (two series of experiments [1&2]) and variable concentrations of ferric ions (table). A second advantage of ferric sulphate is the fact that it is fairly cheap, and it was therefore chosen as oxidising agent for the subsequent experiments.

Amount of Fe^{3+} added g-ion/l	Concentration of thiourea after addition of Fe^{3+} mole/l	
	1	2
0.0	0.065	0.158
0.025	0.065	0.158
0.050	0.065	0.158
0.100	0.065	0.138
0.200	0.065	0.126

The dependence of the dissolution rate of silver on the rotation rate of the disc (fig.3) up to 270 rpm shows unambig-

Fig.3
Dependence of the dissolution rate of silver on the square root of the rotation rate of the disc with a ferric ion concentration of 0.02 g-ion/l at 25°C. Thiourea concentration: 1 – 0.16; 2 – 0.30 mole/l.

ously that the reaction takes place according to diffusion laws: $v = f(n^{1/2})$. The dependence of the dissolution rate of silver on the thiourea concentration with a constant concentration of ferric ions (0.015 g-ion/l, 25°C, n = 0.67 rps) is interesting. Without thiourea the silver dissolves at a rate of $6.8 \cdot 10^{-9}$ g-atom/cm^2·sec, and under the same conditions but with a ferric ion concentration of 0.025 g-ion/l it dissolves at a rate of $7.2 \cdot 10^{-9}$ (fig.4).

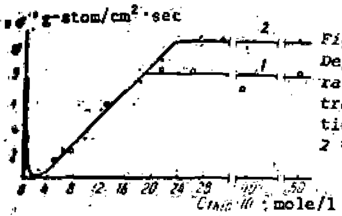

Fig.4
Dependence of the dissolution rate of silver on the concentration of thiourea. Concentration of ferric iron: 1 – 0.015; 2 – 0.025 g-ion/l.

With increase in the thiourea concentration to 0.02–0.04 mole/l the dissolution rate decreases sharply as a result of the formation on the surface of the disc of an insoluble compact greyish film, which is visible with the naked eye and becomes dark in air. Silver, sulphur, and iron were found in this film by microspectral analysis. With increase in the thiourea concentration above 0.04 mole/l a linear increase in the dissolution rate is observed up to a certain constant value V, which depends on the concentration of ferric ions. Curves with such character are always observed during heterogeneous reactions with a complex-forming agent and an oxidising agent. The constant maximum dissolution rate is determined by an insufficiency of one of the components (in the present case an insufficiency of the oxidising agent, i.e., ferric ions). The higher their concentration, the higher the maximum rate. On the sloping section of the curve the rate of the process is controlled by the diffusion of thiourea, and on the horizontal section it is controlled by diffusion of iron ions.

The value of the theroretical rate constant, calculated at 25°C according to the published data5), is equal to:

$$k = \frac{3.40 \cdot 10^{-3} \cdot D^{2/3}}{m} = 6.1 \cdot 10^{-7} \quad (l/cm^2 \cdot sec^{1/2} \cdot rev^{1/2})$$

where D is the diffusion coefficient of thiourea (the diffusion coefficient of urea was used for the published calculations6), equal to $1.25 \cdot 10^{-5}$ cm^2/sec; m is a stoichiometric coefficient of the reaction, equal to 3. The experimental value of the constant, calculated from the curve, is exactly an order of magnitude lower ($6.1 \cdot 10^{-8}$). This effect has been observed more than once in our researches7) and is explained by the formation of compact films on the reaction surface, creating additional diffusion resistance.

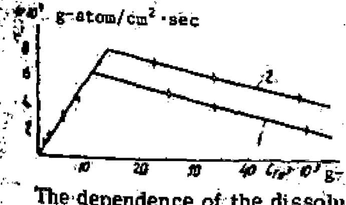

Fig.5
Dependence of the dissolution rate of silver on the concentration of ferric iron at 25°C with n] 6.7 rps. The concentration of thiourea was 0.130 (1) and 0.195 (2) mole/l.

The dependence of the dissolution rate of silver on the concentration of ferric ions with a constant concentration of thiourea (two series of experiments with 0.130 and 0.195 mole/l) is shown in fig.5. In this case too the character of the curves is normal; there are two regions with control by the iron and by the thiourea. In the region controlled by the diffusion of ferric ions the rate constant is $7.1 \cdot 10^{-7}$ l/cm^2·sec$^{1/2}$·rev$^{1/2}$. However, these experiments differ somewhat from the previous experiments. In the post limit region with respect to thiourea there is no horizontal section, since the excess ferric ions (by forming a complex with thiourea) reduce the concentration of its molecules in its solution, and this is accompanied by a decrease in the dissolution rate of silver.

The effect of temperature on the dissolution rate of silver was investigated under the following conditions: Ferric ion concentration 0.02 g-ion/l; thiourea 0.065, 0.16, and 0.30 mole/l; sulphuric acid 0.051 mole/l; temperature from 15 to 35°C; disc rotation rate 0.67 rps. The results from the experiments were treated by the method of least squares. The deviations were small, and only the experimental activation energies are therefore given instead of the Arrhenius curve. They are equal to 9.61, 7.29 and 5.56 kcal/mole for thiourea concentrations of 0.065, 0.16 and 0.30 mole/l respectively.

The zinc and arsenic present in the solution reduce the dissolution rate of silver by approximately a half only at high concentrations in the order of 0.1 g-ion/l, whereas the harmful effect of copper becomes appreciable at concentrations approximately an order of magnitude lower (oxidation of thiourea and the formation of fairly stable copper-thiourea complexes).

The reaction investigated of dissolution of silver in acidified solutions of thiourea in the presence of ferric ions is interesting in its complexity and inconsistency. On the on hand, the experimental dissolution rate is an order of magnitude lower than the theoretical value, and the experimental activation energy reaches almost 10 kcal/mole, which is similar to indications of a kinetic regime. On the other hand, the dissolution rate depends on the square root of the disc rotation rate, i.e., the main indication of a diffusion regime. It has been observed many times7) that the most reliable criterion of the mechanism is the dependence of the rate of the process on the intensity of agitation, while the other criteria can be distorted by the formation of compact films on the reaction surface, which create additional diffusion but not chemical resistance. The investigated reaction is an exceptionally clear confirmation of this fact. The experimental activation energy decreases sharply with increase in the thiourea concentration with a constant concentration of ferric ions (rapid dissolution of the films) and reaches values (5.56 kcal/mole) characteristic of reactions complicated by the formation of comparatively permeable films. The complicating action of the films is also demonstrated by the ratio of the concentrations of the complexing agent and the oxidising agent at the point of transition from the prelimit region to the postlimit region. During the cyaniding of the gold, silver, and copper this ratio is very close to the stoichiometric coefficient of the reaction, and during the cyaniding of palladium and its alloys with silver and the tellurides of gold and silver it is considerably greater than the stoichiometric coefficient and reaches 3008,9). For the reaction which we investigated this ratio is 10-15 instead of 3. In addition, during calculation of the values of the experimental rate constants account was taken of the formal concentration of the reagents, whereas the complexing agent and the oxidising agent react with each other and this is accompanied by a decrease in their active ion concentrations. Finally, trivalent iron in acidic sulphate solutions is present mainly in the form of $Fe(OH)^{++}$ and $FeSO_4^{+}$ and not Fe^{3+} 10). The compact films, the formation of thiourea complexes of trivalent iron, and the hydrolysis of ferric ions are the factors which reduce the rate of the investigated reaction. Nevertheless, it takes place according to diffusion laws, although it is very much complicated by the above-mentioned factors. However, with increase in temperature the discrepancies between the numerical values of the experimental and calculated theoretical rate constants will will become smaller and smaller, since the activation energy of the reaction considerably exceeds the activation energy of diffusion. The physical meaning of this relation between the activation energies signifies that the surface films become thinner and the complexing of the iron ions and thiourea becomes weaker with increase in temperature.

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UDC 546.289+541.12.012

Investigation of the reaction of germanium disulphide with ferric chloride solution

V N Kryukova and G L Lobanova (Institute of Petrochemical and Coal-Chemical Synthesis, Irkutsk State University).

Summary

The kinetics of the reaction of germanium disulphide with an acidic solution of ferric chloride were investigated in the region of temperatures between 60 and 130°C. It was established that at temperatures above 120°C the reaction takes place in the kinetic region. At lower temperatures it takes place in the diffusion region.

The apparent activation energy of the process amounts to 11.7 and 129.6 kJ/mole for low and high tenperatures respectively.

It was shown that in the region of 60-120°C the process of the dissolution of germanium disulphide is described by the equation, previously derived for processes involving retardation:

$$(1/\tau)\ \ln[1/(1-x)] - \beta(x/\tau) = \mu$$

where x is the proportion of reacted substance, τ is the reaction time, and β and μ are coefficients.

UDC 661.417:542.

Diffusion coefficients of beryllium ions in an equimolar mixture of lithium and potassium chlorides

V P Butorov, E A Novikov, I F Nichkov, S P Raspopin, and A A Khamatshin

Summary

The diffusion coefficients of beryllium ions in an equimolar mixture of lithium and potassium chlorides were measured in connection with the production of beryllium by electrolysis of molten alkali-metal halides with additions of beryllium salts. The following empirical relationship was obtained:

$$\log D = -3.11 - 1110/T \pm 0.04$$

The experimental limiting diffusion currents for the discharge of beryllium ions and the values calculated by means of the measured diffusion coefficients agree satisfactorily. The mobility of the beryllium ions and the activation energy of diffusion depend on the ionic composition of the electrolyte.

UDC 661.1

Investigation of the ion-exchange separation of scandium from some accompanying elements

Yu P Kudryavskii, E I Kazantsev, E A Kazantsev, A S Baryshnikov and V N Onosov (Urals Polytechnical Institute. Department of the Metallurgy of Rare Metals)

Summary

The behaviour of scandium and its accompanying elements on a macroporous phosphate cation-exchange resin KFP-8 was investigated. It was shown that the sorbability of scandium exceeds the corresponding values for divalent and trivalent metals to a considerable degree.

Significant differences were found in the behaviour of scandium and the impurity elements during the desorption processes. On the basis of the obtained differences in the ion-exchange behaviour of the elements the quantitative separation of scandium from 5-100-fold amounts of Y, La, Al, Fe (III), Ca, and Mn was realised.

UDC 536.3:669.332

Three-dimensional zone model and calculation of the heat exchange in a copper reverberatory furnace

Yu A Zhuravlev (Krasnoyarsk Institute of Nonferrous Metals. Department of Metallurgical Furnaces).

At the present time the most complete physical method for calculation heat exchange in the working area of combustion furnaces is the zone method. Its use in conjunction with the Monte Carlo method for determination of the generalised

Investigation of the leaching of bauxites from the Ayat' deposit

L P Ni, B E Medvedkov, V I Grigor'ev and R A Abdulvaliev (Institute of Metallurgy and Concentration, Academy of Sciences of the Kazakh SSR)

The Ayat' deposit is confined to the western edge of the Turgay lowlands in northern Kazakhstan. All the bauxites of this region are represented by gibbsite ores[1,2]). It is well known that the bauxites of the deposits of northern Kazakhstan are generally similar in composition. Their differences lie in the ratio of the minerals and lithologic forms and the size of secondary changes[1,3]), having a large effect on the quality of the raw materials. This in turn is reflected in the technology for the production of alumina from the bauxites of the various deposits[4]).

A characteristic feature of the Ayat' bauxites is the inconstancy of chemical composition even within a single deposit: these fluctuations reflect the quantitative ratio of the principal rock-forming minerals. A common feature of the given deposit is the increased content of iron compounds and, in particular, siderite (5-6%) and the preponderance of stony forms.

The present work was devoted to determination of the effect of the principal factors on the technological characteristics and determination of the optimum conditions for the leaching of Ayat' bauxites.

The investigation was carried out with various samples of bauxites (table 1) having silica ratios between 3.6 and 7.3 (composition of recycled solution g/l: 248.0 Na_2O_c, 120.0 Al_2O_3, α_c = 3.41; calculated caustic ratio 1.7; temperature 105°C, duration 2 h). The effect of the composition of the bauxite and its particle size, the concentration of the recycled solution, the time, and the reaction temperature on the leaching process was investigated. The results from the leaching of Ayat' bauxites under various conditions are given below.

Table 1: Results from leaching of various samples of Ayat' bauxites

Experimental Data		Sample No.		
		1	2	3
Composition of bauxite %	Na_2O	0.5	0.5	0.5
	Al_2O_3	43.1	44.8	45.6
	SiO_2	5.9	12.4	7.0
	Fe_2O_3	23.2	16.4	19.7
	TiO_2	1.7	2.0	1.5
	calc. loss	25.0	23.0	23.8
Composition of solution obtained g/l	Na_2O_c	231.0	225.0	236.0
	Na_2O_y	7.0	7.0	6.0
	Al_2O_3	213.5	209.0	220.0
	SiO_2	2.28	2.88	2.01
	α_c	1.78	1.77	1.76
Content in the residue from leaching %	Na_2O	8.9	8.3	9.0
	Al_2O_3	17.3	23.9	15.7
	SiO_2	12.8	24.0	15.4
	Fe_2O_3	48.3	31.2	48.2
	calc. loss	9.0	8.6	7.4
Extraction of Al_2O_3	theor.	86.3	72.3	84.8
	pract.	80.6	72.0	85.9

As a result of the different ratios of the main rock-forming minerals in the bauxite, the results from leaching of the various samples were different (table 1); the extraction of Al_2O_3 was lower than, higher than, or at the level of the theoretically possible value. Three samples of the Ayat's bauxite containing rock-forming minerals (gibbsite, kaolinite, goethite, haematite, magnetite and siderite) and the residues from their leaching were analysed by chemical, crystal-optical, and X-ray diffraction methods.

In sample No.1, crypto-crystalline formations with a yellow-brown colour and variable refractive index (1.5 - 1.62) were found. It is known[3,5]) that in bauxites and iron ores aluminium forms solid solutions with goethite, haematite and maghaemite. The presence of aluminium-iron compounds in the bauxite leads to incomplete extraction of Al_2O_3 during decomposition of such a bauxite.

A similar effect was observed during the leaching of sample No.1, the deficiency in the extraction of which amounted to about 6%. The alumina combined in it passed into the slime without change. The amount of Al_2O_3 in relation to SiO_2 in the leaching residue therefore considerably exceeded the value required for the formation of only hydrated sodium aluminosilicate (HSAS). During the leaching of sample No.2, which contained Al_2O_3 only in the form of gibbsite and kaolinite, the theoretical yield of Al_2O_3 was obtained. The amount of dissolved SiO_2 in this case was the highest, and this was due to its highest content in this sample. The leaching of sample No.3 gave an Al_2O_3 extraction somewhat higher than the theoretical on account of the presence of insoluble forms of SiO_2 in the bauxite.

Leaching time. According to data from chemical analysis of the liquid phases and physicochemical investigation of the solid phases, the leaching time has a considerable effect on the results from the process (fig.1); a maximum is observed on the kinetic curves for the extraction of Al_2O_3 at 105°C.

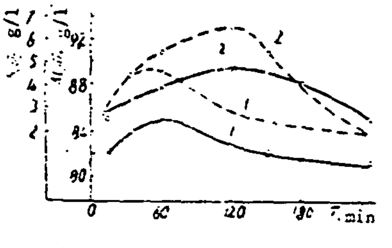

Fig.1 Variation of the concentration of Al_2O_3 (solid lines) and SiO_2 (dotted lines) as functions of the bauxite leaching times. Samples. 1 - No.1; 2 - No.3.

It is known that an increase in the temperature of the process to 180-220°C leads to the disappearance of the extremum. We find an explanation for this in the following. In the first case, during atmospheric leaching there are two opposing processes (dissolution of Al_2O_3 and SiO_2 and crystallisation of HSAS), which are separated in time on account of a difference in rates. The left part of the kinetic curve (fig.1) characterises the dissolution of gibbsite and kaolinite, while the right part characterises the crystallisation of HSAS. Of course, there is no sharp boundary between the end of the dissolution process and the beginning of the crystallisation process. However, when the first process predominates, the kinetic curve passes abruptly into a maximum, and when the crystallisation process predominates the curve decreases more gently.

During autoclave leaching the two processes (dissolution and crystallisation) take place simultaneously, since their rates are commensurable and the kinetic curve in this case reflects the overall effect of the two reactions. During decomposition of a more siliceous bauxite (fig.1) the maximum passage of Al_2O_3 and SiO_2 into solution is reached later (120 min) than in bauxite with a smaller silicon content (60 min). Of course, the maximum concentration of dissolved

SiO_2 is higher in the leaching of the more siliceous bauxite.

Particle size of the bauxite. Table 2 gives the results from the leaching of bauxites with the various particle sizes under the conditions of the nonautoclave variant of the Bayer scheme (composition of recycled solution: Na_2O_c 254 g/l, α_c = 3.38; composition of +0.149 mm fraction %: Al_2O_3, 5.6 SiO_2, 21.4 Fe_2O_3; Composition of -0.149 mm fraction %: 43.3 Al_2O_3, 6.2 SiO_2; 21.0 Fe_2O_3; temperature 105°C, time 2h).

From these data it follows that the extraction of a Al_2O_3 decreases with increase in the amount of the +0.149 mm fraction in the bauxite. The extraction of Al_2O_3 decreases particularly sharply from bauxite containing more than 10% of this fraction.

Table 2: Dependence of the extraction of Al_2O_3 on the content of the +0.149mm fraction in the bauxite

Amount of residue on + 0.149 mm screen %	Composition of obtained solution %					Content in residue %			Extraction %
	Na_2O_c	Na_2O_{carb}	Al_2O_3	SiO_2	α_c	Al_2O_3	SiO_2	Fe_2O_3	
5	253.0	7.0	214.0	3.8	1.95	17.7	11.4	47.0	81.8
10	249.0	7.0	208.0	3.4	1.97	18.3	12.0	47.9	81.4
20	252.0	7.0	199.5	2.1	2.08	24.3	10.6	41.7	71.2

The effect of the concentration of the recycled solution on the extraction of Al_2O_3 at 105°C is shown in fig.2. Increase in the concentration from 156 to 243 g/l in respect of caustic sodium oxide leads to an increase of approximately 10% in the extraction of Al_2O_3.

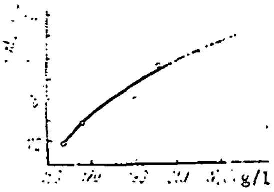

Fig.2 Effect of the concentration of the alkali-aluminate solution (with α_c = 3.4) on the extraction of Al_2O_3.

Leaching temperature. The experiments were carried out at 70, 90 and 105°C. Owing to the fact that the material composition of the residues from leaching at various temperatures may be different, the subsequent operations of desiliconising the aluminate solution and thickening the red mud will be carried out under noncomparable conditions. The experiments were therefore carried out in a system with desiliconising of the aluminate solution and thickening of the red mud according to the standard procedure[4]). The results are given in table 3 (bauxite composition %: 43.1 Al_2O_3; 5.9 SiO_2; 23.2 Fe_2O_3; 25.0 calc. loss; composition of recycled solution: Na_2O_c 247 g/l; α_c = 3.38; calculated ratio 1.7; theoretical extraction 86.3%). Decrease in temperature reduces the extraction of Al_2O_3, while the SiO_2 content of the solution increases.

Table 3: Results from decomposition of bauxite at various temperatures

Operation	°C	Composition of solution g/l				Extraction of Al_2O_3 %
		Na_2O_c	Al_2O_3	SiO_2	α_c	
Leaching	70	241.4	220.9	4.07	1.8	77.8
Desiliconising		144.8	114.5	1.19	2.08	67.0
Thickening		150.0	117.5	1.10	2.10	65.8
Leaching		248.0	199.8	3.82	2.04	69.0
Desiliconising	90	154.8	121.0	1.06	2.10	66.2
Thickening		155.0	121.4	0.86	2.10	66.0
Leaching		240.0	225.0	2.92	1.76	80.6
Desiliconising	105	142.0	132.0	0.70	1.77	77.8
Thickening		150.0	139.0	0.56	1.77	77.3

On the basis of the results from X-ray and crystal-optical analyses of the solid phases it was established that a decrease in the leaching temperature leads to a qualitative change in the composition of the products.

As a result of decomposition of the bauxite at 105°C washed red mud with the following composition was obtained %: 6.2 Na_2O, 18.1 Al_2O_3, 13.4 SiO_2, 47.8 Fe_2O_3, calcination loss 9.3.

From the results it follows that after thickening and washing the composition of the mud changed somewhat compared with the mud after leaching (table 1). The phase composition also changed. Apart from lines for HSAS, in which most of the aluminium and silicon was combined, the X-ray patterns also contained reflections for gibbsite. The appearance of gibbsite in the thickened bauxite mud is a special problem, which is not being considered in the present work. Part of the superfluous (over the HSAS) aluminium oxide is present in aluminium-iron compounds. Under these conditions the kaolinite of the bauxite almost completely decomposed; it could not be detected in the washed thickened red mud by crystal-optical and X-ray methods.

With decrease in the leaching temperature the kaolinite of the bauxite passes into the red mud without change. At 90°C the kaolinite only partly decomposes. During subsequent operations part of the SiO_2 combines in the HSAS. The latter is formed particularly intensively during the thickening of the red mud. At 70°C the kaolinite is hardly decomposed at all. There is quite a small amount of HSAS in the thickened red mud, which contains %: 3.4 Na_2O; 27.1 Al_2O_3; 11.7 SiO_2; 39.4 Fe_2O_3; 11.7 calcination loss. On the X-ray pattern of this mud the lines for kaolinite are appreciably stronger than on the X-ray pattern of the red mud obtained with a leaching temperature of 90°C.

It should be noted that when the leaching temperature is reduced a certain part of the gibbsite which has not passed into solution remains in the red mud. Leaching at even lower temperatures (70°C) leads to even greater losses of gibbsite in the red mud.

Conclusions

1. In the Ayat' bauxites the processes of dissolution of gibbsite and kaolinite and crystallisation of HSAS take place separately.
2. Increase in the alkalinity of the recycled alkali-aluminate solution from 160 to 250 g/l in respect of Na_2O_c leads to an appreciable increase in the extraction of Al_2O_3.
3. The presence of aluminium-iron compounds leads to incomplete extraction of Al_2O_3 (to 6%)

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United States Patent [19]
Tweeton

[11] **4,253,063**
[45] **Feb. 24, 1981**

[54] IMPEDANCE MEASURING METHOD OF AND APPARATUS FOR DETECTING ESCAPING LEACH SOLUTION

[75] Inventor: **Daryl R. Tweeton**, Apple Valley, Minn.

[73] Assignee: **The United States of America as represented by the Secretary of the Interior**, Washington, D.C.

[21] Appl. No.: **950,762**

[22] Filed: **Oct. 12, 1978**

[51] **Int. Cl.**^{3} **G01V 3/20**; G01V 3/02

[52] **U.S. Cl.** **324/323**; 324/324; 324/372

[58] **Field of Search** .... 324/1, 9, 10, 324, 325, 324/366, 368, 372; 166/65 R, 66; 73/155

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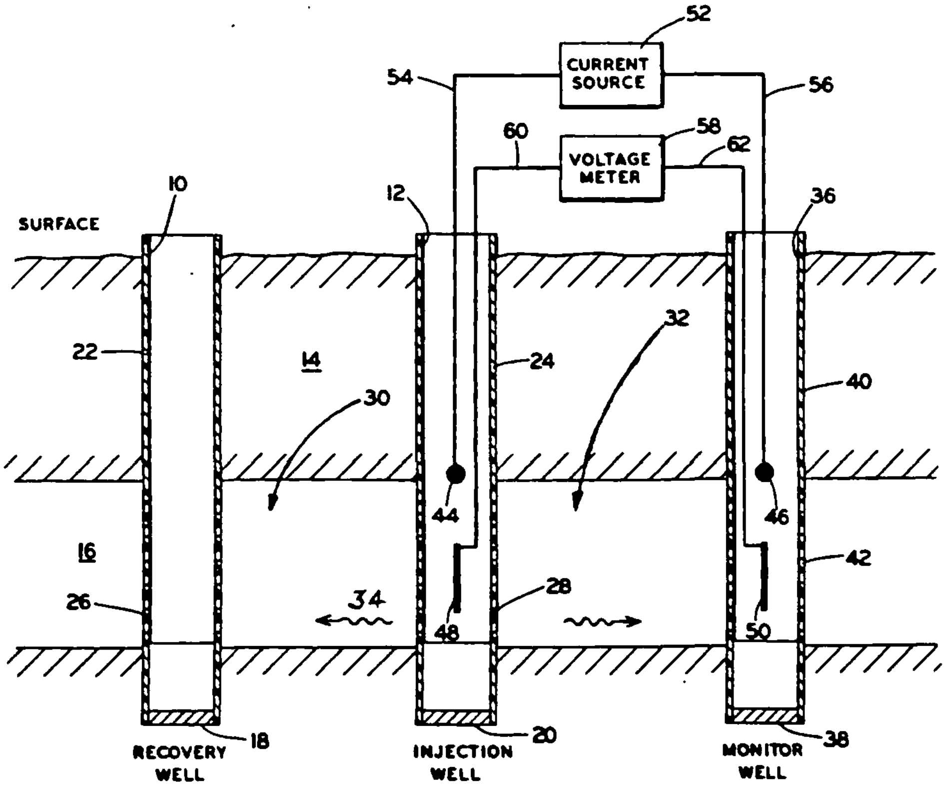
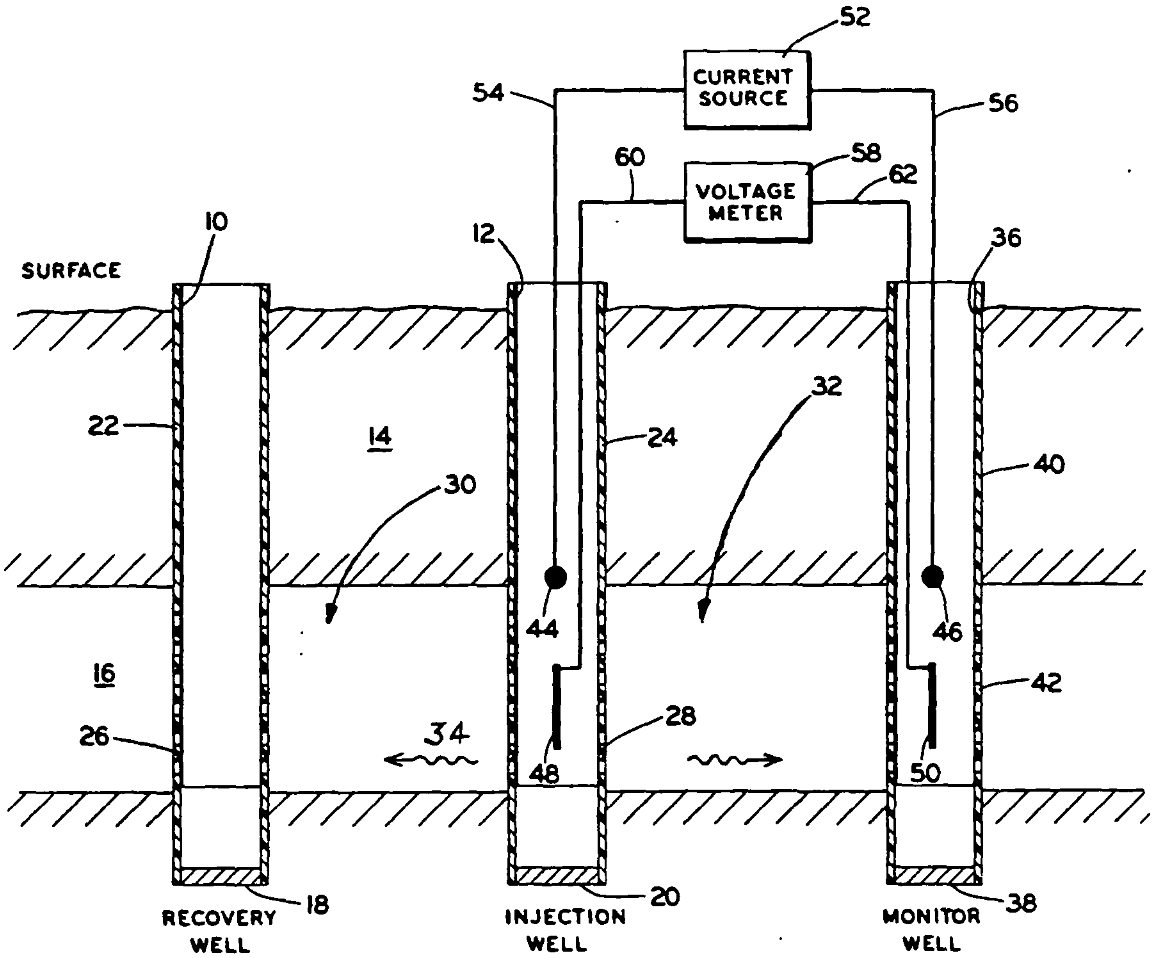
Primary Examiner—Gerard R. Strecker
Attorney, Agent, or Firm—Gersten Sadowsky; Donald A. Gardiner

[57] ABSTRACT

In an in situ uranium leaching process, a method of detecting presence or absence of leach solution escaping from a desired leaching zone involves monitoring the electrical impedance of a zone just outside the desired zone to detect high ionic concentration indicative of leach solution. Electrical impedance is measured by locating monitor wells just outside the leaching zone and positioning pairs of current and voltage probes within the monitor wells and closest injection wells. Low frequency, constant current is generated by each pair of current probes between corresponding injection and monitor wells to develop a zone impedance-dependent voltage drop that is measured by each set of voltage probes and correlated to presence or absence of escaping leach solution. In an alternative embodiment, electrical impedances are measured between a single, central recovery well and a series of distributed, monitor wells to reduce the total number of probes required.

12 Claims, 6 Drawing Figures

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INJECTION WELL
MONITOR WELL

FIG. 1

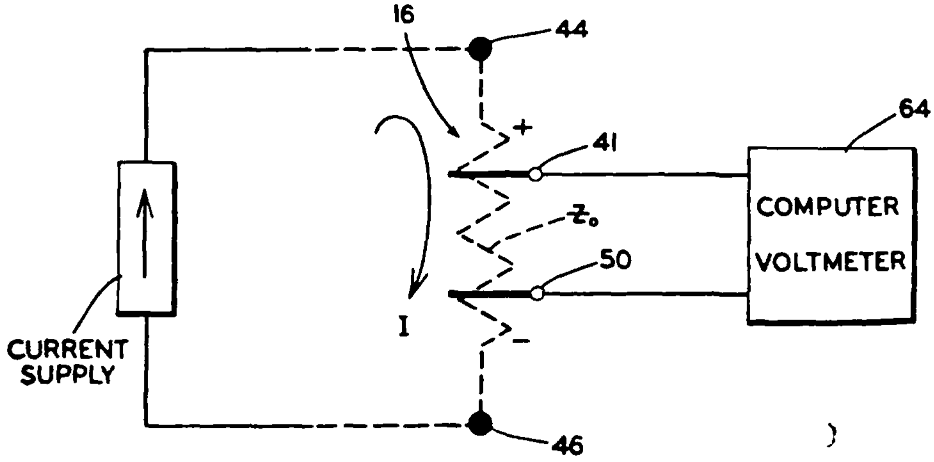
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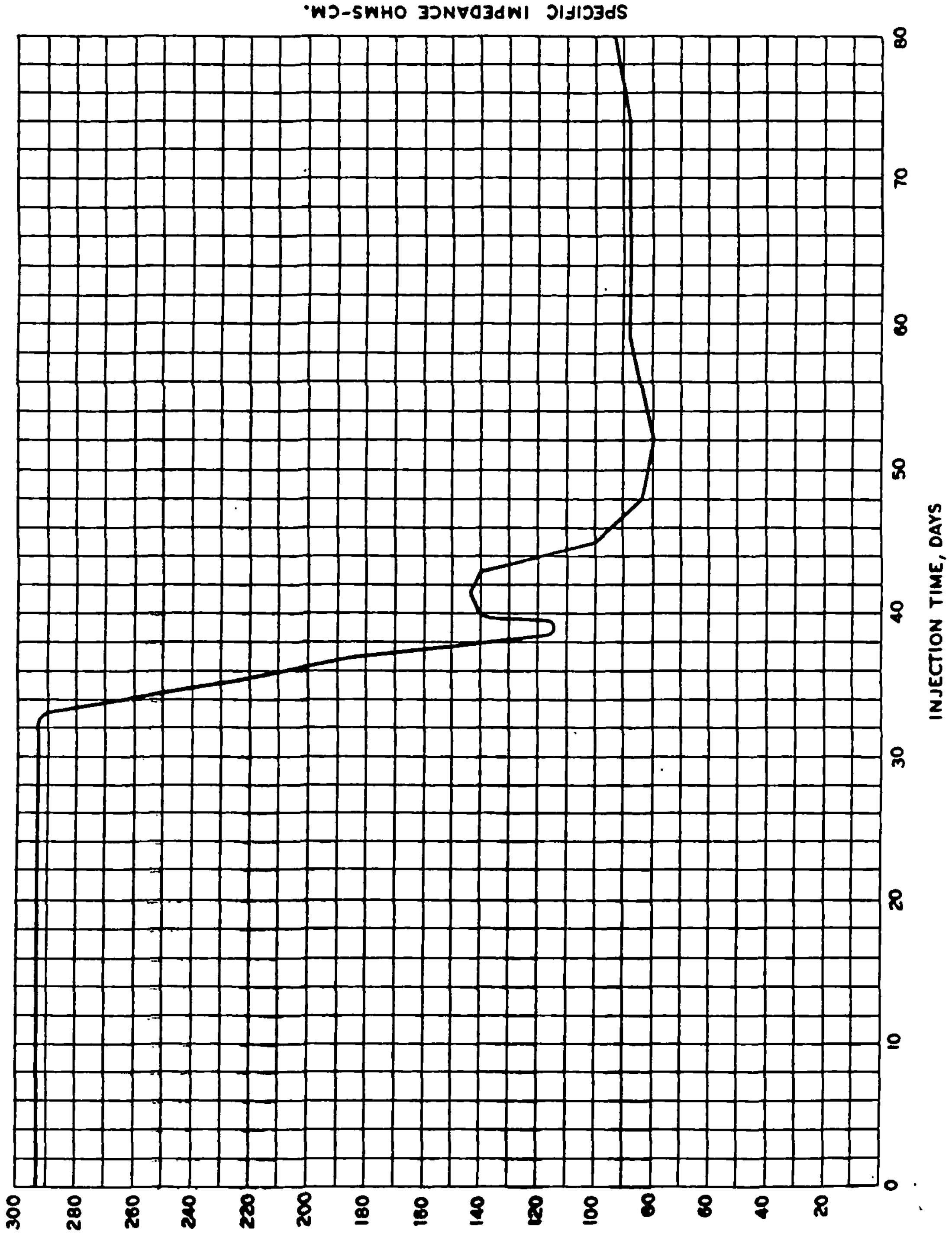
FIG. 2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INJECTION TIME, DAYS

FIG. 3

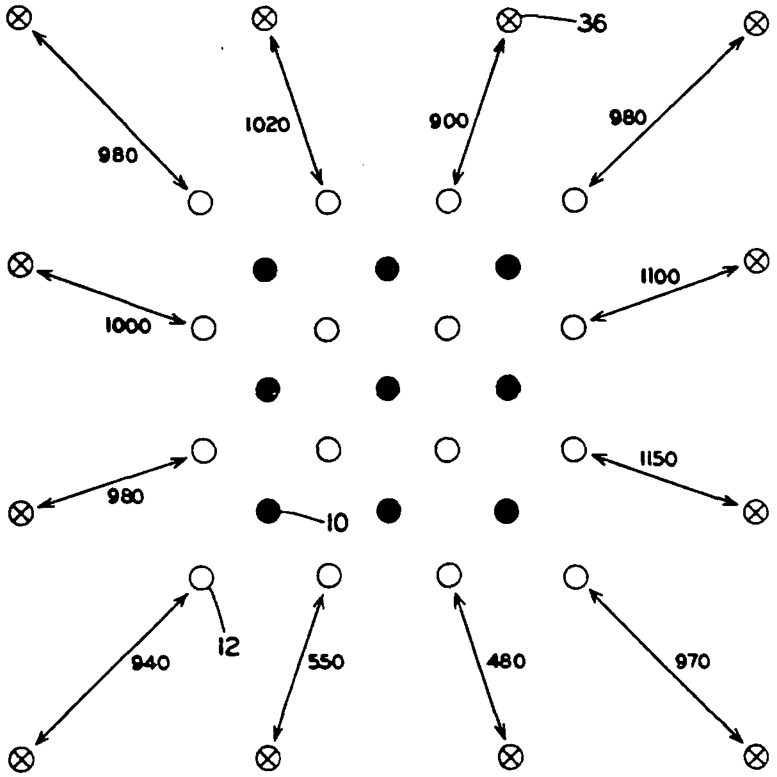


FIG. 4

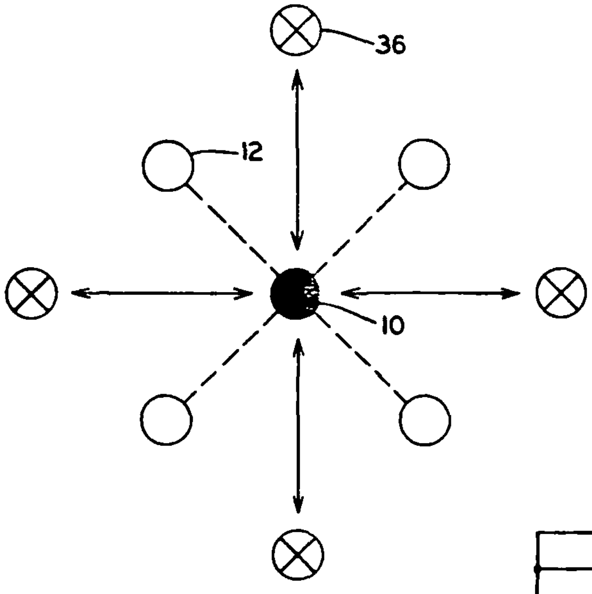
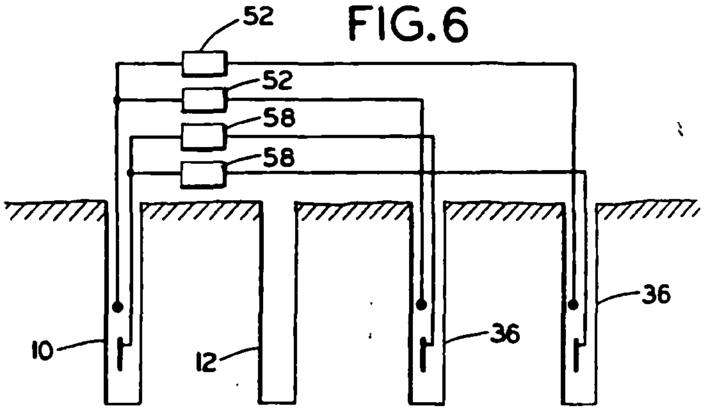


FIG. 5

FIG. 6



IMPEDANCE MEASURING METHOD OF AND APPARATUS FOR DETECTING ESCAPING LEACH SOLUTION

TECHNICAL FIELD

The present invention relates generally to a method of monitoring the presence or absence of leach solution escaping from a desired leaching zone during in situ uranium leaching. The invention relates more particularly to a highly sensitive, improved method of and apparatus for monitoring escaping leach solution by measuring the electrical impedance of a predetermined region outside the desired leaching zone using sets of current and voltage probes and correlating the measured impedance to presence or absence of the solution.

BACKGROUND ART

As an alternative to conventional shaft and strip mining techniques to recover ores containing valuable metals such as uranium and other elements, a technique known as leaching has recently evolved for tapping underground ore bodies, in situ, by treating the underground ore with a leaching solution (lixiviant) which establishes oxidation-reduction reactions for separating and recovering a particular element or mineral from unwanted material in the ore body. The process involves mainly drilling an injection well into an underground ore deposit, and then introducing the leach solution to contact the ore. The leach solution dissolves the mineral within the ore deposit, and thereafter, the pregnant solution is recovered at a recovery well and processed by conventional extraction means to recover desired minerals therefrom.

In order to avoid contaminating an underground region outside of a desired leaching zone, it has been necessary to periodically monitor water samples withdrawn from monitor wells surrounding the leaching site. The water samples are analyzed for ions contained in the water samples. An increase in ion concentration in the samples is considered to be an indication of escaping leach solution in proximity to the monitor wells which are outside the desired leaching zone.

The above method is tedious and requires manual attention by personnel. Even more important, however, it is impossible to determine the presence of escaping leach solution until the solution actually reaches the monitor wells. Detection may therefore be delayed for a substantial period of time after escape begins. Even then, false indications of escaping leach solution sometimes occur because of locally high concentrations of ions in migrating ground water. A need exists, therefore, for a method of detecting escaping leach solution to avoid contamination of regions such as farm land outside the desired leaching zone that is faster and more reliable than previously known methods.

Accordingly, one object of the present invention is to provide a new and improved method of detecting leach solution escaping from a leaching zone.

Another object is to provide a method of and apparatus for detecting escaping leach solution that does not require sampling of solutions from individual monitor wells surrounding the leaching site.

Another object is to provide a new and improved method of and apparatus for detecting escaping leach solution that is faster and more reliable than prior methods.

Another object is to provide a new and improved method of detecting escaping leach solution that is adaptable to automation to reduce personnel requirements.

DISCLOSURE OF INVENTION

The above objects are satisfied by establishing monitor wells surrounding the standard injection wells and recovery wells formed within a desired leaching site. Escape of leach solution beyond the site is detected using current and voltage probes to monitor the electrical impedance of the subterranean regions between the injection wells and nearest monitor wells. A decrease in impedance between pairs of injection and monitor wells is caused by leach solution replacing the natural ground water between the wells and is therefore indicative of escaping leach solution. The impedance between the well pairs are continuously monitored or are monitored periodically over the life of the leaching operation. Occurrence and magnitude of escaping leach solution are periodically reviewed by personnel or are analyzed automatically by computer to determine the condition of the subterranean regions outside the leaching site.

In practice, in order to measure the electrical impedance of the ore formation distributed throughout the leaching site, a series of injection wells and recovery wells are established within the site in a pattern determined by particular mining requirements. Monitor wells are then drilled surrounding the injection and recovery wells outside the site. Each well is jacketed in an electrically insulated, corrosion resistant, casing. A portion of each casing at a preselected depth corresponding to the depth of the ore deposit is formed with a screen to pass leaching solution and dissolved materials. A first current probe is located within the monitor well just above the casing screen and a second current probe is positioned at a corresponding depth in the closest injection well. First and second voltage measuring probes are positioned, respectively, in the two wells adjacent the screens. A constant current source having a magnitude of up to 10 amperes and a frequency in the range of 1-20 Hz is connected to the current probes to establish a constant current flow through the voltage measuring probes, casing screens and ore deposit between the two wells. The voltage measured by the voltage probes is a function of electrical impedance of the ore deposit between the wells which in turn is a function of amount of leach solution present. Thus, any drop in voltage from an expected or nominal voltage is indicative of the presence of escaping leach solution between the injection well and monitor well.

As an alternative configuration, the voltage and current probes may be placed between a single, center recovery well and a series of outer, monitor wells surrounding the injection wells. Electrical impedances are measured between the center recovery well and the monitor wells. Since only a common current probe and a common voltage probe are located in the center recovery well for cooperation with the monitor well current and voltage probes, the total number of probes in the system is reduced by $(M-1)$, where M is the number of monitor wells provided. I am aware that earth resistance monitoring has been used in the past for various purposes, such as porosity logging (e.g., see U.S. Pat. No. 3,975,674). I am also aware that it is known that leach solution has a characteristic impedance or conductance as described, for example, in U.S. Pat. No. 4,071,278. The present invention is based on the realization that escaping leach solution can be detected by monitoring the impedance of an ore formation being mined in situ by leaching, using the probe arrangement and operating parameters, described in detail below. Much higher sensitivity to presence of leach solution is realized by monitoring impedance or conductance from within the monitor and injection or recovery wells in accordance with the invention than by monitoring those parameters at the surface of earth, for example, or by known other methods.

Still other objects and advantages of the present invention will become readily apparent to those skilled in this art from the following detailed description, wherein I have shown and described only the preferred embodiments of the invention, simply by way of illustration of the best modes contemplated by me of carrying out my invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the invention. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a cross sectional view of a subsurface mineral bearing formation penetrated by an injection well, a recovery well and a monitor well equipped with current probes and voltage probes for practicing the invention;

FIG. 2 is a diagram of an equivalent electrical circuit showing the constant current source and voltage drop induced across the ore formation together with a computer for interpreting the results;

FIG. 3 is a graph showing impedance verses time of an ore formation into which leach solution has been injected;

FIG. 4 is a diagram showing an array of injection wells, production wells and monitor wells together with impedance measurement paths at a leaching site in accordance with one embodiment of the invention;

FIG. 5 is a diagram of an alternative array of wells and impedance paths; and

FIG. 6 is a cross sectional side view of the array of FIG. 5 showing probe placement.

BEST MODE FOR CARRYING OUT THE INVENTION

Referring to FIG. 1, a pair of conventional boreholes 10 and 12 are shown drilled into the earth for penetrating overlying strata 14 and a uranium ore or other mineral deposit 16. The lower ends of boreholes 10 and 12 are sealed by conventional caps 18 and 20. The boreholes 10 and 12 are jacketed by electrically insulating, corrosion resistant casings 22 and 24 formed preferably of plastic or fiberglass. A portion of each of the casings 22 and 24 is formed as a screen 26, 28 having slots or perforations that enable leach solution to flow outwardly from borehole 12 and dissolved minerals to flow into the borehole 10 in the usual manner. The borehole 12 is usually referred to as "injection well" while the borehole 10 is referred to as "recovery well" in conventional mineral leaching.

A suitable leach solution (lixiviant), such as ammonium carbonate or sulfuric acid, is distributed into injection well 12 by suitable piping (not shown) and allowed to disperse into the ore formation 16 through screen 28. The screen 28 is positioned at a depth corresponding to the depth of the ore formation, with enough leach solution being supplied to cover a depth that is slightly greater than the depth of the formation 16 to dissolve a maximum amount of mineral. The leach solution chemically reacts with the ore 16 (e.g., UO_3 UO_2 of uranium ore) as the solution penetrates the ore toward the recovery well 10. After some period of time, the zone between injection well 20 and recovery well 24 has been bridged by leach solution and the solution and dissolved ore are withdrawn from recovery well 10 by conventional techniques, such as by pumping through tubing (not shown). The leach solution is pumped to treatment or processing equipment (not shown) where desired minerals are separated for commercial use using conventional chemical separation or refining processes. The recovery process is continued until the desired mineral is leached out to the extent that it is no longer practical to continue the process.

During the leaching process, there is a tendency for leach solution from injection well 12 to escape from the desired leaching zone 30 between injection well 12 and recovery well 10 into an undesired zone 32. To detect the presence of escaping leach solution 34, an additional borehole 36 is drilled into the earth outside the desired leaching zone 30. The borehole 36, identified hereinafter as "monitor well" is equipped with an end plug 38 and casing 40 having a screen 42, in the same manner as described with respect to injection well 12 and recovery well 10. It is to be understood that although only single injection, recovery and monitor wells are shown in FIG. 1, a number of each type of well arranged in a predetermined pattern or array depending upon particular requirements would be provided in practice as shown in FIGS. 3 and 4, for example.

In accordance with the invention, the electrical impedance of zone 32 is monitored by positioning a pair of current supply probes 44 and 46 together with voltage measuring probes 48 and 50 within, respectively, the injection well 12 and monitor well 36. The current supply probes 44 and 46 are located within the two wells at or just above the upper ends of screens 28 and 42. Voltage measuring probes 48 and 50 are positioned beneath the current supply probes 44 and 46 in exposure to each other through the screens 28 and 42. The current supply probes 44 and 46 are preferably located within the range of 5 to 20 feet above the upper ends of the screens 28 and 42, although the exact position within that range is not critical. The voltage probes 48 and 50 preferably extend along the entire length of screens 28 and 42, that is, from just above the upper ends of the screens to just below the lower ends thereof. Shorter probes may be used, however, as shown in FIG. 1, with proportionally reduced sensitivity. The significance of the probe placement described herein is that current is forced to flow along a path through ore formation 16 at a depth defined by the depth of the casing screens 26, 28 because the impedance of the casing 22, 24 at each well to current flow is lowest at said screen.

A constant current source 52 is connected to the current supply probes 44, 46 through conductors 54 and 56. A voltage meter 58 is similarly connected to the voltage measuring probes 48 and 50 through conductors 60 and 62, as shown in FIG. 1. The current source 52 is preferably a constant current, square wave current generator having a frequency of between 1 hertz and 20 hertz. The magnitude of current generated by current source 52 is preferably as high as possible in order to maximize signal-to-noise ratio. In order to reduce power supply requirements, and to avoid disassociation of the leach solution, I have found that a current magnitude of about up to 10 amperes peak is preferred.

Referring to FIG. 2, the impedance of the ore formation 16 between voltage measuring probes 48 and 50 is symbolized by Z_0. The magnitude of this impedance is a function of the amount of leach solution within zone 32, that is, the impedance decreases as the quantity of leach solution within the zone increases. The lower impedance is caused as a result of the ionic concentration of the leach solution which is greater than the ionic concentration of water naturally occurring within the zone 32. Since the nominal impedance of the zone 32 can be determined by measuring the impedance prior to delivery of leach solution into the injection well 12, any significant subsequent decrease in impedance can be attributed to the presence of leach solution that has escaped into the zone 32.

Still referring to FIG. 2, since the amount of current flowing through zone impedance Z_0 is constant, it is evident that the voltage drop across probes 48 and 50 is a function of only the magnitude of impedance Z_0. This voltage is monitored by meter 58 and compared with the predetermined, nominal impedance of the ore formation within zone 32 to determine the presence or absence of escaping leach solution.

FIG. 3 illustrates the measured specific impedance in an acquifer as sulfuric acid leach solution replaced groundwater. The strength of the injected leach solution was increased very slowly for about 30 days, and then was increased more rapidly. FIG. 3 shows that the specific impedance decreased to less than one-third of the initial value. The decrease in specific impedance (ohm-cm) decreased the total impedance (ohm), thereby making the invention feasible.

Monitoring of the voltage drop across probes 48 and 50 can be made continuously or periodically, either manually, or by a programmed, general purpose digital computer 64, as shown in FIG. 2. Of particular significance, the output of voltage probes 48 and 50 is responsive to the presence of any leach solution that escapes into the zone 32 before the solution has migrated toward the monitor well 36. This is in contrast to prior leach solution detection systems of which I am aware that are responsive to the presence of leach solution only after the solution has penetrated the monitor well screen. Accordingly, the presence of escaping leach solution can be detected early, thereby enabling corrective measures to be undertaken.

Referring to FIG. 4, an example of a typical well array at a leaching site is shown. A number of injection wells 12 are distributed within the site and interposed with another number of recovery wells. The number of injection wells 12 in practice may be greater, smaller or equal to the number of recovery wells 10. The leach solution injected into the leaching site through the injection wells 12 is distributed throughout the site, but should not be permitted to extend substantially out of the site. An array of monitor wells 36 are thus distributed around the outer most group of injection wells 36, as shown, to monitor the impedance of the zone between the monitor wells and injection wells shown in FIG. 4. The arrows extending between monitor wells 36 and the closest, corresponding injection wells 12 indicate the paths along which geophysical impedances are monitored by the current and voltage probe pairs described in connection with FIG. 1. Thus, a pair of current and voltage probes are needed for each monitor well 36 and corresponding injection well 12. The voltage outputs of the voltage measuring probes within the corresponding pairs of monitor and injection wells may be supplied to a computer 64 (FIG. 2) to develop a map of the impedances distributed within the monitored zone shown in FIG. 4. It is thereby possible to determine the amount of any leach solution that has escaped into the monitored zone by inspection of the map.

An example of the above mentioned process is shown in FIG. 4, wherein the numbers distributed in the monitored zone defined by the arrows indicate relative voltages that could be measured by voltage probes 48 and 50 at a particular point in time. It can be noted that the voltages measured in the monitored zone at a position of about six o'clock are significantly lower than the remaining measured voltages. It can therefore be presumed that there is an abnormally high ion concentration within the six o'clock region of the monitored zone which is an indication that leach solution has escaped into this region.

Referring to FIG. 5, an alternative array of monitor, injection and recovery wells designed to reduce the total number of probes required for detecting escaping leach solution is shown wherein a single, center recovery well 10 is positioned in communication with four injection wells 12 (the number of injection wells is arbitrary). This type of array is probably not suitable for large mining installations, but is adequate for smaller applications. A number of monitor wells 36 are positioned outside the region surrounded by the injection and recovery wells 12, 10. During a leaching operation, leach solution tends to flow substantially along the paths shown in the dotted lines. Any leach solution flowing along the paths defined by the arrows, however, would have a tendency to escape outside the leaching site and be detected by the monitor wells 36. In accordance with the embodiment of the invention shown in FIG. 5, a single current supply probe and a single voltage measuring probe are positioned in the recovery well 10. An additional current supply probe and voltage measuring probe are also located in each of the monitor wells 36. The current and voltage probes in each of the monitor wells 36 cooperate with the single current probe and voltage probe in the center recovery well 10, that is, each of the constant current sources has one terminal connected to the probe in recovery well 18 and its remaining terminal connected to the current probe in a different one of the monitor wells 36. Similarly, each voltage meter has one terminal connected to the voltage probe in center recovery well 10 and its remaining terminal connected to the voltage measuring probe in a different monitor well. This arrangement is illustrated schematically in FIG. 6 wherein is shown two monitor wells 36 distributed around center recovery well 10. The total number of current and voltage probes saved in the configuration of FIG. 6 compared to the configuration of FIG. 4 is $(M-1)$, where M is the number of monitor wells in the array.

In this disclosure, there is shown and described only the preferred embodiments of the invention, but, as aforementioned, it is to be understood that the invention is capable of use in various other combinations and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein.

I claim:

1. A method of detecting presence or absence of leach solution escaping from a desired underground

leaching zone having an injection well and a recovery well extending thereto from ground above, wherein leach solution is delivered through the injection well to a region of said zone having an ore formation between the two wells, and dissolved minerals are recovered from said recovery well, comprising the steps of establishing a monitor well outside said region between said injection and recovery wells; measuring an impedance of underground formation between said monitor well and one of said injection well and said recovery well at a depth below said ground substantially corresponding to that of said zone; and correlating said measured impedance to a presence or absence of leach solution.

2. The method of claim 1, wherein said measuring step includes the steps of locating a first current probe and a first voltage probe in said monitor well; locating a second current probe and a second voltage probe in one of said injection well and recovery well; generating a constant current between said current probes; and monitoring a voltage drop between said voltage probes.

3. The method of claim 2, wherein said locating steps includes positioning said voltage probes below said current probes within said wells.

4. The method of claim 3, wherein said injection, recovery and monitor wells are jacketed in electrically insulating casings, the casings of said probe-containing wells having a portion formed with apertures, and said locating steps further include the steps of positioning said current probes above said apertures, and positioning said voltage probes for exposure through said apertures, a current flow path thereby being established through said voltage probes at the apertured portions of said well casings.

5. The method of claim 1, wherein said locating steps including positioning said current and voltage probes in said injection well and said monitor well.

6. The method of claim 1, wherein said locating steps include positioning said current and voltage probes in said recovery well and said monitor well.

7. The method of claim 2, wherein said constant current has a frequency in the range of 1-20 Hz.

8. An apparatus for detecting leakage of leach solution outside a desired leaching zone, comprising:

- an injection well into which leaching solution is delivered for dissolving a mineral from an ore formation;
- a recovery well for withdrawing dissolved minerals, said injection and recovery wells being located within the desired leaching zone being mined, and a monitor well located outside said desired leaching zone, wherein each of said wells includes an electrically insulating casing, and a portion having formed therein apertures facilitating flow of said solution and dissolved minerals through said zone;
- a set of impedance monitoring probes located within said monitor well and one of said injection well and recovery well wherein each set of probes, including a current supplying probe and a voltage measuring probe, is located at a depth in said wells substantially corresponding to the position of said apertures;
- means for operating said probes to measure electrical impedance of an earth formation between said probes, and
- means responsive to signals generated by said probes for correlating an impedance measurement to presence or absence of leach solution between said monitor well and said one of said injection well and recovery well.

9. The apparatus of claim 8, wherein said voltage probes are positioned beneath said current probes.

10. The apparatus of claim 9, including a source for supplying a constant current to said current probes.

11. The apparatus of claim 8, wherein said impedance monitoring probes are located in said monitor well and said injection well.

12. The apparatus of claim 8, wherein said impedance monitoring probes are located in said monitor well and said recovery well.

* * * * *

x'x = matrix of the set of normal equations;
x'_p = the vector of the given values of the independent variables;
x' and x_p = the transposed matrix and vector.

As follows from table 2, the predicted values of the fluidised bed temperature do not fall outside the confidence level. The following regression equations were also used in the calculations:

$$\beta = 0.44622S_c + 0.69445 \cdot 10^{-4} S_c^2 - 0.11065 \qquad (11)$$

$$G_d = 284.56 - 18.994S_c + 0.29723S_c^2 \qquad (12)$$

where:
β = the fraction of the concentrate in the dry charge;
G_d = the amount of dust in the charge (kg/100kg of concentrate).

The excess blast coefficient was calculated by means of the equation:

$$\alpha = \frac{V}{P \cdot \beta \left(\frac{100 - W}{100}\right) V_T} \qquad (13)$$

where:
V = the consumption of blast delivered to the furnace m^3/h;
P = the productivity of the furnace in the moist charge ton/h;
V_T = the specific theoretical consumption of blast m^3/ton of concentrate (V_T = 1481.4m^3/ton).

Conclusions

1. By a computer simulation experiment a mathematical model was obtained, relating the temperature in the fluidised bed during the roasting of nickel concentrates from the Severonikel' Combine to the moisture content and sulphur content of the charge, the oxygen content of the blast, and the excess blast coefficient.
2. The adequacy of the model for experimental data obtained on an industrial roasting furnace was established.

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Investigation of the mechanism of oxidative leaching of copper subsulphide

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Recent researches have shown that the reactions in oxidative leaching of sulphides are well reproduced by electrochemical models[1-3]). Since the general content of these reactions largely reduces to two processes, i.e. cathodic reduction of the oxidising agent and anodic dissolution (oxidation) of the sulphides, the localisation of the individual stages possible in the electrochemical method greatly improves and intensifies the investigations. The present report sets out the results from an electrochemical investigation into the oxidative leaching of copper subsulphide, which is of interest in connection with the development of various prospective hydrometallurgical schemes.

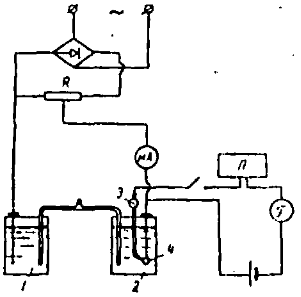

Fig.1 Diagram of the apparatus for measurement of anodic polarisation: 1) cathode compartment, 2) anode compartment; 3) calomel electrode; 4) sample.

The samples for the investigations were prepared from a sample of fused white matte, containing 81.1% Cu and 18.7% S. Its structure was diagnosed by X-ray methods as Chalcocite with small inclusions of metallic copper. These samples in the form of cubes with an edge of 10-15mm were coated with copper electrolytically and attached mechanically to a copper conductor by soldering with tin. The whole electrode was then effectively isolated by BF-2 cement, the working part was reinforced by a self-hardening acrylic plastic, and the surface of the sulphide was carefully ground and polished. A general diagram of the apparatus is shown in fig. 1. The anode compartment was assembled in the form of a beaker with an airtight lid, to which the sulphide electrode and a capillary with a calomel electrode were attached. The observed potentials were read on the hydrogen scale by the usual method. The anolyte (solutions of $CuSO_4$ with concentrations of 0.01, 0.1 and 1M) was thermostated with an accuracy of ± 0.5°C. The cathode compartment was an analogous device with a copper electrode in an acidified solution of copper sulphate.

In the investigated temperature range (25-60°C) the static potentials of the sulphide electrodes were established after a few minutes. They were approximately 0.12V below the equilibrium values calculated by means of the Nernst equation and the standard potential of chalcocite (0.530V) calculated from tables of thermodynamic data. The prelogarithmic coefficients in the temperature and concentration dependences were close to the theoretical values (0.029-0.033). These measurements and also observations on the formation of pale blue deposits of covellite in experiments with prolonged electrolysis and the absence of sulphate formation during analogous electrolysis experiments with copper nitrate solutions showed that the main anodic reaction in the oxidation of chalcocite is the ionisation of copper according to the equation:

$$Cu_2S - 2e = CuS + Cu^{2+}$$

For low current densities the obtained polarisation relationships were found to be practically linear (fig. 2). This showed that the dissolution of chalcocite took place under exchange current control. Its equilibrium values (A/m^2) obtained by means of the equation[4]):

$$D_{0.} = \frac{D_a}{\eta_a} \cdot \frac{RT}{2F}$$

where D_a and η_a respectively are the observed anodic current density (A/m²) and the electrode polarisation (V). are given in the table.

$CuSO_4$ concentration M	Equilibrium values of the exchange current density (A/m²) at temperature °C		
	25	45	60
0.01	0.254	0.680	1.97
0.1	0.510	1.20	2.64
1	0.933	1.60	3.40

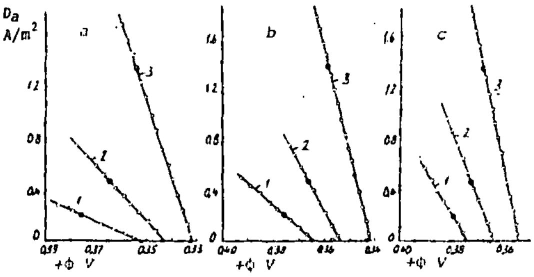

Fig.2 The anodic polarisation of copper subsulphide in $CuSO_4$ solutions M: a) 0.01; b) 0.1; c) 1.0. Temperature °C: 1 - 25; 2 - 40; 3 - 60. ● - static potential; x - calculated value of current density.

In a general assessment they were found to be comparable with the exchange current for pure copper in a solution of 1M $CuSO_4$ + 1M H_2SO_4 at 20°C, which is equal to 30A/m² [6]. Some decrease in the exchange rate in the transition to a more stable chemical compound was quite natural. The concentration dependence of the exchange currents showed that the oxidation rate of copper subsulphide increases appreciably with increase in the $CuSO_4$ concentration.

From the variation of the exchange current with temperature (fig. 3), it was established that the observed activation energy for the ionisation of copper in solutions with copper concentrations of 0.01, 0.1 and 1M $CuSO_4$ is 11.6, 8.9 and 7.5kcal/mole respectively. The direction of the variation in these quantities makes it possible to suppose that the extent of the linear section of the polarisation curves will increase appreciably with temperature, and this increase will be somewhat greater in dilute solutions than in concentrated solutions.

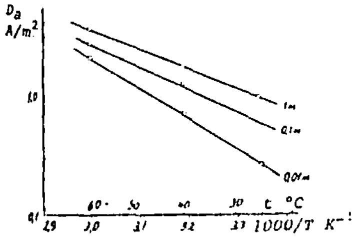

Fig.3 The effect of temperature on the exchange current at $CuSO_4$ concentrations of 0.01, 0.1 and 1.0M.

In addition, the graphs in figs. 2 and 4 show the calculated values of the current density (0.2, 0.46 and 1.34A/m²), obtained from the known temperature dependence of the rate of the autoclave leaching of a sulphide material with similar composition[8]. The positions of the calculated points confirm that the dissolution of copper subsulphide takes place under exchange current control under the leaching conditions.

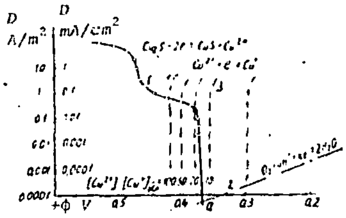

Fig.4 The polarisation curves for the anodic oxidation of copper subsulphide (1), the cathodic reduction of oxygen (2) and the cathodic reduction of Cu^{2+} ions (3).

Of the possible cathodic processes associated with the anodic dissolution of chalcocite of greatest interest is the reduction of molecular oxygen:

$$O_2 + 4H^+ + 4e = 2H_2O$$

the dynamic potential of which is given by the equation:

$$\varphi = 1.229 - \frac{2.303}{F}\,pH + \frac{2.303RT}{4F}\,\lg \cdot P_{O_2} - \eta_c \qquad (1)$$

where η_c is the overpotential for the reduction of oxygen (V). At present the kinetic characteristics of reaction (1) have been poorly investigated, and the available information is practically restricted to investigations in the region of normal temperature[7][8][9]. Since the overpotential for the reduction of oxygen depends to a considerable degree on the cathode material[7][8], and the reduction of oxygen at base metals is masked by self-dissolution effects and by the presence of oxides, we used data on the kinetics of the reduction of oxygen at metallic silver for comparison[9][10]. According to these data, the polarisation of an oxygen electrode at 20°C is given by:

$$\eta_c = a - b'\,pH + b\,\lg D_c$$

where a is a constant determined by the general conditions and by the dimensionality of the current density D_c; b' is a constant obtained experimentally (0.054V) and close to the theoretical value of 2.303RT/F = 0.058V; b is a constant found to be equal to 0.112 on the average and close to the theoretical value of 2.303RT/βF, where β is the transfer coefficient of the cation (~0.5). Correction of equation (1) according to published data[9][10]. gives:

$$\varphi = -0.019 - 0.005pH + 0.127\,\lg P_{O_2} - 0.112\lg D_c \qquad (2)$$

The overpotential for the reduction of oxygen at silver calculated by means of equation (2) is too high. For example, when pH = 1.8, P_{O_2} = 0.21 atm and $D_c = 10^{-2}$ A/m², the dynamic potential of the oxygen electrode amounts to only 0.110V with a polarisation of 0.916V. Comparison of the curve for the cathodic polarisation of oxygen with the anodic curve for chalcocite at 25°C (fig. 4) shows that the dissolution of copper sulphide takes place at an extremely low rate (fig. 4, point a), i.e. approximately four orders of magnitude lower than the calculated value (0.2A/m²). Since the overpotential for the reduction of oxygen at base metals is even higher than that at silver[8], this disagreement between the rates for chalcocite is even greater. In this respect the comparatively slow surface reduction of copper $Cu^{2+} + e = Cu^+$ with subsequent rapid oxidation of Cu^+ ions in the volume of the solution seems more promising:

$$4Cu^+ + O_2 + 4H^+ = 4Cu^{2+} + 2H_2O$$

According to published data[11], at 25°C the equilibrium constant of the reaction $2Cu^+ \rightleftarrows Cu^{2+} + C$ is $K = [Cu^{2+}]/[Cu^+]^2 = 1.7 \cdot 10^6$, which with a Cu^{2+} content of 40g/dm³ and a H_2SO_4 content of 200g/dm³ gives an equilibrium

Cu^+ concentration of 39mg/dm^3. Even gentle bubbling of the solution with oxygen or nitrogen-oxygen mixtures rapidly reduces the equilibrium concentration of Cu^+ to 2-10mg/dm^3. With increase in temperature the equilibrium content of Cu^+ ions and their oxidation rate increase rapidly. In fig. 4 the dotted line shows the approximate position of the kinetic curves for the cathodic process $Cu^{2+} + e = Cu^+$ with an overall copper content of 0.1M and with nominal $[Cu^{2+}]/[Cu^+]_{nom}$ ratios of 100, 50, 20, 10 and 1, calculated from the equilibrium values. Agreement between the expected rates of the anodic and cathodic processes for a calculated current density of 0.2A/m^2 [illegible]) is obtained with the nominal ratio $[Cu^{2+}]/[Cu^+]_{nom} \approx 25$ or with a real Cu^+ concentration of $\approx$0.6mg/dm^3. In view of the high intensity of aeration and the large volume ratio of the solution in the experiments [illegible]), the attainment of such a dynamic equilibrium seems quite tangible.

A further argument in favour of the catalytic action of copper ions is provided by the known observations and conclusions on the existence of an induction period during the oxidative (sulphuric acid) leaching of chalcocite[12][13]. The leaching reactions can evidently only develop to a full extent with a sufficient accumulation of copper ions in the solution. On the potential diagrams the positions of the cathodic curves are determined by the attained dynamic equilibria. Many of the chalcocite leaching characteristics (the observed rate of the process, its temperature dependence etc.) will therefore be determined also by the composition and by the relative amount of the solution, by the intensity of the aeration of pulp, and by certain other specific conditions.

Conclusions

1. From examination of the anodic dissolution potentials of copper subsulphide and the cathodic potentials for the reduction of molecular oxygen it was established that the leaching of copper subsulphide with the direct participation of oxygen takes place at low rates as a result of the high overpotential for the oxygen ionisation reaction.

2. The dissolution of copper subsulphide is appreciably accelerated with the development of the side reactions of cathodic reduction of divalent copper ions: $Cu^{2+} + e = Cu^+$, and the subsequent volume oxidation of the obtained Cu^+ ions:

$$4Cu^+ + O_2 + 4H^+ = 4Cu^{2+} = 2H_2O$$

The leaching rate of copper subsulphide and the temperature dependence of the overall process will therefore evidently be determined also by the composition and relative amount of the solution, by the intensity of the aeration of the pulp, and by certain other specific conditions.

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UDC 669.431.4

Investigation of the reaction of lead sulphide with lead oxide and sulphate at 1150°C

M M Khalmetov and V Ya Zaitsev (Moscow Institute of Steel and Alloys, Department of the Metallurgy of Heavy Non-Ferrous Metals)

The existing classical scheme of lead production (sintering, smelting) has substantial disadvantages. There are greater prospects for the recently developed methods for the production of lead by an autogenous method directly from sulphide concentrates in the liquid state[1-4]. To develop the technological regimes and to obtain a better understanding of such processes it is necessary accumulate a whole series of data on the mechanism and kinetics of the reaction of lead sulphides and oxide compounds at high temperatures. The kinetics of the reactions in the solid state have been studied[5-8], but these data are clearly insufficient to determine the characteristics of the reactions of the components of the lead charge in melts.

The present article sets out the results from an experimental investigation into the reactions of PbS with PbO and $PbSO_4$, realised on the apparatus shown in fig. 1. The alundum crucible 1 with a weighed amount of the charge was placed in a quartz tube 2 closed with an airtight water-cooled stopper, and the tube was placed in a Silit furnace (up to 5kW). The temperature in the reaction tube was measured by means of the thermocouple 3; automatic control of the temperature conditions was realised with an accuracy of ±5°C by means of the KSP-6 instrument 4.

To eliminate fully the possibility of oxidation the argon was purified from oxygen. Argon from the bottle 5 was passed successively through a column of copper filings 6.

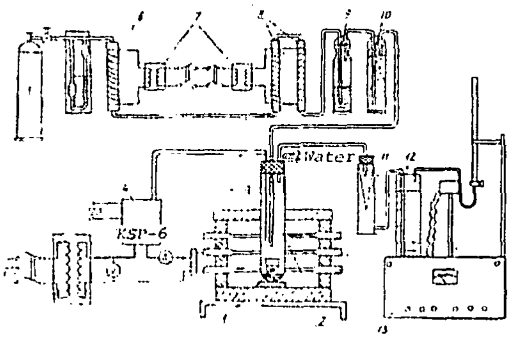

Fig. 1 Diagram of the apparatus.

Columns with an active preparation of copper 8, a Drechsel bottle containing concentrated sulphuric acid 9, and a vessel containing calcium chloride 10. The temperature conditions in the heated gas purification columns were maintained by means of laboratory autotransformers 7.

The gaseous reaction products were passed through a dust collector with a paper filter 11 and were dispersed in a beaker of water 12, where the sulphur dioxide was titrated automatically with a solution of iodine on an automatic titrator TFL-46-2 13. The amount of sulphur dioxide released or the reacted amount of sulphur at each

IDENTIFICATION OF NATIONAL NEEDS WITH INDUSTRY LEADERS COMMENTS ON RESEARCH AND DEVELOPMENT NEEDS IN MINERALS EXTRACTION

Final
Report

October
1980

Contract #J0100077
P.O. #P0101349

Prepared for:

U.S. Department of
the Interior
Bureau of Mines
Washington, DC

By
Alfred Weiss

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New York
Montreal

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DR. ALFRED WEISS
President

October 16, 1980

Dr. Thomas A. Henrie
Chief Scientist
U.S. DEPARTMENT OF THE INTERIOR
Bureau of Mines
2401 E Street NW
Washington, DC 20241

Re: P.O. #P0101349
Contract #J0100077
Identification of National
Needs and Industry Leader
Comments

Dear Dr. Henrie:

Enclosed please find five copies of our final report entitled "Identification of National Needs with Industry Leaders Comments on Research and Development Needs in Minerals Extraction" which includes work performed on the above referenced project order and contract.

I have incorporated the results of our meeting in Washington on October 10 and the comments you made on the draft report submitted earlier.

It has been a pleasure to work with you in this effort and I feel something very meaningful has been accomplished.

With best regards.

Sincerely,

AW/pc
enclosures
cc: Mrs. G. Neubert w/report

Section 1 - Table of Contents

IDENTIFICATION OF NATIONAL NEEDS
with
INDUSTRY LEADERS COMMENTS
on
RESEARCH AND DEVELOPMENT NEEDS
in
MINERALS EXTRACTION

Section 2 - Summary

Approximately forty top level executives were visited at seventeen company locations, seven universities and a number of executives representing three additional corporations were contacted by telephone in order:

1. to discuss a cooperative program in mining-metals research and development proposed by the Office of Science and Technology Policy of the Executive Office of the President, and
2. to identify problem areas reflective of national needs.

Strong expressions of interest were received for participation in an industry-government cooperative R&D program; and national needs with respect to minerals were identified in areas of energy conservation, environmental control, and broad-based research and development in specific phases of the mineral cycle.

Section 3 - Introduction

Early in 1980, Dr. Thomas A. Henrie, Chief Scientist of the U. S. Department of the Interior, Bureau of Mines, discussed with Dr. Alfred Weiss, President of Mineral Systems Inc., plans to contact industry leaders. The principal purpose of such contacts would be the identification of national needs with emphasis on Research and Development (R&D) needs in minerals extraction. Contacts would be established by visits with top management, and initial discussions would center around a possible industry-government cooperative program in mining/metals R&D proposed by the Office of Science and Technology Policy (OSTP) of the Executive Office of the President.

Dr. Weiss' assistance was requested because of his long standing acquaintance with and acceptance by many industry leaders and his familiarity with the planning and evaluation functions of the Bureau of Mines. His involvement included:

a. Assistance in setting objectives as to overall industry leaders' visitation program.

b. Assistance in the identification of key industry leaders.

c. Participation in the preparation and scheduling of visits; in some instances take lead in approaching Chief Executive Officers.

d. Participation in meetings and discussions.

e. Analysis of each meeting/discussion session.

f. Preparation of report on discussions with industry leaders.

This document is submitted to address items E and F of the project.

Section 4 - Subject of Discussion

In contrast with other investigations, it was decided to conduct all discussions with corporate officers before contacting any research and development managers.

Also, while the intention was to keep the discussions unstructured, it was decided to start with a description of the proposed OSTP industry-government cooperative program in mining-metals Research and Development.

The following is a description of the R&D concept which was discussed with industry leaders during the project.

Overall Concept

The basic concept is that the extractive industry would join the Federal Government in a major effort of cooperative research. Such effort may last some 10 years and cost at least a billion dollars. Initially, the program would need to start small, possibly at the ten - twenty thousand dollar level; and grow as the management of such program would be able to effectively steer and guide the activity. By developing a cooperative program, the knowledge and experience derived would flow to all participants, generally in amounts far greater than could be achieved by individual corporate or Federally supported project investment in R&D. Furthermore, through such effort, technology transfer--one of the most troublesome aspects of Federal R&D--would be maximized.

Participants

The program that would be funded is one of basic and applied research and advanced technology development. Universities would participate in the basic research projects oriented toward the total program; government laboratories which combined have larger resources and capabilities would conduct the basic core program; and industry would execute engineering type programs such as pilot plants and demonstrations.

The program would be open to participation by all those firms seeking to join with other firms and the government. Costs would be shared in such a way so as not to impact disproportionately the smaller companies. Entry in the program would be voluntary.

The program would start with Federal government participation through the Department of the Interior (the Bureau of Mines and the U.S. Geological Survey) and the National Science Foundation with the Bureau of Mines assuming a lead role.

Organization of the Research

The cooperative research activities envisioned in the government-industry mining-metals program could be organized in any of several ways. A specific organizational framework could be selected by the contributing companies, which could support research (through grants) at universities. In this case, the research management teams would be guided in their decisions by the agreement of all particpating parties on a research framework.

In another cooperative industry-government cooperative program, the industry funding is contributed to one project account, managed by one agency. Another model might be to establish an independent research organization to which both the government and industry would contribute funding. In any case, an advisory or steering committee would include government, industry, academic and possibly public representatives.

The discussions of these arrangement and other elements of administration, clearance of the program from the antitrust standpoint, patents, etc., would begin if there is a sufficient expression of interest in a cooperative program on the part of a number of firms in the mining-metals industry. At the same time, there would be continuing discussions of the possible research topics that would constitute a cooperative program.

On the basis of its experience with similar research programs and university-industry programs the Bureau of Mines knows of no insurmountable issues that would inhibit successful cooperation between industry and government.

Funding Levels and Duration of the Cooperative Effort

Funding for R&D in mining-metals industry is significantly below that of other major industrial sectors, and Federal support is less than that for some other industry-related work. It is necessary to see what the capacity within the research community is, or can be expected to be after several years of support. Also important is the extent to which there will be funding directed toward applied research or pilot plants.

As a target for discussion, the industrial firms and the government should undertake planning that could lead to an increase of investment of at least $100M, achieved over several years, and then sustained over the rest of the decade.

Next Steps

Joint discussions of this concept would be followed by a more formal series of meetings in autumn, 1980 to seek a decision on an agreement of principles, endorsed by a sufficient number of firms to warrant inclusion of some funding for a sectoral initiative in the 1982 Federal Budget. The discussions will be conducted on the Federal side by the Office of Science and Technology Policy-Executive Office of the President and the Department of the Interior.

The above conceptual framework was discussed face to face with each executive or small group of executives visited and discussions were held in terms of expressing interest and of making suggestions. No promises of commitment or of assured actions were made; emphasis was placed on an OSTP initiative to take the next step.

Section 5 - Analysis of Discussions

THE ANACONDA COMPANY

Discussions at the Anaconda Copper Company took place with Messrs. J. S. Morrison, President and J. Anderson, Senior Vice President. Both men were unaware of the Bureau's research program, but were in favor of participating in a joint R&D program.

They believed, however, that if industry shared in the funding, the individual companies would want to have a say in determining the R&D problem. It was recognized that the problems need to be of a general nature so that industry as a whole and the national economy would benefit.

They were very much in favor of the R&D concept especially those aspects related to an advisory or steering committee in which academia, government labs and industrial groups could all participate.

They believed Anaconda would be most interested in participating and assisting in the development of such programs and wanted to be kept advised.

Problem areas mentioned were:

- Smelting research to meet ambient air standards, or alternatively, substitute for smelter by alternative methods such as hydrometallurgical processes,
- Pit-wall leaching of mines which cannot be mined economically in the conventional manner, and
- Processes and systems related to in-situ leaching of deep-seated copper deposits; both oxides and sulfides.

NEW YORK UNIVERSITY - Center for Science and Technology Policy

Discussion at NYU/Center for Science and Technology Policy took place with Drs. Herbert I. Fusfeld, Director and A. C. Dameske, visiting Professor. A number of pertinent questions related to any possible industry-government research program were addressed. The overall conclusions drawn were that there would be little gain for individual companies to develop technology, and there is sufficient incentive for a major individual effort to participate in a cooperative research and development.

A number of organizational and procedural problems were discussed and a strong interest was expressed on behalf of NYU to contribute to the solution of some of these problems.

The Center for Science and Technology as represented by its Director, Dr. Herbert Fusfeld is most anxious to help the Bureau of Mines in planning any industry-wide meeting or even staging the meeting itself. We were shown facilities which would be ideally suited for such purpose. Dr. Henrie indicated that the first meeting would be held in the Indian Treaty Room at the Old Executive Building in Washington, DC, but that there might be a good opportunity to use the NYU facilities at a later date.

Industry problems of national scale perceived by the Center include:

- Energy Conservation, and
- Environmental Control.

FREEPORT MINERALS COMPANY

Discussion at Freeport took place with Mr. Milton H. Ward, Executive Vice President. Visit was relatively brief because of Mr. Ward's pending departure for Australia and Indonesia.

Strong support was expressed by Mr. Ward on behalf of the company for an R&D program with the Bureau of Mines assuming a lead role. Freeport would like to be informed and Mr. Ward volunteered to represent Freeport in any follow-up meeting.

The late hour and Ward's pending trip to Australia prevented an in-depth discussion of national problems and issues.

ST. JOE MINERALS COPORATION

Discussions at St. Joe took place with Messrs Joseph G. Sevich, Vice President of Technology and John A. Wright, Executive Vice President. We were later joined by Mr. John C. Duncan, Chairman.

St. Joe also expressed strong support for a Bureau of Mines managed R&D program and saw as a potential obstacle the selection of research problem(s). The management through a Steering Committee with federal and industry representation appeared the solution to maintaining broad-based interest and to assuming selection of problems of national scope.

Currently, St. Joe sees as problems of national importance which infringe heavily on mineral producers:

- Wilderness Bill consequences,
- Implications, such as technological obsolescence created by EPA and OSHA regulations,
- Energy problems at the smelter, and
- Competition from imports.

St. Joe oriented problems and concerns include:

- Lead chloride process, and
- Direct reduction of iron process.

UNION CARBIDE CORPORATION

Discussions at Union Carbide took place with Mr. F. J. Shortsleeve, Vice President. While Union Carbide was only retaining their Vanadium, Uranium, and Tungsten business, having sold its domestic plants in the ferroalloy business, Mr. Shortsleeve expressed support for the program we outlined and wanted to be kept informed as to the progress. Furthermore he offered his personal assistance to encourage the concept of any future cooperative research program. He pointed out that Union Carbide had sold its research laboratory in Niagra Falls lending additional weight to our impression that industry finds itself less and less in a position to sponsor its own research activities.

AMAX INC.

Discussions at Amax were held with Dr. Herbert Kay, Vice President of Technology. Dr. Kay, who had previously visited with Dr. Henrie in Washington, DC to seek Bureau of Mines support, was in complete agreement with the concept of an industry-government cooperative R&D program. On behalf of Amax, he offered his personal involvement and those reporting to him at the regional level in Denver, CO.

He stressed Amax's interest in a broad-based program as his company has plans for and is involved in the exploration and/or production of practically all minerals of commercial value. The organizational chart he showed us reflected a broad-based and complex organization. Dr. Kay urged us to contact his associates in Amax's Denver laboratory, and especially to discuss the program with Dr. Eugene Michael.

National problems expressed by Dr. Kay concurred with those listed under St. Joe and Anaconda.

COLUMBIA UNIVERSITY

Discussions at Columbia were held with Professor Stevan Boshkov, Chairman of the Henry Krumb School of Mines, and Herbert Kellogg, Professor of Metallurgy. Professor Boshkov not only expressed strong support for the cooperative R&D program, but pointed out that in many countries such programs are and have been successful and have served to place the respective countries in a strong competitive position.

Professor Kellogg pointed out that the 'old technology' may not be obsolete and that any effective R&D program should not necessarily abandon the old technology; but should examine it to determine which parts of the unit processes should be maintained. He admits that the smelter has many environmental problems and that the blast furnace is not flexible enough to accomodate the various grade and ore characteristics.

Professor Boshkov expressed some apprehension that the industry might not be forward looking enough and might fail to appreciate the effect of an R&D program to maintain a high level of technology. However, with increased involvement of the oil companies in the minerals business and their differing views as to high technology operations, the more traditional segments of the minerals industry may follow with support once it is obtained by the oil companies.

Both gentlemen expressed complete support and offered their personal involvement should this be required.

EXXON CORPORATION

Discussions at Exxon took place with Messrs. W. Cooper, Senior Advisor in Science and Technology, Exxon Corporation, and E. Paul Mortimer, Senior Vice President Exxon Minerals Corp. in charge of Research and Technology Development.

Both gentlemen were extremely interested in the program and pointed out that Exxon is already spending a sizable amount of money in all areas of the mineral business even though its cash flow from minerals is minimal. Mortimer in particular pointed out that aspects of organizational concurrence on research programs and monetary support from industrial companies would be our greatest problem areas as he experienced similar obstacles just within the Exxon family.

After about an hour and a half discussion on the program and some of the concepts and how it would work, Mr. Mortimer thought it best that he be kept abreast of developments and was sure that when the time came Exxon would find a way to support a cooperative program in minerals research and would surely want to be part of it. He had very little doubt that McCardell's (William M. McCardell, President, Exxon Minerals Corp.) feelings would be the same. We felt that it was a productive meeting and that Exxon was quite forward looking in their minerals program.

ASARCO INC.

Discussions at Asarco took place with Messrs. C. F. Barber, Chairman and Chief Executive Officer, R. L. Hennebach, President; Richard Osbourn, Executive Vice President; K. D. Loughridge, Senior Vice President; Bill Roe, Vice President Research; and other staff members.

Mr. Hennebach expressed skepticism and concern regarding the joint government-industry R&D program based on fear for the underlying premises. For instance, an R&D in smelting technology might imply inadequacies of current smelting practices, a subject matter on which Asarco has testified, defended in public hearings, and argued for in numerous court battles.

Mr. Barber had a completely different perspective on any such joint program and viewed such activity more in light of a broad-based R&D program to develop new and more effective ways of mineral extraction.

Further, he offered his personal support as President of the American Mining Congress to see to it that the Executive Committee of the AMC would adopt a resolution in principle supporting a joint government-industry R&D program.

While the initial phase of our meeting started in an adversary way, the meeting concluded very much in a positive and supportive posture.

Mr. Barber suggested that we commit in writing (4 to 10 pages) a synopsis of the R&D program concept and how it would work to be reviewed by a small group of industrialists.

UNIVERSITY OF CALIFORNIA at Berkeley

Discussions at Berkeley took place with Dean A. M. Hopkins and Dr. Sherman. They were quite impressed with the idea of a joint R&D program but were relatively uninformed about industrial research within the extractive minerals industry. Neither appeared to know much about government-industry relations in the R&D area.

Much of the conversation channelled into a discussion concerning the contract and grant policy of the Bureau of Mines and both expressed concern over the publication of technological information policy introduced by the Bureau in the current R&D contracts with the University.

We felt, however, that we could count on the University of California at Berkeley for its support when a joint R&D program is formulated.

BECHTEL CORPORATION

Discussion at Bechtel took place with Mr. Robert Shoemaker, Manager of Metallurgy. The reason for visiting Bechtel was to obtain the reaction of a large engineering-construction firm as to the idea of a cooperative research program between industry and government.

Mr. Shoemaker was extremely supportive and hoped there would be a way the engineering-construction companies could get involved. He pointed out that during engineering of a large mining project the engineering-construction firm, if they were current, would be able, in many areas, to implement innovative technology and to demonstrate such technology through the pilot plant stages.

ENVIROTECH CORPORATION

Discussions at Envirotech took place with Messrs. Bob Byron, Vice President Technology; Booker Moorey, Directory of Research; and Elwood Cone, Project Manager.

Not only did they support the concept of a joint research program, but they urged that we keep them in mind as the involvement of equipment manufacturers would be key to the success of any joint program. They wanted to be kept informed and to be brought into the program as an active participant.

KAISER ALUMINUM COMPANY

Discussions at Kaiser took place with Mr. Don McPherson, Vice Presient of Technology. Mr. McPherson pointed out that two elements would be important in the success of such a research program: development of an objective and the cohesiveness with which the various program objectives will be maintained. He expressed his personal commitment to work with us and would be available for an initial guidelines meeting should we call on him.

He cited numerous projects in which he had extensive experience and in which the two elements cited above were key to the success of such projects.

Mr. McPherson expressed the hope that participants would be obligated to contribute in the funding, thereby committing themselves to an active interest and participation in making the program a success.

KENNECOTT MINERALS COMPANY

Discussions at Kennecott took place with Messrs. G. F. Joklik, President; K. Richards, Vice President, and R. N. Pratt, Vice President. Apprehensions and concerns of these gentlemen centered around three areas: 1) organization, 2) funding, and 3) integration of company proprietary technologies into the joint program. Dr. Joklik pointed out that Kennecott has just curtailed its basic research activities and that as a result of many years of Kennecott's R&D programs, extensive knowledge already exists in the areas of in-situ leaching and ocean mining. His concern therefore was to what degree would the existing technology be integrated and what level of funding would be expected from a company such as Kennecott which already has developed extensive knowledge.

On a personal basis Dr. Joklik had reservations as to the sincerity and Administration commitment of even starting a program since his most recent and extensive involvement in the Minerals Availability study sponsored by the Administration came to no avail.

We felt, nevertheless that the meeting with Kennecott was productive and that the reservations expressed at that meeting could be dealt with effectively.

UNIVERSITY OF UTAH

Discussions at the University of Utah took place with Dr. Larry Latman, Dean of the Mining School and Acting Dean of the School of Engineering. Dr. Latman appeared to be well informed of the cooperative research agreements between industry and government. He appeared extremely interested and would definitely wish the University to be an active participant. He even offered his personal involvement if political pressure on the Utah delegation should be required.

UNIVERSITY OF UTAH RESEARCH INSTITUTE

Discussions at the University of Utah Research Institute took place with Dr. Bill Partridge, the President of the Institute. Dr. Partridge had already been visited by Dr. Henrie so that our meeting was brief and served the purpose of bringing Dr. Partridge up to date on the immediate future plans of the program.

OCCIDENTAL MINERALS COPRORATION

Discussions at Oxy took place with Dr. Paul A. Bailly, President. Dr. Bailly was quite supportive but was hesitant as to his commitment for funding since Oxy Minerals at present has no cash flow and most likely will not be in the black for some time to come. Based on Dr. Bailly's extensive experience he is well aware of research problems in the mineral industry and felt the time had come for industry and government to pool their respective resources and establish a cooperative research program. Having a broad international background, he also indicated the number of industrialized countries which have implemented a nonfuel minerals policy which emphasized mutual support and cooperation between industry and government.

AMAX INC. - Denver

Discussion at Amax, Denver took place with Dr. Eugene Michaels, Director of Research; and Paul Quenau, Research Supervisor. Both gentlemen suppported the general idea of a cooperative research program but pointed out certain problem areas similar to those we encountered in earlier discussions.

COLORADO SCHOOL OF MINES

Discussions took place with Dr. Bill Muellar, Vice President Academic Affairs. While not familiar with the cooperative research program he expressed keen interest and wanted to know what he could do to help further the cause. He felt that the Colorado School of Mines by its very nature is interested in making a contribution either through specific research contracts, through managing parts of the program, or any combination thereof.

DUVAL CORPORATION - Tucson, AZ

Discussions at Duval took place with Messrs. George Edward, Chairman and Chief Executive Office and Royce Hardy, Vice President. Mr. Edwards expressed skepticism and reservations as to the effectiveness of bringing 'all of these people together to develop a research program'. Mr. Hardy, having been an Assistant Secretary in the Department of the Interior was much more positive in his outlook. We felt that if a joint program were to be developed, Duval would lend its support.

ASARCO - Tucson

Discussions took place with Mr. Charles Campbell, General Manager, Western and Southwestern Mines. Mr. Campbell expressed a typical operators' point of view - viewing studies as a means to promulgate more and more regulations causing his already difficult job to become more burdensome. He did express satisfaction concerning our visit with him which he perceived as a follow-up to an earlier meeting he had attended with Dr. Lindsay Norman, Director of the Bureau of Mines. It's our impression that at an operating level, the joint R&D program will be viewed from a much more parochial standpoint; indicative of the necessity to keep any future R&D program broad-based, fundamental, and beneficial industry-wide.

ANACONDA - Tucson

Discussions at Anaconda took place with Mr. Bill Stern, Metallurgical Consultant. Mr. Stern was formerly Manager of Research. Supportive of the cooperative program, he feels especially strong concerning hydrometallurgy to be the answer to future treatment of pyrittic nonferrous ores, especially the McArthur deposit in Australia and many mineralizations in Alaska. His remarks also reflect a much more site-specific view point.

UNIVERSITY OF ARIZONA

Discussions took place with Dr. William Dresher, Dean of the Mining School. Dean Dresher was well apprised of the program having been a staunch supporter of the joint research program concept. He's presently chairman of the COMINTECH Committee of the National Academy of Engineers. Dresher's concern was centered around the timing, pointing out that the program perhaps, should await publication of the COMINTECH report. He would prefer to see the report as a basic instrument in developing the joint R&D program.

GULF RESOURCES AND CHEMICAL CORPORATION

Discussions at Gulf Resources took place with Mr. Jack M. Webb, Vice President Government Relations. Mr. Webb, having had a few bad experiences with Government, including Interior, expressed reservations concerning any cooperative research program. After learning of the Bureau of Mines' involvement, he became much more sympathetic and in the final analysis supportive of a Bureau managed program.

Underlying Mr. Webb's views was his feeling concerning timing. He couldn't help but feel that introducing a joint program at the end of an Administration which has not been supportive of the minerals industry could only be construed as a political gimmick to gain voter support. He expressed suspicion of government and was also of the opinion that government research would lead to more regulations. He would also see some complication of Gulf Resources support since his own organization has essentially curtailed its technical program.

Section 6 - Conclusions

This project entitled Identification of National Needs with Respect to Minerals has served a two-fold purpose: 1) By structuring and centering the discussions around a possible industry-government cooperative program in mining-metals R&D an expression of interest was obtained; and 2) Throughout the discussions, industrialists expressed those R&D needs in minerals extraction reflective of their perception of national mineral problems. Based on this project methodology, the following conclusions may be drawn:

1. Informal expressions were obtained of keen interest by industrial companies in participating in industry-government cooperative programs in mining-metals R&D.
2. Such an interest will continue provided the program is planned and implemented carefully with all parties concerned.
3. Such planning and implementation should include the development of a research agenda and the institutionalization mechanism to begin work in the summer of 1981 (FY1981) or later in the calendar year 1981 (FY82).
4. The most frequently mentioned problem areas reflective of industry views as to national problems were:
    - Smelting research to meet ambient air standards, or alternatively, substitute alternative methods such as hydrometallurgical processes for the smelter,
    - Pit-wall leaching of mines which cannot be mined economically in the conventional manner,
    - Processes and systems related to in-situ leaching of deep-seated copper deposits; both oxides and sulfides,
    - Energy conservation,
    - Environmental control,
    - Wilderness Bill consequences,
    - Implications, such as technological obsolescence created by EPA and OSHA regulations,
    - Energy problems at the smelter,

- Competition from imports,
- Lead chloride processes, and
- Direct reduction of iron process.

Appendix A

Companies Visited

Amax Inc.
Amax Center
Greenwich, CT 06830
(203) 622-3000

Amax Research Laboratory
5950 McIntrye Street
Denver, CO 80212
(303) 279-7636

Anaconda Copper Company
Sub. of The Anaconda Company,
a Sub. of Atlantic Richfield Co.
555 17th Street
Denver, CO 80202
(303) 575-4000

Anaconda Copper Co.
Metallurgical Research Dept.
Box 27007
Interstate 10 E & 8000 South Colbe Road
Tucson, AZ 85726
(602) 889-5361

Asarco Inc.
120 Broadway
New York, NY 10005
(212) 732-9500

Asarco Inc.
Western and Southwestern Mines Division
1150 N. Seventh Ave.
Tucson, AZ 85705
(602) 792-3010

Bechtel Corporation
P.O. Box 3965
50 Beale Street
San Francisco, CA 94119
(415) 768-1234

Duval Corporation
4715 E. Ft. Lowell Road
Tucson, AZ 85712
(602) 327-5941

Envirotech Corporation
3000 Sand Hill Road
Menlo Park, CA 94025
(415) 854-2000

Exxon Corporation
1251 Ave. of the Americas
New York, NY 10020
(212) 398-3000

Freeport Minerals Company
200 Park Avenue
New York, NY 10017
(212) 578-9200

Gulf Resources and Chemical Corporation
1100 Milam Bldg.
Houston, TX 77002
(713) 658-0471

Kaiser Aluminum and Chemical Company
300 Lakeside Drive
Oakland, CA 04643
(415) 271-3300

Kennecott Minerals Company
Box 11248
Salt Lake City, UT 84147
(801) 534-8111

Occidental Minerals Corporation
Div. Occidental Petroleum Corp.
Irongate Bldg. 4
777 S. Wadsworth Blvd.
Lakewood, CO 80226
(303) 988-2200

St. Joe Minerals Corp.
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Hearst Mining Building
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(415) 642-6000

Colorado School of Mines
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(303) 279-0300

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Henry Krumb School of Mines
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New York University
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University of Utah
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In-Place Leaching at Miami Mine, Miami, Arizona

by James B. Fletcher

Leaching of the block caved mine from 1941 through 1970 is described, and the improvements made are listed. Detailed is the increased knowledge of leaching gained through this operation, including methods used in forecasting production, prediction of the economical end point, rate of recovery, and ultimate recovery.

The Miami mine is located near the town of Miami, Gila County, Ariz. The Miami mine started mining in 1910 and finished in July 1959. The ore body was divided and mined as follows:

	Tons	
High Grade	24,400,000	Top slicing, sublevel caving, etc.
Low Grade	105,100,000	Block caving
Mixed ore	9,800,000	Block caving
Low Grade #2	13,100,000	Block caving
Total Mining	152,400,000	

Geology: Ore minerals are largely in Precambrian Pinal schist intruded by tertiary Schultz granite porphyry and covered to some extent by Quarternary Gila conglomerate. The structures are highly faulted and shattered. The Miami fault on the east cuts off the ore and the Pinto fault on the southwest caused reoxidation of enriched sulfides producing mixed ore.

Mineralogy: The chief mineral is chalcocite, with chalcopyrite, bornite, covellite, malachite, azurite, chrysocola, cuprite, native copper; and molybdenite as minor minerals. The ore minerals occur in seams, veinlets, and disseminated particles.

In block caving there is always some dilution, and drawing of ore stops when the grade drops past an economical point. This results in a small amount of copper left in the stopes below the capping. There is some copper in the capping, probably below 0.03% or less than 0.6 lb per ton. Over the low grade No. 2 ore body and portions of the high grade, there was an oxide capping which was not mined. The crushed pillars are another source of copper. The leaching at Miami is an attempt to recover this last remaining copper of a worked-out mine.

The enrichment at the Miami mine had gone more nearly to completion than most ore bodies in the southwest. There is practically no pyrite in the capping and very little in the ore.

Leaching

Leaching started on a small scale in December 1941. Some of the early problems that were met are as follows:

The first leaching was tried through the conglomerate over the high grade mining. No solution came through the fault. There had been mining below the high grade since the first leaching, which had broken the conglomerate for the second time, but this problem has not been completely solved to date.

The next leaching was tried over the mixed ore body with water. The solution came through with very little copper. Water was tried over the sulfide stopes with no recovery of copper. Then acid was added to the water over the mixed ore. The first leaching was started with a 3% H_2SO_4 solution which was immediately dropped to a 0.6% solution. At the present time we try to control the H_2SO_4 feed by the amount of free acid in the pregnant solution. If the acid in the pregnant solution drops much below 0.5 lb H_2SO_4 per ton of solution, the pumps, pipe lines, sumps, etc., are clogged with iron salts.

The early thinking was that the reuse of the ferrous solution from the precipitation plant would clog the caved area and stop the leaching.

In order to leach sulfides it was realized that Fe''' would be necessary, and several attempts were made to manufacture a high Fe''' solution. It was discovered that by adding acid to the off-solution from the precipitating plant, Fe'' was converted to Fe''' as the solution went through the caved ground. The equation for this reaction is:

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{\text{Bacteria}} 2Fe_2(SO_4)_3 + 2H_2O$$

The ferric sulfate reacts with the copper sulfide mineral, chalcocite, to form copper sulfate, ferrous sulfate, and elemental sulfur as shown in the following equation:

$$Cu_2S + 2Fe_2(SO_4)_3 \xrightarrow{\text{Bacteria}} 2CuSO_4 + 4FeSO_4 + S.$$

The ferrous sulfate is then reoxidized by the iron-oxidizing bacteria to form more ferric sulfate, and the cycle is repeated. The elemental sulfur set free in the dissolution of the copper mineral is oxidized by the sulfur-oxidizing bacteria, Thiobacillus Concretivoues, in the presence of oxygen and water, to form sulfuric acid as shown in the following equation:

$$2S + 3\,O_2 + 2H_2O \xrightarrow{\text{Bacteria}} 2H_2SO_4.$$

The iron-oxidizing bacteria, Thiobacillus Ferrooxidan, and the sulfur-oxidizing bacteria, Thiobacillus Concretivoues, are present in the Miami solutions.

Miami reports assay values in terms of pounds per ton of solution. Practically, it is a simple term, because all pumps are rated in gallons per minute and we talk in gallons per minute and days. 1 gal = 8-1/3 lb; therefore 1 gpm for 24 hr = (8-1/3 × 1440/2000 = 6 tons.

Requirements: The Miami plant was designed to treat 2000 gpm and to produce 1,500,000 lb Cu per month or 50,000 lb Cu per day. Therefore

2000 gpm × 6 = 12,000 tons of solution per day

$$\frac{50{,}000}{12{,}000} = 4.17 \text{ lb Cu per ton of solution}$$

$$\begin{array}{rl} +0.04 & \text{Tail} \\ \hline 4.21 & \\ +0.07 & \text{Smelter Loss} \\ \hline 4.28 & \text{Required Assay} \end{array}$$

J. B. FLETCHER, Member AIME, is Leaching Superintendent, Miami Copper Operations, Cities Service Co., Miami, Ariz. SME Preprint 71AS40, AIME Centennial Annual Meeting, New York, March 1971. Manuscript, Nov. 6, 1970. Discussion of this paper, submitted in duplicate prior to Mar. 15, 1972, will appear in SME Transactions, June 1972, and in AIME Transactions, 1972, Vol. 252.

Leaching can best be thought of in four dimensions. The first two dimensions are the surface to be covered. We have approximately 5,000,000 sq ft to cover. One-half of the area was covered in the first 20 years of leaching. The entire area had been covered in the next four years. Since 1963, the entire area has been under leach.

Tailing water from the precipitating plant constitutes the most important source of leach solution. Water losses occur principally from evaporation and at Miami they approximate 10%. Fresh water is used as wash water in the precipitating plant and usually supplies the makeup water to maintain the 2000 gpm from underground. Acid is immediately added to the off-solution at the sump to bring the solution to 0.5 lb H_2SO_4 per ton of the solution. This keeps the iron from precipitating out, which gives us a clean sump, pump, and pipelines to the caved ground. This strength acid does not deteriorate the cement asbestos pipeline. When the solution reaches the caved ground it is measured in weir boxes and additional acid is added to bring the strength up to the acid required at each area. From this point on, the solution is carried in polyethylene plastic pipe to the point of application. We have used ponds, sprays and drill holes to introduce the solution to the caved ground. Due to the uneven surface slope encountered in the caved area, sprays are the most satisfactory. Sprays also allow the solution to be introduced slower than by ponding. Drill holes were used in an attempt to introduce the solution below the conglomerate cover east of the Miami fault.

The solution descends vertically from the point of application except where sealed off by the heavy gouge of the Miami fault. Holes that were drilled through this gouge leached an area approximately 50 ft in diam directly below the hole. To leach this area would required drilling on 50-ft spacing.

The third dimension is the amount of ore and waste to be penetrated. This averages about 600 ft. Of this 600 ft, the bottom 150 ft contains the mixture of ore and waste we are leaching. We try to maintain the underground collecting system so that we have a free flow of water in the main haulage ways and we have a few key sampling points.

The fourth dimension is the time factor. It takes from 3 to 4 weeks after a spray is turned on to the surface for it to come through on the 1000 level. The same spray will drop off in about 2 weeks after it is turned off.

The next point is how long can the spray remain at one place before the grade drops. This depends on the amount of ore in the area being leached. It is pracitcally impossible to correlate the mining extraction records with the material to be leached. So when a new area is to be leached, the spray is turned on and there is a waiting period of 3 to 4 weeks before a sample can be taken underground.

The sprays are left in one place until the grade from that area drops below 2 lb Cu per ton. The spray is then turned off and the area allowed to lie idle for a period of time. The rest and leach periods are alternated over and over. The second time over an area we can remain about one-half the time used originally and recover about one-half the amount of copper. The third time over it is one-half the second, the fourth is one-half the third, etc.

There are several explanations for this. During the rest period oxidation of the sulfides may take place, but since we are leaching with an acid ferric sulfate solution and from observed action on the surface it appears that a reverse capillary action is the best explanation. A copper-bearing boulder can be put in a flow of a leaching solution, then the solution removed, and as the boulder begins to dry, a copper oxide coating forms on its surface. When a copper-bearing rock is broken, it usually cracks on the mineralized seams and shows that the solution is actually penetrating the rock.

The sulfide areas do not give as high grade a pregnant solution as the oxide areas. The leaching of chalcocite, the predominate ore at Miami, seems to take two steps, which are expressed in the following reactions:

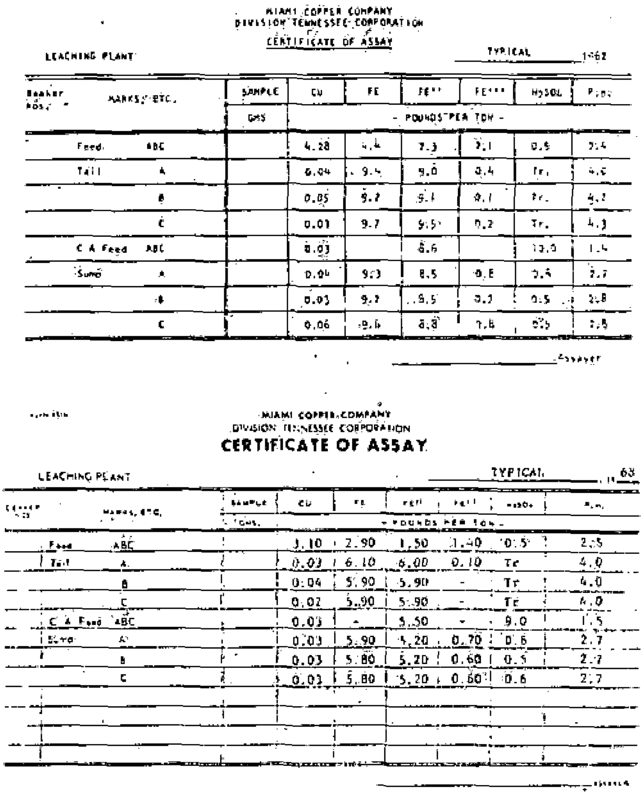
$$(1)\quad Cu_2S + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + CuS$$

$$(2)\quad CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S.$$

The first reaction takes place fairly rapidly. The second reaction is much slower. Chalcopyrite, a minor ore mineral at Miami, does leach but at a much slower rate.

The time to allow for an area to rest is difficult to determine due to the varying depth of the column being leached, and the type and amount of mineralization. With a depth of 600 ft, the minimum rest period seems to be one month.

To Jan. 1, 1970, the Miami mine has produced by leaching 261,000,000 lb of copper. The iron to copper ratio is 1.3 and the acid to copper ratio is 2.4, both figures based on *net smelter returns*. It is apparent that the largest factors affecting the cost per pound of copper are the iron and acid consumption. If the acid in the pregnant solution becomes too high, the iron consumption per pound of copper will go up. (The ferric iron in the pregnant solution also affects the iron consumption.) If the acid strength is too high, the gangue consumption of acid will go up. The acid strength is kept below 15 lb even in the high grade oxide areas unless the ore is very close to the surface. The time lag between the solution entering the caved ground and the same solution appearing underground where it can be sampled and assayed makes this problem of control difficult. The best way we have found is to keep graphs of the assays of the underground sample points. From these graphs we can check the



MIAMI COPPER COMPANY
DIVISION TENNESSEE CORPORATION
CERTIFICATE OF ASSAY

LEACHING PLANT — TYPICAL 1962

Beaker Nos.	Marks, etc.	Sample	Cu	Fe	Fe''	Fe'''	H_2SO_4	P.H.
		GMS	- Pounds per ton -					
Feed	ABC		4.28	4.4	7.3	[illegible]	0.5	[illegible]
Tail	A		0.04	9.4	9.0	0.4	Tr.	4.6
	B		0.05	9.2	9.1	0.1	Tr.	4.2
	C		0.01	9.7	9.5	0.2	Tr.	4.3
C A Feed	ABC		0.03		8.6		13.5	1.4
Sump	A		0.04	9.3	8.5	0.8	[illegible]	2.7
	B		0.03	9.2	8.5	[illegible]	0.5	2.8
	C		0.06	9.6	8.8	[illegible]	0.5	2.8

Assayer

MIAMI COPPER COMPANY
DIVISION TENNESSEE CORPORATION
CERTIFICATE OF ASSAY

LEACHING PLANT — TYPICAL 19 68

Beaker Nos.	Marks, etc.	Sample	Cu	Fe	Fe''	Fe'''	H_2SO_4	P.H.
		Tons.	- Pounds per ton -					
Feed	ABC		3.10	2.90	1.50	1.40	0.5	2.5
Tail	A		0.03	6.10	6.00	0.10	Tr	4.0
	B		0.04	5.90	5.90	-	Tr	4.0
	C		0.02	5.90	5.90	-	Tr	4.0
C A Feed	ABC		0.03	-	5.50	-	9.0	1.5
Sump	A		0.03	5.90	5.20	0.70	0.6	2.7
	B		0.03	5.80	5.20	0.60	0.5	2.7
	C		0.03	5.80	5.20	0.60	0.6	2.7

Assayer

Fig. 1—Typical assay reports for 1962 and 1968.

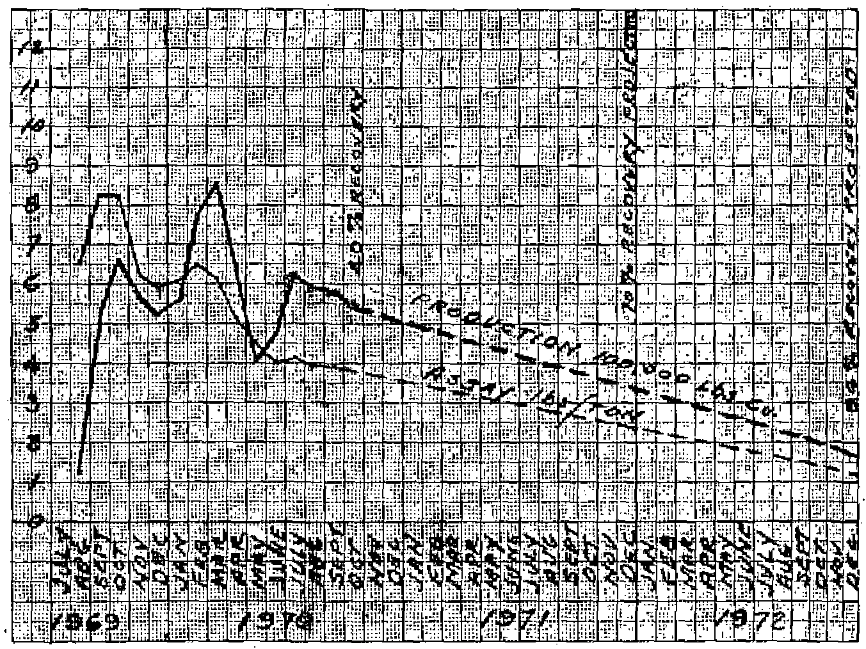


Fig. 2—Assay and copper production by months from start (1969) to November 1970 with a projection to 1972, Miami mine.

trend and anticipate a drop in grade or a decrease in acid consumption.

The operation since 1963, the time when no new areas to leach were added, shows a gradual drop in grade of the pregnant solution from 4.03 lb per ton in 1963 to 3.10 lb per ton in 1968.

Iron salts do precipitate as the solution goes through the caved material. From the assay report, Fig. 1, it can be seen that iron loss from the cave area feed to the precipitation plant feed is 4.2 lb Fe per ton of solution to 1962. In 1968 the loss is 2.6 lb Fe per ton of solution. It has been our experience that there is no plugging action of the cave ground from these basic iron salts. It is not known where the iron precipitates, but is probably high in the column.

Since the tail solution from the iron launders is to be recirculated the argument always occurs; why make a good recovery? It has often been proposed to recirculate low grade solution back through the same area (with addition of acid) in order to upgrade the solution to the iron launders. A strike was called at Miami in August 1954. The pregnant solution was pumped from the mine and stored in a pond on the mill tailings dam. In September this solution, which assayed 5 lb Cu per ton, was pumped back to the leaching areas, more acid was added, and sprayed back on to areas. No pickup in the pregnant solution was noted in the following months. The pregnant solution from the mine continued to assay 5 lb per ton as it had prior to the strike. Miami was again on strike in 1967. Only the minimum amount of washing of the iron launders was allowed. The assay results in Table 1 show that recirculation did not upgrade the solution.

Acid was added to bring the acid strength of the recirculated solution to the normal spray solution.

Miami Copper has two other properties, Castle Dome and Copper Cities, where dump leaching is carried on. In both operations the dumps contain enough pyrite so that acid is not required for leaching. No. 14 dump at Copper Cities mine was producing a low grade solution. In December 1964 it was decided to try recirculating No. 1 dam pregnant solution over this dump with the hope that the Fe''' and H_2SO_4 in the solution would help the leaching. On Dec. 21, 1964, 500 gpm of No. 1 dam solution was started on the dump. The assays for the month of January 1964 showed the results given in Table 2.

From Table 2 it is apparent that no copper is being leached from the dump to date. The copper assay shows such a small drop that it could be in assaying. The only positive reaction is the loss of iron in the dump. The assay from this dump the last time it was run (October 1964) with tail solution is given in Table 3.

In 1969 a portion of the Miami ore body that was too low grade to mine by caving, was mined by open pit and dumped into the caved area adjacent to the mining area. This resulted in 200,000 sq ft of level area ideal for leaching, containing 1,348,172 tons assaying 0.78% total Cu, 0.59% oxide Cu, and 0.19% sulfide Cu or 21,000,000 lb Cu. The solution came through to the 1000 level and mixed with the solution from other parts of the mine. However, we were able to weir and assay this solution. From the results obtained from this area a close approximation of the overall recover can be made. The graph (Fig. 2) shows assay and copper production by

Table 1. Assay Results in 1967

Year 1967	Cu Assay, Lb per Ton Feed to Plant	Cu Assay, Lb per Ton Recirculated Tail Solution
July	2.73	0.05
August	2.69	1.04
September	2.29	1.37
October	2.40	1.07
November	2.30	1.08
December	2.40	0.75

Table 2. Copper Cities Dam No. 1 Assay Report, January 1964

	Gpm	Tons	Assay	Lb Cu	Fe	H_2SO_4
To Dump	477	88,722	1.59	141,067	1.09	0.35
From Dump	396	73,656	1.58	116,376	0.42	0.24
Difference	81	15,066	0.01	24,691	0.67	0.11

Table 3. Copper Cities Dam No. 1 Assay Report, October 1964

	Cu Assay	Fe	H_2SO_4
To Dump	0.01	3.03	0.00
From Dump	1.10	0.20	0.10
Difference	1.09	2.83	0.10

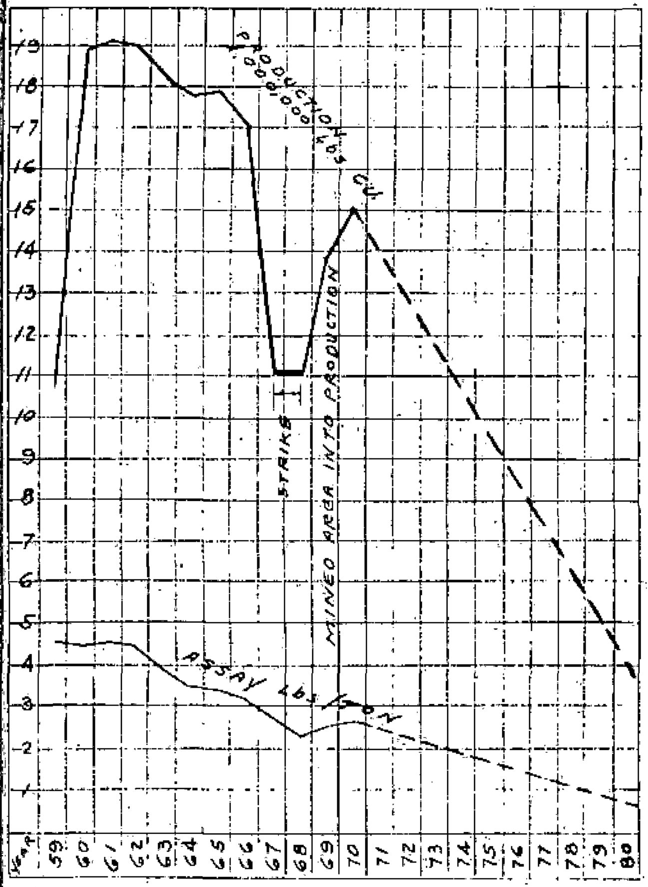


Fig. 3—Projected assays and production, with flow of 2600 gpm, Miami mine.

months from the start to November 1970 with a projection to 1972. The maximum flow that can be sprayed on this area without excessive pooling is 900 gpm. This gives a flow rate of 0.45 gpm per 100 sq ft with a loss of 10% by evaporation and gives a recovery of 800 gpm from this area.

Although the plant was designed for a flow of 2,000 gpm, as the grade dropped the flow was increased in order to keep the production as high as possible. At the present time 2600 gpm is the maximum flow without major changes in the pumping system and precipitation plant. With the 5,000,000 sq ft of area available, if the entire area were covered, it would give a flow rate of 0.052 gpm per 100 sq ft. Using 2600 gpm, a graph of the projected assays and production was made (Fig. 3).

Assuming the following cost and the projected production of 4,000,000 lb for 1980, the economics would be as follows:

Assumed Cost:	Acid	\$25.00 ton, 1.25¢ per lb
	Iron	\$64.00 ton, 3.2¢ per lb

Iron to Cu ratio: 2 (as the grade of the solution decreases, the iron consumption increases due to Fe‴)

Acid to Cu ratio: 2.3

Gives:

1.25¢ × 2.3	=	2.875¢ per lb Cu
3.2¢ × 2	=	6.400¢ per lb Cu
Freight, Smelting, and Refining	=	7.00¢ per lb Cu (Assumed)
Total Fixed Cost		16.275¢

As the production drops, the manpower could probably be cut. But for this study, assume an operation cost of \$3000 per day which would include labor, power, taxes, overhead, etc. Using the projected copper production of 4,000,000 lb for the year 1980 gives:

$$\frac{4{,}000{,}000}{365} = 10{,}959 \text{ lb Cu per day}$$

$$\frac{\$3{,}000}{10{,}959} = 27.375¢ \text{ per lb Cu}$$

16.275¢ + 27.375¢ = 43.65¢ total cost per lb Cu for the year 1980.

Therefore, the ultimate recovery will depend on the price of copper.

The 1,348,172 tons mined in 1969 were dumped into an area of 200,000 sq ft with an average depth of 135 ft. From this dump it is projected to have a recovery of 80% in 3 years. If the area could have been doubled, 1800 gpm of solution could have been sprayed on the dump with a quicker recovery. This dump was mostly oxide which gives a comparably rapid recovery. The ore broke fairly fine with very few rocks over 12 in. in diam.

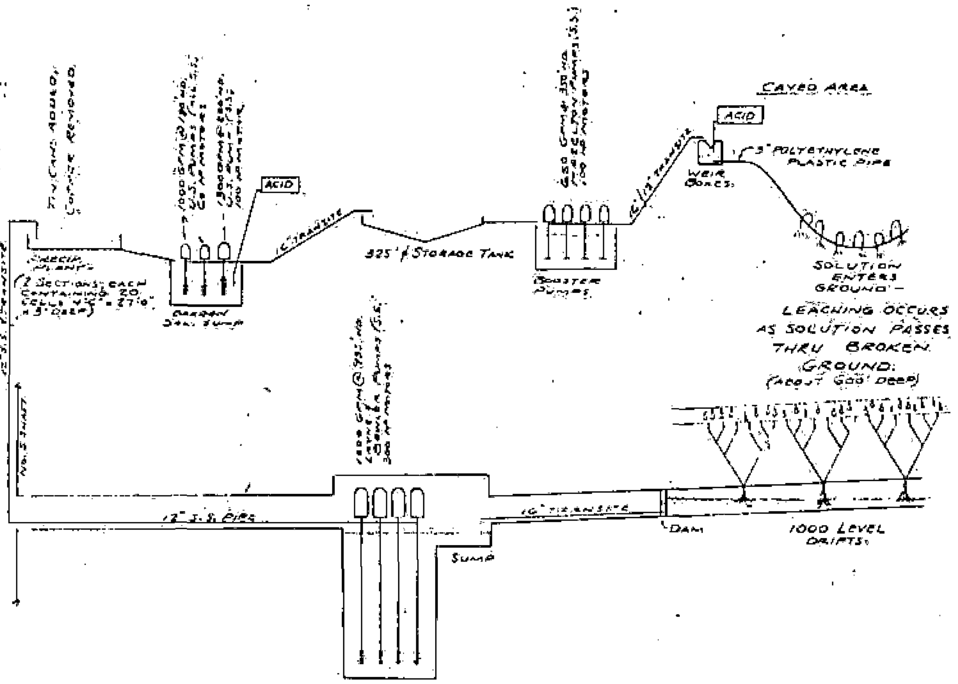


Fig. 4—Schematic of leaching at Miami Copper unit. All pumps are type 316 SS.

Table 4. Operating Crews for Miami Leach Operation

Precipitating Plant, 7-day operation	1 Operator or pumpman	3 shifts
	1 Equipment operator	Day shift
	1 Cave area pumpman	Day shift
	3 Cell washers	Day shift
	1 Foreman	Day shift
Underground, 5-day operation	3 Timber crews, 8 men	Day shift
	2 Hoist engineers	Day shift
	1 Foreman	Day shift
Maintenance crews from Copper Cities, 5-day operation	1 Pipeman	Day shift
	1 Machinist	Day shift
	1 Mechanic	Day shift

At the Copper Cities mine, as the dump material came from lower in the mine, where chalcopyrite was the main mineral, the rate of recovery dropped rapidly. At Castle Dome mine, at the toe of the dumps, which are composed of large boulders, leaching is very slow.

The precipitating plant at Miami is similar to others in the southwest. The only difference is the method of cell loading. Detinned shredded cans are received by rail and unloaded by a magnet. The magnet drops the cans into a hopper which feeds a belt conveyor. The belt travels over the center of the cells and by means of a traveling tripper the cells are evenly charged with iron. The precipitated copper is washed from the cans through wooden screens by high pressure water. The precipitates discharge onto a decant slab. Washing is done on the day shift only. Solutions are drained from the precipitated copper and pumped back to the cells on the afternoon shift. The copper is moved from the decant slab to a drying slab early the next morning before washing begins. The copper is moved with a front-end loader. The same loader loads the dry copper into the railroad car. The copper is shipped to the smelter at Douglas.

The plant operates every day in the year. The copper recovery at the plant is 99% or 0.04 lb Cu per ton of solution tail. The precipitates shipped average 23.5% moisture and assay 79% copper.

The operating crew of the plant is listed in Table 4.

The overall recovery by leaching at Miami will be impossible to determine as we do not know exactly how much copper we had at the start. A percent recovery figure for leaching is a misleading figure. A 50% recovery of a 1% ore body would be poor.

The first 15% or 20% of the copper in place is very easy to recover. It is only possible through careful attention to details to maintain a steady production and to get a good overall recovery by this method.

To give a complete picture of the leaching at Miami, a flowsheet (Fig. 4) and two typical assay reports (Fig. 1) are included.

Summary and Conclusions

1) Leaching in place of a block caved mine recovers the remaining copper.

2) Oxide minerals leached with H_2SO_4 solution.

3) Ferric sulfate solution is necessary for leaching sulfide minerals and can be obtained by utilizing the action of bacteria on the ferrous solution from the iron launders.

4) There is no plugging of the ground by disposition of iron salts from the reclaimed solution.

5) Sprays were found to be the most economical and simplest way to introduce solution to the caved area.

6) Recirculation does not upgrade the solution; therefore, a good stripping of the solution in the iron launders is good practice.

7) A rest period is utilized to induce reverse capillary action.

8) Rate of leaching is controlled by the size of the material, type of mineralization, and the area available.

9) The economical end point and recovery can be closely predicted by graphs of the leaching.

TECHNICAL NOTE

Size Distribution General Law of Fragments Resulting from Rock Blasting

by C. Dinis da Gama

In mining, all unit operations are closely interrelated, and the results of blasting are probably the key factor within that sequence.

The drilling program prior to blasting is just as dependent upon the desired rock fragmentation as are the loading, hauling, and mechanical crushing operations which are economically and technically influenced by the results of blasting, namely, the size and scatter of the product.

What is known today as optimum blasting is the process of designing a blast in order to obtain a certain degree of fragmentation so that overall mining costs are minimized. Applying this criterion often results in a different program than when an individual blasting pattern is chosen only on the basis of the lowest operational cost for that pattern, disregarding what comes before or after the blast. Fig. 1 shows the characteristic variation of mining unit costs with the degree of fragmentation, or the maximum size of blocks obtained from blasting.[2] From the figure, it can be seen that optimum breakage must correspond to the lowest total costs, but reducing drilling-blasting costs only does not achieve such an optimum solution.

Methods of designing surface or underground blasting operations should comply with the optimization criterion, but this compliance is feasible only if a detailed mining system analysis is available. Therefore, predictions of costs of loading, transporting, and mechanical breakage of ore as a function of its size will define a narrow range of variation for drilling and blasting parameters in order to get the minimum total costs.

C. D. DA GAMA, Member AIME, is Assistant Professor, University of Luanda, Angola, Portugal. TN 71AM203. Manuscript, Jun. 19, 1971.

Table 1. Summary of Dewatering Systems at Pine Point Mines, January 1970

Ore Pit	T, Gpd per Ft	S	Number of Wells Drilled	Number of Wells Pumping	Pumpage, Mgd	Drawdown, Ft
N-42	54,000	0.015	6	2	2.2	70
O-42	72,000	0.035	9	9	10.1	73
J-44	±25,000	±0.02	10	10	10.8	71
X-15	34,000	0.006	12	11	7.9	57
K-57	40,000	0.001	10	6	7.9	51
Total			47	38	38.9	

was run under carefully controlled conditions for a total of 17 days. A single well was pumped to waste at 1140 gpm for 13 days and then a second well was turned on at 750 gpm for 4 days. During the entire test period, drawdown measurements were made in the two pumping wells and in 10 observation wells. After 2½ weeks of pumping, about 15 of the required 40 ft of dewatering had been achieved in the center of the ore pit.

Extrapolation of the pumping-test data was done largely by methods described by Cooper and Jacob,[1] to provide a basis for dewatering design. A pattern of six production wells was recommended to provide rapid and complete dewatering at all points of the ore pit, with an adequate safety factor for equipment breakdown. After the additional wells were drilled, a delay in the mining schedule provided sufficient time so that only three of the wells were required to complete the necessary dewatering.

Pumping-test methods were applied to two deep pits by mine personnel and the designs were reviewed by our firm.[2] The testing conducted by mine personnel produced highly satisfactory results. By 1969, the extent of dewatering operations was such that the mine added a hydrogeologist to the staff.

The scope of dewatering at Pine Point Mines is indicated by Table 1, which gives design parameters and results as of January 1970. Ore pits as large as 2000 by 3000 ft in areal extent are being dewatered by peripheral wells. Plans calling for development of new ore pits having several benches that require dewatering will result in greater pumpage in the future.[3] The differences in aquifer transmissibility and storage characteristics highlight the need for individual testing of each ore pit. Costs of dewatering are reported to total 30¢ per ton of ore mined in 1969. These costs are about one-third capital expenditure and two-thirds operating costs.[4]

The results demonstrate that dewatering of open pit mines may be accomplished in a satisfactory manner by high-capacity peripheral wells, provided hydrogeologic conditions are favorable. The separation of such wells from the immediate area of mining activity provides advantages of efficiency, equipment protection and operating convenience. In cold climates, peripheral wells do not have troublesome freeze-up problems during equipment failure that may be experienced with central sump-pump systems in exposed open pits.

Aquifer testing by conventional and relatively simple methods can provide data for dewatering design. Testing programs may be tailored to the hydrologic and economic scope of the ground-water problem. Pumping-test methods permit proper selection of well spacing, aid in production-well design and provide a basis for pump selection; all features that result in efficient and economical dewatering.

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DISCUSSION

In-Place Leaching at Miami Mine, Miami, Arizona

by James B. Fletcher

Transactions SME/AIME, Vol. 250, No. 4, December 1971, pp. 310-314

Harmon E. Keyes (*Chemical & Metallurgical Engineer, Eagar, Ariz.*)—Chemical dissolution of chalcocite by acidic ferric sulfate is well known. Resulting elemental sulfur may be oxidized to sulfuric acid by heated ferric sulfate. Laboratory tests at Southwest Experiment Station, USBM, Tucson, generally confirmed stoichiometric relations of 1 part Cu dissolved to 1.750 parts ferric iron reduced, using CP chemicals, dried ore samples, and apparatus cleaned with potable water. Recirculation with open-drainage percolation to increase copper in leaching solvent was followed successfully when appropriate, both in laboratory and Pinto Valley pilot tests.[1]

Before 1924 attempts to produce ferric sulfate by aerating ferrous sulfate solution were known. Initial oxidation was satisfactory, but rate slowed below practicality as oxidation progressed and acidity increased. Also, due to hydrolysis of ferric sulfate, a ferric precipitate of hydroxide and basic sulfate resulted. Both laboratory and pilot plant tests gave similar results, regardless of whether CP ferrous sulfate or scrap iron cementation discard solution was used.

Rapid oxidation of ferrous hydroxide by air alone is well known to analytical chemists. I demonstrated a process to produce acidic ferric sulfate solutions by precipitating ferrous hydroxide with milk of lime, aerating to form ferric precipitate in matter of minutes, dissolving ferric precipitate with sulfuric acid, and separating the calcium sulfate precipitate. Limestone can be used under similar conditions.

A USBM project was demonstration of a cheap method to produce acidic ferric sulfate solution applicable to leaching chalcocite. The well-documented[2] mixed ore acidic ferric sulfate leaching and electrolysis process at Inspiration was beyond the scope of smaller installations.

The SW Experiment Station, USBM, prior to 1924, proved that acidic ferric sulfate solutions could be produced by aerating ferrous sulfate solution with sulfur dioxide and excess of finely divided air.[3] About 1925 a cooperative agreement was arranged with Pinto Valley Co. Investigations were made and complete pilot plant erected and operated at this company's Castle Dome mine near Miami, Ariz. An objective was accelerating heap leaching of crushed chalcocite ore to compete with vat leaching rates, thereby eliminating tight vats. Stoichiometric relation of ferric iron-copper sulfate was contemplated.

This pilot demonstration[1] noted acid consumption consistently higher than in laboratory tests. Calculations showed that ferric sulfate was regenerated in the leaching columns, giving a higher ratio of copper leached to ferric iron reduced than stoichiometric conditions or previous laboratory tests indicated. This regeneration of ferric iron usually varied inversely with increased percolation rates. Estimates gave possibility of leaching crushed chalcocite ore in about six months, adding acidified *ferrous* sulfate. Accordingly, a patent was issued to Garret Mott, president, and assigned to Pinto Valley Co. about 1928. This covered regeneration of ferric sulfate in heaps.

Independent of these investigations further evidence was secured proving increasing stability of state of iron oxidation as acidity increased, and vice-versa. Research by me on regeneration of waste steel plant pickling liquors in Pennsylvania, about 1939, showed that ferric iron in acid of 10 to 20% strength resisted reduction to ferrous with SO_2 of sulfur burner concentration. A previous book on "inhibition of chemical reactions" verified this conclusion. Contacting this acidic ferric sulfate with SO_2 and activated carbon achieved successful reduction.

The foregoing illustrations show pH as a major factor in controlling oxidation or reduction of iron in sulfate solutions. If iron is oxidized in a separate circuit, ferric precipitate can be dissolved by acid and applied to leaching at any desired strength of acid or ferric iron.

Noteworthy advances in microbiological leaching give new evidence on sulfide extraction.[4-6] However, the unexpected ratio of copper dissolved to ferric iron reduced, demonstrated by Pinto Valley Co. at Castle Dome mine during 1926-27, probably furnished the first documented quantitative account of what now is recognized as biological acceleration of chalcocite leaching.

Local conditions may determine whether direct chemical action with ferric sulfate or biological effects dominates heap leaching of chalcocite.

In conclusion, as stated by Mr. Fletcher[6], a controlling leaching factor is rate ingress and egress of the solution along the mineralized veinlets of an ore boulder. This, and many other variables, may offset differences in effectiveness of various leaching agents.

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Cost of Reclamation and Mine Drainage Abatement, Elkins Demonstration Project

by R. B. Scott, R. C. Wilmoth, and R. D. Hill

A cost breakdown is given for reclamation and mine drainage abatement conducted by the Federal Water Quality Administration's demonstration project near Elkins, W. Va. Costs for construction of control measures have been developed and include backfilling strip mines, sealing subsidence areas, reconstructing stream channels, and installing mine seals to prevent the entrance of water and air.

Acid mine drainage, discharging from coal beds, has polluted our streams and rivers since early times. These pollutants affect water quality by lowering the pH, reducing natural alkalinity, increasing total hardness, and adding undesirable amounts of iron, manganese, aluminum, and sulfates. The tangible damages are the costs involved in replacing equipment corroded by the acid water, additional treatment costs at municipal and industrial water treatment plants, and damages resulting from corrosion of steel culverts, bridge piers, locks, boat hulls, steel barges, pumps, and condensers. Intangible damages, which are real and important, include destruction of biological life of the stream, reduced property values, and streams rendered undesirable for recreational uses.[1]

The major problems of mine drainage occur in the anthracite and bituminous coal regions in Appalachia. However, many of the western mining states have significant mine drainage problems in specific areas, but

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R. B. SCOTT, R. C. WILMOTH, and R. D. HILL, are with Federal Water Quality Administration, U.S. Dept. of the Interior, Elkins, W.Va. SME Preprint 70AG349, SME Fall Meeting, St. Louis, Mo., Oct. 1970. Manuscript, Sep. 23, 1970. Discussion of this paper, submitted in duplicate prior to Sep. 15, 1972, will appear in SME Transactions, December 1972, and in AIME Transactions, 1972, Vol. 252.

IN-PLACE LEACHING RESEARCH AT THE SENECA MINE, MOHAWK, MICH.

by

Peter G. Chamberlain

April 1977

Presented before the Annual Spring Technical Meeting of Upper Peninsula Section, AIME, Michigan Technological University at Houghton, Mich., April 21, 1977.

IN-PLACE LEACHING RESEARCH AT THE SENECA MINE, MOHAWK, MICH.

by

Peter G. Chamberlain[1]

ABSTRACT

The Bureau of Mines is conducting a broad research program to promote in-place leaching of mineral values from ore deposits. One project within that program was designed to develop technology for in situ leaching of ore in underground mines. In this project the Bureau of Mines, in cooperation with Homestake Copper Co., attempted to develop a method of confined blasting suitable for use in underground mines that would create enough fracturing in the native copper ores to permit leaching. Results of tests conducted at the Seneca mine, Mohawk, Mich., indicated that confined blasting without void space to break the rock into is not a practical scheme for preparing deep ore bodies for leaching if the formation is relatively impermeable.

INTRODUCTION

The Bureau of Mines is conducting a broad research program to stimulate in-place leaching operations in the country. Leaching is commercially feasible in dump and heap leaching operations; in situ leaching has been applied with some success to near-surface deposits. Research at the Twin Cities Mining Research Center focuses on fragmenting ore bodies for leaching at surface, shallow, and deep depths. Current and past Bureau research projects in Arizona (1, 3)[2] have provided technology for fragmenting surface and shallow ore bodies for leaching. The work described in this presentation was an attempt to develop a method of fragmenting deep ore bodies for subsequent leaching (Overhead 1).

Access to the ore presents a major obstacle to widespread consideration of leaching deep deposits in-place. There are many ore bodies, particularly on the fringes of old mining districts which are too low grade for conventional mining and too deep to fragment for leaching from surface blastholes. In the project that is the subject of this presentation, the primary interest was developing ore bodies where access is gained via conventional underground mine development openings.

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[1] Geophysicist, Twin Cities Mining Research Center, Bureau of Mines, U.S. Department of the Interior, Twin Cities, Minn.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The Bureau's research in developing a system for fragmenting deep ore bodies for leaching required a suitable field test site. Since Homestake Copper Co. has had an interest in evaluating the leachability of the native copper ores in the copper mining district of Upper Michigan and since that district represented the closest suitable test site for the Bureau's research, the two parties entered into a cooperative agreement for the research (Overhead 2). Homestake's contribution consisted of providing a test site in an underground mine, renovating the site into usable condition, and providing a limited amount of support for the operations. The Bureau designed and conducted all research in the mine and provided most of the services associated with the operations. A service contract was subsequently awarded to Michigan Technological University, Institute of Minerals Research, to perform laboratory "vat" leaching tests, porosity and permeability tests, water analyses, and emergency machine-shop work.

The research approach emphasized developing blocks of virgin ore for leaching rather than leaching existing stopes filled with rubblized gob. Two basic approaches were originally conceived for fragmenting deep ore bodies for leaching--confined blasting from drifts and blasting to relief provided by raises or other mine development openings (Overhead 3). For ease and economy, confined blasting was selected as the first research effort. It was hoped that confined blasts could break rock sufficiently even without swell space to permit leaching fluids to flow through the ore body. Such a system would be much easier to establish than a fragmentation system predicated on removing a percentage of the ore to create appropriate swell space. This presentation will provide results of tests conducted at the Seneca mine to determine the possible application of confined blasting for preparing an ore body to be leached.

SITE SELECTION AND PREPARATION

The resident geologist for Homestake Copper made the preliminary site evaluation. The Kearsarge amygdaloidal basalt seemed the most desirable geological setting for a test site based upon remaining reserves, relatively recent workings which provided access to the ore, and water levels below any potential working locations. After several mines situated on the Kearsarge ore body were visited by Homestake and Bureau personnel, the Seneca No. 2 Mine, third level, was selected as the best test site. The mine had been abandoned since the mid-1960's--no surface facilities were available.

The geology of the district is a series of basaltic flows--often interspersed with conglomerate beds--which were tilted subsequent to their extrusion and now dip toward Lake Superior. In the Seneca mine, the copper occurred in the amygdaloidal top of the Kearsarge basalt. The dip of the flow is about 37° in the mine. Since no stopes are present, the third level of the mine apparently did not contain significant amounts of copper. The drift was surveyed with a metal detector by Homestake to locate copper so that a test site with typical mineralization could be selected.

A mining crew from Homestake rejuvenated the surface facilities at the mine so that it could be used as a test site. Shelters were constructed for the Bureau's air compressor and for a small hoist. Airlines and waterlines were installed down to the third level where a plat was constructed. A man-car brought to the site was modified so that equipment could be easily lowered to the third level. A small amount of retimbering was necessary to restore the shaft.

After Homestake had reconditioned the mine to the third level, a Bureau crew laid airlines and waterlines along the drift to the test site. As a final step preparatory to the research, fractures and joints traversing the test site were mapped.

TEST PROCEDURES

The first research efforts at the Seneca mine were to determine natural permeability, porosity, and fracture characteristics of the amygdaloidal basalt before blasting. These data provide baseline information for evaluating the effects of the blasting schemes tested. They also identify any problems in containing leaching fluids within a specified area in the mine. Several core holes were, therefore, drilled down-dip into the formation for porosity and permeability tests.

Effective porosity was determined by forcing a given amount of compressed air into the formation at a known pressure to estimate the length of paths over which the pores in the formation were interconnected (Overhead 4).

Several schemes for measuring permeability were tested in the core holes. The method which seemed to give best results employed a mechanical packer to seal the hole (Overhead 5). Water was then forced into the formation from the hole at a constant pressure (arbitrarily selected from 60 to 80 psi); the volume of water injected into the formation was recorded as a function of time. Where the extreme "tightness" of the formation precluded measuring injected water with standard water meters, calibrated beakers were used to catch water outflow from adjacent holes and hence determine the volume of water flowing between holes with respect to time.

Baseline fracture characteristics of the formation were obtained from two sources--geological mapping of joints in the drift and analyses of fractures in cores retrieved during drilling. Although mapping is familiar to most attendees at this meeting, analyzing drill cores for fracture characteristics may not be. Over the years the Bureau has determined that the rock quality designation (RQD)--the percentage of core pieces at least 4 inches long--and the average length of core pieces over 1 inch long have given the best quantitative characterizations of fracturing in rock. The number of core pieces in each of several size ranges can be plotted to provide an in-place fragment size distribution profile. A more detailed description of fracture analyses from cores can be found in reference 3.

The basic approach to confined blasting was to drill and shoot blastholes drilled down dip into the formation from the third level drift, located 280 feet below the surface. Parameters such as hole depth, hole diameter, hole spacing, explosive type, and stemming were considered in designing a blast that would break rock without moving it. Hole depth was set at 40 feet; this would minimize the effects of the drift on the blast yet keep drilling costs within the research budget. A 3-inch hole diameter was then selected based on the expected range of burdens associated with the 10-foot ore zone thickness. Finally, a slurry blasting agent suitable for wet conditions was chosen for the shots with a 20-foot powder column and 20 feet of water stemming (Overhead 6).

The only significant blasting parameter remaining for evaluation in the tests--blasthole spacing--held the key to economic feasibility of confined blasting. If the blastholes had to be drilled very close together to create adequate permeability for leaching, confined blasting would be uneconomical. To evaluate fracturing and permeability as a function of blasthole spacing, a blast incorporating three different triangular blasthole patterns was designed (Overhead 7). This design, used successfully in earlier projects in Arizona, permits evaluation of three patterns with only seven holes instead of the nine required for three totally isolated patterns. In addition, three patterns in such a configuration will be affected by fewer variances from geologic inhomogeneities than would three separate patterns. The interaction between shots from adjacent patterns also closely approximates the interaction that would occur in a production blast consisting of many blastholes detonated in one shot.

The three ratios of burden/blasthole-diameter selected for the test series were 10, 14, and 18. These ratios corresponded to blasthole spacings of 2-1/2, 3-1/2, and 4-1/2 feet. The calculated powder factors in the ore around the loaded portions of the blastholes were 8, 4, and 2-1/2 lb/ton, respectively. Three-inch coreholes accordingly were drilled in triangular patterns at the desired spacings with a rotary, pneumatic drill for blasting. Core obtained from these holes was examined for the fracture analysis; permeability tests were also conducted in the blastholes before shooting. Borehole deviation was surveyed to determine the actual blasthole spacing present in the loaded portions of the holes.

After permeability tests were completed, the holes were bottom primed with three 1-inch sticks of power primer. The holes were hand-loaded with three 30-pound bags of water gel in each, which created a 22-foot explosives column. Since the holes were filled with water while the gel was being poured, the water stemming was automatically applied. All three interconnected patterns were detonated in one shot using electric blasting caps.

The fragmentation effectiveness of each blasthole spacing was evaluated with postshot core holes drilled in the center of each triangular pattern. Fracturing in the core was then compared with that in the preshot core: the permeability was also then determined in the postshot core holes for comparison with preshot measurements.

Dyes were injected into the formation after the shot to locate fracture zones capable of transmitting fluids. A two-component fluorescent dye, zinc 8-hydroxyquinolate, was forced from the upper three blastholes to the lower row of holes before the core holes were drilled in the center of each blast pattern. It was hoped that the dye would appear in the postshot core to identify fluid carrying fractures.

DISCUSSION OF RESULTS

All preshot tests and analyses pointed to a "tight" impermeable formation that contained few fractures. Crude measurements of permeability ranged from 0 to 1.5 ft/yr (1.5 millidarcys)(table 1). One major fracture traversing the test zone apparently communicated with the surface ground water supply since it "made" water even before blasting. The test zone had a high RQD and a high average size of core pieces over 1 inch long. Both of these measurements indicate a very competent formation. Effective porosity tests showed that the pores were interconnected for an average of only 1 inch away from the core holes.

The deviation survey indicated that in the powder column, the actual hole spacing was 2-3/4, 3-1/4, and 4-3/4 feet. Blasting did create new fractures, particularly at the closer spacings with their associated high powder factors (Overhead 8). The RQD and average piece length from the postshot core shows a definite trend towards increased fracturing at the 2-1/2- and 3-1/2-foot spacings when measurements on postshot core are normalized to those of the preshot core. At the 4-1/2-foot spacing, no fracturing could be observed. The high scatter in data associated with such a test blast precludes absolute quantification of the fracture damage.

The permeability changes created by the fracturing were disappointingly small. Even with injection pressures of 80 psi, very little fluid could be pushed from one hole to the next. Permeabilities of at least 500 ft/yr (or 500 millidarcys) are normally desired for leaching. Since the best permeability achieved with the close spacings was only 40 ft/yr (40 millidarcys), blasting simply did not create enough permeability to consider leaching. Furthermore, studies of the postshot core to locate fractures containing dye injected into the formation revealed only one 2-foot fracture that contained any traces. The remainder of the core from all three postshot core holes showed no evidence that dye had been transmitted through the formation.

SUMMARY

Confined blasting did not provide an adequate network of permeable cracks for leaching. Although the studies indicated fracturing with closely spaced blastholes, the fractures apparently cannot transmit fluids because the overburden pressure effectively reseals them. It would seem logical, therefore, that if a mining company wished to consider leaching a deeply buried ore body, any of three conditions must be present: (1) Fragmentation must take place where significant swell space allows the rock fragments to jostle and realine themselves; (2) leaching fluids must be injected at pressures significantly higher than stresses from overburden to force open the fractures; or (3) the formation must be permeable enough for leaching without appreciable new fractures. Permeable deep formations occur primarily in sedimentary rocks--uranium deposits in sandstones frequently can be leached without fragmentation. Hydraulically "jacking open" fractures created in a formation is technically feasible. A production leaching operation employing high pressures would, however, be very expensive and much more dangerous than low-pressure systems. Further research in preparing impermeable formations for in situ leaching at depth must, therefore, concentrate on methods whereby significant swell space is provided to allow the fragmented rock to expand and realine.

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DEEP LEACHING

PROBLEM

- Preparing deep ore bodies

OBJECTIVE

- Develop economic fragmentation techniques

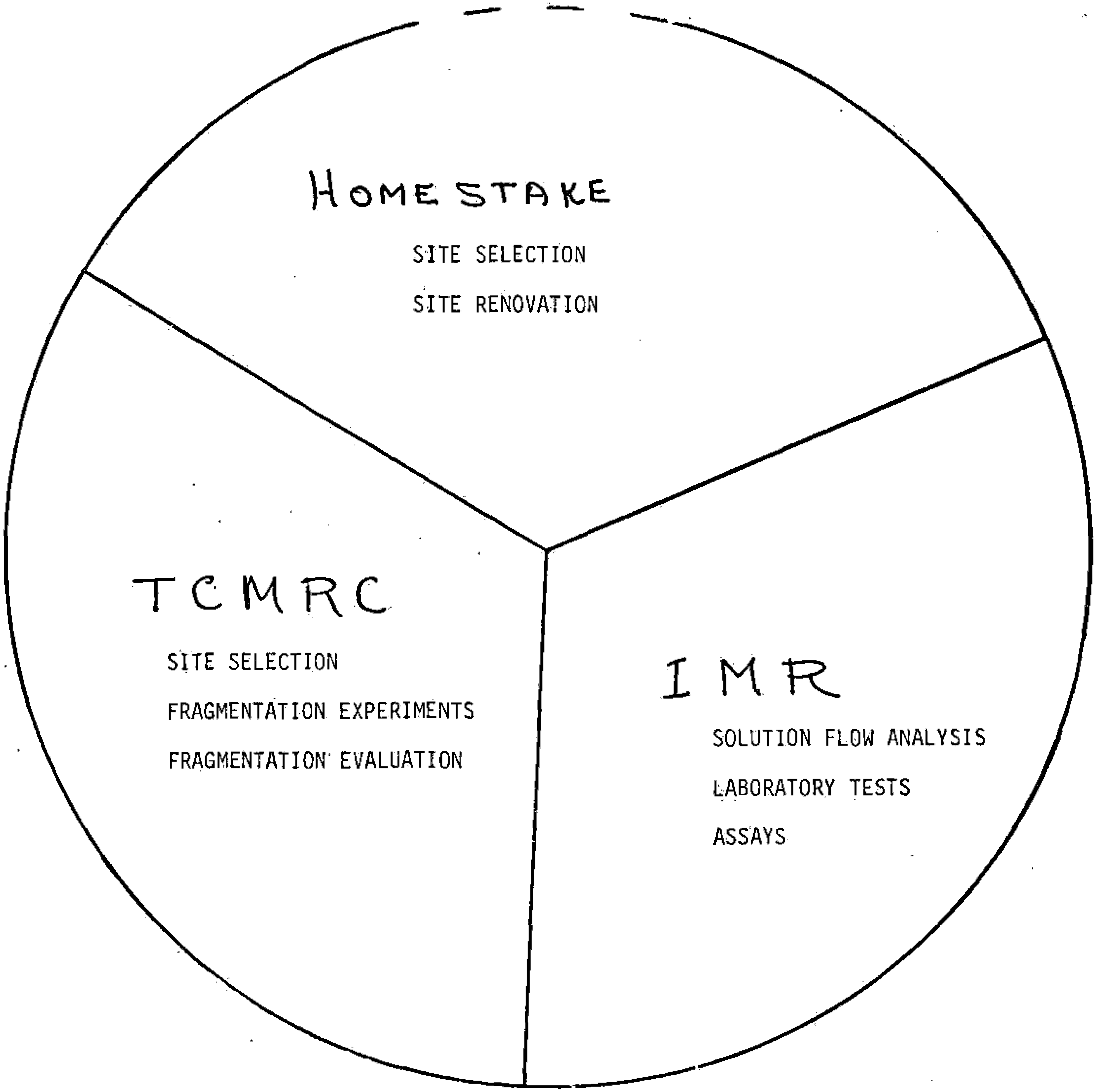
PRODUCT

- Fragmentation technology costs

BENEFICIARY

- Mine operators
    - Copper
    - Uranium
    - Gold

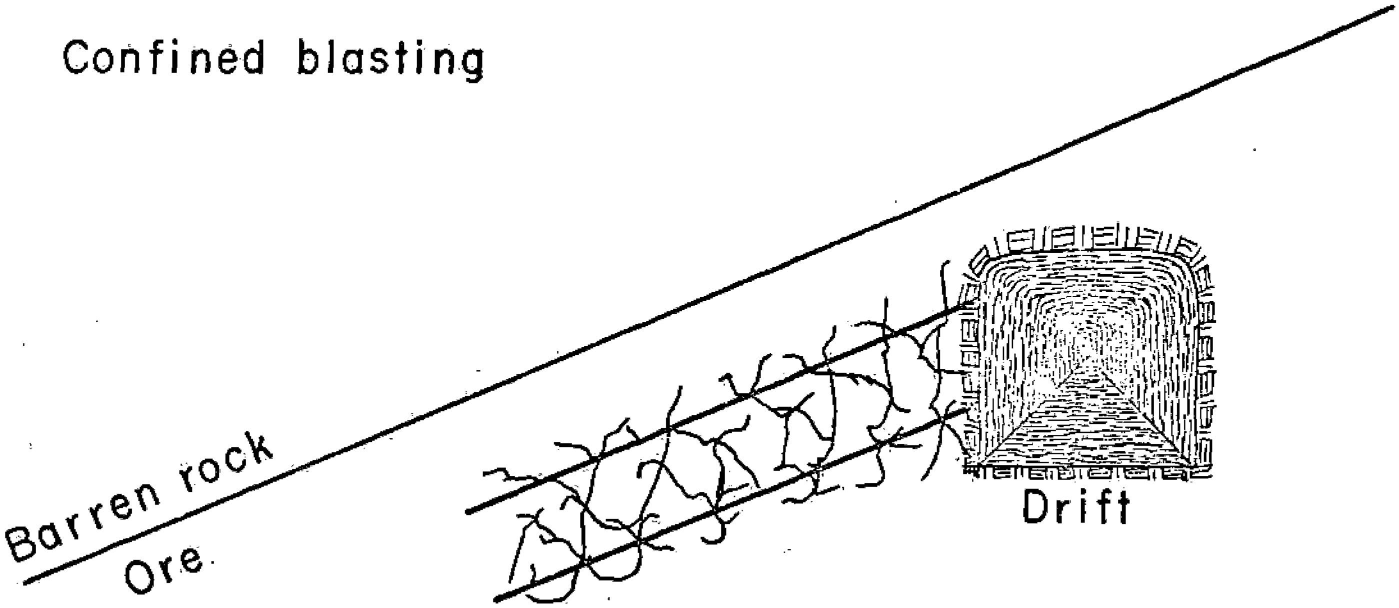
OVERHEAD 1. - Deep leaching research program.



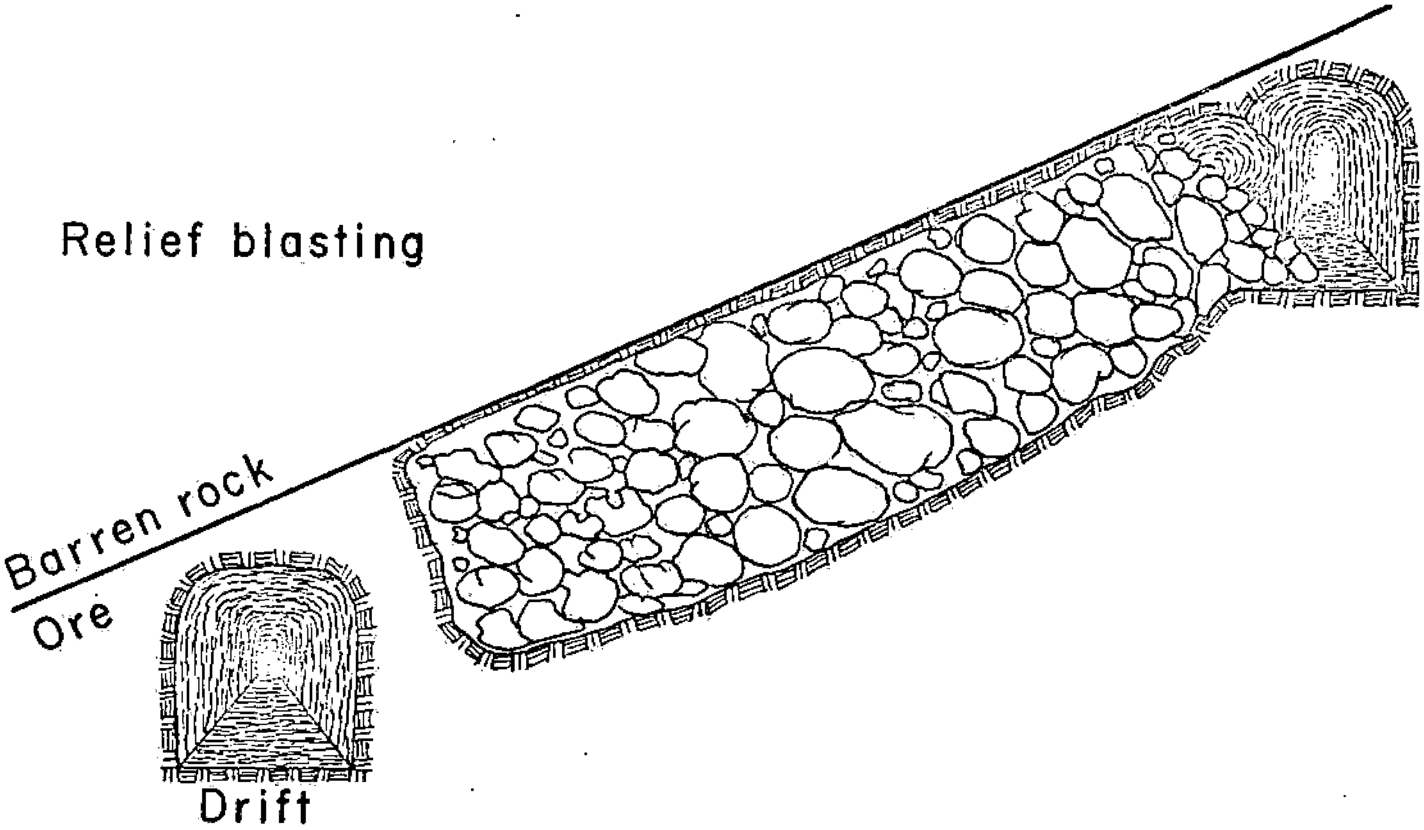
OVERHEAD 2. - Contributions toward cooperative research program.

FRAGMENTATION TECHNIQUES

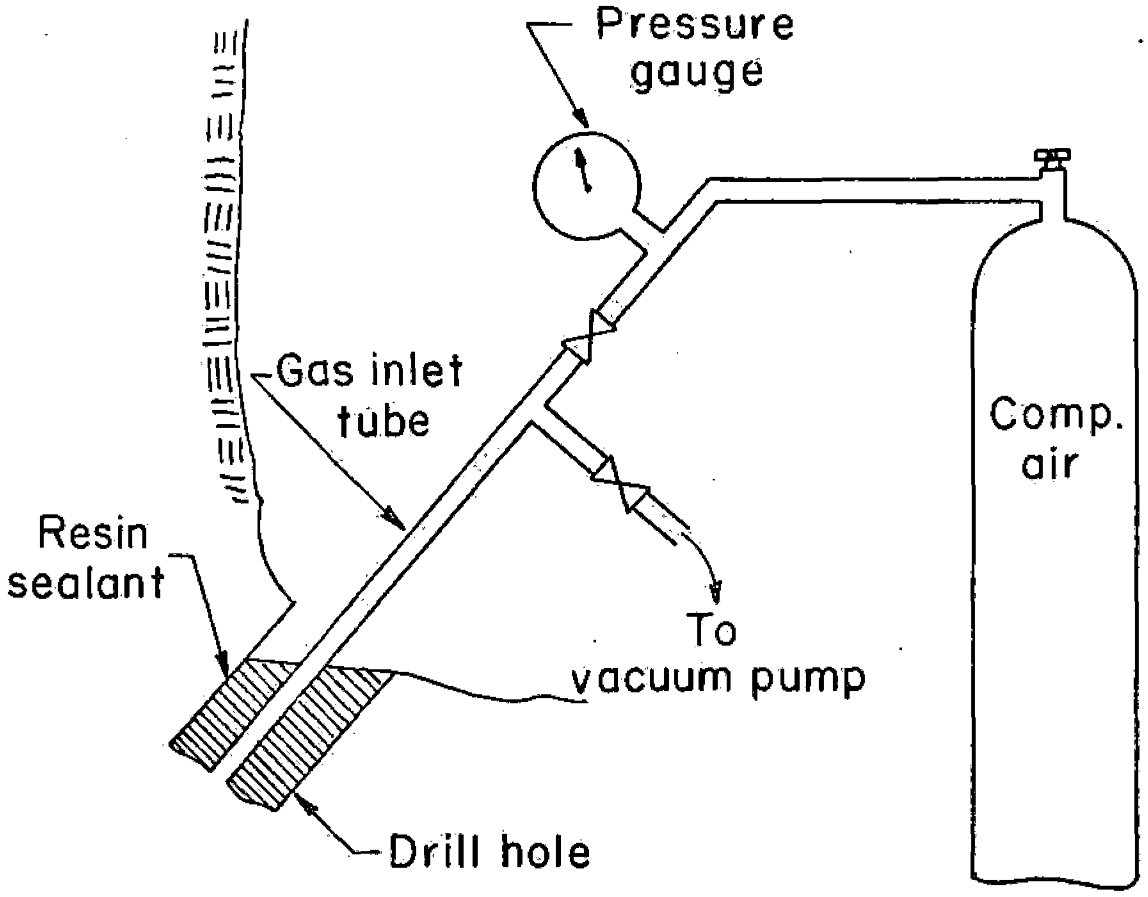
Confined blasting



Relief blasting

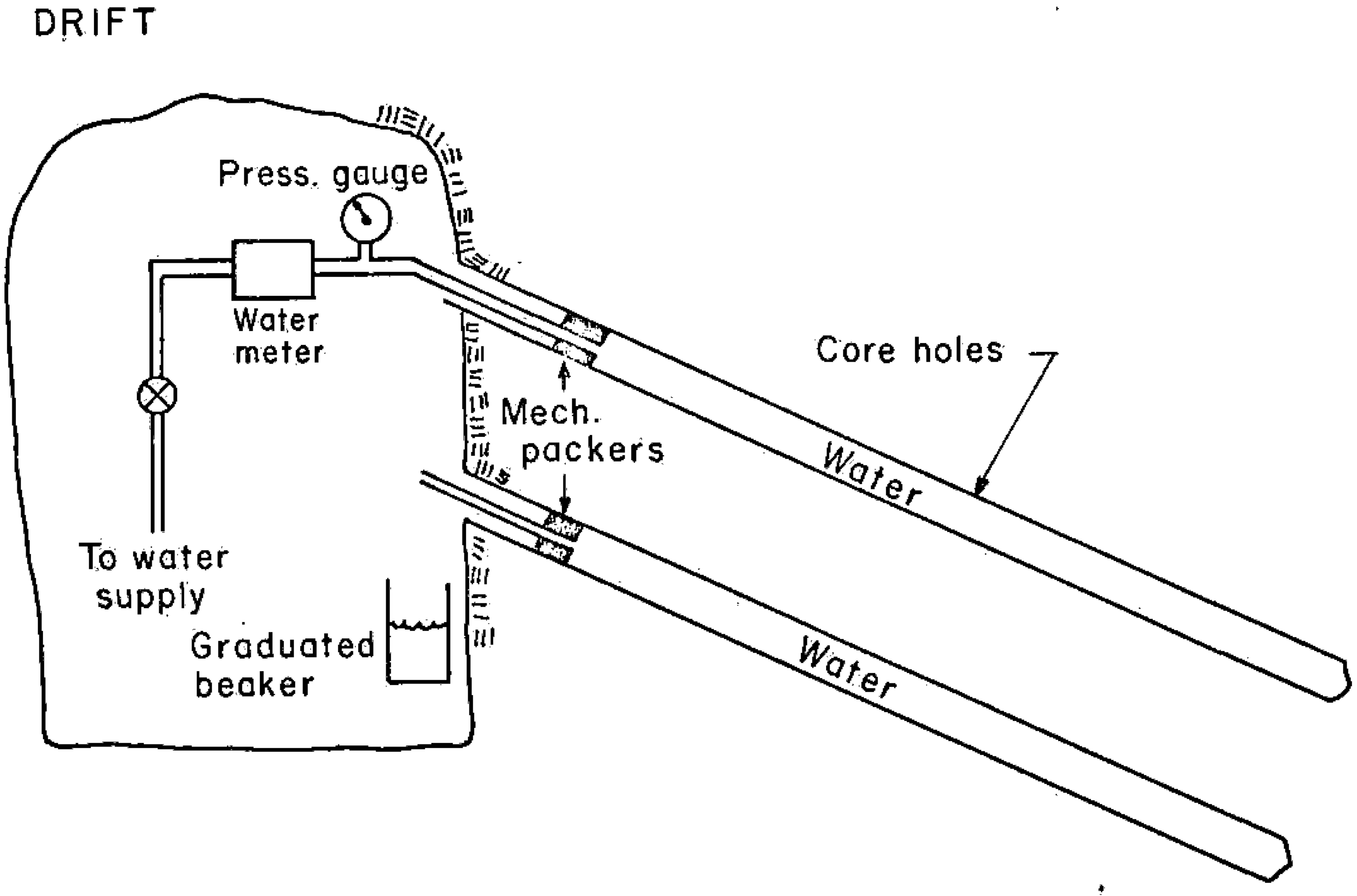


OVERHEAD 3. - Fragmentation techniques.

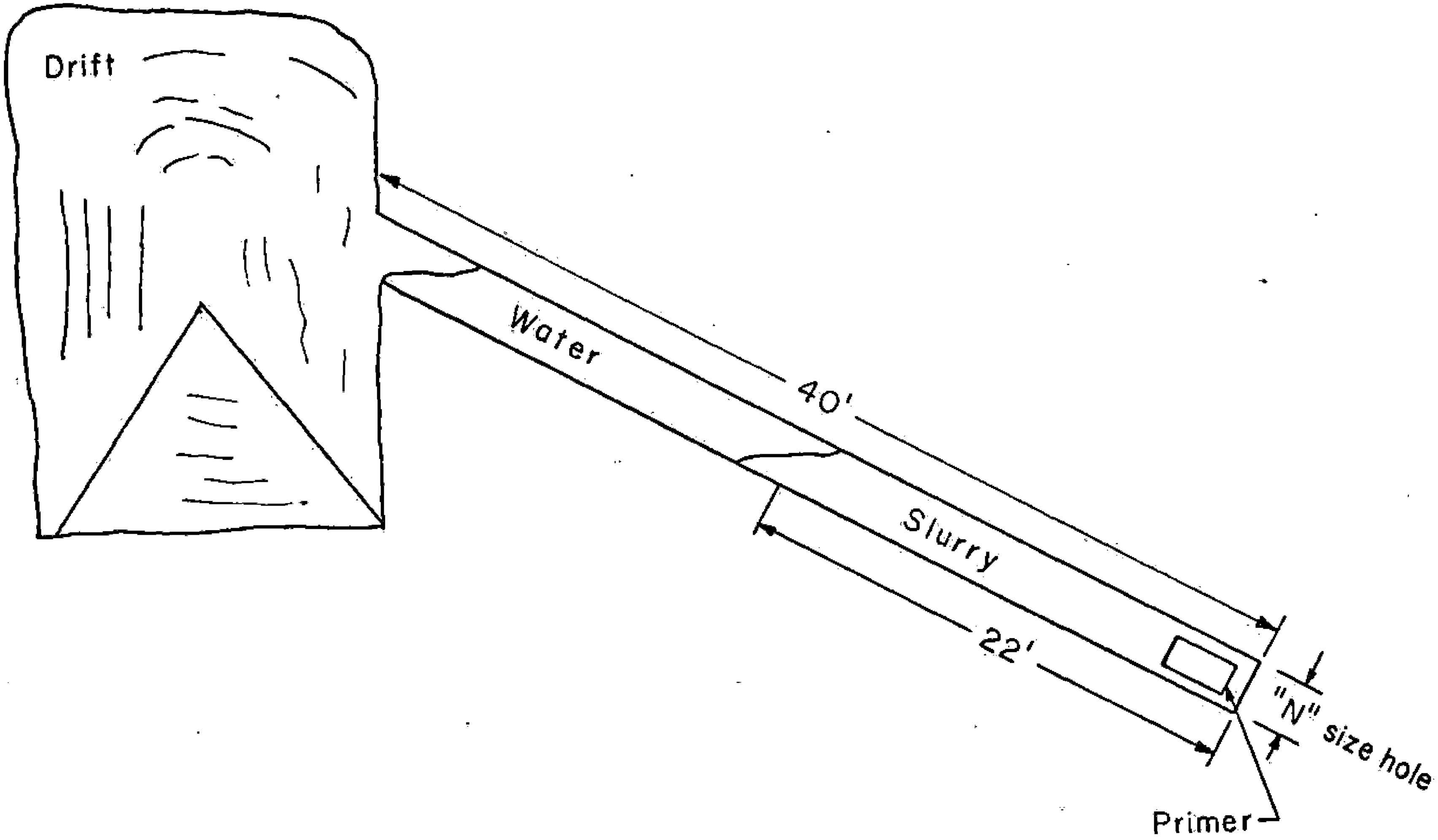


EFFECTIVE POROSITY

OVERHEAD 4. - Effective porosity measuring system.



OVERHEAD 5. - Permeability measuring system.

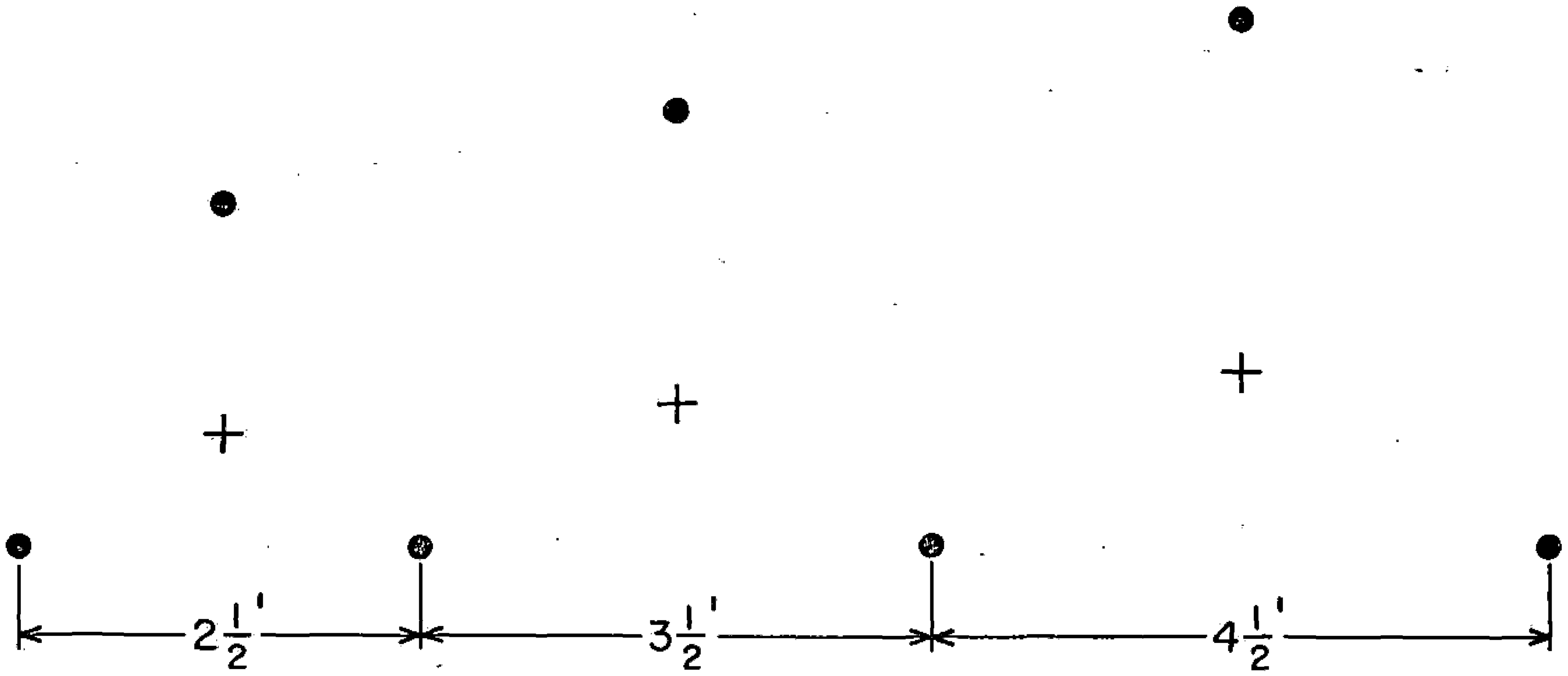


OVERHEAD 6. - Blasthole parameters.

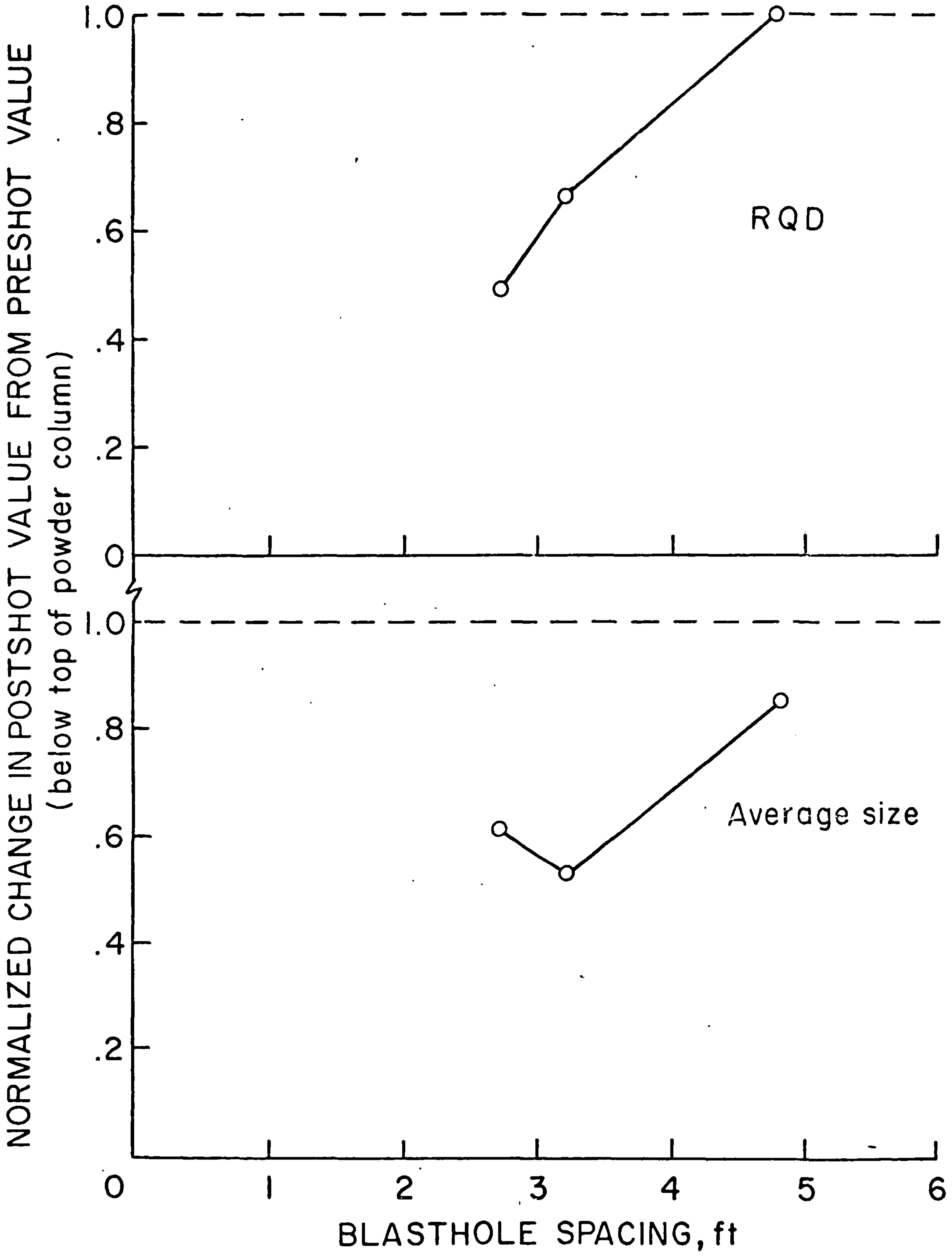
BLASTING PATTERN

● BLASTHOLE

+ CORE HOLES (POSTBLAST)



OVERHEAD 7. - Blasthole pattern.



OVERHEAD 8. - Fracture damage.

N5, 1975

METALLURGY

ALUMINUM, ALUMINA, ELECTRODES

IMPROVING SOLUTION CONCENTRATION BY EVAPORATION IN ALUMINA PRODUCTION

UDC 669.712.1

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Increasing the bulk of evaporating batteries is one way to reduce steam consumption for the concentration of solutions in alumina production. When treating bauxites of varying quality, solutions are evaporated in 3-, 4-, and 5-unit batteries, depending on the required alkali concentration and the soda concentration in the solutions. By employing the current industrial method of leaching diaspore bauxites, the caustic alkali concentration in the evaporated solutions is maintained within 300 g/l. Moreover, the carbonates contained in the solution as soda tend to separate intensively on the heated surfaces. In addition, the alkali-aluminate solutions with the indicated concentration indices show a depression at 16-18°C. In order to keep the batteries from clogging up, it was proposed that the 4-unit direct-flow evaporation batteries of the Urals Aluminum Plant (UAZ) be replaced by 3- and 2-unit installations.

Converting the evaporating batteries to a direct-flow arrangement made it possible to vaporize the water in 3-unit batteries with a capacity of 60-70 tons of evaporated water per hour.

Attempts to increase the number of times that the steam was to be used, by altering the sequence of solution feed to each unit -- in currently-employed apparatus -- were not successful because the production units became encrusted with soda deposits. Therefore, two approaches were used to increase the frequency of steam use: designing an apparatus capable of operating with an increased heat-transfer coefficient for solutions which are supersaturated with respect to soda, and developing a system which would keep soda from encrusting on to the heating surfaces.

Workers at VAMI and at the Bogoslovo Aluminum Plant (BAZ) developed an apparatus with a decreasing film and forced circulation. This apparatus, though it has a number of shortcomings, is being used today at several BAZ batteries and does provide a drop in steam consumption.

At the UAZ, where this apparatus could be introduced at only one of the three batteries without being forced into a major reconstruction of the building, industrial tests are being conducted on a two-stage evaporation system which had been developed in collaboration with SverdNIIkhimmash.

The essence of the approach is as follows:

1. The starting solution is evaporated in a multi-unit countercurrent evaporating battery to a concentration of 240-250 g/l $Na_2O_{caustic}$, i.e., to the start of soda crystallization.
2. The "medium lye" obtained is heated to 140-150°C, and then subjected to step-by-step evaporation in a system of series-connected units of flash-evaporator crystallizers, where the concentration is increased to 300 g/l $Na_2O_{caustic}$; soda will crystallize here.

Reducing the solution concentration in the battery makes it possible:

- to eliminate any soda separating at the heating surfaces; thus, when a constant productivity is maintained, it is possible to increase the period between battery. washes;
- to reduce losses in useful temperature differences by reducing solution depression. This makes it possible to select an evaporating battery for the two-stage system with a larger number of units and, correspondingly, with a lower specific steam consumption;
- to reduce the corrosion rate of the boiler pipes.

In making the industrial tests, I-stage evaporation was performed with a 4-unit countercurrent system. The solution from the production unit, with a 239-249 g/l Na_2O caustic concentration was transferred by a pump through a medium-lye preheater to a chain of 5 flash-evaporator units where, as a result of step-by-step evaporation, up to 290-300 g/l was concentrated. Solutions from the fifth flash-evaporator were fed, at 60-70°C, to a preheater (heated with steam from a heat- and electric-power plant); it was then directed, at 100-105°C, to a soda-settler as a means of separating the soda. In order to maintain the concentration of the circulating solution at a specific level, some part of it was directed to recirculation in the 4th flash evaporator.

In working out the system, questions were resolved with respect to intensifying the heat-exchange in the vacuum unit, reducing the rate at which the flow pipes become overgrown in the flash-evaporator , and with respect to soda separation.

Under conventional conditions, the vacuum units operate at heat-transfer coefficients of 600-800 kcal/(m^2·hr°C). During the tests, in order to intensify the heat-exchange in the vacuum unit, steam and air were blown into the lower solution chamber. Steam was sampled from the gas-exhaust of the 1st unit, the air being sucked in from the atmosphere. The steam-gas mixture -- directed to the lower solution-chamber of the boiler -- preheated the solution and agitated the preheating zone in the pipes, penetrating it in the form of bubbles and forming a two-phase mixture on this section. That kind of hydrodynamic system contributed to an increase in heat-exchange intensity. The heat-transfer coefficient increased to 1200 kcal/(m^2·hr·°C).

Intensive overgrowth of the flow pipes was slowed down through elimination of boiling within the pipes and by the introduction of soda as a seed crystal to the flash evaporation system.

The following indices were obtained during the tests:

Amount of evaporated water, tons/hr................	To 100
Heat-transfer coefficient per unit, kcal/(m^2·hr·°C):	
1..	1100-1300
2..	1500-1800
3..	2100-2200
4..	To 1200
Duration of period between washes:	
with seed crystal added to flash-evaporator, days.	5
with no seed crystal added........................	76-78
Specific steam consumption, t/t evaporated water....	0.39

Heating solutions, after they have passed through flash evaporators of two series-connected preheaters -- with one of them using liquor steam from the 1st installation -- makes it possible to reduce steam consumption to 0.37 tons per ton of evaporated water.

The flash evaporators operated stably, with neither pulsation nor froth being observed. Soda will not always precipitate from the evaporated solutions normally. Moments occurred when there was a deterioration of the discharge from the industrial soda-settler. It was established under laboratory conditions that soda will settle very slowly or that a large part of the soda will float upwards as flocs which include air bubbles. Boiling the circulating solution under laboratory conditions provided a positive effect.

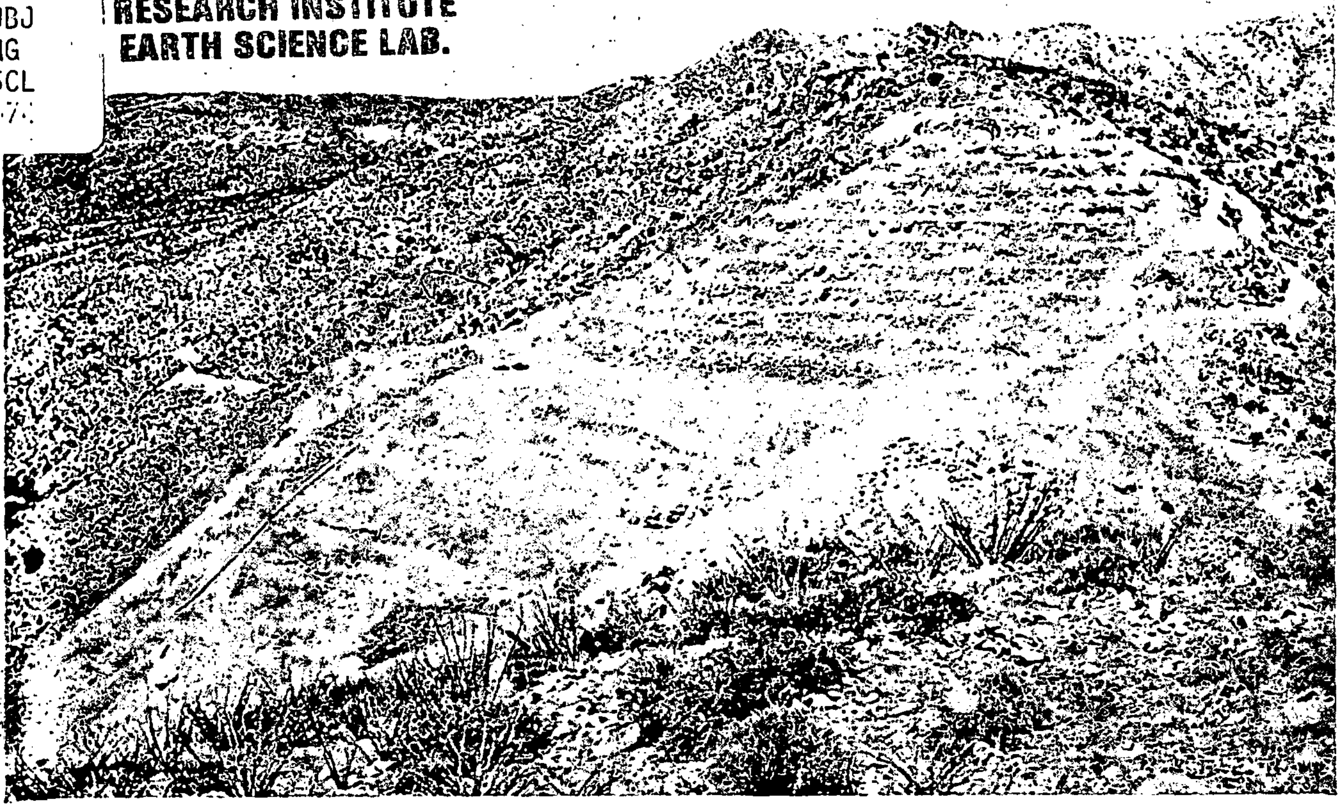
Industrial verification of the efficiency of solution boiling was performed by passing an evaporated solution -- after it has gone through preheaters -- through the production installation of a 3-unit battery. As a result, the potential of the soda to deposit was about the same as from solutions in other shop batteries.

Using the results of laboratory and industrial tests it became possible to set up a system in which solutions -- after passing through flash-evaporators -- were directed to an evaporator which was heated by steam from heat- and electric-power plants. Heating the solution before it reaches the evaporator was performed in a tubular and contact preheater using the liquor steam from this apparatus.

Calculations show that the specific consumption of steam by a two-stage system in which there is a 4-fold use of heat in the battery and employing the given preheating method will amount to 0.365-0.370 t/t of evaporated water.

CONCLUSIONS

1. By using the process of soda crystallization from concentration apparatus to solution flash-evaporators it becomes possible to convert from the use of 3-unit batteries to 4- and 5-fold uses of steam. The average capacity of a 4-unit battery using flash evaporation was about 90-95 tons/hr of evaporated water. The interwash period for the apparatus was 3-5 days.
2. For flash-evaporation of crystallized solutions one can use flash-evaporators with natural circulation. They are sufficiently simple and operate reliably: they operate with a stable circulation with no frothing, discarding solutions into the lower part of the circulating circuit.
3. By introducing small amounts of soda seed crystals into the flash evaporator it becomes possible to slow down encrustation of the flash evaporator.



IN-SITU COPPER LEACHING AT THE OLD RELIABLE MINE

THE Old Reliable Mine located approximately nine miles east of Mammoth, Arizona, U.S. has been sporadically mined since about 1880. The most recent mining, prior to acquisition by Ranchers Exploration and Development Corp., was in 1953-54. The orebody is a near-vertical breccia pipe containing approximately 4 million tons of 0·8 per cent copper with mineralisation occurring as chalcocite, chalcopyrite, malachite, and chrysocolla. The host rocks are extrusive lavas of Cretaceous age which were intruded by the Copper Creek granodiorite.

The ore zone which outcrops on the crest of a ridge, is about 300ft x 600ft in plan with the bulk of the deposit extending from the surface to a depth of approximately 500ft.

The mine, as it existed prior to Ranchers' work, consisted of two levels. The bottom level or 200 level was located just a few feet above the bottom of a wash and consisted of some 1,400ft of drifting and cross-cuts and a few raises. A second level located 100ft above the 200 level consisted of 2,800ft of drifts and cross-cuts and some stopes.

Upon leasing the property from Occidental Minerals Corporation and Siskon Corporation, Ranchers took bulk samples and began column leach tests at its Bluebird Mine lab with additional test work being done by an independent research lab. The results of these tests being satisfactory, additional tests were run on Bluebird and Old Reliable ores to obtain a correlation between the lab tests and actual leaching. The results of this study indicated that the Old Reliable ore was amenable to *in situ* leaching.

During the drilling programme, it was established that the water table was only a few feet below the bottom level. Further investigation revealed that this would be an ideal floor from which to recover solutions. Permeability and porosity tests were undertaken on the samples to analyse the fracture and flow characteristics of the ore, and it was soon apparent that the orebody would have to be shattered to obtain the required degree of permeability.

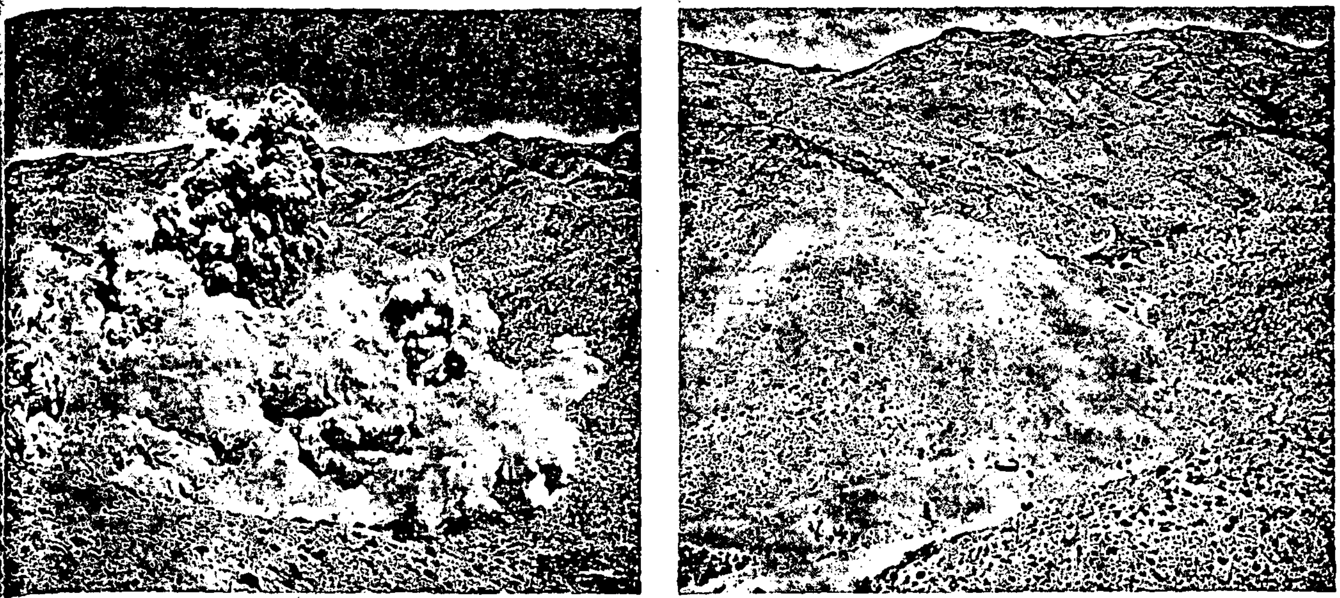
Several types of explosives were considered for breaking the deposit—nuclear, slurry, or ammonium nitrate. After serious study, the nuclear possibility was eliminated primarily because of safety and blast monitoring costs and the time involved. Conventional explosives loaded for coyote blasting was the method eventually selected. The site was well suited for the large blast, being remotely located and situated on the side of a hill so that leaching solutions could be drawn off by gravity at the base.

Blast design

The blast design developed by E. I. du Pont de Nemours & Company called for 4 million lb of ammonium nitrate explosives to be loaded throughout 6,000ft of 6ft x 6ft coyote tunnels on three levels. An over-all powder factor of 0·66 lb of explosives ton or 1·70 lb/yd^3 was used to fracture the 4 million tons of ore and 2·1 million tons of waste.

Additional underground development amounting to 1,300ft on the 200 level, 1,050ft on the 100 level and 1,700ft on a new level located 100ft above the 100 level was accomplished by Kop-Ran Development Corporation.

Fifty - pound bags of ammonium nitrate were packed in pre-determined

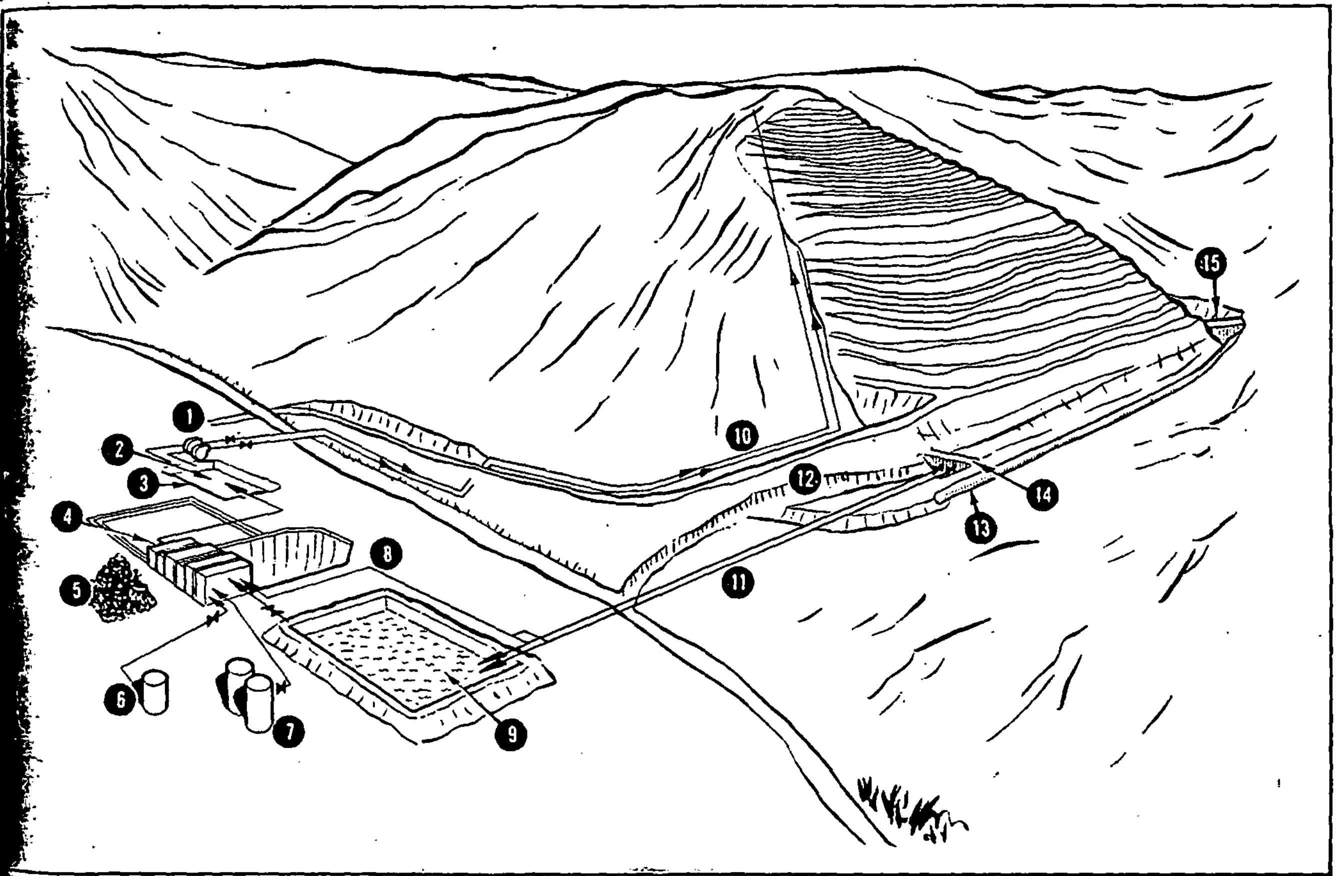


eft: Blast at the Old Reliable deposit. Right: Ore throughout an area measuring approximately 500ft in diameter and 350ft deep as broken into pieces averaging around 9in in diameter

atterns at specific points in the drifts nd cross-cuts. As the ammonium itrate was loaded, approximately 80,000ft^3 of sand stemming was blown in place utilising a Radmark stowing machine and by hand-stacking sacks of sand.

The blast was detonated from a firing bunker one mile from the mine. Completed blasting circuit included lead wires connected to blasting caps, detonating cord, and high explosive primers placed in bags of ammonium nitrate. Dual blasting circuits were utilised to reduce the possibility of a mis-fire. Millisecond delays were attached with instantaneous delay on the top level followed by 100-millisecond delays on the middle level and 150-millisecond delays on the lower level.

Surface disturbance, as anticipated, was minimal with an area of only 450-500ft in diameter being affected. The plant area, which was located downhill and some 800ft from the blast zone, was not disturbed at all. Subsequent



hematic diagram of Old Reliable project. 1. 2 x 500 gal/min leach pumps; 2. Barren solution pond; 3. Make-up water; 4. Precipitation lls; 5. Shredded and de-tinned cans; 6. Fresh H_2O for plant; 7. Acid tanks; 8. By-pass; 9. Pregnant solution pond; 10. 1,000 gal/min top of ore and distribution water sprinklers—dual lines, 6in ø; 11. Approximately 1,000 gal/min pregnant solution; 12. Saloon wash; 12in ø by-pass; 14. Saloon wash collection dam; 15. Diversion dam inspection of the blast area indicates that the shot was a complete success, with an average rock breakage size of 9-10in.

Ore zone survey

Following the blast, the entire ore zone was resurveyed and on March 15, terracing of benches (20ft high and varying from 15 to 180ft wide) was begun. The operation was completed on May 30, 1972. During the same period, a 6-cell precipitation plant, pregnant solution and barren solution storage ponds, and a drying pad were completed. To provide water for leaching solutions, a 6 mile-long, 6in-dameter pipeline was laid from a 17½in O.D. cased well drilled near Mammoth. This well is presently providing up to 200 gal/min of fresh water. The average monthly consumption of fresh water is approximately five million gal or 10½ per cent make-up.

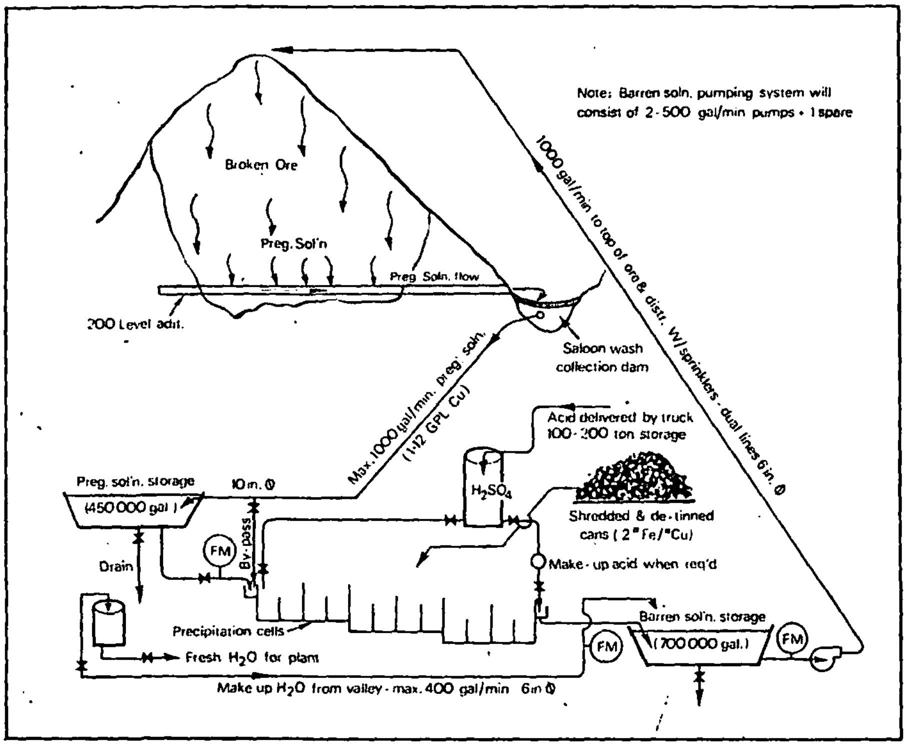
Leach liquor

On August 23, 1972, the first leach liquor was pumped to the ore, and in September, 1972 the initial underflow exited the orebody. In mid-December, 1972, nominal recovery of cement copper was commenced and by February, 1973, the orebody had been completely saturated. From December through February, the cement copper was stockpiled, and in March, 1973 shipment of precipitate began. Mine production capacity of 19,000 to 20,000lb daily was reached in August, 1973.

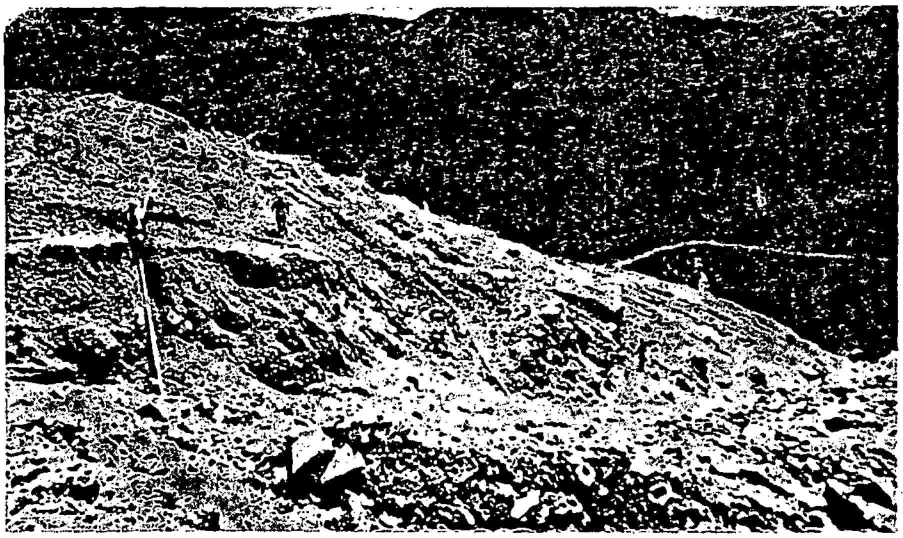
Leach liquor is now being distributed over 245,000 ft^2 of surface at the rate of 1,100 gal/min. The solution is acidified to a pH of 1·8. The ratio is five pounds of acid for each pound of cement copper recovered.

Water used in the leach solution is acidified with sulphuric acid in the barren solution pond and fed by gravity to two 200hp two-stage Goulds centrifugal pumps. Each pump provides solution to a distribution system covering one-half of the terraced area. Each of the systems consist of one 6in main transmission line and several 2in distribution lines. Rainbird sprinkler heads are spaced at 40ft intervals along the distribution lines. The front and rear spray nozzles cover a circular area having a 60ft radius. The pregnant solution exits the orebody at the base of the hill near what was once the 200-level portal. Shown in the drawing above is the general flow diagram of the solutions.

The solution is collected by a concrete catch dam and then directed by two 10in plastic pipes by gravity to the pregnant liquor pond at the plant site. An earthen diversion dam above the



Flow diagram of leaching solutions at the Old Reliable mine

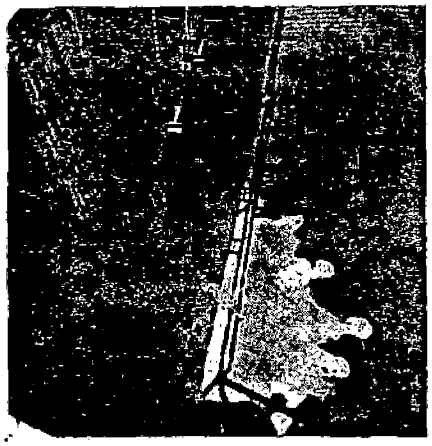


Sprinkling acid and water on the terraces

Copper-bearing solution (left foreground) seeps from the bottom of the orebody

blasted area channels storm run-off through 600ft of 72in culvert around the pregnant liquor collection pond and into the natural drainage system below the mine.

Copper-bearing solutions seeping from the bottom of the orebody towards the precipitation plant



Production of cement copper in the precipitation cells at the plant

From the pregnant liquor pond, the copper-laden solution passes through a magnetic flow meter and into the precipitation cells where shredded iron is added. The six cells are 24ft long by 8ft wide by 4ft deep and are usually operated in parallel, although they may be operated in series. Makeup acid is added to the barren solution in the tailrace of the cells to provide adequate mixing before discharge into the barren solution pond.

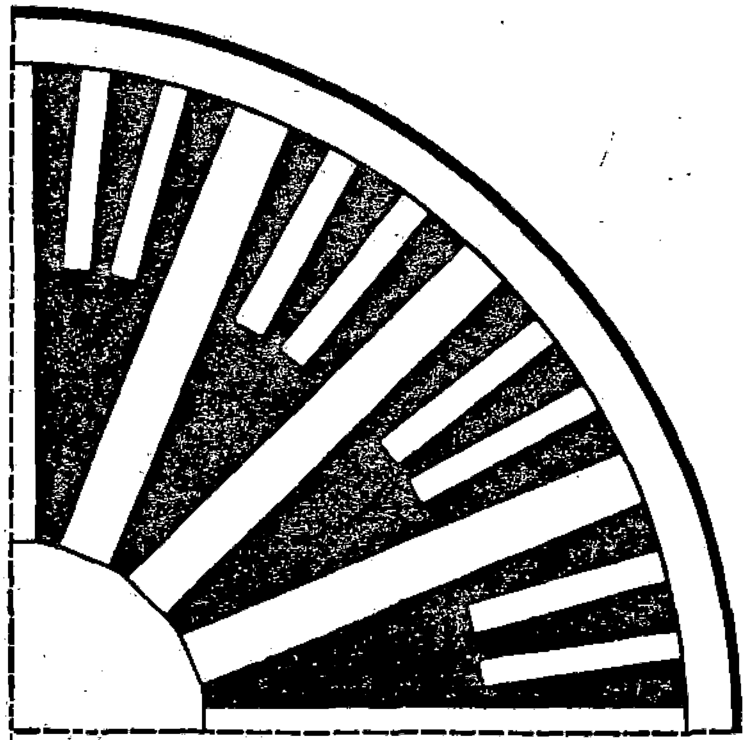
The copper precipitate is washed each day from the cells into a decant sump. The wash water is returned to the feed end of the cells by decanting from the top of the liquid. The precipitate is moved from the sump by a frontend loader to a concrete drying pad to reduce the moisture content to 15 per cent.

The precipitate, which averages 80 to 83 per cent copper, is hauled by trucks to the railhead where it is thereafter shipped for refining into wirebar on a toll basis.

Solution - monitoring wells were drilled above and below and leach area and are continuously monitored for liquid level changes, temperature, pH, total dissolved solids, copper, iron, etc. This monitoring, along with the water balance, indicates there is no solution loss into the ground.

Acknowledgement

Thanks are due to David K. Hogan, Manager, Engineering & Construction, Ranchers Exploration and Development Corp., Albuquerque, New Mexico, for preparing this article for publication in *Mining Magazine*.



Chapter 24

IN SITU COPPER LEACHING RESEARCH AT THE EMERALD ISLE MINE

by Dennis V. D'Andrea[1] and Sidney M. Runke[2]

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ABSTRACT

This paper describes the Bureau of Mines-El Paso Mining and Milling Company cooperative research program at the Emerald Isle mine[3] near Kingman, Ariz. This research program was directed toward developing in situ leaching methods for 200,000 tons of ore exposed in the pit bottom and also 1,500,000 tons of ore under 200 feet of overburden adjacent to the pit. A test area in the pit bottom containing 15,000 tons of ore was blasted and leached. The results of this leach test were encouraging, and the entire pit bottom was leached in-place for about 7 months. Two test blasts under 200 feet of overburden and extending to 290 feet were detonated in an area near the open pit. The results of these blasts were evaluated by core drilling and permeability measurements. An in situ leaching system was designed, but not implemented, to recover copper from the 1,500,000-ton area near the pit. The company decided to terminate operations at the Emerald Isle mine in November 1975.

INTRODUCTION

The Emerald Isle mine located 15 miles northwest of Kingman, Ariz., is owned by El Paso Mining and Milling Company. This copper deposit (principally chrysocolla) was owned by several companies over the

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[3] The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the El Paso Mining and Milling Company, El Paso, Tex.

years and was mined by underground and open pit methods. The ore has been heap leached and most recently treated in a leach-precipitate-float plant. El Paso has mined 1,400,000 tons of 1-percent-copper ore since it acquired the property. Approximately 200,000 tons of 1-percent-copper ore remains exposed in the bottom of the pit, and about 1,500,000 tons of 0.5-percent ore remains under 180 to 250 feet of overburden.

Open pit mining at the Emerald Isle mine ceased in July 1973 because increased stripping requirements made continued operation uneconomical. El Paso decided to develop an in situ leaching system to recover as much of the remaining copper as possible. The Bureau of Mines entered into a cooperative agreement with El Paso Mining and Milling Company in November 1973 to conduct research at the mine related to the development of this system. Both the Twin Cities Mining Research Center and the Salt Lake City Metallurgy Research Center of the Bureau of Mines became involved in this cooperative program. El Paso agreed to pay for all parts of the program that were required for the actual production of copper such as blasthole drilling, explosives, solution distribution and recovery systems, acid, and scrap iron, etc. The Bureau conducted core drilling, drill core analysis, physical property measurements, ground water studies, permeability measurements, laboratory leaching tests, seismic measurements, and assisted El Paso with the design of the blast and the in situ leaching system.

A research program for the Emerald Isle mine was prepared. Phase I of the research program began in January 1974 with a test blast followed by in-place leaching of 15,000 tons of ore in the pit bottom. The information developed from this Phase I test was used to design an in situ leaching system for the remaining 200,000 tons of ore exposed in the pit bottom. Leaching of this ore began in December 1974 and continued for about 7 months. A Phase II test site with again about 15,000 tons of ore was selected in an area under 200 feet of overburden. A Phase II test blast was detonated in July 1974 with seven 280-foot-deep blastholes. Circulation tests with water showed that this blast did not create sufficient permeability for leaching. In August 1975 a second blast was detonated in the Phase II test area with three blastholes. The effects of this second blast were evaluated using core drilling and permeability techniques. In November 1975 El Paso Mining and Milling Company decided to terminate operations at the Emerald Isle mine, and plans to leach the Phase II test area were abandoned.

This paper presents the research program at the Emerald Isle Mine and describes an in situ leaching system which was designed to recover copper from a 1,500,000-ton area under 180 to 250 feet of overburden.

EMERALD ISLE DEPOSIT

Figure 1 is a cross section through the Emerald Isle mine showing the Phase I and Phase II test areas. The deepest portions of the open pit have been excavated to about 200 feet exposing the top of the ore body (Gila Conglomerate). The Gila Conglomerate averages about 70 feet thick and dips approximately 10° to 15° to the southwest. The Gila Conglomerate is overlain by alluvium (quaternary) which is 150 to 250 feet thick and underlain by a granite gneiss. The dominant copper mineral in the Gila Conglomerate at the Emerald Isle mine is chrysocolla.

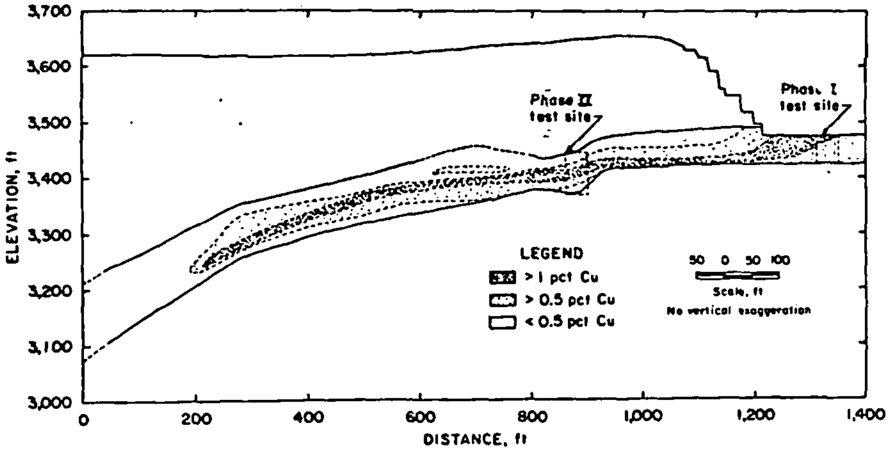

Figure 1. - Cross section through Emerald Isle deposit

Figure 2 is a plan view of the Emerald Isle mine with contours of the copper grade of the Gila Conglomerate. During open pit operation El Paso mined 1,400,000 tons of ore that averaged 1.0 percent copper. The copper mineralization continues beyond the pit in the downdip direction in a channel type distribution that decreases in grade downdip. At about 1,000 feet from the pit crest the grade is about 0.1 percent. Total ore reserves greater than 0.1 percent copper are estimated to be 3,000,000 tons.

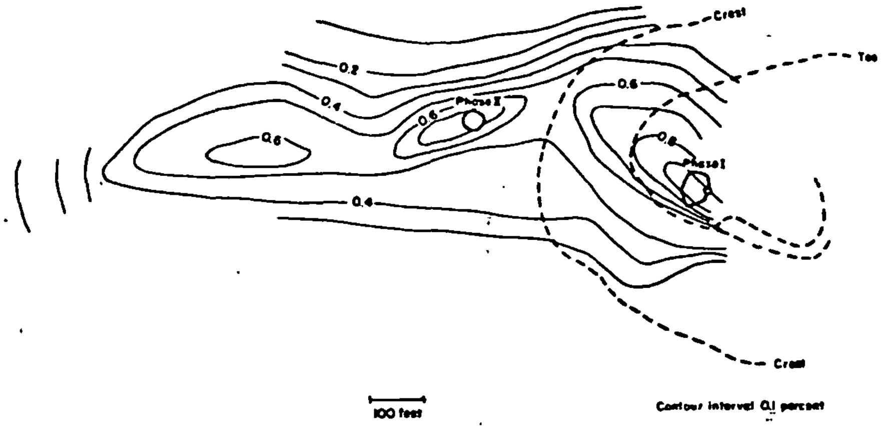

Figure 2. - Contour map of copper grade

Table 1 lists the physical properties of Gila Conglomerate core samples measured in the laboratory. The porosity, permeability, and strength values probably reflect the characteristics of the cementing material in the conglomerate and not the actual in situ values.

TABLE 1. - Physical properties of the Gila Conglomerate

Property	Phase I	Phase II
Porosity......................pct..	20.6	16.3
Density..................g/cu cm..	2.29	2.28
Permeability................darcy..	-	.65
Pulse Velocity.............ft/sec..	8,100	9,500
Torsional Velocity.............do..	4,200	5,100
Compressive Strength..........psi..	2,600	-
Tensile Strength..............psi..	72	-
Young's Modulus...........10^6 psi..	0.85	-

Ground water entering the pit, about 14 gpm, was pumped from a sump area for about 30 hours each week. The ground water table was controlled by sump pumping at about 5 feet below the surface of the pit floor.

PHASE I TEST BLAST

Figure 3 shows the Phase I test blast design. Seven 8-3/8-inch-diameter blastholes, about 50 feet deep were spaced 25 feet apart in a seven-spot pattern with one central blasthole. These blastholes had an average 22-foot powder column with 25 feet of stemming. A total of 4,500 pounds of slurry was detonated without delays. Table 2 lists the blast design data for the Phase I blast and the two Phase II blasts.

TABLE 2. - Blast design data

	Phase I	Phase II 1st Blast	Phase II 2nd Blast
Number of blastholes..........	7	7	3
Blasthole spacing.........ft..	25	20	18
Average hole depth........do..	47	277	277
Average top powder column.do..	25	205	192
Average powder column.....do..	22	72	85
Average stemming..........do..	25	205	192 (90 ft gravel)
Blasthole diameter........in..	8-3/8	9	9
Explosive diameter........do..	8-3/8	7	7-in bags cut
Explosive....................	nonaluminized slurry	smokeless powder slurry	smokeless powder slurry
Total explosives..........lb..	4,500	12,000	7,450
Loading density........lb/ft..	29.2	23.7	29.3
Powder factor[1]........lb/ton..	0.30	-	-
Powder factor[2]............do..	0.78	0.95	1.47
Delays (between each hole)....	Instantaneous	17 ms	25 ms

[1] Powder factor (lb/ton) includes ore above top of powder column

[2] Powder factor (lb/ton) = $1814 \frac{Pe}{Pr} \left(\frac{D}{S}\right)^2$) for ore in powder column zone only

Pe = specific gravity, explosive
Pr = specific gravity, rock
D = blasthole diameter, ft, and
S = blasthole spacing, ft, for infinite triangular pattern, ore zone only.

Topographic surveys were run before and after the Phase I blast so that the blast swell could be calculated. The maximum surface rise was only about 1.5 feet, and the blast swell was 1.4 percent. The volume of ore broken by this blast was estimated to be 15,000 tons.

PHASE II TEST BLASTS

Two blasts were detonated in the Phase II test area under 200 feet of overburden. The first blast had seven blastholes drilled to an average depth of 277 feet. These holes were 9 inches in diameter and 20 feet apart in a seven-spot pattern. Figure 4 shows the blasthole

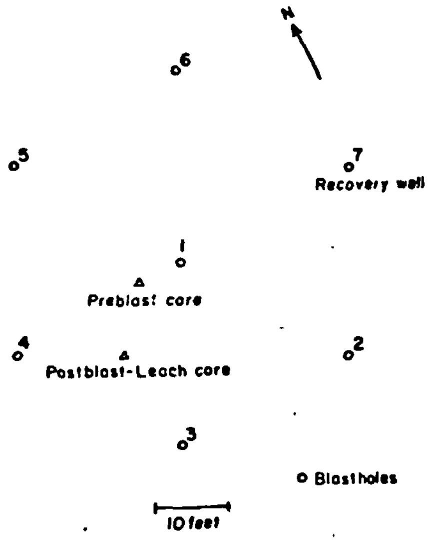

Figure 3. - Phase I test blast design

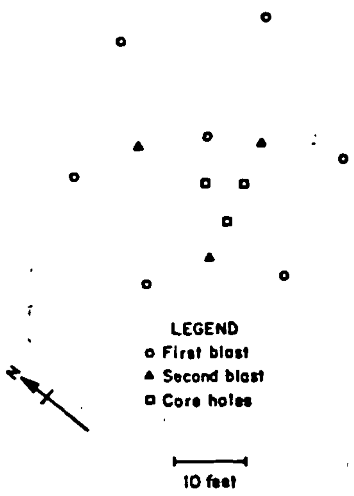

Figure 4. - Phase II test blast design

patterns for the two Phase II blasts. The second blast had three blastholes, 9 inches in diameter, 277 feet deep, and they were spaced 18 feet apart. Table 2 lists the blast design data for the Phase II blasts.

The first blast was loaded with 7-inch-diameter, 50-pound-bags, of smokeless powder slurry in 9-inch-diameter blastholes. The second blast was loaded with the same explosive, but the bags were cut before they were lowered into 9-inch holes. The cutting procedure increased the loading density from 23.7 lb/ft for the first blast to 29.3 lb/ft for the second.

The second blast in the Phase II area was considered necessary after circulation tests with water revealed that the first blast had not created sufficient permeability for successful leaching. After the first blast a recovery well pump was installed at a depth of 290 feet, and drawdown tests were conducted with and without water injection at the 200-foot level. Flow rates from these tests averaged less than 1 gpm over a 24-hour period and were not considered adequate for leaching. In addition the water injected at the 200-foot level did not work its way into the fractured zone and into the recovery well but apparently flowed across the top of the alluvium-conglomerate contact. The water table in the Phase II area was at a depth of 230 feet.

After the second blast the recovery well pump would have been reinstalled and water circulation would have been tested but this plan was not implemented before El Paso closed down the Emerald Isle operation. However, a core hole was drilled after the second blast for fracture analysis. Permeability tests were also run in this core hole and in one of the blastholes that was open to a depth of 250 feet. The core fracture analysis and in-place permeability tests indicated that the second blast substantially improved the breakage and flow.

Detailed topographic surveys before and after each Phase II blast did not reveal any significant surface rise. Elevation increases of 4 to 6 inches were observed near the collars of some of the blastholes that vented.

PHASE I LEACH TEST

The Phase I leach test began in March 1974 and continued for 117 days until July 1974. Leach solutions were distributed over the surface of the broken ore through perforated pipes. Solutions were recovered in a well located on the east side of the blasted zone as shown in figure 3. The recovery well hole was drilled with a churn drill using one of the blastholes that remained open after the blast. The recovery well hole was about 11 inches in diameter, 50 feet deep, and had a 9-inch-diameter casing. The bottom 20 feet of this casing was perforated.

During the 117-day leaching period flow rates averaged 57.4 gpm. Because of ground water dilution of the leach solutions and the desirability of drawing down the water table, a bleed of 9 gpm was established in the flow circuit after discharge from a cementation system and before recharging with acid. The water table was about 5 feet below the surface before leaching, but during the leach test it went to about 20 feet below the surface and reached a maximum of 23 feet drawdown.

Table 3 lists the results of the Phase I leach tests and also data from the pit bottom leaching. The pH averaged 1.18 for the sulphuric acid influent solutions and 1.71 for effluent solutions. Effluent copper grade averaged 0.562 gram/liter, calculated copper production was 245 lb/day, and a total of 29,000 pounds of copper was produced. Copper was recovered by cementation on scrap iron. Iron consumption was 4.7 lb Fe/lb Cu. The acid consumption figure of 15 lb H_2SO_4/lb Cu was high, but this was attributed to the 9 gpm bleed in the solution circulation system, the small size of the test area with important fringe effects, the short duration of the leaching test, and the small difference between the pH of influent and effluent solutions. Figure 5 shows the cumulative copper recovery for the Phase I leach test.

TABLE 3. - Leaching results

	Phase I Leach Test	Pit Bottom Leaching
Ore leached....................tons..	15,000	100,000
Grade of ore...................pct..	1.0	1.0
Duration of leaching.........days..	117	190
Average running time.......hr/day..	20.5	23.2
Leach influent:		
pH.............................	1.18	1.10
Copper......................g/l..	0.147	0.091
Iron........................g/l..	8.5	-
Leach effluent:		
Flow rate...................gpm..	57.4	115.9
pH.............................	1.3	-
Copper......................g/l..	0.562	0.646
Iron........................g/l..	6.2	-
Precipitation effluent:		
pH.............................	1.71	1.62
Copper......................g/l..	0.067	0.076
Acid consumption...lb H_2SO_4 /lb Cu..	15.0	10.0
Iron consumption......lb FE/lb Cu..	4.7	2.75
Copper production..........lb/day..	245	748
Total copper production........lb..	29,000	142,000

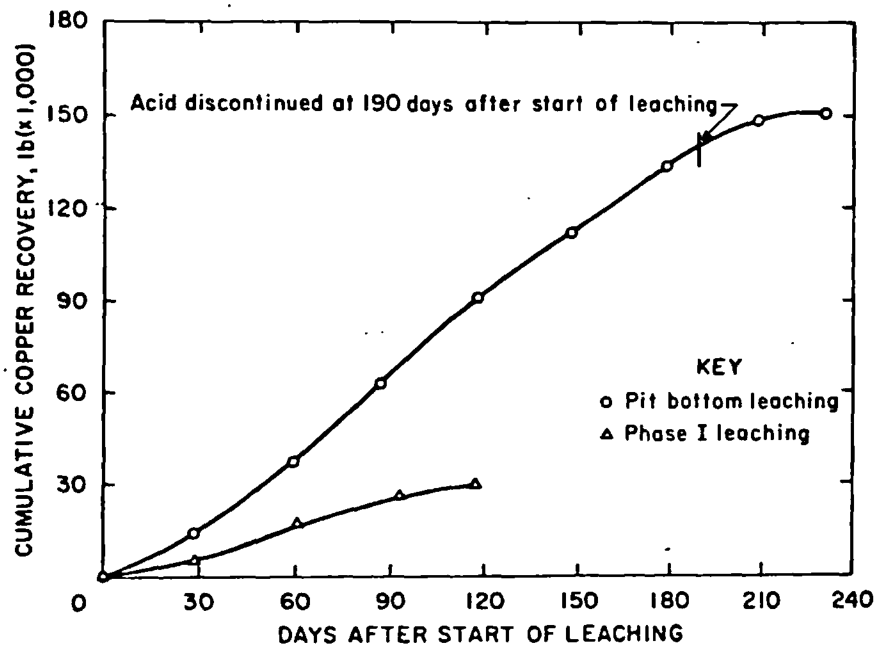

Figure 5. - Cummulative copper recovery - Phase I test and pit bottom leaching

PIT BOTTOM LEACHING

Pit bottom leaching of about 100,000 tons of ore began in December 1974 and continued for 190 days. A system of seven recovery wells was installed. These wells were installed in 12-inch-diameter holes to an average depth of 50 feet and were spaced 50 feet apart. The ore in the pit bottom was not blasted before leaching in the hope that natural permeability was adequate for successful leaching.

Pit bottom leaching results are listed in Table 3. The average flow rate was 116 gpm, pH of influent solution was 1.10, and the copper grade of effluent solutions was 0.646 gram/liter. Calculated copper production averaged 748 lb/day, and a total of 142,000 pounds of copper was produced. Solutions were circulated for 41 days after acid addition ceased to bring up the pH of the solutions remaining in the pit bottom. During this period an additional 9,000 pounds of copper were produced. Figure 5 shows the cumulative copper production for the pit bottom leaching.

During pit bottom leaching acid consumption averaged 10 lb H_2SO_4/lb Cu, and iron consumption averaged 2.75 lb Fe/lb Cu. This was an improvement over the Phase I leach test but was still high. However, acid consumption was dropping as the test continued.

Pit bottom leaching was stopped because the flow rates of leach solutions were not as high as desired. Pit bottom leaching was halted, and the ore was to be blasted to improve permeabilities and flow rates. The drilling and blasting program began, but the Emerald Isle operation closed before the pit bottom ore was leached further.

DESIGN OF FULL-SCALE OPERATION

Based on the experimental blasting and leaching tests, a full-scale in situ system was designed to recover the majority of the remaining copper. However, this plan was not implemented because the mine closed. This plan involved blasting and leaching of first a higher grade area followed by blasting and leaching of a second lower grade area. The first area would include some ore in the pit bottom, some ore under the pit walls, and ore under 180 to 250 feet of overburden along a channel extending 700 feet from the crest of the pit. The 700-foot-channel would follow the high-grade copper mineralization as shown in figure 6. The second area would be along the flanks of the 700-foot-channel and would include lower grade ore. A third area parallel to the second area could be added if leaching of the initial areas were successful.

Fragmentation would be accomplished primarily with vertical blastholes, although some inclined holes from the pit crest and some horizontal holes in the pit bottom would be required to break the ore under the pit walls. The ore in the pit bottom and under the pit

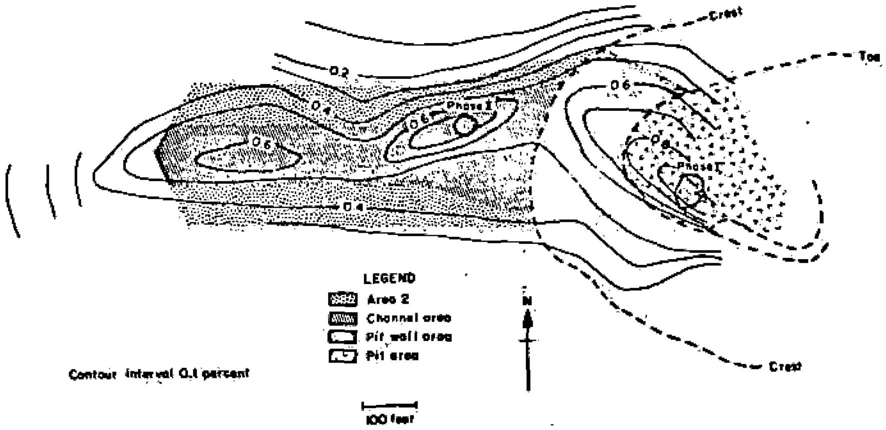

Figure 6. - Blast design for full-scale operation

walls would be broken in one blast while the channel area would be broken in a series of seven-hole blasts beginning at the pit crest and proceeding in the downdip direction. Each of the seven-hole blasts would be detonated as soon as drilling was completed so that this drilling and blasting program would continue for several months. A series of blasts would also break the second area. Table 4 lists the full-scale blast design data.

TABLE 4. - Full-scale blast data

	Area 1			Area 2
	Pit	Walls	Channel	
Area..............sq ft..	59,000	56,000	96,000	88,000
Thickness............ft..	40	69	78	76
Volume............cu yd..	87,000	143,000	276,000	246,000
Weight.............tons..	167,000	274,000	530,000	472,000
Grade................pct..	0.70	.58	.55	.41
Total copper.........lb..	2,300,000	3,200,000	5,800,000	3,900,000
Drilling depth.......ft..	40	125	287	297
Powder factor.....lb/ton..	0.5	1.0	1.5	.75
Total drilling.......ft..	2,200	12,900	76,300	36,000
Total explosives.....lb..	83,000	274,000	795,000	354,000

Leach solution injection would occur primarily in the pit bottom with some vertical injection holes near the pit crest. Solutions would be recovered downdip with a series of recovery wells. It is