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DISTANT BLAST PREDICTIONS FOR EXPLOSIONS[*]

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After one of the first Nevada nuclear tests in early 1951 broke windows
in Las Vegas, 80 miles away, Sandia Laboratories began measurements and research
to develop methods for avoiding recurrences. The techniques we derived are
useful for blast prediction for various explosives where atmospheric refraction
may cause nuisance or hazard outside a controlled danger area. Nuclear test
data collections have been summarized to give a climatology of propagation
amplitudes that may be expected under various meteorological conditions.
These results are at variance with predictions in the Ballistic Research
Laboratories Handbook, BRL-1240, of 1964, which is still used by some military
agencies. That Handbook now appears to be obsolete, and based on limited
data which were available and unclassified during the 1950's.

Atmospheric refraction, by wind and temperature effects, may duct and
even focus blast waves to cause nuisance and possible minor damage at often
unexpected distances from explosions. Blast ray paths may be returned to the
ground, as shown by Figure 1, at ranges even beyond 100 miles, depending on
upper air conditions. Strong propagation in the boundary layer may be carried
downwind by strong winds, or in all directions during night-time surface
temperature inversions. Jet-stream winds, at 25,000 to 40,000 ft altitudes
can cause blast focusing at 30-50 mile downwind ranges. The warm layer in

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the high stratosphere, or ozonosphere, near 150,000 ft, also allows ducting which carries relatively loud noise 100 to 150 miles downwind of seasonal monsoon winds at that altitude.

To predict amplitudes from these atmospheric ducted waves, we begin with a standard explosion overpressure versus distance curve, as shown in Figure 2. At low blast overpressures, below about 1/3 psi or 25 millibars, quasi-acoustic propagation in a homogeneous, calm atmosphere gives overpressures, or peak-to-peak amplitudes, that decrease about in proportion to the -1.2 power of distance. A variety of experimental data have been used to generate and confirm this rule for unrefracted, radially expanding explosive waves. This "standard" curve is shown for a 1-kt (4.2×10^{19} ergs) nuclear-explosive (NE), burst in free air away from reflecting surfaces, in 1000 mb ambient pressure.

Blast wave scaling laws, in Figure 3, show that distances to constant overpressures are proportional to the cube-root of yield as shown in Equations 1 and 2. In consequence, in the low pressure, $R^{-1.2}$ region, amplitudes are proportional to yield raised to the 0.4 power, as shown in Equation 3.

Most atmospheric nuclear tests were fired at or near a reflecting ground surface. Many generated fused Mach-stems, as shown in Figure 4, where incident and reflected waves are merged into one stronger shock wave. The strength of these Mach stem source waves depends primarily on yield-scaled height-of-burst (HOB). Figure 5 shows how apparent yield is enhanced by various scaled burst heights.

Far-field microbarograph records have been normalized to 1-kt HE free-air burst amplitudes, by adjusting for apparent yields, based on HOB, for 1953, 1955, 1957, and 1958 Nevada atmospheric nuclear tests in Figures 6, 7, 8, and

9. In spring and fall, storm winds and generally cooler surface temperatures occasionally caused blast ducting and larger-than-standard pressure amplitudes to propagate to considerable distances. Summer test data usually showed a rapid decrease of amplitude with increased distance because of the normally large gradient of sound velocity with altitude. As was shown earlier in Figure 1, a gradient in the surface layer causes the blast wave to turn away from ground, so that only relatively weak, scattered waves reach our ground level recorders. A rule-of-thumb for gradient propagation is that amplitudes decrease about in proportion to distance squared, beyond about 3km from 1-kt NE.

Nuclear data were usually gathered near or before dawn, when there was a strong surface temperature inversion in Yucca or Frenchman's Flats. This caused ducting and blast amplification on-site and until the wave passed the first range of hills surrounding the Flats. Beyond that distance, free air conditions of gradients or sound ducts determined the distant propagation.

At very high altitudes, near 50 km, relatively warm temperatures, near $0^{\circ}C$, and monsoon winds give downwind ducting into a noisy belt or ring near 200 km range. In winter, west winds at altitude carry blast waves eastward and in summer, east winds carry the blast west. The results are shown in Figures 10 and 11, with amplitudes again normalized for yield and HOB. St. George, Utah, east of Nevada Test Site, typically received "standard" amplitudes in winter, with considerable scatter, of course. Summer propagations, upwind, generally confirmed the R^{-2} rule for gradient propagation. To the west, Bishop, California, showed the monsoon pattern reversal, with strong, ducted waves in summer and weak, upwind waves in winter.

These climatological data were used to estimate off-site effects from several recent large HE tests in Colorado. Project MIDDLE GUST, by the USAF Weapons Laboratory, fired two 20-ton and three 100-ton HE yields near Ordway, in Southeastern Colorado. Proximity to various communities required that these tests be conducted with strong sound velocity-height gradients, to minimize nuisance damage and disturbance. Results from off-site microbarograph measurements of peak-to-peak amplitudes are shown in Figure 12, with an approximate threshold, at 4 mb for beginning window damage. By waiting for appropriate weather conditions, when necessary, it was possible to minimize such off-site damage and maintain good public relations with the neighborhood.

Project MIXED COMPANY, by the Defense Nuclear Agency, fired two 20-ton and one 500-ton HE tests near Grand Junction, in Western Colorado. Microbarograph measurements of the large yield event are shown in Figure 13. Window breaking amplitudes were held to about 20 km range where, under some weather conditions, they could have spread to 80 km. The weather-watch appears to have served its purpose in generally minimizing off-site propagations.

A similar prediction service was performed with a 150-ton HE test by Tooele Army Depot early this year, with successful results as shown by Figure 14. Although barely 4 mb would reach the distance of Ogden or Salt Lake City, the exposed population of near one million people caused need for special caution.

A primary source for empirical data on the nuisance damage from blast waves has been the accident at Medina Base, San Antonio, Texas, where 56-t HE exploded and broke over 3000 windows in the city, in 1963. Evaluation of the damage claims and the exposed pane population led to the relationships in

Figure 15. These have been used with fair success in evaluating other minor incidents in Nevada and Colorado tests. There is, however, no theoretical foundation for these power law relationships to pane area and incident overpressure. These damage probabilities also depend on the actual distribution of pane qualities and sizes -- area and thickness -- in San Antonio, Texas, in late 1963. A better theoretical basis would allow more confidence in extrapolation to other situations.

Figure 16 shows how the Medina result compares with Pittsburgh Plate Glass Co. Report 101, "Glass Product Recommendations - Structural". They assumed a normal distribution for failures with a 25% standard deviation that obviously fails at 4σ and does not account for real problems of actual exposure and installation. Their laboratory data may be re-interpreted with a better-fitting log-normal distribution, but it likewise fails to account for all of the variables in real installations.

A recent assembly of explosion test data, by Wilton and Gabrielsen, in DNA-2906F, is shown to give surprising agreement with the Medina equations, which obviously should fail at high breakage probability. A combination of a log-normal damage model which fits the two main explosion data sets is shown in Figure 17. Hopefully, the log-normal laboratory test data can be used, along with distributions of pane exposure and blast reflection factors, as well as distributions of incident overpressures which are randomized by atmospheric turbulence, to approximate the empirical log-normal connection from Medina data to the strong blast housing test results.

Details on blast prediction methods, as described in this paper, have been assembled for the American National Standards Institute (ANSI) in a draft, "Standard for Single Point Explosions in Air." This document is currently under committee review, and, hopefully, can be distributed during 1974.

SELECTED REFERENCES

B. Perkins, Jr., and W. F. Jackson, "Handbook for Prediction of Air Blast Focusing," BRL-1240, Ballistic Research Laboratories, Aberdeen, Md, February 1964.

S. Glasstone, editor, The Effects of Nuclear Weapons, Rev. Ed., DOD/AEC, U. S. Government Printing Office, Washington, D.C., April 1962.

E. F. Cox, J. H. Plagge, and J. W. Reed, "Meteorology Directs Where Blast Will Strike," Bull. Am. Meteor. Soc., Vol. 35, No. 3, pp. 95-103, March 1954.

J. W. Reed, "Explosion Wave Amplitude Statistics for a Caustic at Ranges of 30- to 45-Miles", SC-RR-67 860, Sandia Laboratories, February 1968.

J. W. Reed, "Climatology of Airblast Propagations for Nevada Test Site Nuclear Airbursts," SC-RR-69 572, Sandia Laboratories, December 1969.

J. W. Reed, "Airblast Overpressure Decay at Long Ranges," J. Geophys. Res., Vol. 77, No. 9, March 20, 1972.

J. W. Reed, B. J. Paper, J. E. Minor, and R. C. DeHart, "Evaluation of Window Pane Damage Intensity in San Antonio Resulting from Medina Facility Explosion on 13 November 1963," Annals of the New York Academy of Sciences, Vol. 152, Art. 1, October 28, 1968, pp. 565-584.

C. Wilton, and B. Gabrielsen, "House Damage Assessment," DNA-2906F, URS Research Co., San Mateo, CA, January 1973.

Pittsburgh Plate Glass Co., "Glass Product Recommendations - Structural," Tech. Service Report No. 101, Pittsburgh, PA (1964).
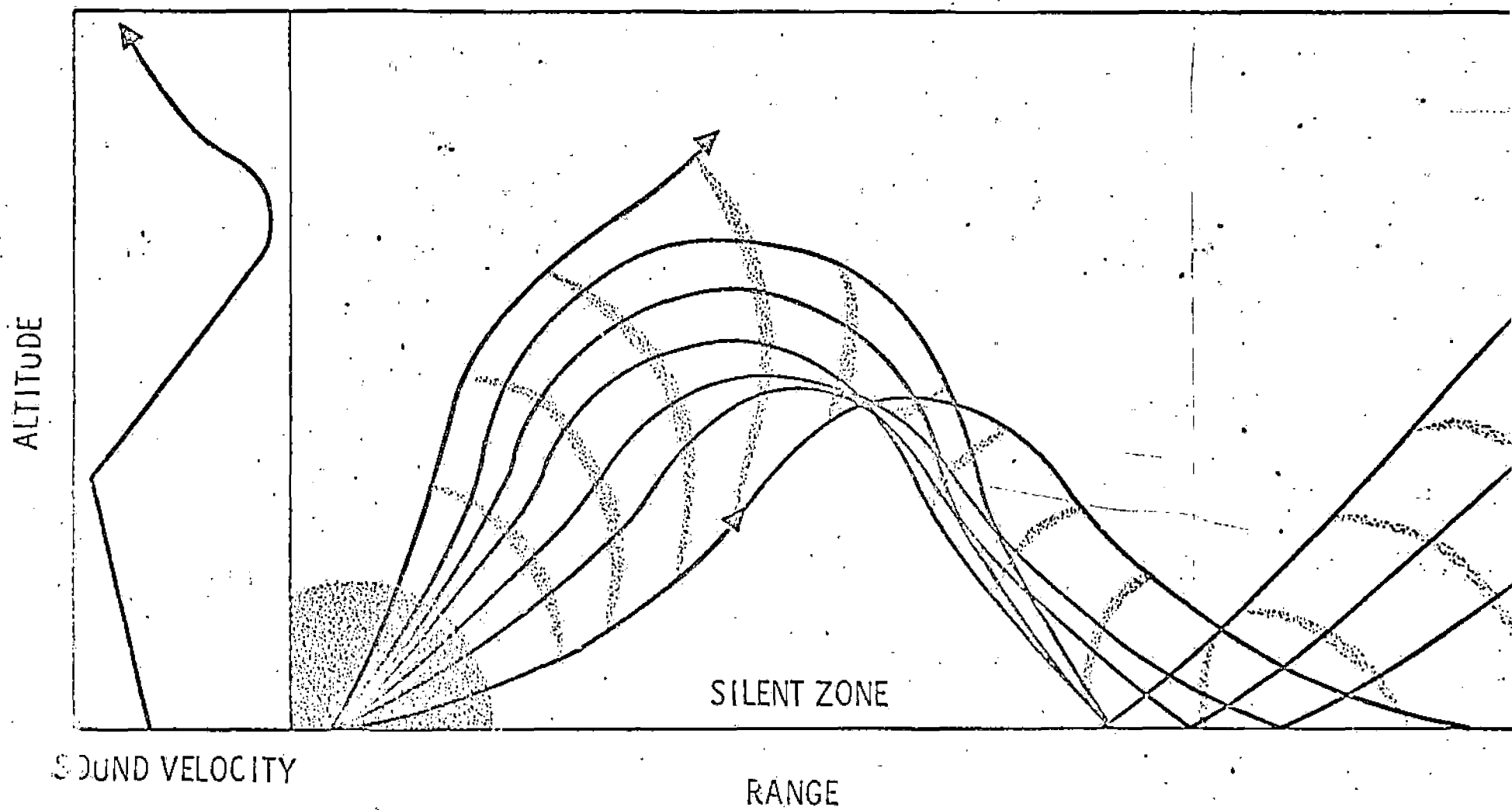
ALTITUDE

SOUND VELOCITY

SILENT ZONE

RANGE

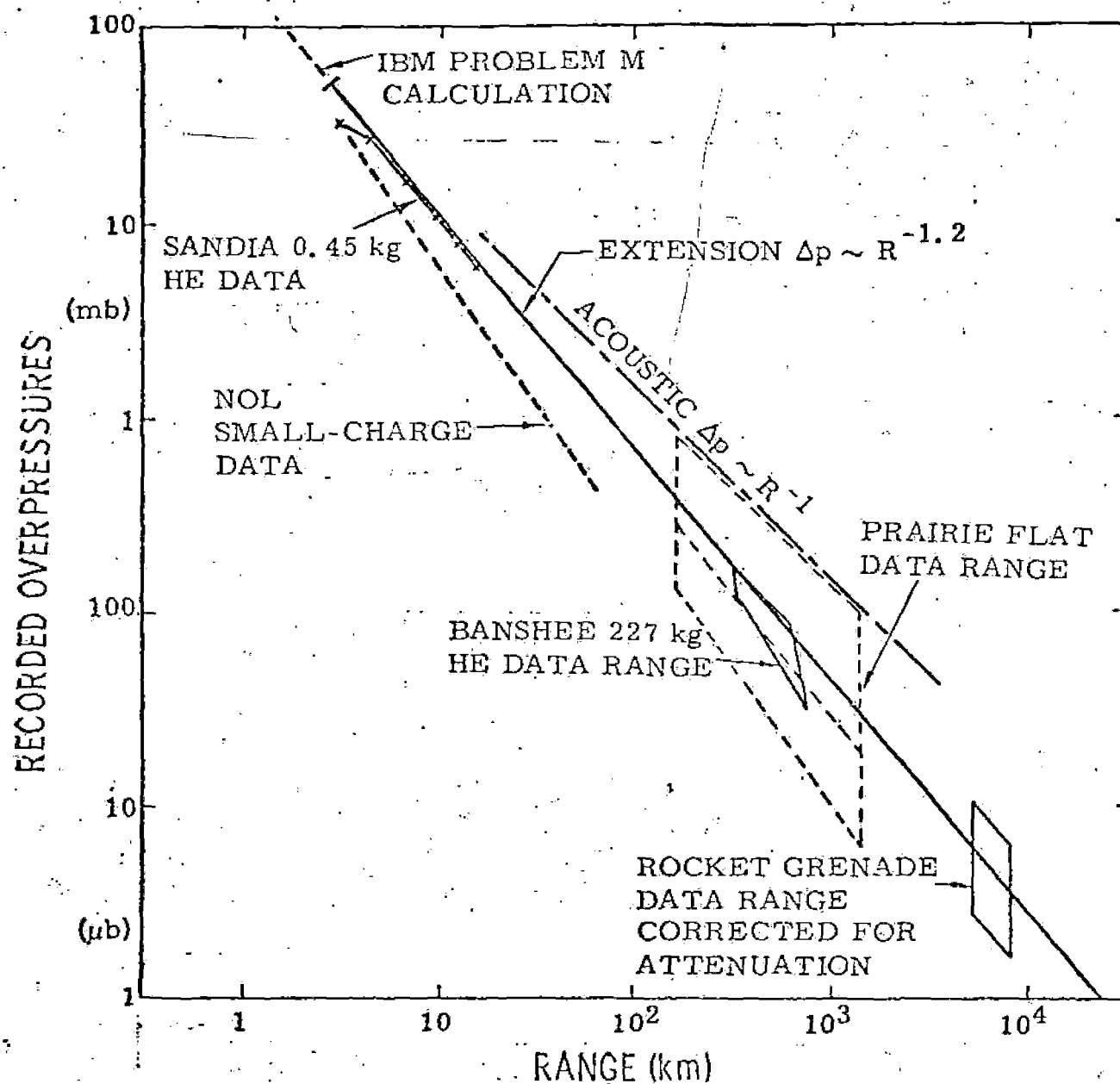FIG. 1 · TYPICAL EXPLOSION RAY PATHS

FIG. 2   LONG-RANGE AIRBLAST DATA
SCALED TO 1-KT NUCLEAR
EXPLOSIVES

FIG. 3

p = pressure

Δp = overpressure

R = slant range

W = yield

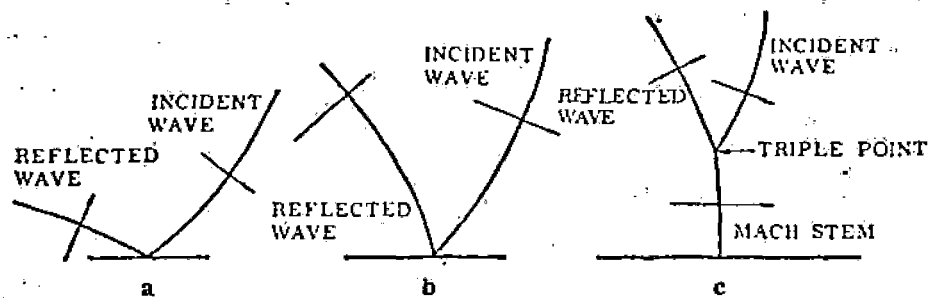## SIMULTANEOUS SCALING EQUATIONS

$$\frac{\Delta p}{p} = \frac{\Delta p_0}{p_0} \qquad (1)$$

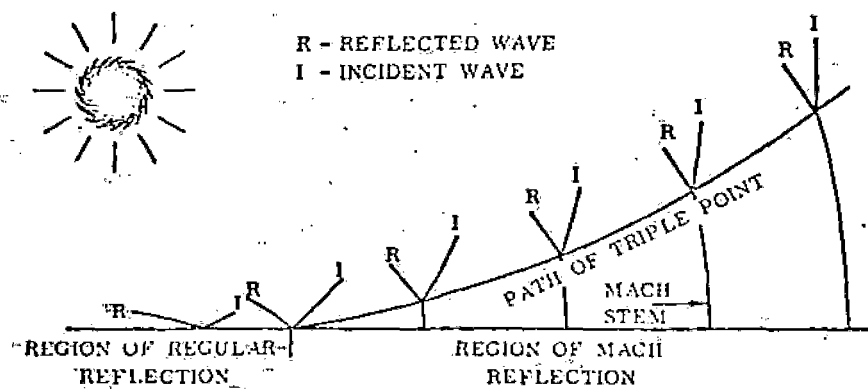$$\frac{R}{R_0} = \left(\frac{W}{W_0} \frac{p_0}{p} \right)^{1/3} \qquad (2)$$

LOW OVERPRESSURE-DISTANCE EQUATION

$$\Delta p = k W^{0.4} R^{-1.2} p^{0.6} \qquad (3)$$

k = constant

FUSION OF INCIDENT AND REFLECTED WAVES

R - REFLECTED WAVE
I - INCIDENT WAVE

PATH OF TRIPLE POINT

MACH STEM

REGION OF REGULAR REFLECTION

REGION OF MACH REFLECTION

BLAST WAVE MOTION IN THE MACH REGION

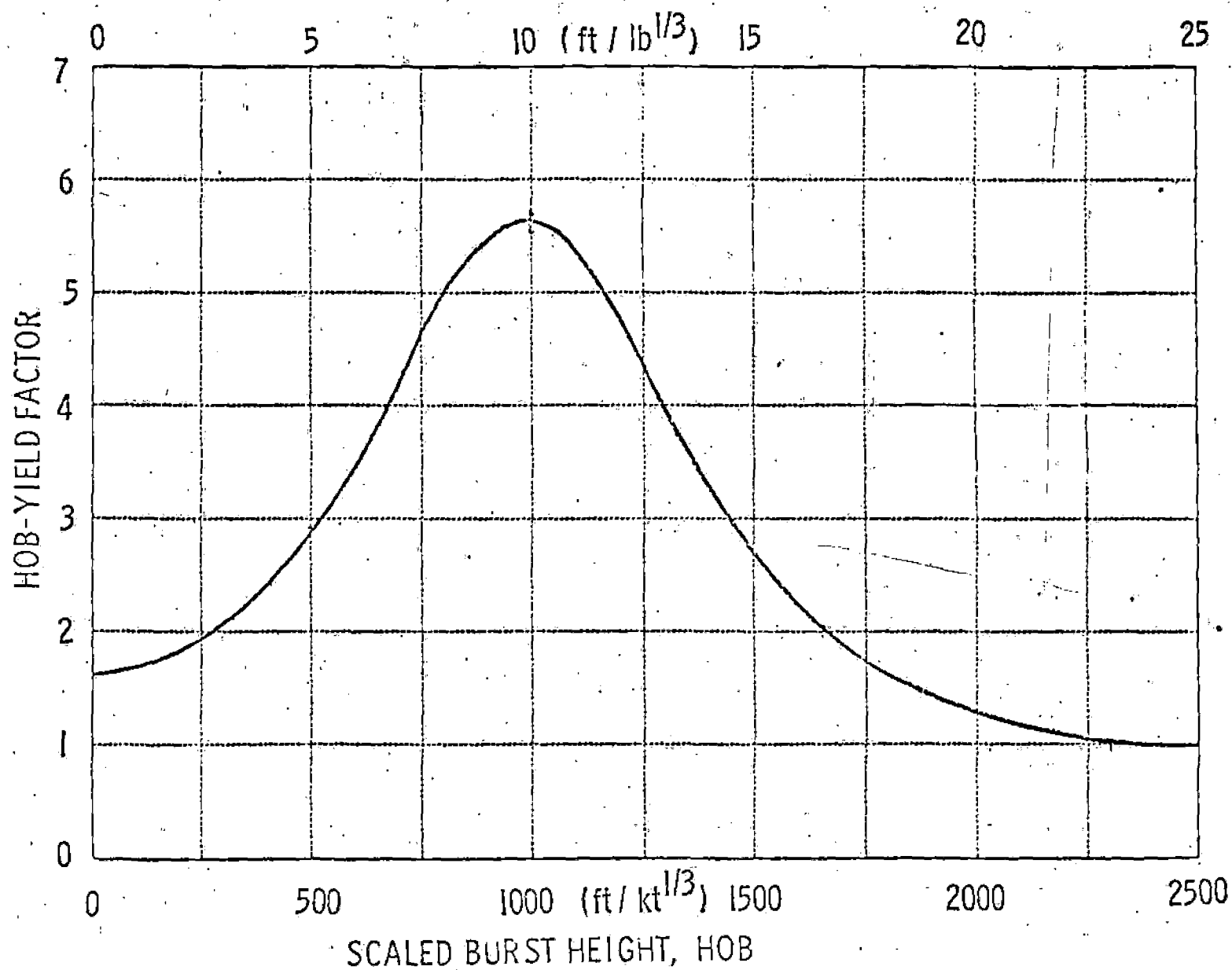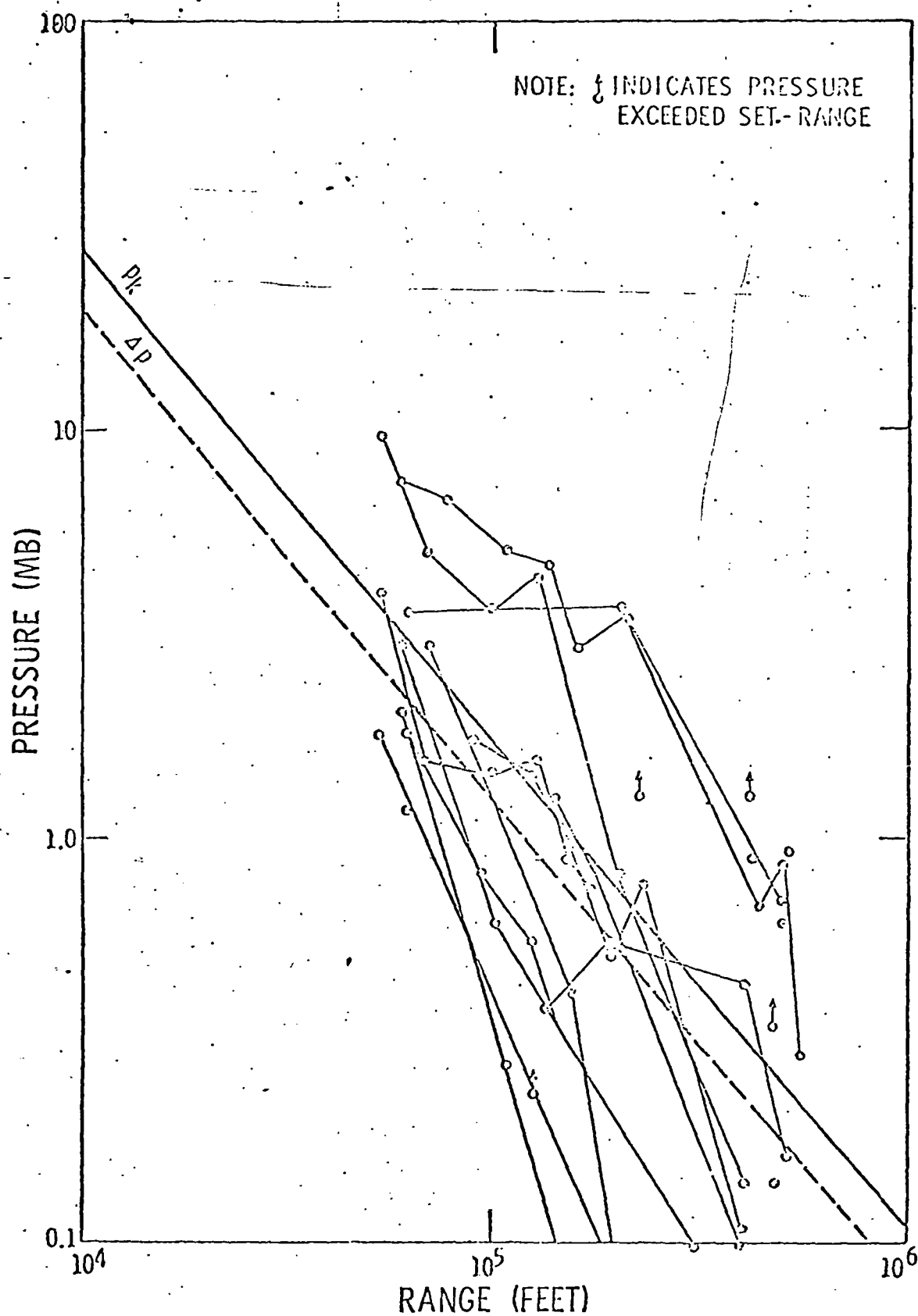FIG. 4   MACH STEM FORMATION FOR ABOVE-GROUND BURSTS

FIG. 5 AIRBLAST HEIGHT-OF-BURST EFFECT ON APPARENT YIELD

SUMMARY OF TROPOSPHERE PROPAGATIONS, UPSHOT-KNOTHOLE,
3/17 - 6/4, 1953 (SCALED TO I-KT NE AIRBURST)

FIG. 6
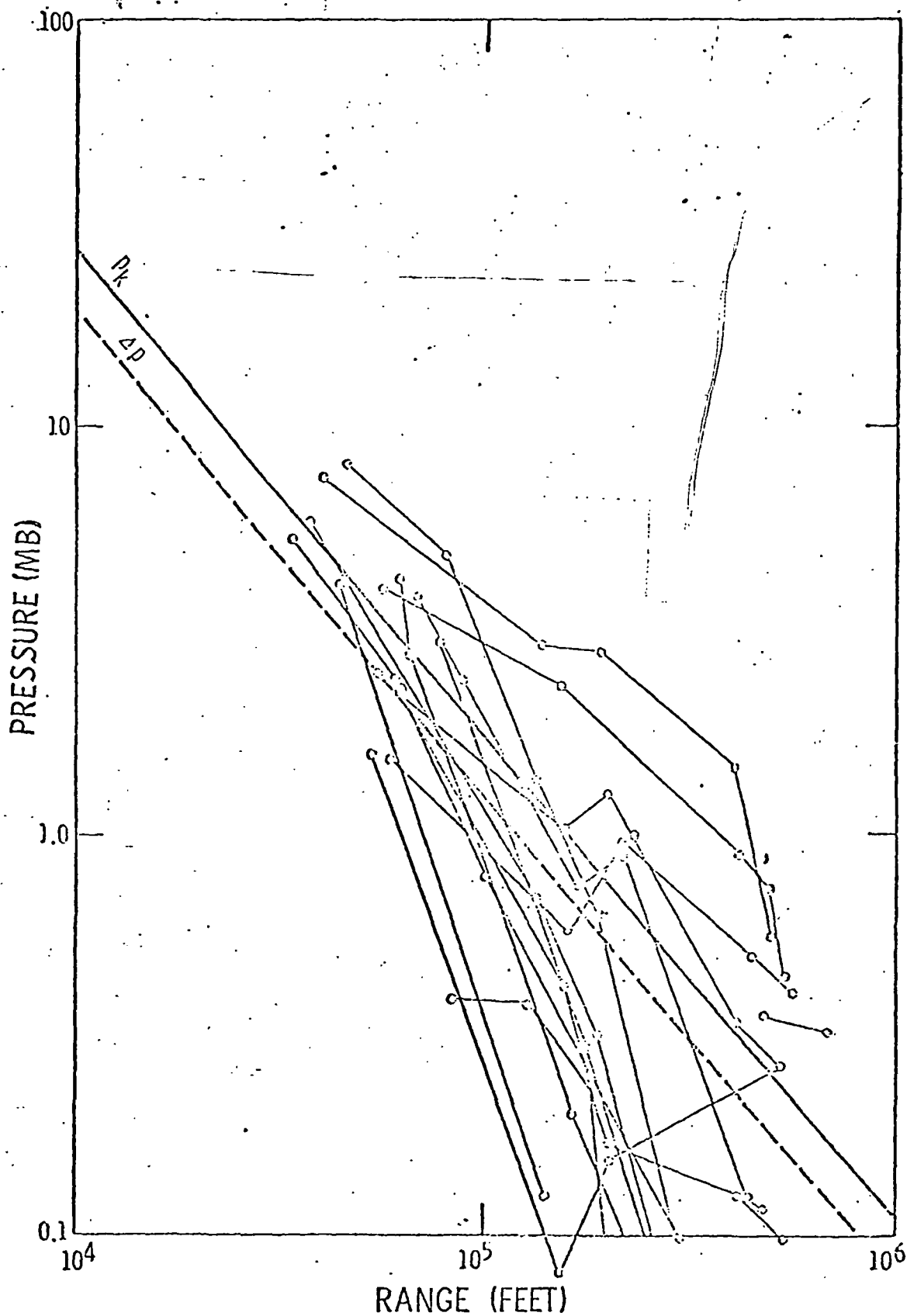
SUMMARY OF TROPOSPHERE PROPAGATIONS, TEAPOT, 2/18 – 5/15, 1955

(SCALED TO 1-KT NE AIRBURST)

FIG. 7

SUMMARY OF TROPOSPHERE PROPAGATIONS, PLUMBBOB, 5/28 - 10/7, 1957

(SCALED TO 1-KT NE AIRBURST)

FIG. 8
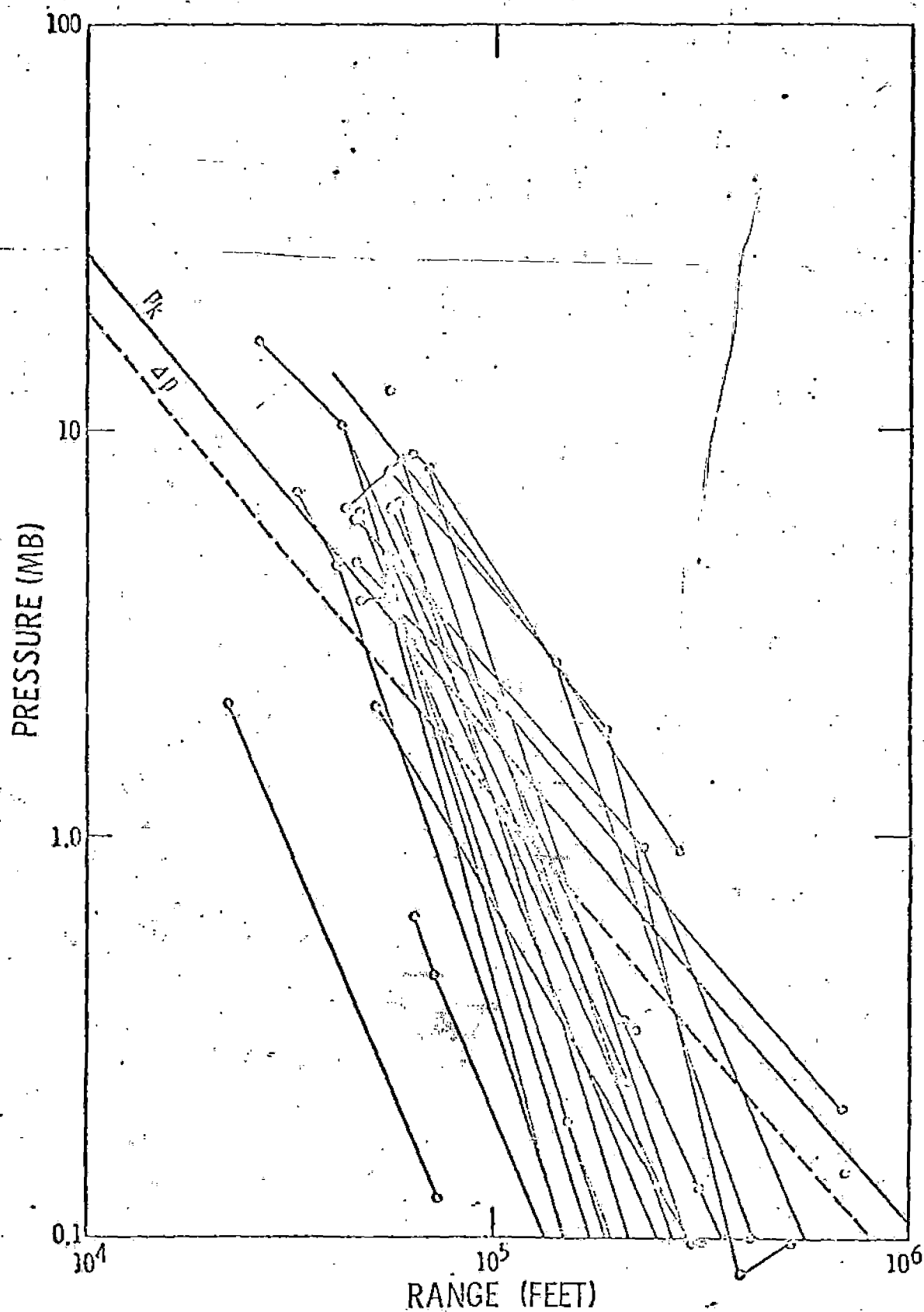
SUMMARY OF TROPOSPHERE PROPAGATIONS, HARDTACK II, 9/19 − 10/29, 1958

(SCALED TO 1-KT NE AIRBURST)

FIG. 9

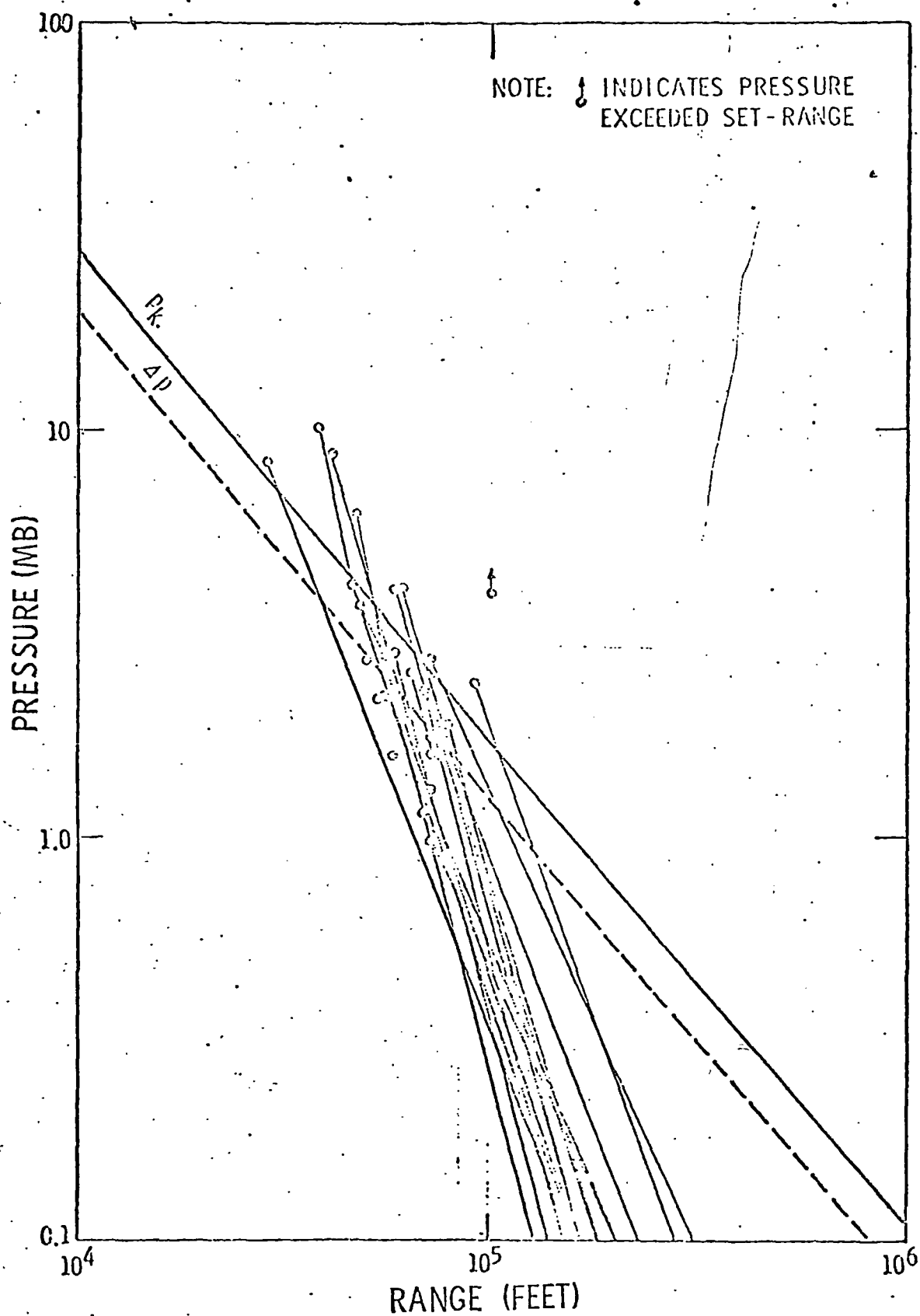FIG. 10   OZONOSPHERE SIGNAL AMPLITUDES, BISHOP, CALIFORNIA, FROM NEVADA NUCLEAR TESTS
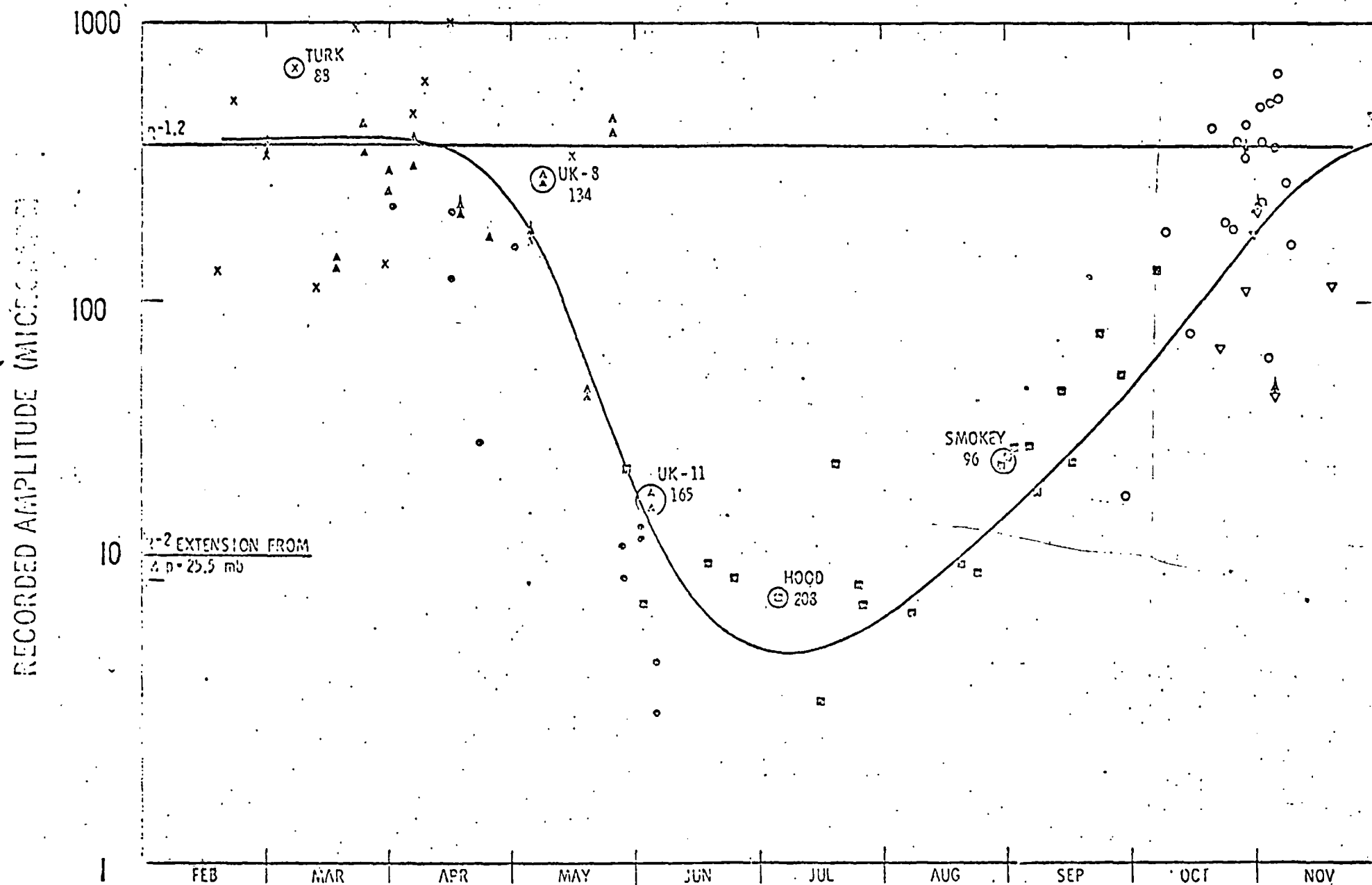
FIG. II OZONOSPHERE SIGNAL AMPLITUDES, ST. GEORGE, UTAH, FROM
NEVADA NUCLEAR TESTS
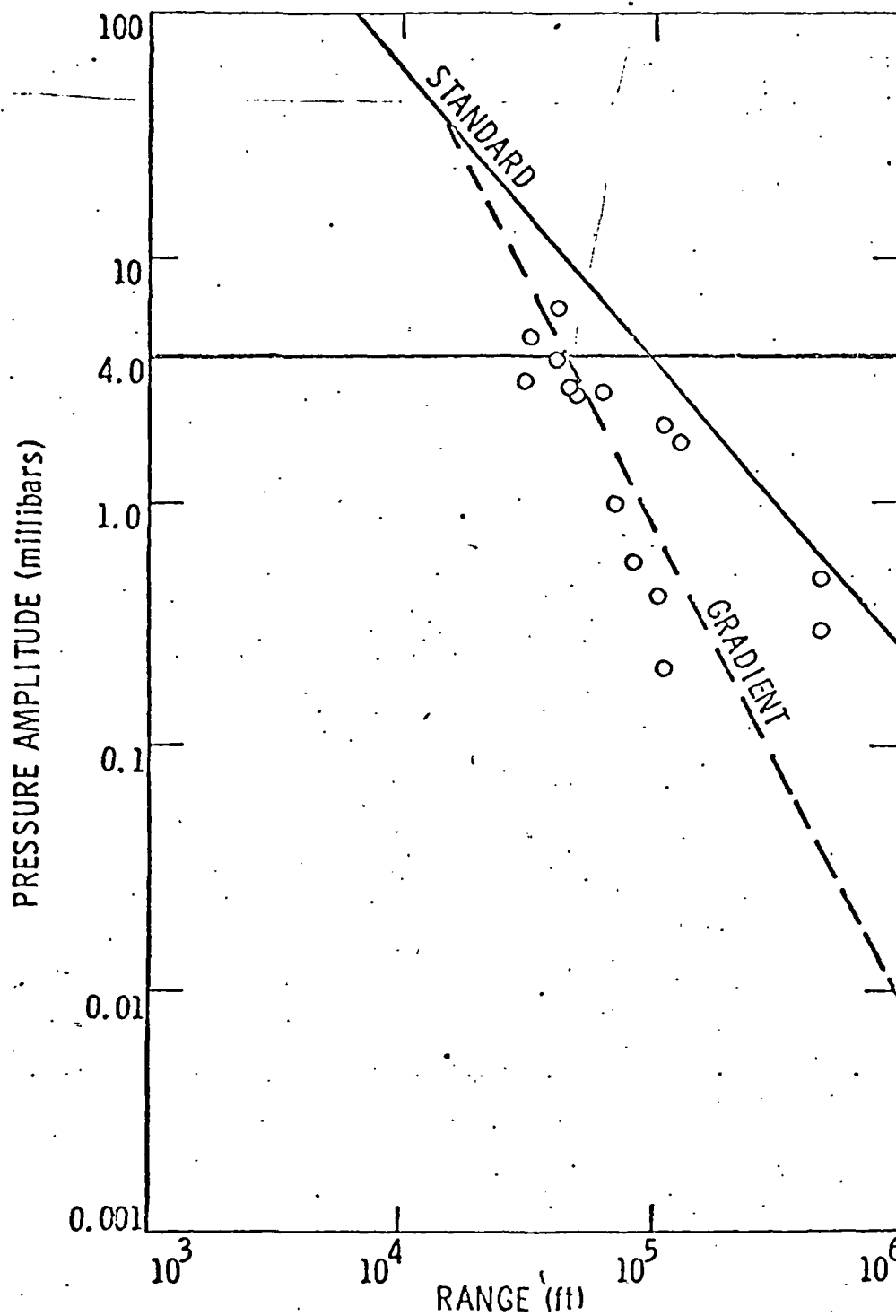
FIGURE 12 MIDDLE GUST SUMMARY OF PRESSURE AMPLITUDES, SCALED TO 1-KT SEA LEVEL FREE-AIR BURST.
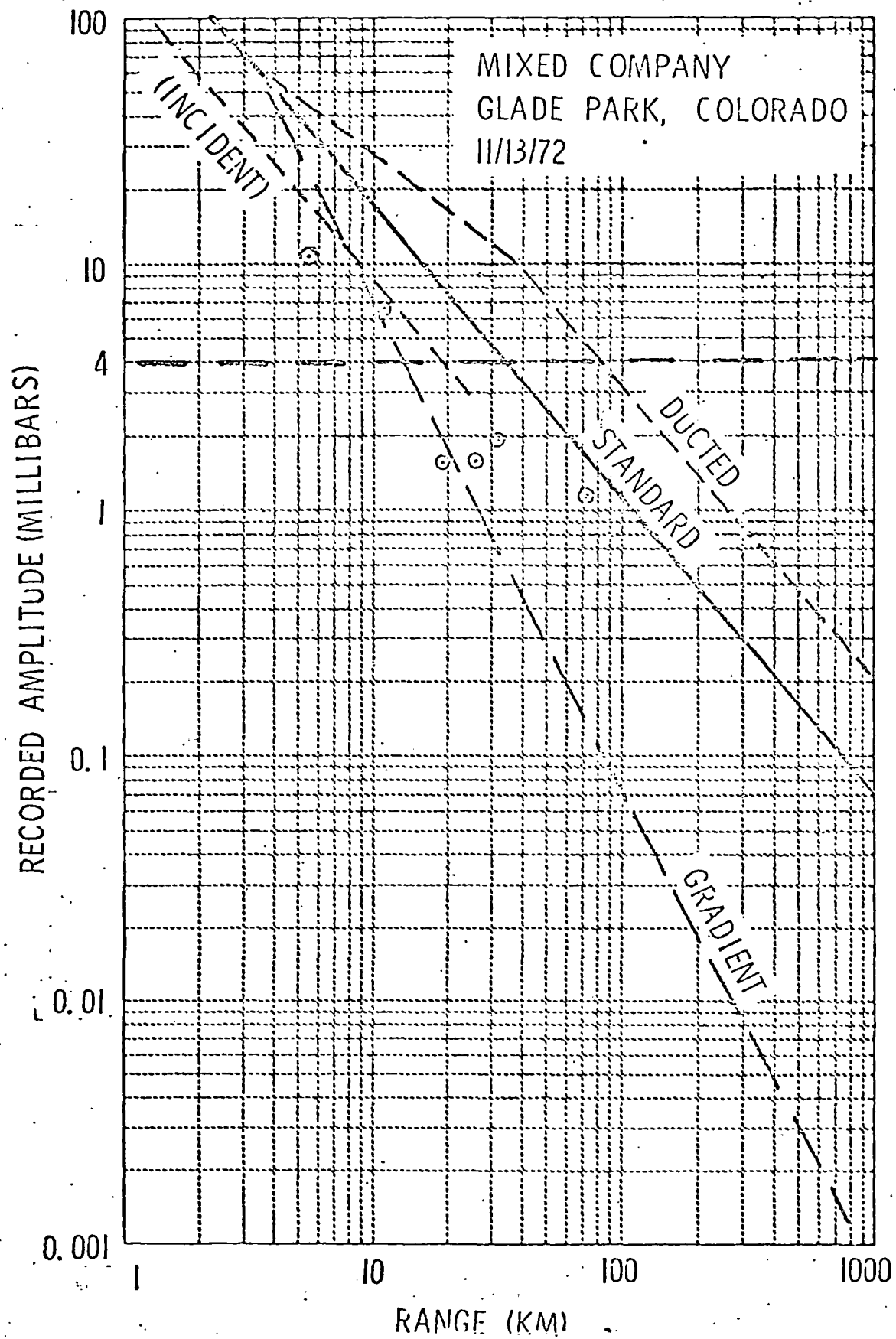
PEAK AMPLITUDES FROM 500-TON HE TEST

FIGURE 13
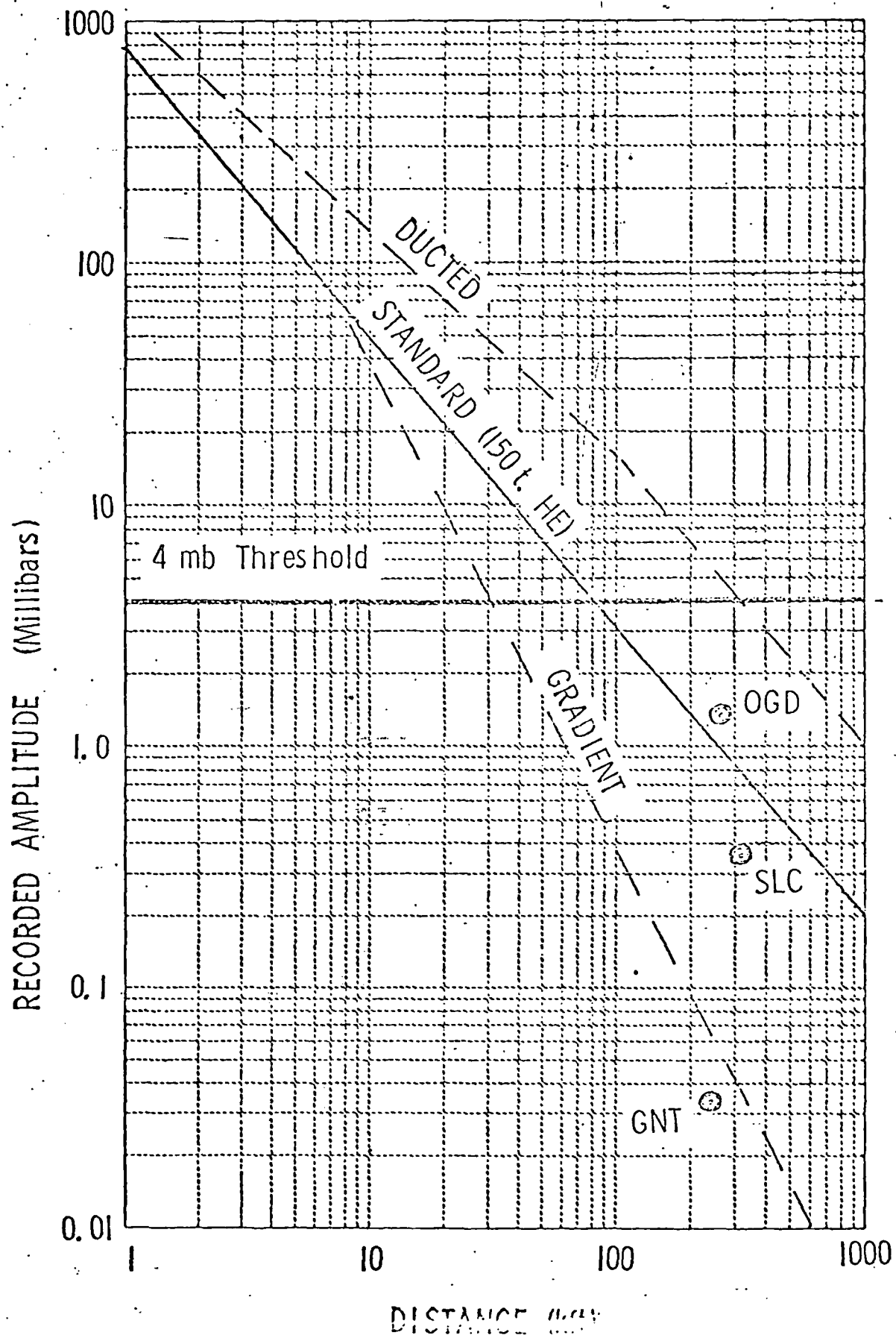
FIG. 14 . TOOELE - HILL TEST
3 FEB. 1973

FIG. 15
WINDOW DAMAGES

DAMAGE PROBABILITY

$$P = 3.71 \times 10^{-6} \, (A \, ft^2)^{1.22} \, (\Delta p \, mb)^{2.78}$$

NUMBER OF BROKEN PANES

$$Q = 1.3 \times 10^{-4} \, N \, (\Delta p \, mb)^{2.78}$$

$$N = \text{Population (people)}$$

From: Medina Base Accident, November 1963,
San Antonio, Texas

FIG. 17

NEW WINDOW DAMAGE EQUATION

$$\Delta p \, (50) = 75 \times (2.5)^{\pm 1} \, mb$$

$$\Delta p \, (50) : \quad 50\% \text{ Breakage Overpressure}$$

$$\text{Log Normal } \sigma = \text{Log}_e \, (2.5)$$
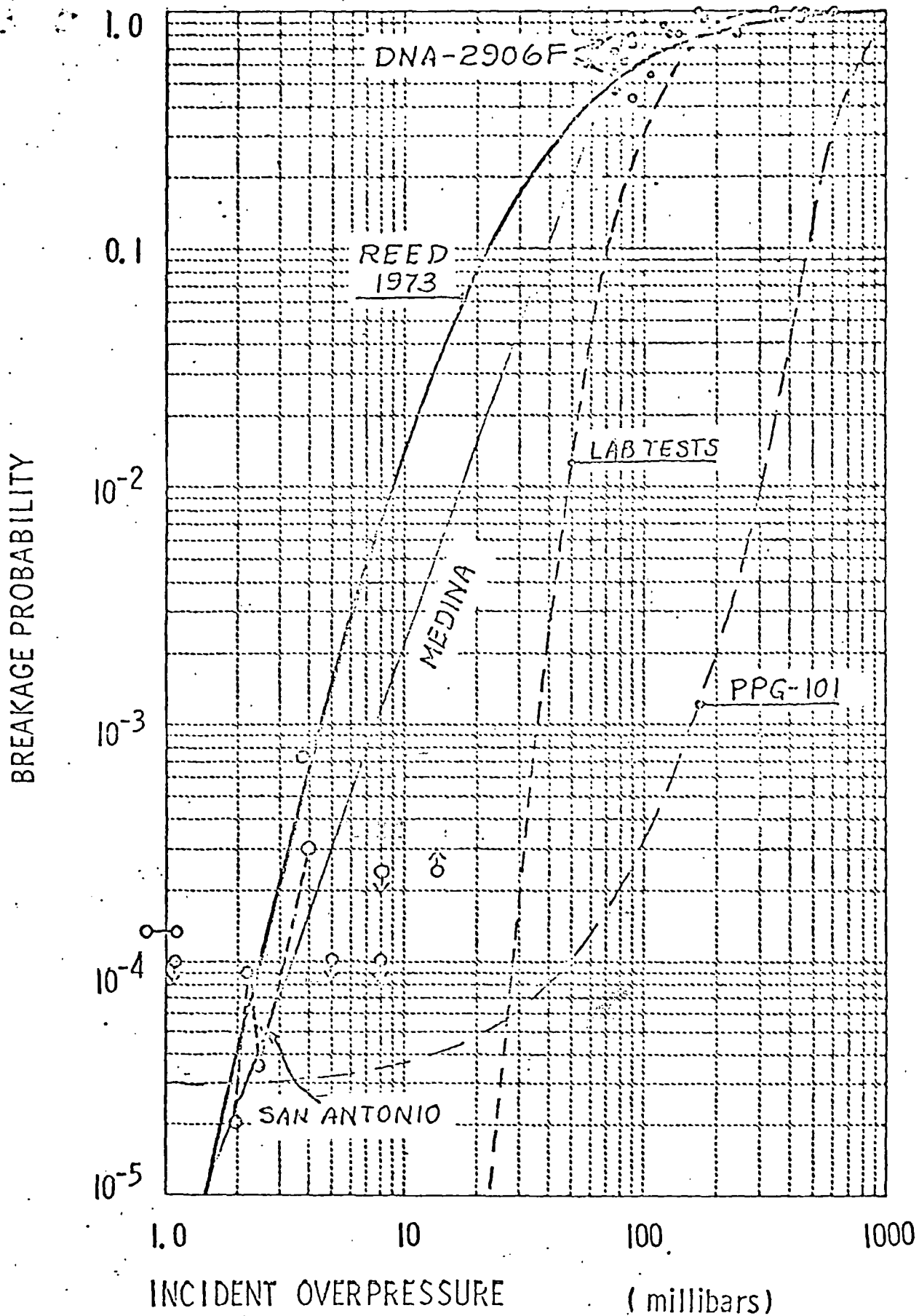
FIG. 16   WINDOW BREAKAGE FROM
AIRBLAST, THEORY & DATA

and copper is the constant presence of an impurity content
of cobalt (0.77-2.3%, table 1). The intermetallic phase with
increased cobalt content is usually found in one concretion
with nickel sulphide. This clearly reflects the geochemical
specialisation of the microlocal generating media of the
slag-forming minerals.

Owing to the exceedingly small dimensions of the main
mass of the silicate phases of the slag it was not possible
to realise their accurate quantitative analysis. Only the
limits of the concentrations of the non-ferrous metals were
determined. The largest segregations (0.05-0.10 mm) of
the silicates are fayalite with an iron content within the
limits of 59.7-63.5 wt.%. They differ from the other silicates
by a higher content of nickel (0.3-2.5%), copper (0.1-0.2%),
and cobalt (up to 0.4%).

There are two forms of olivine-like phases (I and II) with
a nickel concentration not exceeding 0.1% and copper 0.5%(4).
Thus, the nickel and copper in the converter slags are mostly
present in the sulphide form. The nickel phase-concentrators
are the monosulphide and chalcopyrite-pentlandite solid
solutions and intermetallic phase. The copper phase-con-
centrators are the sulphide chalcosine-bornite solid solution
and metallic copper, the proportion of which in the slag is
small. An appreciable amount of copper is found in the
chalcopyrite-pentlandite solid solution, impregnated in the
silicate glass. The remaining sulphide minerals and metallic
alloy are phase-bearers, and the concentration of copper
in them is small.

Cobalt has a sulphide, metallic, and oxide form and bears
a positive correlation with nickel. Its highest concentrations
are observed in the Ni-Fe metallic alloy (up to 6.13%). The
amount of cobalt in the silicate form is evidently determined
by the amount of fayalite.

The wide range of compositions of the sulphide solid solu-
tions in one product is of specific interest from the genetic
standpoint and is a subject for further investigations. The
validity of the separation of two iron-nickel sulphide solid
solutions is confirmed by their repeated detection in various
metallurgical products.

Conclusion

In the silicate phases the nonferrous metal sulphides are
present mainly in the form of a mechanical suspension,
which has solidified together with the silicates and separ-
ates during solidification of the silicates. Here microanaly-
sis of certain microzones of the silicates shows almost
complete absence of non-ferrous metals within the sensi-
tivity limits of the method. This demonstrates the need for
investigations into the conditions for more complete separa-
tion of non-ferrous metals from solid slags. Such conditions
may be special heat treatment, the addition of components
which alter the temperature and rate of crystallisation of
the slag components in the liquid state, and so forth.

References

1) G Springer: Die Berechnung von Korrekturen für die
   quantitative electronenstrahl - Mikroanalyse Forsch.
   Miner 1967, 45, (1), 103.
2) G Kullerud: Experimental petrology and mineralogy
   (Proceedings of the Geophysical Laboratory of the
   Carnegie Institute, No.62), Moscow 1969.
3) G Kellerud: Carnegie Inst. of Washington, B, 61, 1961,
   1962.
4) T R Soboleva et alia: Tsvetnye Metally 1975, (3).

Soviet Non-ferrous metals Research 1976 r.4 N1

UDC 669.334:66:081

Desorption of copper and zinc cyanide compounds by sulphuric acid solutions of oxidising agents with anion-exchange resin AV-17

T D Novikova, M D Ivanovskii and V S Strizhko (Moscow Institute of Steel and Alloys - Department of the Metallurgy
of Heavy Nonferrous Metals)

In the selective flotation of copper-zinc sulphide ores
cyanide liquors are frequently used to suppress the floata-
bility of zinc sulphides, and in the separation of the collec-
tive copper-lead concentrate they are used to depress the
copper minerals. Here oxidised and sulphur compounds of
copper and zinc and also noble metals dissolve to form com-
plexes with various compositions and are concentrated
mainly in the overflows from the copper concentrate thicken-
ers. One of the possible methods for the extraction of all
the valuable components is sorption by ion-exchange resins.
In spite of the effectiveness of the ion-exchange method for
purification of the cyanide effluents, the main difficulty in
the wide-scale introduction of sorption technology into
practice is the lack of satisfactory methods for desorption
of the metals and the treatment of the eluates obtained.

In the currently existing technology at the Zyryanovsk
concentration works the cyanide complexes of copper and
zinc and free cyanide ions are extracted from the overflow
of the copper concentrate thickener by means of the anion-
exchange resin AV-17x4. On account of their small content
in the solution, the gold and silver are previously extracted
by sorption on activated carbon. The desorption of copper
and zinc is realised with an eluent containing 18%NaCl +
2%NaOH. The obtained eluent passes on for electrolysis
to remove the copper. Investigations at the Kazmekhanobr
Institute and practice at the Zyryanovsk works[1] established
that the electrochemical method for the regeneration of the
eluate is extremely ineffective as a result of the impossi-
bility of regenerating the cyanide (the cost of which is greater
than the cost of the copper and zinc taken together), the

impossibility of recycling the eluate on account of the high
residual concentration of metals, and the high electricity
consumption (the current efficiency is not greater than
10-20%).

In the present work the use of acid elution with oxidising
agents is proposed. In addition to selective desorption of
copper and zinc and regeneration of the bulk of the cyanide,
this makes it possible to obtain eluates which do not require
further treatment as a result of their use as flotation rea-
gents.

In the work of Lebedev et alia[2] and by our investigations
it was established that the best sorption and kinetic charac-
teristics in relation to the cyanide complexes of nonferrous
metals are given by strongly basic anion-exchange resins
of the AV-17 and AM types. Experiments under static and
dynamic conditions were carried out on AV-17p x 10 resin
with a grain size of -0.8 to +0.5 mm in the chloride form.
The cyanide solutions were close in composition to the over-
flows of the copper concentrate thickener at the Zyryanovsk
works. Regeneration of the cyanide under dynamic conditions
was realised by blowing air through the layer of eluate under
vacuum (P = 0.3 - 0.4 atm., τ = 3 h) and collecting the HCN
with 2% sodium hydroxide solution. The analysis of the
solutions and resin after combustion was realised by chemi-
cal and atomic-absorption methods.

Fig.1 shows the dependence of the sorption of the cyanide
complexes of the metal and free cyanide from the solution
(mg/l): 620Cu, 330Zn, 270CN$_{free}^-$, 1560CN$_{tot}^-$, pH = 10.8.

The length of contact between the phases amounted to 6 h. For complete extraction of all the components a phase ratio $V_{resin}:V_s$ of 1:25 is required. Here the exchange capacity of the resin has the following values (mg/g): $52.3 Cu, 27.5 Zn, 22 CN_{free}, 130 CN_{tot}$.
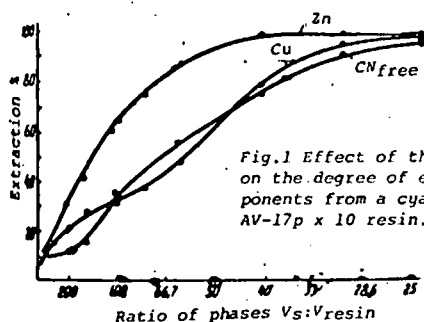

Fig.1 Effect of the ratio of the phases on the degree of extraction of the components from a cyanide solution by the AV-17p x 10 resin.

It is known that during the acid desorption of copper and zinc from anion-exchange resins saturated with the cyanide complexes of these metals the greatest difficulties arise in the case of cyanocuprate ions. Whereas the zinc complexes are decomposed relatively easily by solutions of acids, copper (on account of the greater stability of its cyanide complexes and, largely, on account of the absence of stable compounds of monovalent copper in solutions of mineral acids) only gives up part of the cyanide ions combined with it right up to the transition to the insoluble compound CuCN[3]).

Since solutions of copper and zinc sulphates are used as reagents in flotation, sulphuric acid solutions were used for the desorption of the metals from the AV-17 resin. It was observed that zinc is fully desorbed in 1 h by a 0.5 M solution of sulphuric acid with an organic-aqueous phase ratio $V_o:V_w =$ 1:10. With increase in the acid concentration to 100 g/litre and with increase in the length of contact between the phases to 4 h the extraction of copper increases somewhat but does not exceed 2-3%.

To determine the composition of the copper complex remaining on the resin after acid treatment the infrared spectrum of the resin was determined. This revealed the existence of one absorption band with a frequency $\nu = 2125 \text{ cm}^{-1}$ corresponding to a singly charged dicyanocuprate ion[4]. In addition, during acid elution 60-65% of the total content of the cyanide in the resin was regenerated, and this is 10-15% greater than the difference between the total amount of sorbed cyanide and that combined in $Cu(CN)_2^-$. In all probability, some part of the copper passes into the "simple" cyanide CuCN, which was not detected by the IR spectrum on account of the small amount and of the low extinction coefficient of this compound[4]). The possibility of the utilisation of oxidising agents for the desorption of copper, as a result of its conversion into the unsorbed cationic form, was examined in[5], but the use of the mixture of mineral acid and its ferric salt proposed by these authors is undesirable on account of the formation of poorly decomposable mixed complexes of iron in the resin phase. In the literature[6] a sulphuric acid solution of ammonium persulphate $[2\% (NH_4)_2S_2O_8 + 50 \text{ g/l } H_2SO_4]$ is proposed as a desorbent for copper.

In the present work solutions containing various oxidising agents (hydrogen peroxide, chlorate, persulphate, and nitrate ions) were examined for the purpose of selecting the most effective oxidising agents for copper. To determine the oxidising power of the investigated oxidising agents the equilibrium constants were calculated for the corresponding oxidation reactions of copper present in the solution in the form of $Cu(CN)_2^-$. The values of the thermodynamic functions were taken from the literature[7]. The obtained equilibrium constants and the values for the normal oxidising potentials are given in the table.

It is known that the NO_3 ion is the weakest oxidising agent in the investigated series; HNO_3 only desorbs copper at

fairly high concentrations (2-3 N)[8]). During the desorption of copper by $NH_4NO_3 + H_2SO_4$ and $NaNO_3 + H_2SO_4$ solutions it was noticed that the oxidation of copper with NO_3 ion concentrations up to 1.5-2N takes place very slowly and the extraction of copper after contact for 2h does not exceed 30% (fig.2): Some acceleration of the process is observed with increase in temperature. Full extraction of the copper by a mixture of ammonium nitrate (0.25 N) and sulphuric acid (0.5 M) solutions is achieved after three stages of desorption at 57.5-58°C with a $V_o:V_w$ ratio of 1:10 and a contact time of 2h in each stage.

Equilibrium constant for the oxidation reactions of copper present in the solution in the form of $Cu(CN)_2^-$

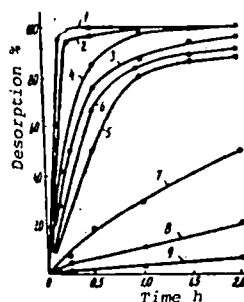| Oxidising agent	Degree of reduction	Equilibrium constants	Normal oxidation potential
NO_3^-	NO	$1.57 \cdot 10^{13}$	+0.8
	NO	$5.37 \cdot 10^{18}$	+0.96
ClO_3^-	Cl^-	$4.3 \cdot 10^{20}$	+1.21
	ClO_2^-	$4.7 \cdot 10^{24}$	+1.45
H_2O_2	H_2O	$1.35 \cdot 10^{30}$	+1.77
S_2O_8''	SO_4''	$3.2 \cdot 10^{33}$	+2.0

Fig.2 Desorption of copper by sulphuric acid solutions of oxidising agents (g/l) as a function of the phase contact time. Hydrogen peroxide: 1-10; 2-6; 3-3g/l. Potassium chlorate: 4-10; 5-5. Ammonium persulphate: 6-20. Concentration $25H_2SO_4$ (expts.1-6). $20NH_4NO_3 + 44H_2SO_4$, $t = 57°C$ (7); the same, $t = 38°C$ (8); the same, $t = 22.5°C$ (9). In all the experiments the $V_o:V_w$ phase ratio was 1:10.

In accordance with the values of the equilibrium constants and the normal oxidation potentials the $S_2O_8^{2-}$ ion is the strongest oxidising agent (table). Investigation of the effect of the concentration of the oxidising agent on the degree of desorption of the copper showed that a large consumption of the oxidising agent not less than $[15 \text{ g/l } (NH_4)_2S_2O_8]$ is required for the persulphate ion compared with hydrogen peroxide (6 g/l) and potassium chlorate (10 g/l) (fig.3). In addition, the desorption of copper by ammonium persulphate solutions takes place slowly, and this is explained by the low rate of oxidation by per-sulphuric acid formed in a sulphuric acid solution[9]). Thus, ammonium persulphate solutions are inferior to perioxide and chlorate solutions in their desorbing characteristics. Figure 3 (curves 4 and 5) also shows the dependence of the desorption of copper by solutions of hydrogen perioxide (3 g/l) and potassium chlorate (5 g/l) respectively on the sulphuric acid concentration.
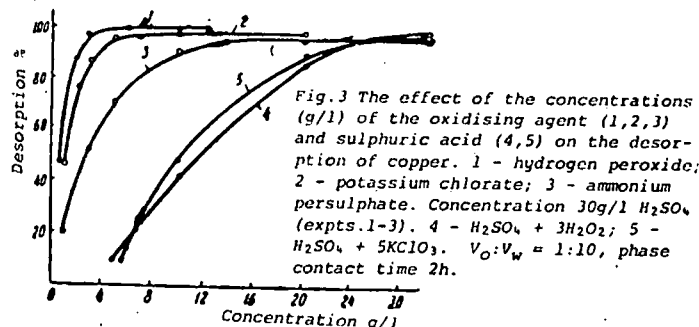
Fig.3 The effect of the concentrations (g/l) of the oxidising agent (1,2,3) and sulphuric acid (4,5) on the desorption of copper. 1 - hydrogen peroxide; 2 - potassium chlorate; 3 - ammonium persulphate. Concentration $30g/l H_2SO_4$ (expts.1-3). 4 - $H_2SO_4 + 3H_2O_2$; 5 - $H_2SO_4 + 5KClO_3$. $V_o:V_w = 1:10$, phase contact time 2h.

During elution of copper by solutions of oxidising agents the question arises as to the oxidation of the cyanide combined with it and also the possible change in the sorption characteristics of the ion exchanger. By laboratory tests at the Zyryanovsk concentration plant it was established that the use of hydrogen peroxide and potassium chlorate

for 10 cycles doe not reduce the sorption characteristics of the AV-17 resin. During selective elution of copper with distillation and collection of the hydrocyanic acid it was observed that when peroxide solutions (6 g/l H_2O_2 + 25 g/l H_2SO_4) are used 30-35% of the total amount of sorbed cyanide or about 90% of the cyanide combined into the $Cu(CN)_3^-$ complex is oxidised. In the case of potassium chlorate (10 g/l $KClO_3$ + 25 g/l H_2SO_4) 8-10% of the total amount of cyanide is oxidised, which amounts to 20-25% of the cyanide combined into the complex. Thus, if the lower degree of oxidation of the cyanide and the lower (by half) cost of chlorate solutions compared with peroxide solutions are taken into account a sulphuric acid solution containing chlorate ions must be considered to be the most effective among the investigated desorbents for copper. The eluate obtained after the desorption of copper by the chlorate solution can be used as reagent in the zinc-pyrite flotation cycle, as was confirmed by laboratory tests at the factory. The sodium cyanide obtained as a result of distillation of the hydrocyanic acid and its collection by alkali (32-37 g/l NaCN) can also be used as a flotation reagent.

Conclusions

1. The desorption of cyanide complexes of copper with sulphuric acid solutions containing various oxidising agents (hydrogen peroxide, chlorate, persulphate, and nitrate ions) was investigated. A sulphuric acid solution of potassium perchlorate with the composition 10 g/l $KClO_3$ + 25 g/l H_2SO_4 is proposed as the most effective desorbent for copper.

2. Together with the selective desorption of copper and zinc and regeneration of the bulk of the cyanide, one of the main advantages of the proposed method of acid elution is the possibility of direct utilisation of the eluates as reagents in flotation: zinc sulphate in the copper-lead cycle and copper sulphate in zinc-pyrite cycle.

References

1) A N Kvyatkovskii et alia: Methods for purification of industrial effluents. Tr. Inst. Kazmekhanobr 1972, 8, (1).
2) K B Lebedev et alia: Synthesis and use of ion-exchange materials and sorbents in non-ferrous metallurgy 1972, p.14-23.
3) I N Plaksin and S A Tetaru: Hydrometallurgy with the use of ion-exchange resins. Metallurgiya 1964.
4) I D Fridman and N D Klyueva: Tsvetnye Metally 1972, (2).
5) Yu A Beilin et alia: Authors' Certificate No.129333, 1960.
6) B P Pimenov et alia: Izv Vuz Tsvetnaya Metallurgiya 1972, (4).
7) M Kh Karapet'yants and M L Karapet'yants: Fundamental thermodynamic constants of inorganic and organic substances. Khimiya 1968.
8) V I Demidov: Tsvetnye Metally 1967,(8).
9) B V Nekrasov: Course of general chemistry. Khimiya 1965, 1.

Some relationships in the cementation of copper by nickel in a fluidized bed under the influence of ultrasonic vibrations

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Cementation in a fluidised bed was proposed and first introduced on an industrial scale at the Severonikel' Combine in 1959 [1] and has been successfully used there from that time. Apparatus with a fluidised bed of a metal cementation agent differs favourably from other apparatus employed in industry in its higher productivity and also in the simplicity of construction and maintenance. In addition, the required degree of purification of the solutions from impurities in fluidised-bed equipment is achieved by the creation of a large excess of the metal cementation agent on account of the low rates of removal of the particles. At the same time, as a result of poorly developed agitation in the fluidised bed, the cemented deposit is poorly removed from the surface of the particles of the metal cementation agent, thereby preventing its full utilisation in the process. Another result of the poor agitation is the formation of spherical conglomerates, which disrupt the hydrodynamics of the bed.
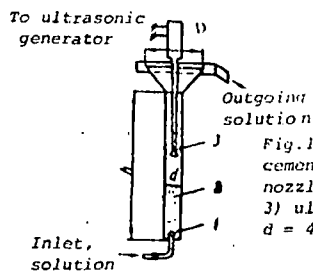

Fig.1 Diagram of the apparatus for cementation in a fluidised bed: 1) nozzle, 2) fluidised bed zone; 3) ultrasonic emitter. D = 170mm, d = 45mm, h = 450mm.

Various papers [1-7] have been devoted to investigation of fluidised-bed cementation, and in the greater part of them questions of the hydrodynamics of the fluidised bed are considered. The purpose of the present investigation was to study the individual relationships governing the cementation process in a fluidised bed and also to establish the possibility of intensifying the process by means of ultrasonic treatment. Cementation was realised in laboratory apparatus with a fluidised bed zone of cylindrical form 45mm in diameter and 450mm high (fig. 1). The introduction of the solution into the apparatus was realised through a nozzle with eight apertures. The solution had the following composition g/l: 70 Ni^{++}, 115 SO_4^{--}, 30 Cl^-, 20 Na^+, 4 H_3BO_3, pH = 2.6. Cementation was realised with nickel powder having the following composition %: 86.0 Ni, 5.97 Cu, 2.64 Fe. The equivalent diameter of the particles of the initial nickel powder d_e was 0.438mm. The source of the ultrasonic vibrations was a UZDN-IV 4.2 instrument with a magnetostrictive converter at a resonance frequency of 22 kHz. The area of the emitter was 1.77 cm^2. The ultrasonic regime was of the cavitation type, the presence and intensity of which was evaluated from the disintegration of aluminium foil.

To obtain a mathematical model of the fluidised bed cementation process the experimental design method was used with the following five factors: the concentration of copper in the solution; the specific amount of nickel powder in the fluidised bed zone; the temperature of the solution; the flow rate of the solution in the fluidised bed zone; the intensity of the ultrasonic vibrations.

Owing to the fact that a linear model was found to be inadequate, we used a central composite rotatable design of second order with fractional replication of the 2^{6-1} type and a total number of trials of 32. The conditions of the trials are given in the table.

The coded values of the factors are as follows:

$$X_1 = \frac{t - 60}{10}, \quad X_2 = \frac{G - 0.200}{0.05}, \quad X_3 = \frac{\nu - 0.04}{0.01}, \quad X_4 = \frac{I - 12.0}{6.0}$$

*) A V Ogarkov took part in the experimental work.

Cockfield is the proposed disposal zone.

During aquifer renovation following leaching, Arco expects to pump an estimated 150 gpm of slightly saline water from the leach pattern, with a probable maximum of 2,000 mg per liter total dissolved solids. This water will be pumped to the disposal well after most of the uranium has been removed. The native water in Cockfield sands is much more saline than the disposal stream.

The surface hole will be drilled 12½-in.-dia and 600 ft deep, through the Oakville aquifer and into the underlying Catahoula clays. H-40, 32.3-lb pipe with a diameter of 9⅝ in. will be set as casing to 600 ft, and Class C cement circulated to the surface. An 8¾-in. hole will then be drilled to 4,500 ft. Upon completion of drilling, electrical and bulk density logs will be run in the hole.

Casing—7-in.-dia, 20-lb, H-40 pipe—will be set on the bottom and cemented in two stages. The first stage will

bring cement to the top of the Cockfield sand, a depth of about 3,500 ft. Utilizing a D-V tool, sufficient additional cement will be pumped to circulate to the surface.

Injection intervals will be determined from electric and gamma-ray logs. Proposed intervals are from 3,580 ft to 3,670 ft and from 3,700 ft to 3,790 ft. The balance of the Cockfield sand between the depths of about 3,790 ft and 4,500 ft is considered a reserve for future disposal, if volumes or pressure gradients exceed present estimates.

When the ore zone of a leaching pattern has been restored, Arco will turn the surface back to normal use. The area will need reseeding, but reclamation in the usually understood sense will be unnecessary. The leaching operations will leave the surface essentially undisturbed. Within a few years after leaching stops, it may be difficult to identify a leach pattern area as ever having been different from the surrounding countryside. □

Developers eye Texas potential for in-situ uranium leaching

Emmy Crawford, McGraw-Hill World News, Houston

IN ADDITION TO the Arco-US Steel-Dalco plant now in production near George West, Tex., several other in-situ uranium leaching projects are in various stages of planning, design, and construction in south Texas.

The most advanced project belongs to Westinghouse's wholly owned subsidiary, Wyoming Minerals, which is building a 250,000-lb-per-year plant near Bruni, Tex., about 40 mi east of Laredo. While Wyoming Minerals has not revealed any details of its process, a source at the Texas Water Quality Board states that the operation will use a weak ammonia leach and a proprietary ion exchange extraction system.

Wyoming Minerals also plans a second commercial uranium in-situ leach plant near Ray Point, north of George West in Live Oak County. The Texas Water Quality Board has received an application for this operation, but as of early June, no date had been set for a hearing.

In Duval County, Union Carbide is considering a pilot-scale in-situ leach operation, but for it too, no hearing date had been set by early June.

(While n t of direct interest to Texas uranium production, a Burlington Northern-Wyoming Minerals joint venture calls for Wyoming Minerals to conduct minerals exploration on 8.4 million acres of Burlington Northern railroad property in Oregon, Washington, Idaho, Wyoming, Montana, North Dakota, Minnesota and Wisconsin. The agreement, which includes gas, oil, and uranium as well as other minerals, will run five to eight years, and Wyoming Minerals will get up to 50% interest in discovered properties, depending on how much money it invests in the project. The joint venture company—called Bur-West—is headquartered in Billings, Mont.)

Mobil pilot plant is under construction

Southeast of Bruni, in Webb County, Tex., Mobil Oil Corp. is building a pilot plant to test the feasibility of a proprietary in-situ uranium leaching method. The plant is

expected to start up around October 1 to leach U_3O_8 in place, at depths of 410 to 430 ft.

Present plans call for an initial 18-month test program, with an overlapping 15-month test at a nearby site if the first program is successful. The capacity of the pilot scale operation will not be determined until solution is actually put into the ground, and Mobil has no present timetable for commercial development.

The Mobil pilot operation will inject a leach solution into the uranium-bearing formation through 15 injection wells and extract it through seven production wells. The solution is identified as a dilute ammonium carbonate made by mixing gaseous ammonia and carbon dioxide with formation water treated with ordinary water softener. An unidentified oxidant is also added. Solution produced will be collected in a surge tank and then pumped to a holding tank at the recovery plant site, about 700 ft away.

A sand filter will remove suspended solids, and an ion exchange column will extract U_3O_8. The barren effluent from the ion exchange column will be pumped to a holding tank where an oxidant and leach chemicals are added, and the solution will be recycled to the injection wells.

Uranium will be extracted from the ion exchange resin by an unidentified chemical, and the U_3O_8-rich eluate will be pumped to a holding tank and then to a precipitation tank for uranium precipitation. Ammonia and carbon dioxide gases generated in the precipitation process will be vented to a 20-ft-high fume scrubber. Water spray in the scrubber will absorb the vapors, and the resulting solution will be recycled to the injection well stream.

Filters, ion exchange, and water softener tanks will be backwashed periodically and the water held in a 500-bbl tank. If backwash water is found to contain excess solid or radioactive material, it will be pumped to an evaporation pit.

A system of eight monitoring wells will determine if there is leakage of chemicals outside the planned injection production pattern.

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cipitation or by an electrolytic process. The "formation of salt by sintering" reactions do not occur in a wet way between MnO_2 and WO_3 or MoO_3, nor with natural sulphides such as FeS_2. They can be realized very easily by sintering.[2]

Sodium nitrate, $NaNO_3$, is a very mild oxidizing reagent (except in the presence of a strong reducing agent), and a very soluble compound, allowing easy penetration into the pores of the ore. It also has a relatively low melting temperature (310°C), and by decomposition at a high temperature (400°C) it furnishes the correspondent nitrite, $NaNO_2$, which is both an oxidant and a solvent for the metallo-acid elements.[3] However, sodium nitrate cannot be recovered.

Chromium trioxide, CrO_3, is an extremely strong and easily soluble oxidizing agent whose oxidizing power increases with decreasing water content of the solvent.[3] It is

layer by electrolytic oxidation, according to the overall equation:

$$Cr_2(SO_4)_3 + 5H_2O + 1½O_2 \rightarrow 2H_2CrO_4 + 3H_2SO_4$$
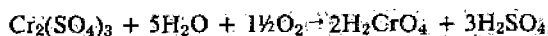
The new process has been tested with good results for the extraction of uranium from low grade refractory uranium ores, such as uraniferous zirconium ores, and from pyrochlore concentrates. □

References

1) McClaine, L. A., E. P. Bullwinkel, and J. C. Huggins, Proceedings of International Conference on Peaceful Uses of Atomic Energy, United Nations, New York, 1968, Vol. 8, p 33.
2) Arnold, H. Z., INORG. CHEM., 88, 1914; p 74.
3) Feigl, F., L. L. Miranda, and H. A. Suter, J. CHEM. EDUC., 21, 1944, pp 18-24.
4) Fieser, L. F., Experiments in Organic Chemistry, Heath, London, 1955, p 309.
5) Brazilian patent No. 5095/74.

PETROLEUM TRANSACTIONS

Distribution in Fracture Permeability of a Granitic Rock Mass Following a Contained Nuclear Explosion

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ABSTRACT

In situ permeability of the rock outside the Hardhat chimney was determined by pressurization of long holes with air. Experimental data indicated a remarkable difference between fracture permeability of the rock near the chimney and that at a considerable distance. Although permeable fault zones were known to exist in the granite stock, the measurements of background permeability were quite low, on the order of tenths to several millidarcies. The observed difference is about two or three orders of magnitude above this background in the region 125 to 215 ft radially from the shot point, or 80 to 165 ft radially from the vertical axis of the chimney. The presence of a collapsed drift immediately beyond this region precluded measurements which could have defined the maximum extent of the zone of high permeability.

INTRODUCTION

Previous exploration has revealed that contained nuclear explosions create cavities which generally collapse, resulting in rubble-filled chimneys and annular fractured zones. These geometries have been shown to result in complex flow regimes which should increase the production rate from hydrocarbon reservoirs.[1] Empirical scaling equations have been developed for estimating chimney radii and heights for a variety of rock media.[2] The extent of the annular fractured zone has been documented and associated permeability changes have been observed qualitatively for several explosions.

This study was begun to establish the nature and magnitude of the permeability of the latter region. It is anticipated that results will be useful in estimating permeability changes and consequent production stimulation which might ensue from a contained explosion in a hydrocarbon reservoir.

The post-shot environment of the Hardhat event (a 5-kt contained nuclear explosion in granitic rock) was chosen for the experimental measurements. The Hardhat device was detonated at a depth of 939 ft, and subsequent exploration revealed a chimney of broken rock with a radius of 65 to 70 ft and a height above shot point of 281 ft.[3] Before the explosion, the Hardhat medium was highly jointed and fractured (Fig. 1). It was expected that differential

rock motion along these and other weaknesses induced during cavity growth and collapse would significantly alter the permeability of the rock mass.

EXPERIMENTAL METHOD

Initially, three 2-in. diameter holes (Nos. 10, 12 and 19) were drilled about 25 ft outward through the walls of the 800-ft level drift (elevation 4,253 ft, Fig. 2). One was drilled near the chimney and two holes, one vertical and the other horizontal, were drilled near the shaft. Order-of-magnitude differences in permeability obtained by pressurization measurements indicated further investigation was warranted.

A series of 3-in. diameter holes was then drilled with water as a coolant into the walls and roof of the drift (Fig. 2). An 11-in. long packer was set from 1 to 8 ft inside each hole and air was injected at measured flow rates. Hole pressures were monitored at the collar.

Permeability was low enough in the holes near the access shaft that pressure could be maintained long enough to obtain good pressure decay rates. In the vicinity of the chimney, however, permeability was so high that this was not possible and air was injected under steady-state conditions.

About one year later, these same holes were retested to

Fig. 1 HARDHAT GRANITE IN TYPICAL PRE-SHOT CONDITION.

determine whether the drilling water in fractures at the time of the earlier measurements had had an effect on the observed permeabilities. For these tests, pipes 2½-ft long were grouted into the holes at the collar to provide a better seal from the drift during pressurization. No significant drilling-water effect was observed.

THEORETICAL TREATMENT OF DATA

Permeabilities were calculated from the field data by means of the steady-state, isothermal, radial-flow equation for ideal gases[1]:

$$k = \frac{q\mu p_b \ln(r_e/r_h)}{19.88\,h(p_r^2 - p_h^2)},$$

where

k = permeability, darcies

q = volume rate of flow in cu ft/D at base pressure p_b

μ = viscosity of the air, cp

p_h = tunnel pressure, psia

r_e/r_h = radius of effects (increased pressure)/radius of hole in consistent units

h = hole length, ft

p_e = absolute pressure at radial distance r_e, psia

p_h = absolute hole pressure, psia.

Radial flow was assumed, since the ratio of hole length to diameter is between 100 and 200. End effects of the tested zones were therefore neglected.

Values of q were determined for the low-permeability holes by means of Boyle's law:

$$q = \frac{1,440\,V_h\,(p_i - p_f)}{t p_b},$$

where

V_h = volume of the hole, cu ft

p_i = initial absolute hole pressure, psia

p_f = final absolute hole pressure, psia

t = time in minutes during which the hole pressure dropped from p_i to p_f.
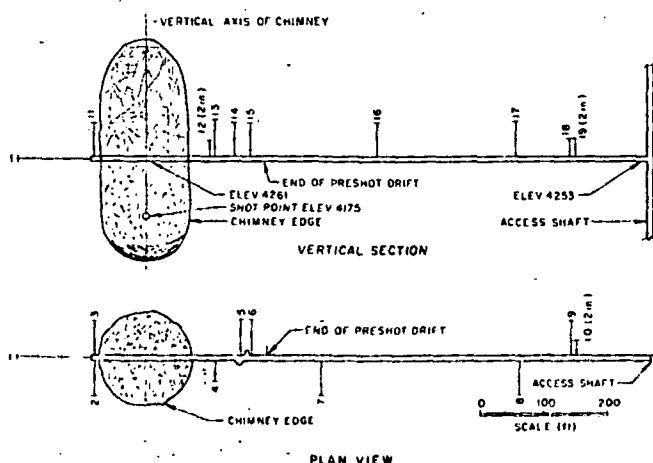

VERTICAL SECTION

PLAN VIEW

Fig. 2—SECTIONS THROUGH HARDHAT EXPLORATORY DRIFT SHOWING HOLES DRILLED FOR PERMEABILITY MEASUREMENTS.

Standard orifice plates ranging in diameter from ⅛ to ½ in. were used to determine values of q for the higher-permeability, close-in holes.

An arbitrary value of 50 ft was used for r_e. Calculated permeabilities are relatively insensitive to variations in this term. As an example of this insensitivity, the natural logarithm of r_e/r_h varies from 4.79 to 5.99, respectively, for variations in r_e from 15 to 50 ft. The absolute pressure in the drift p_h of 12.4 psia was assigned to p_e in all the calculations. An average pressure $(p_e + p_h)/2$, was used for p_h in calculations involving the low-permeability holes. Values of p_h for the high-permeability holes near the chimney were measured with air pressure gauges during steady-state injection.

DISCUSSION

The experimental data taken in May, 1964 are presented in Table 1, and those taken in Feb., 1965 in Table 2. Average radial distances of holes from shot point and center of chimney are given in Table 3. Calculated permeabilities are plotted in Figs. 3 and 4. Rock movements in the drift subsequent to the earlier measurements caused some of the holes to leak rapidly to the drift along breaks when the latest measurements were attempted. Consequently, the 1965 data are not as complete as would be desirable.

The only critical permeability difference noted between earlier and later measurements was that for vertical Hole 16. The earlier values for this hole, and for Hole 7, more or less fall on a straight line, leading to the assumption that the radius of permeability increase is on the order of 400 to 500 ft. The later value for Hole 16, however, is essentially background, indicating a small radius of increase. It is possible that the packer was not set adequately during the earlier measurement. Also, since the pre-shot drift extended to a point ~183 ft from the vertical axis of the chimney, it is possible that the May, 1964 permeability determined for Hole 7 is partly a result of spall associated with shock wave interaction with the drift. Attempts to seal this hole for pressurization were unsuccessful in Feb., 1965.

The permeability determined for the 2-in. diameter Hole 12 from the May, 1964 measurements appears to be anomalously low compared to that of adjacent holes. It is possible that this hole penetrated a rather massive block with fewer open fractures, thus reducing the permeability.

Two holes, Nos. 1 and 2, were drilled in increments of about 30 ft and pressurized upon completion of each increment. It was anticipated that the permeability k_j of the rock surrounding each increment h_j of the hole could be determined by the relationship[1]:

$$\bar{k} = \frac{\sum\limits_{j=1}^{n} k_j h_j}{\sum\limits_{j=1}^{n} h_j},$$

where $\bar{k}$ = average permeability of the entire section. Because of the small differences in steady-state hole pressures observed for these tests (Table 1) this treatment would indicate that the permeability of the succeeding incremental sections is significantly lower than that of the initial section.

Operational difficulties precluded a definitive analysis. Hole 2 was found to be blocked at a depth of 35 ft after it had been drilled to a total depth of 55 ft. Also,

STEADY-STATE MEASUREMENTS

Hole Number	Measured Interval (ft).	Orifice Plate Diameter (in.)	Hole Pressure (psig) for Upstream Pressure (psig) of			Calculated Permeability (darcies) of Upstream Pressure (psig) of		
			25	50	7.	2.	50	75
Horizontal								
1	2-30	1/8	2.7	5.1	7.8	0.50	0.40	0.36
1	2-60	1/8	2.7	5.1	7.6	0.24	0.19	0.17
1	2-90	1/8	1.7	3.6	5.5	0.26	0.19	0.16
1	2-120	1/8	2.4	4.9	7.3	0.13	0.10	0.09
2	2-30	3/8	6.6	14.6	23.5	1.61	0.96	0.69
2*	2-55	3/8	6.1	14.0	23.0	0.92	0.53	0.37
3	2-55	3/8	6.2	14.0	23.0	1.50	0.86	0.60
4	5-30	1/4	4.2	8.7	13.8	1.35	0.94	0.72
5	5-55	3/8	9.3	17.5	26.2	0.58	0.42	0.32
6	1-55	1/4	2.5	5.8	9.7	1.10	0.70	0.52
7	6-55	1/16	7.4	12.2	16.7	0.021	0.019	0.017
Vertical								
11	8-55	3/8	5.8	12.5	20.2	1.13	0.72	0.52
13	5-55	3/8	7.3	15.0	—	0.80	0.52	—
13	5-55	1/4	—	4.7	7.8	—	0.98	0.76
14	3-55	1/8	5.4	9.3	13.2	0.12	0.10	0.09
15	2-55	1/4	5.5	11.3	18.2	0.46	0.31	0.23
16	8-55	1/32	5.7	7.7	9.4	0.010	0.009	0.008
17	2-55	1/32	9.9	15.7	—	0.004	0.003	—

*Hole can be closed at depth of 35 ft.

PRESSURE-DECAY MEASUREMENTS

Hole Number	Measured Interval (ft)	Pressure Drop (psig)	Time (sec)	Calculated Permeability (darcies)
Horizontal				
8	1 - 55	30 - 29	25	0.0006
8	1 - 55	21 - 20	64	0.0004
9	2 - 55	50 - 49	70	0.0001
9	2 - 55	111 - 110	15	0.0001
10**	1 - 25	25 - 24	135	0.00007
10**	1 - 25	17 - 16	210	0.00007
Vertical				
12**	1 - 25	25 - 20	7	0.006
12**	1 - 25	10 - 5	18	0.010
18	6 - 26	50 - 49	195	0.00003
18	6 - 26	120 - 119	60	0.00003
19**	1 - 25	50 - 49	100	0.00003
19**	1 - 25	25 - 24	180	0.00004

**2-in. diameter hole.

TABLE 2—DATA FROM PRESSURIZATION OF LONG HOLES IN ROOF AND WALLS OF HARDHAT DRIFT—FEB., 1965

STEADY-STATE MEASUREMENTS

Hole Number	Depth (ft)	Orifice Plate Diameter (in.)	Hole Pressure (psig) for Upstream Pressure (psig) of				Calculated Permeability (darcies) for Upstream Pressure (psig) of			
			30	40	50	60	30	40	50	60
Horizontal										
1	120	1/8	2.0	3.3	5	6.6	0.192	0.137	0.097	0.082
2	55	1/2	7.5	12.5	17	—	1.59	1.03	0.80	—
3	55	1/2	9.0	15.0	—	—	1.28	1.03	—	—
4	30	3/8	—	20.0	24	28.0	—	0.737	0.673	0.620

Hole Number	Depth (ft)	Orifice Plate Diameter (in.)	Hole Pressure (psig) for Upstream Pressure (psig) of					Calculated Permeability (darcies) for Upstream Pressure (psig) of				
			30	40	50	60	70	30	40	50	60	70
Vertical												
11	55	1/2	—	—	6.0	—	—	—	—	3.07	—	—
13	55	3/8	—	—	8.0	11.0	15.0	—	—	1.21	0.94	0.78
14	55	1/8	3.5	6.0	7.5	8.0	10.0	0.25	0.17	0.14	0.16	0.14
15	55	1/4	—	—	—	9.0	14.0	—	—	—	0.54	0.34

PRESSURE-DECAY MEASUREMENTS

Hole Number	Depth (ft)	Pressure Drop (psig)	Time (sec)	Calculated Permeability (darcies)
Horizontal				
8	55	25 - 20	130	0.0009
8	55	30 - 25	93	0.0009
8	55	35 - 30	75	0.0009
9	55	45 - 43	145	0.0001
9	55	48 - 45	190	0.0001
Vertical				
16	55	30 - 25	120	0.0007
16	55	35 - 30	90	0.0007
17	55	30 - 25	35	0.0024
17	55	35 - 30	25	0.0024
17	55	40 - 35	25	0.0021
18	26	42 - 40	75	0.0002
18	26	50 - 45	85	0.0004

TABLE 3—AVERAGE RADIAL DISTANCES OF VERTICAL AND HORIZONTAL HOLES FROM SHOT POINT AND FROM VERTICAL AXIS OF CHIMNEY.

Hole Number	Average Radial Distance from Shot Point (ft)	Average Radial Distance from Vertical Axis of Chimney (ft)
Horizontal		
1	180	102
2	126	85
3	126	85
4	144	110
5	172	146
6	192	169
7	286	278
8	587	584
9	670	670
10	680	678
Vertical		
11	152	80
12	146	104
13	167	108
14	188	141
15	207	165
16	384	362
17	597	584
18	672	669
19	681	677

a 4-ft thick, clayey zone was encountered during the drilling of the second increment of Hole 1 which probably resulted in some plugging of fractures. Effective clearing of this longest hole of sludge and chips was not possible. The nonlinearity of the holes prevented isolation of the incremental sections by packers to independently measure the resistance to flow of each section. Fractures at the drift walls were monitored for leakage to the drift which might have made the permeability of the initial section appear anomalously high. No leaks were detected.

On the basis of these considerations, the permeability of the incremental sections beyond the initial 30 ft of Holes 1 and 2 is uncertain. Because of this uncertainty, permeabilities were calculated for the total length of hole existing during each test and are presented separately in Table 1 and Figs. 3 and 4.

Permeable fault zones were known to exist in the granite stock.[5] With the exception of these zones, it is believed that the permeabilities determined for the rock near the access shaft are typical pre-shot permeabilities. As a check, 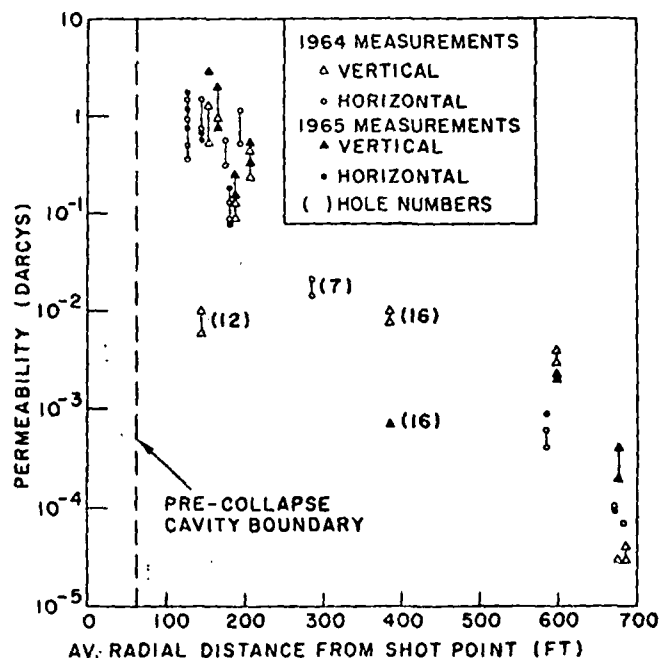two 3-in. diameter horizontal holes were pressurized in a drift below the Hardhat exploratory level. Permeabilities calculated from the pressure decay data from these holes fall within the range obtained for the holes near the Hardhat access shaft.

CONCLUSIONS

The experimental data indicate that there is a remarkable difference between the permeability of the granitic rock mass near the Hardhat access shaft and that near the Hardhat chimney. Although pre-shot control was not available, it is assumed that such a condition did not exist before the Hardhat event. On the basis of this assumption and excepting permeable fault zones, pre-shot permeability was on the order of tenths to several millidarcies, and the increase in permeability is about two to three orders of magnitude in the region 125 to 215 ft radially from the shot point, or 80 to 165 ft radially from the vertical axis of the chimney.

Absence of data in the region immediately beyond these limits and the uncertainty of the data from Holes 7 and 16 preclude an extrapolation to the pre-shot values obtained in the drift immediately beyond the collapsed portion. In view of the magnitude of radial mass displacement[2] (~1 ft) and the relatively high permeabilities near the maximum limits of the inferred region of observed permeability increase (Holes 6 and 15), it is probable that the observed limit can be extended.

There is apparently little, if any, significant difference between the permeabilities obtained from the vertical holes and those obtained from the horizontal holes. The 1965 data indicate that the permeability of the vertical holes is possibly somewhat greater. The paucity of data, however, may be responsible for the apparent differences.

Because of the spread of data, the relative influence of cavity growth as opposed to cavity collapse on the observed permeabilities is not evident from a comparison of the plots of permeability vs radial distance from shot point and from the vertical axis of the chimney. Consequently, the geometry of the zone of enhanced per-

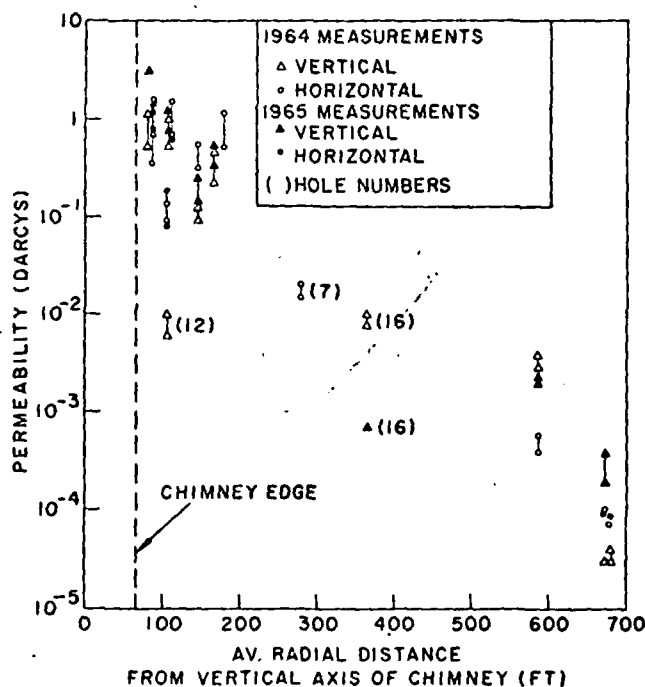FIG. 3—PERMEABILITY VS RADIAL DISTANCE FROM SHOT POINT.

FIG. 4—PERMEABILITY VS RADIAL DISTANCE FROM VERTICAL AXIS OF CHIMNEY.

meability, whether spherical because of the influence of cavity growth or cylindrical from cavity collapse, is not certain. A combination of the two symmetries is likely.

ACKNOWLEDGMENTS

The field support was supplied by Glenn Clayton of REECO, and the experimental apparatus was designed and built under the direction of Charles Meier. Analysis of the earlier data by Howard Rodean of LRL-Livermore and Carroll Knutsen of Continental Oil Co. is gratefully acknowledged. Critical reading of the manuscript by members of LRL and Bruce Bray of Continental is appreciated.

REFERENCES

1. Coffer, H. F., Bray, B. G. and Knutsen, C. F.: "Applications of Nuclear Explosions to Increase Effective Well Diameters", Proc., Engineering with Nuclear Explosives: Third Plowshare Symposium, U. S. Atomic Energy Commission TID-7695 (1964) 269.
2. Boardman, C. R., Rabb, D. D. and McArthur, R. D.: "Responses of Four Rock Mediums to Contained Nuclear Explosions", Jour. Geophysical Research (Aug. 15, 1964) 69, No. 16, 3457.
3. McArthur, R. D.: "Geologic and Engineering Effects of the Hardhat Event (Preliminary)", Lawrence Radiation Laboratory (Nev.) GNI-63 (Feb., 1963) (unpublished report).
4. Amyx, J. W., Bass, D. M. Jr. and Whiting, R. S.: Petroleum Reservoir Engineering, McGraw-Hill Book Co., Inc., New York, N.Y. (1960).
5. McArthur, R. D.: private communication.   ★★★

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Development of the Leaching Operations of the Union Minière du Haut Katanga

By Archer E. Wheeler* and H. Y. Eagle,* New York, N. Y.

The copper industry in the Province of Katanga, in the Belgian Congo, which is now controlled and operated by the Union Minère du Haut Katanga, had its inception many years ago in the vision of a Scotsman, Robert Williams, now Sir Robert Williams, Baronet. He it was who personally negotiated the mineral concession with King Leopold of Belgium, sent in the prospecting parties who located most of the present mines of the company, later arranged for the Belgian participation from which the present company was formed, and has been its active mentor ever since. The idea back of his efforts was the establishment of an industry on the Congo-Zambezi divide, of sufficient importance to draw up to it the head of the Cape to Cairo Railroad, the dream of Sir Cecil Rhodes, and the consummation of which he had left as a legacy to Mr. Williams, his successor.

The reports of the prospecting expeditions showed that copper in profitable quantity was there, but many difficulties lay in the way of the establishment of the infant industry. The isolated location of the mines, various tribal wars, the Boer War, and many other factors contributed to making progress very slow. However, in spite of these difficulties the railroad was finally built and a blast-furnace plant erected at Lubumbashi, near Elisabethville, the capital of the Province. Operations of this plant were started in 1911, treating high-grade oxidized ores and producing pig copper by a reducing smelting. Production has been continuous since that time and the company has grown so that at present it ranks as the largest individual copper producer in the industry. It is a fitting monument to the foresight, optimism and driving force of its founder, and the progressive policies of his Belgian colleagues.

In January, 1914, the Union Minière du Haut Katanga engaged as its consulting engineer, Archer E. Wheeler, metallurgical engineer, at that time general superintendent of the Great Falls plant of the Anaconda Copper Mining Co. Mr. Wheeler was commissioned by the Board of Directors to proceed into Katanga, and make all necessary investigations to enable him to report on a comprehensive development program, and to recommend a scheme of treatment particularly for their low grade

* Consulting Metallurgical Engineer.

ores.   He reached Katanga in June, 1914, where he was joined by P. W. Snow, mining engineer, formerly connected with the Great Falls smelter and the Ray and Chino properties, whom he had engaged as his assistant.

The first step in the investigation was an extended inspection trip to the mines and prospects on the company concession.   This involved a

FIG. 1.—INSPECTION SAFARI ON TREK.
FIG. 2.—KAMBOVE, ONE OF THE MINES OF THE UNION MINIÈRE.

trek through the bush with a native safari of about 120 boys, and covered the period from Aug. 12 to Dec. 24.   The trip involved a journey on foot (Fig. 1) and cycle of about 500 miles, and included visits to four operating mines and about 43 prospects.   The mines were surveyed, mapped, described and sampled to the extent that outcrops and existing development and old native workings permitted.   The mine at Kambove is shown in Fig. 2.   The conclusions drawn from the results of the inspection trip can be summarized as follows:

1. It was estimated that the mines visited would yield an ore of an average grade of 6.5 to 7 per cent.

2. It was estimated that would result from mining op per cent if a grade of 15 per

3. Practically all the ores mineral being malachite, with cuprite, native copper and oc

4. A remarkable similar deposits.   The copper minera quartzose association, which

5. It was obvious that ar be one to treat ores of a mu practice of direct blast-furn or more of copper.

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The desirable treatment, commercially amenable, thu obviating all selective mining son of these methods, a thorou the development of unit costs following principal points.

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2. Cost of white and n expenses and allowances.

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With these figures as a and production costs were w from the various mines.   F general conclusion was draw under the existing condition

2. It was estimated that the amount of direct smelting ore which would result from mining operations would be small, probably not over per cent if a grade of 15 per cent were required.

3. Practically all the ores were completely oxidized, the predominating mineral being malachite, with very minor amounts of azurite, chrysocolla, cuprite, native copper and occasional evidences of sulfides.

4. A remarkable similarity existed in the ores from the various deposits. The copper mineral was mainly found in shales, sandstones and quartzose association, which were siliceous in character.

5. It was obvious that any scheme of treatment recommended must be one to treat ores of a much lower grade than the existing Katanga practice of direct blast-furnace smelting of ores carrying 14 per cent or more of copper.

6. Sufficient ore was in sight in mines close to the railroad to justify the erection of a low-grade treatment plant.

7. The character of the ore occurrence and the lay of the ground at the various mines indicated that cheap steam-shovel mining could be applied in most cases for a low-grade treatment program.

The next step in the investigation was the study of a scheme of treatment, the methods naturally presenting themselves being:

1. Smelting of ores direct from the mine.

2. Water concentration, or flotation concentration, followed by smelting of the concentrates.

3. Leaching.

4. Combinations of any or all of these.

The desirable treatment, of course, was one to which all ores were commercially amenable, thus requiring only one type of plant and obviating all selective mining. As a necessary preliminary to a comparison of these methods, a thorough study was made of local conditions, and the development of unit costs to use in the estimates. This involved the following principal points.

1. Transportation costs on fuels, fluxes, ores, concentrates and copper.

2. Cost of white and native labor, including housing, traveling expenses and allowances.

3. Investigation of the available water power sites in the concession.

4. Cost of power from wood as fuel and coal as fuel.

5. Cost of power from the various possible hydroelectric developments.

6. Cost of operating and repair supplies.

7. Cost of mining, by various methods.

With these figures as a basis, complete direct smelting calculations and production costs were worked out for all the different types of ores from the various mines. From the results of these calculations, the general conclusion was drawn that ores to be profitable for direct smelting under the existing conditions should contain from 10.5 to 13.5 per cent

copper, depending upon the kind of ore. In order to furnish a reasonable margin of profit, somewhat higher grades than these would be required. In view of the probable small yield of this grade of ore from mining operations, it was obvious that direct smelting by itself did not furnish the solution of the problem.

CONCENTRATION AND LEACHING TESTS

As no data existed as to the amenability of Katanga ores to concentration, it was necessary to do a great deal of experimental work along this line. The work was started in the laboratory on a very small scale, with hand-operated equipment. Later these were supplemented by tests on a larger scale run in a small test plant erected for the purpose, which provided facilities for hand picking, screening, jigging and tabling with the necessary intermediate crushing steps. Based on the test results, detailed smelting calculations and operating costs were worked out for the concentrates of various grades, as produced from the various ores. The general conclusions drawn from this work were as follows:

1. All the different types of Katanga ores can be enriched by water concentration, but generally with comparatively poor recoveries.

2. Most ores of a grade less than 12 per cent need to be enriched to be made to pay.

3. The best average grade of concentrate to be produced is around 25 per cent Cu.

4. The greatest economy in operation lies in concentrating the ore as close to the mine as possible.

5. Under the then existing conditions, the existing smelter at Lubumbashi was the most economical place to smelt the concentrates.

6. In the state of the art, as it then existed, oil flotation held out no promise for the concentration of Katanga ores.

In order to determine the possibilities of the leaching process, small-scale tests were first instituted in the laboratory. These included upward and downward percolation leaching tests, upward and downward percolation washing tests, bottle agitation tests and decantation washing tests. On the basis of the data obtained from these tests, a small experimental plant was built and the small-scale tests were supplemented by tests on a larger scale. The general conclusions drawn from the results of this work were as follows:

1. Downward percolation of the solution through the total ore is not possible with Katanga ores of any allowable size.

2. Downward percolation is possible if material finer than 200 mesh (0.074 mm.) is removed.

3. Upward percolation of solution through the total ore is not possible keeping the slimes in the upward percolation system.

4. Leaching by all agitation or a simple flow sheet.

5. The copper in the comp soluble in sulfuric acid solution

6. The strength of solution the solutions can be used effect

7. Any size of ore from 3 n reasonable time.

8. The time required for le ⅜-mesh (6.680-mm.) material, a being indicated.

9. The chemical consumpt average of 0.04 kg. per kilograr for all ores treated.

10. Continuous counter-cur feasible means of recovery of v

11. In general, it appears er Katanga ores by sulfuric acid l solution is concerned.

In determining a method fo solutions, consideration was t precipitants for copper, such a sulfide and sulfur dioxide. Ur type of solution proposed, none ing a commercial solution of t concentrated on the recovery o with insoluble anodes. As soc leaching tests, experiments were were run using (1) Antisell ba laced lead anodes; (3) plain lea

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4. Leaching by all agitation is indicated as the most feasible method for a simple flow sheet.

5. The copper in the company's oxidized ores is almost completely soluble in sulfuric acid solutions.

6. The strength of solution required to effect the solution is low, and the solutions can be used effectively at ordinary temperatures.

7. Any size of ore from 3 mesh (6.680 mm.) down can be treated in a reasonable time.

8. The time required for leaching is short; approximately 48 hr. for 3-mesh (6.680-mm.) material, and 9 hr. for 10-mesh (1.651-mm.) material being indicated.

9. The chemical consumption of sulfuric acid is not excessive, an average of 0.04 kg. per kilogram of gangue being indicated as an average for all ores treated.

10. Continuous counter-current decantation is indicated as the most feasible means of recovery of values in entrained solution in the tailings.

11. In general, it appears entirely practicable to treat all grades of the Katanga ores by sulfuric acid leaching, as far as getting the copper into solution is concerned.

In determining a method for recovering the copper from the leaching solutions, consideration was first given to various possible chemical precipitants for copper, such as scrap iron, sponge iron, lime, hydrogen sulfide and sulfur dioxide. Under the existing local conditions and the type of solution proposed, none of these held out any promise of furnishing a commercial solution of the problem. Accordingly, attention was concentrated on the recovery of the copper from solution by electrolysis with insoluble anodes. As soon as solution became available from the leaching tests, experiments were started on electrolytic deposition. Tests were run using (1) Antisell basket anodes (carbon); (2) Antisell coke-faced lead anodes; (3) plain lead anodes.

A long series of tests was run to determine the effect of depolarization of the anodes by introducing SO_2 gas into the solution. Tests were also run to determine the effect of impurities in the solution on the electrolysis and the probable practical limits of iron in solution. The general conclusions drawn from the test work were as follows:

1. Copper can be recovered readily from the sulfuric acid leaching solutions by electrolysis with insoluble anodes, and in a high degree of purity.

2. Carbon anodes of either the basket or coke-faced type disintegrate unless they can be completely depolarized.

3. Depolarization with SO_2 is partly effective with carbon anodes, but not sufficiently so to prevent them from disintegrating.

4. Introducing SO_2 into the solution results in very little depolarization of plain lead anodes.

5. Plain lead anodes are quite suitable for use in the solutions, and while the required voltage is high, ampere efficiencies are high, and the pounds of copper per kilowatt-hour are reasonable.

6. None of the impurities which accumulated in solution have any marked effect on electrolysis, except iron.

7. The presence of ferric iron in the electrolyte in any considerable quantity results in low ampere efficiency. When small in amount, its effect is not marked and a concentration of 3 grams per liter in the electrolyte was fixed as a probable practical operating condition.

Using the results of this test work as a basis, complete treatment costs by leaching were worked out for the Katanga ores of various grades. These were supplemented by comparisons of the costs by the various treatment schemes, from which it was concluded: (1) that leaching offers the most profitable method of treatment for the large bulk of Katanga ores; (2) that ores of a much lower grade can be treated at a profit by this method than by any of the other methods; (3) that leaching is the only scheme that does not involve a great deal of expensive selective mining.

The complete details of the results of the inspection trip, test work and calculations were embodied in a voluminous report which was completed and submitted to the Board of Directors in August, 1916. As a final conclusion to this report, Mr. Wheeler recommended the adoption, in principle, of leaching as the basis of the future treatment program, and the immediate installation of a plant of large capacity.

4000-TON CONCENTRATOR

While these investigations were in progress, the world war began, and it was necessary to move the company's head office from Brussels to London, where it was operated until after the armistice, in conjunction with the offices of the British Associates of the Union Minière du Haut Katanga, Messrs. Robert Williams & Co., now Sir Robert Williams & Co. The Board of Directors approved Mr. Wheeler's recommendations in principle and authorized him to get out the designs of a large treatment plant, together with estimated construction and operating costs. Since war conditions at this time rendered it impossible to procure in London the necessary engineering force for this work, Mr. Wheeler was commissioned to return to the United States and carry it out there. He and Mr. Snow established offices in New York in December, 1916, and assembled an engineering force under H. Y. Eagle, electrometallurgist, who had been associated with the Engineering and Electrolytic departments of the Anaconda Copper Mining Co. at Anaconda and Great Falls, Mont. Preliminary designs and estimates for a leaching-electrolytic plant to produce 30,000 metric tons of copper per year were immediately put in hand, and the estimated construction and operating costs submitted to the Board in October, 1917. War conditions, with

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plant and necessary water-power development, and the board decided
that this major project would have to be laid aside until the end of the
war and until more normal price conditions prevailed.

At about this time it became apparent that unless steps were taken
to provide additional sources of supply for the existing blast-furnace
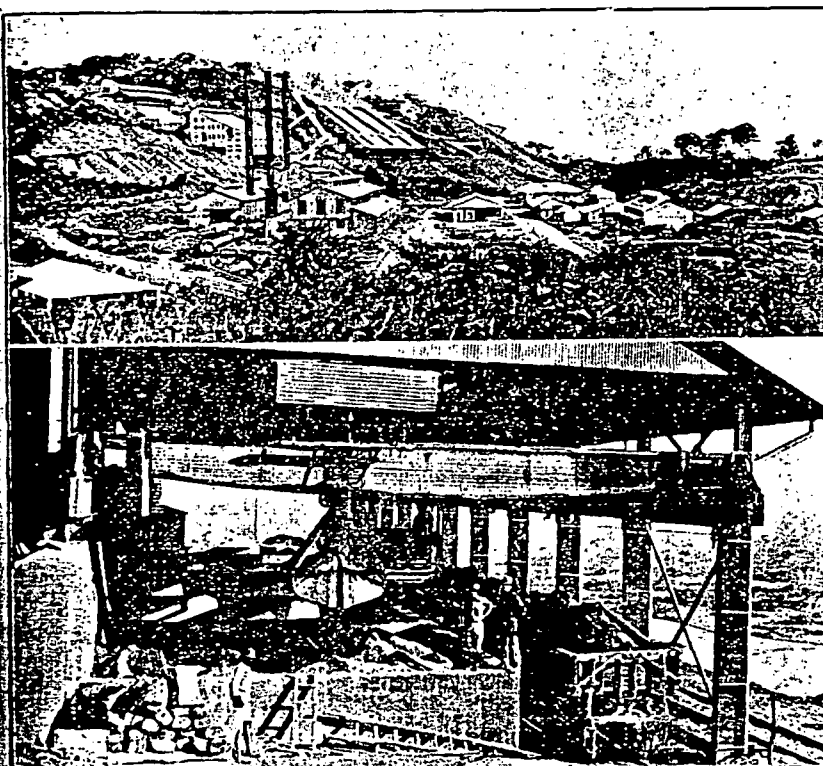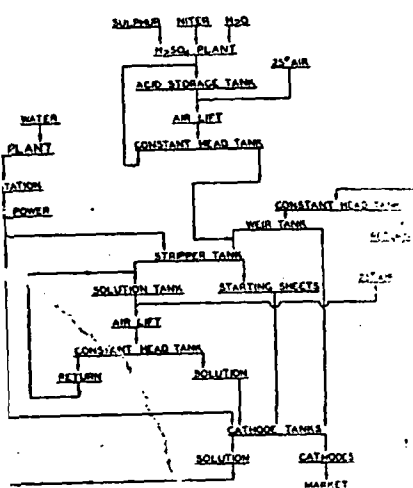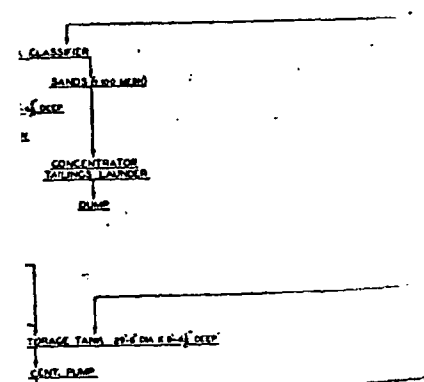operations, the exhaustion of high-grade direct smelting ores would make

FIG. 3.—THE 4000-TON PANDA CONCENTRATOR.
FIG. 4.—LOADING CONCENTRATES FROM BINS TO CARS.

necessary to cut the company's output of copper. This, with the war
going on and all the company's output being turned over to the British
Ministry of War Munitions for war purposes, was not to be thought of.
The matter of building a concentrator to treat ores below smelting grade
and supply concentrates suitable for the smelter had been under con-
sideration for a long time. The experimental work in Katanga had
shown the project to be possible, though the recoveries were such that the
method under normal conditions would represent abortive metallurgical

practice. In view of the necessities of the situation and the fact that tailings could be impounded for future leaching, Mr. Wheeler recommended, as a lower cost alternative to the leaching scheme, the installa-

FIG. 5.—FLOW SHEET OF EXPERIMENTAL LEACHING PLANT.

tion of a 4000-ton concentrator at Panda, and the Board approved the project in November, 1917. The engineering force in New York was at once started on the work, and the purchase and shipment of material was accomplished as fast as war conditions would permit. The designs, purchase and shipment of material were completed by the end of

1918, construction carried out into operation in the middle o

EXPERIME!

Since the concentrator in: expansion of the company's c afforded for a more leisurely c capital expenditure for the la felt that a commercial demon to expedite its eventual finar design of the concentrator was of the smallest unit that coul type proposed for the large p such a unit in November, 1918 1919. The work of design wa from the concentrator design material was completed early i field as fast as men became av force, and the plant was compl

The crushing divisions of t ore for the experimental plant end of the concentrator bin 100 metric tons of cathode co unit, a dry-crushing unit, stora a leaching and filtration unit chamber sulfuric acid plant to wet grinding in water were s Since this method involved an rator was provided to remove fact that in practice the solut impurities rendered the eva alternate was never used. T given in Fig. 5. The principa ing hydrometallurgical practic

1. The process is continuo
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WATER
PLANT
AIR LIFT
CONSTANT HEAD TANK
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POWER
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STRIPPER TANK
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1918, construction carried out during 1919 and 1920, and the plant put into operation in the middle of 1921. (Fig. 3.)

EXPERIMENTAL LEACHING PLANT

Since the concentrator installation provided means for the desired expansion of the company's output for some years to come, time was afforded for a more leisurely consideration of the leaching project. The capital expenditure for the latter installation was so large that it was felt that a commercial demonstration of the process would be desirable to expedite its eventual financing. Mr. Wheeler, therefore, while the design of the concentrator was in progress, recommended the construction of the smallest unit that could use machines of commercial size of the type proposed for the large plant. The Board approved the design of such a unit in November, 1918, and authorized its construction in March, 1919. The work of design was started as soon as men became available from the concentrator design work, and the purchase and shipment of material was completed early in 1920. Construction was carried on in the field as fast as men became available from the concentrator construction force, and the plant was completed by the middle of November, 1921.

The crushing divisions of the concentrator were utilized to crush the ore for the experimental plant and the ore stored in, and drawn from, one end of the concentrator bins. The plant had a capacity of about 100 metric tons of cathode copper per month. It consisted of a drying unit, a dry-crushing unit, storage bins for ground ore, a wet-grinding unit, a leaching and filtration unit, an electrolytic tank house, and a small chamber sulfuric acid plant to furnish the necessary acid. Facilities for wet grinding in water were supplied as an alternate to dry grinding. Since this method involved an addition of water to the circuit, an evaporator was provided to remove this water from the leach solution. The fact that in practice the solutions normally ran at saturation in certain impurities rendered the evaporation scheme impractical, and this alternate was never used. The flow sheet of the plant as operated is given in Fig. 5. The principal features in which it departed from existing hydrometallurgical practice in copper are as follows:

1. The process is continuous, not batch.
2. Leaching is accomplished by agitation instead of percolation, this being dictated by the character of the Katanga ores.
3. Continuous washing of sand tailings is accomplished in multideck Dorr classifiers arranged counter-current.
4. Continuous washing of slime tailings on vacuum filters was installed on the basis of tests run by the manufacturer on Katanga ores. This was substituted for the original idea of installing counter-current decantation, one or the other of which methods was dictated by the character of the Katanga ore. The filtration method, if practicable, involved a much smaller initial capital expenditure than decantation.
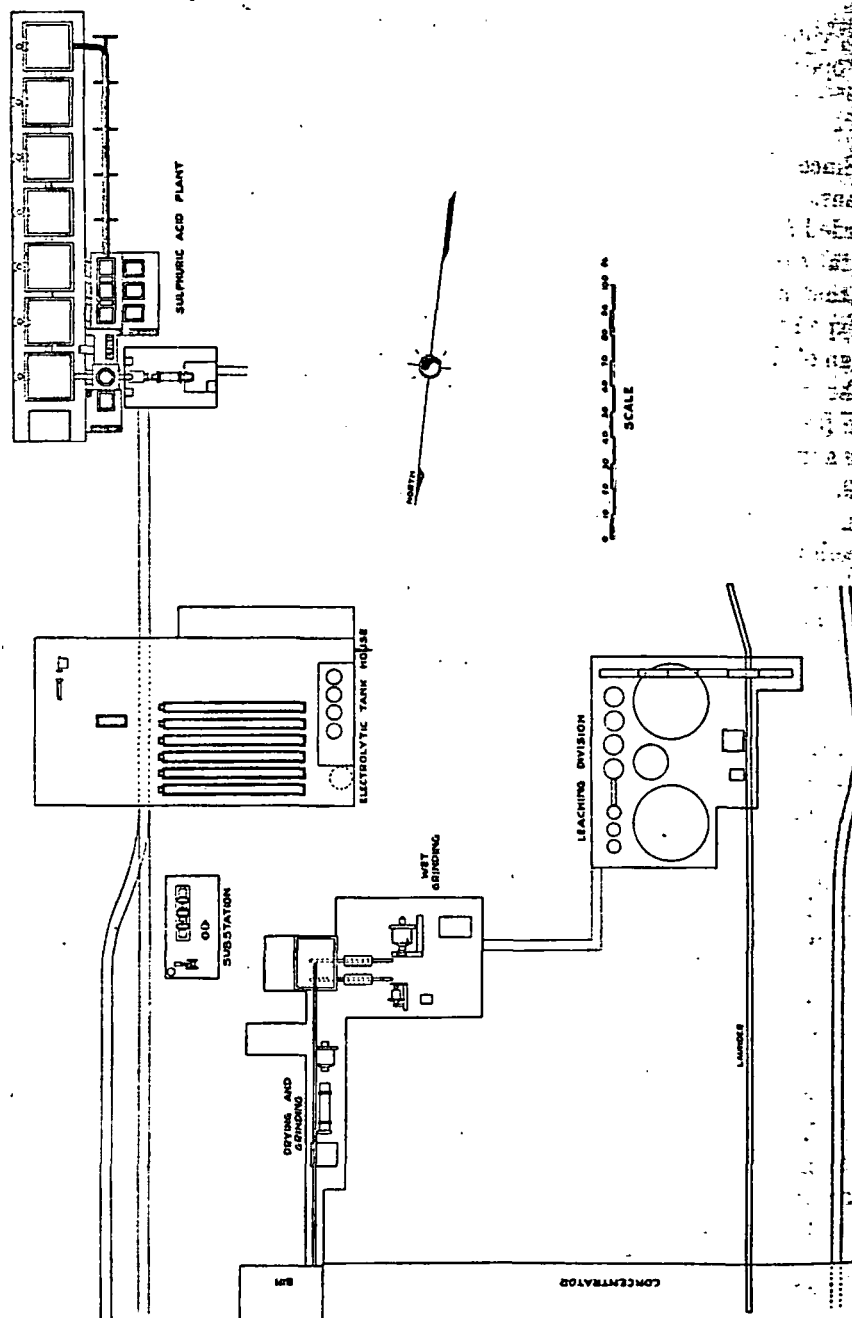
FIG. 6.—GENERAL PLAN OF EXPERIMENTAL LEACHING PLANT.

ARCHER E. W

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causes: (1) inability of the a
promised by the manufacturer
slimes tailings; (3) failure of r
corrosive solutions.

The agitators would not pr
the accumulation of this mate
the series. After the system
it became apparent that the
Experiments were then started
coarse material through the ta
tors was finally developed, whi
of the grinding was decreased
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proved the device effective for

In spite of the fact that la
Katanga ores had indicated th
dling the slime, actual operatic
Excellent vacuum conditions c
cake that formed did not cracl
thickness, the filtration stopp
ineffective, because of its imp
thickness was not practical, i
plan of counter-current decant
tion thickener was converted
run long enough to demonstra
type of washing. During the
handled by the filters or washi
the thickener spigots.

[1] U. S. Patent 170
[2] U. S. Patent 143
[3] Trans. Amer. El
[4] U. S. Patent 165

SCALE

LEACHING DIVISION

5. Provision was made for a continuous system of purification[1] by neutralization of a part of the solution with original ore or concentrates, to maintain the iron content of the solutions at a practical operating figure.

6. Electrolytic tanks[2] were installed which utilized in their design a principle not previously recognized.

The general arrangement of entire plant is shown in Fig. 6. A complete description of the electrolytic tank house is contained in another paper[3] and can be found elsewhere.

The experimental leaching plant was put into operation in November, 1921, and operated from then until the end of August, 1922, under the immediate direction of Mr. Eagle. Numerous difficulties were encountered in the early stages of the work, due primarily to the following causes: (1) inability of the agitators to handle the 35-mesh material promised by the manufacturer; (2) inability of the filters to handle the slimes tailings; (3) failure of much so-called acidproof equipment in the corrosive solutions.

The agitators would not progress the coarse material in the pulp and the accumulation of this material quickly plugged the first agitator in the series. After the system had been dug out a number of times, it became apparent that the agitators simply could not do the work. Experiments were then started with various expedients to progress the coarse material through the tanks. A simple attachment[4] for the agitators was finally developed, which did this so effectively that the fineness of the grinding was decreased to 20 mesh, and even small quantities of accidental coarse oversize up to $\frac{1}{4}$ in. caused no trouble. Experiment proved the device effective for agitators of the Dorr or Pachuca types.

In spite of the fact that laboratory tests by the manufacturer with Katanga ores had indicated the vacuum filters as being capable of handling the slime, actual operation did not confirm the results of these tests. Excellent vacuum conditions could be maintained on the filters and the cake that formed did not crack, but after building up to about $\frac{1}{8}$ in. in thickness, the filtration stopped. The washing of this cake, too, was ineffective, because of its impervious character. Since a cake of this thickness was not practical, it was necessary to revert to the original plan of counter-current decantation to effect the washing. The purification thickener was converted for a time into a washing thickener and run long enough to demonstrate the feasibility and effectiveness of this type of washing. During the test work, such slime tails as were not handled by the filters or washing thickener were discarded directly from the thickener spigots.

[1] U. S. Patent 1703435.
[2] U. S. Patent 1431574.
[3] Trans. Amer. Electrochem. Soc. (1924) 45, 365.
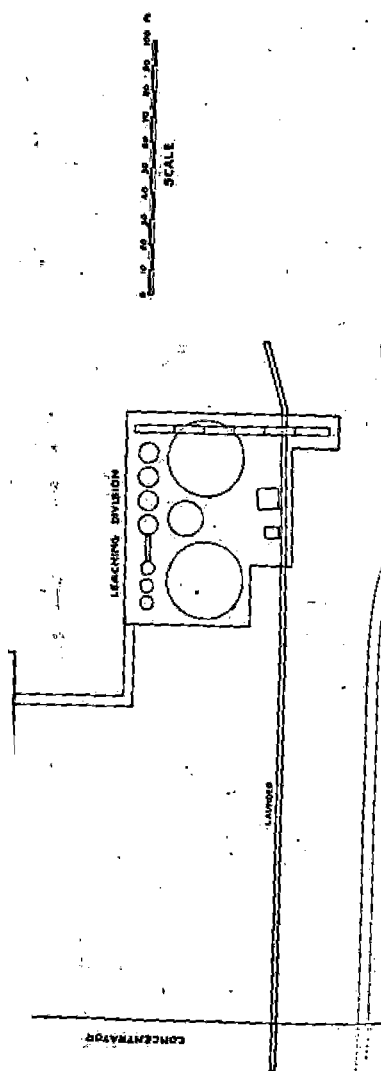[4] U. S. Patent 1651680.

The leaching solutions proved to be extremely corrosive, and copper, brass and bronze in contact with them went into solution with unbelievable rapidity. The bronze bolts in the leaching mechanisms, scrapers and

TABLE 1.—*Details of Experimental Leaching Plant Operations*
QUANTITIES AND AVERAGE GRADE OF ORES TREATED

	Dry, Metric Tons	Cu, Per Cent	Cu, Metric Tons
Impregnated shales.................	3533.309	9.07	320.360
Talcose ores......................	324.875	7.97	25.891
Quartzose ores....................	1516.621	8.67	131.565
Fines from dumps.................	515.539	13.73	70.784
Total and average................	5890.344	9.31	548.600

AVERAGE COMPOSITIONS OF ORES, PERCENTAGE OF DRY SOLIDS

	Impregnated Shales	Talcose Ores	Quartzose Ores	Fines Dump	Average Ore
Cu.................	9.07	7.97	8.67	13.73	9.31
SiO$_2$..............	63.95	60.57	68.17	56.19	64.17
Al$_2$O$_3$.............	8.48	6.98	4.85	7.93	7.42
Fe.................	3.40	4.73	2.45	3.23	3.21
CaO................	1.32	0.89	1.30	1.36	1.29
MgO...............	4.88	9.22	4.52	5.13	5.05

TYPICAL AVERAGE SCREEN ANALYSES AFTER DRY GRINDING, INDICATING CHARACTER OF FEED TO LEACHING DIVISION, CUMULATIVE PERCENTAGE

Mesh	Impregnated Shales	Talcose Ore	Quartzose Ore	Fines Dump
+28	10.07	1.96	5.91	5.90
+35	16.93	4.87	13.69	11.74
+48	23.24	10.54	21.44	18.14
+65	29.65	17.63	29.62	26.46
+100	35.08	26.42	36.97	31.46
+200	48.98	40.22	51.85	44.87
Total................	100.00	100.00	100.00	100.00

valves of the filters, bronze filtrate pumps, etc., etc., all failed in quick succession, and had to be replaced by lead parts or steel parts covered with lead. The work developed the fact that only lead, duriron, rubber, asphalt mastic, glass and porcelain could safely be used in contact with the solutions. Later experiments added to the above list several alloys of the chrome-nickel-iron series.

The various troubles encountered w
plant put on as nearly a regular basis
the experimental investigation perm
the experimental work are given in Ta

The copper content of all these or
accustomed to think in terms of the
original survey of the company's min
grade of ore would be approximately
was requested for the experimental
attempts to meet the request resulte
worthy effort was made to furnish the
a so-called low-grade ore and d
Unfortunately, the barren material
dolomite and when this material stru
can well be imagined. After this exp
of as low a grade as the existing n
calculations depended upon to inte
average ore conditions.

As will be noted from the flow sh
plant are a sand tailing, an acid sl
tailing. Due to the inability of the
experiments with counter-current w
charged in three different ways dur

TABLE 2.—*Average An*

	Sand Tails	Acid Fi Cak
AVERAGE COMPOSITION OF TAIL		
Cu.................	0.331	0.2
SiO$_2$..............	84.20	68.5
Al$_2$O$_3$.............	4.65	10.3
Fe.................	2.65	4.1
CaO................	1.20	1.3
MgO...............	3.08	7.5
PERCENTAG		
Solution per cent..	30.25	31.
ENTRAINED SOLUTION, C		
Cu.................	1.46	16
Free H$_2$SO$_4$.......	0.12	4

s proved to be extremely corrosive, and copper,
ct with them went into solution with unbeliev-
e bolts in the leaching mechanisms, scrapers and

f Experimental Leaching Plant Operations
ND AVERAGE GRADE OF ORES TREATED

	Dry, Metric Tons	Cu, Per Cent	Cu, Metric Tons
....	3533.309	9.07	320.360
....	324.875	7.97	25.891
....	1516.621	8.67	131.565
....	515.539	13.73	70.784
....	5890.344	9.31	548.600

ONS OF ORES, PERCENTAGE OF DRY SOLIDS

	Talcose Ores	Quartzose Ores	Fines Dump	Average Ore
	7.97	8.67	13.73	9.31
	60.57	68.17	56.19	64.17
	6.98	4.85	7.93	7.42
	4.73	2.45	3.23	3.21
	0.89	1.30	1.36	1.29
	9.22	4.52	5.13	5.05

RES AFTER DRY GRINDING, INDICATING CHARACTER
G DIVISION, CUMULATIVE PERCENTAGE

	Talcose Ore	Quartzose Ore	Fines Dump
	1.96	5.91	5.90
	4.87	13.69	11.74
	10.54	21.44	18.14
	17.63	29.62	26.46
	26.42	36.97	31.46
	0.22	51.85	44.87
	.00	100.00	100.00

. etc., etc., all failed in quick
rts or steel parts covered with
only lead, duriron, rubber,
ely be used in contact with
he above list several alloys

The various troubles encountered were gradually eliminated and the plant put on as nearly a regular basis of operation as the various lines of the experimental investigation permitted. The principal features of the experimental work are given in Table 1.

The copper content of all these ores must be rather startling to men accustomed to think in terms of the ores of the United States. The original survey of the company's mines had indicated that the average grade of ore would be approximately 6.5 per cent Cu, and that grade was requested for the experimental work. The mining department's attempts to meet the request resulted as shown in Table 1. One noteworthy effort was made to furnish the low-grade ore asked for, by mining a so-called low-grade ore and diluting it with barren material. Unfortunately, the barren material happened to be largely calcite and dolomite and when this material struck the leaching solutions, its effect can well be imagined. After this experience, straight ores were requested of as low a grade as the existing mining development permitted, and calculations depended upon to interpolate the results to the eventual average ore conditions.

As will be noted from the flow sheet, the tailings discharged from the plant are a sand tailing, an acid slime tailing and a purification slime tailing. Due to the inability of the filters to handle the slimes, and to the experiments with counter-current washing, the acid slime tails were discharged in three different ways during various periods of the investiga-

TABLE 2.—*Average Analyses of Tailing Products*

	Sand Tails	Acid Filter Cake	Acid Thickener Spigot	Washing Thickener Spigot	Purification Filter Cake
AVERAGE COMPOSITION OF TAILINGS, PERCENTAGE OF DRY SOLIDS					
Cu..............	0.331	0.245	0.176	0.169	2.40
SiO_2..............	84.20	68.56	75.41	74.62	64.91
Al_2O_3..............	4.65	10.36	8.77	9.01	11.40
Fe..............	2.65	4.14	2.99	3.40	3.94
CaO..............	1.20	1.32	1.17	1.31	0.88
MgO..............	3.08	7.26	4.72	5.86	5.47
PERCENTAGE OF WET PULP					
Solution per cent..	30.25	31.79	50.61	50.96	40.83
ENTRAINED SOLUTION, CONTENTS IN GRAMS PER LITER					
Cu..............	1.46	16.11	34.34	24.09	31.08
Free H_2SO_4.......	0.12	4.90	4.30	0.96	0.00

TABLE 2.—(Continued)

AVERAGE SCREEN ANALYSES, CUMULATIVE PERCENTAGE

Mesh	Sand Tailings	Acid Slime Tailings	Purification Slime Tailings	Purification Classifier Sands
+ 28	9.13	0.01		9.22
+ 35	22.16	0.08		23.53
+ 48	39.47	0.25	0.05	39.76
+ 65	63.09	0.80	0.16	59.75
+100	78.29	3.01	0.29	73.96
+200	93.29	13.80	4.02	91.88
Total..................	100.00	100.00	100.00	100.00

tion: viz., as acid filter cake, acid thickener spigot and washing thickener spigot. The average analyses of all the tailing products are given in Table 2.

The test results of the experimental plant indicated that the copper content of all the ores was readily soluble in sulfuric acid solutions, the average extraction (copper into solution) for all the ores treated being 97.44 per cent. An agitation time of 4 hr. was found to be sufficient to extract the copper from −20-mesh material. Inasmuch as the greater part of the slime tailings was discarded directly from the acid thickener spigot with no washing, the losses in entrained solution were very high and he over-all recovery was only about 80.31 per cent. The experiments and calculations on washing, however, demonstrated that this washing loss could be cut down by counter-current decantation to any desired figure which would justify the required initial capital expenditure.

During the experimental period, a total of 426 metric tons of cathode copper was produced. Table 3 shows averages of operating conditions.

TABLE 3.—Averages of Operating Conditions and Analyses of Solutions

426 Metric Tons Cathode Copper Produced

Cathode current density, amps. per sq. m.................... 98.24
Cathode current density, amps. per sq. ft.................... 9.13
Ampere efficiency, per cent............................... 83.33
Copper, kg. per kw-hr.................................... 0.508
Copper, lb. per kw-hr.................................... 1.120

TYPICAL ANALYSES OF SOLUTIONS TO AND FROM ELECTROLYTIC TANK HOUSE

	Free H_2SO_4	Cu	Fe, Total	Fe, Ferrous	Fe, Ferric	Al_2O_3	MgO	CaO
Solution from leaching plant, grams per liter...........	15	35	5	2	3	10	7	1
Solution return to leaching plant, grams per liter.....	60	15	5	3	2	10	7	1

The solutions at times carried
to the slow settling properties of
was mechanically entrapped in
itself was of high electrolytic gra
yielded wire bar of high quality
rendered them soft and brittle a
Europe. For this reason fire refi
necessary part of an eventual tre

Tests in the purification secti
ore in excess, an agitation time
would give an effective eliminati
solutions. It was also demonsti
precipitated material was regen
With the equipment as installe
high in grade, but tests showed th
and a finer point of classification
could readily be maintained be
small quantity of purification t
satisfactory. Typical assays of
agitators are given below:

Cu.....................
Free H_2SO_4.......................
Fe, total........................
Al_2O_3.........................

The purification method used is
for precipitation of iron and alu
plant is the first, within the w
applied it. The fact that ore in
from copper leach solutions ha
loss of copper in the excess pre
cipitate in some subsequent ste
idea to be discarded. The fir:
the pulp from the neutral agitat
the great majority of the exces
recovered. The second difficul
classifier overflow, which cont
separate thickening-washing ci
trality. These two simple ex
and furnished an effective m
the solution.

ntinued)

UMULATIVE PERCENTAGE

d Slime ailings	Purification Slime Tailings	Purification Classifier Sands
0.01		9.22
0.08		23.53
0.25	0.05	39.76
0.80	0.16	59.75
3.01	0.29	73.96
13.80	4.02	91.88
00.00	100.00	100.00

ier spigot and washing thickener
ie tailing products are given in

plant indicated that the copper
le in sulfuric acid solutions, the
i) for all the ores treated being
hr. was found to be sufficient to
erial. Inasmuch as the greater
directly from the acid thickener
ined solution were very high and
31 per cent. The experiments
lemonstrated that this washing
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nitial capital expenditure.
al of 426 metric tons of cathode
rerages of operating conditions.

ions and Analyses of Solutions

opper Produced

.... 98.24
.... 9.13
.... 83.33
.... 0.50S
.... 1.120

OM ELECTROLYTIC TANK HOUSE

Fe, Ferrous	Fe, Ferric	Al₂O₃	MgO	CaO
2	3	10	7	1
3	2	10	7	1

The solutions at times carried considerable slime in suspension, owing to the slow settling properties of some particular ore, and some of this was mechanically entrapped in the deposited cathodes. The copper itself was of high electrolytic grade, and on subsequent furnace refining yielded wire bar of high quality. The slime content of the cathodes rendered them soft and brittle and unsuitable for regular shipment to Europe. For this reason fire refining of the cathodes was indicated as a necessary part of an eventual treatment plant in Katanga.

Tests in the purification section indicated that with ordinary copper ore in excess, an agitation time of 17 hr. in the purification agitators would give an effective elimination of Fe and Al_2O_3 from the leaching solutions. It was also demonstrated that the acid combined with the precipitated material was regenerated and used for dissolving copper. With the equipment as installed the purification tailings were rather high in grade, but tests showed that with proper control of the ore excess, and a finer point of classification on the purification classifier, this grade could readily be maintained below 1 per cent. This, in view of the small quantity of purification tailing produced, was considered quite satisfactory. Typical assays of solutions to and from the purification agitators are given below:

	Solution to Purification, Grams per Liter	Solution from Purification, Grams per Liter
Cu	35	56
Free H_2SO_4	15	0
Fe, total	5	2
Al_2O_3	10	6

The purification method used is not a new idea insofar as neutralization for precipitation of iron and alumina is concerned, but the experimental plant is the first, within the writers' knowledge, that has successfully applied it. The fact that ore in excess will precipitate iron and alumina from copper leach solutions has been known for a long time, but the loss of copper in the excess precipitant, and the re-solution of the precipitate in some subsequent step in the process, has always caused the idea to be discarded. The first difficulty was removed by classifying the pulp from the neutral agitators and sending the sands, which contain the great majority of the excess copper, to the acid circuit, where it is recovered. The second difficulty was eliminated by sending the neutral classifier overflow, which contains practically all the precipitate, to a separate thickening-washing circuit which is always maintained at neutrality. These two simple expedients rendered the scheme operative and furnished an effective means for controlling the iron content of the solution.

The consumption of sulfuric acid in the experimental plant confirmed the results of the earlier test work, the average chemical consumption for all the ores treated averaging 0.0376 kg. per kilogram of gangue. Due to the fact that most of the acid slimes were discharged from the acid thickener spigot with no washing, the entrained losses during the test period were high. As a result of this the total acid consumption for the entire period was 0.791 kg. per kilogram of copper recovered. The tests and calculations on counter current washing indicated that the washing loss could be cut down by this means to any desired figure which would justify the initial capital expenditure.

By the end of August, 1922, all necessary points bearing on the design of a large plant had been determined, the plant was at that time turned over to the operating management, and the consulting engineer's staff returned to New York. It is interesting to note that while the small plant was operated by the African organization from 1922 to 1929, no change was developed in the flow sheet which was submitted after the first nine months of work.

30,000 METRIC TONS PANDA LEACHING PLANT

The results of the experimental leaching plant were so satisfactory that the Board of Directors immediately authorized the final designs of a plant to produce 30,000 metric tons of wire bar per year, and this work was at once put in hand in the New York office. Estimates of construction and operating costs of the new plant were submitted in April, 1923, but the construction of the plant was not approved until March, 1925. A combination of circumstances then united to delay the construction of the plant, which could have been completed easily in two years. In the first place, the work was turned over to the company's newly developed African construction department, and, at the same time, the construction of a large reverberatory plant was authorized, the two projects to be carried on simultaneously. It was soon found that more had been undertaken than could be accomplished, and work on the leaching plant was finally stopped altogether until the reverberatory plant was completed, therefore the leaching plant was not ready to begin work until April, 1929, and was not really completed until the early part of 1930.

The flow sheet about which the 30,000 metric ton Panda leaching plant is designed is given diagrammatically in Fig. 7, and indicates the character of the equipment and the quantities of flow. The principal differences between this flow sheet and that of the experimental plant, which were developed by the test work, are as follows:

1. Ore bedding was substituted for bins for the storage of crushed ore. This was done both because Katanga ores are extremely difficult to handle in bins in the wet season, and also because it was desirable

FIG. 7.—

PRIMARY CRUSHING PLANT

ORE IN R.R. CARS ①

2-4' GRIZZLIES

OVERSIZE (+4) ②   UNDERSIZE (-4+0) ③

1-48"x36" JAW CRUSHER (SET 4) ②   2-HOPPERS 80 M.T. CAP. (EA) ③

2-48" BELT FEEDERS ③

1-60"x12'-0" TROMMELS ②   2-60"x12'-0" TROMMELS ③

UNDERSIZE (-1+0) ⑦ OVERSIZE (-4+1) ⑧   OVERSIZE (-4+1) ⑤ UNDERSIZE (-1+0) ④

1-24" BELT CONVEYOR ⑧   1-24" BELT CONVEYOR ⑨

SECONDARY CRUSHING PLANT

2-NO.3 GYRATORYS (SET 2) ⑧

2-60"x12'-0" TROMMELS ⑧

OVERSIZE (-2+1) ⑩   UNDERSIZE (-1+0) ⑪

2-SETS 54X16" ROLLS (SET 1) ⑩

1-24" BELT CONVEYOR ⑫

ORE STORAGE PLANT

3-24" DISTRIBUTING CONVEYORS (1 IN USE) ⑫

3-ORE PILES 3800 M.T. CAPACITY (EA)

2-RECLAIMING MACHINES (1 IN USE) ⑬

3-24" RECLAIMING CONVEYORS (1 IN USE) ⑬

1-24" COLLECTING CONVEYOR ⑬

1-24 BELT CONVEYOR ⑬

DRYING AND GRINDING PLANT

3-HOPPERS 30 M.T. CAPACITY (EACH)

3-24" BELT FEEDERS (4 IN USE) ⑭

WOOD FUEL ⑳

8-7'-8" DIA. X 55'-0" DOUBLE SHELL DRYERS (4 IN USE) ⑭

3-14"X7' BUCKET ELEVATORS (4 IN USE) ⑮

3-16" SCREW FEEDERS (4 IN USE) ⑮

10-8'-0" HAMMER SCREENS (8 IN USE) ⑮

RODS ㉑   OVERSIZE (-1+20 MESH) ⑯   UNDERSIZE (-20 MESH +0) ⑰

5-6'X12'-0" ROD MILLS (4 IN USE) ⑯

FINE ORE BINS-2000 M.T. CAPACITY

TO LEACHING PLANT

FIG. 7.—(Part I)

LEACHING PLANT

PURIFICATION SECTION — LEACHING SECTION

LUFIRA PROJECT — PANDA CENTRALE — ELECTR

H_2SO_4 STORAGE TANK

FIG. 7.—FLOW SHEET OF 30,000-TON PANDA LEACHING PLANT (Parts 2 and 3).

LUFIRA PROJECT   PANDA CENTRALE   ELECTROLYTIC PLANT

TRANSMISSION LINE   TRANSMISSION LINE H_2SO_4 STORAGE TANK

H_2SO_4 (55)   56-STARTING SHEET TANKS

SUBSTATION   STARTING SHEETS (58) SCRAP (56) SOLUTION (57)

POWER   COMP. AIR   144-CATHODE TANKS   2-PUMPS (1 IN USE) (57)

TO VARIOUS DEPTS.   SOLUTION (56)   CATHODES (60)

FURNACE REFINERY

COAL, FUEL (61)   POLES (62) CHARCOAL (63)

2-13'X27'-6' REFINING FURNACES (1 IN USE) (64)

SLAG (65)   REFINED COPPER (66)

SMELTER

2-COPPER CASTING WHEELS (1 IN USE) (66)

REJECTS (67) WIRE BAR INGOTS, ETC. (68) ANODES (69)

MARKET

QUANTITY REQUIREMENTS ON THE BASIS OF TREATING A 6.5% ORE AND PRODUCING 30000 M.T. OF WIRE BARS PER YEAR

ORES

REF. NO.	MAX. DRY SOLIDS 24 PER HR. DAY M.T.	MAX. WET TONNES HANDLED BY MACH. PER DAY	PER HOUR	HRS. OF OPERAT'N PER 24 HR. DAY	REF. NO.	MAX. DRY SOLIDS PER 24 HR. DAY M.T.	MAX. WET TONNES HANDLED BY MACH. PER DAY	PER HOUR	HRS. OF OPERATION PER 24 HR. DAY
1	1600	1860	23.5	8	11	800	832	85	8
2	400	421	75	8	12	1600	1860	23.5	8
3	1600	1880	23.5	8	13	1800	1860	23.5	24
4	1400	1828	220	8	14	1800	1880	100	24
5	800	842	120	8	15	3000	3060	170	24
6	200	211	30	8	16	1400	1429	70	24
7	300	316	50	8	17	1600	1633	70	24
8	1000	1053	130	8	18	300	306	15	24
9	1600	1880	23.5	8	19	1300	1327	60	24
10	400	421	65	8					

PULPS AND SOLUTIONS 24 HOUR SERVICE

REF. NO.	M.T. DRY SOLIDS PER HR.	LITERS SOLUTION PER HR.	PULP PER HOUR M.T.	LITERS	REF. NO.	M.T. DRY SOLIDS PER HR.	LITERS SOLUTION PER HR.	PULP PER HOUR M.T.	LITERS
20	37.8	243000	337.0	264700	39		267100		
21	30.4	250200	338.5	289200	40		267100		
22	33.0	243000	312.5	295400	41				
23	17.4	7300	25.8	13800	42		25400		
24		7300			43		241700		
25	17.4	14600	32.5	21100	44	12.5	25400	41.7	30100
26		7300			45	8.0	24100	35.7	27200
27	17.4	7300	24.7	13800	46	3.4	1300	4.8	2600
28	33.0	278000	352.7	290400	47	6.0	34500	47.7	37500
29		243000			48		34100		
30	33.0	35000	73.2	47500	49	8.0	10400	18.9	13400
31	33.0	70000	113.5	82500	50	8.0	20800	31.9	23800
32		35000			51		10400		
33	33.0	35000	73.2	47500	52	8.0	10400	18.9	13400
34		35000			53		158600		
35	58.4	208300	273.4	230300	54		10400		
36		243000			55		2000		
37		243000			56		241700		
38					57		38000		

MISCELLANEOUS

REF. NO.	METRIC TONNES PER YEAR	PER DAY	REF. NO.	METRIC TONNES PER YEAR	PER DAY	REF. NO.	METRIC TONNES PER YEAR	PER DAY
58	3150	8	63	350	1.0	68	30000	85.7
59	1050	3	64	39900	114.0	69	4200	12.0
60	33800	96	65	900	2.6	70	70000	2000
61	8750	25	66	39450	112.7	71	175	0.5
62	1750	3	67	5230	15.0	56	28700	82.0

PANDA LEACHING PLANT (Parts 2 and 3).

that the grade of the ore fed to the leaching plant should be as uniform as possible.

on account of the higher washing effic classifier than with slimes in the thicke

3. The primary classifiers in the ac type instead of standard, in order to in for the reasons given above.

4. The purification classifier was n the amount of sand discharge, and t of grade of the purification slimes.

5. Counter-current washing was i values in entrained solution in slim decided upon for the initial installatic more could be added in the future if c

6. The electrolytic tanks were n arranged with three electrical groups i

7. Starting sheets were made from tion circuit, instead of with insoluble This was done because it was a more c satisfactory sheets, and also because grade of the solutions in the leaching washing losses.

8. A furnace refinery was installed bar, to make the starting sheet anod product quite suitable for shipment to

A short description of each of the below. Fig. 8 shows a general plan. throughout, of good materials. The Coast fir; brick and cement are of t structural steel and most of the machi of Belgian manufacture. The plant i extended on the present site to double tons of wire bar per year.

Crushing and

The primary crushing building i 0 in. by 47 ft. 2 in. in plan, sheathed anc steel. It has four operating floors. screening equipment, which is of Allis-(in the flow sheet (Fig. 7). The buildin trestle 56 ft. 5½ in. maximum height ore is brought to the receiving hoppers bottom railroad cars. A 20-ton ha provides facilities for heavy repairs.

The secondary crushing building is by 57 ft. 0 in. in plan, sheathed and

FIG. 8.—GENERAL PLAN OF 30,000-METRIC TON PANDA LEACHING PLANT.

2. Rod mills were substituted for ball mills for dry grinding and the fines scalped from the feed to the mill. Both these features were adopted to increase the amount of sand tailings from the ore. This was desirable

iching plant should be as uniform

FIG. 8.—GENERAL PLAN OF 30,000-METRIC TON PANDA LEACHING PLANT.
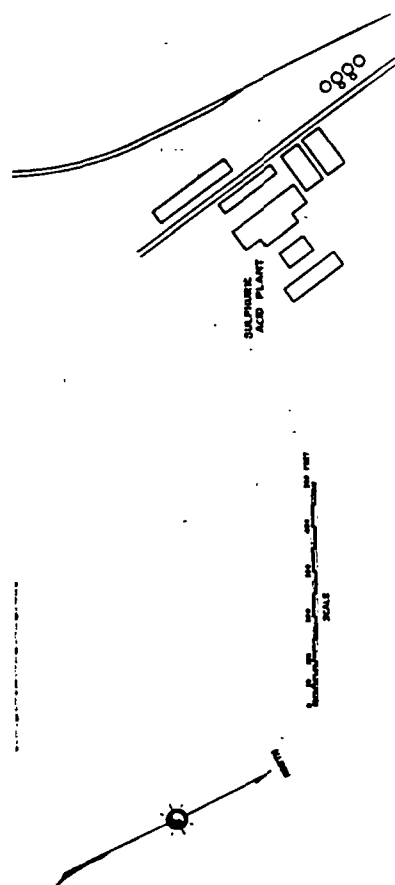
SULPHURIC ACID PLANT

ball mills for dry grinding and the
   Both these features were adopted
s from the ore.   This was desirable

on account of the higher washing efficiency obtained with sands in the classifier than with slimes in the thickeners.

3. The primary classifiers in the acid section were made of the bowl type instead of standard, in order to increase the amount of sand tailings, for the reasons given above.

4. The purification classifier was made of the bowl type to increase the amount of sand discharge, and to attain the consequent lowering of grade of the purification slimes.

5. Counter-current washing was installed for recovery of solution values in entrained solution in slimes tailings. Three washes were decided upon for the initial installation, but the plant so laid out that more could be added in the future if conditions warranted it.

6. The electrolytic tanks were made somewhat longer but were arranged with three electrical groups instead of five.

7. Starting sheets were made from soluble anodes in a separate solution circuit, instead of with insoluble anodes from the leaching solution. This was done because it was a more certain method of regularly making satisfactory sheets, and also because it permitted the lowering of the grade of the solutions in the leaching division and thus decreased the washing losses.

8. A furnace refinery was installed to convert the cathodes into wire bar, to make the starting sheet anodes, and incidentally to furnish a product quite suitable for shipment to Europe.

A short description of each of the departments of the plant is given below. Fig. 8 shows a general plan. The plant is substantially built throughout, of good materials. The construction lumber is Pacific Coast fir; brick and cement are of the company's local manufacture; structural steel and most of the machinery not specifically identified are of Belgian manufacture. The plant is arranged so as to permit it to be extended on the present site to double its initial capacity of 30,000 metric tons of wire bar per year.

Crushing and Grinding

The primary crushing building is a steel-frame structure 45 ft. 0 in. by 47 ft. 2 in. in plan, sheathed and roofed with corrugated galvanized steel. It has four operating floors. The character of the crushing and screening equipment, which is of Allis-Chalmers manufacture, is indicated in the flow sheet (Fig. 7). The building is served by a double-track steel trestle 56 ft. 5½ in. maximum height by 378 ft. 0 in. long, by which the ore is brought to the receiving hoppers in standard (3 ft. 6 in. gage) drop-bottom railroad cars. A 20-ton hand-power crane over the crusher provides facilities for heavy repairs.

The secondary crushing building is a steel-frame structure, 40 ft. 0 in. by 57 ft. 0 in. in plan, sheathed and roofed with galvanized corrugated

steel and arranged with five operating floors. The crushing and screening equipment is as noted on the flow sheet and is of Allis-Chalmers manufacture. I-beam crawls and Yale & Towne trolleys and chain blocks over the various machines furnish means for heavy repairs. Conveyors bring the ore from the primary crushing and deliver the crushed product to the ore-bedding system.

The ore-storage building is a steel-frame structure 198 ft. 0 in. by 304 ft. 0 in. in plan, roofed and sheathed with galvanized corrugated steel and provided with two main operating levels. It consists of three bays, each housing an ore pile which is built up by the discharge of the self-propelling, self-reversing tripper on the conveyor above. Ore is reclaimed from the pile by a standard Messiter reclaimer, as manufactured by the Robins Conveying Belt Co., and is delivered by conveyor to the dryer bins. One pile is being built, one being fed, and the other standing by at any one time. A transfer car is provided to shift the reclaimers from one pile to the other. The conveyors in this division as well as throughout the rest of the plant, are equipped with ball-bearing idlers of Stephens-Adamson manufacture, and the belting was supplied by the Goodyear and Goodrich companies. Weightometers, from the Merrick Scale Co., are provided wherever necessary, to indicate and record the tonnage handled by the conveyors.

The drying and grinding building is a steel-frame structure, 114 ft. 0 in. by 140 ft. 0 in. in plan, sheathed with corrugated galvanized steel, roofed with wood decking covered with built-up roofing, and arranged with four main operating levels. The character of the equipment is indicated in the flow sheet, the dryers being furnished by the Ruggles-Coles Mfg. Co., the rod mills by the Allis-Chalmers Mfg. Co., and the vibrating screens by the W. S. Tyler Co. The rod mills are provided with individual synchronous motor drive through a Cutler-Hammer magnetic clutch. A 20-ton hand-power traveling crane over the mills provides facilities for heavy repairs.

The bins, holding 2000 metric tons, are of heavy steel construction, 20 ft. 6 in. by 95 ft. 0 in. in plan by 35 ft. 0 in. high. The bin bottom is of the catenary suspension type. An exhauster fan maintains the atmosphere in the bin at a small negative pressure, and this eliminates to a great extent the dust nuisance from the vibrating screen operations.

Leaching Division

The agitator building of the leaching division is a steel-frame structure, 102 ft. 0 in. by 115 ft. 6 in. in plan, sheathed with asbestos-protected metal, roofed with wood decking covered with built-up roofing, and provided with three main operating levels. Agitators are of the standard, cone-bottomed Pachuca type, built of steel and lined with 10-lb. chemical lead sheet. They are equipped with the device developed to progress

coarse material through the tank, and about 30-lb. gage, controlled from the ators are arranged in five acid sections tion section consisting of two rows of fc The solution from the electrolytic tank
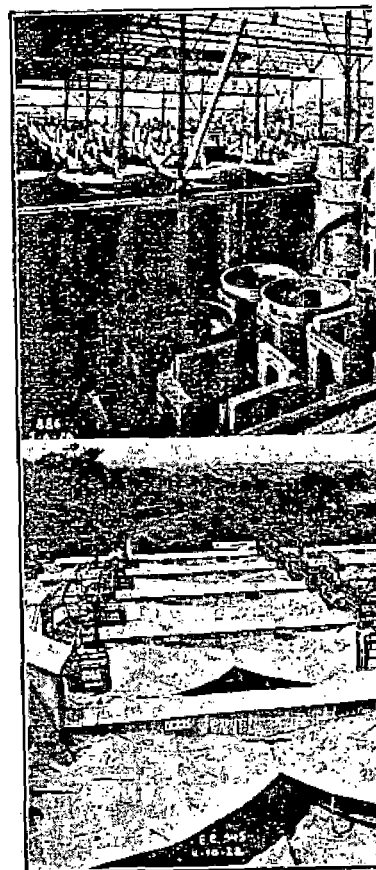
FIG. 9.—AGITATORS AND CLASSIFII
FIG. 10.—THICKENER SECTION

ing by gravity and is distributed to the five-compartment weir box. The solut feed to that section in a mixing box agitator in the series. The solution f pumped from the first storage thicke maintain the total iron content of the sc per liter. Fig. 9 shows agitators and cl

The classifier building of the leachii ture, 109 ft. 6 in. by 99 ft. 0 in. in plan,

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A transfer car is provided to shift
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exhauster fan maintains the atmos-
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the vibrating screen operations.

Division

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coarse material through the tank, and provided with an air supply of about 30-lb. gage, controlled from the main operating floor. The agitators are arranged in five acid sections of four in series, and one purification section consisting of two rows of four in series, arranged in parallel. The solution from the electrolytic tank house flows to the agitator build-
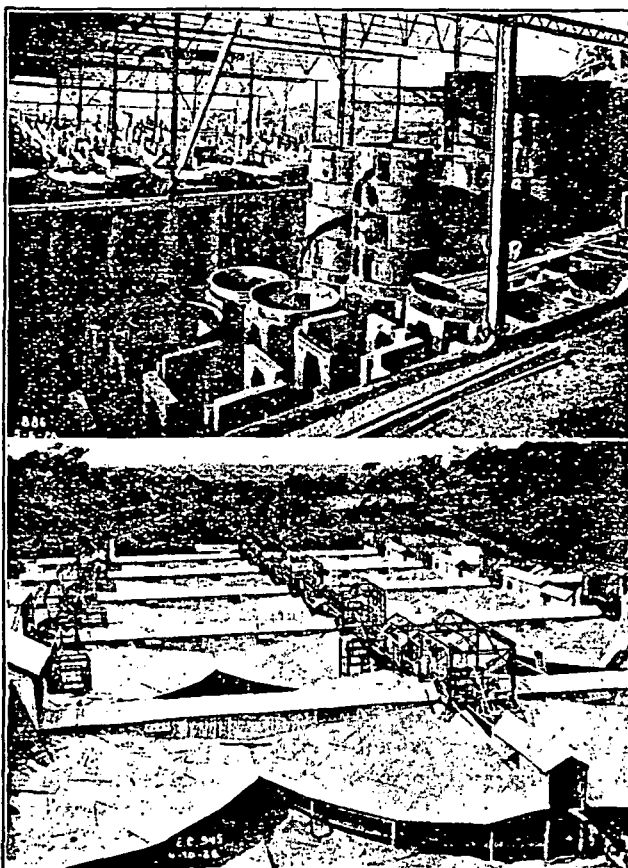
FIG. 9.—AGITATORS AND CLASSIFIERS UNDER CONSTRUCTION.
FIG. 10.—THICKENER SECTION UNDER CONSTRUCTION.

ing by gravity and is distributed to the five acid sections by means of a five-compartment weir box. The solution to each section joins the ore feed to that section in a mixing box immediately ahead of the first agitator in the series. The solution feed to the purification section is pumped from the first storage thickener in an amount necessary to maintain the total iron content of the solutions at approximately 6 grams per liter. Fig. 9 shows agitators and classifiers under construction.

The classifier building of the leaching division is a steel-frame structure, 109 ft. 6 in. by 99 ft. 0 in. in plan, sheathed with asbestos-protected

metal, roofed with wood decking covered with built-up roofing, and provided with two main operating levels. The classifiers are arranged in six sections, five of which correspond to the five acid agitator sections, and one spare. Each section consists of a primary bowl classifier, followed by and built integral with a three-deck washing classifier. The sands are progressed successively through the four decks, which are arranged for counter-current washing, and the discharge from the last washing deck is the finished sand tailing. Water is added in the last washing deck in an amount equal to the entrained solution in the sands from this deck. The bowl-classifier overflow is laundered to the primary thickener feed wells. The classifier tanks are constructed of reinforced concrete lined with 2 in. of asphalt mastic. The mechanisms are of steel, and where in contact with solution, are covered with 12-lb. chemical lead sheet. The rake blades are of duriron.

The thickener section of the leaching division consists of twenty-eight 70-ft. dia. Dorr thickeners, arranged on 75-ft. centers in both directions, in five horizontal benches, each bench 3 ft. 4 in. lower than the one above. There are six thickeners in each of the four top rows and four thickeners in the bottom row. The top row is the third wash, the next lower row is the second wash, the next lower row is the first wash, and the next lower row is the primary thickener. The first row of thickeners on the left looking up the hill is the purification section. The other five rows of thickeners are acid thickener sections corresponding to the same division in the agitator and classifier sections. One thickener in the bottom row is a spare used to hold the contents of any thickener that must be emptied for repairs; one is a clarifying thickener, which receives the overflows of all the primary acid thickeners, and the other two are simply solution-storage tanks. Each thickener is roofed individually and walkways are provided over the top connecting all the thickeners. This superstructure is of steel framing and the roofing of corrugated galvanized steel; walkway floors are of wood. The thickener tanks have concrete bottoms, steel sides and are lined with 8-lb. chemical lead sheet. Under each row of thickeners up and down the hill is a concrete tunnel which provides access to the cast-lead discharge cones, valves and piping, and which terminates in a sump and pump house. The latter provides facilities for disposal of pulp and solution drained from the tanks. The thickener mechanisms are constructed of steel with wood extension arms, the steel being covered with 12-lb. chemical lead sheet wherever in contact with the solution. Duplex Dorrco pumps progress the spigot discharge up the hill from one tank to the next, and the solution overflow flows by gravity from one tank to the next. Wash water is added in the last washing thickeners in an amount equal to that discarded as entrained solution in the finished slime tailing from this thickener. The feed to the five acid thickeners is distributed by a five-

PLAN VIEW

ELEVATION

END VIEW

FIG. 11.—(PART 1)

Fig. 11.—(Part 2)

SECTION AT CATHODE

SECTION AT STARTING SHEET BLANK
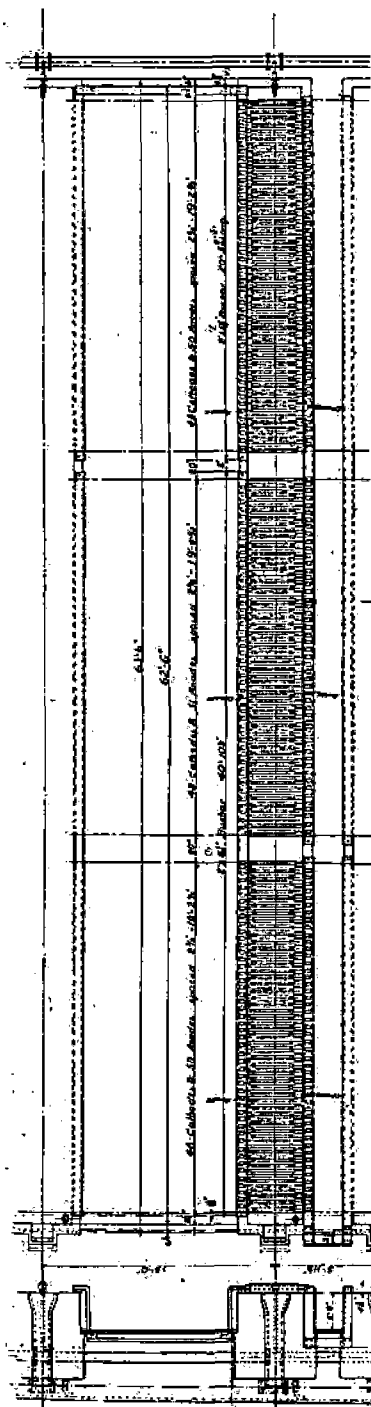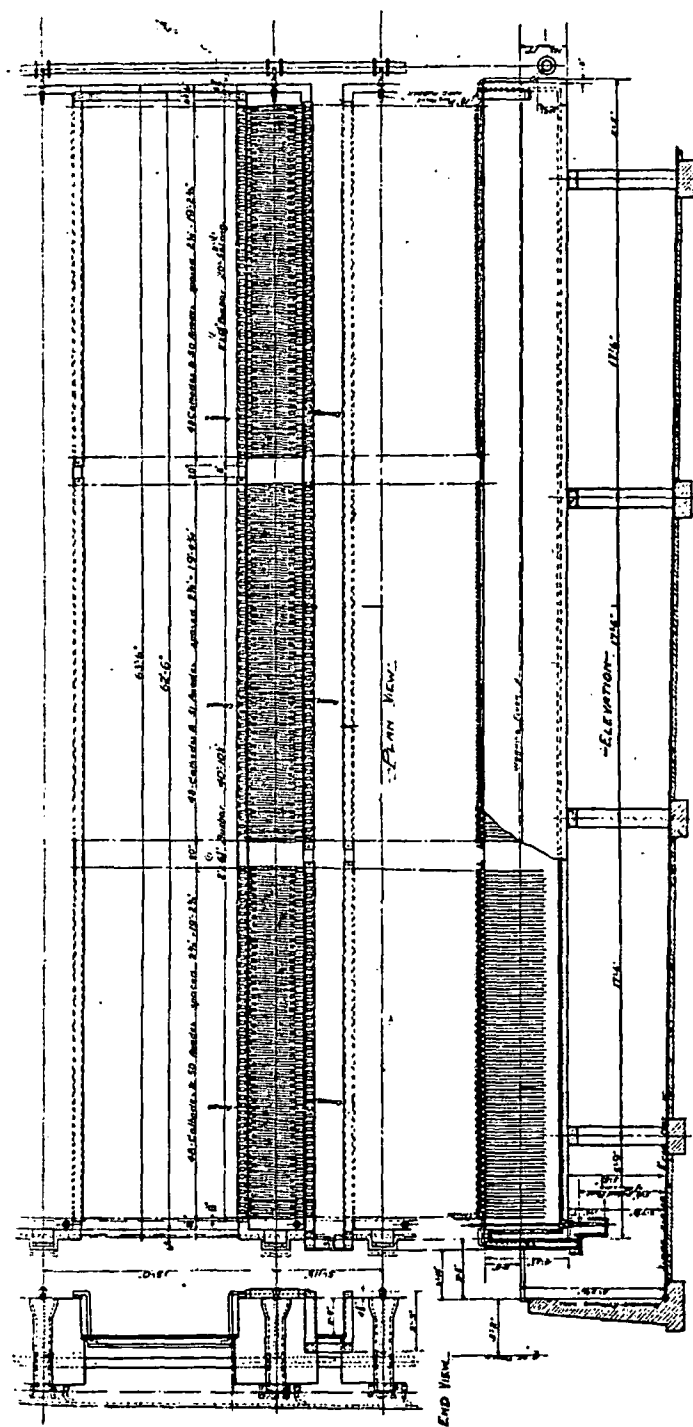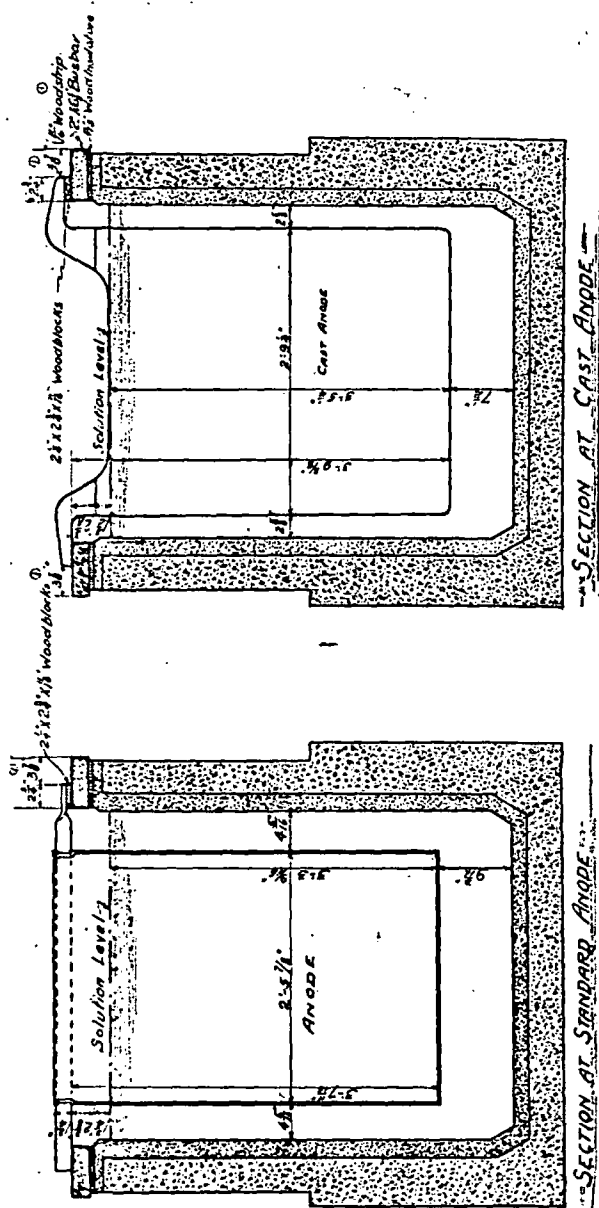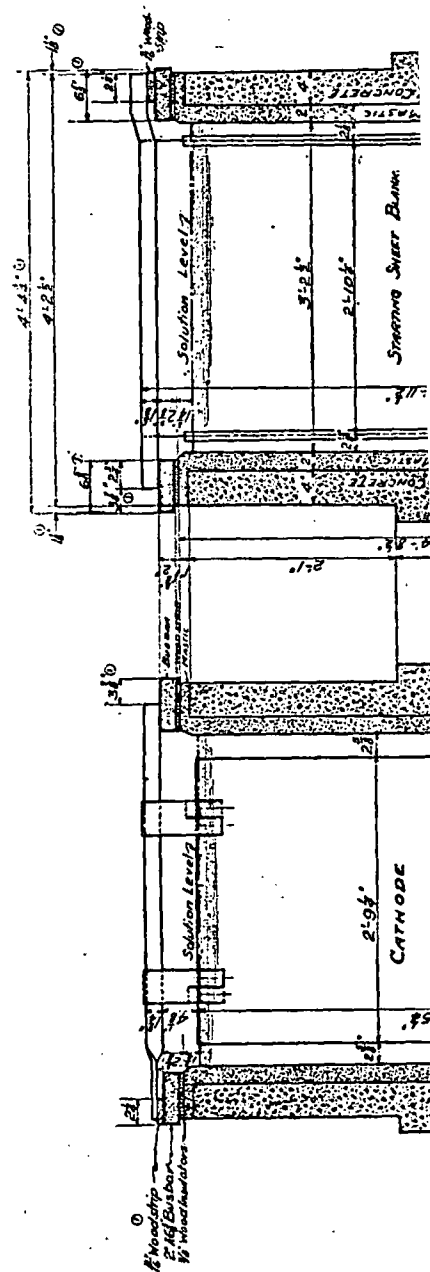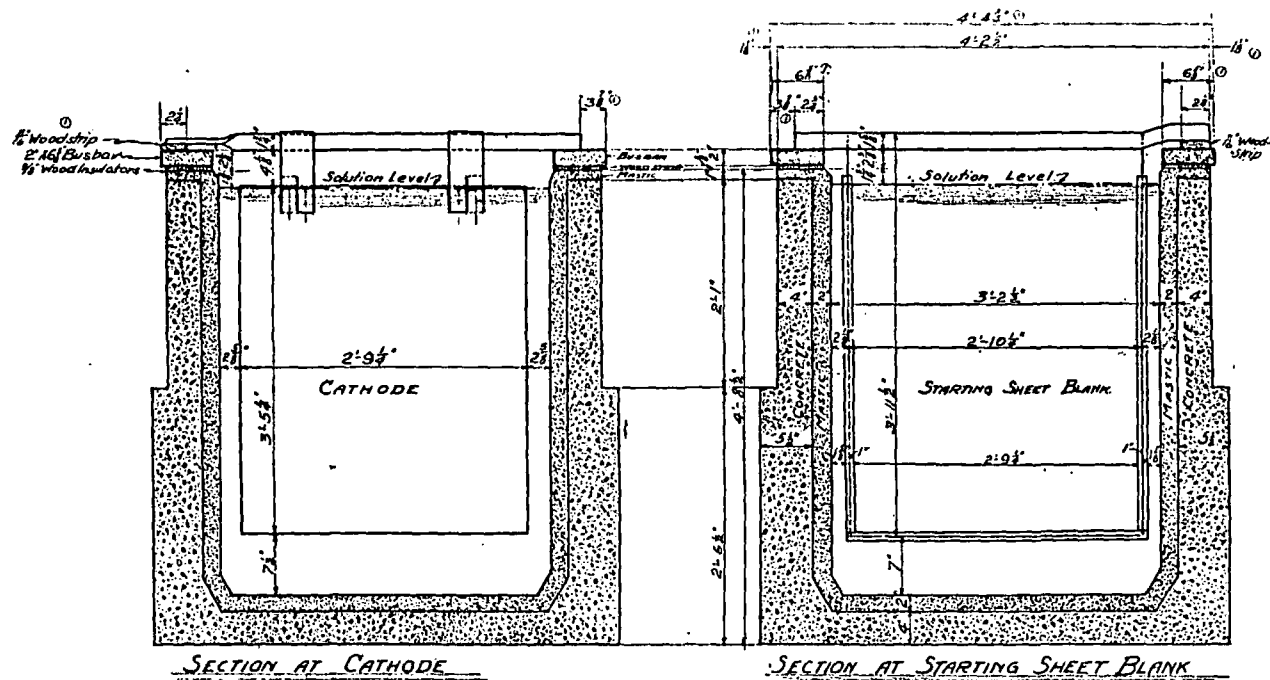
Fig. 11.—(Part 3)

Fig. 11.—General arrangement of electrolytic tanks.

compartment weir box and launder systems. Launders throughout the plant are of wood, lined with 6-lb. or 8-lb. chemical lead sheet, and where necessary are provided with renewable wood liners to protect the lead. Tailings are laundered to a gully below the plant site, which leads to a tailings pond constructed to impound them. Fig. 10 shows thickener section under construction.

Two small pump houses of brick and steel construction are provided near the thickeners, one to pump the solution from the last storage tank to the electrolytic tank house, the other to pump the solution for purification from the first storage tank to the purification agitators. Direct-connected electrically driven duriron centrifugal pumps are used, 8 by 6 in. for the first service and 6 by 4 in. for the latter. The sumps in the thickener tunnels and the agitator basement are also equipped with 6 by 4-in. duriron centrifugal pumps. All solution piping under high head is of steel, lead lined, and low-head piping is of extruded chemical lead. The sheet lead and pipe for the plant were fabricated in the company's own rolling and extruding mill, erected for the purpose. The pig lead was shipped in from the Broken Hill smelter in Rhodesia or from Europe.

Electrolytic Plant

The electrolytic tank house is a steel-frame structure, 266 ft. 6 in. by 405 ft. 0 in. in plan, sheathed with asbestos-protected metal and roofed with a wood deck covered with built-up roofing. The building is arranged with four crane aisles with a crane transfer at one end, to provide means for shifting cranes from one aisle to the other. The main operating floor is all on one level, and a basement is provided with ample head room for tank inspection and launder installation. There are 160 electrolytic tanks in the building, each 62 ft. 6 in. long, 3 ft. 2½ in. wide and 4 ft. 2½ in. deep inside (Fig. 11). The tanks are of reinforced concrete lined with 2 in. of asphalt mastic, and are equipped with a feed pipe at one end, an overflow dam at the other, and a hard lead plug and seat in the bottom for draining and cleaning out. The solution pumped from the leaching division is split into two equal parts by a weir tank in which the sulfuric acid requirement of the process is added continuously. The solution from the weir compartments is laundered to two constant-head tanks from which hard rubber header and riser pipes distribute the feed to the individual tanks. The overflow solution from the tanks is collected by a launder system in the basement and laundered through a tunnel to the agitator section of the leaching division. Conductor bars 2 by 6⅝ in. in cross-section are supported on wood insulating strips on the tank walls. The electrodes are arranged in three separate electrical groups in each tank, the groups being in series and the electrodes in multiple. The entire tank house is laid out in

two main electrical circuits, each t
60 volts. The center point of each
low resistance in order to protect
the electrolytic tanks are equipp

FIG. 12.—ELECTROLYTIC TANK H
FIG. 13.—TANK-HOUSE INTERIO

separate circulation of pure solution,
used to produce the necessary starting
remainder of the tanks are equipped w
Electrodes are handled to and from the
of the stiff-leg type. Forty-eight-hou
racks at the end of the building, looped
tapped on tables and suspended in rack
Finished cathodes, 10 to 14 days old,

launder systems. Launders throughout
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½ in. in cross-section are supported on
walls. The electrodes are arranged in
each tank, the groups being in series
The entire tank house is laid out in

two main electrical circuits, each taking normally 8000 amp. at about
460 volts. The center point of each electrical system is grounded through
a low resistance in order to protect the workmen from injury. Sixteen
of the electrolytic tanks are equipped so that they can be fed with a
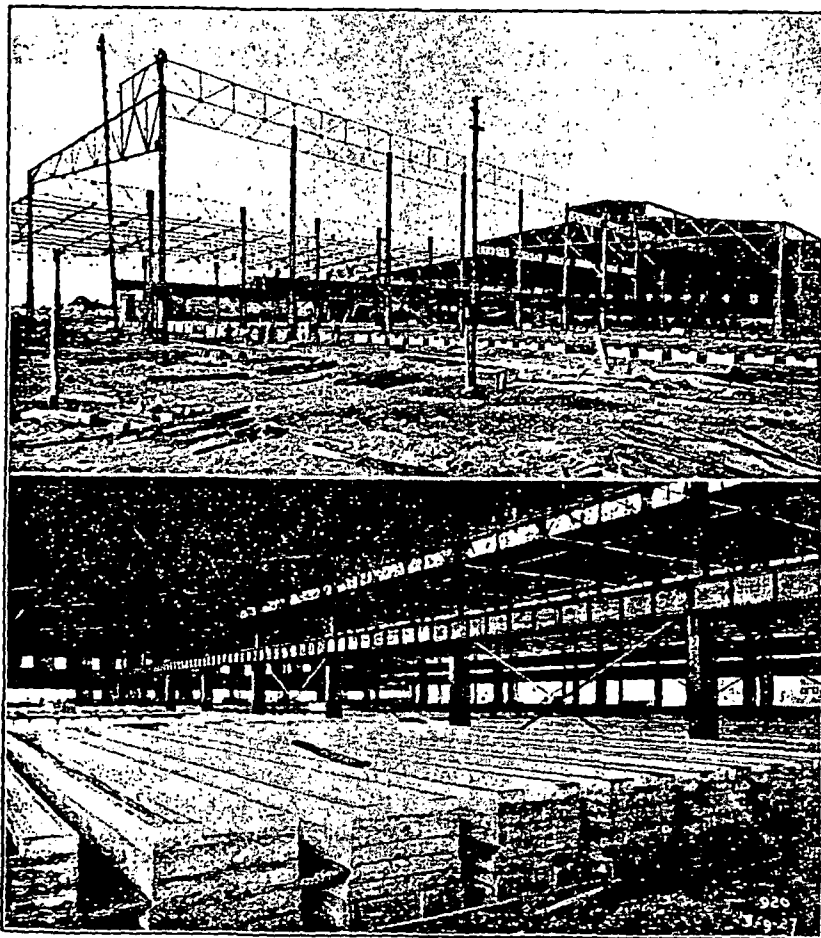
FIG. 12.—ELECTROLYTIC TANK HOUSE UNDER CONSTRUCTION.
FIG. 13.—TANK-HOUSE INTERIOR UNDER CONSTRUCTION.

separate circulation of pure solution, and enough of these tanks are so
used to produce the necessary starting sheets from soluble anodes. The
remainder of the tanks are equipped with insoluble anodes of hard lead.
Electrodes are handled to and from the tanks by 5-ton tank-house cranes
of the stiff-leg type. Forty-eight-hour starting sheets are stripped on
racks at the end of the building, looped on standard Morrow clip machines,
flapped on tables and suspended in racks ready for charging by the crane.
Finished cathodes, 10 to 14 days old, are drawn from the tanks by the

crane, spray-washed and unloaded on cathode loading machines of the Great Falls type, which deposit them in piles on cars going to the furnace refinery. Figs. 12 and 13 show the electrolytic tank house under construction.

Furnace Refinery

The furnace refinery building is a steel-frame structure, 124 ft. 8 in. by 234 ft. 0 in. in plan, sheathed and roofed with corrugated galvanized steel, and arranged with two operating levels. The building is equipped with two 130-ton refining furnaces, each provided with a 38-ft. dia. casting wheel of the Clark type, together with bosh and inspection conveyors. The charging bay is served by a 7000-lb. charging crane, made by the Wellman Engineering Co., and the casting bay by a standard 5-ton crane. An outside runway equipped with a standard 5-ton crane provides handling facilities over the storage and shipping yard. The furnaces were originally designed for grate firing, but on installation were equipped for pulverized coal firing with Heyl and Patterson burners and feeders. The furnaces are constructed with air-cooled brick bottoms; each has its individual stack, but no waste-heat boiler. A small coal-pulverizing plant is next to the furnace refinery. Wankie coal from Rhodesia is dried in a rotary shell dryer, pulverized in conical air-swept ball mills and delivered to the furnace bins by screw conveyor.

Acid Supply and Electric Power

Sulfuric acid is supplied for the leaching from a plant built close to the thickener section by a subsidiary company of the Union Minière. It is a contact process plant, burning sulfur shipped in from the Texas fields and utilizing as a catalyst platinized silica gel.

The electrical substation, which distributes power to the entire plant, is a steel-frame structure with brick walls and a concrete slab roof covered with built-up roofing. The main building is 39 ft. 4 in. by 175 ft. 0 in. in plan, and houses the following equipment:

One main switchboard, 31 panels, remote control.

Three 4000-kw. motor-generator sets for electrolysis, each consisting of a synchronous motor driving two direct-current generators, each capable of delivering 4000 amp. at 500 volts. One of these sets is a spare.

Three 175-kw. motor-generator sets for supplying 250 volts direct-current excitation and auxiliary power. One of these sets is a spare.

Two air compressors with direct-connected synchronous motor drive, capable of delivering 3650 cu. ft. of free air per min. at 4600-ft. altitude and a pressure of 40 lb. These units, one of which is a spare, provide air for solution agitation, etc.

A lean-to on one side of the building, 28 ft. 3 in. by 122 ft. 6 in. in plan, houses the high-tension switches, auxiliary power transformers

air washers for building ventilati and a storage-battery room. A ba ment is provided under part of main building and the high-tens switch compartment, and houses direct current breakers, main dir current buses, and switchboard a iliaries. Power is supplied to substation from the Panda ste plant or the Lufira hydroelectric pl at three-phase, 50 cycles, 6600 vo The electrical equipment was larg supplied by the International G eral Electric Co. and the compress by the Ingersoll-Rand Company.

Besides the major departme described above, the plant is equip with its own general offices, mech cal shop, carpenter shop, warehou locomotive shop, laboratory, etc., The ensemble provides a comp self-contained unit which turns marketable copper from original Fig. 14 shows a panorama of plant.

Details of Operation

The first unit of the new p was ready to be started up in A 1929, and was put into operation a locally organized crew. As fa additional units were completed, were put into operation, and b end of the year the entire plant operating, except for four of purification agitators, which lacked some of their interior fitt The plant was staffed with men v training had practically all bee tained in the experimental lea plant, and the operating crew was posed of men who had little if experience with the type of equip installed. The inexperience o

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air washers for building ventilation
and a storage-battery room. A base-
ment is provided under part of the
main building and the high-tension
switch compartment, and houses the
direct current breakers, main direct
current buses, and switchboard aux-
iliaries. Power is supplied to the
substation from the Panda steam
plant or the Lufira hydroelectric plant
at three-phase, 50 cycles, 6600 volts.
The electrical equipment was largely
supplied by the International Gen-
eral Electric Co. and the compressors
by the Ingersoll-Rand Company.

Besides the major departments
described above, the plant is equipped
with its own general offices, mechani-
cal shop, carpenter shop, warehouses,
locomotive shop, laboratory, etc., etc.
The ensemble provides a complete
self-contained unit which turns out
marketable copper from original ore.
Fig. 14 shows a panorama of the
plant.

Details of Operation

The first unit of the new plant
was ready to be started up in April,
1929, and was put into operation with
a locally organized crew. As fast as
additional units were completed, they
were put into operation, and by the
end of the year the entire plant was
operating, except for four of the
purification agitators, which still
lacked some of their interior fittings.
The plant was staffed with men whose
training had practically all been ob-
tained in the experimental leaching
plant, and the operating crew was com-
posed of men who had little if any
experience with the type of equipment
installed. The inexperience of the

FIG. 14.—PANORAMA OF 30,000-TON PANDA LEACHING PLANT.

operating force and the fact that construction was being carried on side by side with operation were the principal difficulties to be surmounted in starting operations. Mr. Eagle was sent into Katanga as the consulting engineer's representative to act in an advisory capacity during the final construction and starting up of the plant.

In general, the equipment installed gave excellent service. One major difficulty was encountered with the classifier mechanisms. The manufacturers supplied a mechanism which was not sufficiently strong to take care of the extra weight added by the lead covering specified for acid-proofing, therefore mechanical breakage occurred when the units were placed in operation. After new and stronger mechanisms were installed, there were no further difficulties. The screw conveyors in the drying and grinding division did their work satisfactorily, but maintenance of the intermediate bearings was excessive, and indicated the desirability of shifting the thrust bearing to the discharge end. The slope of the sand-tailings launder needed to be increased, because when the plant capacity rose nearly to its normal, the tendency of this clean material, free of slimes, to drop out of solution caused the launder as installed to overflow. The wood interior fittings of the Pachuca agitators were made too light to give long life and were replaced by heavier construction. The long electrolytic tanks, while ideal for use with insoluble anodes, resulted in such excessive solution segregation in the stripper tanks using soluble anodes that poor starting sheets were made. It was found necessary to insert baffles between the three electrical groups in these tanks to break up this segregation, and after this was done no further trouble was experienced. Except for the items mentioned above, practically no trouble of any moment was experienced with the equipment as installed.

TABLE 4.—*Summary of Plant Operations for December, 1929*

CRUSHING, STORAGE, DRYING, ETC.

Wet ore crushed, metric tons, total	40,056
Moisture in wet ore crushed, avg. per cent	13.20
Cu in dry ore crushed, avg. per cent	6.57
Wet ore to driers, metric tons, total	39,984
Moisture in drier discharge, avg. per cent	0.24

LEACHING DIVISION

Dry ore fed to leaching, metric tons, total	32,631.109
Dry concentrates fed to purification, metric tons, total	1,057.966
Cu in ore fed to leaching, avg. per cent	6.539
Cu in concentrates fed to purification, avg. per cent	28.700
Cu in classifier sands (per cent of dry solids), avg. per cent	0.442
Solution in classifier sands, avg. per cent	29.19
Cu in entrained solution in classifier sands, avg. grams per liter	11.84
Free H_2SO_4 in entrained solution in classifier sands, avg. grams per liter	0.00

TABLE

Cu in acid slime tails (per cent of dry
Solution in acid slime tails, avg. per ce
Cu in entrained solution of acid slime
Free H_2SO_4 in entrained solution of acid
Cu in purification slime tails (per cent
Solution in purification slime tails, avg.
Cu in entrained solution of purification
Free H_2SO_4 in entrained solution of pur.
  per liter
Extraction (copper into solution), avg.
Recovery (copper to tank house), avg.
H_2SO_4 consumed per kilogram Cu recov
Sand tails, per cent of total tails
Acid slime tails, per cent of total tails
Purification slime tails, per cent of total
Metric tons total tails from 1 m.t. ore
Metric tons total tails from 1 m.t. concer

ELECTROLY

Fine copper in cathodes drawn, metric to
Cu produced per kw-hr., avg. kg
Ampere efficiency, avg. per cent
Amperes for month per circuit, avg
Volts for month per circuit, avg
Volts per electrical group (commercial), av
Volts per electrical group (stripper), avg.
Starting sheets stripped, total number
Good sheets, per cent
Starting sheet tanks in service, total numb
Commercial tanks in service, total number.
Tanks in service, total number

FURNACE F

Furnace charges, total number
Hours per charge, avg
Metric tons to furnace per charge, avg
Metric tons production per charge, avg
Metric tons treated, total number
Metric tons produced, total number
Metric tons Wankie coal per charge, avg

SUBSTA

Alternating current power for deposition, k
Alternating current auxiliary power, kw-hr.
Alternating current power, total, kw-hr

No process troubles were encount
where the troubles were entirely the
operating force and the fact that the
developed to the degree of accurac

at construction was being carried on side
he principal difficulties to be surmounted
agle was sent into Katanga as the consult-
to act in an advisory capacity during the
up of the plant.

t installed gave excellent service. One
red with the classifier mechanisms. The
hanism which was not sufficiently strong
ght added by the lead covering specified
hanical breakage occurred when the units
ter new and stronger mechanisms were
er difficulties. The screw conveyors in
n did their work satisfactorily, but main-
earings was excessive, and indicated the
t bearing to the discharge end. The slope
eded to be increased, because when the
its normal, the tendency of this clean
p out of solution caused the launder as
d interior fittings of the Pachuca agitators
g life and were replaced by heavier con-
c tanks, while ideal for use with insoluble
ive solution segregation in the stripper
at poor starting sheets were made. It
affles between the three electrical groups
segregation, and after this was done no
Except for the items mentioned above,
ment was experienced with the equipment

lant Operations for December, 1929

rORAGE, DRYING, ETC.

....	40,056
cent............................	13.20
....	6.57
....	39,984
cent............................	0.24

uNG DIVISION

otal............................	32,631.109
ietric tons, total..............	1,057.966
t...............................	6.539
avg. per cent..................	28.700
iolids), avg. per cent..........	0.442
nt.............................	29.19
nds, avg. grams per liter......	11.84
sifier sands, avg. grams per liter	0.00

TABLE 4.—(Continued)

Cu in acid slime tails (per cent of dry solids), avg. per cent..........	0.177
Solution in acid slime tails, avg. per cent...........................	49.39
Cu in entrained solution of acid slime tails, avg. grams per liter......	9.52
Free H$_2$SO$_4$ in entrained solution of acid slime tails, avg. grams per liter	0.00
Cu in purification slime tails (per cent of dry solids), avg. per cent...	0.426
Solution in purification slime tails, avg. per cent....................	57.20
Cu in entrained solution of purification slime tails, avg. grams per liter	11.33
Free H$_2$SO$_4$ in entrained solution of purification slime tails, avg. grams per liter........................	0.00
Extraction (copper into solution), avg. per cent.....................	96.53
Recovery (copper to tank house), avg. per cent.....................	88.34
H$_2$SO$_4$ consumed per kilogram Cu recovered, kg...................	0.696
Sand tails, per cent of total tails..................................	40.54
Acid slime tails, per cent of total tails.............................	56.08
Purification slime tails, per cent of total tails.....................	3.38
Metric tons total tails from 1 m.t. ore.............................	0.869
Metric tons total tails from 1 m.t. concentrates....................	0.491

ELECTROLYTIC DIVISION

Fine copper in cathodes drawn, metric tons, total..................	2,486.097
Cu produced per kw-hr., avg. kg..................................	0.471
Ampere efficiency, avg. per cent.................................	78.53
Amperes for month per circuit, avg...............................	7,460
Volts for month per circuit, avg..................................	444.69
Volts per electrical group (commercial), avg......................	1.97
Volts per electrical group (stripper), avg.........................	0.39
Starting sheets stripped, total number............................	64,176
Good sheets, per cent..	92.43
Starting sheet tanks in service, total number.....................	12
Commercial tanks in service, total number........................	148
Tanks in service, total number...................................	160

FURNACE REFINERY

Furnace charges, total number...................................	13
Hours per charge, avg...	29.15
Metric tons to furnace per charge, avg...........................	100.383
Metric tons production per charge, avg...........................	86.454
Metric tons treated, total number................................	1,304.977
Metric tons produced, total number..............................	1,123.896
Metric tons Wankie coal per charge, avg.........................	24.905

SUBSTATION

Alternating current power for deposition, kw-hr...................	5,458,000
Alternating current auxiliary power, kw-hr.......................	876,000
Alternating current power, total, kw-hr..........................	6,334,000

No process troubles were encountered, except in the furnace refinery, where the troubles were entirely the reflection of the inexperience of the operating force and the fact that the laboratory technique had not been developed to the degree of accuracy required by this rather delicate

operation. The matter of turning out a furnace refinery product that
will meet the requirements of the fabricators is a difficult operation at the
best, and the company exhibited a great deal of courage in attempting the
job with a crew of the limited experience of the men they had.

TABLE 5.—*Typical Solution Assays and Screen Analyses*

AVERAGE SOLUTION ASSAYS

| | Tank House | | Acid Agitation Discharge, Grams per Liter | Purification | |
	Feed, Grams per Liter	Discharge, Grams per Liter		Feed, Grams per Liter	Discharge, Grams per Liter
Cu..............	30.51	16.26	30.53	30.17	44.98
Free H₂SO₄......	5.50	34.35	12.22	11.17	0.00
Fe, Total........	5.63	5.63	6.65	5.81	1.99
Fe, Ferric........	5.43	3.97	6.34	4.98	1.42
Fe, Ferrous.......	0.20	1.66	0.31	0.83	0.57
Al₂O₃...........	11.00	11.00	11.70	10.88	7.50

OTHER IMPURITIES ACCUMULATED IN THE SOLUTIONS, GRAMS PER LITER

Co	Mn	MgO	SiO₂	P₂O₄	CaO
10.03	6.50	13.60	1.72	3.80	0.34

AVERAGE SCREEN ANALYSES FOR DECEMBER, CUMULATIVE PERCENTAGE

Mesh	Ore to Leaching	Sand Tails	Slime Tails
+ 20	8.05	14.07	—
+ 35	22.95	42.09	—
+ 48	29.70	54.60	—
+ 65	35.95	66.98	—
+100	42.30	75.79	0.73
+150	47.25	82.07	2.08
+200	51.55	85.77	5.84
Total.................	100.00	100.00	100.00

Conditions in the copper industry had become so serious by the end
of December, 1929, that the output of the new leaching plant was ordered
curtailed in January. As a result of this, the largest month's production
during the observation of the operations by the consulting engineers was
obtained in December, with the plant still partly incomplete. A sum-
mary of the plant operations for that month is given in Table 4. Typical
solution assays covering the principal constituents of the solution at
various points in the process cycle are given in Table 5.

At the conclusion of the per
new plant at the end of Janua
sonable degree of efficiency, bu
on what would be considered a
ever, had amply demonstrated
the promises made as to capac
consumption, power consumpti
satisfying complement to these
of construction cost indicated
original estimate submitted in

D.

(Francis

F. R. PYNE, Perth Amboy, N.
leaching solution. Was that due to

H. Y. EAGLE.—We do not know
not sufficient, as far as we can see, t
solution. We had various bronze ar
two weeks the pumps were like sieve
tion line in the agitators and the n
amount of ferric iron in the solution

F. R. PYNE.—The amount of ferri
powerful corrosive effect. There cou

H. Y. EAGLE.—No nitrates and no
for it, but we do not know. The s
ordinary refinery solutions; the amo
neighborhood of 10 grams per liter wa

MEMBER.—To what extent do the
of the Katanga ores, or what proport
proportion smelted?

H. Y. EAGLE.—That is pretty m
opinion is that from the standpoint of
which are leached, the more profitabl
of production presented by leaching i
the total production of about 139,000

E. L. JORGENSEN, Irvington, N. J
material by agitation in preference t
for the coarser material, and the met

H. Y. EAGLE.—We did considera
came to was that it is all well and goo
possible to leach the coarse Katanga
percolation leaching is a good deal
but when designing a slime plant t
amount of very fine material in the
must be provided to take care of the
taken out or not, or practically so.

ION MINIÈRE DU HAUT KATANGA

; out a furnace refinery product that
bricators is a difficult operation at the
great deal of courage in attempting the
rience of the men they had.

n Assays and Screen Analyses

LUTION ASSAYS

'ge, per	Acid Agitation Discharge, Grams per Liter	Purification	
		Feed, Grams per Liter	Discharge, Grams per Liter
6	30.53	30.17	44.98
5	12.22	11.17	0.00
3	6.65	5.81	1.99
7	6.34	4.98	1.42
3	0.31	0.83	0.57
)	11.70	10.88	7.50

N THE SOLUTIONS, GRAMS PER LITER

SiO₂	P₂O₄	CaO
1.72	3.80	0.34

ECEMBER, CUMULATIVE PERCENTAGE

ıg	Sand Tails	Slime Tails
	14.07	—
	42.09	—
	54.60	—
	66.98	—
	75.79	0.73
	82.07	2.08
	85.77	5.84
	100.00	100.00

y had become so serious by the end
f the new leaching plant was ordered
this, the largest month's production
ons by the consulting engineers was
nt still partly incomplete. A sum-
month is given in Table 4. Typical
al constituents of the solution at
e given in Table 5.

At the conclusion of the period of observation of the operations of the new plant at the end of January, 1930, it had been brought up to a reasonable degree of efficiency, but had still a considerable way to go to get on what would be considered a proper operating basis. The plant, however, had amply demonstrated its ability to meet without undue difficulty the promises made as to capacity, copper extraction and recovery, acid consumption, power consumption and over-all operating costs. A rather satisfying complement to these results was the fact that the final records of construction cost indicated that the plant had been built within the original estimate submitted in 1923.

DISCUSSION

(Francis R. Pyne presiding)

F. R. PYNE, Perth Amboy, N. J.—The authors mention (p. 620) the corrosive leaching solution. Was that due to ferric iron or something else?

H. Y. EAGLE.—We do not know. The chemical composition of the solution is not sufficient, as far as we can see, to explain the extremely corrosive nature of the solution. We had various bronze and brass pumps, for example, in use. Inside of two weeks the pumps were like sieves. We could drive copper nails below the solution line in the agitators and the next day they were gone. I do not believe the amount of ferric iron in the solution was sufficient to account for it.

F. R. PYNE.—The amount of ferric iron appeared to be rather small to have such a powerful corrosive effect. There could not be nitrates very well.

H. Y. EAGLE.—No nitrates and no chlorides. The presence of cobalt might account for it, but we do not know. The solutions were very much more corrosive than ordinary refinery solutions; the amount of cobalt in the solution somewhere in the neighborhood of 10 grams per liter was the only thing that to us seemed to be unusual.

MEMBER.—To what extent do the authors think leaching may supersede smelting of the Katanga ores, or what proportion of the ores is likely to be leached and what proportion smelted?

H. Y. EAGLE.—That is pretty much a matter of company policy, but our own opinion is that from the standpoint of costs the more of the ores amenable to leaching, which are leached, the more profitable it will be. Up to date, however, the amount of production presented by leaching is comparatively small. I think that in 1930 of the total production of about 139,000 metric tons only 21,000 of it was from leaching.

E. L. JORGENSEN, Irvington, N. J.—Why was it decided to treat relatively coarse material by agitation in preference to separating coarse and fines, using percolation for the coarser material, and the method you are using for the finer material?

H. Y. EAGLE.—We did considerable figuring on that basis and the conclusion we came to was that it is all well and good to separate the coarse material, and it is quite possible to leach the coarse Katanga material by percolation. There is no doubt that percolation leaching is a good deal more efficient metallurgically than is agitation, but when designing a slime plant the size of the slime plant is determined by the amount of very fine material in the ore. That is, the amount of settling area that must be provided to take care of the slimes is the same whether the coarse material is taken out or not, or practically so. So it meant that if we put in a coarse percolation

treatment for the coarse, we still had to build just as big a plant for the slimes, and it ran into too much money.

F. R. PYNE.—Is the source of the Katanga power water or fuel?

H. Y. EAGLE.—The new leaching plant was started on the basis of steam power. I left Katanga in February, 1930, and in May of that year the new Lufira power plant was scheduled to deliver hydropower to the leaching plant; I suppose that is now in operation.

A. GRÖNNINGSATER, Sudbury, Ont.—I believe that is due to the ferric sulfate. I have had experience with that kind of solution, in which I know there was no impurity except a small amount of iron. Only one or two grams per liter will eat up copper. If you take out the iron and leave everything else in, copper will withstand corrosion for years.

H. Y. EAGLE.—The small amount of ferric iron in our solution has not seemed to us to explain the cause. In refinery practice there may be quite a bit of iron in the solution, and usually it splits up about fifty-fifty; that is, about 50 per cent ferric and 50 per cent ferrous. Often the amount of ferric iron in a refinery solution will greatly exceed the amount we had and still we never noticed that particularly corrosive action there. We were looking for the cause, but never hit upon a satisfactory explanation.

I would like to speak of our long electrolytic tanks. The long electrolytic tank, when it was presented at a meeting of the Electrochemical Society was looked upon more or less as a fish story. The energy efficiencies as high as 1⅛ lb. per kilowatt hour, which we obtained, were a good deal higher than the usual practice. The tanks, as they are now operating, while they are not yielding as much as that, owing to the low ampere efficiency produced by a new crew, will, I believe, yield a considerably higher figure eventually.

F. R. PYNE.—Has it been your experience that lengthening the tank increases the power efficiency?

H. Y. EAGLE.—Yes.

F. R. PYNE.—I should think it would because there is the same solution throughout no matter how long the tank is. And a high acid can be run whereas in a short tank the same beneficial results are not obtained.

H. Y. EAGLE.—I should like to know whether in any other industry, for example in electrolytic zinc, or other copper plants, the same thing has been experienced.

F. R. PYNE.—We have not tried long tanks for copper—I have never seen any long tanks—but we have experienced the thing to which you refer in the paper; that is, that when the circulation in the tank is slow, it is practically constant from one end of the tank to the other, except possibly where the solution comes into it. I presume you find the same condition in the new longer tanks.

H. Y. EAGLE.—It persists up to 60 ft., as far as we have tried it.

W. C. SMITH, New York, N. Y.—What experience have you had with insoluble anodes?

H. Y. EAGLE.—The insoluble anodes that we first used in the experimental plant were made of chemical lead, and naturally we ran into a lot of trouble. The warping that developed after a short time was serious, and we had to take the anodes out of the tank repeatedly and beat them straight. The oxidation was very serious and the chemical lead anodes did not last very long. We tried out lead anodes of various antimony contents, and finally fixed on one with a content of about 6 per cent anti-

mony, that being a point that ga
to be as resistant to warping and

W. C. SMITH.—Have you had
anodes?

H. Y. EAGLE.—I have tried t
tried the perforated anodes on th
Raritan. Perhaps Mr. Pyne can
practice at Raritan to operate the

F. R. PYNE.—Yes, some years
there. It was abandoned so I sh
was due to the poor casting of the
of the anodes, I cannot say.

H. Y. EAGLE.—It was general
voltage was obtained for a given lit
it was a considerable saving in lead
with all insoluble anodes, the savi
weight could be cut out. We tried
anode density. Apparently tank
density. At least, that was our ex

A. GRÖNNINGSATER.—The new
There is said to be no increase in
thick were they?

H. Y. EAGLE.—They were cast
⅜ in. thick. At the expiration of r
eight months, there seemed to be no
get anywhere up to 10 years out of t

About ten amperes current densi
the basis of 100 amp. per square m

E. L. JORGENSEN (written discu
Copper Co., we carried out in 1914
conditions. We compared grid and
have described with sheet-lead ano
surfaces, the sheet-lead anodes show
current densities at the cathode of 1
sq. ft. this advantage was lost. A
increased rapidly 75 to 80 per cent
no increase at all after 70 days of s
40 per cent.

Based on 70 days operation, we
remelted oftener than every four ye

Another important observation
grid anodes but not with sheet-lead
tion of oxygen was concentrated on
good circulation where it was most
5 in. on centers.

The findings given are so much
some details should be given. The
the others of chemical sheet lead.
higher than on the sheet-lead anode
in the experimental tanks: copper,

I MINÈRE DU HAUT KATANGA

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mony, that being a point that gave practically no shrinkage in the mold and seemed to be as resistant to warping and corrosion as any of the others tried.

W. C. SMITH.—Have you had any experience with the silver-lead or perforated anodes?

H. Y. EAGLE.—I have tried the perforated anodes but not the silver-lead. We tried the perforated anodes on the basis of some tests which I think were run at Raritan. Perhaps Mr. Pyne can confirm this. Was it not at one time standard practice at Raritan to operate the liberator tanks with a grid anode?

F. R. PYNE.—Yes, some years ago, but it has not been done since I have been there. It was abandoned so I should imagine it was unsatisfactory. Whether it was due to the poor casting of the anodes, or some other defect inherent in the shape of the anodes, I cannot say.

H. Y. EAGLE.—It was generally considered at Raritan, I think, that the same voltage was obtained for a given liberator tank, irrespective of the anode density, and it was a considerable saving in lead to make it a grid. In a leaching plant, of course, with all insoluble anodes, the saving in lead would be enormous if a quarter of the weight could be cut out. We tried it, but the voltage ran up perceptibly with added anode density. Apparently tank voltage is dependent on both cathode and anode density. At least, that was our experience.

A. GRÖNNINGSATER.—The new copper refinery at Sudbury is using a grid anode. There is said to be no increase in voltage. How were your anodes cast, and how thick were they?

H. Y. EAGLE.—They were cast in a cast-iron chill, and if I remember rightly were ⅜ in. thick. At the expiration of my stay at Katanga, when they had been in about eight months, there seemed to be no perceptible depreciation. I have an idea we may get anywhere up to 10 years out of them.

About ten amperes current density is being used. The design of the plant was on the basis of 100 amp. per square meter.

E. L. JORGENSEN (written discussion).—When I was in Chile with the Braden Copper Co., we carried out in 1914 and 1915 extensive experiments under operating conditions. We compared grid anodes cast in a similar manner to that which you have described with sheet-lead anodes. When starting with new anodes with clean surfaces, the sheet-lead anodes showed 5 per cent lower voltage than the grids, with current densities at the cathode of 10 to 15 amp. per sq. ft. With 15 to 40 amp. per sq. ft. this advantage was lost. After a very short period of service, the voltage increased rapidly 75 to 80 per cent with sheet-lead anodes, whereas the grids showed no increase at all after 70 days of service. The saving in power with grids was over 40 per cent.

Based on 70 days operation, we estimated that the grids would not have to be remelted oftener than every four years, with the possibility of much longer life.

Another important observation was that we could make good starting sheets with grid anodes but not with sheet-lead anodes. The reason for this was that the evolution of oxygen was concentrated on a small surface and acted as an air-lift to promote good circulation where it was most needed. The cathodes and anodes were spaced 5 in. on centers.

The findings given are so much at variance with the observations of others that some details should be given. The grids were made of 6 per cent antimonial lead and the others of chemical sheet lead. The current density on the grids was 3.4 times higher than on the sheet-lead anodes. The electrolyte had the following composition in the experimental tanks: copper, 17 to 20 grams per liter; ferrous iron, 20 to 26;

ferric iron, 11.5; sulfuric acid, 45 to 70; nitric acid, none; chlorine, none. The temperature was 50° to 55° C.

Since I am talking of the Braden Copper Co., a few remarks on leaching operations there might not be out of order. We roasted sulfide concentrate and leached with sulfuric acid solutions. We removed ferric iron from neutralized solutions as basic sulfate and separated the precipitate from partially leached pulp by classification, as you did later at Katanga. This was a relatively simple matter when working with concentrate from Wilfley tables. With the much finer flotation concentrate this classification was not so good. The difficulty was overcome, experimentally at least, with magnetic separators covered with lead. The basic iron sulfate was nonmagnetic and partially leached calcine was strongly magnetic.

C. W. EICHRODT, Laurel Hill, N. Y.—I am not with Chile Copper Co. now, but in 1924 I presented a paper on the electrolytic tank house for that company at the same time that Mr. Eagle did. At that time we had experimented with larger tanks, but failed to mention the matter. Our experience in this connection was that we lost in ampere efficiency more than we gained in reduced voltage. Our development along these lines was somewhat a matter of secondary consideration. In order to improve the flow of electrolyte between tanks or cells of our electrolytic sections, which consisted of 16 tanks in series, a new type of construction was developed. The section was built as one large tank with partitions that divided it into the individual cells; openings in the partitions were provided for the flow of electrolyte through the series. The size of these openings was increased until the final development was a tank containing 16 electrode sets in series with partitions between sets consisting only of mastic-covered supporting columns for the beams carrying the intermediate transfer bars. The voltage was lower, mainly, I believe, because of irregular current distribution, and the ampere efficiency loss for the same reason was lowered to the point that the net power efficiency decreased.

H. Y. EAGLE.—Did you have baffles between the various tanks?

C. W. EICHRODT.—No, in the one tank mentioned we did not. Any suitable material for baffles would not stand up in our electrolyte. We made little mention of our development and immediately replaced portions of the mastic partitions, which might be considered baffles.

H. Y. EAGLE.—We found that in order to cut down the leakage between the various electrical groups in the tank it was essential to put at the end of each electrical group one anode or one sheet of lead, which was absolutely not in circuit. That meant that for current to leak from one group to the next, there would necessarily be two voltages of decomposition. This lead screen absolutely stopped the leakage from one group to the other and kept ampere efficiency up.

C. W. EICHRODT.—Our individual electrode sets consisted of 56 anodes and 55 cathodes, with an anode at each end. This might be considered a long tank unit in itself. It was the partitions between the sets in series that we removed. No screen or baffle between sets was practical because no inexpensive material that was suitable would stand up in our solutions, which contained nitric, hydrochloric and sulfuric acids and ferric iron. With the improved alloys now available, something might be developed, but I doubt whether it would prove practical.

You mentioned that you did not have much success with acid-resisting materials. I am inclined to believe that cobalt and not ferric iron is basically responsible. Ferric iron behaves in no consistent manner. I have seen four or five grams per liter apparently do no harm, and again under practically the same conditions one gram per liter cause trouble. It depends upon the agents causing alternate oxidation and reduction

of the iron. If the solution is satur
In this connection, the presence of c
is important. There is apparently
up the oxidation and reduction of i
inclined to believe is cobalt. The c
the iron takes part in the corrosion

F. R. PYNE.—When talking wit
property I understood that there i
wood. What are you using for pol

H. Y. EAGLE.—There is no scar
of what is called "bush," and it is
gnarled wood. It is not suitable fo

F. R. PYNE.—Is it a hard wood

H. Y. EAGLE.—It is a bastard m

C. W. EICHRODT.—How much l
solution circuit per ton of ore leache

H. Y. EAGLE.—I cannot give y
amount of wash water added in t
entrained solution in the classifier
moisture. The same figure applies
treatment, one volume for each vol
the slime tails average about, 50 pe
of the relative amounts of sands
the two different kinds of tails, you
water per ton of ore. Does that ar

C. W. EICHRODT.—Not exactly.
equal to the water added, or the cir
in the way of evaporation or delibe

H. Y. EAGLE.—There is no disc

C. W. EICHRODT.—The water u
moisture?

H. Y. EAGLE.—Absolutely.

B. H. STROM, New York, N. Y.
chlorine in the electrolysis of zinc su
one-tenth gram per liter chlorine th
half gram per liter the anodes becar
influence anode corrosion in zinc e
story. I know of one case where th
liter chlorine. The anodes last for
could easily be made to last for
a change advisable.

Coming back to the leaching p
used to prevent segregation and pl
given, and I would like to have a li

H. Y. EAGLE.—I do not know w
When the material is lifted from th
the coarse drops out before the solu

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Co., a few remarks on leaching operations
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the flow of electrolyte through the series.
til the final development was a tank con-
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ir electrolyte. We made little mention
ced portions of the mastic partitions.

cut down the leakage between the vari-
ial to put at the end of each electrical
was absolutely not in circuit. That
to the next, there would necessarily be
en absolutely stopped the leakage from
ncy up.

e sets consisted of 56 anodes and 55
ght be considered a long tank unit in
a series that we removed. No screen
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ned nitric, hydrochloric and sulfuric
s now available, something might be
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success with acid-resisting materials
iron is basically responsible. Ferric
en four or five grams per liter appar-
e same conditions one gram per liter
ng alternate oxidation and reduction

of the iron. If the solution is saturated with air, trouble from iron may be aggravated. In this connection, the presence of other metals even in relatively negligible quantities is important. There is apparently what might be called a catalytic action in speeding up the oxidation and reduction of iron, exerted by certain metals, one of which I am inclined to believe is cobalt. The cobalt would be the primary source of trouble while the iron takes part in the corrosion reaction.

F. R. PYNE.—When talking with Mr. Wheeler some years ago about the Katanga property I understood that there is either a scarcity of wood or that it is all dwarf wood. What are you using for poling in the furnace refining?

H. Y. EAGLE.—There is no scarcity of wood in Katanga. There is an abundance of what is called "bush," and it is not dwarf wood by any means, but an extremely gnarled wood. It is not suitable for construction but for poling it is quite all right.

F. R. PYNE.—Is it a hard wood?

H. Y. EAGLE.—It is a bastard mahogany, mostly.

C. W. EICHRODT.—How much fresh water for washing is added to the leaching-solution circuit per ton of ore leached?

H. Y. EAGLE.—I cannot give you that in definite figures, but I can say that the amount of wash water added in the classifiers is one volume for each volume of entrained solution in the classifier tails. These tails go out at about 30 per cent moisture. The same figure applies to the amount of wash water added in the slime treatment, one volume for each volume of entrained solution in the slime tails, and the slime tails average about 50 per cent moisture. From the figures in the paper of the relative amounts of sands and slimes, and the relative moisture contents of the two different kinds of tails, you can figure out for yourselves the amount of wash water per ton of ore. Does that answer your question?

C. W. EICHRODT.—Not exactly. The amount of moisture in the tailings must be equal to the water added, or the circuit will build up in volume unless there is an aid in the way of evaporation or deliberate discard.

H. Y. EAGLE.—There is no discard in the system.

C. W. EICHRODT.—The water used in washing ore is equivalent to the tailings' moisture?

H. Y. EAGLE.—Absolutely.

B. H. STROM, New York, N. Y.—I have had some experience with the effect of chlorine in the electrolysis of zinc sulfate solution, using anodes of soft lead. Above one-tenth gram per liter chlorine the corrosive action became noticeable; with one-half gram per liter the anodes became perforated in a few days. Many other factors influence anode corrosion in zinc electrolysis, and chlorine does not tell the whole story. I know of one case where the solution generally runs as high as 0.08 grams per liter chlorine. The anodes last for years; in fact, I have been informed that they could easily be made to last for eight years, if other conditions did not make a change advisable.

Coming back to the leaching plant: I noticed a reference to a patented device used to prevent segregation and plugging of the Pachuca tanks. No description is given, and I would like to have a little more information on the subject if possible.

H. Y. EAGLE.—I do not know whether I can do it without a sketch, but I will try. When the material is lifted from the bottom of the agitator to the surface, naturally the coarse drops out before the solution gets over to the outflow of the tank, and the

result is that a comparatively small amount of coarse will go out from the ordinary type of agitator, either a Dorr or Pachuca.

We found that out after digging the system out a number of times, and came to the conclusion that our 35-mesh material simply could not be handled in a Dorr agitator with $2\frac{1}{2}$ to 1 density. So we tried out various schemes, and finally came to one, which in substance is this: We take all of the discharge of the central air-lift, put it into a launder, take that launder directly to the outer part of the tank. Besides the outlet port, there is at that point a very much larger port, which permits the solution to run back into the tank. The size of the exit port is such that it will discharge the amount of feed to the tank with a comparatively small head, and the port is equipped with a constricting gate, which provides for any possible and necessary adjustment. When the tank is started, and there is the condition of a given amount of inflowing pulp and a certain rate of circulation of the central air-lift, you adjust the constricting gate on the exit port from the tank until the level in the tank will maintain itself just about at the point that will smother the weir of the discharge from the collecting launder back into the tank. When this is done, the tank will automatically maintain its level with comparatively little attention, the reason for it being that if more solution goes out of the tank from the exit port than comes in, the solution level in the agitator will fall. As soon as it falls it takes the smother off the weir. That automatically increases the discharge of the weir and brings back the level again. If less goes out of the tank than is coming in, the solution level in the tank rises, raises the head on the outlet port and automatically increases the discharge from the exit port. Since all the coarse and fine material in the internal circulation is given an equal chance to leave the tank, the amounts of these discharged are in the same proportion as they exist in the feed.

The device actually works and we are handling 1600 tons daily without trouble. Often when there is a breakage of copper screens, we get considerable oversize in the bins, and even up to as high as $\frac{1}{2}$ in. it is handled successfully.

E. L. JORGENSEN.—How are the extractions in the $\frac{1}{2}$-in. material?

H. Y. EAGLE.—Not good. The extractions we get under the average grinding conditions are given in the paper, and naturally in the coarse material the extractions run downward.

E. L. JORGENSEN.—It would improve if you gave it time?

H. Y. EAGLE.—Yes. On the other hand, I would not recommend anybody to try to agitate stuff that is ground through $\frac{1}{2}$ inch.

E. L. JORGENSEN.—In Chile, we leached coarser material by percolation for an extended period of time. Have you any conclusions for Katanga ore on this point?

H. Y. EAGLE.—I hope you understand that we are not presenting this process as an argument that agitation is better than percolation. We would have been pleased to leach on a basis of percolation if we could have done so, but Katanga ores are not amenable to percolation. Our extraction and recovery on 6.5 per cent ore looks like very poor work, but it is the best we can do under the existing conditions.

E. L. JORGENSEN.—What characteristic of Katanga ore makes it unsuitable for percolation?

H. Y. EAGLE.—In the first place, the mineral in the Katanga ores is largely malachite, which is a carbonate. You know what happens when you put acid on a carbonate. The upper percolation will not work because the tremendous gas evolution takes every bit of the fines out of the tank, and the downward percolation will not work for the same reason. But even were it not for that, the Katanga ores are largely malachite.

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in shales and sandstones, and the amount of colloidal clayey material is great enough
so that the solution will not percolate through it on a downward basis.

MEMBER.—I should like to ask the gentleman from the Chile Copper Co. about the
use of antimonial lead anodes containing a high percentage of arsenic, say 2 per cent
arsenic, or over.

C. W. EICHRODT.—While I was there we did not use antimonial lead anodes
except in laboratory experiments. I do not believe that we ever tried arsenic in
the anodes.

MEMBER.—I am not asking the question from the standpoint of an electrolytic
copper man but rather from the standpoint of the producer of antimonial lead. I
had heard that certain plants in South America were using antimonial lead high
in arsenic.

F. R. PYNE.—I have never seen it used in copper refining, but I would like to hear
some results from it if anybody has tried it out.

C. R. HAYWARD, [Cambridge, Mass.—I know nothing definite regarding high-
arsenic anodes, but in the early days of experimentation on the Chuquicamata process
I examined a good many anodes, lead and otherwise, and it was rather interesting
to note that those that were cast in a flat mold corroded only slightly on the side
that was chilled; that is, the side that came in contact with the mold, whereas the
upper side went to pieces rapidly.

A. B. YOUNG.—The plant referred to is the Potrerillos plant of the Andes Copper
Co. The anodes were high in arsenic, 2 per cent or better. However, it is my under-
standing that the arsenic did not prove to be of any particular benefit.

R. C. DALZELL, Trenton, N. J.—I have always found pH control very helpful in
an iron precipitation such as takes place in the purification section described in this
paper. Neutrality covers a broad field, and I should like to know the approximate
pH of the neutral thickener solution referred to on p. 623, third line from the bottom.
I notice that the solution from purification contains 2 grams per liter of iron. I
assume that this is ferrous iron, and that chemical oxidation of it is more expensive
than would be justified. Air oxidation might be applicable here. A method that
appeals to me because of its simplicity and cheapness consists in circulating the solu-
tion downward through a sort of chimney, in which are placed criss-crossed baffles.
These break up the solution, presenting a very large surface for oxidation by the air
drawn up through the chimney. The hot solution creates a natural draft in the
chimney. The only operating expenses are power for circulating the solution and
steam for heating the solution. The operation is very effective and has been in use
for some years by a large European refinery.

adhesion of the product to the cathode rod. It was shown that the experimentally obtained degree of coverage of the compact zinc composition with zirconium (α = 0.79) is close to the coefficient (α' = 0.74) corresponding to maximum close packing. The full realisation of the possibilities of pulsed electrodeposition for the purposes of maximum saturation of zinc with zirconium was explained by the small effect of disturbances due to the Archimedes force on account of the similarity in the densities of the intermetallic compound $ZrZn_2$ (6.64 g/cm³) and of the saturated metallic solution (6.69 g/cm³).

Reaction of molten Zn-La and Zn-Al-La alloys with molten salt mixtures containing lead chloride

B D Vasin, A A Kayurov, I F Nichkov and S P Raspopin (Urals Polytechnical Institute, Department of the Metallurgy of Rare Metals)

Summary

The exchange process between Zn-La and Zn-Al-La alloys and a molten equimolar mixture of sodium and potassium chlorides containing lead ions as oxidising agent was used to extract lanthanum from zinc-base alloys. The experimental data (table) show the degree of extraction of lanthanum from the alloys into the molten salt mixtures.

Initial alloy	Initial content of lanthanum in alloy wt.%	Length of contact between phases, min	Final lanthanum content of alloy, wt.%	Degree of extraction of lanthanum %	Remarks
Zn-La	0.236	10	0.037	84.5	
	0.550	20	0.016	97.1	
	0.435	40	0.016	96.3	
	1.000	150	0.025	97.5	
	1.000	300	0.028	97.2	
	0.483	315	0.010	98.2	5 wt.% NaF added to electrolyte
Zn-Al-La	0.472	10	0.035	92.6	
	0.630	40	0.010	98.4	
	0.520	120	0.510	1.9	5 wt.% NaF added to electrolyte

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Deposition of metals of the platinum group from acidic sulphate solutions with elemental sulphur in an autoclave

V Sh Barkan and T N Greiver (Leningrad Mining Institute, Department of Light and Rare Metals)

The separation of platinum metals and of iridium, in particular, from acidic sulphate solutions is only possible with high parameters. Thiourea, hydrogen, hydrogen sulphide, etc. can be used as reagents[1]. It is well known that elemental sulphur precipitates copper at sufficiently high temperatures[2][3]. The present work gives data from an investigation into the possibility of using sulphur for the precipitation of platinum metals with elemental sulphur. On the basis of a thermodynamic analysis we showed (fig.1) that whereas the

fig.1 The dependence of the change in isobaric potential on temperature for the reaction
$Me_2(SO_4)_3 + 6S \rightarrow Me_2S_3 + 6SO_2$ or $MeSO_4 + 2S \rightarrow MeS + 2SO_2$.

precipitation of the sulphides with sulphur is extremely probable for platinum and palladium even at normal temperature (and its probability increases with increase in temperature) for the other platinum metals it becomes thermodynamically probable only at temperatures above 200°C. An experimental check was made on solutions from the sulphatisation of nickel slimes, containing 200-220 g/l sulphuric acid, 50 g/l total copper and nickel, 120 mg/l rhodium, 40 mg/l ruthenium, 20 mg/l iridium, 140 mg/l tellurium, and 100 mg/l

selenium; palladium, platinum, gold, and silver were absent. The experiments were carried out in rotating autoclaves with a volume of 1 l. The following parameters were varied: The consumption of sulphur; temperature; the length of the experiment. As seen from the data shown in fig.2, platinum
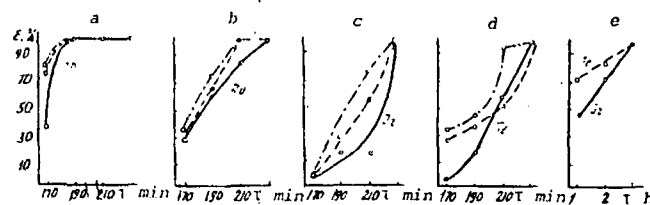
Fig.2 The extraction of evious metals from solution.
Composition of solution: 200-220g/l H_2SO_4,
50-60g/l total heavy metals; 120 rH, 40 Ru,
20 Ir, 150mg/l Te. Process time 3h (for figs.
a-d). The sulphur consumption rate for experie was 24g/l.

metals begin to precipitate at a lower temperature than follows from thermodynamic calculations for the precipitation of the individual sulphides. The most difficult to extract are tellurium and iridium (complete precipitation is only achieved at 230°C), and tellurium must be completely precipitated for full precipitation of the iridium. Variation in the sulphur consumption rate in the range of 5-30 g/l has an effect on the rate of the process but not on the the final result; with a sufficiently long holding time a high degree of separation of all the platinum metals is achieved even with

the smallest sulphur consumption rate. The metals are separated from the solution in the following order: Rhodium, ruthenium, tellurium, iridium. Excess sulphur is consumed in the precipitation of copper and is therefore undesirable. The concentrates obtained contained up to 4% of the platinum metals in the form of sulphides and ~2-3% of selenium and tellurium, and the remainder was copper sulphide. By calcination followed by leaching with dilute sulphuric acid it is possible to obtain concentrates containing about 40% of the platinum metals.

References

1) S I Ginzburg et alia: Analytical chemistry of platinum metals. Nauka, Moscow 1972.
2) I Yu Leshch et alia: Autoclave method for purification of solutions from copper by means of elemental sulphur. Tr. Inta Giproñikel', Voprosy Tekhnologii No.38, 1968, 126-139.
3) Ya M Shneerson et alia: Method for purification of acid or neutral solutions containing nickel and cobalt from copper. Author's Certificate No.178992, 18.05.64, Byull. Izobr., No.4

UDC 661.183.12:546.161

Sorption of the ions of some group III elements from ammonium fluoride solutions with granulated iron hydroxide

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Summary

Experimental data on the sorption of boron, aluminium, gallium, indium, and thallium (and of trivalent chromium and iron, for comparison) from MeF_3 (H_3BO_3)-NH_4F-H_2O solutions with granulated iron hydroxide are examined and discussed. The sorption was investigated under dynamic conditions in aqueous 0.01N solutions of boric acid and metal fluorides with various concentrations of ammonium fluoride. As a rule, the sorbability decreases with increase in the ammonium fluoride concentration in the initial solution, and the main reason for this is the competing sorption of the fluoride ions, which possesses a high affinity towards the OH groups of the hydroxide. For indium the relationship is more complex, indicating the existence of chemical interaction between the sorbed indium ions and the iron hydroxide. As shown in the discussion, the high affinity of the trivalent elements towards the OH group promotes their effective sorption by iron hydroxide by a co-polymerisation mechanism. Gallium, indium, aluminium, chromium (III), and iron ions are not eluted by water or by ammonium fluoride solutions up to a concentration of 0.5 M NH_4F. For the amphoteric gallium it was found that even dilute solutions of sodium hydroxide desorb the metal effectively and fully from the iron hydroxide. An acetate buffer solution can be used for indium. Thallium sorbed from neutral and acidic solutions can be eluted from the hydroxide even with water. Thus, the data obtained show that it is possible to extract the elements quantitatively from ammonium fluoride solutions by means of granulated iron hydroxide. The differences in the behaviour of the elements in the sorption and desorption processes can be used for the solution of specific problems on the separation and purification of fluorides from impurities.

UDC 669.1

Electrolytic purification of nitrate effluents from chromium ions

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Summary

The results are given from investigations into the purification of nitric acid pickling solutions from chromium by electrolysis with a soluble iron anode. The electrochemical method involved anodic dissolution of the iron electrode, reduction of hexavalent chromium to trivalent chromium, and separation of the latter as a precipitate. The initial solution contained 60-70 g/l of chromium as potassium bichromate and concentrated nitric acid. Potassium iodide, sodium chloride, sodium fluoride, ammonium fluoride, and calcium chloride were used as depolarisers to prevent the passivation of the iron electrode, and sodium chloride and potassium iodide were found to be the most effective.

The degree of purification of the solution from chromium depends on the pH value, and a concentrated solution of ammonia was used for neutralisation. The best results were obtained at pH 2.5-4.0, where the residual chromium content in the purified solution varied between 0.22 and 0.11 g/l. The ammonia consumption rate amounted to 1.11 for 1 l of solution. It is recommended that the electrolytic separation of the chromium can be carried out effectively at a current density of 1000 A/m², an electrolysis time of 1.5h, 1:8 dilution of the initial solution, at pH2.5-4.0, and with a sodium chloride concentration of 40 g/l. A technological scheme for purification of the solutions is proposed.

UDC 621.745.552/557.001.57

Optimisation of the reductive cyclone smelting of carbonaceous and clay materials

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Summary

A mathematical model of the reductive cyclone smelting of carbonaceous and clay materials in the form of multiple regression equations characterising the relations between the quality indices of the charge, the technological parameters, and the smelting products was used for optimisation of the process. By the method of random search specific values were obtained for the amount of flux CaO in the charge, the productivity of the plan in respect of the charge, the amount of air for combustion, and the temperature. By means of these values it was possible to reduce the germanium content of a slag by half and to increase its concentration in the sublimates by 30-32%.

low that side processes (e.g. desiliconising) play a perceptible role.

Conclusions

1. The effect of sodium salts (sodium carbonate, sodium sulphate, sodium fluoride) on the leaching of hydrargillite bauxite of the Turgai deposit was investigated.

2. The positive role of sodium carbonate and the negative role of sodium sulphate and sodium fluoride on the extraction of aluminium oxide from bauxite into solution, were demonstrated.

d. The kinetics of the leaching of hydrargillite may be described by Drozdov's equation for self-retarding reactions.

References

1) S I Beneslavskii: Mineralogy of bauxites: Gosgeoltekhizdat, Moscow 1963.
2) F I Tsymbal: Tr. VAMI, Glavalyuminii 1945, 28, 64.
3) Ya I Mikhailenko: Course of general and inorganic chemistry; Moscow 1966.
4) N S Mal'ts and L F Verbov: Tsvetnye Metally 1971, 5, 35.

Decomposition of mixed zincate-aluminate solutions

N I Zabolotnov, V V Grachev, V K Kuznetsova, T V Bogacheva and N G Vinogradov (Urals Polytechnical Institute - Urals Branch, All-Union Aluminium and Magnesium Institute)

In the earlier work[1] it was established that supersaturated alkaline zincate solutions possess the ability to decompose comparatively rapidly when mixed with a seed of zinc oxide. Here, if the concentration of Na_2O amounts to 90g/l or more zinc oxide separates from the solutions, and with a concentration of Na_2O below 90g/l zinc hydroxide separates. At low concentrations the solutions decompose at a high rate without a seed. The length of the decomposition of alkaline zincate solutions containing about 100g/l Na_2O amounts to 3-4h. After stirring for 4h the degree of decomposition of the solutions amounts to 50-55%, and it remains practically unchanged with increase in the length of stirring. Since the solubility of zinc oxide in alkaline solutions varies little with variation of temperature, it can be considered with some fraction of error that the degree of decomposition of the solutions with not change on heating. However, the decomposition rate increases with increase in temperature. The decomposition of alkaline zincate solutions is greatly retarded by silica impurity.

It is of great interest to investigate the decomposition of mixed zincate-aluminate solutions. For the technology of alumina production it is important to know the behaviour of the zinc impurity during the decomposition of aluminate solutions. It was established that aluminium hydroxide contaminated with zinc oxide separates during the decomposition of aluminate solutions containing zinc as impurity. The decomposition rate of the aluminate solutions decreases with increase in the zinc oxide content. Here, more coarse-grained aluminium hydroxide is obtained[2].

We set out to investigate the decomposition of mixed zincate-aluminate solutions from the standpoint of determining the possibility of combining the production of zinc oxide with the production of alumina. The hydrometallurgical method for the production of zinc oxide from materials containing it, i.e., the concentrates of oxidised zinc ores and the slimes from the wet gas purification of blast furnaces, is well known[3]. The method consists in the leaching of the zinc-containing material with strong alkali followed by dilution and separation of the undissolved parts of the slime. The zincate solution is decomposed by mixing with a seed of zinc oxide. The mother solution separated from the obtained zinc oxide is evaporated and passed on for leaching the zinc-containing material. This method is distinguished by its great simplicity and by the low cost of the obtained zinc oxide.

It is also possible to use recycled alkaline aluminate solutions from alumina production for the extraction of zinc oxide. In this case mixed zincate-aluminate solutions will be obtained. The higher decomposition rate of the zincate solutions compared with aluminate solutions gives hope for the production of pure zinc oxide from the mixed solution. In the first series of experiments we studied the leaching of zinc oxide with aluminate solutions having various concen-

trations. The aluminate solutions were obtained by dissolving aluminium hydroxide of analytical grade in alkaline solutions. The prepared solutions had one and the same caustic ratio, equal to 3.4, but different concentrations: 50, 100, 150, 200, 250, 275, 300, and 325g/l Na_2O. With these solutions we leached zinc oxide, which was used in a small excess calculated on its solubility in alkaline solutions. The leaching was carried out in glass flasks, which were placed in an air agitation-type thermostat at 90-105°C for 1h. During leaching we obtained zincate-aluminate solutions containing various amounts of zinc oxide (tables 1 and 2).

Table 1: The results from the leaching of ZnO in synthetic recycled aluminate solution. $a_{caustic} = 3.4$; $t = 95°C$; $\tau_{leach} = 1h$

Na_2O_{in}, g/l	Al_2O_{3in}, g/l	Na_2O_{fin}, g/l	Al_2O_{3fin}, g/l	ZnO, g/l	a_{fin}	a_{in}
51.21	26.72	51.36	24.96	4.88	3.2	3.4
101.85	49.98	100.59	48.96	8.13	3.4	3.4
155.68	76.54	154.87	75.99	16.52	3.3	3.4
197.04	103.02	199.93	99.96	34.17	3.2	3.3
245.6	125.46	255.08	127.5	50.45	3.2	3.3
279.40	138.72	275.96	137.5	61.02	3.3	3.3
296.85	148.02	296.16	148.02	73.23	3.3	3.3
323.51	159.12	325.14	159.12	78.92	3.3	3.4

Table 2: The results from leaching of ZnO with synthetic recycled aluminate solution. $a_{caustic} = 3.4$, $t = 105°C$, $\tau_{leach} = 1h$

Na_2O_{in}, g/l	Al_2O_{3in}, g/l	Na_2O_{fin}, g/l	Al_2O_{3fin}, g/l	ZnO, g/l	a_{in}	a_{fin}
39.98	18.36	39.33	18.36	0.8	2.95	3.5
79.28	38.25	79.08	37.71	3.56	3.4	3.4
116.84	60.18	120.22	59.67	13.12	3.2	3.3
164.54	79.56	161.89	81.09	25.55	3.4	3.3
204.47	97.92	204.60	100.77	35.8	3.4	3.34
213.30	100.08	223.8	110.36	43.12	3.31	3.34
232.0	116.28	246.35	133.42	48.00	3.28	3.36
256.74	124.44	267.35	131.07	56.14	3.4	3.36

From the data in tables 1 and 2 and in the figure it follows that the extraction of zinc oxide into aluminate solutions increases greatly with increase in the concentration of Na_2O. With Na_2O concentrations of 300-325g/l it is possible to obtain zincate-aluminate solutions with a high content of zinc oxide (73-79 g). In the range of 90-105°C the temperature has practically no effect on the extraction of zinc oxide into aluminate solutions. The curves for the extraction of zinc oxide are curved towards the abscissa axis. This makes it possible to obtain supersaturated solutions with respect to zinc oxide by dilution of strong zincate-aluminate solutions. The strong zincate-aluminate solutions obtained during the leaching of zinc oxide were diluted with distilled water to 100, 150, 200, and 250g/l Na_2O and were then analysed for zinc oxide content. A seed of zinc oxide

analytical grade was added to the diluted solutions. The seeding ratios (the ratio of the weight of ZnO in the seed to the weight of ZnO in the solution) were 0, 0.5, and 1.0. The solutions were agitated with the seed in glass flasks, which were placed in a thermostat with an agitating device, at 90°C for 3h. Samples of the pulp for analysis were taken each hour.
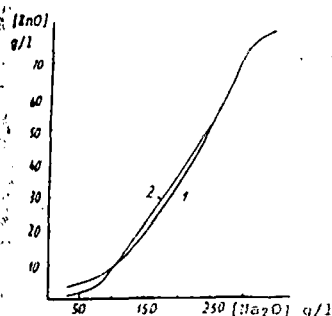
The concentration of zinc oxide in an alkaline aluminate solution with a caustic ratio of 3.4 with the length of the process 1h at 95 (1) and 105 (2) °C.

The indicated agitation conditions were selected on the following considerations. As is known, in alumina production the recycled aluminate solutions are obtained by evaporation of the mother solutions. Under the temperature conditions for the decomposition of the aluminate solutions (initial temperature 60-65°C and final temperature 45-50°C) the mother solutions are weakly supersaturated with respect to aluminium hydroxide (hydrargillite). It is not therefore expedient to realise the decomposition of the mixed zincate-aluminate solutions under the temperature conditions of decomposition in alumina production, since aluminium hydroxide may be precipitated in addition to zinc oxide. When heated to 90-100°C the dilute zincate-aluminate solutions become unsaturated with respect to aluminium hydroxide (in this case boehmite). Aluminium hydroxide will not therefore be released during their decomposition. The solutions remain supersaturated with respect to zinc oxide.

Table 3: The degree of decomposition of zincate-aluminate solutions at various concentrations with an agitation time of 3h. t = 90°C, τ = 3h

ZnO_{in} g/l	ZnO_{fin} g/l	Al_2O_3 g/l	Na_2O g/l	Percentage decomposition of solution (in ZnO)	α_{fin}
29.70	15.46	47.94	100.45	47.9	3.45
40.43	24.41	69.56	146.94	39.7	3.47
55.33	42.31	92.82	171.96	23.5	3.05
69.49	66.72	121.38	260.13	4.0	3.53

The results from the experiments on the decomposition of zincate-aluminate solutions at various concentrations are given in table 3. The degree of decomposition of the solutions with respect to zinc oxide increases with dilution. In the investigated range of concentrations the highest percentage decomposition of the solution was obtained after agitation with a Na_2O concentration of 100g/l for 3h (47.9%). With decrease in the length of agitation the degree of decomposition of the solutions was somewhat lower. The results from experiments on the decomposition of a zincate-aluminate solution containing 100g/l Na_2O when agitated with a seed (seeding ratio 1.0) for 2 and 4h at 90°C are given in table 4. From table 4 it is seen that during the agitation of a zincate-aluminate solution with a seed for 2h the zinc oxide content decreases, whereas the aluminium oxide concentration remains unchanged. The degree of decomposition of the solution with respect to zinc oxide amounts to 54.4%. After agitation for 4h the degree of de-

composition with respect to zinc oxide increases very little (by 1.6%). Here, to judge from analysis of the solution, aluminium hydroxide begins to separate.

Table 4: The results from experiments on decomposition of zincate-aluminate solutions containing 100 g/l Na_2O

Solution	Composition of solution					Percentage decomposition of solution (in ZnO)
	Na_2 g/l	Al_2O_3 g/l	ZnO g/l	α(Al)	α(Zn)	
Initial	100.0	36.3	24.2	4.47	5.33	0
After agitation with ZnO for 2h	101.0	37.0	11.2	4.47	11.70	54.4
After agitation with ZnO for 4h	102.0	36.3	10.7	4.60	12.12	56.0

After separation from the mother solution and thorough washing to a negative reaction against phenolphthalein, the obtained precipitates were submitted to spectral analysis, in order to determine the contents of aluminium and other impurities. For spectral emission analysis we used an ISP-28 quartz spectrograph (slit width 0.015mm, excitation source D-2 generator). The sample was burnt between carbon electrodes. The powdered sample was placed in a channel in the lower electrode (depth 4mm, diameter 4mm), the second carbon electrode was sharpened to a truncated cone, and the interelectrode gap was 2mm. In a sample of zinc oxide isolated from a solution containing 100g/l Na_2O, 36.3g/l Al_2O_3, and 24.2g/l ZnO after 2h the lines for aluminium (3082.15 Å, 3092.71 Å), tin (3034.12 Å), and silicon (2516.11 Å) were found in addition to the lines of zinc. From these lines in the spectrum it is possible to determine the content of the elements semiquantitatively: 0.001-0.003%Al, 0.0001%Sn, 0.001Si. In zinc oxide precipitated from the same solution, after 4h the aluminium line (2652.49 Å, which may indicate a content of up to 0.03%) was detected in addition to the above-mentioned lines of zinc and small tin and silicon impurities.

The aluminium content of the zinc oxide was also determined by the photometric method with luminol[4]. We found 0.01%Al in the first sample and 0.1% in the second. Thus, the aluminium content of the zinc oxide increases a little with increase in the length of agitation of the solution with a seed from 2h to 4h. It was also established that the rate of the decomposition process decreases sharply with decrease in the temperature of the solutions to 70-80°C, as a result of which the degree of decomposition of the solutions with agitation for 2h and 4h decreases.

Thus, it is possible to select conditions for the decomposition of mixed zincate-aluminate solutions with which only zinc oxide is separated from them, whereas the aluminium hydroxide remains in solution. Such conditions are as follows: Optimum concentration of solution (about 100g/l Na_2O), and the presence of a zinc oxide seed. In order to obtain the most pure zinc oxide the length of agitation of the solution with the seed should amount to 2h. The results make it possible to conclude that alumina production by the Bayer process can be combined with zinc oxide production by the above-described hydro-metallurgical method. It is recommended that part of the recycled solutions from alumina production be used for the leaching of zinc-containing materials.

References

1) S I Kuznetsov et alia: Izv. Vuz Tsvetnaya Metallurgiya 1975, (1).
2) L P Ni and L G Romanov: Physical chemistry of hydroalkaline methods for alumina production. Izd. Akad. Nauk KazSSR Alma-Ata 1975, p.265.
3) S I Kuznetsov et alia: Author's Certificate No. 467124.
4) Analytical chemistry of elements. Aluminium. Nauka, Moscow 1971, p.216.

DISTRIBUTION OF OSMIUM IN THE SULFURIC ACID STAGE OF COPPER-NICKEL PRODUCTION AND OPPORTUNITIES FOR ITS EXTRACTION

UDC 669.233

V. Sh. Barkan, E. V. Popov, V. M. Kosover, and M. D. Ostrobrod

The distribution of osmium among the products of the sulfuric acid stage in copper production from copper sulfide ores was studied in [1]. Osmium has been detected in both scrubber acid and in sulfuric acid slimes.

When copper-nickel sulfide ores are processed, osmium is driven off mainly during the fluidized-bed roasting of nickel concentrate from Bessemer matte flotation and to a lesser extent during converting to produce Bessemer matte [2].

The distribution of osmium in the sulfuric acid stage of copper-nickel production was studied in the present work.

The sulfuric acid shop operates a standard contact scheme (Fig. 1) and includes a scrubber section for special purification of gases.

The sulfuric acid shop was investigated by sampling all the liquid and solid products, then analyzing them for osmium. All the solid products were washed prior to analysis in water at 80°C for 2 hr to remove sulfuric acid and water-soluble sulfates; under these circumstances, no more than 1-3% Os went into
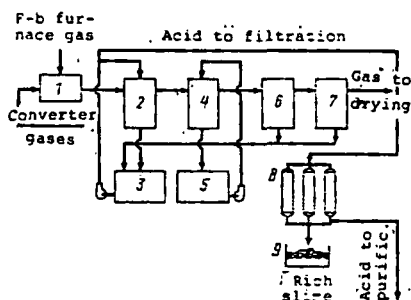
Fig. 1. Sulfuric acid shop gas-cleaning scheme:
1 - mixing chamber; 2 - scrubber tower I; 3 - scrubber tower I acid collector; 4 - scrubber tower II; 5 - scrubber tower II acid collector; 6, 7 - two-stage electrostatic precipitator; 8 - filter columns; 9 - Nutsch filter.

Behavior of Osmium in Production of Selenide, Sulfoselenide, and Selenosulfate Solution

Leaching method	Os distribution, %		Predominant forms of selenium in solution
	residue	solution	
With alkali and aluminum powder	80,0	20,0	Unsaturated chalcogenides: mono- and diselenides
	80,0	20,0	
	99,8	0,2	Saturated chalcogenides: sodium tetraselenides
	99,1	0,9	
	95,5	4,5	
	99,6	0,4	
With sodium sulfide	71,0	29,0	Saturated polysulfides and sulfoselenides
	70,0	30,0	
	99,8	0,2	Saturated polysulfides and sulfoselenides
With sodium sulfite	100,0	0	Sodium selenosulfate

solution. The analysis results showed that osmium was present in all the sulfuric acid shop products including monohydrate, the finished product. This indicates that the sulfuric acid shop scrubber section does not ensure complete extraction of osmium from the gases. The highest osmium concentration occurs in slimes washed out of the mixing chamber (0.05-0.12%) and in dusts from the gas conduits before the mixing chamber (0.1-0.2%); osmium was also detected in selenium slimes from the sulfuric acid shop scrubber section (0.02-0.07%). It is a striking fact that these products are extremely rich in selenium, and contain 20-80% Se after repulping with water. A considerable osmium content was found in the sulfuric acid shop solutions (0.3-9 mg/liter).

The following percentages show the Os distribution among the sulfuric acid shop products: extraction into scrubber
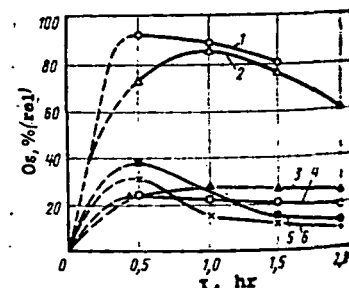
Fig. 2. Effect of H_2SO_4 concentration and air blowing time upon Os absorption in absorber I (t = 10-15°C, amount of Os driven off 2 mg; V_{air} = 1.3 liters/min; V_{abs} = 50 ml). Percentage concentration of H_2SO_4 in absorber:
1 - 0; 2 - 20; 3 - 40; 4 - 60; 5 - 80; 6 - 98.

acid comes to about 40; into slimes it is about 20, while into production acid, it is ∿ 40. Laboratory experiments in OsO_4 distillation with consecutive absorption in 3 diffusers were conducted to study the reasons for incomplete trapping of Os by scrubber sulfuric acid solutions. The first two units were filled with sulfuric acid solution, and the 3rd contained 10% caustic soda solution for final trapping of Os. The absorbers were thermostatically controlled. The behavior of Os was monitored by reference to the radioactive isotope [191]Os, using a PS-02-08 scaler unit with an NaI crystal and an FEU-19M photomultiplier.

The experimental results (Fig. 2) indicate that sulfuric acid (300 g/liter) saturated with sulfur dioxide is not effective enough as an absorbing agent for Os. The higher the H_2SO_4 concentration and the temperature, the greater the breakthrough, and passing air through the absorbers is accompanied by volatilization of part of the Os already absorbed. Accordingly, the lower the Os content of the initial gases the worse the Os absorption must be. Absorption of Os from rich gases from roasting nickel slimes, using a system of five diffusers filled with water, enabled the authors of [3] to record complete absorption.

The introduction of reducing agents and complexing additions ($SnCl_2$, thiourea) used in analytical practice increases Os absorption. Since the methods of extracting Os from sulfuric acid solutions are well known [4], we have studied ways of extracting Os from selenium slimes. Hydrometallurgical selenide, sulfide, and sulfite methods [5] are the most effective for selenium extraction from rich sulfuric acid production slimes. With respect to the effect of selenium forms in chalcogenide solutions (the presence or absence of forms unsaturated with selenium and sulfur) upon the solubility of silver, gold, and copper established by Greiver and Zaitseva [6], the effect of this factor upon Os solubility was studied in this work.

The theoretically necessary reagent consumption was adopted in the first and second case to produce saturated forms; excess of reagents was added to produce unsaturated forms. Processing of slimes and dusts by the selenide method involved dissolution of selenium in an alkaline solution (50-60 g/liter NaOH) with formation of sodium selenide in the presence of a reducing agent (aluminum powder), filtration, and aeration of the produced solution, which is accompanied by precipitation of crystalline selenium sulfide. In processing slimes and dusts by the sulfide method, these were leached with sodium sulfide solutions. The selenium was also brought out of solution by aeration. In the third method, the initial products were leached with sodium sulfite solution (200 g/liter, 100°C, τ = 4 hr). After filtration, the selenium was separated out by acidifying the solution with sulfuric acid.

The test results (see Table) show that most of the Os concentrates in the insoluble residue, no matter what slime processing method is used. It was noted when processing Se products by the selenide and sulfide methods that a certain proportion of the Os went into solution, the extent of the transition being dependent upon the form of Se in the solution. Os passage into solution is least in Se-saturated tetraselenide and sulfoselenide solutions. Thus, the leaching process must involve production of saturated forms of selenides and sulfoselenides, i.e., there must be no excess of reagents, to avoid Os losses with the solution.

Losses of osmium with the solutions do not occur when slimes and dusts are treated with sodium sulfite solution.

Pilot-plant checking of selenium-bearing sulfuric acid slime and dust processing by the sulfite method entirely confirmed the results of the laboratory investigations.

REFERENCES

1. V.D. Nagibin, S. K. Kalinin, L. I. Mekler, et al., Vestnik Akad. Nauk Kazakh. SSR, 1974, No. 7, 53-55.   1974, No. 7, 53-55.
2. T. N. Greiver, V. M. Kosover, V. Sh. Barkan, and N. V. Popkov, Tsvetnye Metally, 1976, No. 3, 14-16.
3. A. S. Ladygo, V. F. Borbat, A. M. Orlov, and N. M. Sinitsyn, in: Analysis and Technology of Precious Metals, Moscow, Metallurgiya, 1971, pp. 399-404.
4. R. K. Alekseeva and T. G. Khateeva, Tsvetnye Metally, 1972, No. 12, 61-62.
5. Principles of Metallurgy, edited by N. S. Greiver, Vol. IV (Chapter "Selenium and Tellurium"), Moscow, Metallurgiya, 1967, pp. 493-536.
6. T. N. Greiver and I. G. Saitseva, Zh. Prikl. Khim., 1971, V. 446, No. 8, pp. 1689-1699.

EFFLUENT PROTECTION

DEVELOPING A PYROLUSITE TECHNOLOGY FOR ARSENIC REMOVAL FROM SULFURIC-ACID PRODUCTION EFFLUENTS

UNIVERSITY RESEARCH INSTITUTE EARTH SCIENCE LAB.

UDC 628.543:661.25

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Removal of arsenic from industrial effluents in non-ferrous metallurgy and in the copper industry in particular is a vital task for the national economy. Coprecipitation based upon formation of relatively insoluble polyvalent metal arsenates and arsenites is one method of removing arsenic from effluents. The solubility of metal arsenates is within the permitted public health norms on conversion to arsenic, whereas the arsenites of these metals have much greater solubility and also require burial in special concrete-lined trenches.

Arsenic is present in sulfuric-acid production effluents in trivalent form, which leads to the need for preliminary oxidation to the pentavalent state. Use of pyrolusite, a natural manganese dioxide, of all the various oxidizing agents for these purposes seems to be the most desireable for the following reasons.

In oxidizing trivalent arsenic, the tetravalent manganese in the dioxide is reduced to the bivalent state and will combine with the arsenate ion when the solution is neutralized to form manganese arsenate $Mn_3(AsO_4)_2$ with a solubility product of 1.9×10^{-29}

2. Unreacted pyrolusite is a natural sorbent, and will sorb additional arsenic.

3. Using pyrolusite as an oxidizing and precipitating agent from arsenic will greatly simplify the apparatus layout and make it possible to limit it to single-stage precipitation.

This work gives the results of laboratory studies of arsenic oxidation and precipitation with pyrolusite[1] and of pilot-plant studies on the technology.

Pyrolusite was added to beakers containing 0.5 liters of effluent with continuous mixing, and the arsenic was oxidized. The effect of the following factors was studied in order to find the optimum process parameters: pyrolusite consumption, solution acidity and temperature, and oxidation time. Grade III pyrolusite (peroxide) from the Chiatura deposit in the Georgian SSR was used in the experiments.

It is apparent from Fig. 1 that increasing the MnO_2 consumption improves the arsenic oxidation process appreciably, and with a four- to six-fold excess the arsenic is practically completely oxidized in a 3 hour period.

The kinetics of the process of trivalent arsenic oxidation by pyrolusite in aqueous solutions can be satisfactorily described by a first-order reaction equation. Changes in the reaction-speed constant according to MnO_2 consumption (see Fig. 2) are exponential in nature, increasing the pyrolusite consumption above a sixfold excess
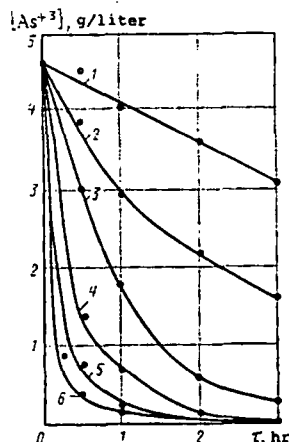
Fig. 1. Kinetic curves for As^{3+} oxidation by pyrolusite at various manganese dioxide consumption rates: 1 - theoretical consumption; 2 - twofold; 3 - threefold 4 - sixfold; 5 - eightfold; 6 - tenfold excess. Experimental conditions: Solution acidity - 34 g/1 H_2SO_4; $t = 25\pm1°C$
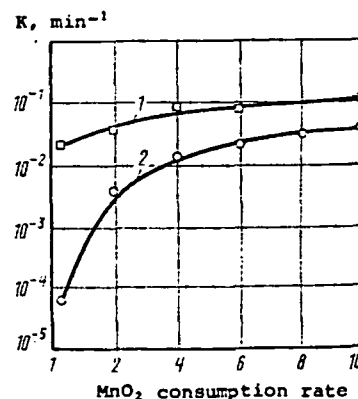
Fig. 2. Relationship of reaction-speed constant in As^{3+} oxidation by pyrolusite to MnO_2 consumption rates at the following temperatures, °C: 1 - 25±1; 2 - 70±10.

[1] M. E. Koshkarova participated in the work.

barely increases the rate of the oxidation reaction at all.

Oxidation speed increases when the temperature rises (see Fig. 2). Thus, at 70±10°C the oxidation reaction speed constant is fairly high, even with a two-fold excess of MnO_2 and provides at least 98% arsenic oxidation over a 3-hour period.

The optimum solution acidity was determined, to ensure minimum consumption of neutralizing reagent and the minimum yield of arsenical cake which has to be sent for burial. The optimum solution acidity to conform to these requirements was 30-40 g/lit H_2SO_4.

Thus, the laboratory investigations revealed the optimum conditions for arsenic oxidation by pyrolusite: a fourfold excess of MnO_2 as the pyrolusite consumption, solution acidity 30-40 g/liter H_2SO_4, t = 70-80°C, and τ = 3 hr.

Arsenic was precipitated as follows: following the operation of arsenic oxidation under optimum conditions the test solution, containing 4.32 g/liter As and with an acidity of 30-40 g/liter H_2SO_4, was neutralized to pH 8-9. The neutralizing agent used was milk of lime, the cheapest, most readily available, and convenient reagent. A fourfold excess of MnO_2 was adopted instead of a twofold excess, so that the solution should contain more bivalent manganese than was essential to the formation of manganese arsenate. In addition, the sulfur dioxide left in the effluent after degassing the solution will also participate in the oxidation-reduction process and will supply additional bivalent manganese to the solution.

The results of filtrate analysis showed that the solution arsenic content, following precipitation, did not exceed the maximum permitted concentration (0.05 mg/liter).

Control tests, using the radioactive indicator method, were conducted to reveal the mechanism of arsenic precipitation. An aqueous solution of sodium arsenate Na_3AsO_4, tagged with [74]As was used to monitor the behavior of arsenic in the effluents. In these experiments, the solution was neutralized after oxidation of the arsenic with milk of lime and with soda for comparison. In both cases, the activity of the filtrate after oxidation and precipitation of arsenic did not exceed the background activity. This indicates that the arsenic passes entirely into the precipitate formed as manganese arsenate.

The chemical composition of the cake (%) is 5-10 As, 10-12 S_{total}, 5-7 $S_{sulfate}$, 22.4-24.4 CaO, 25-27 Mn, 3.18-4.5 Fe, 1.0 (Zn+Cu); the rational composition (%) is: 20-30 $CaSO_4$, 15-30 $Mn_3(AsO_4)_2$, 5.7-8.6 $Fe(OH)_3$, and 24-30 $[MnO_2+Mn(OH)_2]$.

In by far the greater number of experiments, the water-soluble arsenic content of the cake produced did not exceed thousandths of one percent. This made it possible to propose burial of the arsenical cake in trenches with clay linings.

The results of the investigations suggest the following chemical mechanism for the process. Arsenic is present in sulfuric acid production effluent in the form of arsenous acid anions.

Initial waste soln. 4-10 g/l As; 30-40 g/l H_2SO_4.

Degassing (t = = 80°C; τ = 1 hr)

Pyrolusite (75% MnO_2) 4 g MnO_2 per g As

Oxidation (t = = 80°C; τ = 3 hr)

Milk of lime, 10%; 0.65 g CaO per g H_2SO_4

Neutralization and precipitation (pH=8-9; τ=30-40 min)

Filtration (0.4- -0.5 tons/$m^2 \cdot$hr)

Solution, 0.05 mg/l As^{+} Cake for burial (yield 15-18%, moisture 40%)
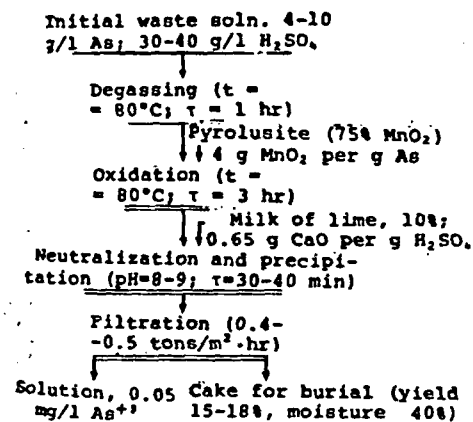
Fig. 3. Flowchart for neutralization of concentrated arsenical effluents using pyrolusite.

Results of Pilot-Plant Experiments on the Oxidation and Precipitation of Arsenic with Pyrolusite*

Initial soln.			Oxid. conditions			As content in filtrate after neutralization, mg/l
V, lit	[As] g/l	[H_2SO_4] g/l	MnO_2 consumption rate	t, °C	τ, hr	
60	2.74	31.4	4	80	3.0	0.02
60	8.5	80.0	4	70	2.5	0.06
60	12.37	42.9	4	80	2.45	Traces
350	3.17	32.0	4	75	3.0	»
670	3.55	23.1	4	70	3.0	0.05
670	12.37	42.9	4	80	3.0	0.05
670	4.4	49.1	4	80	2	0.035

*The solution was neutralized to a pH of 8-9, following oxidation of the arsenic. Water-soluble arsenic (As^{1+}) was not detected in the cake.

The following reaction takes place when arsenic is oxidized by pyrolusite in an acid medium:

$$H_3AsO_3+MnO_2+H_2SO_4=H_3AsO_4+MnSO_4+H_2O. \tag{1}$$
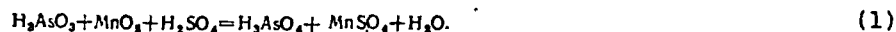
In addition, the reaction of tetravalent manganese reduction to the bivalent form will occur when SO_2 is present in the solution:

$$SO_2 + H_2O = H_2SO_3$$
$$\frac{H_2SO_3 + MnO_2 = MnSO_4 + H_2O}{SO_2 + MnO_2 = MnSO_4.} \tag{2}$$

The following reactions occur when the solution is neutralized with milk of lime:

$$3H_2SO_4 + 3MnSO_4 + 6Ca(OH)_2 = \downarrow CaSO_4 + 3Mn(OH)_2 + 6H_2O$$
$$\frac{3Mn(OH)_3 + 2H_3AsO_4 = \downarrow Mn_3(AsO_4)_2 + 6H_2O}{3H_2SO_4 + 6Ca(OH)_2 + 3MnSO_4 + 2H_3AsO_4 = \downarrow Mn_3(AsO_4)_2 + \downarrow CaSO_4 + 12H_2O.}$$

(3)

A flowchart for the thorough elimination of arsenic from acid effluents has been suggested on the basis of the investigation results (Fig. 3).

The volume of effluent for purification in the pilot-plant tests varied widely, from 60 to 600 liters. With respect to the fact that actual sulfuric acid production effluents are variable in their arsenic and sulfuric acid content, the effect of these factors upon the results of the scheme was checked. The test results (see Table) showed that variations in the solution arsenic content do not affect the purification process parameters. The unit consumption of pyrolusite (4 g MnO_2 per g of arsenic in the solution) remains constant whatever the arsenic content of the effluents.

The optimum sulfuric acid content was 30-40 g/liter, as in the laboratory investigations. Optimum characteristics, in terms of pyrolusite consumption, temperature, and oxidation time were confirmed.

Report of Investigations 8280

Design Requirements for Uranium Ion Exchange From Ammonium Bicarbonate Solutions in a Fluidized System

By D. E. Traut, I. L. Nichols, and D. C. Seidel

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TABLE

DESIGN REQUIREMENTS FOR URANIUM ION EXCHANGE FROM AMMONIUM BICARBONATE SOLUTIONS IN A FLUIDIZED SYSTEM

by

D. E. Traut,[1] I. L. Nichols,[2] and D. C. Seidel[3]

ABSTRACT

A fluidized countercurrent ion-exchange system was developed, operated, and evaluated by the U.S. Department of the Interior, Bureau of Mines. The system consisted of integrated multiple-compartment absorption and elution columns in which the solution flows were continuous except for short periods when resin increments were withdrawn. The exchange of uranyl carbonate between a simulated in situ uranium leach liquor and a strong-base ion-exchange resin together with the subsequent elution with an ammonium chloride solution was studied. The effects of the number of sections, section height, amount of resin withdrawal, solution flow rate, and column diameter were investigated. The kinetic and equilibrium relationships for the absorption and elution steps were also examined. The experimental data indicate a strong interdependence between variables. Solution retention time appears to be a major limiting variable in the absorption process, while resin residence time is the determining factor in the elution process. The column was efficient over a range of conditions, but close control was needed for optimum operation.

INTRODUCTION

Bureau of Mines uranium research is conducted in support of its objective to help assure an adequate supply of uranium for national needs by making technological improvements in the processes for extracting uranium from ores and low-grade uraniferous materials. Part of the research is concerned with development of ion-exchange extraction procedures for recovering uranium at less cost from in situ leaching solutions.

The initial application of ion exchange for the recovery of uranium from alkaline leach liquors occurred during the 1950's, but the use was not extensive. Recently interest has revived because the technology is being used to

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recover uranium from alkaline leach liquors produced by in situ leaching operations. The uranium-bearing alkaline leach liquor is contacted with an anionic resin and the uranium exchanges as an anionic uranium carbonate complex. This complex is then eluted from the resin by displacing the uranium complex with

FIGURE 1. - Multiple-compartment ion-exchange column.

another anion such as Cl^-. The uranium is recovered from the eluate by various precipitation techniques; the final uranium mill product is designated as "yellow cake," which is normally shipped to other operations for further refining and conversion to UF_6.

A variety of ion-exchange systems have been used; some of these systems have been described by Merritt (3).[4] Each of the systems has both advantages and limitations; for example, some systems can handle only clarified feed solutions, while other systems require relatively large resin inventories and higher capital investments. During research by the Bureau of Mines on recovery of uranium from dilute mine waters, a new low-cost system of ion exchange was developed that is applicable to both clear solutions and many slime slurries (1, 5, 7, 9). The primary component of this system has been designated as the multiple-compartment ion-exchange (MCIX) column; a generalized schematic is shown in figure 1. In this column, the upflowing feed solution fluidizes the ion-exchange resin in a series of compartments. The compartments are separated by orifice plates; the orifice openings constitute about 5 percent of the column cross-sectional area. The feed solutions flow upward at rates of about 10 to 20 gallons per minute per square foot. This fluidizes the resin in each compartment, but the flow through the orifices prevents the resin from dropping into a lower compartment. Periodically, the feed stream is momentarily interrupted, a discharge valve is opened, and an increment of resin is discharged. This operational cycle permits the increments of resin to move down through the column countercurrent to the solution flow. A similar column arrangement can also be used for elution of the loaded resin.

A 14-inch-diameter MCIX absorption column and a 4-inch-diameter fixed-bed upflow elution column were field tested on uranium-bearing mine water at Bingham Canyon, Utah, and Grants, N. Mex. The same system was tested on alkaline leach slurry at Moab, Utah. A 6-foot-diameter column was hydraulically tested in Salt Lake City, Utah. A 20-inch-diameter absorption column was tested on acid leach slurry at Edgemont, S. Dak. Laboratory testing with a 2-inch-diameter column showed that it was feasible to use a compartmented column for countercurrent elution (6).

Previous cost estimates indicated considerable savings over conventional resin-in-pulp (RIP) basket-type operations because the resin requirement for the compartmented columns was determined to be about 35 percent of the amount needed by basket-type RIP circuits of the same throughput capacity. Based on 1972 costs and milling 2,000 tons of ore per day, it was determined that the capital required for a hypothetical ion-exchange plant using MCIX columns was 73 percent of the amount for a solvent-extraction plant and the operating costs for the ion-exchange plant were 81 percent of the solvent extraction plant.

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.
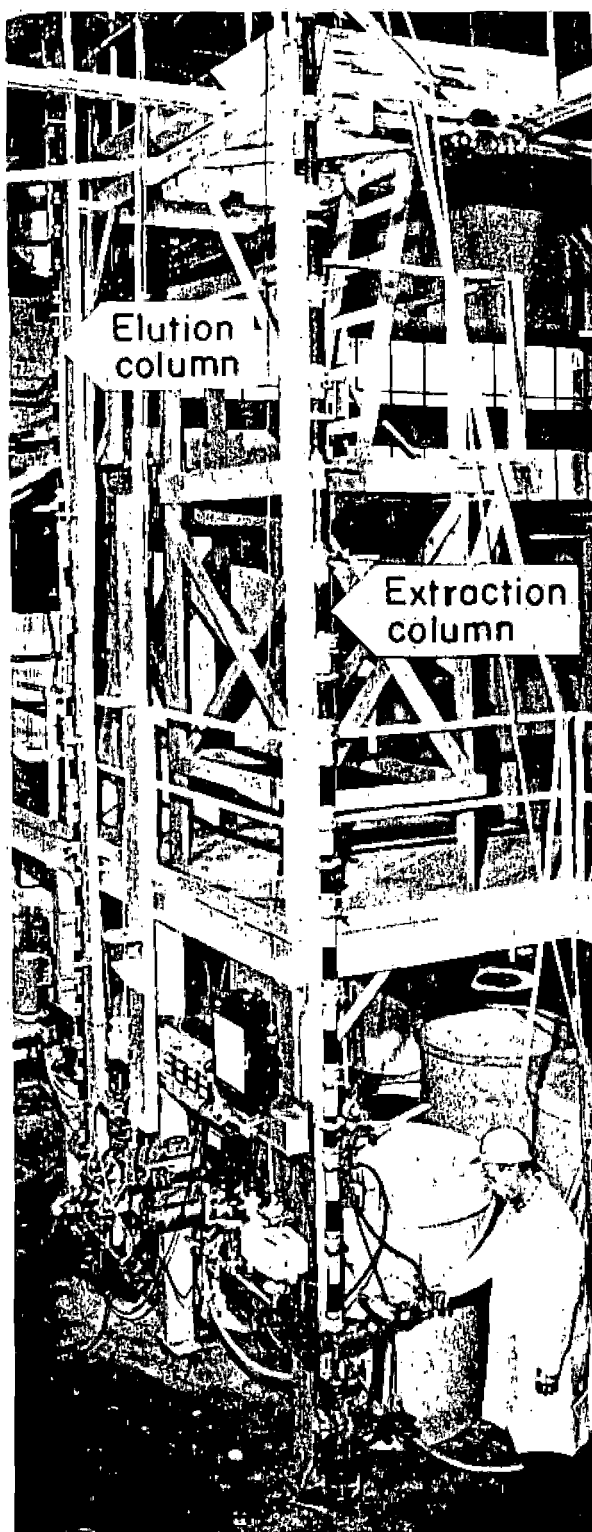
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FIGURE 2. - Overall view of the two mul-
tiple-compartment columns
systems.

MCIX columns are in commercial use
for gold recovery from cyanide solutions
using coarse activated carbon particles,
and prototype columns are in use for
uranium absorption and elution.

During the past year, the Bureau of
Mines has conducted experimental studies
to determine MCIX column design require-
ments for the absorption of uranium from
ammonium bicarbonate solutions similar
to those produced by in situ leaching
operations. Design criteria were also
developed for the elution of the loaded
resin with an ammonium chloride eluant.
This work is a continuation of similar
work on acid solutions (8). Both indi-
vidual and integrated absorption and
elution circuit arrangements were used
during this work.

EQUIPMENT

The main component of the absorp-
tion equipment used in the current
experimental program was a 2-inch-inside-
diameter (ID) by 16-foot-high glass col-
umn composed of 1-foot sections as shown
in figure 2. The elution studies used
1-, 2-, and 4-inch-ID columns. The
1-inch-ID column was composed of 6-inch-
high sections while the 2- and 4-inch-ID
columns were composed of 12-inch-high
sections. The maximum total height of
the 1- and 2-inch-ID columns was 22 feet
and 16 feet, while the maximum height of
the 4-inch-ID column was 17 feet. A
detailed flowsheet of the columns system
is shown in figure 3. Individual com-
partments were separated by orifice
plates that had openings equivalent to
approximately 6 percent of the column
cross-sectional area. The column was
constructed so that the compartment
height could be modified by substituting
full-diameter couplings for the orifice
plate couplings. Rosenbaum and Ross
state the following about the use of
these orifice plates:

FIGURE 3. - Flowsheet of the MCIX columns system.

"Observation has shown that when a regulated flow of solution passes upward through a column of closely sized resin at a rate sufficient to fluidize the resin, vertical mixing occurs over the length of the column. In effect, the entire column serves as a gently agitated reactor; and under these conditions, equilibrium stringently limits the absorption kinetics and efficiency. By assembling the resin column out of short segments, each separated by a perforated plate, vertical mixing still occurs within each segment of expanded-bed resin, but the net overall effect is of multiple-stage absorption or elution yielding more rapid and complete ion transfer than obtainable in a noncompartmented column of equivalent height.

"Under ideal operating conditions, each compartment is nearly full of fluidized resin in equilibrium with the upflowing solution. If the quantity of resin in any compartment is initially in excess of the equilibrium volume, the excess resin moves up through the perforated plate into the next compartment. If the quantity of resin is less than the equilibrium volume, the compartment will not

be completely filled. Downward movement of resin between compartments can occur only when the velocity of the solution flow through the holes in the perforated plates is less than the terminal settling velocity of the resin particles. An increase in solution flow rate or density will cause the resin bed to expand. When using coarse bead resins, minus 16-mesh plus 20-mesh (Tyler), perforated plates that have an open area of approximately 5 percent are satisfactory."

COLUMN OPERATION

The column is operated with a continuous, upflow of solution except for the scheduled resin withdrawals. During these resin withdrawals, the automatic solution inlet valve closes, and the automatic resin outlet valve opens to discharge a programed amount of resin from the column. The discharge periods are approximately 3 to 6 seconds for the 1-inch-ID column and 6 to 12 seconds for the 2- and 4-inch-ID columns. The time interval between withdrawals from the absorption column is determined by the amount of resin to be discharged per withdrawal cycle, and this is a function of feed solution flow rate, feed solution concentration, and desired resin loading. The time interval between withdrawals from the elution column is also determined by the amount of resin to be discharged per withdrawal cycle; this time interval is a function of feed resin concentration, eluant flow rate, desired resin elution, and desired eluate grade. The actual time during which the resin discharge valve must be open to discharge a programed amount of resin is a function of the valve opening configuration and the bed expansion. During column operation, the solution flows were controlled by automatic instruments; and the open time interval on the resin discharge valve was set by trial and error adjustments. Figure 4 shows the sequence for one cycle of the resin discharge operation. The 4-foot compartment shown is made up of 1-foot glass sections and full-diameter couplings.

The solution flow rate controller is a critical component of the system. Some of the previous work did not have the precise flow rate control necessary to assure steady-state operation. Without this control, the resin migrates from one compartment to another at random, and the column conditions remain transient. Solution flow control for the 2- and 4-inch-ID columns was maintained by an automatic system which consisted of a magnetic flowmeter, a controller, and an air diaphragm valve. This system had a precision of ±1 percent of the maximum flow rate through the magnetic flowmeter. A head tank and rotameter maintained the flow rate for the 1-inch-ID column. Both the absorption and the subsequent elution were conducted at room temperature.

SOLUTION DESCRIPTION

The absorption column feed solution used for these tests simulated the composition of a uranium leach liquor obtained from a Texas in situ pilot plant operation. The composition and pH of this clear, simulated mill solution are listed in table 1.

TABLE 1. - Analysis of synthetic feed solution in grams per liter
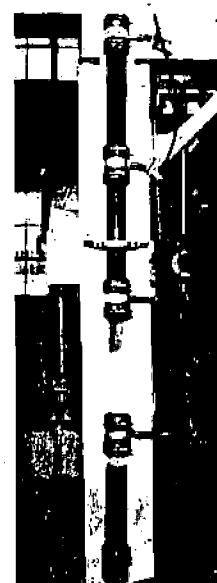
U_3O_8	NH_4HCO_3	Mg	PO_4	K	Na	Cl	Al	Ca	SO_4	pH
0.15	1.0	0.12	<0.001	0.30	0.20	0.75	<0.01	0.20	0.75	7.2

| O second | 2 seconds | 7 seconds |

| 9 seconds | 20 seconds | 60 seconds |

RESIN WITHDRAWAL CYCLE

O sec - start - resin bed at steady-state level.
9 sec - end of withdrawal.
60 sec - resin bed approaching steady-state level.

FIGURE 4. - Sequence of resin withdrawal cycle from MCIX absorption column.

8

EQUILIBRIUM AND KINETIC TESTS

Laboratory tests were made to collect uranium equilibrium data during absorption and elution of a strong-base anionic resin. Kinetic data were determined for the elution step. This information was used for both the planning and the evaluation of the column operations.

The equilibrium isotherm for the absorption feed solution and Rohm and Haas Amberlite IRA 430 resin[6] is shown in figure 5. This isotherm was obtained by a crosscurrent, pyramid-type, absorption technique similar to that used in solvent extraction shakeout tests described by Treybal (fig. 6). The isotherm

FIGURE 5. - Equilibrium isotherm for uranium-NH_4HCO_3 solution and IRA 430 resin.

[6]Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

Steps

FIGURE 6. - Contact pyramid for resin and solution to obtain an equilibrium isotherm for the system.

is extremely favorable for absorption in this system and indicates that low tails (<0.001 gram per liter (g/1) $U_3 O_8$) are possible even with slightly loaded recycle resin (<10 g/1 $U_3 O_8$).

FIGURE 7. - Elution equilibrium isotherm.

The equilibrium isotherm for the eluant and Amberlite IRA 430 is shown in figure 7. This isotherm was developed by the cross-current, pyramid-type, absorption technique. The eluant used for these tests was a 1.5-$\underline{M}$ $NH_4 Cl$ and 0.1-$\underline{M}$ $NH_4 HCO_3$ solution with a natural pH of approximately 7.3.

Experimental kinetic data for the system are shown in figure 8. These kinetic data were obtained by contacting the eluant and the resin in a stirred reactor and withdrawing solution samples at predetermined times.

FIGURE 8. - Kinetic data on elution with ammonium chloride and IRA 430 resin.

ABSORPTION COLUMN TESTS

Operating characteristics of the countercurrent 2-inch-ID absorption column were determined using a coarse bead (approximately 16 by 20 mesh), strong-base anionic resin Amberlite IRA 430 with the synthetic feed solution previously described. The orifice plates were perforated with one centered 29/64-inch-diameter hole per plate, and the column was divided by these plates into various equal height sections for the different tests. The column was fitted with motorized valves actuated by electric timers to control the on-off flows of the solution and resin. Precision control of the solution flow rate was obtained with an automatic air diaphragm valve coupled to a magnetic flow-meter control system.

The following characteristics of the absorption column were studied:

1. Solution flow rate.

2. Compartment height.

3. Spacing above the resin bed.

Effect of Solution Flow Rate

The optimum solution flow rate per unit area of column diameter is a major consideration when designing a column system. The limiting maximum flow

rate is the flow that will carry resin over the top of the column. The minimum solution flow rate to the column is that which will provide the minimum amount of resin fluidization required for mechanical transfer of the resin during the withdrawal cycle. However, as the flow rate increases above this minimum, the solution residence time per foot of column height decreases.. When this solution residence time decreases to the minimum time necessary for efficient absorption, a taller column may be required. Optimum economic design would require tradeoffs among the four parameters of column diameter, column height, solution flow rate, and uranium recovery.

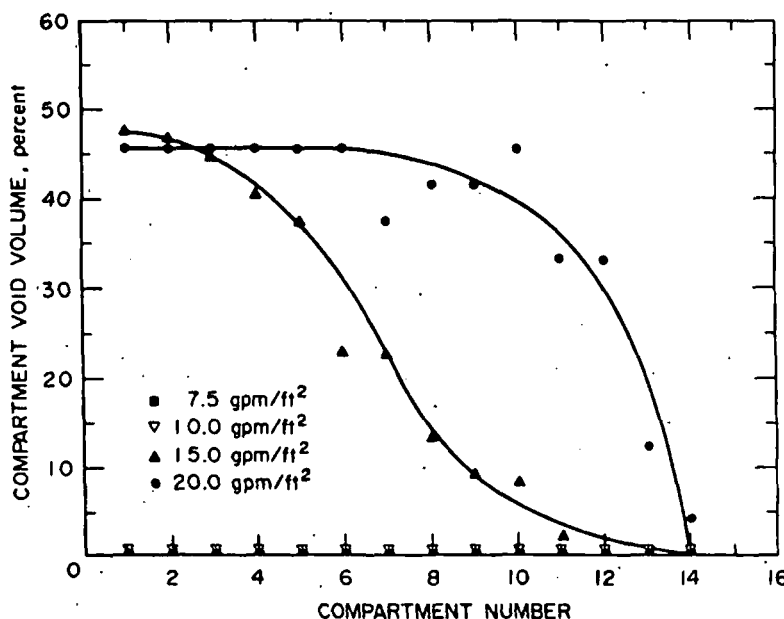FIGURE 9. - Effect of solution flow rate on uranium absorption (2-inch-ID column, 1-foot compartments, aqueous:resin 200:1).

FIGURE 10. - Effect of solution flow rate on uranium absorption (2-inch-ID column, 1-foot compartments, aqueous:resin 400:1).

The effect of solution flow rate is illustrated in figures 9-10 which show the solution column absorption profile for four solution flow rates with 1-foot compartments and aqueous-to-resin flow (A:R) ratios of 200:1 and 400:1. The A:R flow ratio is the ratio of solution flow rate to resin flow rate. For both A:R ratios, increasing the solution flow rate increased the length of column required to obtain the same amount of uranium absorption from the solution. The optimum solution flow rate for a column of approximately fourteen 1-foot compartments with a similar solution and resin would be 15 gallons per minute per square foot (gpm/ft^2).

This optimum can be attributed to solution retention time; that is, the solution must be in contact with the resin for a certain minimum time. With higher solution flow rates, the time requirement forces the absorption to take place in a higher compartment. The effect of this contact time can be illustrated by the experimental kinetic data shown in figure 11. As shown in figure 11, the

FIGURE 11. - Kinetic data on NH_4HCO_3-uranium solution and IRA 430 resin.

initial portion of the rate curve for uranium absorption from fresh feed solution onto unloaded resin is extremely steep. Changing the contact time of the solution and resin in this steep part of the curve by changing the flow rate of the solution would significantly affect the absorption efficiency.

Effect of Compartment Height

The multiple-compartment column can be considered as an assemblage of individual agitated stages in which absorption is achieved by a series of mass transfers from the solution to the resin. To be effective, the column must provide the required number of transfer stages, each having sufficient solution retention time for a reasonable approach to equilibrium mass transfer. As discussed in the previous sections, the solution retention is critical because the transfer of uranium from the solution to the resin sites is not instantaneous.

The stage height is of particular consequence because it can affect both the column construction cost and the inventory of resin required to fill the column.

Figure 12 shows the uranium extraction profile of the column when operating the 1- and 2-foot compartments. The solution flow rate was 10 gpm/ft^2 with a 200:1 A:R ratio. These curves indicate a marked decrease in absorption with the 2-foot compartments. By segregating the resin into compartments, extraction has been improved. Therefore, the optimum compartment height recommended is 1 foot.

FIGURE 12. - Effect of compartment height on uranium absorption (solution flow rate 10 gpm/ft², 2-inch-ID column, aqueous:resin 200:1).

FIGURE 13. - Effect of solution flow rate on spacing above resin bed in absorption column (2-inch-ID column, 1-foot compartments, aqueous:resin 400:1).

Spacing Above the Resin Bed

During the normal operation of the absorption column, eluted resin is fed into the top compartment of the absorption column and the resin level is maintained by an automatic controller. The eluted resin is the lightest resin in the column and, therefore, the resin bed in this top compartment is the most expanded bed in the column. As a resin increment is withdrawn from the bottom of the column, the resin in the rest of the column compartments moves down. When steady-state operation has been achieved, only a fixed amount of resin is transferred from compartment to compartment during each discharge cycle. As the resin in each individual compartment absorbs the uranium from the solution passing through that compartment, the density of the resin beads increases causing less bed expansion in that compartment. This decrease in bed expansion coupled with the transfer of equal numbers of resin beads gives rise to empty spaces above the resin in the compartments below the top compartment. Solution density changes are considered negligible (maximum 0.007 percent).

The open spacing above the resin beds for the various stages is shown in figure 13 for several solution flow rates at an A:R ratio of 400:1. Increasing the solution flow rate stretches the working length of the column. In other words, for the 7.5 and 10 gpm/ft², as shown in figure 10, the loading is completed in the first 5 and 8 feet of the column. No spacing occurs for these flow rates. For 15 and 20 gpm/ft² the loading occurs higher in the column, and the density change associated with it also occurs in the upper compartments.

ELUTION COLUMN TESTS

Operating characteristics of the countercurrent elution column were deter-mined using the strong-base anion resin Amberlite IRA 430 with the 1.5-$\underline{M}$ NH_4Cl and 0.1-$\underline{M}$ NH_4HCO_3 eluant previously described. For the individual tests the resin was loaded to approximately 60 g/l U_3O_8 from a uranyl carbonate circuit in a Utah uranium mill. To obtain a low effluent value from the absorption column, a resin eluted down to 5 g/l U_3O_8 was set as the requirement for the present series of tests. The orifice plates were perforated with one centered hole per plate as follows for the three column diameters tested:

1-inch-ID column = 5/16-inch-diameter hole.

2-inch-ID column = 29/64-inch-diameter hole.

4-inch-ID column = 15/16-inch-diameter hole.

The columns were divided by these orifice plates into various equal-height sec-tions for the different tests. The columns were fitted with motorized valves actuated by electric timers to control the on-off flows of the solution and resin. Precision control of the solution flow rate was obtained with an auto-matic air diaphragm valve coupled to a magnetic flowmeter control system for the 2- and 4-inch-ID columns. A head tank and rotameter controlled the solu-tion flow to the 1-inch-ID column.

The following characteristics of the MCIX elution column were studied: (1) solution flow rate, (2) A:R flow ratio, (3) column diameter, and (4) sec-tion height. Both solution flow rate and A:R flow ratio determine resin resi-dence time; these relationships are discussed in the following sections.

Resin Residence Time

The amount of time the resin is in contact with the solution in the column is designated as the resin residence time. Test data indicate that this resin residence time shows a direct relationship with the degree of uranium elution. Resin residence time is plotted against overall column elu-tion efficiency in figure 14. This resin residence time is a function of the following parameters:

1. Solution flow rate.

2. Aqueous-to-resin flow ratio.

3. Column height.

FIGURE 14. - Effect of resin residence time on elution efficiency.

The column height was held constant throughout the present series of tests and the effects of changes in the solution flow rate and the A:R ratio are discussed in the next sections.

Effect of Solution Flow Rate

There are major design considerations when determining the eluant flow rate. Because better elution is obtained with longer resin residence times, the lowest possible eluant flow rate is desirable. However, the minimum solution flow rate to the column is determined by the resin fluidization required for mechanical transfer of the resin during the withdrawal cycle. This flow rate is approximately 2.0 gpm/ft^2. As in the absorption column design, the optimum design would require tradeoffs among the four parameters of column diameter, column height, solution flow rate, and desired resin elution.

The effect of solution flow rate is shown in figures 15-18. The minimum eluant flow rate as mentioned previously is approximately 2.0 gpm/ft^2. Approaching this value would approximate the optimum eluant flow rate that would give the maximum resin residence time for a given column length while still being able to mechanically operate the resin withdrawal system of the column. The two eluant flow rates studied in this series of tests were 2.7 and 4.0 gpm/ft^2. These tests were made to investigate the effect of increased flow rates on elution. At a constant A:R flow ratio, increases in the eluant flow rate reduce the resin residence time. For the tests shown in figures 15 and 17 with A:R ratios of 10:1, the resin residence time was still adequate at the higher eluant flow rate of 4.0 gpm/ft^2 to allow resin elution of 90 percent or greater. However, at the A:R ratio of 6:1, resin elution is reduced significantly with the increase in eluant flow rate as shown in figures 16-18. Therefore, an eluant flow rate of 2 to 2.7 gpm/ft^2 is considered optimum and allows a maximum resin residence time while still permitting mechanical operation of the resin withdrawal system of the elution column.
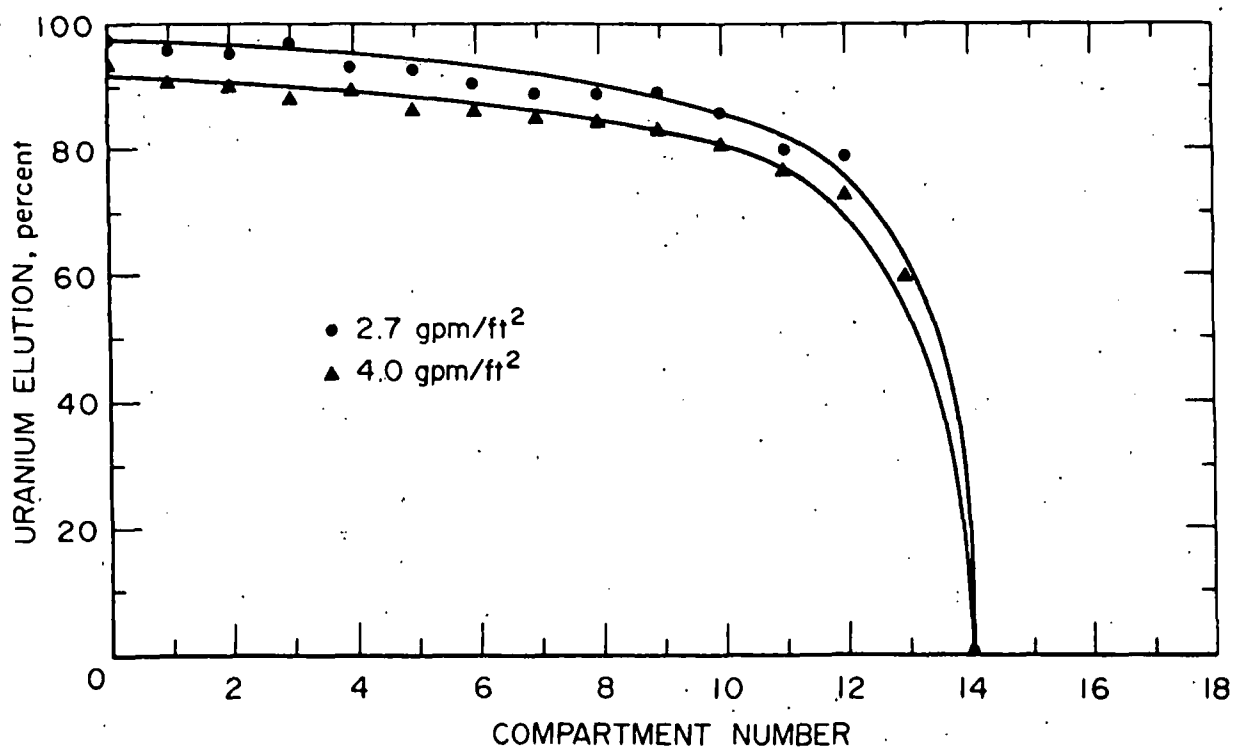
FIGURE 15. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 1-foot compartments, aqueous:resin 10:1).
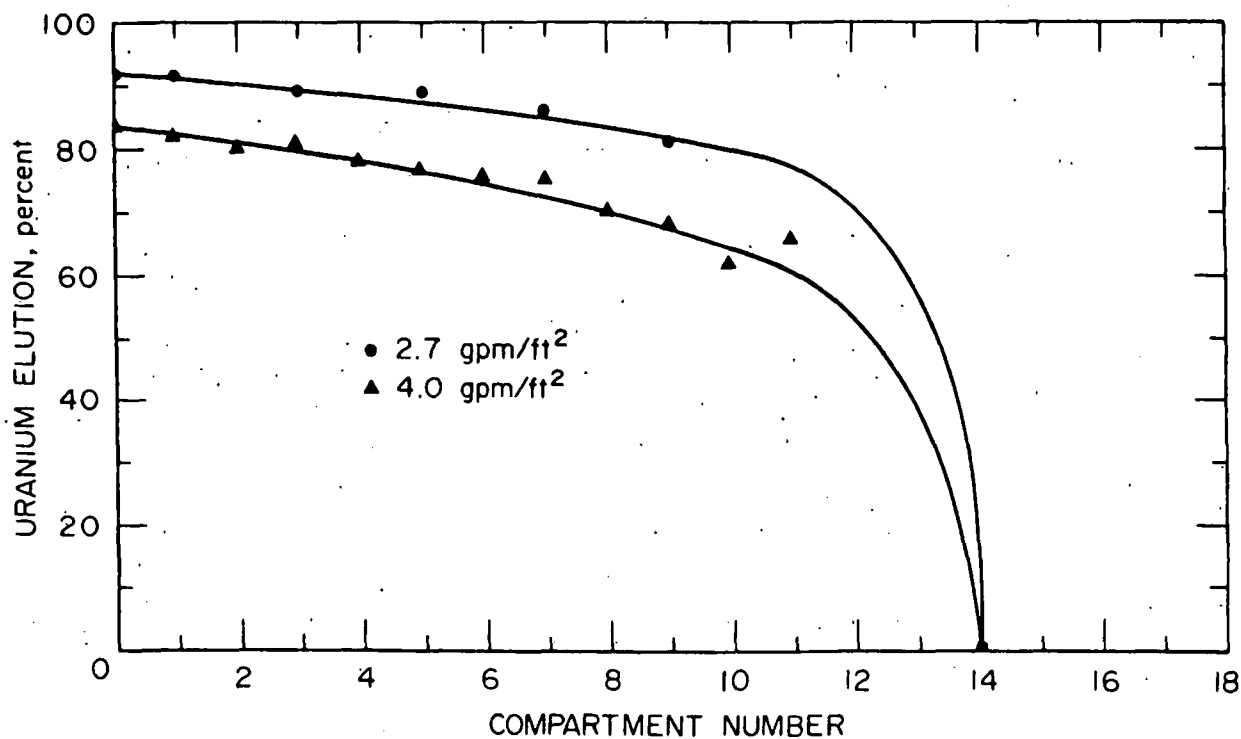

FIGURE 16. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 1-foot compartments, aqueous:resin 6:1).
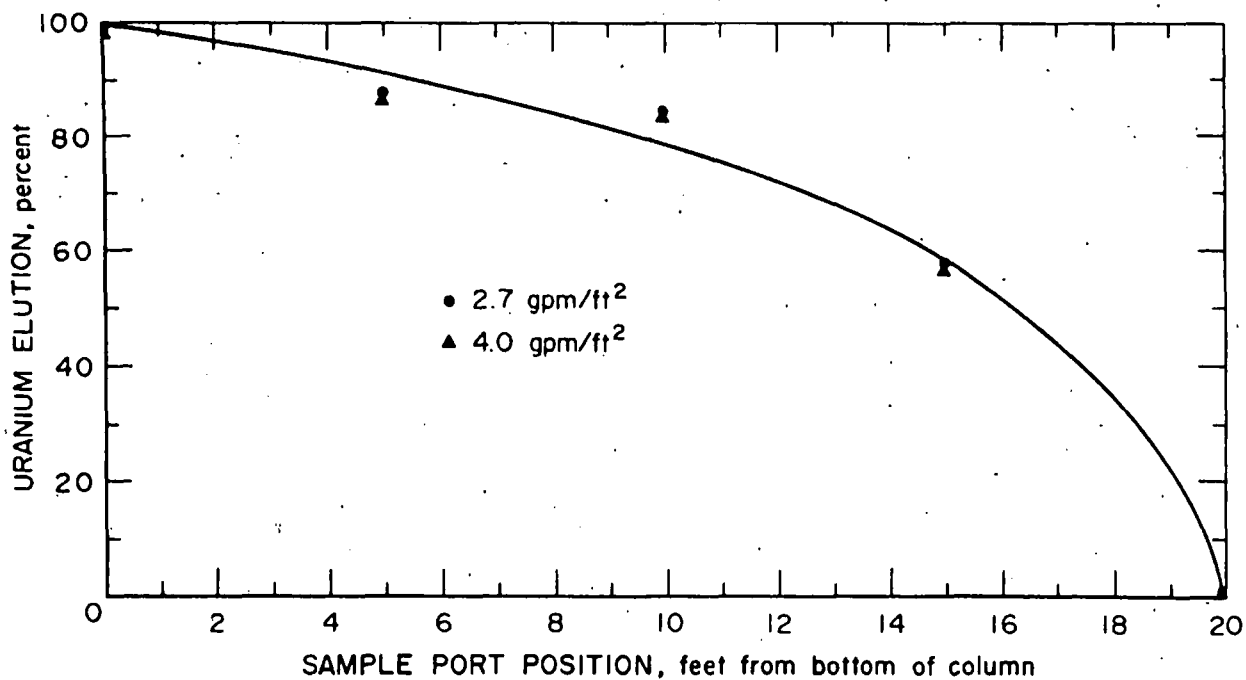
FIGURE 17. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 5-foot compartments, aqueous:resin 10:1).
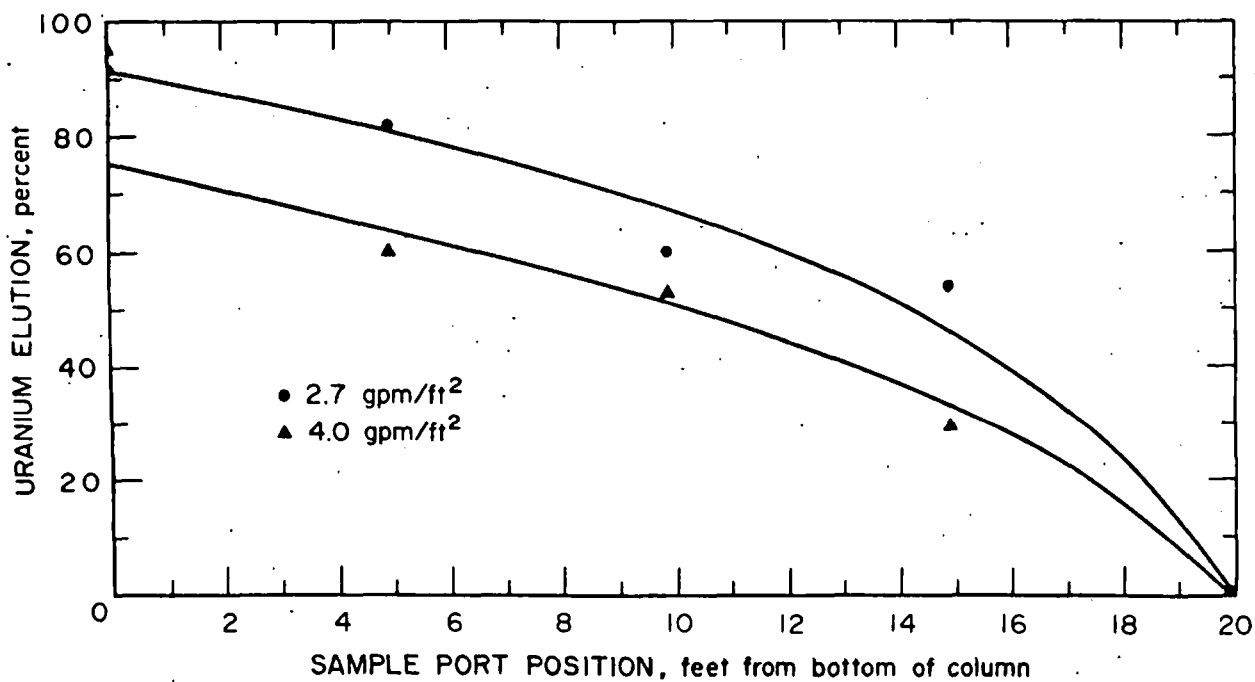

FIGURE 18. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 5-foot compartments, aqueous:resin 6:1).

Effect of Aqueous-to-Resin Flow Ratio

The A:R flow ratio influences both the degree of resin elution and the eluate grade. The equilibrium isotherm in figure 7 shows about a 2:1 A:R flow ratio constraint when plotting a McCabe-Thiele operating line (2). In addition, a mechanical constraint involving the entrained eluant withdrawn with the resin limits the minimum A:R flow ratio to about 4:1. To obtain low effluent values from the absorption circuit, a well eluted resin (<5 g/l U_3O_8) from the elution column is desirable. Also desirable from the elution column is a high eluate grade (>10 g/l U_3O_8) for ease in the subsequent uranium precipitation and reduced eluant chemical requirements. In the present series of tests, ammonium uranyl carbonate precipitated out of eluates exceeding about 4.5 g/l U_3O_8. The addition of 0.05 $\underline{M}$ Na_2CO_3 to the eluant has been suggested to avoid this precipitation problem and to allow eluate grades of at least 12 to 14 g/l U_3O_8. This modification should be considered for future investigation.

As mentioned previously, the effect of the A:R ratio directly determines the resin residence time. To obtain a high-grade eluate (>10 g/l U_3O_8) the A:R ratio would have to be 6:1 or less when using an entering resin concentration of approximately 50 to 60 g/l U_3O_8. With the minimum solution flow rate of 2.0 gpm/ft^2, the desired A:R ratio of 6:1 or less limits the final uranium concentration on the resin at the column heights tested. With a taller column sufficient resin time would be obtained with the minimum eluant flow rate and an A:R ratio of 4:1 to 6:1.

The effects of the A:R ratio from 10:1 to 6:1 for different flow rates, section heights, and column diameters are shown in figures 19-24. In every comparison of elution performance, the reduced A:R ratio of 6:1 decreased the elution efficiency. As stated previously, with a taller column sufficient resin residence time could have been obtained at 6:1 A:R and elution efficiency increased.

Effect of Column Diameter

Column diameter is determined by the eluant flow rate, the amount of resin to be eluted, and the A:R ratio. Wall effects that might hinder mixing in the smaller diameter columns and change the elution characteristics were studied in this series of tests. Tests utilizing the same conditions were run using 1-, 2-, and 4-inch-ID columns. The results from these tests are shown in figures 25-26 and indicate very little difference in elution efficiency between the three column diameters. Because of differences in the total length of column used for the various experiments, the abscissa of the graphs are marked with offset scales.
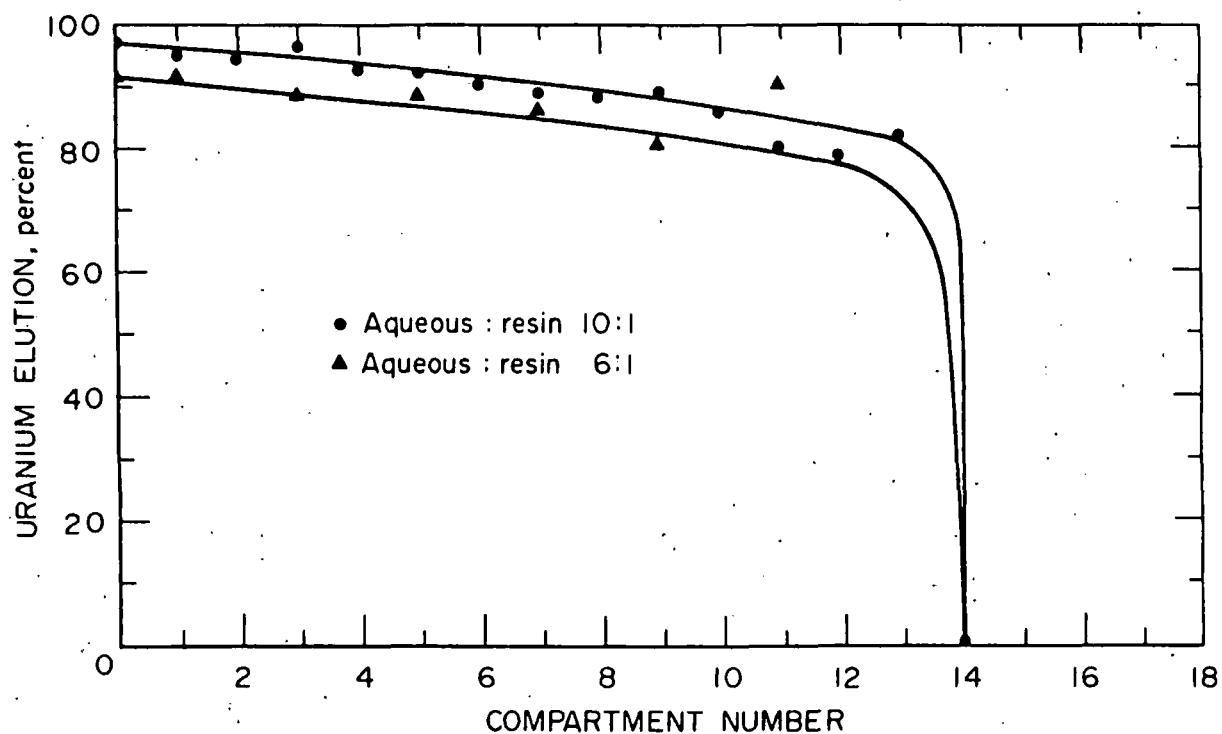
FIGURE 19. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 1-foot compartments, solution flow rate 2.7 gpm/ft²).
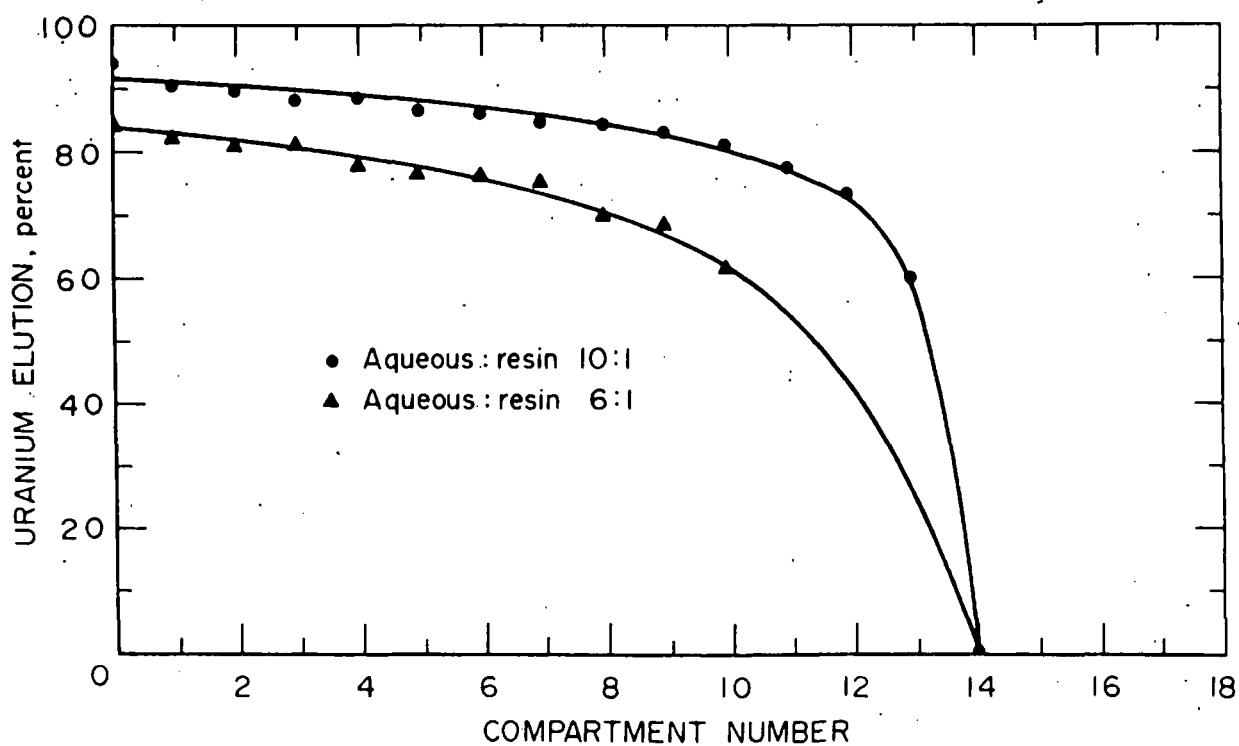

FIGURE 20. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 1-foot compartments, solution flow rate 4.0 gpm/ft²).
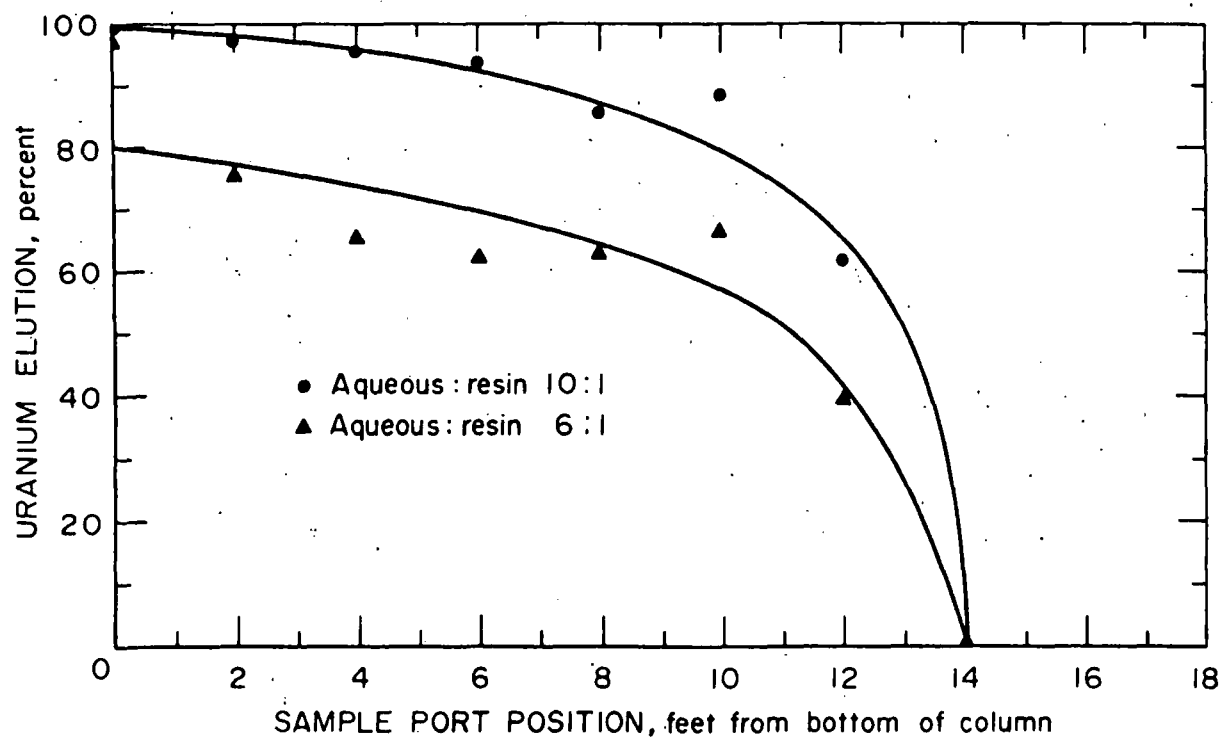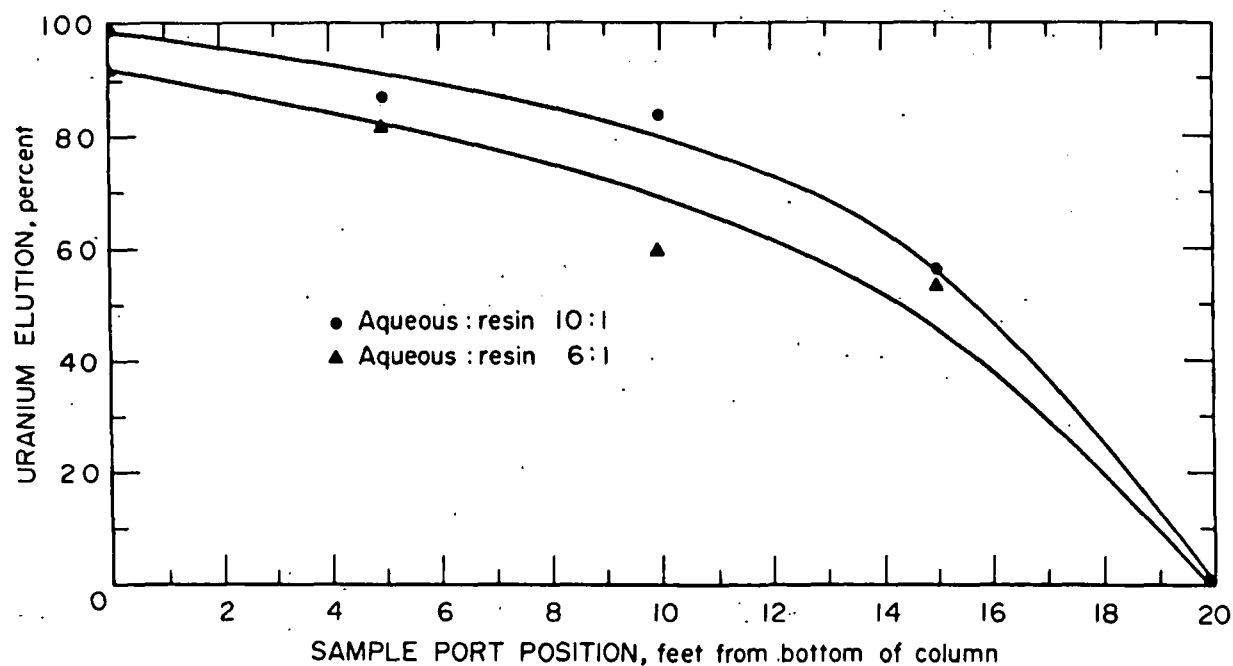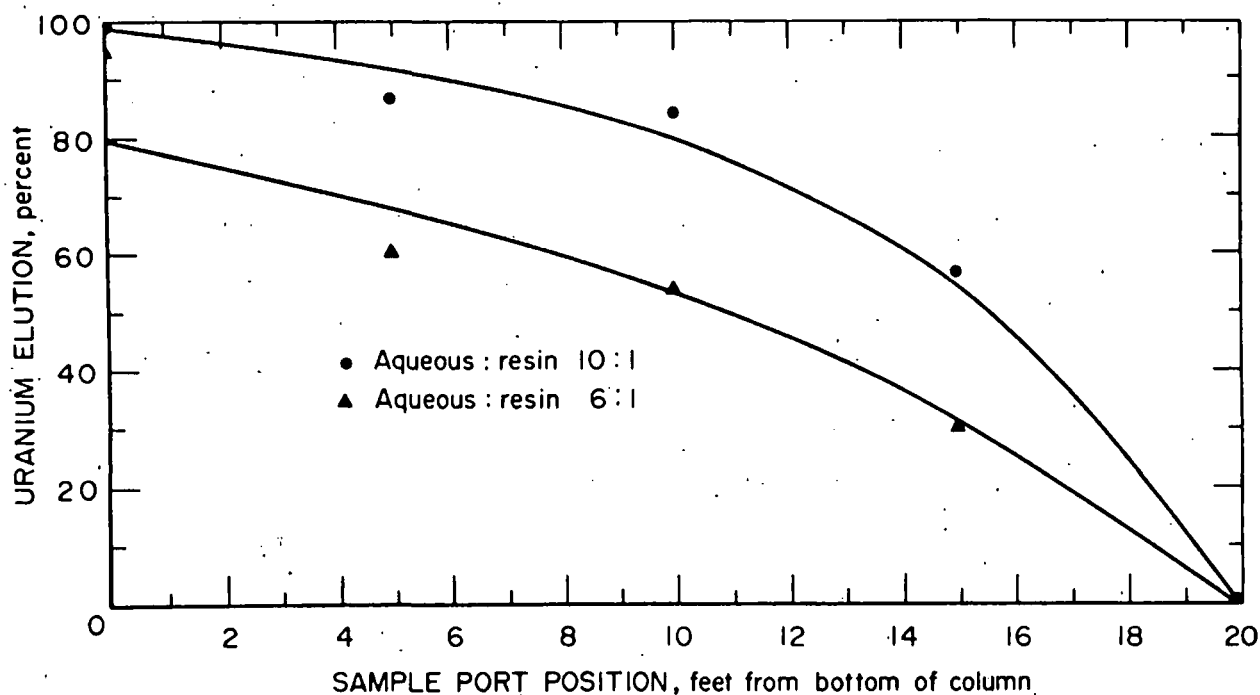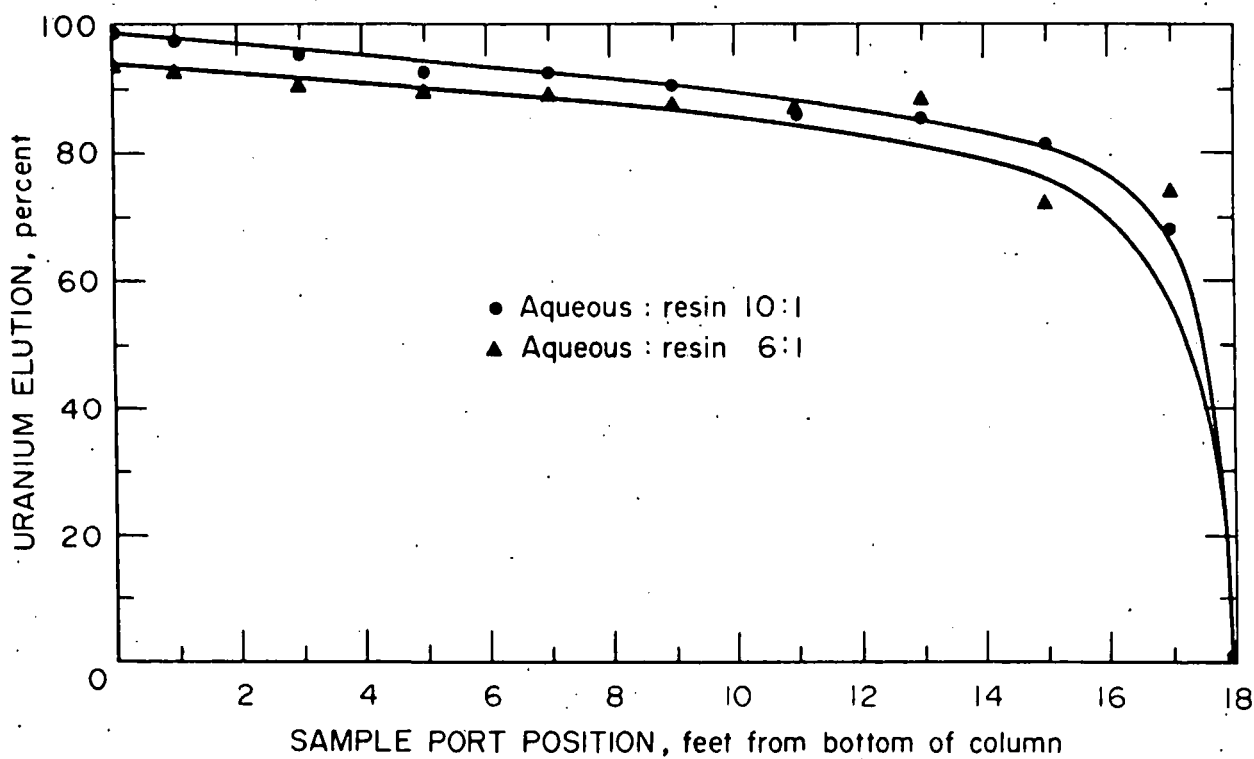
FIGURE 21. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 2-foot compartments, solution flow rate 2.7 gpm/ft²).
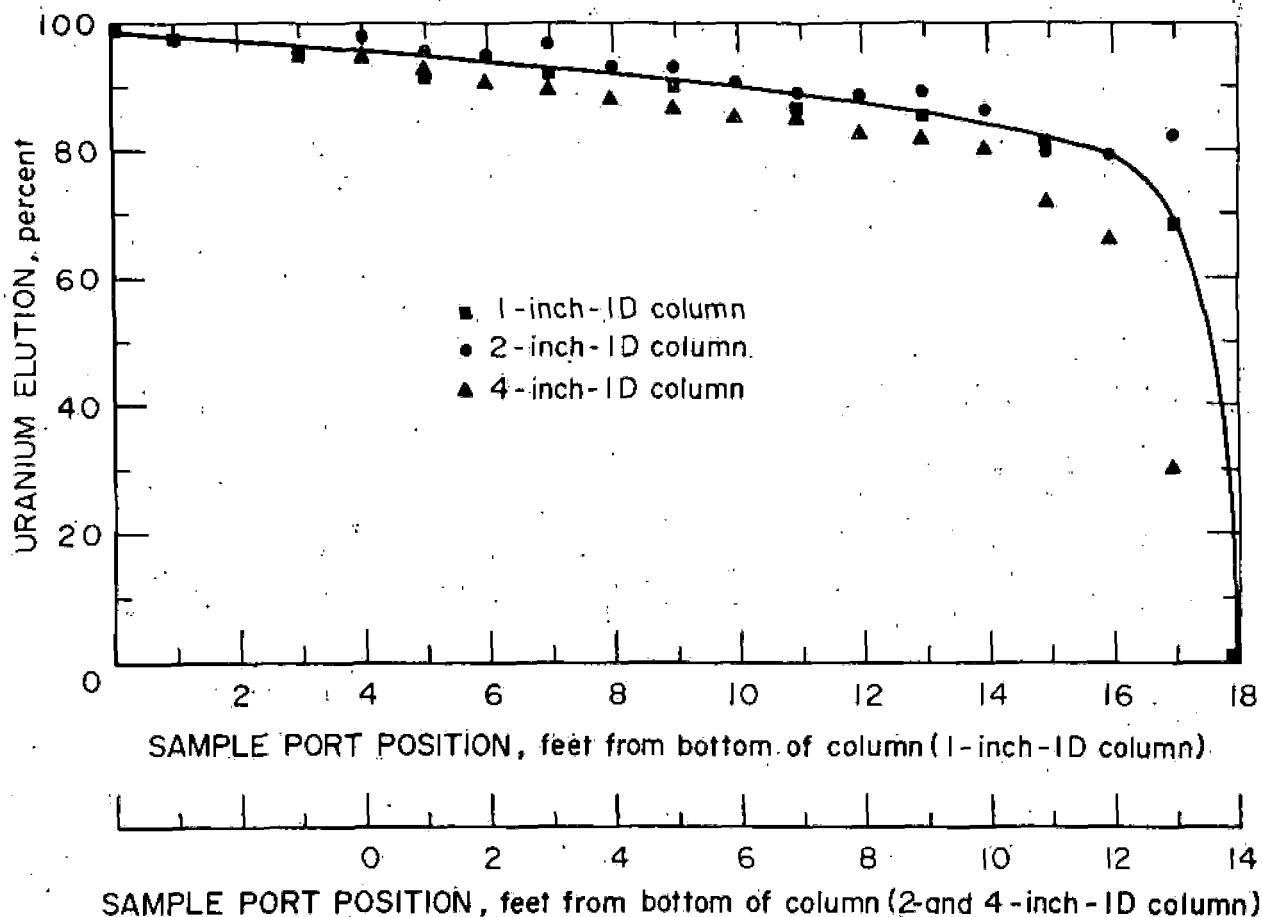

FIGURE 22. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 5-foot compartments, solution flow rate 2.7 gpm/ft²).

FIGURE 23. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 5-foot compartments, solution flow rate 4.0 gpm/ft²).

FIGURE 24. - Effect of aqueous-to-resin flow ratio on elution efficiency (1-inch-ID column, 2-foot compartments, solution flow rate 2.7 gpm/ft²).

FIGURE 25. - Effect of column diameter on elution efficiency (1-foot compartments, solution flow rate 2.7 gpm/ft², aqueous:resin 10:1).

Effect of Compartment Height

In the elution column, separation into stages is critical. Resin density changes are favorable in the absorption column, but the reverse is true in the elution column. Loaded resin, which is the highest density resin, is transferred from the bottom of the absorption column to the top of the elution column. As the resin moves down through this column, it is eluted and its density decreases thereby increasing its bed expansion. This bed expansion can cause the lighter resin beads to be pushed into the next higher compartment which contains denser resin beads. If this trend continues, top-to-bottom mixing (heavy loaded beads to the bottom and eluted beads to the top) would occur and be detrimental to the elution operation. The 1.3 percent density change of the solution is negligible. Exact full resin withdrawals are very important in elution. Fractional resin withdrawals draw out the heavy or more loaded resin in the bottom compartments leaving the more eluted resin in the column.
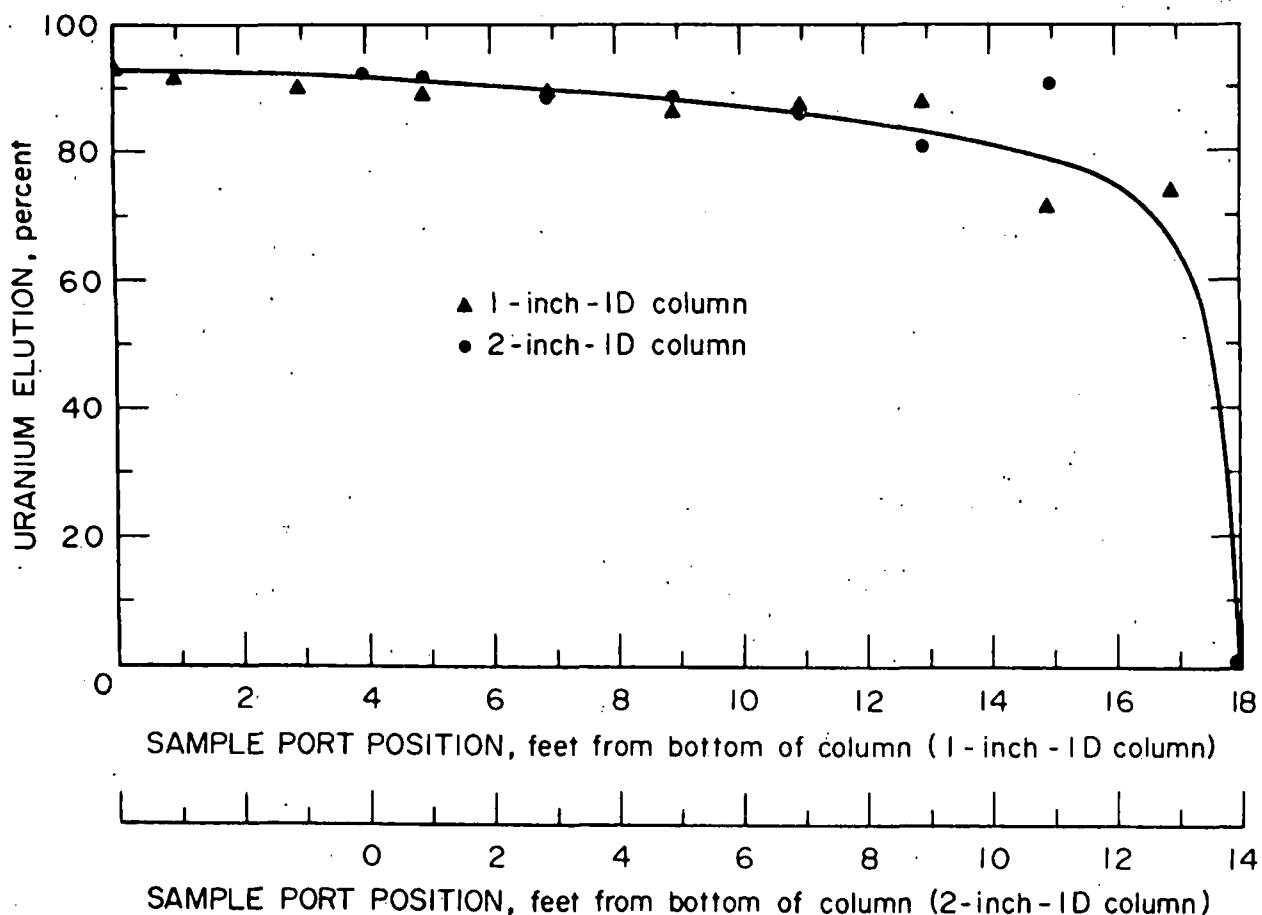
FIGURE 26. - Effect of column diameter on elution efficiency (2-foot compartments, solution flow rate 2.7 gpm/ft², aqueous:resin 6:1).

As shown in figure 27, when using an A:R ratio of 10:1 and holding all other variables constant, the increase from 1- to 2-foot section heights had little effect on elution efficiency. When the section height was increased to 5 feet, a significant decrease in elution efficiency occurred. This decrease also occurs at a higher flow rate of 4.0 gpm/ft² as shown in figure 29. In figure 28, which shows tests having an A:R ratio of 6:1, the increase of the section height from 1-foot to the 2- and 5-foot heights caused a marked decrease in elution efficiency. When the A:R ratio is decreased from 10:1 (fig. 27) to 6:1 (fig. 28), the resin residence time becomes more critical. As shown in figure 27, ample time allowed the elution efficiency in the 2-foot section height to approach the 1-foot results. The results shown for the 5-foot sections in figures 27-28 and the 2-foot sections in figure 28 indicate that increased resin residence time could not overcome the detrimental effect of the mixing in the longer sections. This is also shown at a higher flow rate in figure 30. The data indicate that a compartment height of 1-foot produced the most efficient elution per foot of column height over a range of operating conditions.
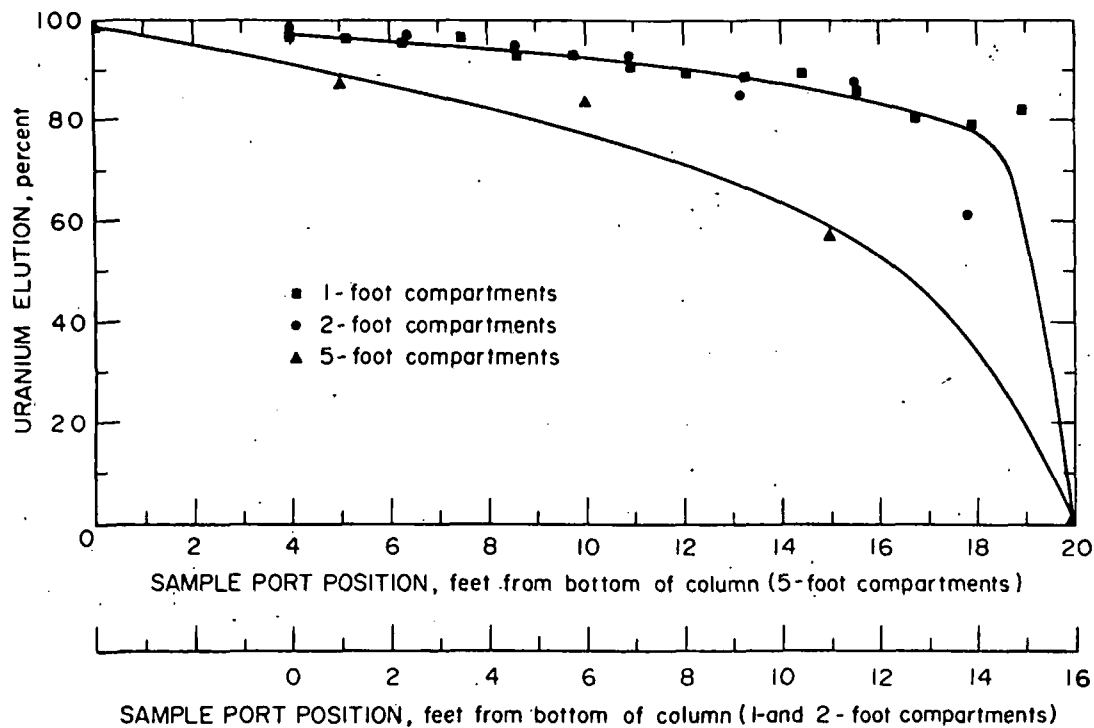
FIGURE 27. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 2.7 gpm/ft², aqueous:resin 10:1).
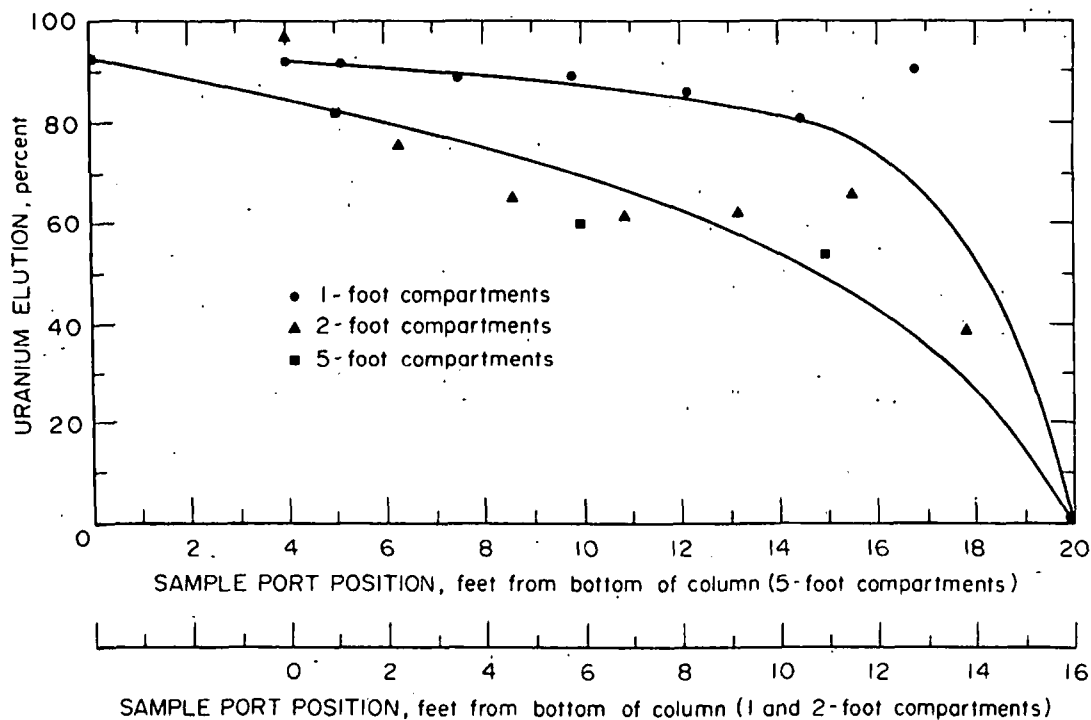

FIGURE 28. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 2.7 gpm/ft², aqueous:resin 6:1).
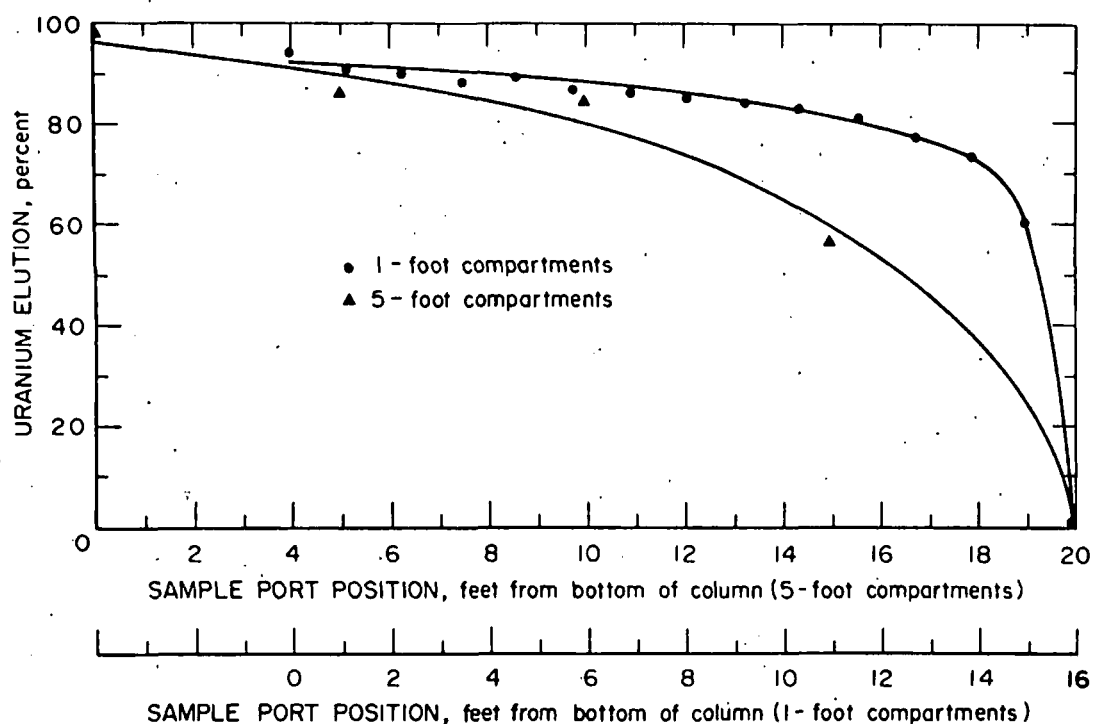
FIGURE 29. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 4.0 gpm/ft^2, aqueous:resin 10:1).
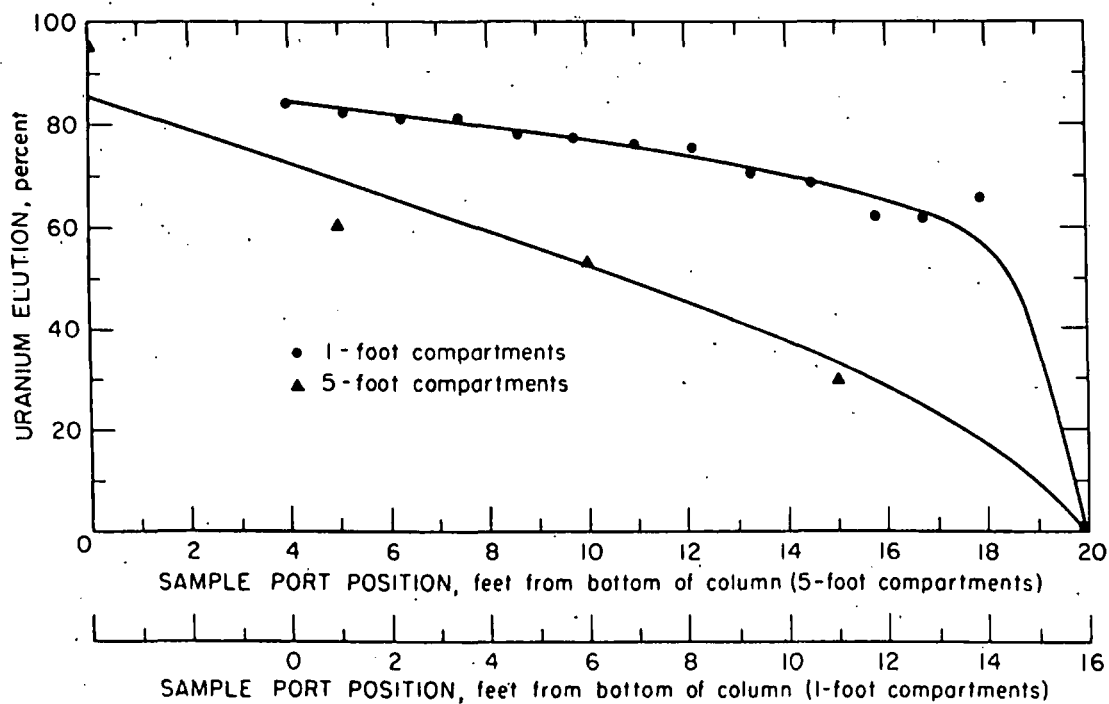

FIGURE 30. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 4.0 gpm/ft^2, aqueous:resin 6:1).

SUMMARY

This work was done to support recent developments of in situ ammonium bicarbonate leaching of uranium ores. The application of the multiple-compartment, ion-exchange columns system provides an efficient method of processing the leach liquor.

For the 16-foot tall absorption column (fourteen 1-foot compartments) with the recommended 1-foot compartment height, a feed solution flow rate of 15 gpm/ft^2 with an A:R ratio of 400:1 was considered optimum and achieved 99 percent absorption of uranium from the 0.15-g/1 U_3O_8 leach liquor. This provides a 60-g/1 U_3O_8 loaded resin for the elution circuit.

For the elution circuit a 16-foot-tall column with the recommended 1-foot compartment height and an eluant flow rate of 2.7 gpm/ft^2 would attain about 92 percent elution of uranium from the resin. This is at an A:R ratio of 6:1 and would provide a 9-g/1 U_3O_8 eluate grade and a 5-g/1 U_3O_8 exiting resin concentration. Higher eluate grades and/or lower exiting resin concentration could be obtained by increasing the column length. Resin residence time was the critical factor in determining resin elution efficiency. The indicated resin residence time required to produce an eluted resin containing <5 g/1 U_3O_8 was 160 to 190 minutes.

REFERENCES

1. George, D. R., J. R. Ross, and J. D. Prater. Byproduct Uranium Recovered With New Ion-Exchange Techniques. Min. Eng., v. 20, January 1968, pp. 1-5.

2. McCabe, W. L., and J. C. Smith. Unit Operations in Chemical Engineering. McGraw-Hill Book Co., Inc., New York, 2d ed., 1967, pp. 526-530.

3. Merritt, R. C. The Extractive Metallurgy of Uranium. U.S. Atomic Energy Commission, Colo. School of Mines Research Inst., Golden, Colo., 1971, 576 pp.

4. Pizarro, R., J. D. McBeth, and G. M. Potter. Heap Leaching Practice at the Carlin Gold Mining Co., Carlin, Nev. Solution Min. Symp., AIME, Dallas, Tex., ch. 19, 1974, pp. 253-267.

5. Rosenbaum, J. B., and D. R. George. Cost Reductions in Ion-Exchange Processing of Uranium Ores--The Recovery of Uranium. Proc. IAEA Symp., Sao Paulo, Brazil, August 1970, pp. 297-309.

6. Rosenbaum, J. B., and J. R. Ross. A Countercurrent Column for Fluid-Bed Ion Exchange of Uranium Ore Slurries. Internat. Symp. on Hydrometallurgy, AIME, Chicago, Ill., ch. 20, 1973, pp. 535-551.

7. Ross, J. R., and D. R. George. Recovery of Uranium From Natural Mine Waters by Countercurrent Ion Exchange. BuMines RI 7471, 1971, 17 pp.

8. Traut, D. E., I. L. Nichols, and D. C. Seidel. Design Criteria for Uranium Ion Exchange in a Fluidized System. Trans. AIME, v. 260, March 1976, pp. 24-28.

9. Treybal, R. E. Liquid Extraction. McGraw-Hill Book Co., Inc., New York, 2d ed., 1963, pp. 361-368.

Design Requirements for Uranium Ion Exchange From Ammonium Bicarbonate Solutions in a Fluidized System

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UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

BUREAU OF MINES

This publication has been cataloged as follows:

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DESIGN REQUIREMENTS FOR URANIUM ION EXCHANGE FROM AMMONIUM BICARBONATE SOLUTIONS IN A FLUIDIZED SYSTEM

by

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ABSTRACT

A fluidized countercurrent ion-exchange system was developed, operated, and evaluated by the U.S. Department of the Interior, Bureau of Mines. The system consisted of integrated multiple-compartment absorption and elution columns in which the solution flows were continuous except for short periods when resin increments were withdrawn. The exchange of uranyl carbonate between a simulated in situ uranium leach liquor and a strong-base ion-exchange resin together with the subsequent elution with an ammonium chloride solution was studied. The effects of the number of sections, section height, amount of resin withdrawal, solution flow rate, and column diameter were investigated. The kinetic and equilibrium relationships for the absorption and elution steps were also examined. The experimental data indicate a strong interdependence between variables. Solution retention time appears to be a major limiting variable in the absorption process, while resin residence time is the determining factor in the elution process. The column was efficient over a range of conditions, but close control was needed for optimum operation.

INTRODUCTION

Bureau of Mines uranium research is conducted in support of its objective to help assure an adequate supply of uranium for national needs by making technological improvements in the processes for extracting uranium from ores and low-grade uraniferous materials. Part of the research is concerned with development of ion-exchange extraction procedures for recovering uranium at less cost from in situ leaching solutions.

The initial application of ion exchange for the recovery of uranium from alkaline leach liquors occurred during the 1950's, but the use was not extensive. Recently interest has revived because the technology is being used to

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recover uranium from alkaline leach liquors produced by in situ leaching operations. The uranium-bearing alkaline leach liquor is contacted with an anionic resin and the uranium exchanges as an anionic uranium carbonate complex. This complex is then eluted from the resin by displacing the uranium complex with

FIGURE 1. - Multiple-compartment ion-exchange column.

another anion such as Cl⁻. The uranium is recovered from the eluate by various precipitation techniques; the final uranium mill product is designated as "yellow cake," which is normally shipped to other operations for further refining and conversion to UF_6.

A variety of ion-exchange systems have been used; some of these systems have been described by Merritt (3).[4] Each of the systems has both advantages and limitations; for example, some systems can handle only clarified feed solutions, while other systems require relatively large resin inventories and higher capital investments. During research by the Bureau of Mines on recovery of uranium from dilute mine waters, a new low-cost system of ion exchange was developed that is applicable to both clear solutions and many slime slurries (1, 5, 7, 9). The primary component of this system has been designated as the multiple-compartment ion-exchange (MCIX) column; a generalized schematic is shown in figure 1. In this column, the upflowing feed solution fluidizes the ion-exchange resin in a series of compartments. The compartments are separated by orifice plates; the orifice openings constitute about 5 percent of the column cross-sectional area. The feed solutions flow upward at rates of about 10 to 20 gallons per minute per square foot. This fluidizes the resin in each compartment, but the flow through the orifices prevents the resin from dropping into a lower compartment. Periodically, the feed stream is momentarily interrupted, a discharge valve is opened, and an increment of resin is discharged. This operational cycle permits the increments of resin to move down through the column countercurrent to the solution flow. A similar column arrangement can also be used for elution of the loaded resin.

A 14-inch-diameter MCIX absorption column and a 4-inch-diameter fixed-bed upflow elution column were field tested on uranium-bearing mine water at Bingham Canyon, Utah, and Grants, N. Mex. The same system was tested on alkaline leach slurry at Moab, Utah. A 6-foot-diameter column was hydraulically tested in Salt Lake City, Utah. A 20-inch-diameter absorption column was tested on acid leach slurry at Edgemont, S. Dak. Laboratory testing with a 2-inch-diameter column showed that it was feasible to use a compartmented column for countercurrent elution (6).

Previous cost estimates indicated considerable savings over conventional resin-in-pulp (RIP) basket-type operations because the resin requirement for the compartmented columns was determined to be about 35 percent of the amount needed by basket-type RIP circuits of the same throughput capacity. Based on 1972 costs and milling 2,000 tons of ore per day, it was determined that the capital required for a hypothetical ion-exchange plant using MCIX columns was 73 percent of the amount for a solvent-extraction plant and the operating costs for the ion-exchange plant were 81 percent of the solvent extraction plant.

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

FIGURE 2. - Overall view of the two mul-
tiple-compartment columns
systems.

MCIX columns are in commercial use
for gold recovery from cyanide solutions
using coarse activated carbon particles,
and prototype columns are in use for
uranium absorption and elution.

During the past year, the Bureau of
Mines has conducted experimental studies
to determine MCIX column design require-
ments for the absorption of uranium from
ammonium bicarbonate solutions similar
to those produced by in situ leaching
operations. Design criteria were also
developed for the elution of the loaded
resin with an ammonium chloride eluant.
This work is a continuation of similar
work on acid solutions (8). Both indi-
vidual and integrated absorption and
elution circuit arrangements were used
during this work.

EQUIPMENT

The main component of the absorp-
tion equipment used in the current
experimental program was a 2-inch-inside-
diameter (ID) by 16-foot-high glass col-
umn composed of 1-foot sections as shown
in figure 2. The elution studies used
1-, 2-, and 4-inch-ID columns. The
1-inch-ID column was composed of 6-inch-
high sections while the 2- and 4-inch-ID
columns were composed of 12-inch-high
sections. The maximum total height of
the 1- and 2-inch-ID columns was 22 feet
and 16 feet, while the maximum height of
the 4-inch-ID column was 17 feet. A
detailed flowsheet of the columns system
is shown in figure 3. Individual com-
partments were separated by orifice
plates that had openings equivalent to
approximately 6 percent of the column
cross-sectional area. The column was
constructed so that the compartment
height could be modified by substituting
full-diameter couplings for the orifice
plate couplings. Rosenbaum and Ross
state the following about the use of
these orifice plates:

ELUTION CIRCUIT   ABSORPTION CIRCUIT

FIGURE 3. - Flowsheet of the MCIX columns system.

"Observation has shown that when a regulated flow of solution passes upward through a column of closely sized resin at a rate sufficient to fluidize the resin, vertical mixing occurs over the length of the column. In effect, the entire column serves as a gently agitated reactor; and under these conditions, equilibrium stringently limits the absorption kinetics and efficiency. By assembling the resin column out of short segments, each separated by a perforated plate, vertical mixing still occurs within each segment of expanded-bed resin, but the net overall effect is of multiple-stage absorption or elution yielding more rapid and complete ion transfer than obtainable in a noncompartmented column of equivalent height.

"Under ideal operating conditions, each compartment is nearly full of fluidized resin in equilibrium with the upflowing solution. If the quantity of resin in any compartment is initially in excess of the equilibrium volume, the excess resin moves up through the perforated plate into the next compartment. If the quantity of resin is less than the equilibrium volume, the compartment will not

be completely filled. Downward movement of resin between compartments can occur only when the velocity of the solution flow through the holes in the perforated plates is less than the terminal settling velocity of the resin particles. An increase in solution flow rate or density will cause the resin bed to expand. When using coarse bead resins, minus 16-mesh plus 20-mesh (Tyler), perforated plates that have an open area of approximately 5 percent are satisfactory."

COLUMN OPERATION

The column is operated with a continuous upflow of solution except for the scheduled resin withdrawals. During these resin withdrawals, the automatic solution inlet valve closes, and the automatic resin outlet valve opens to discharge a programed amount of resin from the column. The discharge periods are approximately 3 to 6 seconds for the 1-inch-ID column and 6 to 12 seconds for the 2- and 4-inch-ID columns. The time interval between withdrawals from the absorption column is determined by the amount of resin to be discharged per withdrawal cycle, and this is a function of feed solution flow rate, feed solution concentration, and desired resin loading. The time interval between withdrawals from the elution column is also determined by the amount of resin to be discharged per withdrawal cycle; this time interval is a function of feed resin concentration, eluant flow rate, desired resin elution, and desired eluate grade. The actual time during which the resin discharge valve must be open to discharge a programed amount of resin is a function of the valve opening configuration and the bed expansion. During column operation, the solution flows were controlled by automatic instruments; and the open time interval on the resin discharge valve was set by trial and error adjustments. Figure 4 shows the sequence for one cycle of the resin discharge operation. The 4-foot compartment shown is made up of 1-foot glass sections and full-diameter couplings.

The solution flow rate controller is a critical component of the system. Some of the previous work did not have the precise flow rate control necessary to assure steady-state operation. Without this control, the resin migrates from one compartment to another at random, and the column conditions remain transient. Solution flow control for the 2- and 4-inch-ID columns was maintained by an automatic system which consisted of a magnetic flowmeter, a controller, and an air diaphragm valve. This system had a precision of ±1 percent of the maximum flow rate through the magnetic flowmeter. A head tank and rotameter maintained the flow rate for the 1-inch-ID column. Both the absorption and the subsequent elution were conducted at room temperature.

SOLUTION DESCRIPTION

The absorption column feed solution used for these tests simulated the composition of a uranium leach liquor obtained from a Texas in situ pilot plant operation. The composition and pH of this clear, simulated mill solution are listed in table 1.

TABLE 1. - Analysis of synthetic feed solution in grams per liter

U_3O_8	NH_4HCO_3	Mg	PO_4	K	Na	Cl	Al	Ca	SO_4	pH
0.15	1.0	0.12	<0.001	0.30	0.20	0.75	<0.01	0.20	0.75	7.2

O second	2 seconds	7 seconds

9 seconds	20 seconds	6C seconds

RESIN WITHDRAWAL CYCLE

O sec - start - resin bed at steady-state level.
9 sec - end of withdrawal.
60 sec - resin bed approaching steady state level

FIGURE 4. - Sequence of resin withdrawal cycle from MCIX absorption column.

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Laboratory tests were made to collect uranium equilibrium data during absorption and elution of a strong-base anionic resin. Kinetic data were determined for the elution step. This information was used for both the planning and the evaluation of the column operations.

The equilibrium isotherm for the absorption feed solution and Rohm and Haas Amberlite IRA 430 resin[6] is shown in figure 5. This isotherm was obtained by a crosscurrent, pyramid-type, absorption technique similar to that used in solvent extraction shakeout tests described by Treybal (fig. 6). The isotherm

FIGURE 5. - Equilibrium isotherm for uranium-NH_4HCO_3 solution and IRA 430 resin.

[6]Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

Steps

FIGURE 6. - Contact pyramid for resin and solution to obtain an equilibrium isotherm for the system.

FIGURE 7. - Elution equilibrium isotherm.

is extremely favorable for absorption in this system and indicates that low tails (<0.001 gram per liter (g/l) U_3O_8) are possible even with slightly loaded recycle resin (<10 g/l U_3O_8).

The equilibrium isotherm for the eluant and Amberlite IRA 430 is shown in figure 7. This isotherm was developed by the cross-current, pyramid-type, absorption technique. The eluant used for these tests was a 1.5-$\underline{M}$ NH_4Cl and 0.1-$\underline{M}$ NH_4HCO_3 solution with a natural pH of approximately 7.3.

Experimental kinetic data for the system are shown in figure 8. These kinetic data were obtained by contacting the eluant and the resin in a stirred reactor and withdrawing solution samples at predetermined times.

FIGURE 8. - Kinetic data on elution with ammonium chloride and IRA 430 resin.

ABSORPTION COLUMN TESTS

Operating characteristics of the countercurrent 2-inch-ID absorption column were determined using a coarse bead (approximately 16 by 20 mesh), strong-base anionic resin Amberlite IRA 430 with the synthetic feed solution previously described. The orifice plates were perforated with one centered 29/64-inch-diameter hole per plate, and the column was divided by these plates into various equal height sections for the different tests. The column was fitted with motorized valves actuated by electric timers to control the on-off flows of the solution and resin. Precision control of the solution flow rate was obtained with an automatic air diaphragm valve coupled to a magnetic flowmeter control system.

The following characteristics of the absorption column were studied:

1. Solution flow rate.

2. Compartment height.

3. Spacing above the resin bed.

Effect of Solution Flow Rate

The optimum solution flow rate per unit area of column diameter is a major consideration when designing a column system. The limiting maximum flow

rate is the flow that will carry resin over the top of the column. The minimum solution flow rate to the column is that which will provide the minimum amount of resin fluidization required for mechanical transfer of the resin during the withdrawal cycle. However, as the flow rate increases above this minimum, the solution residence time per foot of column height decreases. When this solution residence time decreases to the minimum time necessary for efficient absorption, a taller column may be required. Optimum economic design would require tradeoffs among the four parameters of column diameter, column height, solution flow rate, and uranium recovery.

FIGURE 9. - Effect of solution flow rate on uranium absorption (2-inch-ID column, 1-foot compartments, aqueous:resin 200:1).

FIGURE 10. - Effect of solution flow rate on uranium absorption (2-inch-ID column, 1-foot compartments, aqueous:resin 400:1).

The effect of solution flow rate is illustrated in figures 9-10 which show the solution column absorption profile for four solution flow rates with 1-foot compartments and aqueous-to-resin flow (A:R) ratios of 200:1 and 400:1. The A:R flow ratio is the ratio of solution flow rate to resin flow rate. For both A:R ratios, increasing the solution flow rate increased the length of column required to obtain the same amount of uranium absorption from the solution. The optimum solution flow rate for a column of approximately fourteen 1-foot compartments with a similar solution and resin would be 15 gallons per minute per square foot (gpm/ft^2).

This optimum can be attributed to solution retention time; that is, the solution must be in contact with the resin for a certain minimum time. With higher solution flow rates, the time requirement forces the absorption to take place in a higher compartment. The effect of this contact time can be illustrated by the experimental kinetic data shown in figure 11. As shown in figure 11, the

FIGURE 11. - Kinetic data on NH_4HCO_3-uranium solution and IRA 430 resin.

initial portion of the rate curve for uranium absorption from fresh feed solution onto unloaded resin is extremely steep. Changing the contact time of the solution and resin in this steep part of the curve by changing the flow rate of the solution would significantly affect the absorption efficiency.

Effect of Compartment Height

The multiple-compartment column can be considered as an assemblage of individual agitated stages in which absorption is achieved by a series of mass transfers from the solution to the resin. To be effective, the column must provide the required number of transfer stages, each having sufficient solution retention time for a reasonable approach to equilibrium mass transfer. As discussed in the previous sections, the solution retention is critical because the transfer of uranium from the solution to the resin sites is not instantaneous.

The stage height is of particular consequence because it can affect both the column construction cost and the inventory of resin required to fill the column.

Figure 12 shows the uranium extraction profile of the column when operating the 1- and 2-foot compartments. The solution flow rate was 10 gpm/ft^2 with a 200:1 A:R ratio. These curves indicate a marked decrease in absorption with the 2-foot compartments. By segregating the resin into compartments, extraction has been improved. Therefore, the optimum compartment height recommended is 1 foot.

FIGURE 12. - Effect of compartment height on uranium absorption (solution flow rate 10 gpm/ft², 2-inch-ID column, aqueous:resin 200:1).

FIGURE 13. - Effect of solution flow rate on spacing above resin bed in absorption column (2-inch-ID column, 1-foot compartments, aqueous:resin 400:1).

Spacing Above the Resin Bed

During the normal operation of the absorption column, eluted resin is fed into the top compartment of the absorption column and the resin level is maintained by an automatic controller. The eluted resin is the lightest resin in the column and, therefore, the resin bed in this top compartment is the most expanded bed in the column. As a resin increment is withdrawn from the bottom of the column, the resin in the rest of the column compartments moves down. When steady-state operation has been achieved, only a fixed amount of resin is transferred from compartment to compartment during each discharge cycle. As the resin in each individual compartment absorbs the uranium from the solution passing through that compartment, the density of the resin beads increases causing less bed expansion in that compartment. This decrease in bed expansion coupled with the transfer of equal numbers of resin beads gives rise to empty spaces above the resin in the compartments below the top compartment. Solution density changes are considered negligible (maximum 0.007 percent).

The open spacing above the resin beds for the various stages is shown in figure 13 for several solution flow rates at an A:R ratio of 400:1. Increasing the solution flow rate stretches the working length of the column. In other words, for the 7.5 and 10 gpm/ft², as shown in figure 10, the loading is completed in the first 5 and 8 feet of the column. No spacing occurs for these flow rates. For 15 and 20 gpm/ft² the loading occurs higher in the column, and the density change associated with it also occurs in the upper compartments.

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ELUTION COLUMN TESTS

Operating characteristics of the countercurrent elution column were determined using the strong-base anion resin Amberlite IRA 430 with the 1.5-$\underline{M}$ NH$_4$Cl and 0.1-$\underline{M}$ NH$_4$HCO$_3$ eluant previously described. For the individual tests the resin was loaded to approximately 60 g/l U$_3$O$_8$ from a uranyl carbonate circuit in a Utah uranium mill. To obtain a low effluent value from the absorption column, a resin eluted down to 5 g/l U$_3$O$_8$ was set as the requirement for the present series of tests. The orifice plates were perforated with one centered hole per plate as follows for the three column diameters tested:

1-inch-ID column = 5/16-inch-diameter hole.

2-inch-ID column = 29/64-inch-diameter hole.

4-inch-ID column = 15/16-inch-diameter hole.

The columns were divided by these orifice plates into various equal-height sections for the different tests. The columns were fitted with motorized valves actuated by electric timers to control the on-off flows of the solution and resin. Precision control of the solution flow rate was obtained with an automatic air diaphragm valve coupled to a magnetic flowmeter control system for the 2- and 4-inch-ID columns. A head tank and rotameter controlled the solution flow to the 1-inch-ID column.

The following characteristics of the MCIX elution column were studied: (1) solution flow rate, (2) A:R flow ratio, (3) column diameter, and (4) section height. Both solution flow rate and A:R flow ratio determine resin residence time; these relationships are discussed in the following sections.

Resin Residence Time

The amount of time the resin is in contact with the solution in the column is designated as the resin residence time. Test data indicate that this resin residence time shows a direct relationship with the degree of uranium elution. Resin residence time is plotted against overall column elution efficiency in figure 14. This resin residence time is a function of the following parameters:

1. Solution flow rate.

2. Aqueous-to-resin flow ratio.

3. Column height.

FIGURE 14. - Effect of resin residence time on elution efficiency.

The column height was held constant throughout the present series of tests and the effects of changes in the solution flow rate and the A:R ratio are discussed in the next sections.

Effect of Solution Flow Rate

There are major design considerations when determining the eluant flow rate. Because better elution is obtained with longer resin residence times, the lowest possible eluant flow rate is desirable. However, the minimum solution flow rate to the column is determined by the resin fluidization required for mechanical transfer of the resin during the withdrawal cycle. This flow rate is approximately 2.0 gpm/ft^2. As in the absorption column design, the optimum design would require tradeoffs among the four parameters of column diameter, column height, solution flow rate, and desired resin elution.

The effect of solution flow rate is shown in figures 15-18. The minimum eluant flow rate as mentioned previously is approximately 2.0 gpm/ft^2. Approaching this value would approximate the optimum eluant flow rate that would give the maximum resin residence time for a given column length while still being able to mechanically operate the resin withdrawal system of the column. The two eluant flow rates studied in this series of tests were 2.7 and 4.0 gpm/ft^2. These tests were made to investigate the effect of increased flow rates on elution. At a constant A:R flow ratio, increases in the eluant flow rate reduce the resin residence time. For the tests shown in figures 15 and 17 with A:R ratios of 10:1, the resin residence time was still adequate at the higher eluant flow rate of 4.0 gpm/ft^2 to allow resin elution of 90 percent or greater. However, at the A:R ratio of 6:1, resin elution is reduced significantly with the increase in eluant flow rate as shown in figures 16-18. Therefore, an eluant flow rate of 2 to 2.7 gpm/ft^2 is considered optimum and allows a maximum resin residence time while still permitting mechanical operation of the resin withdrawal system of the elution column.

FIGURE 15. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 1-foot compartments, aqueous:resin 10:1).

FIGURE 16. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 1-foot compartments, aqueous:resin 6:1);

FIGURE 17. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 5-foot compartments, aqueous:resin 10:1).

FIGURE 18. - Effect of solution flow rate on elution efficiency (2-inch-ID column, 5-foot compartments, aqueous:resin 6:1).

Effect of Aqueous-to-Resin Flow Ratio

The A:R flow ratio influences both the degree of resin elution and the eluate grade. The equilibrium isotherm in figure 7 shows about a 2:1 A:R flow ratio constraint when plotting a McCabe-Thiele operating line (2). In addition, a mechanical constraint involving the entrained eluant withdrawn with the resin limits the minimum A:R flow ratio to about 4:1. To obtain low effluent values from the absorption circuit, a well eluted resin (<5 g/l U_3O_8) from the elution column is desirable. Also desirable from the elution column is a high eluate grade (>10 g/l U_3O_8) for ease in the subsequent uranium precipitation and reduced eluant chemical requirements. In the present series of tests, ammonium uranyl carbonate precipitated out of eluates exceeding about 4.5 g/l U_3O_8. The addition of 0.05 $\underline{M}$ Na_2CO_3 to the eluant has been suggested to avoid this precipitation problem and to allow eluate grades of at least 12 to 14 g/l U_3O_8. This modification should be considered for future investigation.

As mentioned previously, the effect of the A:R ratio directly determines the resin residence time. To obtain a high-grade eluate (>10 g/l U_3O_8) the A:R ratio would have to be 6:1 or less when using an entering resin concentration of approximately 50 to 60 g/l U_3O_8. With the minimum solution flow rate of 2.0 gpm/ft^2, the desired A:R ratio of 6:1 or less limits the final uranium concentration on the resin at the column heights tested. With a taller column sufficient resin time would be obtained with the minimum eluant flow rate and an A:R ratio of 4:1 to 6:1.

The effects of the A:R ratio from 10:1 to 6:1 for different flow rates, section heights, and column diameters are shown in figures 19-24. In every comparison of elution performance, the reduced A:R ratio of 6:1 decreased the elution efficiency. As stated previously, with a taller column sufficient resin residence time could have been obtained at 6:1 A:R and elution efficiency increased.

Effect of Column Diameter

Column diameter is determined by the eluant flow rate, the amount of resin to be eluted, and the A:R ratio. Wall effects that might hinder mixing in the smaller diameter columns and change the elution characteristics were studied in this series of tests. Tests utilizing the same conditions were run using 1-, 2-, and 4-inch-ID columns. The results from these tests are shown in figures 25-26 and indicate very little difference in elution efficiency between the three column diameters. Because of differences in the total length of column used for the various experiments, the abscissa of the graphs are marked with offset scales.

FIGURE 19. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 1-foot compartments, solution flow rate 2.7 gpm/ft ^{2}).

FIGURE 20. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 1-foot compartments, solution flow rate 4.0 gpm/ft ^{2}).

FIGURE 21. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 2-foot compartments, solution flow rate 2:7 gpm/ft²).

FIGURE 22. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 5-foot compartments, solution flow rate 2:7 gpm/ft²).

FIGURE 23. - Effect of aqueous-to-resin flow ratio on elution efficiency (2-inch-ID column, 5-foot compartments, solution flow rate 4:0 gpm/ft²).

FIGURE 24. - Effect of aqueous-to-resin flow ratio on elution efficiency (1-inch-ID column, 2-foot compartments, solution flow rate 2:7 gpm/ft²).

FIGURE 25. - Effect of column diameter on elution efficiency (1-foot compartments, solution flow rate 2.7 gpm/ft², aqueous:resin 10:1).

Effect of Compartment Height

In the elution column, separation into stages is critical. Resin density changes are favorable in the absorption column, but the reverse is true in the elution column. Loaded resin, which is the highest density resin, is transferred from the bottom of the absorption column to the top of the elution column. As the resin moves down through this column, it is eluted and its density decreases thereby increasing its bed expansion. This bed expansion can cause the lighter resin beads to be pushed into the next higher compartment which contains denser resin beads. If this trend continues, top-to-bottom mixing (heavy loaded beads to the bottom and eluted beads to the top) would occur and be detrimental to the elution operation. The 1.3 percent density change of the solution is negligible. Exact full resin withdrawals are very important in elution. Fractional resin withdrawals draw out the heavy or more loaded resin in the bottom compartments leaving the more eluted resin in the column.

FIGURE 26. - Effect of column diameter on elution efficiency (2-foot compartments, solution flow rate 2.7 gpm/ft², aqueous:resin 6:1).

As shown in figure 27, when using an A:R ratio of 10:1 and holding all other variables constant, the increase from 1- to 2-foot section heights had little effect on elution efficiency. When the section height was increased to 5 feet, a significant decrease in elution efficiency occurred. This decrease also occurs at a higher flow rate of 4.0 gpm/ft² as shown in figure 29. In figure 28, which shows tests having an A:R ratio of 6:1, the increase of the section height from 1-foot to the 2- and 5-foot heights caused a marked decrease in elution efficiency. When the A:R ratio is decreased from 10:1 (fig. 27) to 6:1 (fig. 28), the resin residence time becomes more critical. As shown in figure 27, ample time allowed the elution efficiency in the 2-foot section height to approach the 1-foot results. The results shown for the 5-foot sections in figures 27-28 and the 2-foot sections in figure 28 indicate that increased resin residence time could not overcome the detrimental effect of the mixing in the longer sections. This is also shown at a higher flow rate in figure 30. The data indicate that a compartment height of 1-foot produced the most efficient elution per foot of column height over a range of operating conditions.

FIGURE 27. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 2.7 gpm/ft², aqueous:resin 10:1).

FIGURE 28. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 2.7 gpm/ft², aqueous:resin 6:1).

FIGURE 29. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 4.0 gpm/ft², aqueous:resin 10:1).

FIGURE 30. - Effect of compartment height on elution efficiency (2-inch-ID column, solution flow rate 4.0 gpm/ft², aqueous:resin 6:1).

SUMMARY

This work was done to support recent developments of in situ ammonium bicarbonate leaching of uranium ores. The application of the multiple-compartment, ion-exchange columns system provides an efficient method of processing the leach liquor.

For the 16-foot tall absorption column (fourteen 1-foot compartments) with the recommended 1-foot compartment height, a feed solution flow rate of 15 gpm/ft^2 with an A:R ratio of 400:1 was considered optimum and achieved 99 percent absorption of uranium from the 0.15-g/l U_3O_8 leach liquor. This provides a 60-g/l U_3O_8 loaded resin for the elution circuit.

For the elution circuit a 16-foot-tall column with the recommended 1-foot compartment height and an eluant flow rate of 2.7 gpm/ft^2 would attain about 92 percent elution of uranium from the resin. This is at an A:R ratio of 6:1 and would provide a 9-g/l U_3O_8 eluate grade and a 5-g/l U_3O_8 exiting resin concentration. Higher eluate grades and/or lower exiting resin concentration could be obtained by increasing the column length. Resin residence time was the critical factor in determining resin elution efficiency. The indicated resin residence time required to produce an eluted resin containing <5 g/l U_3O_8 was 160 to 190 minutes.

REFERENCES

1. George, D. R., J. R. Ross, and J. D. Prater. Byproduct Uranium Recovered With New Ion-Exchange Techniques. Min. Eng., v. 20, January 1968, pp. 1-5.

2. McCabe, W. L., and J. C. Smith. Unit Operations in Chemical Engineering. McGraw-Hill Book Co., Inc., New York, 2d ed., 1967, pp. 526-530.

3. Merritt, R. C. The Extractive Metallurgy of Uranium. U.S. Atomic Energy Commission, Colo. School of Mines Research Inst., Golden, Colo., 1971, 576 pp.

4. Pizarro, R., J. D. McBeth, and G. M. Potter. Heap Leaching Practice at the Carlin Gold Mining Co., Carlin, Nev. Solution Min. Symp., AIME, Dallas, Tex., ch. 19, 1974, pp. 253-267.

5. Rosenbaum, J. B., and D. R. George. Cost Reductions in Ion-Exchange Processing of Uranium Ores--The Recovery of Uranium. Proc. IAEA Symp., Sao Paulo, Brazil, August 1970, pp. 297-309.

6. Rosenbaum, J. B., and J. R. Ross. A Countercurrent Column for Fluid-Bed Ion Exchange of Uranium Ore Slurries. Internat. Symp. on Hydrometallurgy, AIME, Chicago, Ill., ch. 20, 1973, pp. 535-551.

7. Ross, J. R., and D. R. George. Recovery of Uranium From Natural Mine Waters by Countercurrent Ion Exchange. BuMines RI 7471, 1971, 17 pp.

8. Traut, D. E., I. L. Nichols, and D. C. Seidel. Design Criteria for Uranium Ion Exchange in a Fluidized System. Trans. AIME, v. 260, March 1976, pp. 24-28.

9. Treybal, R. E. Liquid Extraction. McGraw-Hill Book Co., Inc., New York, 2d ed., 1963, pp. 361-368.

DETERMINING THE SOLUBILITY OF ALUMINUM HYDROXIDE IN ALUMINATE SOLUTIONS AND THERMODYNAMIC ASSESSMENT OF SOLUTION STABILITY

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In general, alumina is produced by the Bayer method using a technology which contains two basic processes (leaching and aluminate decomposition) and a series of ancillary operations designed to prepare the raw material and the intermediate products. The speed of the heterogeneous processes of aluminum hydroxide solution during bauxite leaching and of aluminum hydroxide crystallization during decomposition of the aluminate solution can be described by the heterogeneous kinetics equation

$$v = kF (C_0 - C),$$
(1)

where k is the coefficient of solution or crystallization speed, F is the phase interface, C is the concentration of dissolved material in the solution, and C_0 is the concentration of material in a saturated (equilibrium) solution, its solubility.

Under conditions in which thermodynamic factors have a decisive effect, i.e., the reaction is limited by attainment of the equilibrium state, the absolute supersaturation of the solution may serve as a numerical index defining the stability of the solution [1]:

$$\beta = C - C_v.$$
(2)

This has a negative value for an unsaturated solution, and can be used to define the capacity of a solution to dissolve or to precipitate the dissolved material quantitatively in absolute units.

Equation (1) takes the following form when applied to alumina production processes:

$$\frac{da}{d\tau} = kF (a_{eq} - a),$$
(3)

where a and a_{eq} are the Al_2O_3 concentrations in the aluminate solution and in its corresponding equilibrium solution respectively.

However, when aluminum hydroxide passes into or out of aluminate solution a change takes place in the weight and volume of the solution, accompanied by changes both in the aluminum oxide concentration and in the alkali concentration in the solution, in spite of the fact that the amount of alkali in it does not alter.

This interrelationship makes it impossible to define the amount of aluminum hydroxide added to or taken from a unit of volume or weight of two aluminate solutions unequivocally by reference to the difference in the aluminum oxide concentrations of these solutions. In addition, if allowance is made for the fact that it is the amount of alkali in the solution that determines the solubility of aluminum hydroxide in it, it becomes clear that the aluminate solution alkali concentration in explicit form cannot be used for quantitative assessment of the potential of a solution to dissolve aluminum hydroxide.

Consequently the concentration values for an equilibrium aluminate solution, though defining the state of the solution as a system with zero chemical potential, do not permit a quantitative assessment of the deviation of an actual solution from that state. In other words, the use of the term $(a_{eq} - a)$ in (3) is incorrect.

The most reliable experimental data and observations in research on aluminate solutions are reconcilable with recognition of the ionic nature of the solution. Let us consider the aluminate solution as a caustic soda solution in which the alkali is present in the form of Na^+ and OH^- ions; as aluminum oxide dissolves in it, the OH^- ions are replaced by AlO_2^- ions according to the equation

$$Al_2O_3 + 2OH^- = 2AlO_2^- + H_2O.$$
(4)

In this case the equilibrium aluminate solution can be described as an equilibrium homogeneous system consisting of AlO_2^- and Na^+ ions in an aqueous medium. The corresponding ion concentrations in such a solution can be calculated by reference to known concentrations for an equilibrium aluminate solution

$$C_N = \frac{1000 n}{31 \left(100 - \frac{46}{62} n - \frac{118}{102} a\right)} g$$
(5)

$$ion/1000 \, g.H_2O,$$

$$C_A = \frac{1000a}{51\left(100 - \frac{46}{62}n - \frac{118}{102}a\right)} \text{ g} \cdot$$
$$\text{ion/1000 g H}_2O,$$

(6)

where n and a are the aluminate solution Na_2O and Al_2O_3 concentrations, wt. %.

The chemical potential of each of the ions can be described in the following form [2]:

$$\mu_a = \mu_a^0 + RT \lg \gamma_a \cdot C_A.$$

(7)

$$\mu_n = \mu_n^b + RT \lg \gamma_n \cdot C_N.$$

(8)

where μ_a^0 and μ_n^0 are the chemical potential of the AlO_2^- and Na^+ ions respectively in an infinitely dilute aqueous solution, R is the universal gas constant, T is the temperature, and γ_a and γ_n are the respective activity coefficients of AlO_2^- and Na^+ respectively.

In view of that fact that aluminum hydroxide and oxide are practically insoluble in water it may be assumed that $\gamma_a = 1$.

It is assumed in the case of salts whose cations and anions have similar physical properties that cation activity is equal to anion activity [2]. This permits the assumption as a first approximation that the activity coefficient γ_n is equal to the average activity coefficient for NaOH. Data on the activity coefficients of NaOH solutions with a concentration of 0 - 17 mole per 1000 g of water in the 0 - 70° C range are given in [3].

The following may be written for an equilibrium aluminate solution, as for any equilibrium system:

$$\nu_a\mu_a + \nu_n\mu_n = 0,$$

(9)

where $\nu_a = \nu_n = 1$ are the respective stoichiometric coefficients.

It follows from (9), taking account of (7) and (8), that

$$C_A = e^{\frac{\mu_n^0 - \mu_a^0}{RT}} \gamma_n C_N.$$

(10)

where C_A is the concentration of AlO_2^- ions in the equilibrium (saturated) aluminate solution.

The C_A value defines the solubility of aluminum oxide in NaOH solution according to its concentration and temperature.

Relationship of aluminate oxide solubility to NaOH solution activity at various temperatures, °C:
1) 30; 2) 40; 3) 60;
4) 70.

The Figure shows the relationship of solubility of aluminum oxide in NaOH solution to the activity of that solution. The relationships were plotted from concentration values for equilibrium aluminate solutions at 30, 40, 60, and 70° C [4-8], converted using formulas (5,6). The γ_n values were calculated from reference data in [3] according to the C_N concentration and the temperature.

The practically linear nature of the relationship for a constant temperature leads to the conclusion that the solubility of aluminum oxide in NaOH solution at a given temperature is directly proportional to the activity of that solution.

In alumina production by the Bayer method, at temperatures not exceeding 100° C aluminum hydroxide trihydrate is the principal product of reaction between the solid phase and the solution, in both the solution and the decomposition processes. In these circumstances three molecules of water are introduced or taken out with each aluminum oxide molecule, which amounts to 0.529 g of water with each gram of aluminum oxide. The change in the NaOH solution concentration and the corresponding change in its activity caused by this phenomenon can be taken into account if the concentration of the NaOH solution is calculated by the formula

$$N = \frac{129n}{100 - 1,529a} \% .$$

(11)

In these circumstances the following amount of aluminum hydroxide trihydrate is dissolved in each 100 g of such a solution:

$$A = \frac{152,9a}{100 - 1,529a} \text{ g} \cdot$$

(12)

Obviously the A values calculated by formula (12) for equilibrium aluminate solutions will be the solubilities of aluminum hydroxide trihydrate in NaOH solutions with concentrations calculated by formula (11).

Analysis of empirical data on NaOH solution activity coefficients showed that the relationship of γ_n to concentration and temperature can be fairly well represented by an expression in the following form in the range corresponding to alumina production by the Bayer method:

$$\gamma_n = b_1 + b_2 N + b_3 T + b_4 NT + b_5 N^2. \tag{13}$$

Taking account of (10), the analytic expression for the relationship of aluminum hydroxide trihydrate solubility to concentration and temperature will take the following form:

$$A_p = e^{\frac{b_6}{T}} (b_1 + b_2 N + b_3 T + b_4 NT + b_5 N^2) N, \tag{14}$$

where b_i are constants.

In view of the fact that the range of changes in the variables A_p and N is great and not evenly represented by experimental findings, the minimum sum of the squares of the relative errors should be chosen as the criterion of approximation in seeking the coefficients in (14).

Identification of model (14) is made difficult by the fact that not all the coefficients are included in it linearly. Generally known methods of minimizing the functionals such as gradient or random searches are very laborious, requiring a large number of mathematical iterations. These methods often fail to ensure good convergence.

A method was used to find the b_i coefficients included in model (14) in which the parameter evaluation algorithm in matrix form is reduced to the following.

Let us use the following notation: Y is the m column vector of measurements of the output variable; $\psi (x,b)$ is the empirical formula; B is the p column vector of the unknown parameters; X - m x z is the matrix of measurements of the output variable.

A linearized problem is solved at each step in the iteration process, for which the (p = 1) vector of parameters B_i, $i = 1, 2, \ldots, p$, (p + 1), is recorded. The following procedure meets the standard of the method of least squares.

1. The error column vectors are computed

$$D_l = Y - \psi (x,\ B_l),\quad l = 1,\ 2,\ \ldots,\ p,\ (p+1).$$

2. Matrices are compiled

$$T = |D_1 | D_2 | \ldots | D_l | \ldots | D_{p+1}|$$

$$H = \left[\frac{B_1}{1} \Big| \frac{B_2}{1} \Big| \ldots \Big| \frac{B_l}{1} \Big| \ldots \Big| \frac{B_{p+1}}{1} \right].$$

3. The matrix of coefficients of equations of hyperplanes corresponding to the linearized problem

$$L = TH^{-1}.$$

is computed.

4. Matrix L is broken down into matrices S (the first p columns) and P: [the (p = 1)-th column, the signs of the column elements being replaced by the opposite signs].

5. The next approximation to the desired solution is calculated by the method of least squares:

$$B^* = -(S'S)^{-1} S'P.$$

6. An iteration process is formed by defining a new set of parameters taking account of B* and the repetition of the procedure set out, if the condition of process termination has not been fulfilled.

It is known from [9] that algorithms similar to that discussed have a tendency to degenerate when the parameter vectors are replaced one at a time. To avoid this and to make computation of matrix L less laborious, a simplex algorithm was developed; a feature of this algorithm is the use of a parameter basis in the form of a regular p-dimensional simplex. The orthogonal properties of the latter make it possible to obtain matrix L without solving systems of equations in explicit form. The next approximation of B* (or the point obtained with allowance for it) is used as the center of a new simplex, the size of which varies according to the course of search for the solution.

An analytic expression for the solubility of aluminum hydroxide trihydrate was obtained by processing data on aluminate solution equilibrium composition on a "Nairi" computer, using the algorithm given:

$$A_{ph}= e^{-\frac{3131}{T}}\,(-4387.67 + 1644.15N + 22.27T - 4.36NT + 1.606N^2)\,N,$$

(15)

where T is the temperature, K.

The results computed using expression (15) show a fairly close coincidence with the equilibrium composition data if allowance is made for the fact that these data were obtained by a wide range of both Soviet and foreign researchers, using various methods. The error exceeds 7% in only 10 of the 128 equilibrium composition values processed.

The overwhelming majority of deviations do not exceed 5%. The standard deviation in relation to the range of changes in solubility examined is 1.2%.

The relationships obtained can be used to express analytically the absolute supersaturation of aluminate solution with aluminum hydroxide trihydrate. If allowance is made for the fact that there are (100 - 1.529 a) grams of NaOH solution with concentration N in 100 g of aluminate solution, we can write the following, taking account of (2):

$$\beta = (A - A_p)\,\frac{100 - 1.529a}{100} = \left|1.529a - A_p\,\frac{100 - 1.529a}{100}\right.$$

(16)

The absolute supersaturation β computed in accordance with (16) quantitatively defines the stability of the aluminate solution. It defines the potential capacity of the solution to dissolve or to precipitate aluminum hydroxide trihydrate.

An adequate mathematical model of alumina production processes can be constructed on the basis of Eq. (3), using supersaturation β, with a view to optimizing these processes.

Work is in progress at present at the Dneprovsk Aluminum Plant to set up an automation system for a number of processes in alumina production, using the results discussed.

REFERENCES

1. E. V. Khamskii, Crystallization from Solutions. Leningrad, Nauka, 1967, 150 pp.; ill.
2. I. A. Izmailov. Electrochemistry of Solutions. Moscow, Khimiya, 1966, 930 pp., ill.
3. G. Harned and B. Owen. Physical Chemistry of Electrolyte Solutions. Moscow, Izd-vo Ionostrannoi Literatury, 1952, 628 pp.; ill.
4. R. Fricke and P. Jucaitis. Zs. Anorg. Chem., 1930, vol. 191, pp. 129-149.
5. A. Russell, J. Edwards, and C. Taylor. J. Metals, 1955, v. X, pp. 1123-1128.
6. V. A. Mazel'. Alumina Production. Moscow, Metallurgizdat, 1955, 431 pp.; ill
7. A. N. Lyapunov, A. G. Khodakov, and Z. G. Galkina. Tsvetnye Metally, 1964, No. 3, pp. 48-51.
8. S. M. Tsirlina. Legkie Metally, 1936, No. 7, pp. 28-37.
9. B. T. Polyak. Ekonomia i Matematicheskie Metody, 1967, vol. 3, No. 6, pp. 881-902.

Dodecyl Mercaptan: A Superior Collector for Sulfide Ores

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Abstract—*Normal dodecyl mercaptan was evaluated as a collector for flotation of sulfide minerals and precious metals. The reagent is from the class of normal mercaptoalkanes (n-alkyl thiols), and is commercially available in the form of a mixture of n-dodecyl mercaptan, the primary constituent, and a water-soluble dispersant, under the trade name Pennfloat(TM) 3. * Reported are results of bench-scale flotation experiments on many commercially treated base metal and precious metal sulfide ores. Dosages, points of addition, and flotation pH were among the variables studied. Most notable results were increased copper, molybdenum, and precious-metals recoveries. Dosages of dodecyl mercaptan on some ores were considerably lower than required for conventional collectors. The reagent was shown to be a highly effective and versatile collector on virtually all of the more than 30 sulfide ore types examined.*

Introduction

An analysis of a commercial flotation operation cannot be undertaken without considering the effectiveness and characteristics of the mineral collector. While many operations show satisfactory metallurgical performance, others are characterized by low recoveries of certain metals. Factors such as inadequate liberation, surface oxidation of sulfide minerals, or the adverse or depressing action of some modifying agents, often inhibit high recoveries. Under such conditions, it is the collector that often controls the ultimate metallurgical performance.

Perhaps the best example of the limitations of some collectors is in byproduct recovery of molybdenum from copper ores. Recoveries at many plants have traditionally been low, being ascribed to molybdenite locking with gangue minerals or because of low ore grades. To illustrate the impact of low recoveries, consider that in 1976, over 204 Mt of porphyry copper-molybdenum-bearing ore were milled in the US. Of the nearly 40 kt of contained molybdenum metal, fully 51%, or about 20 kt of molybdenum, were discharged to tailings areas. In today's metal markets, this translates to a considerable dollar value. A similar situation exists for other metals (copper, nickel, precious metals, etc.) although to lesser extents. What is required to increase the recoveries of molybdenum and other metals is a mineral collector with powerful adsorption properties.

One type of collector was found to be very efficient for sulfide mineral flotation and, moreover, has resulted in significant increases in recoveries of molybdenum, copper, precious metals, and other metals from numerous ore types.

Earliest studies of dodecyl mercaptan were done at the laboratories and pilot plant of Palabora Mining Co. in South Africa by A. Wiechers. The reagent is presently used in Palabora's main concentrator, resulting in a 5% increase in copper recovery over that obtained with more conventional collectors.

In early 1977, Pennwalt Corp. authorized Hazen Research Inc. to begin studies of a newly developed flotation reagent, normal dodecyl mercaptan, as a collector for sulfide minerals. Dodecyl mercaptan, a long-chained collector from the class n-alkyl thiols, is now commercially available from Pennwalt Corp. under the trade name Pennfloat 3. The commercial reagent is a

mixture of n-dodecyl mercaptan, the primary constituent, and a water-soluble dispersant.

Initial studies with dodecyl mercaptan at Hazen Research's Tucson laboratories centered on copper-molybdenum ores from US operations. After encouraging initial results on these ores, especially with respect to increased metal recoveries, study of dodecyl mercaptan branched out to other types of sulfide ores, including several from Canada.

The object of the research program was to evaluate normal dodecyl mercaptan, in the form of Pennfloat 3, as a collector for a variety of base metal and precious metal sulfide ores in direct comparison with other collectors under bench-scale conditions. This direct approach was chosen in lieu of more fundamental studies, to offer an early indication of the collector's characteristics and its potential applicability in commercial flotation operations. Such practical data would be available for more detailed optimization studies at the commercial operation.

Reagent Description

Pennfloat 3, in its commercially available form, is a mixture of n-dodecyl mercaptan, the primary constituent, and a water-soluble dispersant. The reagent is used full strength and can be handled and distributed in the plant in the same manner as other full strength collectors. Pennfloat 3 has a flash point of greater than 93°C and a specific gravity of 0.873. The reagent has a stable and lengthy shelf life and is biodegradable.

Experimental Procedures

Samples of various ore types designated for study were furnished by commercial operators. A representative sample of mill feed (grinding circuit feed) was obtained. Upon receipt at Hazen's Tucson laboratory, the ore was prepared for test work and head assays examined initially for confirmation with the operator's estimated values.

Standard or operational laboratory flotation conditions, furnished by the operators, were used for initial tests on most ores. On some, for which no laboratory information was supplied, bench conditions were designed to simulate typical operating practice.

A requirement was that no modifications would be made to the operators' standard conditions, such as fineness of grind, flowsheet, flotation times, and major reagent practice (pH modifiers, depressants, activators, etc.). Occasionally, however, minor changes were made to the reagent scheme to examine other conditions and provide additional data on the collector.

Initial tests on each ore involved control tests to reproduce, as possible, typical results using standard laboratory conditioning and reagents, and to provide data for direct comparison with tests using dodecyl mercaptan (Pennfloat 3). The correlation

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Ore	Collector Type	Dosage, g/t	Product	Weight %	Assays, g/t Au	Distribution % Au
A	Z-11, Z-6	105	Rougher concentrate	15.54	77.83	89.5
			Rougher tailing	84.46	1.68	10.5
	Z-11, Z-6	60	Rougher concentrate	16.28	73.71	93.3
	Pennfloat(TM)3	40	Rougher tailing	83.72	1.03	6.7
B	Z-11, Z-6	100	Rougher concentrate	11.25	36.00	95.4
			Rougher tailing	88.75	0.240	5.0
	Z-11, Z-6	50	Rougher concentrate	12.03	38.69	97.7
	Pennfloat(TM)3	20	Rougher tailing	87.97	0.103	2.3
C	Z-11	55	Bulk concentrate	8.76	19.54	84.6
			Tailing	91.24	0.411	15.4
	Z-11	45	Bulk concentrate	10.67	15.43	87.0
	Pennfloat(TM)3	25	Tailing	89.33	0.274	13.0

Copper rougher concentrate plus pyrite rougher concentrate

Precious Metal Ores.

Gold ores. Dodecyl mercaptan (Pennfloat 3) was evaluated as a collector for flotation of gold values in ores from three foreign operations. The occurrence of gold values in each ore was largely associated with iron sulfides; discrete gold was uncommon. The results of test comparing dodecyl mercaptan with the standard xanthate collectors are shown in Table 4.

The most effective use of dodecyl mercaptan was in conjunction with reduced dosages of the operational collectors (xanthates). Gold recoveries were from 2.4 - 4% greater than obtained with operational collectors. Although seemingly only a slight increase in gold recovery, the 2.4% increase, for example, would represent a potential increase in operating revenue of approximately $840 000 annually (based upon 2.3 kt/d and gold value of $8/g.

The experimental collector was also very effective as a primary collector in the absence of xanthates. High gold recoveries, comparable to those obtained under standard conditions, were obtained with dosages of dodecyl mercaptan as low as 70% of standard collector dosages.

It was concluded from these studies that dodecyl mercaptan was very effective for flotation of gold values associated with iron and other sulfide minerals. The potential for applying the reagent successfully to other ore types which contain gold values was indicated.

Platinum group metals ore. The effectiveness of dodecyl mercaptan (Pennfloat 3) for flotation of platinum group metals,

gold, and nickel values was examined on one ore from a foreign operation. The ore was characterized by its very low sulfide mineral content and by an abundance of talc. Test results comparing dodecyl mercaptan with the operational collectors are shown in Table 5. Grade-recovery curves for nickel, platinum group metals, and gold flotation with dodecyl mercaptan are shown in Figs. 5-7.

Dodecyl mercaptan was found effective for flotation of platinum group metals, gold, and nickel, and resulted in significantly improved recoveries. Highest recoveries were obtained using the experimental collector in conjunction with the operational collector, sodium isobutyl xanthate. Nickel and platinum group metal recoveries increased approximately 13% and 10%, respectively, while gold recovery increased about 27% over those obtained with xanthate alone.

Dodecyl mercaptan was also effective as a primary collector on this ore. Recoveries of nickel and precious metals increased over those of the operational collector, but not to the same extent as with dodecyl mercaptan as the auxiliary collector.

Although metal recoveries increased with dodecyl mercaptan, selectivity in rougher flotation was reduced as a result of excess talc flotation. Higher dosages of the talc depressant, sodium carboxymethyl cellulose, would likely be required to control selectivity. However, in cleaning tests, conducted with standard talc depressent dosages, upgrading of rougher concentrates provided concentrate grade of 7 - 9% Ni, or just slightly lower than in the control test.

In light of the obvious high value of platinum group metals and gold, the use of dodecyl mercaptan appears attractive on this and other similar ores.
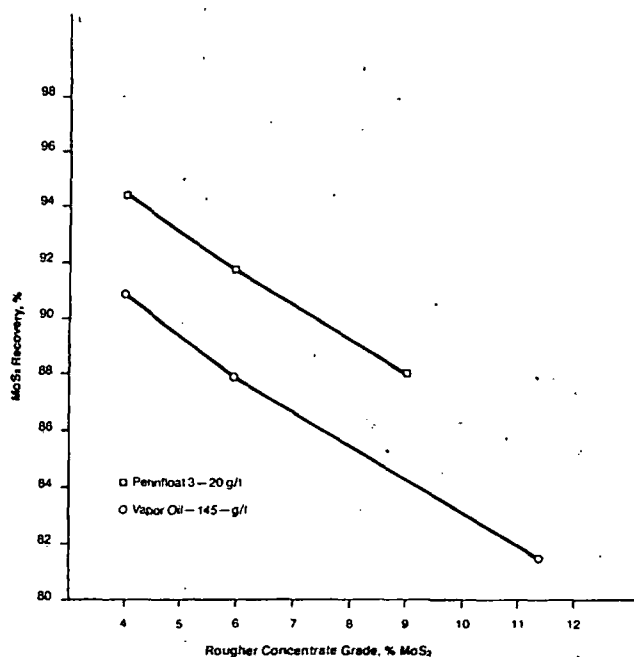
Fig. 4—Molybdenum grade-recovery relationship primary molybdenite ore.
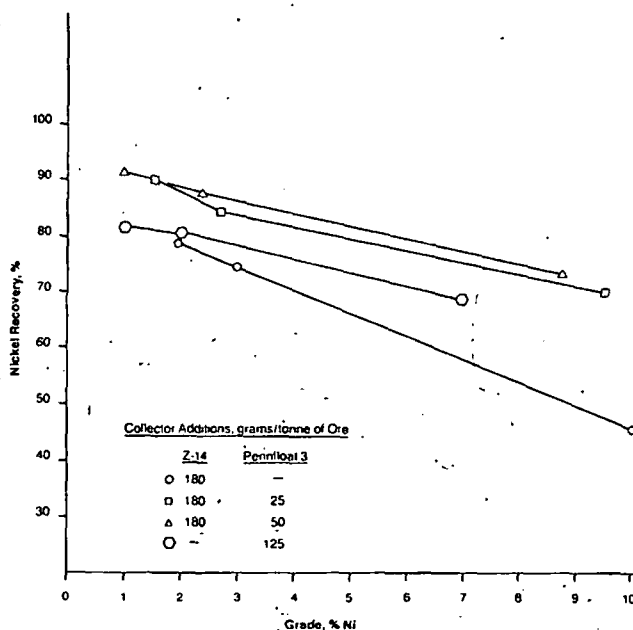
Fig. 5—Nickle grade—recovery relationship.

Developments in Solution Mining Portend Greater Use for In Situ Leaching

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In this year's review, the concept of solution mining has been expanded to include total solution as well as the technology of leaching, or partial solution methods. Leaching methods continue to make strides in the processing of metallic minerals, particularly in copper and uranium production. No quantitative data are available on the increase of leach operations; however, it is known that there were more systems installed in 1969 and that the estimated 15% of U.S. domestic production of copper produced in 1968 was by leach methods.[1] While the number of publications appearing during the year were few,[2,3] there were special sessions in this field at the AIME Annual Meeting and SME Fall Meeting in 1969 and more scheduled for these meetings in 1970. Significant areas that should be mentioned are: the continuing interest in bacteria to convert sulfide sulfur to acid thus reducing reagent costs in both copper and uranium sulfide ores, the exploration of leaching agents other than common mineral acids or alkaline solutions,[4] kinetic studies of leach mechanisms and the development of microfractures for increased leach solution penetration by use of chemical or atomic explosives.[6,7]

Nuclear Explosives and Solution Mining as a Team

The experimental copper leach "Project Sloop" proposed by Kennecott,[8] using an atomic explosive to fracture the low grade oxidized copper zone near Safford, Ariz., continued to be postponed due to lack of funds and other problems. The experiments in gas sands in New Mexico and Colorado, "Gasbuggy" and "Rulison," were completed successfully so that some of the containment objections have been minimized.

The status of technology of total solution mining was well reviewed in papers given at the AIME Annual Meeting, Solution Mining Symposium in February, and the papers given at the Third Symposium on Salt, April 21-24, 1969, held at Cleveland, Ohio, sponsored by the Northern Ohio Geological Society and the Solution Mining Research Institute. The importance of solution mining of salt is reflected in the growing number of brining operations which accompany salt production for the chemical industry. It is estimated that approximately 50% of the salt which goes into chlorine production is now produced by brining or solution mining methods. Of major significance is the growing number of LP gas storage installations which are located in salt beds. Of the 236 LP gas storage facilities in operation in 1966, 177 were located in salt strata. Of these, 76 were single cavities in salt domes and 101 were in bedded salt. The storage capacity in salt represented 110 million bbl of the 125 million total capacity.[9] The storage capacity of LP gas is projected to reach 150 million bbl capacity by 1970,[10] thus one can anticipate a continuing development of new cavities. The solution mining of potash has been accomplished in Canada by Kalium for a number of years. The application of hydraulic fracturing and controlled potash removal in these beds was reported at the Solution Mining Symposium.[17]

Two Well Systems Capture The Most Attention

The mechanism of solution of salt for a single well seems to be sufficiently understood to satisfy present operations. Husband and Shook, of the Saskatchewan Research Council,[11] reported on their continuing research of the single well system. Current research and development seems to have turned to interest in the two-well system. On the theoretical side, Jessen presented his work on a multiwell system including the solution mechanisms taking place in horizontal and vertical fractures.[12,13] The technique of connecting wells by hydraulic fracturing and removing the soluble salt seems to be sufficiently well established to practice on an operational basis.[14,15,16,17] Brief mention of solution removal of trona and borax was reported at the Third Salt Symposium.

In summary, the technique of leaching of metallic ores, particularly in copper, continues to grow with uranium leaching also being important. In-situ leaching is in an interesting experimental stage. Its application to various field situations can be anticipated. In the total solution extraction area, there is considerable evidence that the mechanisms of removal in the multiwell, in-situ system are receiving more thorough study and that the hydraulic fracturing technique is being used as a practical operative technique. The next few years should show some interesting developments in solution extraction methods, particularly applications in in-situ recovery.

References

1 Potter, George, "Solution Mining," Mining Engineering, Vol. 21, February 1969, p 68.
2 Allman, M. B., and Harris, J. A. "An Experiment in Heap Leaching," Mining Congress Journal, Vol. 55, 1969, p 28.
3 McGregor, R. A., "Uranium Dividends from Bacterial Leaching," Mining Engineering, Vol. 21, 1969, p 56.
4 Johnson, P. H., and Bhappu, R. B., "Solution Mining—A Study of Leaching Agents," Paper presented at the AIME February Meeting, 1969.
5 Grenstead, R. R., Davis, J. C., and Chadsworth, R. K., "Mixed Ionic Extractants—Organic Salts as Extractants for Inorganic Salts," Paper presented at the AIME February Meeting, 1969.
6 Griswold, George, "Rock Fracturing Techniques for In-Place Leaching," Paper presented at the AIME February Meeting, 1969.
7 Rabb, D. D., "Penetration of Leach Into Rocks Fractured by a Nuclear Explosive," Paper presented at the AIME February Meeting, 1969.
8 Michaelson, C. D., "Outlook for Sloop," Mining Congress Journal, Vol. 55, No. 2, 1969, p 142.
9 "LP Gas Underground Storage Capacity," Oil & Gas Journal, Vol. 63, No. 42, 1965, pp 115-118.
10 Katz and Coats, "Storage in Salt Cavities," Underground Storage of Fluids, 1968, Ulrich's Books, Inc., Ann Arbor, Michigan.
11 Husband, W. H. W., and Shook, C. A., "Mass Transfer for High Vertical Surfaces to Liquids Under Free Correction Conditions," Paper presented at NOGS, Third Salt Symposium, 1969.
12 Jessen, F. W., "Mechanism of Salt Solution in a Ten-Well System," Paper presented at NOGS, Third Salt Symposium, 1969.
13 Jessen, F. W., "Effects of Solution Mining Operation in the Presence of Vertical and Horizontal Fracture Systems," Paper presented at NOGS, Third Salt Symposium, 1969.
14 Jacoby, C. H., "Storage of Hydrocarbons in Cavities in Bedded Salt Deposits," Paper presented at NOGS, Third Salt Symposium, 1969.
15 Harmsen, Bezalel, "Hydraulic Fracturing and Extraction of Minerals Through Wells," Paper presented at NOGS, Third Salt Symposium, 1969.
16 Manker, E. A., "Hydraulic Fracturing of Salt—Potash Fermenters," Paper presented at NOGS, Third Salt Symposium, 1969.
17 Davis, J. G., and Shock, D. A., "Solution Mining of Thin Bedded Potash," Paper presented at AIME February Meeting, 1969.

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Nuclear Explosives and Solution Mining as a Team

The experimental copper leach "Project Sloop" proposed by Kennecott,[8] using an atomic explosive to fracture the low grade oxidized copper zone near Safford, Ariz., continued to be postponed due to lack of funds and other problems. The experiments in gas sands in New Mexico and Colorado, "Gasbuggy" and "Rulison," were completed successfully so that some of the containment objections have been minimized.

The status of technology of total solution mining was well reviewed in papers given at the AIME Annual Meeting, Solution Mining Symposium in February, and the papers given at the Third Symposium on Salt, April 21-24, 1969, held at Cleveland, Ohio, sponsored by the Northern Ohio Geological Society and the Solution Mining Research Institute. The importance of solution mining of salt is reflected in the growing number of brining operations which accompany salt production for the chemical industry. It is estimated that approximately 50% of the salt which goes into chlorine production is now produced by brining or solution mining methods. Of major significance is the growing number of LP gas storage installations which are located in salt beds. Of the 236 LP gas storage facilities in operation in 1966, 177 were located in salt strata. Of these, 76 were single cavities in salt domes and 101 were in bedded salt. The storage capacity in salt represented 110 million bbl of the 125 million total capacity.[9] The storage capacity of LP gas is projected to reach 150 million bbl capacity by 1970,[10] thus one can anticipate a continuing development of new cavities. The solution mining of potash has been accomplished in Canada by Kalium for a number of years. The application of hydraulic fracturing and controlled potash removal in these beds was reported at the Solution Mining Symposium.[17]

Two Well Systems Capture The Most Attention

The mechanism of solution of salt for a single well seems to be sufficiently understood to satisfy present operations. Husband and Shook, of the Saskatchewan Research Council,[11] reported on their continuing research of the single well system. Current research and development seems to have turned to interest in the two-well system. On the theoretical side, Jessen presented his work on a multiwell system including the solution mechanisms taking place in horizontal and vertical fractures.[12,13] The technique of connecting wells by hydraulic fracturing and removing the soluble salt seems to be sufficiently well established to practice on an operational basis.[14,15,16,17] Brief mention of solution removal of trona and borax was reported at the Third Salt Symposium.

In summary, the technique of leaching of metallic ores, particularly in copper, continues to grow with uranium leaching also being important. In-situ leaching is in an interesting experimental stage. Its application to various field situations can be anticipated. In the total solution extraction area, there is considerable evidence that the mechanisms of removal in the multiwell, in-situ system are receiving more thorough study and that the hydraulic fracturing technique is being used as a practical operative technique. The next few years should show some interesting developments in solution extraction methods, particularly applications in in-situ recovery.

References

[1] Potter, George, "Solution Mining." Mining Engineering, Vol. 21, February 1969, p 68.

[2] Allman, M. B., and Harris, J. A. "An Experiment in Heap Leaching." Mining Congress Journal, Vol. 55, 1969, p 28.

[3] McGregor, R. A., "Uranium Dividends from Bacterial Leaching." Mining Engineering, Vol. 21, 1969, p 56.

[4] Johnson, P. H., and Bhappu, R. B., "Solution Mining—A Study of Leaching Agents," Paper presented at the AIME February Meeting, 1969.

[5] Grenstead, R. R., Davis, J. C., and Chadsworth, R. K., "Mixed Ionic Extractants—Organic Salts as Extractants for Inorganic Salts," Paper presented at the AIME February Meeting, 1969.

[6] Griswald, George, "Rock Fracturing Techniques for In-Place Leaching," Paper presented at the AIME February Meeting, 1969.

[7] Rabb, D. D., "Penetration of Leach Into Rocks Fractured by a Nuclear Explosive," Paper presented at the AIME February Meeting, 1969.

[8] Michaelson, C. D., "Outlook for Sloop," Mining Congress Journal, Vol. 55, No. 2, 1969, p 142.

[9] "LP Gas Underground Storage Capacity," Oil & Gas Journal, Vol. 63, No. 42, 1965, pp 115-118.

[10] Katz and Coats, "Storage in Salt Cavities,"Underground Storage of Fluids, 1968, Ulrich's Books, Inc., Ann Arbor, Michigan.

[11] Husband, W. H. W., and Shook, C. A., "Mass Transfer for High Vertical Surfaces to Liquids Under Free Correction Conditions," Paper presented at NOGS, Third Salt Symposium, 1969.

[12] Jessen, F. W., "Mechanism of Salt Solution in a Ten-Well System," Paper presented at NOGS, Third Salt Symposium, 1969.

[13] Jessen, F. W., "Effects of Solution Mining Operation in the Presence of Vertical and Horizontal Fracture Systems," Paper presented at NOGS, Third Salt Symposium, 1969.

[14] Jacoby, C. H., "Storage of Hydrocarbons in Cavities in Bedded Salt Deposits," Paper presented at NOGS, Third Salt Symposium, 1969.

[15] Harmsen, Bezalel, "Hydraulic Fracturing and Extraction of Minerals Through Wells," Paper presented at NOGS, Third Salt Symposium, 1969.

[16] Manker, E. A., "Hydraulic Fracturing of Salt—Potash Fermenters," Paper presented at NOGS, Third Salt Symposium, 1969.

[17] Davis, J. G., and Shock D. A., "Solution Mining of Thin Bedded Potash," Paper presented at AIME February Meeting, 1969.

United States Patent [19]

Coursen

[11] **3,973,497**

[45] **Aug. 10, 1976**

[54] **DIRECTED-THRUST BLASTING PROCESS**

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[73] Assignee: **E. I. Du Pont de Nemours and Company, Wilmington, Del.**

[22] Filed: **Sept. 24, 1974**

[21] Appl. No.: **508,888**

[52] **U.S. Cl.** 102/23; 299/13
[51] **Int. Cl.²** F42D 3/00
[58] **Field of Search** 102/22, 23; 166/299; 299/13

[56] **References Cited**

UNITED STATES PATENTS

60,572	12/1866	Shaffner	102/23
2,772,632	12/1956	Aitchison et al	102/23
3,024,727	3/1962	Hradel	102/23
3,466,094	9/1969	Haworth et al	299/13
3,792,906	2/1974	Kuck	299/13
3,863,987	2/1975	Lampard	102/23

Primary Examiner—Verlin R. Pendegrass

[57] **ABSTRACT**

Directed thrusts are generated in rock by detonating explosive charges in groups of drill holes therein, the drill holes being aligned so that the maximum thrust from the substantially simultaneous detonation of charges in a group of holes is exerted in a direction close to one in which the rock has been found to be particularly vulnerable to failure, i.e., a direction that is at an angle of 60° to a representative normal of a densely populated set of joints in the rock and that also is close to a direction of maximum principal tectonic stress should one be found.

17 Claims, 8 Drawing Figures

FIG.1

BHP   BHP   BHP   BHP

BHP'

NORMAL BOREHOLE
PLANES BHP'

BHP'

BHP'

NORMAL TO
JOINT PLANE

BHP'

NORMAL TO BOREHOLE
PLANES BHP

JOINT PLANE

JOINT SYSTEM

FIG. 2

N

MIN. HORIZON-
TAL PRINCIPAL
TECTONIC STRESS

830 P.S.I.

MAX. HORIZON-
TAL PRINCIPAL
TECTONIC
STRESS

W

E

210 P.S.I

S

FIG. 3

N (0°)

1

90°

60°

30°

3

2

0°

(270°) W

E (90°)

4

4

4

S (180°)

FIG.5

FIG.4

FIG.7

FIG.6

FIG.8

1
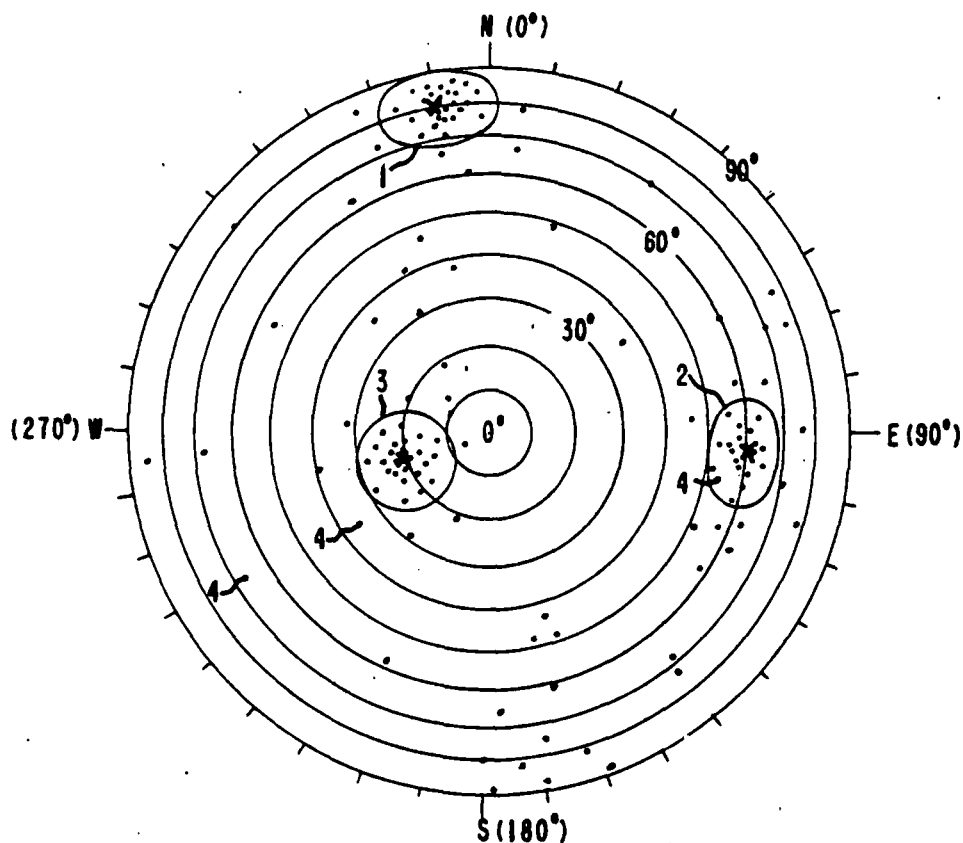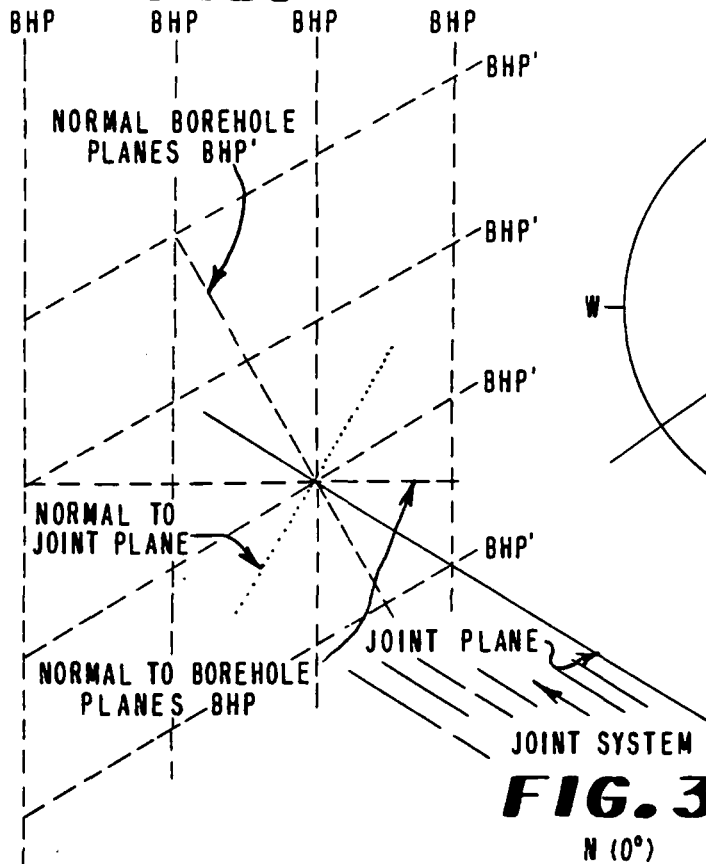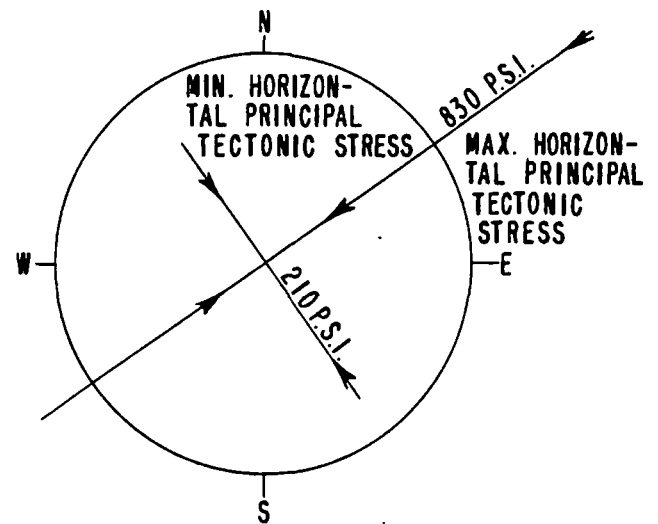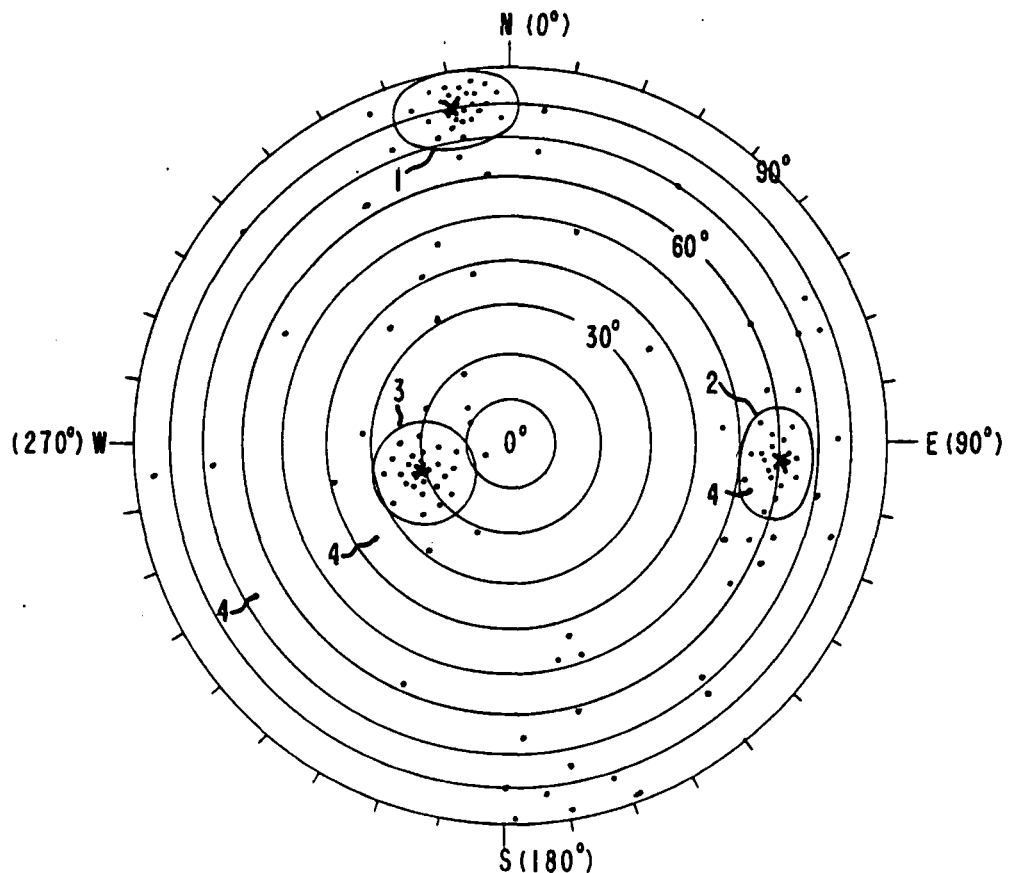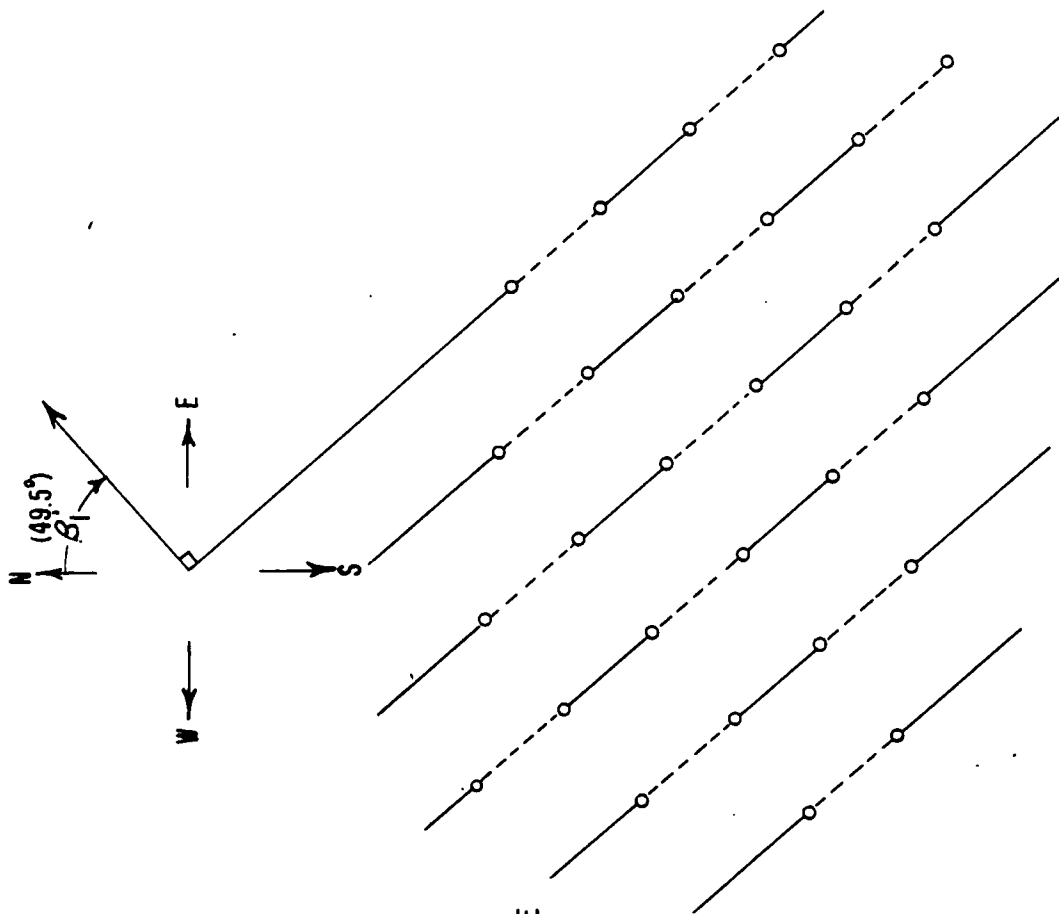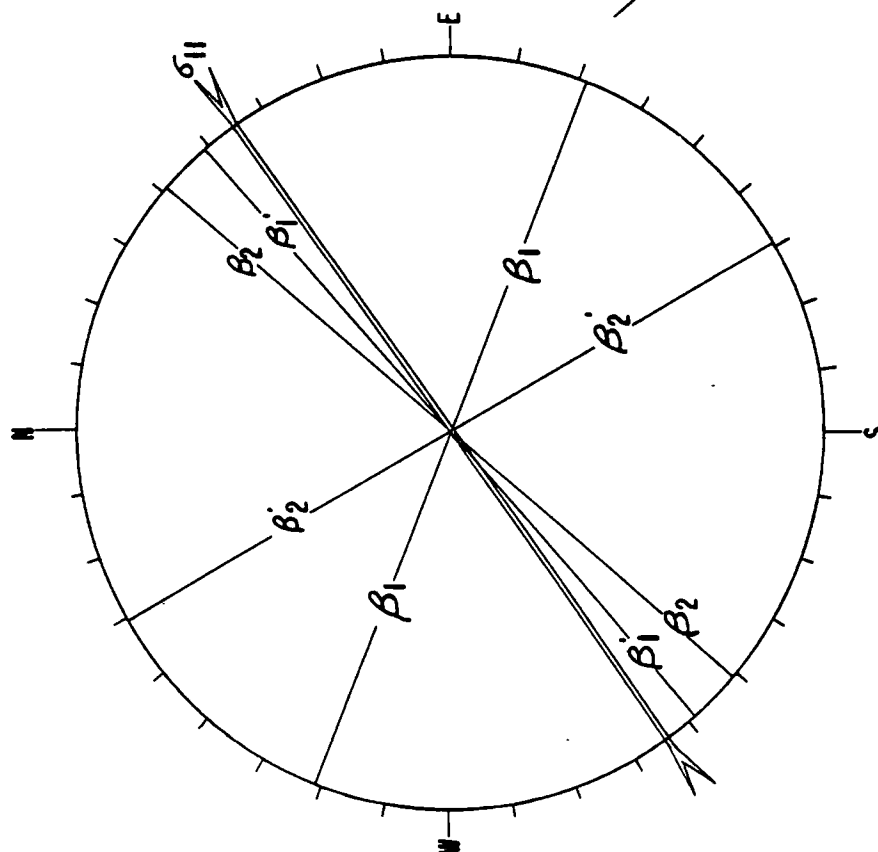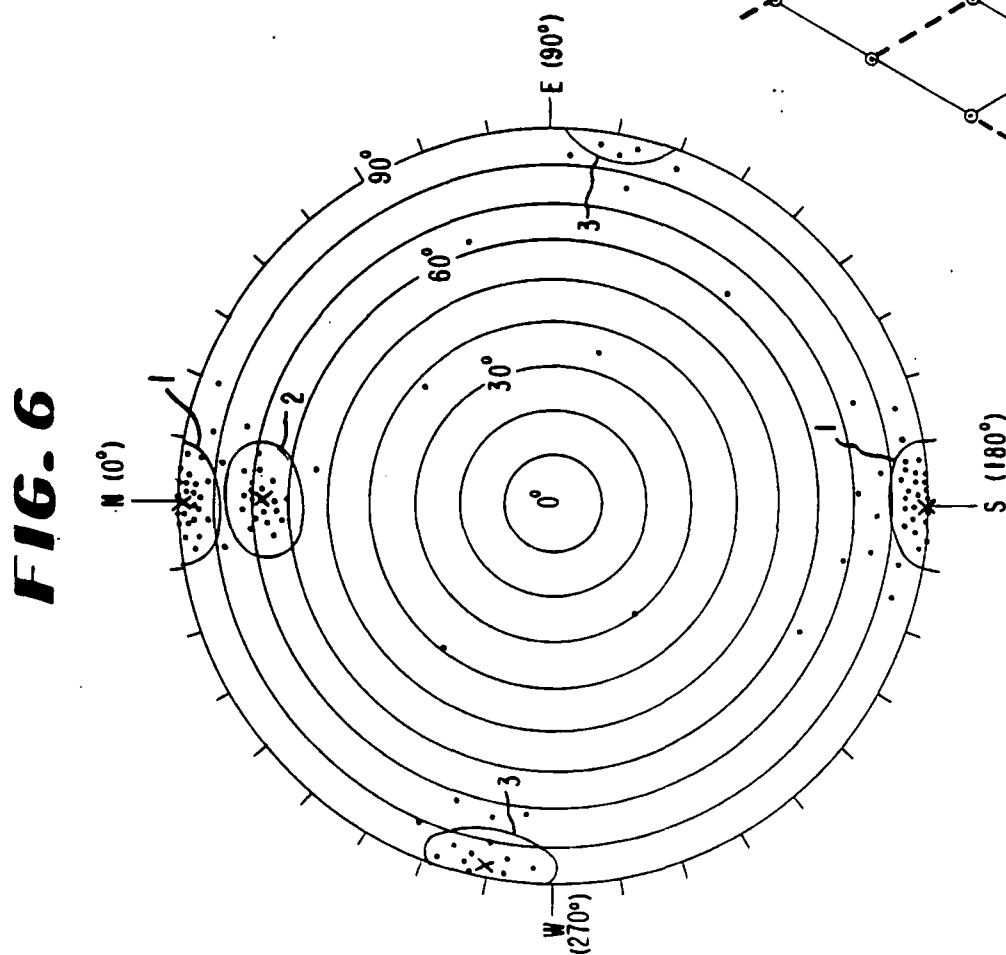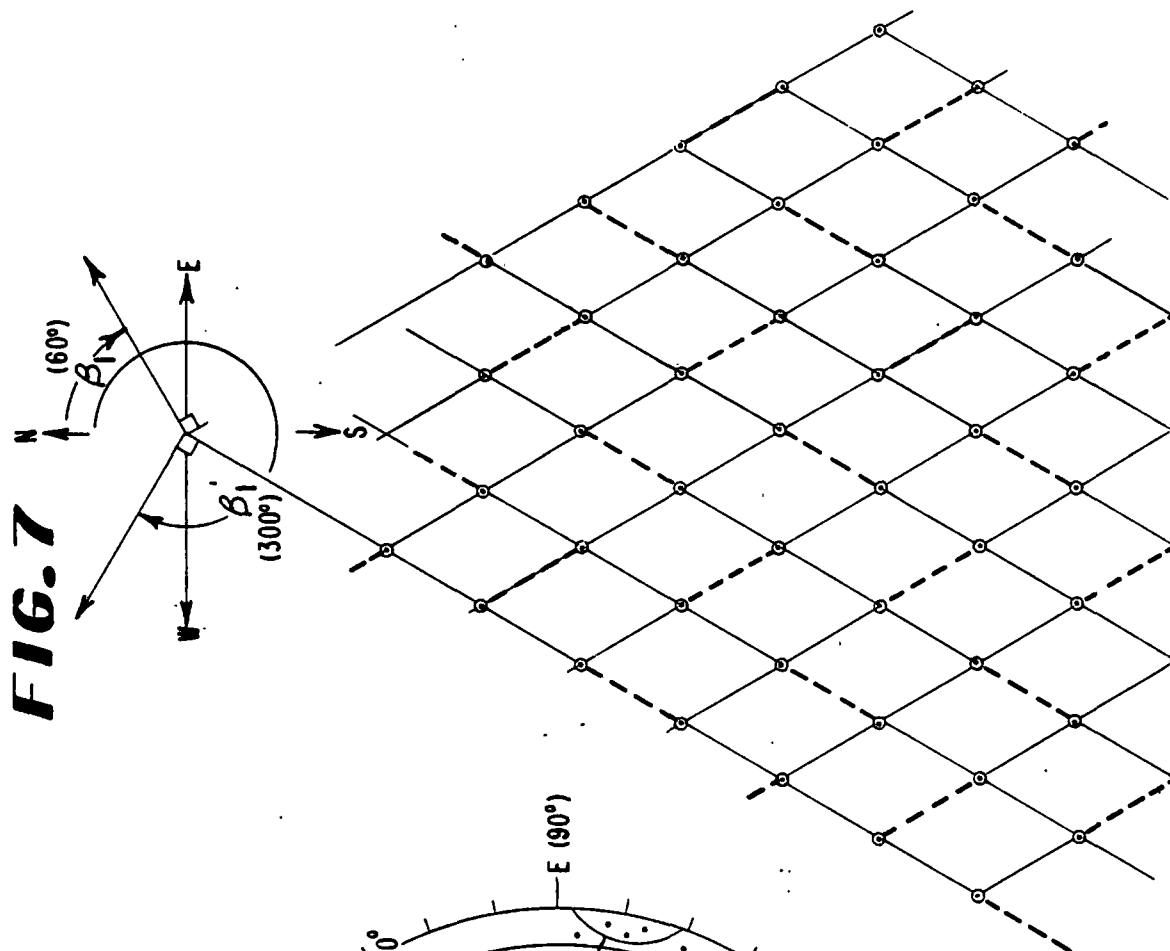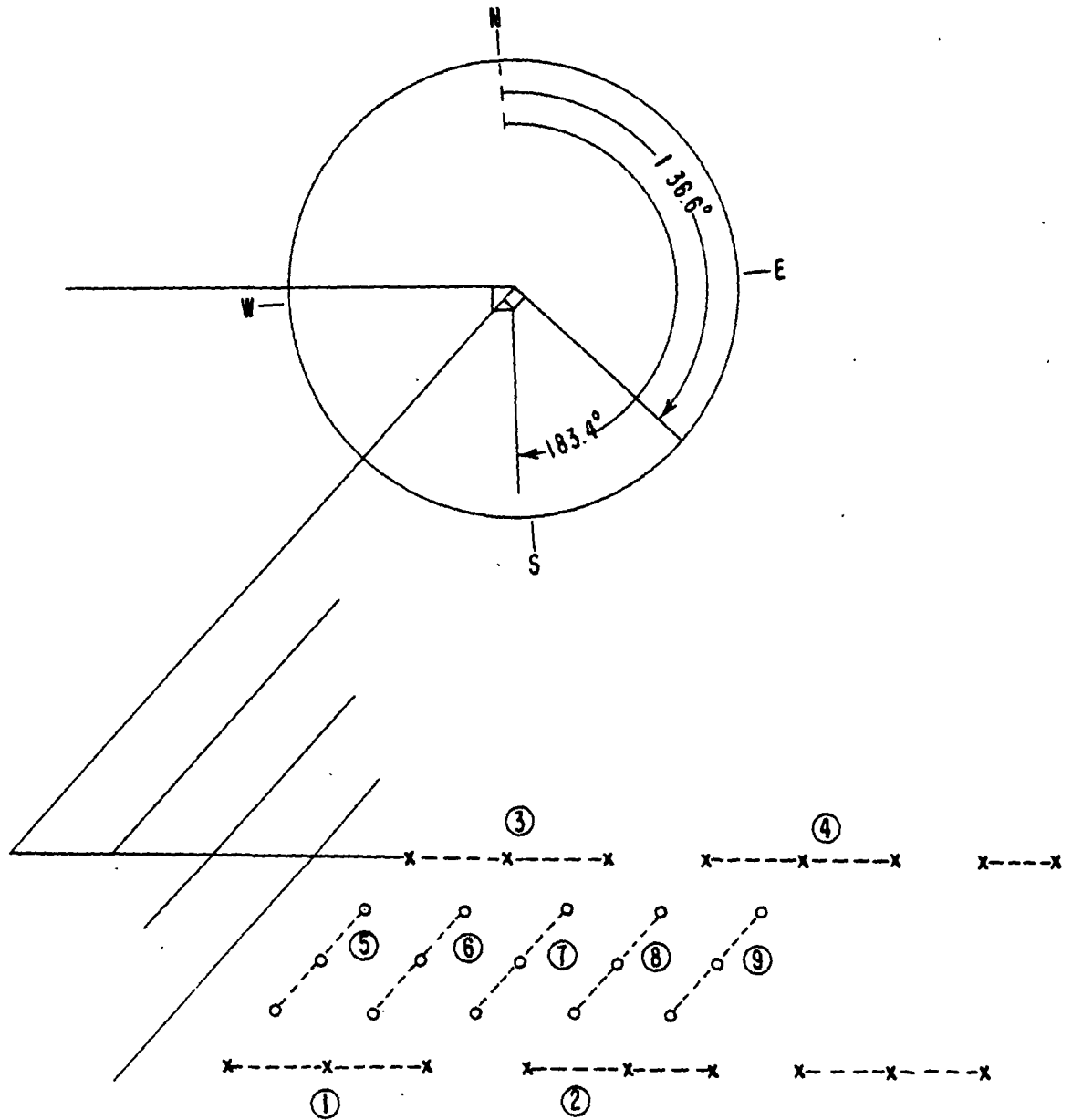
DIRECTED-THRUST BLASTING PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of blasting wherein one or more explosive thrusts are generated in rock in directions in which the rock has been found to be particularly vulnerable to failure.

2. Description of the Prior Art

Blasting processes have long provided man with a powerful tool for performing useful work, affording the energy required, for example, for excavation operations of various kinds, i.e., operations in which material is dug out and removed at or below the earth's surface either to form a useful cavity or to derive profit from the removed material, e.g., in mining. More recently, blasting processes for fracturing deep rock have become increasingly important as it has become necessary to tap deep mineralized rock masses, e.g., ore bodies or oil or gas reservoirs located from about 100 feet to about a few thousand feet beneath the earth's surface, in order to supplement or replace dwindling energy sources and minerals supplies. The fracturing procedure is required to prepare the masses for such in situ recovery operations as leaching of ore or retorting of oil shale in place.

The preparation of large volumes of deep rock for in situ operations by blasting requires the emplacement of enormous amounts of explosives in the regions to be fractured, which in turn entails the drilling of vast numbers of shot holes therein. To some extent, drilling costs can be reduced by drilling holes of smaller diameter than is required to accommodate the size of the explosive charges to be employed, and enlarging or "springing" the lower parts of the shot holes, located in the segment of rock to be fractured, to produce chambers having the volumes required to hold the explosive charges. Nevertheless, the costs of such large blasts will be substantial. Therefore, any procedure which can increase the effectiveness of the blasting process, i.e., produce more useful work (e.g., fracturing) in a given volume of rock per weight of explosive used, and thereby allow larger separations between shot holes or a smaller explosive charge per shot hole would add considerably to the value of the blasting process.

SUMMARY OF THE INVENTION

The invention provides a method of generating a directed thrust, and preferably a succession of directed thrusts, in rock, each by the substantially simultaneous detonation of explosives in an oriented coplanar group of holes in the rock, comprising:

a. forming one or more groups of drill holes in the rock, the holes in each group being a rank of adjacent holes lying substantially in a common plane whose normal defines a predetermined thrust direction, and said plane being oriented in a manner such that the thrust direction is within about 20° of, and preferably substantially coincides with, a direction in which the rock has been found to be particularly vulnerable to failure by virtue of existing jointing anisotropy and possibly also by virtue of anisotropic tectonic stresses;

b. loading the drill holes with explosive charges; and

c. detonating the charges in each group of drill holes substantially simultaneously, whereby the group-detonation exerts a thrust against the rock in the predetermined thrust direction. With multiple groups of drill

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holes, the substantially simultaneously detonated groups of charges are detonated in succession with respect to other such groups, the time interval between the detonations of successive groups of charges being sufficient to permit the pressure in the vicinity of the next group of charges to return to its ambient level.

Directions in which the rock is particularly vulnerable to failure are thrust directions which are optimum for sliding the joints in a densely populated set of joints in the rock, especially joints that are already under shear stress for sliding in the same direction, owing to existing tectonic stresses in the rock. Accordingly, a direction of vulnerability to failure generally will be a direction which is at an angle of 60° to a representative normal of a densely populated joint set in the rock, and preferably also close to a direction of maximum principal tectonic stress if the rock is under anisotropic tectonic stresses.

Because the common plane in which the drill holes of each group lie has its normal oriented along the maximum thrust exerted by the detonations in the holes of the group, this normal is purposely oriented close to a direction of the rock's vulnerability to failure. This orientation of the plane containing the drill holes allows the energy produced by the detonation to work in combination with the pre-existent directions of weakness in the rock, thus utilizing the explosive energy more effectively and thereby reducing the cost of explosive fracturing processes.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic representation showing the edges of planes in which drill holes are to be located with respect to a specific joint system in the present process;

FIG. 2 is a plot of the measured principal tectonic stresses described in Example 1;

FIG. 3 is a plot of joint normal positions used to determine dense jointing directions as described in Example 1;

FIG. 4 is an angular plot of the direction of maximum principal tectonic stress and dense jointing directions described in Example 1;

FIG. 5 is a drill hole pattern laid out for the direction of vulnerability to failure found in Example 1;

FIG. 6 is a plot of joint normal positions used to determine dense jointing directions as described in Example 2;

FIG. 7 is a drill hole pattern laid out for the directions of vulnerability to failure found in Example 2; and

FIG. 8 is a drill hole pattern laid out for a trenching operation described in Example 3.

In the present process, explosive charges in a plurality of drill holes are detonated in a manner such that there is at least one, and preferably a succession of multiple-hole detonations, each detonation being a group-detonation, i.e., the substantially simultaneous detonation of charges in a group of adjacent holes in rank. The holes in each group or rank lie substantially in a common plane and their detonation exerts a maximum thrust normal to the common plane, i.e., in a horizontal direction when the plane is substantially vertical. Consequently, a succession of detonations produces a succession of thrusts into the surrounding rock mass, the direction of each thrust being dependent on the orientation of the common plane in which the holes of the group lie. In the present process, the orientation of the common plane is such that the thrust

direction, i.e., the normal to the plane, is aligned in a direction chosen to cause maximum shear displacement of existing joints in the rock. To accomplish this, the common plane has a normal that is oriented at an angle close to (i.e., ± about 20°) 60° to the normal of a densely populated joint set in the rock. In some cases, there may be more than one direction of dense jointing, and the common planes of some drill hole groups can be oriented so that the explosive thrust will be exerted to cause maximum sliding of one set of joints, and the common planes of other drill hole groups to cause maximum sliding of another set of joints.

In the present process the orientation of the common plane of the group of drill holes is related to the jointing and stresses in the rock, but the orientation of this plane with respect to the horizon is not critical. However, in most blasting situations the holes will lie in a substantially vertical common plane, and the maximum thrust exerted by the group-detonations therefore usually will be substantially horizontal. Accordingly, the direction of the rock's vulnerability to failure generally is referred to herein as a horizontal direction, and the tectonic stress as a horizontal stress.

Referring now to FIG. 1, the lines (dashed) denoted as BHP represent the edges of a first set of parallel vertical borehole planes spaced evenly apart from one another. Lines BHP' (dashed) represent the edges of a second set of evenly spaced-apart parallel vertical borehole planes that intersects the first set. Multiple, spaced boreholes are to be drilled in one or both of the borehole planes. The normals to the two sets of borehole planes (dashed lines) are horizontal and are oriented at an angle of 60° to the normal (dotted line) of a plane of the indicated densely populated vertical joint system. In this manner the thrusts from the detonations of explosive charges in the holes in borehole planes BHP and BHP', which are normal to planes BHP and BHP', are made at an angle of 30° to the plane of the joint system. Thrusts made at such an angle generally are optimum for sliding the joints existent in the rock. When the tectonic stresses in the rock are such that a maximum principal tectonic stress is not present, a single joint plane system preferably is subjected to a succession of thrusts from alternately reversed directions, e.g., by the simultaneous detonation of a group of charges in a BHP plane alternating with the detonation of a group of charges in a BHP' plane (FIG. 1). In this manner, the thrust of each group-detonation reverses the direction of shear from the thrust of the previous detonation. Two joint plane systems can be worked by generating a succession of thrusts from alternately different directions, one to preferentially shear the joints in the first system, followed by a thrust from a different direction to preferentially shear the joints in the second system.

In the present process, when the rock is found to be under anisotropic tectonic stresses, i.e., when the difference between the maximum and minimum principal tectonic stresses is 200 psi or more, the normal of the common plane of each group of boreholes preferably also is as close as possible to the direction of maximum principal tectonic stress (horizontal stress for a vertical plane). In such a case, blasting will reinforce the tectonic shear and the set of joints will fail more easily. The blasting thrusts should be exerted so as to persistently shear the set of joints showing the greatest tectonic stress, and the thrusts should be in the same direction that reinforces the tectonic stress.

Prior to laying out a drill hole pattern in the present process, it is necessary to identify the various directions in which the rock to be blasted is most densely jointed. Often, the jointing will be relatively simple, with the great majority of the joints easily being assigned membership in a major set of joints by inspection, the joints in each major set being nearly parallel and the mean direction of each major set being clearly distinct from the mean direction of every other major set. In such cases, the directions in which the rock is most densely jointed can often be closely estimated by measuring the colatitude and azimuth of the normal (that is, the amount of dip and its compass direction) of a typical joint in each set. The proportion of joints belonging to each set can be estimated by choosing a random sample of joints and counting those that belong in each major set, assignment of each joint to a set being done by inspection.

In most cases, however, such a direct approach will not be acceptable owing to the complexity of the jointing system or the limited amount of data available, or the desirability of avoiding bias arising from the assignment of joints to a set by inspection. Well-developed methods exist for obtaining the directions of most dense jointing in such cases. Such methods are described, for example, in *Structural Geology*, M. P. Billings, Ed. 3, Englewood Cliffs, N.J., Prentice Hall Inc., 1972; and in the United States Bureau of Mines Reports of Investigations RI 7669 (Mahtab et al., 1972) and RI 7715 (Mahtab et al., 1973). Typically, these methods involve (a) measuring the colatitude and azimuth of the normal of each joint in a randomly chosen set of, for example, 100–1000 joints; (b) plotting these measured coordinates of each normal as the point where it will intersect a sphere centered on the normal, and (c) determining the density of the plotted points as a function of position on the surface of the sphere. This density usually is expressed as a percentage of the plotted points that lie within a circular area centered on the point to be assigned a density, each circular area having 1/200 of the area of the surface of the sphere. Such a circular area is one whose radius subtends 10.37° from the center of the sphere. Those positions on the surface of the sphere where the density of plotted points reaches relatively high values represent the normals to planes in the rock that are nearly parallel to relatively large proportions of the joints. A Lambert azimuthal equal-area (or Schmidt) projection can be used to make an equivalent plot in a plane instead of on a spherical surface.

The strikes and dips can be measured on oriented core, or on exposed joints on nearby underground or surface outcrops. One may use, for example, an acoustic imaging and mapping method wherein acoustic signals are reflected from anomalies in the surrounding rock with the emitting and receiving transducers mounted in a drill hole drilled in the rock, as described in Engineering & Mining Journal, Feb. 1970, pp. 93–96.

In the present process, a direction of most dense jointing is a direction such that at least 5% of a measured random sample of joint normals lie within 10.37° of it, and preferably such that it coincides with the mean direction of all joint normals lying within 10.37° of it.

The mean direction of a group of joint normals (in this case, for a group of joints that are nearly parallel) can be calculated from the measured dips and azimuths

by Relationships (4) and (5) found on pages 8 and 9 of the above-mentioned Bureau of Mines Report of Investigations RI-7669, as follows:

$$\hat{\phi}_i = \tan^{-1} \frac{[(\epsilon l_i)^2 + (\epsilon m_i)^2]^{1/2}}{\epsilon n_i}$$

$$\hat{\sigma}_i = \tan^{-1} \frac{\epsilon m_i}{\epsilon l_i}$$

where

$l_i = \sin \phi_i \cos \sigma_i$

$m_i = \sin \phi_i \sin \sigma_i$

$n_i = \cos \phi_i$

$i = 1, 2, - N$

$j = 1, 2, - M$ and

$\hat{\phi}_j$ = mean dip of a group of joints designated j (that is, the colatitude of the mean normal of the group of joints)

$\hat{\sigma}_j$ = azimuth of the mean dip of the group of joints (that is, azimuth of the horizontal component of the mean normal of the group of joints)

N = number of joints whose normals plot within the circle having 1/200 of the area of the sphere

M = number of most densely jointed directions

ϕi = dip of the ith joint

σi = azimuth of the dip of the ith joint.

A direction of dense jointing ($\hat{\phi}_j$, $\hat{\sigma}_j$) which also coincides with the mean direction of all joint normals lying within 10.37° of it, can be found by the following process of successive approximations. Any of the directions of dense jointing close to a local density maximum is chosen as a starting point, or a local density maximum calculated by a computer program such as that described in the United States Bureau of Mines Information Circular IC-8624, *A Computer Program for Clustering Data Points on the Sphere* (Shanley et al., 1974) can be used. The mean direction of all measured joints lying within 10.37° of this first direction is calculated, using the relationships given above. The calculated direction becomes a new starting point and again the mean direction of the new set of joints lying within 10.37° of it is calculated. The procedure is repeated until the calculated mean direction coincides with the one previously calculated.

Directions of vulnerability to failure are found by determining the horizontal directions (β_j and β_j') that make an angle of 60° with the normals that map each of the most densely jointed directions dipping at least 30° (i.e., for which 30° ≤ $\hat{\phi}_j$ ≤ 90°.

For dense jointing that is along vertical or nearly vertical planes, whose normals therefore lie within a few degrees of the horizontal plane, and which therefore have values of $\hat{\phi}_j$ that are close to 90°, this is easily done by simply taking compass directions (β_j and β_j') that are ± 60° from the value of $\hat{\sigma}_j$ corresponding to each of these densely jointed directions. In the general case, however, β_j and β_j' can be found graphically or by solving the following equation for β_j, for each of M directions that are most densely jointed directions:

$$\beta_m = \hat{\sigma}_m - \cos^{-1} \left[\frac{\cos 60°}{\sin \hat{\phi}_j} \right]$$

This equation will have two solutions (β_j and β_j') for 30° < $\hat{\phi}_j$ <150°, one solution for $\hat{\phi}_j$ = 30°(or 150°) and no solutions for 0° ≤ $\hat{\phi}_j$ <30°and 150° < $\hat{\phi}_j$ ≤ 180°.

Lemma:

$\hat{\phi}_j$ $\hat{\theta}_j$	dips and azimuths of dense jointing directions having direction cosines (l_j, m_j, n_j)
α_j β_j	dips and azimuths of directions that are inclined 60° to ($\hat{\phi}_j$, $\hat{\sigma}_j$) with direction cosines (l_j, m_j, n_j)

$\cos 60° = \hat{l}_j l_j + \hat{m}_j m_j + \hat{n}_j n_j = \sin \hat{\phi}_j \cos \hat{\sigma}_j \sin \alpha_j \cos \beta_j + \sin \hat{\phi}_j \sin \hat{\sigma}_j \sin \beta_j + \cos \hat{\phi}_j \cos \alpha_j$

For horizontal directions, $\alpha_j = 90°$

∴ $\cos 60° = \sin \hat{\phi}_j \cos \hat{\sigma}_j \cos \beta_j + \sin \hat{\phi}_j \sin \hat{\sigma}_j \sin \beta_j$

∴ $\frac{\cos 60°}{\sin \hat{\phi}_j} = \cos \hat{\sigma}_j \cos \beta_j + \sin \hat{\sigma}_j \sin \beta_j = \cos (\hat{\sigma}_j - \beta_j)$

$\cos^{-1} \left[\frac{\cos 60°}{\sin \hat{\phi}_j} \right] = \hat{\sigma}_j - \beta_j$

$\beta_j = \hat{\sigma}_j - \cos^{-1} \left[\frac{\cos 60°}{\sin \hat{\phi}_j} \right]$

Preferably the magnitude and direction of the horizontal components of the tectonic stress in the rock is also determined. This can be done by any one of several stress relief methods or by an hydraulic fracturing method.

The stress relief methods all rely on either measurement of the change in dimensions exhibited by a small volume of rock when it is cut loose from a rock formation that is under stress, or on measurement of the stresses required to restore the original dimensions to such a volume of rock (F. T. Williams and A Owens, Tunnels & Tunnelling (London) 5, 138–42 (1973) No. 2).

The hydraulic fracturing method, as presently practiced, relies on a determination of the hydraulic pressures required to initiate fracture of the wall of drill holes in an unstressed sample, and also of a drill hole in the formation in question, and the pressure required to hold the latter fracture open, once it is formed, and the compass orientation of the fracture in the borehole wall. This method is reviewed by B. C. Haimson, Symp. Soc. Internat. des Roches, Nancy, 1971, Vol. II, Paper No. 30, with a specific example of stress determination in deep rock using this method.

For determination of the magnitude and direction of the horizontal components of the tectonic stress in deep rock accessible only through boreholes drilled down from the surface, the hydraulic fracturing method is the easiest to use at the present state of the art, and is therefore preferred.

If the difference between the maximum and minimum principal horizontal tectonic stresses measured as described above is 200 psi or more, then the value of β_j or β_j' that is selected is the one which is closest to the measured azimuth of the maximum principal horizontal tectonic stress. If several values of β_j or β_j' lie within 10° of this direction, and they are derived from directions of appreciably differing jointing density, then the one derived from the more densely jointed direction is selected.

If the difference between the measured minimum and maximum principal horizontal tectonic stresses is less than 200 psi, then one can choose either (a) a value of

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β_j or β_j' derived from the most densely jointed direction, or if there are several choices derived from about equal jointing density, preferably one that is close to those from one or more other densely jointed directions or (b) two or three values of β_j or β_j' that are oriented within $90° \pm 10°$ or $120° \pm 10°$ of each other.

Once the direction(s) of vulnerability to failure (β_j and β_j') have been found, a two-dimensional pattern of drill hole locations is laid out, the locations being evenly spaced on a horizontal line or on a set of horizontal, evenly spaced parallel lines that are perpendicular to the chosen value (or values) of β_j or β_j'. If several values of β_j or β_j' have been chosen, then a horizontal line or a set of evenly spaced horizontal parallel lines is laid out perpendicular to each chosen value of β_j or β_j'. A substantially vertical borehole is drilled at each location.

If the rock is to be blasted in a single thrust, all of the drill holes on one horizontal line perpendicular to β_j or β_j' comprise a single group, and the explosive charges loaded therein are detonated substantially simultaneously. In most instances, however, it will be beneficial to subject the rock to a succession of thrusts and therefore to form multiple groups of drill holes on one or more horizontal lines perpendicular to each chosen value of β_j or β_j', and to detonate in succession the charges loaded into the groups of holes. Subjecting the rock to multiple explosive thrusts in succession allows one, inter alia, to take advantage of the incremental swelling of fracture zones that is achievable when blasting is conducted in flooded rock, as described in my co-pending U.S. patent application Ser. No. 382,845, filed July 26, 1973 now U.S. Pat. No. 3,902,422. Therefore, in a preferred embodiment of the present process the drill holes form a pattern of multi-hole groups, the holes of each group lying on the same line (i.e., in a common plane), and groups preferably being located on a set of parallel lines (i.e., in a set of parallel planes) with multiple groups per line, and with the groups evenly distributed in plan view. If the difference between the maximum and minimum horizontal principal tectonic stresses has been found to be greater than 200 psi, then the groups of holes are laid out on a set of parallel lines all running in the same direction, i.e., lines perpendicular to the β_j which is closest to the direction of the maximum principal tectonic stress. If the difference between the stresses is less, then two intersecting sets of parallel lines perpendicular to β_j and β_j' may be constructed and groups of holes drilled on both sets of lines.

The explosive charges in each drill hole group are detonated substantially simultaneously, and the groups are detonated in succession. When the holes lie in intersecting planes, the detonation of a group of holes in one of the sets of planes alternates with that of a group of holes in the other set. The time between successive group-detonations is sufficient to permit the pressure resulting from one detonation to return to its ambient level in the vicinity of the next group in the succession. As a rule, when the successive groups of holes are adjacent to each other, the time interval between group-detonations is at least $2d/C$, where d is the spacing between a hole in one group and a hole that is closest thereto in an adjacent group, and C is the velocity of compressional waves in the rock.

The size of the drill hole groups can vary, e.g., about from two to eight holes per group, but in most instances small groups, e.g., groups of about from two to four

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holes, are preferred in order to avoid vibration problems associated with larger blasts.

Adequate directivity of the thrust of the planar charge group requires that all explosive in the group be consumed in a very short length of time. Variables that tend to reduce such directivity are: large variability in cap initiation times, a high velocity of sound in the rock, a low detonation velocity of the explosive comprising the array, and a large spacing between detonators in a charge. In general, the spacing between detonators in a hole should be governed by the following relation in order that the maximum thrust be exerted in a direction within $10°$ of the desired direction:

$$R \leq 2D \, [0.03 \, \frac{S^2}{C^2} - \delta^2]^{1/2}$$

where:

R = separation of electrically fired detonators in a borehole

D = detonation velocity of the explosive to be initiated

S = separation of holes in the group C = velocity of sound in the rock

δ = standard deviation of the explosion times of simultaneously initiated blasting caps, for the type of cap and firing current to be used.

Lemma:

$$(\Delta t)^2 = \delta^2 + T^2 \leq (\frac{S}{C} \sin 10°)^2 = (0.17 \frac{S}{C})^2$$

where $T = \frac{R}{2D}$ and Δt = total variability of the initiation points

$$\therefore R \leq 2D \, [0.03 \, \frac{S^2}{C^2} - \delta]^{1/2}$$

For sufficiently short charges, one detonator per charge should be sufficient, but the use of longer charges requires the use of a larger number of detonators spaced along the charge. Thus, the above equation can be used to specify the required simultaneously of the initiators, and the maximum allowable spacing between initiators having a given timing variability. In general, a charge no longer than $R/2$ can be initiated with a single initiator placed anywhere in the charge, a charge no longer than R can be initiated with a single initiator placed no farther than $R/2$ from either end of the charge, and charges longer than R will require two or more initators separated by a distance no greater than R and no farther than $R/2$ from either end of the charge.

If the rock to be blasted is above the phreatic surface, it is preferable to flood the rock in the vicinity of each group of holes with water before detonating them. If the rock to be blasted is below the phreatic surface, it is preferable to allow ground water to percolate into open fractures left by the previous blast, before the next blast is made adjacent to it. Thus, the present process preferably is carried out in conjunction with the process for blasting in flooded rock described in my above-mentioned co-pending U.S. patent applicatin Ser. No. 382,845 now U.S. Pat. No. 3,902,422, the disclosure of which is incorporated herein by reference. Aluminum-containing water gel explosives are the preferred explosive for this type of blasting because of their high energy density, good water resistance,

ability to fill a borehole to high loading density, safety, and reasonable cost.

For boreholes where the barren overburden is at least as thick as the underlying rock, e.g., ore, to be worked by blasting, it is particularly desirable to minimize the amount of drilling required to emplace the charges. This can be done by increasing the volumes of the boreholes at the depths where the charges are to be placed. The volume of a hole can be increased by springing it to a larger volume with one or more preliminary explosive charges or by reaming the deep parts of the hole to larger volume, using an expansion bit.

The following examples serve to further illustrate specific embodiments of the process of the invention.

Example 1

A body of copper ore lying between the depths of 320 and 570 feet is to be fragmented by explosives to prepare it for the leaching-out of copper values in place.

a. Three tectonic stress measurements are made by the hydraulic fracturing method at depths of 370, 445, and 520 feet in each of three coreholes drilled into the ore at widely separated positions (about 500 feet apart) in the ore to be blasted. The average horizontal principal tectonic stresses obtained from these measurements, which are plotted in FIG. 2, are:

	Magnitude (psi)	Azimuth (Degrees True)
Maximum Horizontal Principal Stress (σ_{11})	830 (Compressive)	55°
Minimum Horizontal Principal Stress (σ_{22})	210 (Compressive)	145°

b. The strikes and dips of the joints are measured in oriented core, previously taken with a triple core barrel from the 320–570 feet depth interval in the three holes used in obtaining the tectonic stress condition in Step (a). A Schmidt projection of the resulting data for 131 joints is shown in FIG. 3. In this figure, 4 denotes the plotted positions of joint normals where they intersect the upper half of a sphere centered on the normal; and 1, 2, and 3 denote circles having 1% of the area of the hemisphere (which plot as ovals of the same area on a Schmidt projection) centered on the mean positions of all joint normals that plot in the circle. The several most densely jointed directions are identified by crosses. Their coordinates are as follows:

Center of Circle 1: $\beta_1 = 80°$ $\gamma_1 = 350°$
Center of Circle 2: $\beta_2 = 60°$ $\gamma_2 = 95°$
Center of Circle 3: $\beta_3 = 20°$ $\gamma_3 = 250°$

c. The horizontal directions that make angles of 60° with the most densely jointed directions found in Step (b) are found by solving the following equation:

For 60° from the joint normal represented by the center of Circle 1:

$$\beta_1 = 350° - \cos^{-1}\left[\frac{\cos 60°}{\sin 80°}\right]$$

The values of β_1 which satisfy this equation are:

$$\beta_1 = 290.5°, \beta_1' = 49.5°$$

For 60° from the joint normal represented by the center of Circle 2:

$$\beta_2 = 95° - \cos^{-1}\left[\frac{\cos 60°}{\sin 60°}\right]$$

The values of β_2 which satisfy this equation are:

$$\beta_2 = 40.3°, \beta_2' = 149.7°$$

No horizontal directions exist that bear 60° from a joint normal represented by the center of Circle 3.

d. The maximum horizontal principal stress direction (σ_{11}) and the values of $\beta_1, \beta_1', \beta_2,$ and β_2' that represent thrust directions found above to be optimum for shearing joints are plotted in FIG. 4. The direction β_1' (49.5°) is seen to be the optimum direction along which to direct the thrust of the explosions, because it is quite close to the direction of the maximum principal stress (55°).

e. Six evenly spaced, horizontal parallel lines are laid out perpendicular to β_1', on a spacing appropriate for the separation of ranks of boreholes in this rock, for the charge diameters that are to be used. For example, using an explosive comprising a gelled mixture of 29.6% monomethylamine nitrate, 18.9% ammonium nitrate, 10.5% sodium nitrate, 11.0% water, and 30% powdered aluminum (by weight) in 10-inch-diameter boreholes (to be chambered by reaming) in monzonite porphyry rock, a spacing of about 90 feet between lines is used. Evenly spaced hole positions are laid out on each of these parallel lines, as shown in FIG. 5, the spacing between holes being the same as the spacing between the lines. The substantially vertical boreholes are drilled one or a few at a time and then chambered by under-reaming the ore body in the 320–570 foot interval. This procedure increases the hole volume at this depth interval by a factor of about seven in this rock. Pairs of chambered holes, the holes of each pair lying on the same parallel line (and shown connected by a dashed line in FIG. 5), and the pairs of holes being in staggered position on adjacent lines, are then loaded with the same explosive and one pair of holes detonated at a time so as to exert a succession of thrusts on the rock in the β_1' direction. The fragmentation of the ore is increased, as evidenced by a reduction of the average length of core fragments at least 2 inches long to about half the length obtained before blasting.

EXAMPLE 2

An oil shale formation lying between the depths of 600 and 850 feet is to be fragmented by explosives to prepare it for retorting in place.

a. Tectonic stress measurements made by overcoring methods in drill holes bored from underground workings in the shale show that the principal tectonic stresses at these depths are as follows:

	Magnitude (psi)	Azimuth (degrees true)	Inclination from vertical (degrees)
σ_{11}	1100 (compressive)	35	169
σ_{22}	280 (compressive)	92	100
σ_{33}	170 (compressive)	181	84

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Inasmuch as σ_{22} and σ_{33} are nearly horizontal and differ by only 110 psi, the shear provided by horizontal tectonic stresses is too small to have an important influence on the blasting results.

b. The strikes and dips of a random sample of joints exposed in the underground workings are measured and plotted on a Schmidt projection, shown in FIG. 6. Three directions of dense jointing as follows are disclosed by this plot:

Center of Circle 1:	$\phi_1 = 90°$	$\sigma_1 = 0°$
Center of Circle 2:	$\phi_2 = 66°$	$\sigma_2 = 0°$
Center of Circle 3:	$\phi_3 = 87°$	$\sigma_3 = 280°$

c. Since tectonic stresses can be neglected, and since the center of Circle 1 defines a nearly vertical jointing direction that contains a clear majority of joints, horizontal directions β_1 and β_1' that are inclined 60° from a densely jointed direction are $\beta_1 = 60°$ true and $\beta_1' = 300°$ true.

d. Sets of 25 horizontal evenly spaced (80 feet) parallel lines are constructed perpendicular to the directions 60° true and 300° true (i.e., perpendicular to β_1 and β_1'), as shown in FIG. 7. The intersections of these two sets of lines are evenly spaced locations on the lines, and are chosen as borehole locations. The borehole locations are paired as shown in FIG. 7 so that members of each pair lie on the same line and approximately equal numbers of evenly interspersed pairs lie along both of the sets of parallel lines. (Other arrangements that meet these conditions also exist.) The boreholes are then drilled to a depth of at least 850 feet. The holes are then reamed with an expansion bit to increase their diameter over the depth interval 600–850 feet. Pairs of boreholes, as chosen above, are loaded with explosives up to approximately the 600 foot level and detonated simultaneously. Another adjacent pair of holes is then loaded and detonated simultaneously. The borehole size and explosive are the same as those in Example 1. This process is continued until all boreholes in the pattern have been detonated, the detonations alternating from one set of parallel lines to the other to shear the shale back and forth. The fragmentation of the shale is increased as evidenced by core fragment size measurements.

EXAMPLE 3

Blasting is to be undertaken and then a trench excavated along the center of a city street so as to obtain good rock breakage, yet to minimize the amount of explosive required per round and to maximize the amount of rock broken per pound of explosive. The rock is a sedimentary formation that is densely jointed parallel to well-defined bedding planes that dip 33° in the direction 160° true. The trench is to run in the direction 100° true.

In this case, tectonic stresses are neglected. The blasting is arranged to exploit the jointing parallel to the bedding.

The strike and dip of the bedding give:

$$\phi_1 = 33°$$

$$\sigma_1 = 160°$$
$$\beta_1 = 160° + 23.4° = 183.4°$$
$$\beta_1' = 160° - 23.4° = 136.6°$$

The borehole arrangement based on these values is shown in FIG. 8. In order to minimize backbreak, the rock is pre-sheared with reduced charges shot in 1.5-

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inch-diameter holes drilled along the outline of the trench (groups of holes denoted 1, 2, 3, and 4). The direction in which the trench is being driven makes β_1' a more favorable thrust direction than β_1. Consequently, each set of holes to be simultaneously detonated (i.e., groups denoted 5, 6, 7, 8, and 9) to break up the rock within the pre-sheared perimeter is drilled on a line perpendicular to 136.6° true. The explosive used to similar to that described in Example 1, but contains no aluminum. The groups are detonated in numerical order starting with Group 1.

The holes in each of these groups of holes are detonated simultaneously, and there is an appreciable time interval between the detonation of one group and that of the next. The rock is effectively broken from the detonations.

I claim:

1. A method of generating a directed thrust in rock comprising:
   a. forming in the rock a group of adjacent drill holes which lie substantially in a common plane whose normal defines a predetermined thrust direction, said plane being oriented in a manner such that the thrust direction is at an angle in the range of about from 40° to 80° to a representative normal of any densely populated joint set in the rock;
   b. loading the drill holes with explosive charges; and
   c. detonating the charges in the group of drill holes substantially simultaneously, whereby the group-detonation exerts a thrust against the rock in the predetermined thrust direction.

2. A method of claim 1 wherein said group of drill holes are formed so as to lie in a substantially vertical common plane.

3. A method of claim 1 wherein said group of drill holes are formed in a manner such that the thrust direction defined by the normal to their common plane is a direction which, in addition, is closest to the direction of a maximum principal tectonic stress.

4. A method of claim 1 wherein multiple groups of drill holes are formed, the substantially simultaneously detonated groups of charges being detonated in succession with respect to other such groups, whereby each group-detonation in the succession exerts a thrust against the rock.

5. A method of generating a succession of directed thrusts in rock, each by the substantially simultaneous detonation of explosives in an oriented coplanar group of adjacent holes in the rock, comprising:
   a. forming substantially vertical drill holes in the rock in a pattern of a plurality of groups of adjacent drill holes, the holes in each group lying substantially in a common plane whose normal defines a predetermined thrust direction, said plane being oriented in a manner such that the thrust direction is a substantially horizontal direction that is at an angle in the range of about from 40° to 80° to a representative normal of any densely populated joint set in the rock;
   b. loading the drill holes with explosive charges; and
   c. detonating the charges in a pattern such that the charges in each drill hole group detonate substantially simultaneously and the substantially simultaneously detonated groups of charges are detonated in succession with respect to other such groups, whereby each group-detonation in the succession exerts a thrust against the rock, the time interval between the detonations of successive groups of

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charges being sufficient to permit the pressure in the vicinity of the next group of charges to return to its ambient level.

6. A method of claim 5 further including the step of determining said representative normal of a densely populated joint set by (a) measuring the colatitude and azimuth of the normal of each joint in a randomly chosen sample of joints, (b) plotting the measured coordinates of each normal as the point where it will intersect a sphere centered on the normal, and (c) determining the density of the plotted points as a function of position on the surface of the sphere, the direction of the representative normal of a densely populated joint set being a direction such that at least 5% of the sample of joint normals lie within 10.37° of it.

7. A method of claim 5 wherein said group of drill holes are formed in a manner such that the thrust direction defined by the normal to their common plane is a direction which, in addition, is closest to the direction of a maximum horizontal principal tectonic stress.

8. A method of claim 7 further including the step of measuring the magnitude and direction of the horizontal components of the tectonic stress in the rock by a stress relief method.

9. A method of claim 7 further including the step of measuring the magnitude and direction of the horizontal components of the tectonic stress in the rock by an hydraulic fracturing method.

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10. A method of claim 5 wherein said group of drill holes are formed in a manner such that the thrust direction defined by the normal to their common plane is at an angle of substantially 60° to said representative normal of any joint set.

11. A method of claim 5 wherein successive groups of charges are detonated at intervals of at least about 10 milliseconds.

12. A method of claim 5 wherein about from two to eight drill holes are formed in the rock per group lying substantially in a common plane.

13. A method of claim 12 wherein two drill holes are formed in the rock per group lying substantially in a common plane.

14. A method of claim 5 wherein said drill hole groups lie in a plurality of parallel planes.

15. A method of claim 14 wherein the holes of a plurality of said drill hole groups lie in a common plane.

16. A method of claim 15 wherein said drill hole groups are formed in a manner such that said plurality of parallel planes intersect a plurality of parallel planes in which other such drill hole groups lie, and drill hole groups are detonated, alternating between groups lying on the two intersecting sets of parallel planes.

17. A method of claim 1 wherein said directed thrust is generated in a deep segment of mineralized rock so as to produce a network of fractures therein to prepare said segment for the in situ recovery of mineral values therefrom.

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Dynamic Tensile Strength of Lunar Rock Types

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The dynamic tensile strengths of four rocks have been determined. A flat plate impact experiment is used to generate ~1-μs-duration tensile stress pulses in rock samples by superposing rarefaction waves to induce fracture. A gabbroic anorthosite and a basalt were selected because they are the same rock types as occur on the lunar highlands and mare, respectively. Although these have dynamic tensile strengths which lie within the ranges 153–174 MPa and 157–179 MPa, whereas Arkansas novaculite and Westerly granite exhibit dynamic tensile strengths of 67–88 MPa and 95–116 MPa, respectively, the effect of chemical weathering and other factors, which may affect application of the present results to the moon, have not been explicitly studied. The reported tensile strengths are based on a series of experiments on each rock where determination of incipient spallation is made by terminal microscopic examination. These data are generally consistent with previous determinations, at least one of which was for a significantly chemically altered (hydroxylated) but physically coherent rock. The tensile failure data do not bear a simple relation to compressive results and imply that any modeling involving rock fracture consider the tensile strength of igneous rocks under impulse loads distinct from the values for static tensile strength. Generally, the dynamic tensile strengths of nonporous igneous rocks range from ~100 to 180 MPa, with the more basic, and even amphibole-bearing samples, yielding the higher values.

INTRODUCTION

Central to impact and explosive cratering processes, underground explosive excavation and fragmentation, and planetary accretion via large body interactions is the dynamic fracture behavior of rock. Experimental high velocity impact craters (submillimeter to decicentimeter radius range) produced in pristine rock and glass show that a major portion of the mass fractured by impact is in the form of plates spalled concentrically about the crater [*Hörz*, 1969; *Vedder*, 1971]. Excavation processes and consequently the final ejecta distribution and partitioning of energy strongly depend upon the brittle tensile failure characteristics of the rock, probably more so than compressional failure mechanisms. Laboratory experiments and numerical modeling show that crater evolution and ultimate shape are sensitive to the failure behavior of rocks [*Quaide and Oberbeck*, 1968; *O'Keefe and Ahrens*, 1976; *Melosh*, 1977].

Developing predictive capabilities in the field of explosive cratering has required examination of the dynamic fracture and fragmentation of rock [*Shockey et al.*, 1975; *Curran et al.*, 1977], and the possibility of in situ retorting of coal and oil shale, which requires prior rubblization, has attracted attention to its behavior under dynamic loads as well [*Murri et al.*, 1977]. Furthermore, *Matsui and Mizutani* [1977] propose that the dynamic strength and deformation behavior of rocks composing planetesimal surfaces may have been important in controlling accretion of planetesimals in the early stages of planetary formation.

Most studies of the strength of rock have been in the quasi-static regime of hydraulic or mechanical press experiments with strain rates as low as 10^{-8} per second ranging up to 3 × 10^3 per second obtainable with Hopkinson-bar apparatuses. The tensile fracture strength of rock exhibits very little dependence on strain rate at rates below 10^3 per second but increases dramatically at the higher strain rates produced by shock waves in explosion, impact, and the highest strain rate Hopkinson-bar experiments [*Rinehart*, 1965; *Stevens*, 1974; *Kumar*, 1968; *Grady and Hollenbach*, 1977]. Quasi-static tensile tests, such as employing the Brazilian geometry, demonstrate a stronger dependence on specimen size and geometry than strain rate [e.g., *Price and Knill*, 1967]. Care must be exercised in comparing fracture strength values over the range of strain rates, since the low strain rate experiments all maintain uniaxial stress states, in the test material, while the shock wave techniques produce uniaxial strain. Nevertheless, Kumar's examination of temperature effects upon the compressive fracture strength of rock suggests that a thermal activation process dominates at low strain rates, but inertial and frictional shearing controlled failure appear to dominate failure processes at strain rates between 10^3 and 10^4 per second [*Janach*, 1976]. *Grady and Lipkin* [1980] have examined a series of tensile failure models and point out several previous models and a wide class of data suggesting that tensile fracture strength is proportional to the cube root of strain rate. However, sufficient data on the behavior of various brittle materials, under high rate loading, are lacking.

In this study we have selected two basic igneous rocks, a basalt and a gabbroic anorthosite, because these are the same rock types as occur on the lunar mare and highlands, for determination of dynamic tensile fracture strength. Two other rocks, Arkansas novaculite and Westerly granite, were also tested for comparison with previous studies and different techniques. At a strain rate between 10^4 and 10^5 per second the rock samples are subjected to 1-μs-duration tensile stress pulses in a flat plate impact experiment. The stress level is varied to determine the stress which produces fracture initiation and growth. This is detected by microscopic examination for incipient spall cracks in polished thin sections made from the recovered samples. While such an approach does not determine the strain rate dependence, the conditions of fracture are appropriate for cratering and other dynamic tensile fracturing processes.

EXPERIMENTAL DESIGN

A dynamic tensile stress pulse is produced by superposing, along the midplane of the study sample, two converging planar rarefaction waves, each originating from a free surface reflection of a compressive wave [*Shockey et al.*, 1973; *Curran et al.*, 1973]. Protected recovery of the free-flying rock target,
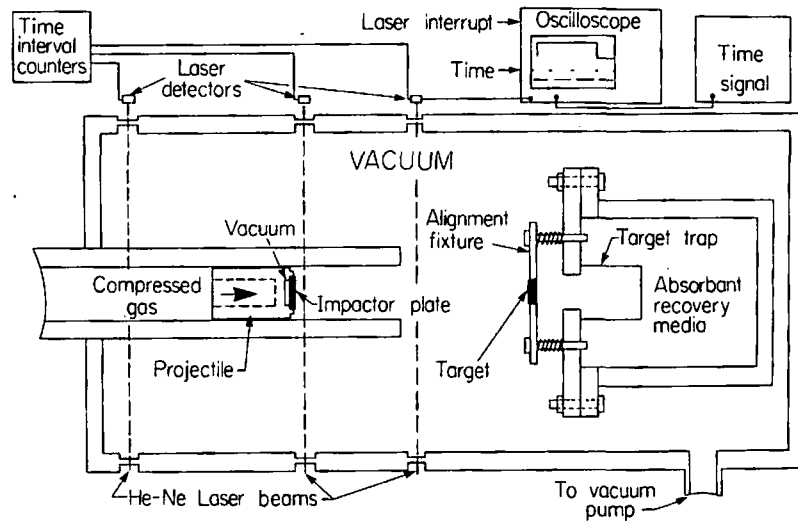
Fig. 1. Sketch of muzzle area of gas gun showing recovery tank, sample holder, and alignment fixture. The velocity of the projectile is determined both by the travel time between laser beams and by the duration of the interruption of the third beam by the projectile. After impact the sample breaks its supports and flies freely into the target trap, where it is protected from further damage.

after the initial impact, allows it to be sectioned and microscopically examined.

The experimental system (Figure 1) utilizes a 40-mm bore powder gun fitted, for these experiments, with a compressed gas breech firing system which provides velocity control in the desired range of 10 to 90 m/s. This produces tensile stresses between 27 and 243 MPa (0.27 to 2.43 kbar). The 75-g projectile, machined from polycarbonate, fits in the barrel without O rings or other seals to resist motion. Resting in the barrel during evacuation to 100 μm Hg, it is retained by a strand of fine magnet wire which breaks when the stored charge of compressed air is dumped through the breech.

The impact plate is mounted on the front of the projectile. Polymethylmethacrylate (PMMA) sheet stock is used for the impact plate material in these experiments, since it has a low shock impedence [Barker and Hollenbach, 1970]. The impact plate is press fitted into the projectile so that it is supported circumferentially, making its rear face a free surface.

Tension is produced in the rock target by superposing two converging, planar rarefaction waves in a uniaxial strain configuration (Figure 2). The initial impact between the impact plate and the rock target produces compressional shock waves propagating away from the plane of contact into each medium, putting both into uniaxial compression. The wave trav-
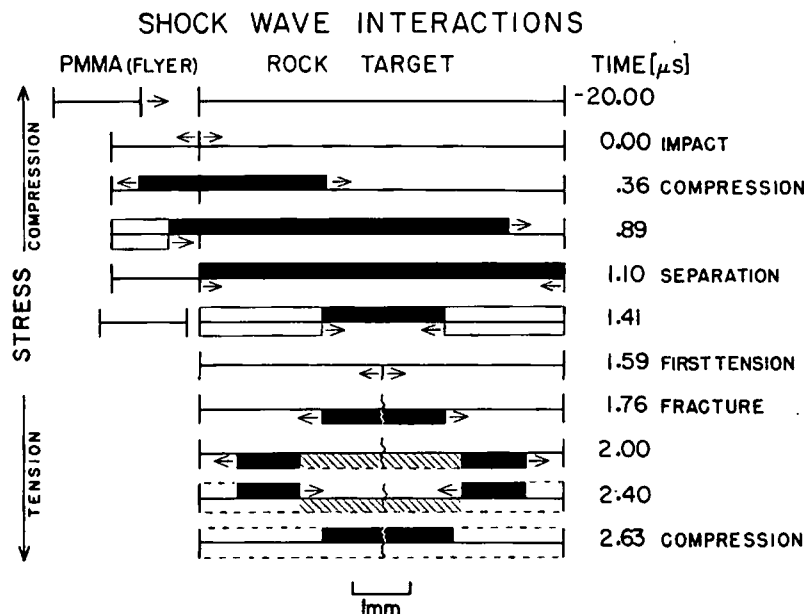
Fig. 2. Diagrammatic representation of sequence of 11 states produced upon interaction of shock waves developed at impact. In the diagram encompassing both target and impactor the vertical direction represents stress. Initial compressional waves propagate away from the impact plane, are reflected from the free surfaces of the target and impactor plate, and then superpose in the middle of the target to create uniaxial extension with ~1-μs duration. The timing of the events depicted depends on the wave velocity and thickness of the target and impactor plate, while the stress level is controlled by the material impedances and impact velocity.

eling into the impact plate reflects off of the free rear surface as a relief wave and propagates back to the contact plane, reducing the stress in the plate to zero. The geometry, in each experiment, is chosen so that the impact plate relief wave reaches the contact plane, reducing the stress to zero at the same time that the forward propagating wave in the target reflects from the target's free surface as a relief wave; this corresponds to the fifth state depicted in Figure 2. The two rarefaction waves propagating in from the surfaces of the target drop the stress in the target to zero, but each wave is accelerating material away from the plane of potential tensile failure so that when they meet, they superpose to produce tension, shown in the seventh state, 1.59 μs after impact. The figure depicts two cases. If no fracture occurs, then the two waves propagate to the sample's surfaces, bringing the whole target into tension; this is shown by the dashed lines. The two waves each reflect from the free surfaces as compressive waves and propagate to the midplane, dropping the stress to zero in their path, and superpose in the middle to produce compression, beginning a new cycle. This cycle repeats until the energy is dissipated. The midplane of the target is held in tension for at most ~1 μs between states 7 and 11. This interval is controlled only by the velocities of propagation and the thickness of the target and impact plate; it can be increased by using proportionally thicker elements.

In the case where fracture does occur, the free surface created by the fracture radiates a compression wave which drops the stress in the target to zero as it propagates away from the fracture surface. This is depicted in Figure 2 by ignoring the dotted lines and hatching. If fracture is induced in the target, the period of tension is reduced to the time interval between initial tension and the development of the fracture so that in practice, while unfractured samples experience ~1-μs intervals in tension, samples which do fracture are held in tension for shorter periods of time.

The rock target is machined to approximately 20-mm diameter and 6-mm thickness with parallel faces, one slightly beveled to aid identification in thin section. The target is then finished on a surface grinder and hand-lapped to within 5 μm of flatness across the face. Using a brittle wax tooling compound, it is suspended in a loose-fitting annulus so that its impact surface projects forward slightly. The mounting annulus and target are then fastened to the recovery vessel by three spring-loaded alignment screws. The impact surface of the target is oriented normal to the axis of the barrel by reflecting an axial laser beam back down the barrel. The impact plate on the projectile is also carefully fitted normal to the axis of the projectile to insure planar impact.

The target assembly is positioned in front of an aperture in the recovery vessel, as shown in Figure 1. This permits the rock sample to fly freely into the recovery vessel after snapping its wax supports upon impact but prevents the larger-diameter projectile from following. The target, or target pieces if fragmentation occurs, collects in a cloth sack which seals as it flies free of its support. The sack and enclosed rock target are decelerated and cushioned by loosely stuffed rags and foam rubber in the recovery chamber.

During the experiment, only the impact velocity of the projectile is recorded, from which the dynamic stress may be calculated, as described below. The velocity of the projectile

TABLE 1. Properties of Rocks

Rock	Minerology, % by volume	Grain Size, mm	Texture	Flaw Structure	Density, g/cm³	Ultrasonic P Velocity, km/s	K, PMMA Impact Plate, 10⁶ kg/m²/s
Arkansas novaculite	100% quartz	0.01	equigranular, occasional 100-μm fragments	oriented cracks up to 0.5 mm [Shockey et al., 1974]	2.6*	6.0*	2.7
Westerly granite	37% K feldspar 30% plagioclase (An 10–20) 26% quartz 6% mica 1% opaques	0.1–0.8 0.2–1.0 0.2–0.6	equigranular subhedral	cracks up to 0.3 mm [Hadley, 1976]	2.6*	5.0*	2.6
Beaver Bay gabbroic anorthosite	67% plagioclase (An 60–90) 26% pyroxene 5% opaques 2% limonite	0.4–0.7 0.1–0.7	intergranular, euhedral equigranular subhedral		3.0†	6.8†	2.8
Ralston basalt	63% feldspar 15% plagioclase (An 70–90) 15% pyroxene (augite) 5% opaques 2% limonite	<0.1 0.7–1.2 1–1.5	fine grained feldspar matrix euhedral phenocrysts euhedral phenocrysts		2.8†	6.4†	2.8

The modal fractions, from Rosiwal analysis, are approximate.
*Grady and Hollenbach [1978].
†This study.

prior to impact is determined by the sequential interruption of three laser beams, one at the muzzle and two which traverse the barrel (Figure 1), during the final 40 cm of projectile travel. Each beam is monitored by a photodiode detector that triggers a time interval counter which is halted when the next beam is interrupted. The counters provide an accuracy of ±10 μs, and beam spacing is measured to ±0.5 mm, resulting in an overall precision of ±0.5% for average interval velocities [Ahrens et al., 1971]; however, over the velocity range of 10 to 90 m/s the projectile is still accelerating as it approaches the muzzle of the barrel so that increases of 20% were not uncommon between the first and second average interval velocities. We relied instead on the velocity of the projectile as it leaves the barrel, which was measured by recording, on a dual-trace oscilloscope, the signal from the third laser detector with a calibrated 10-kHz time signal on the second trace. The velocity is then determined from the length of the projectile and the time interval that the laser beam is blocked. Measuring the interrupt time from the photographic record of the oscilloscope trace is the principal limit on accuracy. The overall accuracy varied from ±1% to ±4% depending how close the actual velocity is to the predicted velocity and hence whether the signal occupies most of the oscilloscope sweep.

To maintain a state of uniaxial strain in the target samples during the tensile pulse, the sample must have a sufficiently large diameter that relief waves from the edges do not propagate into the region of interest. As the tensile state ends, at each point, after the shock wave has traversed at most twice

the thickness of the sample beyond that point, the minimum diameter to assure strictly uniaxial strain in the center of the target is 4 times the thickness. In this experiment the target must be smaller than the projectile to allow recovery so that in practice, a ratio of 3 to 1 is employed. Consequently, relief waves from the initial compressional phase will reach the center of the target during the tensile phase, shifting the dynamic stress state somewhat by increasing the tension acting on planes normal to the impact plane and increasing the axial stress level approximately 15%, but the greatest principal stress will still act normal to the impact plane. Our calculations of stress levels assume uniaxial strain, ignoring this effect.

Induced tensile spall fractures are expected to lie normal to the axis of greatest principal tension and will therefore be parallel to the impact face. In this experiment the strain rate and length of time at tension are held essentially fixed while the stress level is varied by varying the impact velocity; thus it is the stress level at which crack growth is initiated, under dynamic loading, that is determined.

DYNAMIC STRESS LEVEL

The intensity of the tensile stress created by combining the two relief waves in the target is a function only of the densities and wave velocities of the target and impact plate, and of the impact velocity. We have assumed that the relief waves travel at the same velocity as the compression waves and that attenuation of the stress waves is low so that the magnitude of the

| (a) ARKANSAS NOVACULITE | 85 MPa | (b) WESTERLY GRANITE | 106 MPa |
| (c) WESTERLY GRANITE | 125 MPa | (d) WESTERLY GRANITE | 154 MPa |

1 mm
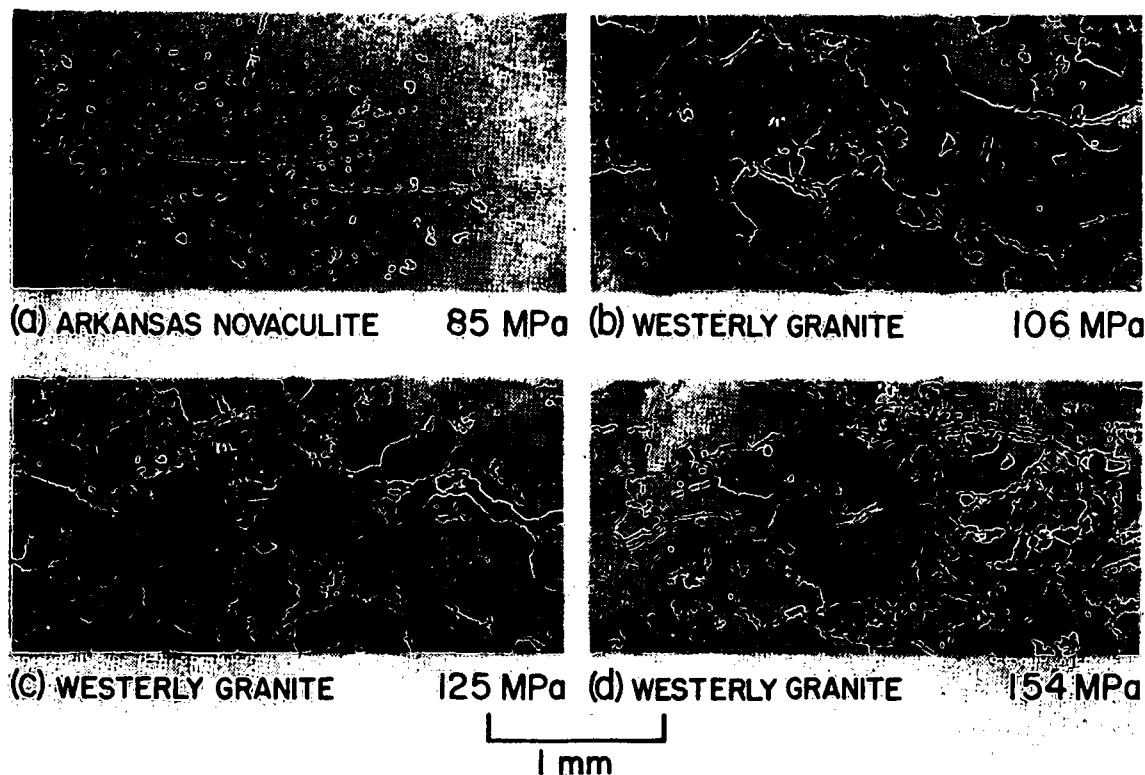
Fig. 3. (a) Reflected light photomicrograph of overlap of two adjacent induced cracks in Arkansas novaculite in a sample which showed 11 2- to 4-mm cracks running entirely across both cross sections. (b–d) Westerly granite targets stressed at increasing levels to demonstrate fracturing, indicating that the dynamic tensile strength is exceeded (Figures 3b and 3c), and the widening and fracturing on multiple planes and fragmentation that develops at higher stresses Figure 3d. The impact plane is parallel to the long dimension in each image.

tensional stress developed equals the compressional stress level in the first phase of compression.

The level of compressional stress is governed by the familiar momentum and stress equations. Let us define the following parameters:

ρ_i, ρ_t respective initial state densities of the impact and target materials;

u_i, u_t respective particle velocities, after passage of initial shock waves, relative to the laboratory;

c_i, c_t respective longitudinal (P) wave velocities of impact and target materials;

σ_i, σ_t principal stress component acting normal to plane parallel to impact surface, for impact plate and target;

U_p impact velocity of the projectile.

Then the momentum equation, applied both to target and impact plate, becomes

$$\sigma_t = \rho_t c_t u_t \qquad \sigma_i = \rho_i c_i (U_p - u_i) \qquad (1)$$

At the impact plane we have continuity of both displacement and stress, yielding

$$u_t = u_i \qquad \sigma_t = \sigma_i$$

$$\sigma_t = \rho_i c_i \left(U_p - \frac{\sigma_t}{\rho_t c_t} \right)$$

and

$$\sigma_t = \frac{\rho_i c_i \rho_t c_t}{\rho_i c_i + \rho_t c_t} U_p = K U_p \qquad (2)$$

which relates the stress level, in the target, to known quantities.

The impact plate material, PMMA, has been extensively studied by *Barker and Hollenbach* [1970]. Its density is 1.18 g/cm^3, and, in the low-stress regime relevant to this study, it has a shock wave-speed of 2.8 km/s. The speed of rarefaction waves exceeds that of the compressional waves by no more than 5%, at these stress levels, and this difference is ignored. As only the impact velocity is measured during the experiment, the actual shock wave velocities in the target and impact plate, for each experiment, are unknown. However, the measured variation of shock wave velocity with stress level is small in PMMA over the range of interest. While rock materials show substantial increases in longitudinal velocity under uniaxial stress conditions between stresses of zero and 50 MPa [*Tocher*, 1957], it is shown below that these variations are not important to the determination of stress levels. For the rock samples it is assumed that the shock wave velocity is equal to the ultrasonic longitudinal velocity measured in this study. We also assume that the elastic moduli and consequently the propagation velocity do not change significantly as the rock goes from compression to extension. Failure of this assumption would imply that the tensile stress produced is different from the compressive stress which is determined by (2). The shape of the stress wave as it propagates through the target is also unknown; however, in Grady and Hollenbach's experi-
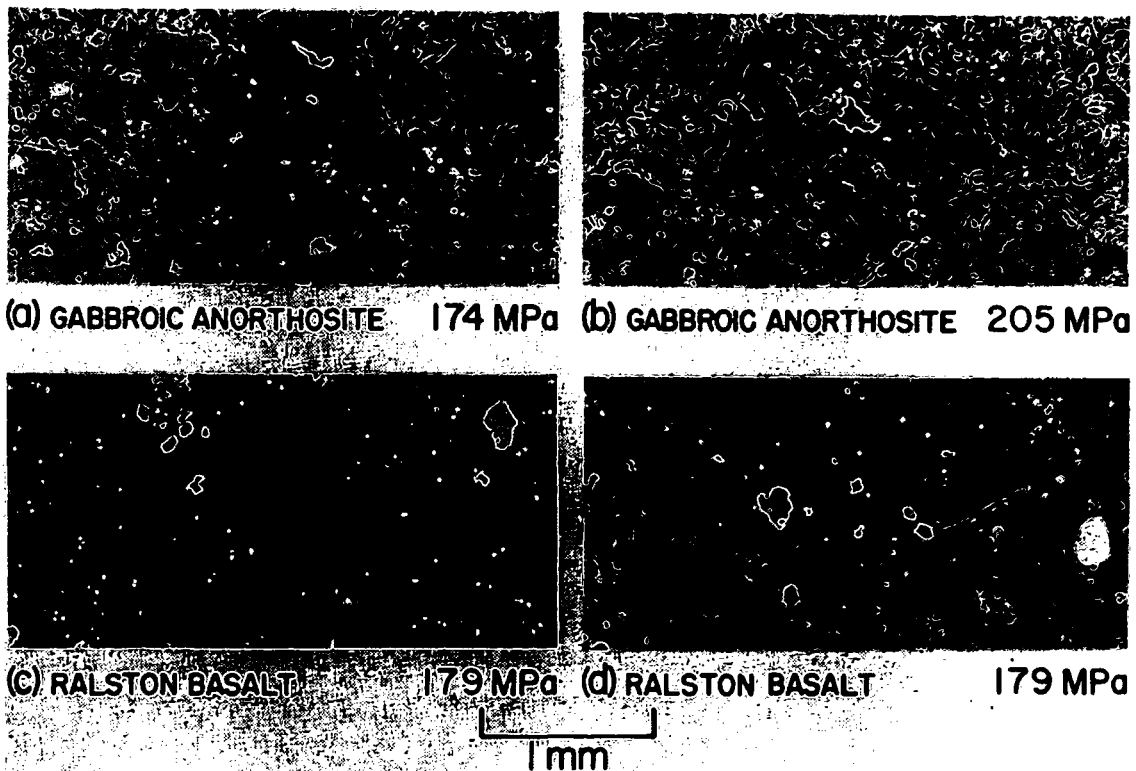
Fig. 4. (a-d) Reflected light photomicrograph of cracks in gabbroic anorthosite and Ralston basalt indicating that the dynamic tensile strength is exceeded. In each of these samples a series of cracks traverses the entire cross section close to its midplane. Propagation of fractures both through grains and along grain boundaries is illustrated by different views of the same sample of Ralston basalt (Figures 4c and 4d). The impact plane is parallel to the long dimension in each image.

TABLE 2. Record of Shots for Each Rock

Impact Velocity, m/s	Stress, MPa	Comments
		Arkansas Novaculite
14.9	40	0.3-mm crosshatched grid of cracks presumed induced by thin sectioning, since cracks are also seen in mounting material
21.0	57	0.3-mm crosshatched grid of cracks presumed induced by thin sectioning, since cracks are also seen in mounting material
21.6	58	no cracks
24.7	67	no cracks
28.3	76	0.3-mm crosshatched grid of cracks also in mounting material
32.7	88	11 2.0- to 4.0-mm-long cracks
34.7	94	2 2.0- to 4.0-mm-long cracks
38.8	105	3 chains, perpendicular to impact plane, of 0.5-mm cracks trending ~45° to impact plane
86.9	235	fragmented
		Westerly Granite
29.2	76	no cracks
36.4	95	no cracks
39.2	102	18 2.0- to 4.0-mm-long cracks
44.8	116	coalesced cracks across entire section
46.2	120	coalesced cracks across entire section
52.1	135	coalesced cracks across entire section
57.2	149	coalesced cracks across entire section and macroscopic fracture/failure
101.5	264	fragmented
		Gabbroic Anorthosite
38.3	107	no cracks
38.5	108	no cracks
39.8	111	no cracks
42.0	118	3 4-mm cracks normal to impact plane
50.6	142	2 6-mm-long chains of cracks normal to impact plane
51.6	144	no cracks
52.1	146	1 2-mm crack parallel to impact plane
54.8	153	5 2- to 4-mm cracks at midplane
62.0	174	coalesced cracks across entire section
73.3	205	coalesced cracks across entire section
73.8	207	coalesced cracks across entire section
		Ralston Basalt
21.5	60	no cracks
22.7	63	no cracks
34.6	97	no cracks
37.6	105	no cracks
41	115	no cracks
42.7	119	no cracks
43.1	120	no cracks
45.8	128	no cracks
56.0	157	no cracks
63.8	179	10 2- to 4-mm cracks across entire section
70	195	spall along midplane; half with free surface in one piece, impact half in four pieces

ments, where a record of free surface velocity rather than sample recovery is obtained, rise times corresponding to strain rates of 10^4–10^5 per second are observed for rarefaction waves [*Grady and Hollenbach*, 1977, 1979].

While the shock wave velocities of the rocks studied are not measured, the effect of these uncertainties in K, the proportionality factor relating impact velocity and induced stress in

(2), is small. This is due to the low shock impedence, I_i (product of density and wave velocity), of PMMA compared to the rocks studied. From (2) we have

$$\frac{\partial \sigma_t}{\partial c_t} \frac{c_t}{\sigma_t} = \frac{c_t}{K} \frac{\partial K}{\partial c_t} = \frac{I_i}{I_i + I_t} \tag{3}$$

which relates fractional change in shock wave velocity to resulting fractional change in the value determined for stress. Substituting the values for PMMA and selected rocks (Table 1) into (3) yields

$$\frac{\partial \sigma_t}{\partial c_t} \frac{c_t}{\sigma_t} < 0.2.$$

which shows that a 10% variation in the elastic wave velocity produces less than 2% change in the value of stress determined. Thus the difference between the shock wave velocity, in a particular experiment, and the ultrasonic velocity used to calculate stress may be neglected. The values of K relating stress in megapascals to projectile velocity in meters per second range between 2.6 and 2.8, shown in Table 1 for the selected rocks.

LITHOLOGIES OF ROCKS

Four competent, low-porosity rocks were selected for dynamic tensile fracturing in this study. A range of textures is explored. The most finely textured material is a 10-μm grained quartzite (novaculite). The remaining three rocks have igneous origins with grain sizes ranging from 0.1 mm to 1.5 mm. All samples of each lithology were made from the same piece of source rock at the same orientation. No effort has been made to examine variations in behavior due to orientation, since *Shockey et al.* [1973] concluded in their study of Arkansas novaculite, which shows a strong preferred flaw orientation, that dynamic strength properties are independent of orientation. One sample of each material was selected for thin sectioning to establish a baseline crack distribution for comparison to the cracks produced by the impact experiment. None of these control sections showed flaws greater than 0.5 mm in length, nor were any preferred orientations of the larger flaws observed which might confuse identification of induced spall cracks in a target when examined microscopically after recovery. In addition to the control samples, for each rock several tests were made at low stress levels which failed to produce spall cracks, and so the above statements apply to these sections as well, confirming the general absence of cracks which we identify as spall cracks, in unstressed samples. The distinguishing properties of each of the four rocks are given below and in Table 1.

Novaculite, from Hot Springs, Arkansas, is a microcrystalline (10-μm grain size), homogeneous quartzite composed of uniform-sized, randomly oriented quartz grains cemented with silica. This material is transparent to a thickness of about 0.2 mm, permitting extensive microscopic examination. Its dynamic tensile strength and fragmentation properties have been studied by *Shockey et al.*, [1973, 1974], who also report an intrinsic, oriented system of flaws up to 1-mm maximum diameter (sample courtesy of D. Grady).

Gabbroic anorthosite, from Beaver Bay, Minnesota, is a homogeneous, fine grained (0.2–0.7 mm) rock composed primarily of plagioclase and pyroxene. Under microscopic examination it shows only slight alteration and no porosity, cracks, or flaws, although these are assumed to exist on some scale.

TABLE 3. Dynamic Tensile Strength and Crack Lengths

Rock	Dynamic Tensile Strength, MPa	Stress, MPa	Crack Distribution (Full Length)		
			1.5–2.4 mm	2.5–3.4 mm	3.5–4.4 mm
Arkansas novaculite	67–88	88	1	8	2
Westerly granite	95–116	102	2	9	7
Gabbroic anorthosite	153–174	153	2	2	1
Ralston basalt	157–179	179	4	5	1

The dynamic tensile strength, as defined in the text, is shown for each rock along with the stress level and distribution of cracks, by size, for the sample tested at the lowest stress level producing dynamic tensile failure.

Westerly granite, quarried in Westerly, Rhode Island, is a widely studied, medium grained (0.1–1.0 mm) granite primarily of feldspar and quartz. The crack density and geometry in Westerly granite are reported by *Hadley* [1976]. She observed no cracks greater than 0.3 mm, with a scanning electron microscope, in unstressed samples.

Ralston basalt, quarried near Golden, Colorado [*Mizutani et al.*, 1977], is a homogeneous, fine grained (0.2–1.5 mm) unweathered porphyritic basalt which shows no porosity or 0.5- to 5-mm cracks when examined microscopically (sample courtesy of H. Spetzler).

Ralston basalt and the Beaver Bay gabbroic anorthosite were chosen mainly because these are nominally the same rock types as are present on the lunar mare and highlands, respectively. Thus the behavior of the basalt and gabbroic anorthosite is expected to be representative of the pristine lunar crust under impact cratering processes. The other rocks were chosen for comparison to previous studies, some using different techniques to determine the same properties.

ANALYSIS AND RESULTS

Targets are removed from the recovery vessel in the cloth sack in which they are sealed after flying free of the mounting annulus. In general, they are intact and competent, exhibiting no visible failures at the surface, except for very highly stressed samples, which may spall into two equal pieces along their midplane or fragment. Some Arkansas novaculite samples, because of the transparency of this rock, displayed obvious internal crack surfaces. The sample disks are cut diametrically. The two halves are mounted with impact faces together and impregnated with epoxy. The cut surface is polished and mounted on a slide, and a thin section is cut and polished, resulting in two separate parallel section views of the internal fracturing of the sample.

Cracks 0.1–4 mm are easily delineated and photographed (Figures 3 and 4) using reflected light microscopy. In transmitted light, the high contrast between adjacent grains, particularly in the igneous rocks, enables easy identification of grain boundaries but obscures the crack traces which often follow along them. Since the cracks are generally not open, Figure 3d being an exception, the accentuation due to the polishing process is necessary to see them at all.

Distinguishing possibly preexisting cracks from induced cracks is problematical, since the samples cannot be examined prior to testing. Consequently, it is assumed that every crack observed in thin section was produced by the impact experiment. This is in general untrue, since Arkansas novaculite and Westerly granite have documented natural flaws with maximum diameters less than 1 mm [*Shockey et al.*, 1974; *Hadley*,

1976] and the Ralston basalt and gabbroic anorthosite presumably also have natural populations of flaws. Nevertheless, examination of targets recovered from low-stress shots and those never stressed show that the population of 0.5-mm and larger cracks is low, since none were observed in 24 thin sections. In addition, induced cracks are expected to lie parallel to the impact surface, as most of those observed were found; naturally occurring cracks would not be expected to show such a preference.

The number, location, and orientation of cracks are recorded for each recovered target. Figures 3 and 4 show some examples of the observed cracks in each of the rocks studied. In each photomicrograph the impact face is parallel to the long dimension so that the observed cracks are normal to the maximum principal tension, as expected. Crack initiation and growth begin, for each rock, over a range of stress levels presumably reflecting statistical variations in the distribution of flaws from sample to sample. This effect is demonstrated in Table 2. Stress levels at or slightly above the level which pro-

TABLE 4. Comparison of Dynamic Tensile Strengths by Various Authors

Method	Dynamic Tensile Strength, MPa	Author
Arkansas Novaculite		
Free surface velocity pullback signal	149	*Stevens* [1974]
Free surface velocity pullback signal	73–108	*Grady and Hollenbach* [1979]
Terminal examination	38–42	*Shockey et al.* [1973]
Terminal examination	67–88	this study
Westerly Granite		
Free surface velocity pullback signal	127	*Stevens* [1974]
Free surface velocity pullback signal	45	*Grady and Hollenbach* [1979]
Terminal examination	95–116	this study
Basalt (Various)		
Free surface velocity pullback signal	114	*Stevens* [1974]
Free surface velocity pullback signal	130	*Grady and Hollenbach* [1979]
Terminal examination	157–179	this study

The terminal examination method is described herein. Tensile strength may also be determined by measuring the drop in velocity of the target's free surface due to the arrival of the compression wave generated by the expanding tensile crack. The technique is described by *Grady and Hollenbach* [1979].

duces crack growth cause several fractures to form. Adjacent fractures tend to terminate with slight overlap of their respective crack tips as in Figures 3a and 4b.

We define the dynamic tensile strength to be the tensile stress which produces a chain of nearly coplanar cracks traversing the whole cross section of the target; however, this stress is less than the stress which produces strength failure, since the cracks need not coalesce. Figures 3a–3c and 4a–4d show cracks induced by dynamic tensile stresses close to the dynamic tensile strength of the particular rock. The fractures are essentially confined to one surface intersecting any traverse through the target except where adjacent crack tips overlap. Applying the above definition of dynamic tensile strength yields a range of values of stress as shown in Table 2. At the low end is the maximum stress consistently failing to produce a series of tensile cracks at the midplane of the target. At the high end is the minimum stress which repeatably produces cracks along the entire cross section. Consequently, we prefer to view the dynamic tensile strength of each of these rocks as a range of stress levels, as shown in Table 3, rather than a single value with associated error bars.

The two 'lunar' rock types exhibit the highest dynamic tensile strength of the rocks tested. Gabbroic anorthosite failed over the range 153–174 MPa, and Ralston basalt at 157–179 MPa. Westerly granite also demonstrated exceptional strength at 95–116 MPa, and Arkansas novaculite, with a dynamic tensile strength range 67–88 MPa, showed itself stronger under dynamic loads than most other sedimentary rocks [Grady and Hollenbach, 1979]. In calculations where a simple dynamic fracture strength criterion is sufficient, these values are more appropriate to describe rock behavior under shock loading than are static fracture strengths, which have often been applied but which are considerably lower.

While terminal analysis provides no direct observations of the fracturing process, it does permit us to place constraints on the crack growth velocity in the sample. Table 3 displays the distribution of cracks, tabulated according to full observed length, for the lowest stress shot, for each rock, which produced a continuous line of spall cracks at the midplane of the sample. The longest crack traces observed, in each rock, are slightly greater than 4 mm long. If we assume bilateral crack growth, then the maximum crack tip propagation is approximately 2 mm, and if this occurs during the first tensile cycle, which lasts ~1 μs, it implies an average crack velocity close to one-third the longitudinal wave velocity, which has been observed by Shockey et al. [1973].

DISCUSSION

The values for dynamic tensile strength determined by the terminal examination method of this study and Shockey et al. [1973], and by Stevens [1974] and Grady and Hollenbach [1979], using the drop in free surface velocity due to the compression waves radiating from the induced spall crack, do not agree well, as shown in Table 4. Besides disagreement in values determined by the two different techniques, which can be attributed to experimental differences, there also exist disagreements between values determined by separate studies using the same methods. Table 4 shows that these disagreements are not systematic.

It is perhaps tempting to ascribe these differences to sample variability, but more likely the inconsistency is due to the inadequate description of rock brittle failure by the single-parameter dynamic tensile strength. Nevertheless, where a

simple failure criterion is desired and its imprecision is tolerable, the presently determined dynamic tensile strength provides a useful description of the dynamic failure of rock. Table 4 shows that with the exception of a single experiment on one sample, the dynamic tensile strength of nonporous igneous rocks ranges from 100 to 180 MPa, with the more basic rocks producing the higher values. We believe the greater tensile strength of basic rocks, which includes Grady and Hollenbach's [1979] Dresser basalt which contains significant quantities of amphibole, is an unexpected but significant result. The dynamic tensile strengths of igneous rocks are much higher than ever determined under quasi-static tensile conditions. The static strength of granite, for example, measured by Rhinehart [1965], is 6.8 MPa, while the dynamic values in Table 4 range between 45 and 127 MPa.

It is clear that igneous rocks, and the lunar rock types in particular, are highly resistant to short-pulse tensile stresses in the range 100–150 MPa, much greater than the values assumed in previous crater modeling studies [O'Keefe and Ahrens, 1976]. The present high values of the dynamic tensile strength should be used in future efforts to model both accretion and fragmentati , processes relating to the formation of solar system objects, ..nd for impact and explosive cratering and excavation studies.

REFERENCES

Ahrens, T. J., J. H. Lower, and P. L. Lagus, Equation of state of forsterite, J. Geophys. Res., 76, 518–528, 1971.

Barker, L. M., and R. E. Hollenbach, Shock wave studies of PMMA, fused silica and sapphire, J. Appl. Phys., 41, 4208–4226, 1970.

Curran, D. R., D. A. Shockey, and L. Seaman, Dynamic fracture criteria for polycarbonate, J. Appl. Phys., 44, 4025, 1973.

Curran, D. R., D. A. Shockey, L. Seaman, and M. Austin, Mechanisms and modes of cratering in earth media, in Impact and Explosion Cratering, edited by D. J. Roddy, R. O. Pepin, and R. B. Merrill, pp. 1057–1087, Pergamon, New York, 1977.

Grady, D. E., and R. E. Hollenbach, Rate controlling processes in the brittle failure of rock, Rep. SAND 76-0659, Sandia Lab., Albuquerque, N. Mex., 1977.

Grady, D. E., and R. E. Hollenbach, Dynamic tensile fracture in rock, Rep. SAND 78-0531, Sandia Lab., Albuquerque, N. Mex., 1978.

Grady, D. E., and R. E. Hollenbach, Dynamic fracture strength of rock, Geophys. Res. Lett., 6, 73–76, 1979.

Grady, D. E., and J. Lipkin, Criteria for impulsive rock fracture, Geophys. Res. Lett., 7, 255–258, 1980.

Hadley, K., Comparison of calculated and observed crack densities and seismic velocities in Westerly granite, J. Geophys. Res., 81, 3484–3494, 1976.

Hörz, F., Structural and mineralogical evaluation of an experimentally produced crater in granite, Contrib. Mineral. Petrol., 21, 365–377, 1969.

Janach, W., The role of bulking in brittle failure of rocks under rapid compression, Int. J. Rock Mech. Min. Sci. Geomech. Abstr., 13, 177–186, 1976.

Kumar, A., The effect of stress rate and temperature on the strength of basalt and granite, Geophysics, 33, 501–510, 1968.

Matsui, T., and H. Mizutani, Why is a minor planet minor, Nature, 270, 506–507, 1977.

Melosh, H. J., Crater modification by gravity: A mechanical analysis of slumping, in Impact and Explosion Cratering, edited by D. J. Roddy, R. O. Pepin, and R. B. Merrill, pp. 1245–1260, Pergamon, New York, 1977.

Mizutani, H., H. Spetzler, I. Getting, R. J. Martin III, and N. Songa, The effect of outgassing upon the closure of cracks and the strength of lunar analogues, *Proc. Lunar Sci. Conf. 8th,* 1235-1248, 1977.

Murri, W. J., C. Young, D. A. Shockey, R. E. Tokheim, and D. R. Curran, Determination of dynamic fracture parameters for oil shale, final report to Sandia Laboratories, *Rep. PYD-5046,* Stanford Res. Inst., Menlo Park, Calif., 1977.

O'Keefe, J. D., and T. J. Ahrens, Impact ejecta on the Moon, *Proc. Lunar Sci. Conf. 7th,* 3007-3025, 1976.

Price, D. G., and J. L. Knill, A study of the tensile strength of isotropic rocks, in *Proceedings of the 1st Congress of the International Society of Rock Mechanics,* vol. I, pp. 439-442, Laboratório Nacional de Engenharia Civil, Lisbon, 1967.

Quaide, W. L., and V. R. Oberbeck, Thickness determinations of the lunar surface layer from lunar impact craters, *J. Geophys. Res., 73,* 5247-5270, 1968.

Rinehart, J. S., Dynamic fracture strength of rocks, in *Proceedings of the 7th Symposium on Rock Mechanics,* vol. I, p. 209, American Institute of Mining, Metallurgical and Petroleum Engineers, New York, 1965.

Shockey, D. A., C. F. Petersen, D. R. Curran, and J. T. Rosenberg, Failure of rocks under high rate tensile loads, in *New Horizons in Rock Mechanics,* p. 709, edited by H. R. Hardy, Jr., and R. Stefanko, American Society of Civil Engineers, New York, 1973.

Shockey, D. A., D. R. Curran, L. Seaman, J. T. Rosenberg, and C. F. Petersen, Fragmentation of rock under dynamic loads, *Int. J. Rock Mech. Min. Sci., 11,* 303-317, 1974.

Shockey, D. A., D. R. Curran, M. Austin, and L. Seaman, Development of a capability for predicting cratering and fragmentation behavior in rock, final report, *DNA 3730F,* Def. Nucl. Agency, Washington, D. C., 1975.

Stevens, A. L., Spall strength of selected geological materials (abstract), *Eos Trans. AGU, 55,* 421, 1974.

Tocher, D., Anisotropy of rocks under simple compression, *Eos Trans. AGU, 38,* 89-94, 1957.

Vedder, J. F., Microcraters in glass and minerals, *Earth Planet. Sci. Lett., 11,* 291-296, 1971.

ENVIRONMENTAL ASPECTS AND THE FEASIBILITY
OF ECONOMIC RECOVERY OF
METALS AND ENERGY FROM COAL WASHER WASTE DEPOSITS

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Abstract. Metal sulfides, chiefly pyrite and minor sphalerite associated with the Herrin (No. 6) coal member of the Pennsylvania Carbondale Formation, have been concentrated in a coal refuse deposit in southern Illinois. Oxidation of pyrite has produced highly acid waters with high concentrations of iron, zinc (up to 200 parts per million) and toxic trace elements that have leached downward to a water system perched on glacial drift.

Chemical, petrographic, low-temperature ashing and x-ray diffraction were performed on cores. The data show that economic recovery of zinc and other trace metals is unlikely at this site. Energy (coal) recovery at the Superior Washer site is possible if resultant environmental problems are considered in the planning.

Introduction

Coal after mining requires beneficiation to remove excess rock and mineral matter. After crushing, the low-density coal is separated from the more dense rock and mineral waste in a fluid medium. The rejected material is known as gob. Turbid waste water from spent separation fluids and coal rinsing is sent to a holding pond for clarification by settling. The fine, laminated sediment accumulated in such an impoundment is known as slurry. Slurry deposited prior to the development of more efficient extraction methods can contain large quantities of fine coal.

In the past, coal wastes were deposited near the preparation plant with economic convenience being the only consideration. Easily eroded gob and slurry deposits were abandoned after mining and processing operations ceased (Wewerka, et al., 1976; Schubert, et al., 1978).

Illinois Basin and Appalachian bituminous coals contain pyrite, much of which becomes concentrated in coal wastes. The pyrite, when exposed to atmospheric moisture and oxygen, is oxidized and dissolved. This releases iron, sulfate and hydrogen ion to meteoric water infiltrating through the wastes. Catalized by an iron oxidizing bacterium, Thiobacillus Ferroxidans, the oxidation of pyrite proceeds rapidly (Singer and Stumm, 1970). Highly acid, iron sulfate waters developed in the wastes leach alkaline earths and heavy metals from associated minerals. Sulfide-bearing coal waste deposits are characterized by a lack of vegetation, rapid erosion and serious degradation of surface drainages by silting and objectionable runoff quality.

Currently, there are over 14,000 acres of abandoned coal wastes in the Illinois Basin. There are over 1,000 abandoned deposits in Illinois and 711 of these pose serious environmental problems (Schubert, et al., 1978).

Proposals for the solution of these problems are numerous and vary widely in approach. They fall into three basic categories: 1) Chemical treatment of the wastes or the acidic runoff; 2) Recovery of industrial clays, metals and energy or use of coal wastes as construction aggregates or fill material; 3) Burial of wastes by back-filling of abandoned mine voids or reclaiming the land by grading, liming and revegetation. Since processing methods varied with time and place and because of spatial variations in coal seam mineralogy, no two waste deposits are chemically and physically identical. The questions of treatment, materials recovery, or burial and reclamation may have to be evaluated for each deposit individually (Wewerka, et al., 1976).

In 1978, a project was funded by the Office of Surface Mining through Argonne National Laboratory to study one such waste deposit for the following environmental and economic purposes: 1) to determine mineral distributions and their relationships to subsurface water chemistry; 2) To determine the possible economic content of the deposit in terms of metals and energy; 3) To suggest how such information may be used in planning for economic recovery or reclamation of the land.

Site Description

The Superior Coal Company washer is located in Macoupin County, Illinois (Figure 1) where previous underground mining has exhausted the Herrin (No. 6) Coal (Smith and Bengal, 1975). Selection of the study site was based upon 1) ease of access to vehicles and equipment, 2) proximity to Consolidated #14, a similar coal waste site recently reclaimed and being monitored by the Land Reclamation Program of Argonne National Laboratory, and 3) proximity to other sites, whose poor quality runoff collectively degrades Cahokia Creek, the major drainage in this area. In a 15 square mile area of its headwaters Cahokia Creek receives acid drainage from at least 10 abandoned coal waste deposits of varying size.

The No. 6 Coal is a member of the Pennsylvanian Carbondale Formation and is about 330 feet (101 m) below the surface in this area. The Carbondale is overlain by about 250 feet (76 m) of shales, limestones and thin coals of the Pennsylvanian Modesto Formation. If present the overlying Shoal Creek Limestone of the Pennsylvanian Bond Formation is thin and is covered by about 40 feet (12 m) of Illinoian glacial till and 10 feet (3 m) of Wisconsin loess (Smith, 1961; Willman, et al., 1975).

The Superior Coal Company operated four shaft mines between 1904 and 1954. The mine products were processed at the

central washer site. During that time, over 900,000 cubic yards (688,000 m3) of coal wastes were produced, covering roughly 58 acres.

Two small gob piles near the center of the site rise 50 and 60 feet (15 and 18 m) above a much larger area of low, graded gob. One small (1 acre) exposure of slurry, about 2 feet (.6 m) thick, lies on the northeast boundary of the site (Figure 2). Evidence for more slurry can be seen around the entire northern perimeter of the graded gob area where erosional gullies dissect the gob embankment, buried soil and loess. Outcrops of slurry, roughly 3.3 feet (1 m) thick, can be found lying on the soil and buried by about 2 meters of gob. Similar evidence of thin, discontinuous buried slurry is found along drainages south and east of the gob piles. Undulations in the upper slurry contact and the normally flat slurry-sediment laminations indicate that gob was graded over the slurry material while it was still wet and plastic. The slurry materials are otherwise typical in appearance, being grey-black, laminated, and ranging from sand to clay in particle size.

The gob materials are distinctly inhomogeneous, showing a wide range in size and composition. Blocks of massive pyrite can be found along with pyritic nodules and impure coal and shale fragments containing finely disseminated pyrite. Shale, claystone and coal fragments are present in very small sizes. Green, yellow and white metal sulfates are often found on the more weathered shale and coal partings and also impart color to the ubiquitous clays.

The gob material transported by storm runoff is better sorted and homogenous. This gob is primarily composed of small, well sorted fragments of grey shale with some coal (Figure 2).

The entire deposit rests upon a flat lying Wisconsinan loess surface (Figure 3). The loess surface slopes gently to the east toward Spring Creek (Figure 2), the upper northeast branch of the Cahokia Creek system. Erosional gullies dissecting the gob are more numerous in the northeast and southeast sectors of the deposit and form two peripheral drainage systems which flow separately into Spring Creek (Figure 2).

The streambeds of all surface are filled with several feet of silt and are highly unstable, carrying significant subsurface flow. Surface flow is generally not apparent in lower portions of the larger gullies, but is perennial in the peripheral systems and drainages to Spring Creek. Reconnaissance of the site in May of 1978 yielded specific conductivities between 4940 and 8900 umohs/cm at 17°C and pH values near 3.0 for peripheral drainages south and southeast of the gob piles.

Sampling and Methodology

In June of 1978, 34 cores were collected from gob and slurry materials at 11 stations at the Superior washer site (Figure 2). To study the weathering profile, a maximum of four samples were taken at each station at depths ranging from 0.1 (.3 feet) to 6.7 (22 feet) meters. Some of the cores were analyzed for mineralogy using X-ray diffraction and petrographic techniques. They were also analyzed for total carbon, BTU and whole rock elemental content. All cores were analyzed for total sulfur, sulfate, sulfide, and organic sulfur and were also ashed in a low-temperature oxygen-plasma asher using methods described by Rao and Gluskoter (1973).

After coring, the hole at each station was augered to a depth below the water table and cased with PVC pipe for later water sample collection. With the exception of the monitoring well at station 2 (Figure 2) in the exposed slurry area, the water table was consistently found to be above the gob/loess contact (Figure 3).

Field measurements for water samples include specific conductance, temperature, pH, Eh and dissolved oxygen. Sample splits for anion analyses were refrigerated and analyzed within four days of collection. Cation sample splits were filtered and then acidified for later analysis. All analyses were performed using standard wet chemical, selective ion electrode, and atomic absorption techniques. The results for well waters collected in March of 1979 are reported in Table 1.

Metals

The waters are highly concentrated in iron and sulfate and have a low pH (Table 1) as a result of pyritic oxidation and leaching. The chemically aggressive acid waters have also leached significant amounts of the common ions, Ca^{2+}, Mg^{2+}, Na^+, and K^+. X-ray diffraction analyses of solids showed gypsum, illite, montmorillonite, and possibly a regular illite-montmorillonite mixed layer clay as the likely sources of these ions. No carbonate sources for Ca^{2+} or Mg^{2+} were found by either X-ray or petrographic techniques.

The high aqueous aluminum values of up to 11,100 ppm (Table 1) also indicate the importance of clay minerals to leachate chemistry. No other aluminum sources (e.g. feldspars) could be found in the mineralogic analyses. Kaolinite was found on X-ray traces, but the diffraction peaks were well defined, indicating little or no destruction of the crystal structure. Kaolinite is more resistant to acid attack than the other clays and probably is not a significant contributor to the high aqueous aluminum concentrations.

Seven gob cores were analyzed by ICAP spectroscopy (Lechler and Leininger, 1979) for a number of elements, including aluminum (Table 2). According to Robl, Bland, and Rose (1976), economic recovery of aluminum from coal wastes is marginal at 9.5 weight percent. This is twice the highest aluminum value (core 7-1) and over three times the seven core average (2.85 %) from the Superior coal washer wastes.

Aqueous zinc concentrations are generally much lower than the major ions, but are proportionally higher than normal, reaching a maximum of 559 ppm for monitoring well 11 (Table 1). Sphalerite is known to concentrate in the No. 6 coal and some authors have suggested the potential for zinc recovery from sphalerite concentrated in coal wastes (Robl et al., 1976; Cobb, et al., 1979).

For the Superior washer wastes, sphalerite was identified by reflected light petrography for only the deeper cores. Particularly for station 10, sphalerite was not found in the two shallower cores from 0.1 and 1.54 meters, but was found at 3.0 meters and, more abundantly, at 6.6 meters. When the whole rock elemental zinc analyses are plotted against core sample depth (Figure 4), a similar increase with depth is indicated. Apparently sphalerite has been more severely leached near the gob deposit surface, and the zinc values from deeper cores may be more representative of the wastes as they were deposited.

The highest zinc value obtained (core 804, Table 2) for any sample was 0.12 weight percent. This is 25 times lower than the 3% tenor for zinc ore indicated by the Bureau of Mines (1975). Even though the wastes are easily accessible and handling costs would be low compared to mining operations, economic recovery of zinc or any other trace metals from the Superior washer site is not indicated.

Energy

Sub-samples from all 34 cores were ashed in a low-temperature oxygen plasma asher. Because of the abundance of coal fines concentrated in the slurry, the eight slurry cores had lower ash content than any of the gob samples. The weight loss upon ashing (100 % - % ash) for the 34 gob and slurry samples is shown as a frequency distribution in figure 5.

Using the ash values as a guideline, three slurry samples were selected for total carbon and BTU analysis; those having the highest, lowest and nearest to mean ash content. The gob sample having the highest ashing weight loss was also analyzed. Total carbon was analyzed on a LECO carbon determinator and the thermal content was obtained using a Parr oxygen bomb calorimeter.

The relationship of thermal content to ashing weight loss for the three slurry samples and one gob sample can be seen in figure 6. With more such analyses, a good regression relationship could likely be established, but the figure indicates that the slurry samples selected for thermal analysis are representative of the range to be found at the Superior washer. Total carbon also increased with increasing BTU content and ashing weight loss for the four samples. In ascending order, the total carbon values were 41.2, 52.7, 56.3 and 62.5 weight percent for samples 10-1, 4-2, 3-3 and 5-3 respectively. In the absence of detectable carbonate minerals, most of the carbon is likely to be organic carbon from coal.

With the exception of the exposed slurry at station 2, all slurry found at the Superior washer is buried under gob. Figure 2 shows the location and thickness of slurries encountered in core sampling as well as the approximate position of the main slurry pond before burial. Using the average thickness in this area (1.19 m), an estimated 1.4×10^4 m^3 of slurry may be buried in the north half of the site. Discontinuous buried slurry south of the gob piles are not included in the estimate.

Bulk density measurements for seven slurries from two nearby sites (Miller and Cameron, 1978) averaged .713 g/cm^3 (range .66 to .76 g/cm^3). Using this average and the above volume estimate gives a total mass estimate of 1.0006×10^8 kilograms. Using the median slurry heat content (average ash for 8 slurry samples) of 8960 BTU/lb (4980 cal/g) yields a total energy estimate of 1.98 $\times 10^{12}$ BTU or 5.79×10^8 Kw hr. If all the above assumptions are valid then the total energy estimate for the slurry materials at the site is thought to be reasonable.

Environmental

Four forms of pyrite were found at the Superior washer; massive pyrite, cleat coat pyrite, plant replacement pyrite and finely disseminated framboidal pyrite. Carruccio and others (1977) concluded that the finer pyrite forms, notably framboidal pyrite, are more readily oxidized due to their greater reactive surface area. Framboidal pyrite and plant cell replacement pyrite were identified petrographically in the deepest samples from two stations. Secondary cleat coat pyrite (< .5 mm thick) was identified visually in the deeper samples, having apparently oxidized to white and yellow sulfates on cleats of coal fragments from the shallowest samples at each station. Massive pyrite fragments were found in samples from all depths.

Quantitative sulfur analyses performed on all 34 cores (Table 3) gave evidence of a rough increase in sulfide

sulfur with sample depth, but a more clear relationship may have been masked by random sampling of the reactive massive pyrite blocks. Sulfate sulfur, however, showed no correlation to sample depth. The reasons for this lack of correlation is that aside from gypsum, sulfate solid concentrations would be a function of reactive sulfide availability and the degree of sulfate saturation in waters percolating through the solids. Sulfates formed near the surface are likely to be dissolved by undersaturated waters and transported downward to zones of increasing sulfate saturation.

In order to reduce sample bias effects and maximize the depth dependence of oxidized versus unoxidized sulfur, a ratio of sulfate to sulfide was plotted against sample depth (Figure 7). When compared to the site-wide average, a marked increase in the sulfate: sulfide ratio is noted for depths less than two meters. In this two meter zone, called the oxidized zone in Figure 2, the sulfide oxidation and leaching has been more intense than at greater depth.

Since the production of acid depends upon the oxidation of pyrite oxidation (Singer and Stumm, 1970), the presence of an oxidized zone may be important environmentally. The well water samples from the gob pile area are generally higher in total dissolved solids than are those from the graded gob area (Table 1). It may be in part due to the longer percolation path to the water table (Figure 3) but it is also possible that waters in the gob pile area encounter a proportionally larger amount of acid producing sulfides below the oxidized zone.

Recovery of coal from the slurry at the Superior washer would require disturbing the gob materials at the risk of exposing fresh pyrite to oxidation. Proper management of such sites is essential to prevent further degradation of ground water.

Conclusions

1) The coal wastes at the Superior washer contain no economically recoverable concentrations of metals. 2) They do, however, contain roughly 2.0×10^{12} BTU 9or 5.8×10^8 Kw-hr) of recoverable slurry energy. 3) Recovery of slurry would necessitate disturbing gob materials, possibly exposing fresher acid producing pyrite to the atmosphere. 4) The portion of the gob requiring disturbing is thin and mostly oxidized. It would not be necessary to disturb the gob piles where larger concentrations of sulfide may occur at depth. 5) Understanding of oxidation and leaching in coal waste piles can aid in sound reclamation planning and further environmental damage to ground water can be avoided.

References

Caruccio, F. T., Ferm, J. C., Horne, J., Geidel, G. and Baganz, 1977, "Paleoenvironment of Coal and Its Relation to Drainage Quality," U. S. Environmental Protection Agency Research Reporting Series, EPA-600/7-77-067, June, 107 p.

Cobb, J. C., Steele, J. D., Treworgy, C. G. and Helfinstine, R. J., 1979, "Abundance and Recovery of Sphalerite and Fine Coal from Mine Waste in Illinois," Illinois State Geological Survey, IMN 71, 11 p.

Lechler, P. J. and Leininger, R. K., 1979, "Analysis of Black Shales by ICAP Spectroscopy," Jarrel-Ash Plasma Newsletter, Vol. 2, No. 1, pp. 8-10.

Miller, M. R. and Cameron, R. E., 1978, "Microbial Ecology Studies at Two Coal Mine Refuse Sites in Illinois," Argonne National Laboratory Report, ANL/LRP-3, 37 p.

Rao, C. P. and Gluskoter, H. J., 1973, "Occurrence and Distribution of Minerals in Illinois Coals," Illinois State Geological Survey, Circular 476, 56 p.

Robl, T. L., Bland, A. E. and Rose, J. G., 1976, "Kentucky Coal Refuse: a Geochemical Assessment of its Potential as a Metals Source," Second Symposium on Mine and Preparation Plant Refuse Disposal, Proceedings of the National Coal Association, Louisville, Ky., pp. 152-159.

Schubert, J. P., Olsen, R. D. and Zellmar, S. D., 1978, "Monitoring the Effects of Coal Refuse Disposal and Reclamation on Water Quality in Southwestern Illinois, Fourth Joint Conference on Sensing of Environmental Pollutants, Proceedings of the American Chemical Society, pp. 725-731.

Singer, P. C. and Stumm, W., 1970, "Acidic Mine Drainage, the Rate-Determining Step," Science, Vol. 167, pp. 1121-1123.

Smith, W. H. and Bengal, L. E., 1975, "Coal Reserves of Illinois-Herrin (No. 6) Coal," Illinois State Geological Survey, Map, scale 1:500,000.

Wewerka, E. M., Williams, J. M., Wanek, P. L. and Olsen, J. D., 1976, "Environmental Contamination from Trace Elements in Coal Preparation Wastes: a Literature Review and Assessment,"

Interagency Energy-Environment Research
and Development Program Report, U. S.
Energy Research and Development. Admin-
istration LA-660 -MS, U. S. Environ-
mental Protection Agency, EPA-600/7-76-
007, 60 p.

Table 1. Groundwater quality within the Superior Mining Company coal wastes (3/10/79). Concentration units are in parts per million.

| | Wells in Graded Gob Area | | | | | | Gob Pile Wells | |
	MW-1	MW-2	MW-3	MW-4	MW-5	MW-7	MW-9	MW-11
TDS	9070.	3830.	12330.	14780.	14100.	8800.	173790.	260210.
T(°C)	3.0	1.0	2.0	2.7	3.0	0.0	15.5	12.6
Acidity (as CaO_3)	1050	800	12400	12000	10400	6800	39700	75800
pH	1.42	3.20	1.30	1.62	2.27	1.65	2.47	3.35
Eh(mv)	+323	+290	+327	+353	+242	+380	+182	+70
Ca	523.	365.	355.	309.	47.	347.	568.	522.
Mg	13.1	380.	22.8	47.2	14.5	31.9	34.6	53.7
Na	114.	246.	18.8	41.5	106.	16.3	188.	209.
K	73.1	1.3	25.2	35.2	183.	9.6	268.	87.8
Al	294.	6.9	596.	1260.	1260.	330.	4620.	11100.
Fe	3840.	33.1	5040.	4910.	5290.	2350.	25700.	49900.
Zn	2.54	0.75	1.22	10.1	6.07	7.39	138.	559.
Cd	0.09	0.09	0.09	0.14	0.17	0.12	1.07	0.87
Mn	0.54	37.3	7.00	6.00	--	--	--	--
SO4	4000.	2600.	6100.	8000.	7000.	5600.	142,000.	198,000.
Cl	10.	90.	6.	20.	43.	9.	25.	13.
SiO_2	190.	50.	140.	120.	120.	92.	200.	290.

*MW – monitoring well at station #

Table 2. Elemental analyses of core samples from the study area.

	gob core 7-1	gob core 7-2	gob core 8-1	gob core 8-4	gob core 9-1	gob core 9-2	gob core 9-3
Depth	0.13 m	1.09 m	0.10 m	5.87 m	0.13 m	1.37 m	2.97 m
Al	4.66	3.77	1.72	4.11	1.67	1.11	2.94
Fe	4.01	6.64	6.37	13.78	8.39	6.29	13.43
Mg	0.22	0.32	0.08	0.17	0.07	0.04	0.13
Ca	1.55	0.63	2.06	1.32	0.99	2.44	1.31
Na	0.34	0.36	0.14	0.11	0.33	0.07	0.15
K	0.8?	0.90	0.71	0.65	0.92	0.90	0.67
Mn	0.002	0.005	0.002	0.008	0.002	0.001	0.008
Ti	0.293	0.250	0.285	0.197	0.345	0.251	0.207
P	0.22	0.70	0.04	0.16	0.05	0.05	0.10
Ba	0.277	0.00	0.0309	0.0102	0.0434	0.0260	0.0185
Cd	0.001	0.0003	0.0002	0.0029	0.0004	0.003	0.0016
Cu	0.0018	0.0060	0.0016	0.0044	0.0025	0.0028	0.0035
Mo	0.0013	0.0024	0.0006	0	0.0004	0.0011	0
Pb	0.0036	0.0024	0.0043	0.0052	0.0054	0.0036	0.0041
Sr	0.0147	0.0072	0.0116	0.0101	0.0124	0.0134	0.0122
Th	0.0005	0.0001	0.0005	0.0007	0.0005	0.0005	0.0005
U	0.8064	0.0161	0.0029	0.0056	0.0038	0.0030	0.0058
Zn	0.0026	0.0166	0.0031	0.1205	0.0052	0.0056	0.0589

*All gob core solids were analyzed by ICAP spectroscopy according to methods described in Lechler and Leininger (1979). Elemental analytical values reported above are all given in units of weight percent of whole sample.

Table 3. Forms of sulfur, as wt. % S in whole sample, in 34 cores (11 stations) from the Superior coal washer (SL = slurry, GB = gob).

Sample (sta-#)	Type	Depth (m)	Total S	Sulfide S	Sulfate S	Organic S
1-1	GB	0.13	2.28	0.50	1.15	0.63
1-2	GB	0.62	3.33	0.86	1.82	0.65
1-3	SL	1.10	2.46	0.58	1.01	0.87
1-4	SL	1.82	1.72	0.43	0.51	0.79
2-1	SL	0.16	1.31	0.14	0.45	0.73
3-1	GB	0.10	1.92	1.00	0.04	0.88
3-2	GB	1.46	15.89	13.41	1.29	1.19
3-3	SL	1.56	1.49	0.67	0.14	0.68
4-1	GB	0.10	1.74	0.60	0.38	0.76
4-2	SL	1.50	2.32	0.75	0.67	0.91
5-1	GB	0.10	2.75	0.57	1.70	0.48
5-2	GB	1.53	7.37	4.49	1.59	1.30
5-3	SL	3.05	2.60	1.15	0.35	1.10
6-1	GB	0.11	3.87	0.47	2.91	0.49
6-2	GB	1.50	3.66	2.91	0.49	0.26
6-3	GB	2.73	5.59	3.91	0.97	0.72
7-1	GB	0.13	2.95	0.53	1.81	0.61
7-2	GB	1.09	5.18	2.30	2.30	0.58
7-3	SL	1.48	2.39	0.96	0.58	0.84
7-4	SL	2.25	2.13	0.86	0.53	0.73
8-1	GB	0.10	6.50	2.16	3.70	0.65
8-2	GB	1.32	17.30	14.60	2.05	0.65
8-3	GB	3.11	22.48	19.89	1.80	0.78
8-4	GB	5.87	16.52	14.52	1.23	0.75
9-1	GB	0.13	4.61	1.85	2.20	0.56
9-2	GB	1.37	6.37	0.86	4.32	1.18
9-3	GB	2.97	9.46	6.31	2.67	0.48
10-1	GB	0.10	2.90	1.05	0.87	0.98
10-2	GB	1.54	3.20	0.67	1.73	0.80
10-3	GB	2.98	21.41	19.97	0.16	1.28
10-4	GB	6.55	12.09	8.66	2.48	0.95
11-1	GB	0.11	5.79	2.02	3.23	0.54
11-2	GB	1.57	3.75	1.56	1.31	0.88
11-3	GB	3.04	11.59	7.63	3.10	0.86
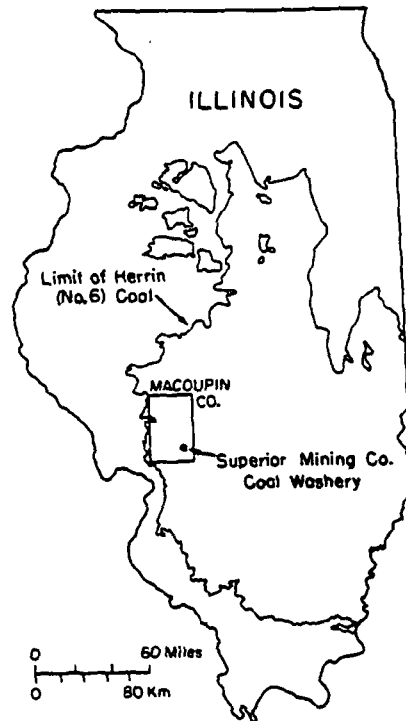
Figure 1. Location of study area showing limit of
           Herrin (No. 6) coal.
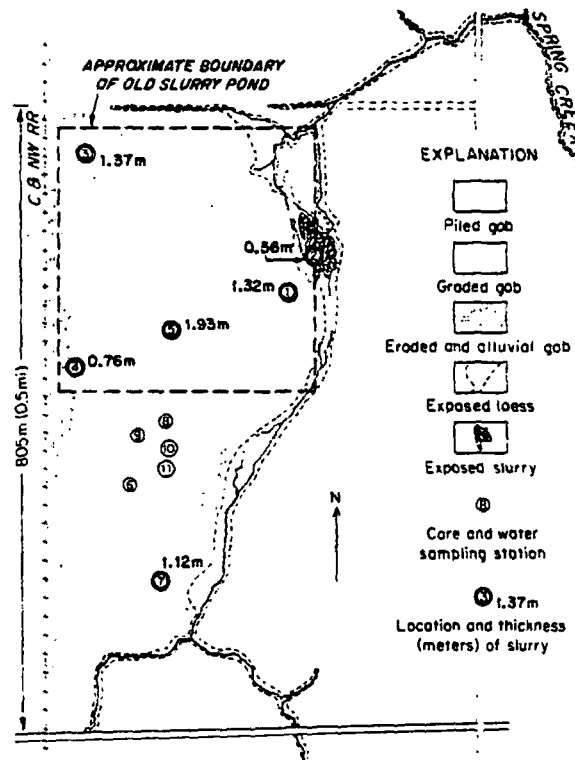
Figure 2. Distribution of materials and location of
           sampling stations at the Superior coal washer.
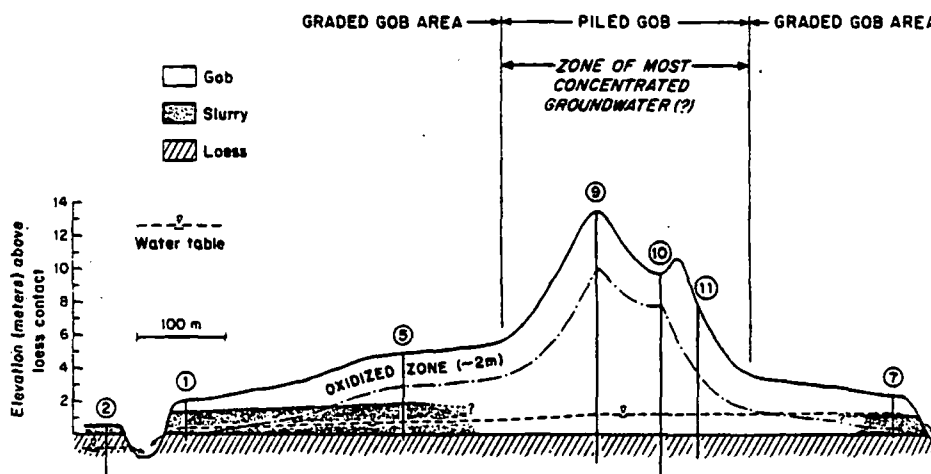
Figure 3.   Diagramatic cross-section of materials at the
            Superior washer (vertical scale exaggerated),
            1 = station number.
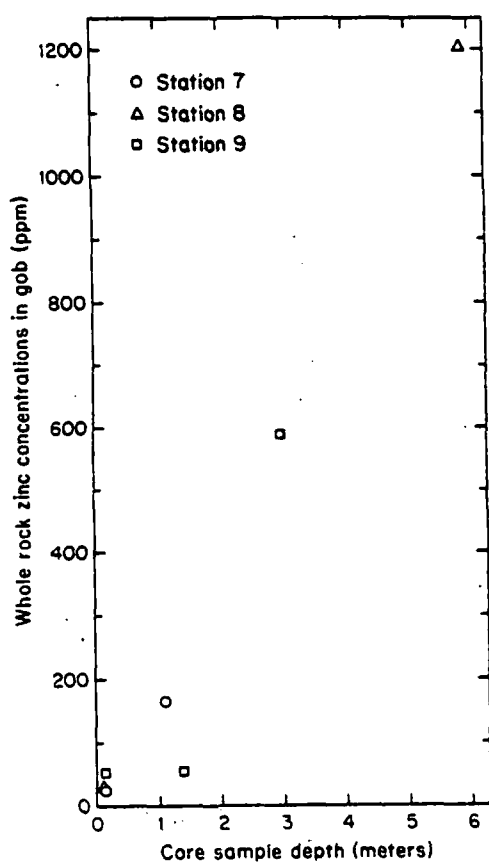
Figure 4.   Whole rock zinc concen-
            tration in gob vs. depth
            of sample.
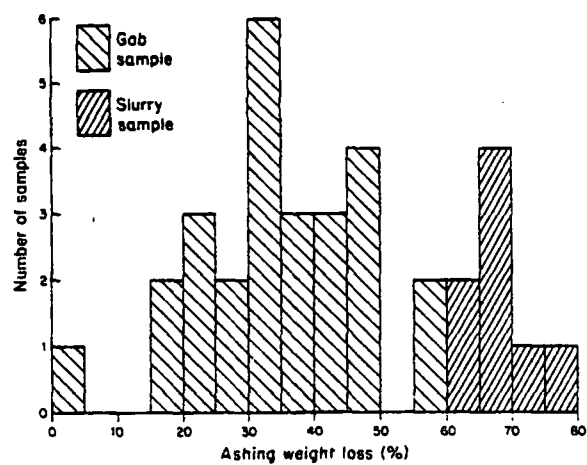
Figure 5.   Frequency distribution of
            ashing weight loss for 34
            cores of gob and slurry
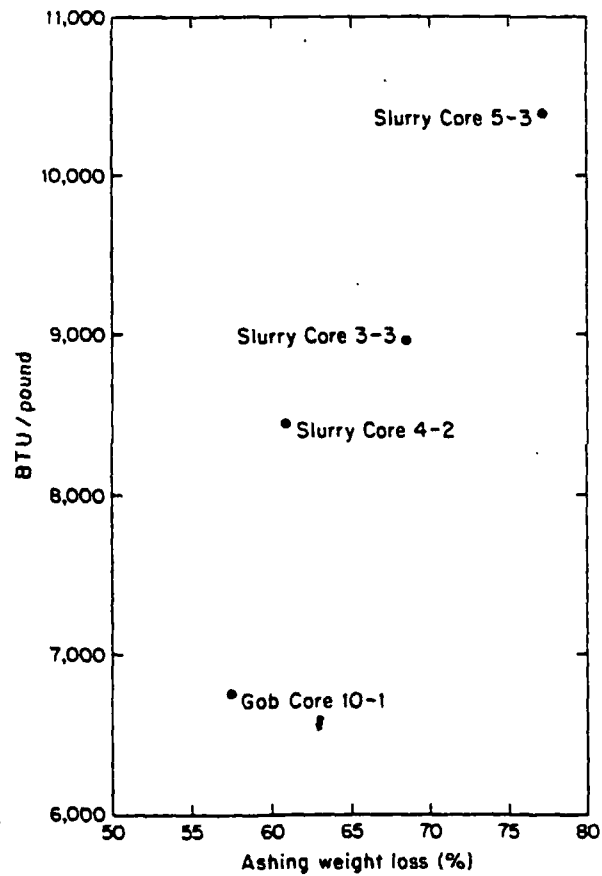
Figure 6. Heat content (BTU/lb) vs. weight
loss upon low temperature ashing.
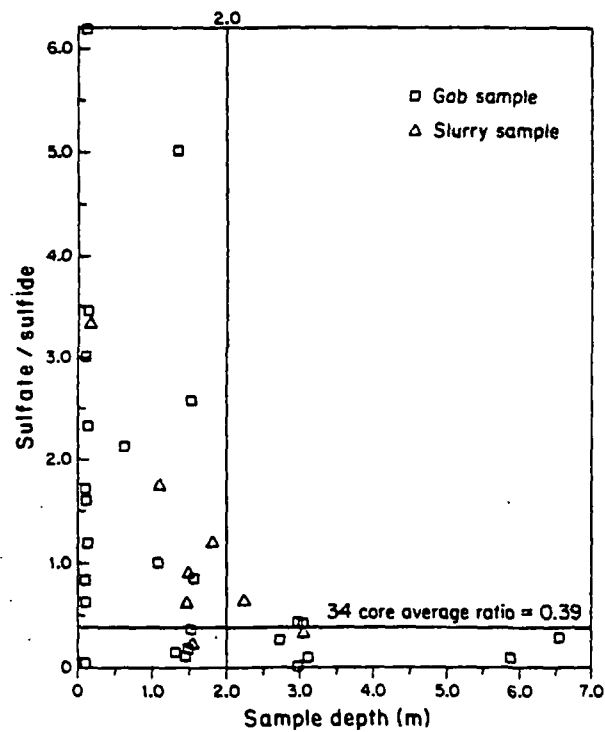
Figure 7. Ratio of sulfate to sulfide vs. sample depth
for 34 cores from the Superior coal washer.

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EFFECT OF ALUMINATE SOLUTION CONCENTRATION UPON NEPHELITE CAKE LEACHING[1]

UDC 669.712.1

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Compounds containing aluminum oxide and alkalis $Na_2O \cdot Al_2O_3$ and $Na_2O \cdot Fe_2O_3$ decompose in the process of cake leaching; the extent of their decomposition is governed by the fineness of cake grinding and by leaching time and temperature. Extraction of aluminum oxide from calcium aluminates also depends upon the aluminate solution soda content.

In addition, the calcium silicates $2CaO \cdot SiO_2$, $Na_2O \cdot CaO \cdot SiO_2$, and $2Na_2O8CaO \cdot 5SiO_2$ decompose in part in the process of leaching, and the silica goes into solution. In these circumstances the liberated calcium and part of the silicon oxide react with the solution constituents, leading to secondary losses of alumina and alkali due to the formation of hydrogarnets $3CaO \cdot Al_2O_3 \cdot nSiO_2 \cdot (6-2)H_2O^*$ and sodium hydroalumosilicates $Na_2O \cdot Al_2O_3 \cdot 1 \cdot 7SiO_2 2H_2O$.

The processes of secondary losses of alumina and alkali in leaching and the reactions in autoclave and thorough desiliconization are identical, being expressed by the following chemical equations:

$$2CaO \cdot SiO_2 + 2H_2O \rightarrow CaO \cdot SiO_2 \cdot H_2O + Ca^{2+} + 2OH^-. \tag{1}$$

$$CaO \cdot SiO_2 \cdot H_2O \rightarrow Ca^{2+} + SiO_3^{2-} + H_2O. \tag{2}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCo_3. \tag{3}$$

$$3Ca^{2+} + 2AlO_2^- + 0.5SiO_3^{2-} + 3OH^- + 3.5H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 0.5SiO_2 \cdot 5H_2O. \tag{4}$$

$$2Na^+ + 2AlO_2^- + 1.7SiO_3^{2-} + 3.7H_2O \rightarrow Na_2O \cdot Al_2O_3 \cdot 1.7SiO_2 \cdot 2H_2O + 3.4OH^-. \tag{5}$$
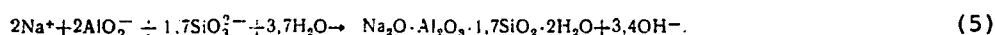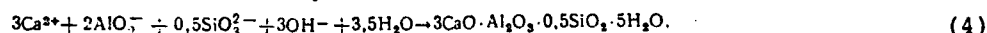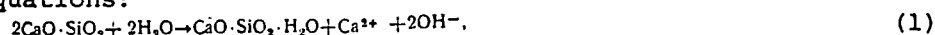
Reactions (1-5) take place in leaching and autoclave desiliconization, reactions (3,4) take place in thorough desiliconization.

It follows from these equations that the speed of the reactions is governed by the aluminate solution concentration, i.e., by its $Al_2O_3 (AlO_2^-)$, $Na_2O_{c.t} (OH^-)$, and $Na_2O_{carb} (CO_3^{2-})$ content.

In processing nephelites, the concentration of the solutions in hydrochemical cake processing usually alters as follows in the stages from leaching to desiliconizing: from 80-90 to 70-80 g/liter Al_2O_3, from 70-80 to 65-76 g/liter $Na_2O_{c.t}$ (α_c from 1.4-1.45 to 1.6-1.7), and from 15-16 to 9-10 g/liter Na_2O_{carb}. The reduction in concentration is due to solution desiliconization and causticization.

Partial hydrolysis of aluminum oxide, i.e., reaction (6) is also possible, in view of the fact that the solution composition is in the hydrargillite formation region in the $Na_2O - Al_2O_3 - H_2O$ system at the caustic ratio values adopted in the technology, $\alpha_c = 1.4 = 1.7$:

$$AlO_2^- + 2H_2O \rightarrow Al(OH)_3 + OH^-. \tag{6}$$

These reactions relate to the system $Na_2O - Al_2O_3 - CaO - SiO_2 - CO_2 - H_2O$, which has been studied in the form of separate simple subsystems by a number of researchers in recent years: N. I. Eremin, I. Z. Pevzner, V. M. Sizyakov, and others [1-3]. The available data are essential for defining the ranges of existence of the various phases and to reveal the chemical mechanism of the reactions. However, the difficulty of studying this six-constituent system and the effect of kinetic factors upon the process make it essential to study the effect of the basic parameters upon cake and solution processing results to obtain the best possible figures.

The effect of the solution caustic ratio was studied under laboratory conditions with the cake used in the leaching stage at the Achinsk Alumina Combine.

The cake had an alkali ratio $R_2O : Al_2O_3 = 1$, a lime ratio $CaO : SiO_2 = 2.01$, and 19.2% porosity in paraffin (for the -10+5 mm fraction); extraction in standard leaching 84.5% Al_2O_3, 85% R_2O. The -10+5 mm cake fraction contained 22.3% fused material (moisture capacity w = 6.8%), 60.2% of material intermediate between fused and normal (w = 15.2%), 11.6% normal material (w = 26%), and 5.9% green material (w = 37.2%).

Agitation leaching of the cake was simulated in the laboratory investigations; the cake was ground to less than 1 mm in size (6.5% over 1 mm, 32.5% under 0.08 mm) and leached at a liquid-to-solid ratio of 2.5 for 15 min to produce aluminate solution of

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* In leaching and autoclave desiliconization n ≈ 0.5, in thorough desiliconization n ≈ 0.1.

[1] L. E. Beletskaya and Z. V. Dmitrieva participated in the work.

the prescribed composition. The mud was agitated three times for 15 min each time in solutions with a twofold reduction in concentration in each successive repulping and then washed with hot water at a liquid-to-solid ratio of 3. Plant solutions containing ~ 1.2 g/liter SiO_2 were used as the initial solutions.

The leaching experiments were carried out at 60-85°C with a final aluminate solution content of 75-95 g/liter Al_2O_3, ~ 15 g/liter Na_2O_{carb} and $\alpha_c = 1.3-1.8$. The results obtained with a constant alumina concentration in the aluminate solution (85 g/liter Al_2O_3) at 65, 75, and 85°C are shown in Fig. 1 in the form of the relationship of alumina and alkali extraction from the cake to the aluminate solution caustic ratio. It is apparent that a rise in $\alpha_c > 1.3-1.4$ in the solutions leads to a substantial (5-7%) reduction in alumina extraction; raising the leaching temperature from 65 to 85°C also causes a substantial (3-4%) reduction in alumina extraction. Alkali extraction from the cake remains practically unchanged when α_c rises, falling somewhat (about 2%) when the temperature rises from 65 to 85°C.

The effect of temperature upon the leaching process [acceleration of the dicalcium silicate decomposition reaction (1,2) and desiliconization reactions (4,5)] is well known [4,5].

The results of changes in the solution carbonate alkali content (the difference in the Na_2O_{carb} concentration in the initial and final solutions) are also given in Fig. 1, for an analysis of the reasons for the effect of the solution α_c upon losses of alumina during leaching.

The change in carbonate content is obviously similar to the slope of the alumina extraction curves. This indicates that causticization of soda, reaction (3), takes place in the region of relatively low aluminate solution α_c values ($\alpha_c < 1.45-1.5$), due to carbonate formation by the calcium ions which pass into solution when dicalcium silicate decomposes. Causticization of carbonates is insignificant at α_c values > 1.45-1.55, because in this case the calcium reacts mainly according to reaction (4), which leads to the formation of hydrogarnets and to increased losses of alumina from the solution.

It is observed on analyzing the experimental results obtained that there is a relationship between the caustic ratio of the solution corresponding to the beginning and to the sudden change in alumina extraction from the cake and the temperature and concentration of the aluminate solution. If the caustic ratio of the solution at a given aluminum oxide concentration and temperature proves to be equal to or greater than the values which correspond to the curves shown (Fig. 2), the reduction in alumina extraction from the cake will be very substantial: over 3-4% (solid lines) or ~ 1% (dashed line).

The changes in the degree of solution causticization according to the caustic alkali content correspond to equilibrium in the $Na_2O - CaO - Al_2O_3 - SiO_2 - CO_2 - H_2O$ system. In view of the presence of areas of existence of calcite and hydrogarnet in it when the α_c values are reduced, the solutions prove to be in the $CaCO_3$ formation region. This leads to a reduction in the secondary losses of alumina when dicalcium silicate decomposes under leaching conditions, due to the reactions of solution causticization, combination of calcium to form calcite, and reduced hydrogarnet formation.

The experimental results obtained take into account the effect both of equilibrium (including the concentration of aluminum oxide and silicon in the solution) and of kinetic factors governed by temperature, the composition of the solution, and the surface of the controlling solid phase upon the causticization process (Fig. 3).

The compositions of the final solutions are close to the practical equilibrium when the carbonate content does not alter significantly during the leaching time.

It follows from the data given that it is desirable to obtain α_c values < 1.4-1.45 in the aluminate solution during leaching in order to increase alumina extraction from the cake.
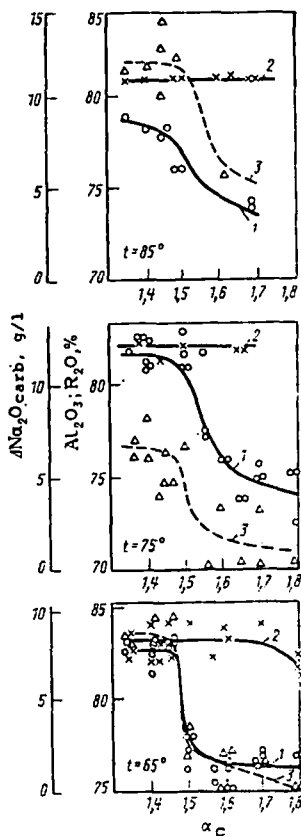
Fig. 1. Changes in extraction of constituents from cake and in carbonate content according to caustic ratio of aluminate solution containing 85 g/liter Al O and 15 g/liter Na O_{carb} at 65, 75, and 85°C: 1 - Al O extraction, %; 2 - R O extraction, %; 3 - changes in concentration of soda Na O, g/liter.

In view of the fact that there may be losses of alumina due to solution hydrolysis at reduced α_c values, special investigations were carried out which showed that there is no solution hydrolysis under leaching conditions at a temperature over 70°C, an Al_2O_3 content of 15-80 g/liter, and $\alpha_c > 1.2$-1.25. The solutions decompose extremely slowly with prolonged standing or cooling. The reason for the increased stability of the solutions is the presence of silicon, which has a stabilizing influence.

The effect of carbonate alkali upon the agitation leaching process was studied with Achinsk Alumina Combine cake characterized by extraction in standard leaching of 84.6% Al_2O_3 and 83.7% R_2O with an alkali ratio of 1.032 and a lime ratio of 1.99. Porosity of the -10+5 mm fraction in paraffin was 25.4%. In the initial cake the -10+5 mm fraction contained 1.5% green material (moisture capacity w = 28.6%), 14% normal cake (w = 18.4%), 69.6% of cake between normal and fused in quality (w = 15.4%), and 14.9% fused material (w = 10.6%). Prior to leaching the cake was ground to 4.5% over 1 mm and 27.9% under 0.08 mm.

Fig. 2. Relationship of maximum α_c value corresponding to changes in alumina extraction from cake to aluminate solution concentration at the following temperatures: 1,4 - 65°C; 2,5 - 75°C; 3,6 - 85°C; change in Al_2O_3 extraction of 3-4% (———) and approximately 1% (— — —).

Leaching was carried out at 60-90°C with 55-120 g/liter Al_2O_3, 5-55 g/liter Na_2O_{carb}, and α_c = 1.4-1.7. Plant solutions were used for the experiments.

The experimental results of studying the effect of carbonates upon alumina and alkali extraction from cake are given in Fig. 4. An increase in carbonates from 5 to 15-20 g/liter helps to increase alumina extraction by 1-3% at 60-75°C, but at 90°C it leads to reduced alumina extraction. Extraction of alkali from the cake decreases somewhat as the carbonate concentration rises, especially when the leaching temperature rises above 75°C.

It follows from the data in Fig. 5 that the beneficial effect of carbonate alkali in agitation leaching is intensified when the aluminate solution concentration rises above 70 g/liter. At α_c = 1.7, however, the beneficial effect of carbonates upon alumina extraction is not apparent.

In analyzing the experimental material, the available data on the Na_2O - CaO - Al_2O_3 - SiO_2 - CO_2 - H_2O system [1,3] and also the results obtained relating to aluminate solution SiO_2 content should be taken into account in qualitative form.

Thus solutions containing more than 5-10 g/liter Na_2O_{carb} are apparently in the $CaCO_3$ formation range when the Al_2O_3 concentration is low, < 70 g/liter, and α_c = 1.4. Therefore an increase in the carbonate content of 10-15 g/liter Na_2O_{carb} leads to causticization of the solution, also helping to increase the solubility of SiO_2 and consequently contributing to an increase in the degree of decomposition of $2CaO \cdot SiO_2$ and to secondary losses of alumina and alkali as a result of formation of sodium hydroalumosilicates (1,2,5).

Fig. 3. Changes in soda concentration in cake leaching at 65, 75, and 85°C with the following Al_2O_3 concentrations, g/liter: 1 - 75; 2 - 85; 3 - 95; the upper part of the curves shows the Na_2O_{carb} content of the initial solutions, the lower part the final solution content.

With an Al_2O_3 concentration of > 70 g/liter, α_c ~ 1.7, and 20-40 g/liter Na_2O_{carb} the solutions are probably in the hydrogarnet formation range; this is indicated by the low causticization of soda. Changes in the carbonate content in this range do not therefore lead to combination of calcium to form calcite.

The equilibrium carbonate concentration for a concentration of 70-100 g/liter Al_2O_3 and α_c = 1.4 is apparently close to 5-10 g/liter Na_2O_{carb}. Increasing the solution soda content therefore leads to increased causticization as a result of the decompo-
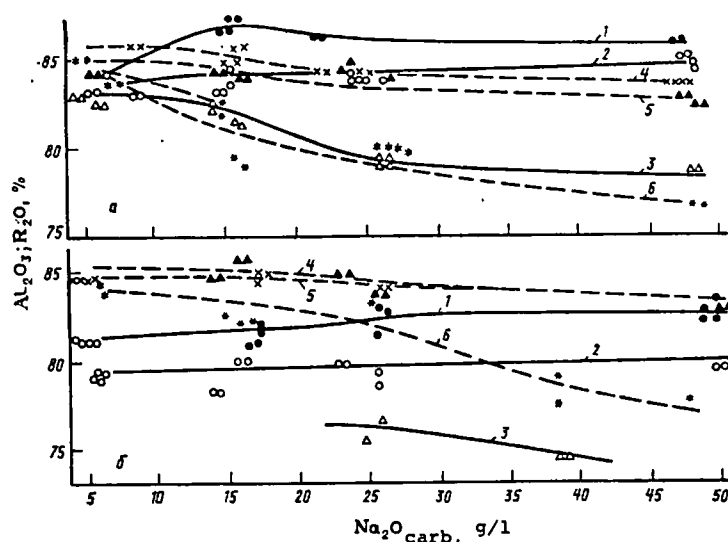
Fig. 4. Relationship of extraction of Al_2O_3 (1-3) and R_2O extraction (4-6) to soda content in cake leaching, in aluminate solution containing 85 g/liter Al_2O_3 at $\alpha_C = 1.43$ (a), $\alpha_C = 1.70$ (b): 1,4 - at 60°C; 2,5 - at 75°C; 3,6 - at 90°C.
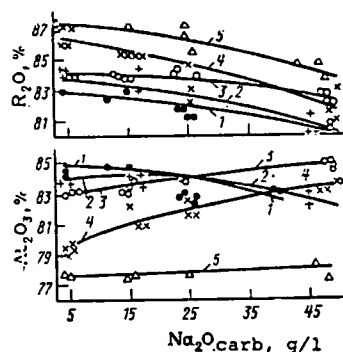
Fig. 5. Relationship of Al_2O_3 and R_2O extraction to aluminate solution composition at 75°C, $\alpha_C = 1.4$; Al_2O_3 concentration, g/liter: 1 - 55; 2 - 70; 3 - 85; 4 - 100; 5 - 120.

sition of dicalcium silicate and the formation of calcium carbonate. Hydrogarnet formation is reduced in these circumstances, which cuts the losses of alumina and increases extraction from the cake.

CONCLUSIONS

1. It was established that alumina extraction increased by 3-4% in cake leaching as a result of reducing the caustic ratio from 1.6 to 1.3-1.4 in aluminate solution containing ~ 15 g/liter Na_2O_{carb}; a subsequent reduction in α_C has little effect.

2. It was established that alumina extraction from cake increased by 1-3% with an increase in the carbonate alkali content from 5 to 15-25 g/liter Na_2O_{carb} at an aluminate solution concentration $Al_2O_3 > 70$ g/liter, $\alpha_C \sim 1.4$, and a temperature of ~ 60-75°C. An increase in temperature, and also an increase in the caustic ratio of the solution, lead to a reduction in the effect of carbonates upon alumina extraction. Increasing the solution carbonate content leads to some reduction in alkali extraction from the cake.

3. The reason for these effects of aluminate solution composition upon alumina extraction is the decomposition of dicalcium silicate when the cake is leached, calcium and silicon oxide going into solution. In view of the presence in the system of regions where calcite and hydrogarnet exist, changes in the composition of the solution govern the degree of causticization of soda and the formation of hydrogarnet, which is one of the main sources of alumina losses in leaching.

REFERENCES

1. N. I. Eremin and M. S. Durandina, Alumina Production, Collection No. 64, Leningrad, All-Union Aluminum and Magnesium Institute, 1968, 16-24.
2. I. Z. Pevzner, A. I. Lainer, I. M. Kontorovich, and V.Ya. Abramov, Izv. Vuzov, Tsvetnaya Metallurgiya, 1968, No. 4, 35-38.
3. V. M. Sizyakov, G. M. Vysotskaya, M. G. Pavlenko, and B. I. Arlyuk, Tsvetnye Metally, 1971, No. 9, 29-32.
4. M. N. Smirnov, Tsvetnye Metally, 1966, No. 1, 52-55.
5. B.I. Arlyuk, E. M. Steshenko, Yu. N. Busygin, et al., Tsvetnye Metally, 1972, No. 8, 42-45.

5) Flotation reagents and processes for their production. Ékspress-
Informatsiya, OPI 1976, (39), 3-10.

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Effect of the composition of the culture medium on the bacterial decomposition of aluminosilicates

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In connection with the continuing increase in the production of alumina the question of extending the mineral-raw material base of the aluminium industry becomes more and more acute, particularly with respect to the processing of high-silica aluminium ores, the effective utilisation of which is only possible with the development of effective methods for desiliconising. One of the promising methods in this respect is microbiological desiliconising, i.e., leaching of aluminosilicates by means of micro-organisms.

Of the whole range of micro-organisms the most active in the decomposition of these minerals are bacteria of the Bacillus mucilarginosus type, the so-called "silicate" bacteria. These bacteria were isolated from soil by V G Aleksandrov and were called "silicate" on account of their ability to break down aluminosilicates with the release of silicon. In the dense nitrogen-free medium A-27 a pure culture of "silicate" bacteria gives round, complex, transparent colonies with uniform rounded edges reminiscent of a drop of colorless liquid. The bacteria have the form of rods, the average size of which is $(4.2-6.0) \times (1.2-1.4) \mu$. They are Gram-negative and covered by a capsule of significant dimensions. The spores are of oval form an measure $2.6 \times 1.3\mu$.

The effect of the culture medium on the variation in the pH of the suspension as a function of the leaching time was investigated. A strain of "silicate" bacteria isolated from soil with an increased phosphorus content was used. Ore with the following composition was submitted to leaching %: $38.5 Al_2O_3$; $35.8 SiO_2$; $1.3 FeO$; $2.3 Fe_2O_3$; $0.3 P_2O_5$; $0.6 CaO$; $1.5 CO_2$. The ratio of the weight of aluminium oxide to silicon dioxide (the silica ratio) amounted to 1.07.

The experiments were carried out in a 1-litre flask shaken periodically on a shaker. The sample size was 50g. The solid content of the pulp was 10%. The concentration of microorganisms was 5tu (turbidity units, corresponding to $5 \cdot 10^8$ cells/ml). The particle size of the investigated material was 0.1mm. The experiments were carried out at a constant temperature of $28-30^\circ C$ in a thermostat with fourfold repetition. The reproducibility of the experiments was good. The investigations were carried out in three versions: 1) Ore + bacteria + 1% solution of glucose; 2) ore + bacteria + boiled water, i.e., the growth of the bacteria in the pulp was realised on the mineral medium;

3) ore + boiled water (control).

The bacterial solutions were changed after 12 days contact between the microorganisms and the ore. The results from experiments on the effect of the composition of the culture medium on the variation in the pH of the pulp with time are shown in the figure. Both in a carbohydrate medium and in the mineral medium the pH of the suspension decreased (acidification of the medium) with increase in the length of contact between the bacteria and the ore, and in the control experiment the pH was in the range of 7.4-7.6. The pH decreases more significantly when the medium with carbohydrates is used. In six days the pH had decreased from 7.2 to 5.5, i.e., by 1.7 units, and then in the next six days it only decreased to 5.0, i.e., by 0.5 unit. After replacement of the bacterial liquid (the old solution was decanted and fresh solution was added in the same volume) the form of the curve for the variation of the pH remained close to that in the first twelve days. A similar pattern was observed during leaching in a carbohydrate-free (mineral) medium except that the decrease in the pH of the medium here was rather slower than in the medium with the carbohydrate.

Analysis of the metabolism products showed the presence of amino acids such a lysine, arginine, aspartic acid, and threonine, a small amount of glutamic acid, glycine, alanine, and valine (total content of amino acids 1.381 g/l), and also organic acids (citric, oxalic, malic, tartaric), which it was possible to determine quantitatively, in the medium after bacterial treatment of the minerals. The appearance of organic acids in the suspension is evidently the main reason for the decrease in the pH of the suspension. Since the content of acids in the suspension is a function of the number of competent microorganisms, the significant reduction in the pH of the solution in the medium containing carbohydrates is a consequence of the more rapid growth of micro-organisms in it.

Analysis of the form of the curves in the figure makes it possible to conclude that it is expedient periodically to renew (change) the bacterial suspension, and the length of a single application of the suspension should not exceed 5-6 days. The main factor which reduces the intensity of growth and multiplication of the bacteria is clearly the accumulation of deleterious metabolites and ore decomposition products which depress the micro-organisms. Thus, periodic or continuous replacement of the bacterial solutions is a necessary condition for the development of a rational technique of bacterial leaching for aluminosilicates.

A specific relationship is observed between the variation in the pH of the medium with time and the composition of the culture medium with the degree of leaching of the aluminosilicates (table).

The data in the table show that "silicate" bacteria actively leach silica from the ore, irrespective of the composition of the culture medium, but most extensive desiliconization occurs with the use of a medium containing carbohydrates (glucose) at a concentration of 1%. The quality of the concen-

Results from bacterial desiliconising of aluminium-containing silicate ores

Product	Yield %	Content %		Extraction %		$\frac{Al_2O_3}{SiO_2}$	Experimental conditions
		Al_2O_3	SiO_2	Al_2O_3	SiO_2		
Concentrate	91.7	39.0	35.5	93.0	91.0	1.10	Ore + water, length of bacterial treatment 30 days, without replacement of the solution
Solution	8.3	32.5	39.0	7.0	9.0	0.83	
Initial ore	100	38.5	35.8	100	100	1.07	
Concentrate	64.0	43.5	30.9	72.2	55.0	1.41	Ore + bacteria + water, length of treatment 30 days, without replacement of solution
Solution	36.0	29.6	44.7	27.8	45.0	0.66	
Initial ore	100	38.5	35.8	100	100	1.07	
Concentrate	56.6	46.3	25.5	68.0	40.4	1.80	Ore + bacteria + 1% solution of glucose. Length of treatment 30 days without replacement of solution
Solution	43.4	28.4	48.2	32.0	59.6	0.59	
Initial ore	100	38.5	35.8	100	100	1.07	
Concentrate	58.0	46.9	19.0	71.1	32.5	2.50	As in previous experiments. Two replacements of bacterial solutions
Solution	42.0	26.3	57.5	28.9	67.5	0.46	
Initial ore	100	38.5	35.8	100	100	1.07	

trate obtained under these conditions is improved by 1.68 times (the ratio of the silica ratios) compared with the initial ore with 68% extraction of the aluminium into the concentrate. About 60% of the silica here is transferred to the liquid phase. With other conditions equal, in the mineral culture medium the quality of the obtained concentrate is improved by 1.37 times with 72.2% extraction of the aluminium into the concentrate. In this case only 45% of the silica is removed from the initial ore.

More extensive desiliconising of the ore is achieved under conditions where the bacterial solutions are changed. Thus, in a microbiological culture medium with two changes of the bacterial solution after 12 and 24 days, the quality of the obtained concentrate is 2.4 times higher compared with the initial ore, and the extraction of aluminium into the concentrate amounts to 71.1%. In this case more than 85% of the silica is leached from the ore and transferred to the liquid phase.

Conclusions

1. The development and activation of "silicate" bacteria in the presence of aluminous ore occur most effectively in a carbohydrate culture medium.
2. The fundamental possibility of replacing the carbohydrate culture medium by a mineral medium was demonstrated. This is an extremely important factor in the industrial utilisation of the method.
3. An essential condition for effective leaching of silica from ores is periodic (after 3-5 days) or continuous replacement of the bacterial solutions in order to remove metabolites and leaching products from the process.
4. Further investigations must be undertaken in the isolation of mutant strains of "silicate" bacteria which develop vigorously in mineral (carbohydrate-free) culture media and are capable of actively decomposing silicates and aluminosilicates.
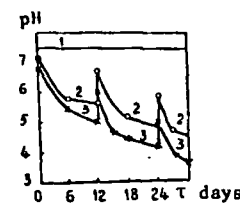

Fig. Effect of the length of leaching of silicate aluminium ores by the strain of "silicate" bacteria and of the composition of the culture medium on the variation in the pH of the bacterial suspension. Composition of medium: 1 - Ore + boiled water, 2 - ore + bacteria + boiled water, 3 - ore + bacteria + 1% solution of glucose.

Evaporation and thermal dissociation of mercuric sulphide (Discussion)

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Summary

The temperature dependence of the saturated vapour pressure of the black modification of HgS was determined:

$$\lg P^o_{HgS_\beta} \text{ (mm Hg)} = -\frac{5584.2}{T} + 9.3166$$

The relation between the dissociation constant of this sulphide and temperature was obtained for 573-773°K

$$\lg K_{HgS_\beta} = \lg(P^2_{Hg} \cdot P_{S_2}) = -\frac{20237}{T} + 17.338 \text{ atm}^3$$

It was shown that the degree of dissociation of HgS vapour in equilibrium with solid HgS$_\beta$ at 300-500°C is not greater than 1%.

Kinetics and mechanism of hydrothermal reaction of sphalerite with copper sulphate

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The reaction of copper salts with sphalerite has been mentioned in papers on mineral formation[1]; Hengelein and Hirsch[2]) and, more recently, other investigators have investigated the catalytic effect of copper ions in the autoclave oxidation of sulphides; in work by A A Tseft and others this effect was used in schemes for salt-type leaching of lead-zinc raw material and then, in order to increase the selectivity, in the autoclave dezincing of copper-zinc materials[3]). However, there have hardly been any theoretical investigations into the effects which arise in the sphalerite-copper sulphate-sulphuric acid-water system at increased temperatures. Below, as a supplement to the previously published material[4]), we examine the kinetics of the reaction of sphalerite with an acidified solution of copper sulphate.

We used synthetic and natural samples of sphalerites. The former (the α-ZnS modification) was obtained by the method of gas-transport reactions[5]), and the natural samples were isolated from single minerals from a number of Soviet deposits. After grinding the required particle size class was class was washed out on standard screens. The working solutions were prepared in distilled water from reagents of chemically pure and analytical grades. The experiments were carried out in a 1-litre autoclave designed by the Gipronikel' Institute; in order to determine the mechanism of the process more accurately we used a rotating thermostated vessel (V = 45ml); contact between the sulphide and the solution was secured only at the beginning of agitation (on the attainment of the required temperature).

In the solutions we determined copper, iron (II and III), zinc, and sulphuric acid. The initial sulphides and activated residues were investigated by chemical, mineral-petrographic, Xray, derivatographic, and Xray crystallographic microanalysis methods. The change in the volume of the solution on account of the removal of samples was taken into account in the calculations. The criterion for the development of the process was the extraction of zinc (iron) and the degree of precipitation of copper present in the initial solution.

The kinetic curves had parabolic form, which is characteristic of processes with diffusion resistance increasing with time on account of the formation of a thickening film. (Its presence was established by mineral-petrographic and Xray crystallographic microanalyses). The kinetic data were treated by means of the Ginstling-Brounshtein equation (6), which proved suitable particularly for a degree of conversion (α)$\geqslant$0.2. To analyse the kinetic data we used the nominal rate constant (K, min^{-1}) of the above-mentioned equation. The investigated parameters, their variation intervals, and the results are given in table 1.

The transfer of zinc into solution increases with increase in the amount of copper sulphate added. In the initial period of the reaction ($\tau\leqslant$30min) or with a deficiency of copper the zinc dissolves more rapidly than the copper is precipitated. However, even with $CuSO_4/ZnS\geqslant$1.0-1.3 the extraction of zinc increases less appreciably. The higher the initial acidity (with $CuSO_4/ZnS>$1), the less the zinc dissolves and the less the copper is precipitated. With $CuSO_4/ZnS<$1 increase in acidity promotes the extraction of zinc. Temperature has the greatest effect on the extraction of zinc (E_a = 74.5 kJ/mole) and particularly on the precipitation of copper (E_a = 96 kJ/mole), and the acidity of the final solutions increases at the same time. With increase in temperature from 140 to 200°C the content of elemental sulphur in the residues from the treatment increases from 0.3 to 6.8%. The effect of the intensity of agitation on the distribution of copper and zinc and also on the nominal rate constant is small. In the cakes the proportion of copper in the form of secondary sulphides amounted to 96-97%. Chalcocite and covelline were detected by mineral-petrographic analysis. Their presence was confirmed by Xray crystallographic (URS-60, ... K RKD camera, asymmetric recording) and Xray microanalysis (Cameca instrument).

The data from phase analysis of the residues and the character of the dissolution of zinc, the precipitation of copper, and the accumulation of acid make it possible to suppose that the reaction of sphalerite with an acidified solution of

copper sulphate is described by the following overall reactions:

$$CuSO_4 + ZnS \longrightarrow CuS + ZnSO_4 \qquad \Delta G^{\circ}_{298} = -62.3 \text{ kJ/mole}.$$

$$3CuSO_4 + 5CuS + 4H_2O \longrightarrow 4Cu_2S + 4H_2SO_4 \quad \Delta G^{\circ}_{298} = -193.1 \text{ kJ/mole}$$

$$8CuSO_4 + 5ZnS + 4H_2O \longrightarrow 4Cu_2S + 5ZnSO_4 + 4H_2SO_4$$
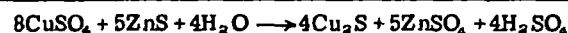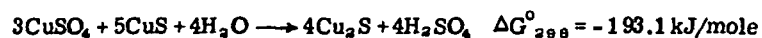
$$\Delta G^{\circ}_{298} = -386.9 \text{ kJ/mole}$$

We called process (1) the simple exchange reaction and process (3) the acid exchange reaction. These processes and the effect of the main parameters on them were investigated in a series of balancing tests (0.5M solution of copper sulphate); the weight of sphalerite (44μ fraction) was calculated with allowance for the chemical and phase analysis of the samples, their acid content (0.157g H_2SO_4/g), and the stoichiometry of the reactions. During treatment of the experimental data we assumed that the zinc was only represented by sulphide forms and the dissolution rates of the sulphide and oxidised forms of iron were the same. From the zinc content of the solution we calculated the amount of precipitated copper and the amount of covelline formed (reaction 1), and from the varying acidity we calculated the amount of copper in the chalcocite form and, accordingly, the proportion of reacted covelline and copper sulphate (reaction 2). On the basis of these data we estimated the degree of conversion of covelline to chalcocite and the discrepancy between the calculated and experimental (from the content in the final solution) amounts of precipitated copper; the discrepancy between the calculated and experimental data was used as a criterion for the reliability of the method. When the vessels were rotated at a rate of 30-60rpm (τ = 30min, 0.1M sulphuric acid, t = 200°C, natural sample, 44μ fraction), 91.5 ±0.2% of the copper was precipitated, and 51.3 ± 1.2% of the zinc was dissolved, i.e., over the indicated range the intensity of agitation does not affect the characteristics of the process; subsequent experiments were carried out with n = 60rpm.

In the experiments with samples of various particle size (t = 200°C, natural sample, 0.1N sulphuric acid) it was established that with the sphalerite fraction of -44μ the copper was fully precipitated after 60min, and here 55.2% of the zinc and 75.5% of the iron passed into solution. With the (74-44)μ fraction 79.5% of the copper was precipitated, and 47.8% of the zinc and 55.4% of the iron were dissolved, and comparable characteristics were obtained only after 2h. Thus, the characteristics of the process are improved significantly with increase in the degree of dispersion of the sphalerite. Subsequent experiments were carried out with the -44μ fraction of sphalerite.

In the experiments with various samples of sphalerite (t = 160°C, 0.25M sulphuric acid, τ = 60-120min) it was established that the synthetic sulphide is characterised by the lowest reactivity: Extraction of zinc 10-15% lower and precipitation of copper 25-40% lower than for natural samples of

sphalerite. A direct correlation was found between the iron content of the sample and the precipitation of copper or dissolution of zinc. With a lead content of more than 0.8% in the sphalerite the extraction of zinc deteriorates, and the precipitation of copper increases proportionally. Evidently, the positive role of isomorphous impurities is due to an increase in the crystal lattice parameters, which weakens the Me-S bond. This leads to an increase in the reactivity of the natural samples compared with the synthetic sphalerite.

Data on the effect of temperature, the initial acidity, and the reaction time are given in table 2. The agreement between the calculated and experimental data is quite satisfactory. (The relative error is not greater than 1-6%). The results are consistent with the data in table 1. With increase in temperature the process develops more rapidly and more fully, the free acidity increases at the same time, and the proportion of chalcocite in the final residue increases. With increase in the initial acidity (> 0.25M sulphuric acid) the extraction of zinc and iron into the solution and, particularly, the precipitation of copper decrease, the increase in the amount of free sulphuric acid is less appreciable, and the bulk of the copper is precipitated in the covelline form. An increased temperature (200°C) retains the general pattern of the process, but the degree of conversion of covelline into chalcocite becomes more appreciable. The E_a value of zinc and iron in reactions (1-3) amounts to 79.5, 105.3, and 95.5 kJ/mole respectively, and this indicates an identical mechanism for the dissolution of zinc and iron, while the precipitation of copper is the result of reactions (1) and (2). The role of process (2) becomes particularly appreciable at increased temperatures (>160°C). According to reaction (3), the sphalerite reacts with copper sulphate in a ratio of 1.6:1 (or 62% of the stoichiometry of reaction 1). Experiments carried out with this ratio showed that 96.8% of the copper is precipitated only after 5h; 83% of the zinc and 89% of the iron pass into solution, and the covelline is converted almost completely (> 95.3%) into chalcocite. More complete breakdown of the sphalerite clearly requires an increased consumption of copper sulphate and a much longer treatment time.

Chemical, phase, and Xray diffraction analyses, Xray microanalysis, and mineral-petrographic analysis of the residues from the reaction of sphalerite with copper sulphate confirmed the existence of covelline, chalcocite, and compounds of the $Cu_{2-x}S$ type (where 0<x<1). The sphalerite grain was surrounded by chalcocite, and here substitution of sphalerite by chalcocite occurred from the periphery of the grain towards its centre. Individual grains of sphalerite completely converted into chalcocite were observed. Its colour was greyish-blue (in contrast to the light-grey colour of natural chalcocite), and this was due to the covelline impurity. Covelline is encountered fairly frequently (no less than 10% of the area of the section), and its formations precede the formations of chalcocite. On the derivatogram of the sphalerite treated with copper sulphate solution two clearly defined endothermic effects appear (at 470 and 590°C), corresponding to the dissociation of compounds of the $Cu_{2-x}S$ and CuS type. The

Table 1: Conditions and characteristics of the reaction of sphalerite with acidified solution of copper sulphate (natural sample, wt 13.5g, V = 0.8 litre, τ = 60min)

Experimental conditions				Content in sol. g/l			Yield residue %
$\frac{[CuSO_4]}{[ZnS]}$	$[H_2SO_4]$	$t°C$	V m/c	Zn	Cu	H_2SO_4	
0.25	0.1	180	0.53	2.11	0.006	7.2	91.2
0.5				2.63	0.014	11.2	97.2
1.0				3.02	0.05	11.0	97.5
1.3				3.17	2.55	10.9	97.6
1.8				3.5	5.8	11.0	98.5
2.4				3.8	9.5	11.4	99.7
0.7	0.05	180	0.53	2.2	−0.03	6.9	99.2
(1.2)**				(3.65)	(3.35)		
	0.1			(3.4)	(3.37)		
	0.2			3.5	0.16	21.0	95.2
				(2.9)	(4.5)		
	0.4			3.7	0.06	35.9	100
				(2.2)	(5.4)		
1.3	0.1	140	0.53	1.35	6.95	10.6	103
		160		2.15	5.6	11.3	104
		180		3.17	2.55	14.0	109
		200		4.7	0.01	15.8	136
1.0	0.1	180	0.23	2.64	0.6	10.9	97.8
			0.43	2.80	0.35	11.0	96.0
			0.53	3.02	0.05	11.0	97.5
			1.06	3.64	0.02	−	99.8

Content in residue %			Extraction %		$K \cdot 10^* \ min^{-1}$		$\frac{Q_{Cu}}{Q_{Zn}}$
Cu	Zn	S	Cu	Zn	Zn	Cu	
13.4	39.3	28.2	99.9	19.2	0.13	8.0	0.84
28.4	30.5	28.3	99.7	27.9	0.2	5.6	1.24
28.8	34.4	28.3	98.4	34.4	0.35	3.5	2.32
-	31.3	28.5	70.1	43.4	0.47	-	2.15
28.7	29.5	27.9	56.6	43.6	0.52	-	2.00
29.0	23.9	27.0	42.6	52.1	0.87	-	1.9
26.9	31.0	28.8	99.6	18.8	0.51	5.4	1.06
			(65.4)	(50.7)	(1.1)	(0.6)	(1.06)
			(65.0)	(46.8)	(0.44)	(0.49)	(1.1)
25.2	31.6	29.4	98.6	29.3	0.29	3.8	1.31
			(55.4)	(39.8)	(0.6)	(0.45)	(1.28)
26.3	29.2	28.5	99.0	30.8	0.21	2.7	1.32
			(41.4)	(30.7)	(0.2)	(0.3)	(1.32)
15.3	-	27.0	23.6	18.4	0.1	0.2	1.7
21.6	22.0	26.9	37.7	29.1	0.25	0.4	1.7
13.7	16.3	24.3	70.1	43.4	0.47	1.8	2.15
40.8	11.9	23.3	99.2	65.6	3.16	10.0	2.0
			84.2	29.8	0.26	2.7	2.4
25.0	31.8	29.6	91.0	31.5	0.30	3.2	2.34
21.8	34.4	28.3	98.4	34.4	0.35	3.5	2.32
26.9	30.5	28.8	95.9	41.0	0.42	4.0	1.92

*) K is the nominal constant in the Ginstling-Brounshtein equation
**) The data in brackets relates to the experiment with $CuSO_4/ZnS = 1.2$

Table 2: Effect of temperature, acidity, and reaction time on the reaction of sphalerite with copper sulphate solution (CuSO$_4$: ZnS = 1)

t °C	τ min	$C^0_{H_2SO_4}$ M	Extraction %		ΔH$_2$SO$_4$ tr.	Precipitation of copper			$\frac{Q_e - Q_c}{Q_e}$	Degree of conversion of CuS into Cu$_2$S %
						Total		Including by reaction (1)		
			Zn	Fe		Q^*_c	Q^{**}_c			
160	15	0.1	19.1	24.5	6.2	30.8	31.6	70.2	2.6	71.0
	30		28.3	32.5	8.1	42.4	44.7	72.4	5.3	63.6
	60		37.5	42.2	10.5	56.0	58.9	72.8	5.2	62.1
	120		45.1	54.9	14.4	73.9	74.3	70.4	0.6	70.1
	180		50.8	65.4	17.1	86.5	85.4	69.3	1.3	73.6
180	15		32.4	27.0	12.3	54.0	54.0	65.4	0.0	88.5
	30		39.2	41.4	15.3	68.8	68.8	65.8	0.2	86.0
	60		48.9	58.1	18.8	88.1	84.6	66.7	2.8	82.9
	120		55.2	71.6	21.2	100	96.5	66.6	3.5	83.5
200	15		45.0	44.0	17.2	74.9	76.7	65.8	2.5	86.8
	30		52.0	64.6	20.4	91.2	91.4	65.8	0.5	86.4
	60		55.2	75.5	21.2	100	97.2	66.6	2.8	83.7
160	180	0.10	50.8	65.4	17.1	86.5	85.3	69.4	1.3	73.6
		0.25	48.8	64.0	13.2	79.4	77.3	73.9	2.5	59.1
		0.50	47.1	62.0	9.9	74.7	70.2	78.6	6.1	45.6
		0.75	47.1	61.0	7.1	71.2	65.8	83.7	7.6	32.8
		1.00	47.0	60.3	4.0	69.5	64.1	85.9	7.9	27.8
200	60	0.10	55.2	75.5	21.2	100	97.2	66.6	2.8	83.7
		0.25	57.9	75.5	19.6	99.9	97.5	69.3	2.5	73.9
		0.50	58.2	74.8	18.3	99.8	95.9	70.8	4.0	69.0
		0.75	57.0	72.5	17.7	95.9	93.5	70.9	2.4	67.8
		1.00	54.3	68.6	16.7	92.4	88.0	71.7	5.0	66.5
200***	60	0.10	59.9	63.7	13.9	67.7	63.6	66.4	6.1	83.8
	120		69.2	73.3	17.1	78.9	75.4	65.4	4.3	88.6
	180		76.5	82.2	19.8	86.7	84.7	64.4	2.2	92.4
	300		82.8	89.3	22.1	96.8	92.9	63.6	4.0	95.3
	240		79.1	85.7	20.9	92.0	88.5	63.9	3.7	94.2

*) Amount of precipitated copper by analysis of solution
**) Amount of precipitated copper calculated by the equation for reactions (1)-(3)

loss in weight of the initial sphalerite at 1050°C by 6.5 abs.% is lower ~~than~~
for the treated material. These data also confirm the change in the phase
composition of sphalerite after its hydrothermal treatment with copper
sulphate solutions.

The kinetics of the investigated process are complicated by the films of
secondary copper sulphides with form; their continuity, evaluated in the
first approximation from the value of the Pilling-Bedworth criterion[7]
(K_{P-B} for the ZnS-CuS system in reaction 1 and ZnS-Cu_2S system in reaction 3 amounts to 0.84 and 0.92 respectively) is extremely significant. At
the beginning of the process the copper is precipitated on the sphalerite
mainly in the form of CuS, and the formation of sulphides of the Cu_2S type
(the film of which is less permeable) is a secondary process and occurs
as a result of reaction of the covelline with copper sulphate. This process
promotes the precipitation of copper and develops intensively at temperatures above 160°C. For more complete precipitation of copper from the
solution with sphalerite (zinc concentrate) it is expedient to use increased
temperature and to add the precipitant on the basis of ZnS/$CuSO_4 \geqslant 1$; in
order to dissolve the zinc (e.g., from a collective concentrate) moderate
temperatures (not more than 160°C) and an increased consumption of copper sulphate, i.e., $CuSO_4/ZnS \geqslant 1$, are more suitable.

The high values for the apparent activation energy are evidently due to
the specific characteristics of the diffusion of the hydrated copper ions
towards the surface of the sphalerite through the layer of insoluble reaction products. A detailed study of the mechanism of the process requires
special investigations.

References

1) S S Smirnov: The oxidation zone in sulphide deposits. Akad. Nauk SSSR,
    Moscow-Leningrad 1955, 381 pages with illustrations.
2) F Hengelein et alia: Z. Erzbergbau und Metallhüttenwesen
    1961, 14, (1), 172-177.
3) S S Noboichenko et alia: Tsvetnye Metally 1972, (8), 20-23.
4) S S Naboichenko et alia: Proceedings of First All-Union conference
    on hydrometallurgy. Moscow 1974, p. 18.
5) B D Stepin et alia: Methods for the production of specially pure inorganic materials. Khimiya, Leningrad 1969, 480 pages with illustrations.
6) A M Ginstling et alia: Zh. Prikl. Khim., 1950, 23, 1249-1259.
7) A N Zelikman et alia: Theory of hydrometallurgical processes.
    Metallurgiya 1975, 504 pages with illustrations.

UNDERGROUND MINING

An all new rig for Magmont shaft would have cost twice as much as new and used parts

Component part	New	Up-graded	Cost
Engines (3 @ $30,000.00)......$	90,000.00	—	$ 90,000.00
Drawworks.................:.....	—	$20,000.00	20,000.00
Mud pumps			
1—1,000...................	60,000.00	—	60,000.00
1— 850...................	—	—	—
Power transmission........:....	—	20,000.00	20,000.00
Substructure.................	—	15,000.00	15,000.00
Derrick......................	—	3,000.00	3,000.00
Blocks, hook, etc..............	40,000.00	—	40,000.00
Miscellaneous.................	—	5,000.00	5,000.00
Drill string...................	134,000.00	—	134,000.00
Choke manifold (10,000 psi)....	25,000.00	—	25,000.00
Total..................$	349,000.00	$63,000.00	$412,000.00

All new rig	Cost
Engines (3)..$	90,000.00
Drawworks..	90,000.00
Mud pumps (2) 1—1,000....................................	115,000.00
1— 850....................................	—
Power transmission.......................................	52,000.00
Substructure	
Derrick...	150,000.00
Blocks, hook, etc..	40,000.00
Miscellaneous auxiliary equipment..........................	65,000.00
Drill string...	282,000.00
Choke manifold (10,000 psi)................................	25,000.00
Total...$	909,000.00

The estimated cost of a nuclear leaching experiment on copper ore

Project Sloop, a proposal by Kennecott Copper Corp. to the Atomic Energy Commission, would provide for a joint $13-million contained 20-kiloton nuclear blast and solution mining experiment at its Safford, Ariz., copper porphyry. If the project is approved by Congress and proceeds as planned, it should go a long way in proving or disproving the feasibility of nuclear blasting for the preparation of an oxide zone of low-grade deposit for in-situ recovery of copper. After the blast, the recovery would further be accomplished by using solution recovery holes and piping in underground access drifts below the chimney created by the blast. The pregnant solution would be pumped to the surface precipitator (see E/MJ, November 1967, p 116).

Some comparisons of the nuclear shot with other big blasts in mining indicate that more rock has been broken with conventional blasts than the estimated 1.3-million tons that the proposed 20-kiloton nuclear device would break. Other production blasts, however, have broken to one or more free faces, while the proposed nuclear shot would be a contained experiment. Other large blasts in the recent past include:

1) International Nickel Co.—Frood mine—5.25-million tons with 464 tons of powder.

2) Climax Molybdenum—1.25-million tons in a glory hole blast with 208 tons of explosives.

3) Minnesota taconite mine—broke 1.3-million tons using 850 tons of high energy slurry (Hercules Powder Co. report).

Cost estimates for Project Sloop

Phase 1
Field start-up and initial support facilities
Pre-shot sampling holes
Site safety studies
Total Phase 1..$750,000

Phase 2
Project start-up and support facilities
Rehabilitation of existing workings
Scientific program and explosive diagnostics
Emplacement hole
Emplacement, stemming
Operational support
Communications
Post-shot drilling, re-entry and testing
Miscellaneous construction
Engineering inspection
Total Phase 2..$5,750,000

Phase 3
Underground re-entry and rehabilitation
Leach solution and recovery system
Post-shot sample and solution input holes
Underground process piping and pumping system
Copper precipitation plant
Process water supply
Leach plant operating costs—one year
Public and industrial safety monitoring
Project evaluation
Total Phase 3..$6,675,000
Total Project Sloop...$13,175,000

The cost of leaching U₃O₈ in stopes and pumping solution to the surface

The economic advantages of microbiological processing have given new life to some mines and, in other cases, will allow the leaching of low-grade ore (see E/MJ, October 1967, p 75). At Stanrock Uranium Mines Ltd., Stanrock, Ontario, Canada, the use of bacteria leaching provided the answer to the question of "how to stay in business," in the face of skyrocketing costs by conventional mining methods.

The high-pressure washing of stopes at Stanrock, beginning in 1963, increased production from 27,100 lb of U_3O_8 in 1962 to 105,300 lb in 1963. Uranium recovery from mine water at that time was 7% of total production.

Between July and October of 1964, mining costs increased to $5.09 per lb of U_3O_8 recovered. This allowed only 41¢ per lb profit. As a result of the high costs the entire mine was converted to bacteria operation at the end of October 1964. By the summer of 1965, bacterial leaching was credited with lowering production costs to $3.30 per lb of U_3O_8. Heating of mine intake air during the winter added 50¢ to total U_3O_8 costs. The conversion to corrosion-resistant materials in the mine solution circuit resulted in a 50¢ per lb U_3O_8 direct savings in chemicals and pump maintenance supplies.

Stanrock is recovering 15,000 to 16,000 lb of U_3O_8 monthly from 1,200 stopes having an average floor area of 6,000 sq ft each.

To eliminate the need of neutralizing mine solutions, 316 stainless-steel pump components, rubber-lined solution lines in the shaft, and plastic distribution lines were installed in the mine.

$$Al_2OF_4 = AlOF + AlF_3 \qquad (3)$$

$$2AlF_3 + 3H_2O = Al_2O_3 + 6HF \qquad (4)$$
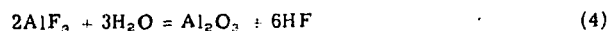
Only peaks for aluminium fluoride are found on the X-ray pattern. Aluminium oxide and oxyfluoride are amorphous to X-rays.

At 630°C the water is finally removed, and the Al-O-H group changes into an Al-O group. Only peaks for aluminium fluoride were found by X-ray phase analysis.

At 680°C sublimation of aluminium fluoride, formed by reaction (3), begins. With further heating of the material the aluminium oxyfluoride dissociates to form aluminium fluoride and α-alumina according to the reaction:

$$3AlOF = AlF_3 + Al_2O_3 \qquad (5)$$

This process is exothermic, which was confirmed many times by a thermal method. Consequently, the possible reactions in the sublimation of the compound when heated to 1000°C (mass-spectrometric analysis) can be represented in the following form:

$$2Al(OH)F_2 \cdot 3H_2O_{(solid)} \rightarrow 2Al(OH)F_{2\,gas} + 3H_2O_{gas} \qquad (6)$$

$$2Al(OH)F_2 \cdot 3H_2O_{(solid)} \rightarrow AlOF_{gas} + AlF_{gas} + 4H_2O_{gas} \qquad (7)$$

$$2Al(OH)F_2 \cdot 3H_2O_{(solid)} \rightarrow Al_2OF_{4\,gas} + 4H_2O_{gas} \qquad (8)$$

$$2Al(OH)F_{2\,(solid)} \rightarrow Al_2O_{3\,(solid)} + AlF_{3\,gas} + 3HF_{gas} \qquad (9)$$

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*) $Al_2O_{3\,solid}$ was found in the residue of the evaporation cell.

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Extractive capacity of organic sulphides

V S Chekushin (Krasnoyarsk Institute of Non-Ferrous Metals - Department of the Metallurgy of Noble and Rare Metals)

The use of organic monosulphides as extractants for noble metals arises from specific characteristics of the heteroatom. The reactivity of sulphides in the chemical reactions which accompany extraction is determined by the electron-donating and electron-accepting power of the sulphur atom, which depend to a considerable degree on the composition and structure of the groups of substituents associated with it and are expressed in the different displacements of the electron density at the heteroatom.

At the present time experimental data from investigation of the reactivity of monosulphides in relation to compounds of metals in groups III and IV of the periodic system and halogens have accumulated together with data on the electron donating characteristics of aliphatic and cyclic compounds [1][2].

The aim of the present work was to undertake further investigations into the reactivity of sulphides with various compositions and structures. As subjects for investigations we took aliphatic sulphides with chain lengths between C_2 and C_7 having normal structure and their isomers, diphenyl sulphide, and the fractions of petroleum sulphides obtained from Arlansk oil [3]) and largely represented by combinations of monocyclic (fraction 1), bicyclic (fraction 2), and tricycle (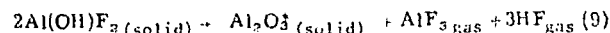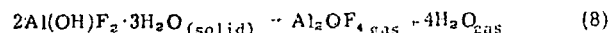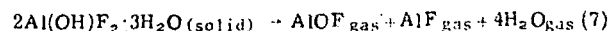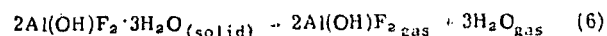fraction 3) compounds. The reactivity of the extractants was assessed by means of the thermodynamic characteristics, which were determined from the concentration constants for the extraction of $[PtCl_4]^{2-}$ by the integral form of the Van't Hoff equation [4]). In the calculations of the extraction constants we started from the assumption that monomolecular bisulphates with the composition $[PtCl_4 \cdot 2S]$, where S is

Conclusions

1. During the heat treatment of $Al(OH)F_2 \cdot 1.5H_2O$ the following processes take place in succession: At 300°C 0.5 molecule of water is removed, and the compound changes into $Al(OH)F_2 \cdot H_2O$; at 400°C one molecule of water is removed, and the compound changes to $Al(OH)F_2$; at 475-630°C $Al(OH)F_2$ is completely dehydrated, changing into Al_2OF_4 and then into AlOF: the AlF_3 which forms is partly hydrolysed: at 680°C AlF_3 begins to sublime: at 750-850°C AlOF dissociates to form AlF_3 and α-Al_2O_3

References

1) L J Bellamy: Infrared spectra of complex molecules: Wiley, New York 1963.
2) L Little: Infrared spectra of adsorbed molecules: Moscow 1969.
3) K Nakanishi: Infrared spectra and structure of organic compounds: Moscow, Mir 1967, p. 219.
4) E Hartel and O Z Glemser: Electrochem. 1956, 60, 746.
5) I I Plyushina: Infrared spectra of silicates: Izd. MGU 1967.
6) Yu M Ivanov and A V Vanykov: Elektronnaya Tekhnika Ser. 14, 1967, 4. 36.
7) Yu M Ivanov and A V Vanyukov: Zavod. Lab. 1970, 11, 1355.
8) N F Kashcheev and N V Lazarev: Method, for the production of aluminium oxyfluoride: Author's Certificate 46256, 1933.
9) S P Kamenetskii and N F Kashcheev: Method for the production of alumina, aluminium oxyfluoride and hydrofluoric acid: Author's Certificate 42064, 1935.
10) M H Read: Bell Telephone Labs. Murry Hill, New York 1958.
11) M Cowley and T R Scott: J. Amer. Chem. Soc. 1948, 70, 105.

the extractant, accumulate in the organic phase. The ΔH, ΔS and ΔG values for extraction are not standard but can be used for the arguments which follow (table 1).

Table 1: The thermodynamic characteristics of extraction by organic sulphides in toluene (298°K)

Extractant	ΔH_e kcal/mole	ΔS_e eu	ΔG_e kcal/mole
Diethyl sulphide	19.6	70.6	-2.20
Dipropyl sulphide	15.5	54.6	-1.35
Diisopropyl sulphide	16.3	58.6	-1.9
Dibutyl sulphide	12.8	45.0	-1.0
Diisobutyl sulphide	13.0	46.0	-1.2
Diamyl sulphide	11.5	40.2	-0.9
Isoamyl sulphide	12.7	44.6	-1.05
Dihexyl sulphide	10.5	35.8	-0.5
Diheptyl sulphide	10.51	36.6	-0.74
Diphenyl sulphide	8.12	27.2	-0.28
Fraction 1	14.4	51.5	-1.5
Fraction 2	12.8	45.3	-1.2
Fraction 3	8.12	31.0	-1.43
Fraction 4	7.94	28.2	-0.76

The extraction of metals by sulphides is accompanied by the formation of stable co-ordination bonds M-S with redistribution of charge between the interacting atoms. The polarisability of the partners is therefore of important significance. The refractions of the sulphur atom $R_D(S)$ in the compounds were distributed by means of the experimental values of the molecular refractions (MR_D) and the group increments for the hydrocarbon radicals [5]). From table 2 it is seen that $R_D(S)$ in aliphatic sulphides depends little on the composition and structure of the radicals and

Table 2: The characteristics of the reactivity of organic monosulphides

Reagent	I_S eV [6]	$K_B \cdot 10^6$	MR_D cm^3	$R_D(S)$ cm^3 [c]	$\Delta H_f^r R_2S$ kcal/mole [7]	$\Delta H^r R$ kcal/mole [7]	$E(C-S)^*$ kcal/mole	ΔX_S	ν_{C-C} cm^{-1}	$E_1(S)$V
$(C_2H_5)_2S$	8.43	1.26	28.59	7.99	19.95	34.00	77.07	0.380	1258	-0.54
$(C_3H_7)_2S$	8.31	1.82	37.99	8.06	29.96	23.10	71.18	0.366	1235	-0.63
$(IZO-C_3H_7)_2S$	8.38	2.16	38.06	8.11	37.76	17.60	69.58	0.361	1248	.-
$(C_4H_9)_2S$	8.23	2.62	47.28	8.11	39.96	17.2	70.2	0.362	1222	-0.66
$(IZO-C_4H_9)_2S$	8.36	2.97	47.39	8.12	-	13.0	-	-	1216	-
$(C_5H_{11})_2S$	-	2.98	56.61	8.15	49.84	10.1	68.12	0.360	1214	-0.71
$IZO-C_5H_{11}SC_5H_{11}$	-	3.08	56.56	8.16	-	-	-	-	-	-
$(C_6H_{13})_2S$	-	3.34	65.87	-	59.69	4.2	67.04	0.356	1208	-0.77
$(C_7H_{15})_2S$	-	3.4	75.24	-.	69.57	-0.2	67.62	0.357	1202	-0.73
$(C_6H_5)_2S$	7.8	8.31	-	-	55.3	70	75.45	0.377		-0.83
Fraction 1		15.4								-0.61
Fraction 2		15.4								-0.65
Fraction 3		27.6								-0.73

*) $\Delta H^p S$ was taken as equal to 66.2kcal/mole [9]

varies between 7.99 and 8.16cm^3 in the transition from diethyl to diamyl sulphide.

The electron-donating potentialities of the hetero-atom were assessed by means of the ionisation potentials I_S [3]) and the basicity constant K_B, determined by a conducto-metric method [4]). From table 2 it follows that the nucleophilic capacity of the reagents increases somewhat with increase in the chain length of the hydrocarbon radical and also with increase in the number of rings in the molecule. The thermal effect of extraction varies in line with the variation of K_B for the sulphides and decreases with increase in their ionisation potentials.

The electronegativity concept is based on the electrochemical difference in the interacting particles and is essentially a function of the bond energy [°]). It is natural that the effective electronegativity will differ from that of the atom, depending on the nature of the groups added to the sulphide sulphur. In the literature [10-12] electronegativity scales were proposed for radicals, but they are evidently far from complete and cannot be used for theoretical evaluation of the effective electronegativity of the sulphur. The bond energies E(S-C) of the extractants were therefore determined by a thermochemical method [13]) (table 2). The obtained values for E(C-S) are the thermal effects of bonding and consequently only characterise the actual bond energy approximately.

The order of variation in the bond energies of a hetero-atom with substituents can often be traced in the character and direction of the shifts of the corresponding frequencies of the vibrations of the bonds in the IR region of the spectrum. Since the band for the stretching vibrations of the C-S bonds in sulphides, located in the region of 700-550cm^{-1} [14]), is weak in intensity and is not suitable for qualitative and semi-qualitative investigations, the band for the stretching vibrations of the C-C bonds of the hydrocarbon skeleton $\nu_{C-C} = 1200$-1300cm^{-1} was used as a characteristic [15]). The orders of variation were similar for E(C-S) and ν(C-C) (table 2), and this can provide evidence for the regular decrease in the effective electronegativity of the sulphur atom (ΔX_S) with increase in the chain length of the alkyl radicals. Compared with dialkyl sulphides, the sulphur in the diphenyl sulphide molecules is the most electronegative. The obtained data are consistent with the orders of variation in K_B and I_S.

The nucleophilic characteristics of sulphide sulphur are extremely restricted and, as was shown above, depend little on the structure and composition of both aliphatic and cyclic compounds. In addition, they cannot explain the high strength of the M-S bonds in the solvates which form. It can be supposed that additional interactions are possible in the M-S system on account of the manifestation of the electron-accepting characteristics of the extractants. There are references to the electro-

philic characteristics of sulphide sulphur in the literature [16]). As a characteristic of the accepting characteristics of the hetero-atom we used the half-wave potential for the cathodic reduction of the extractant $E_1(S)$, which is not a strictly correct expression for the electrophilicity of the sulphur but is evidently functionally related to it.

The relation between the half-wave potentials for the cathodic reduction of palladium from the PdCl$_2 \cdot 2S$ solvates and the $E_1(S)$ value for the relation of the sulphides is given in fig. 1. There is a correlation between these values: increase in the electron-accepting characteristics of the sulphides leads to a shift of the reduction potential of palladium towards negative values. In turn, there is a relation between $E_1(S)$ for the reduction of the sulphides and its effective electronegativity (table 2), and this confirms the regular increase in the electron-accepting characteristics of the sulphur atom with decrease in the chain length of the hydrocarbon radical in the extractant. Consequently, some decrease in the nucleophilicity of the reaction centre of the extractant in the aliphatic and cyclic compounds is compensated by the increase in its electrophilic potentialities.
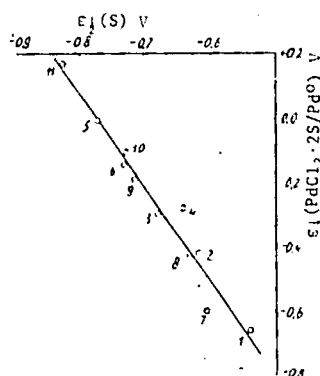
Fig.1
The dependence of the half-wave potential for the reduction of PdCl$_2 \cdot$ 2S on E_1 for the reduction of the sulphides:
1) $(C_2H_5)_2S$; 2) $(C_3H_7)_2S$;
3) $(C_4H_9)_2S$; 4) $(C_5H_{11})_2S$;
5) $(C_6H_{11})_2S$; 6) $(C_7H_{15})_2S$;
7) fraction 1; 8) fraction 2; 9) fraction 3; 10) fraction 4; 11) $(C_6H_5)_2S$.

The participation of the sulphur as an electron acceptor in M-S bonding during the formation of the extracted solvate is confirmed by the existence of a relation between the changes in free energy of extraction and the half-wave potential for the reduction of the sulphides (tables 1 and 2). Here the shift of $E_1(S)$ into the region of negative values as a rule leads to an increase in ΔG_e. A characteristic feature of the extraction process for the chloride complexes of divalent platinum with organic sulphides is the comparatively small change in free energy, while the enthalpy and entropy change within wider limits (table 1). The greater the heat of extraction, the smaller the change in the entropy of the system. It can be supposed that the thermal effect of extraction increases with increase in the nucleophilicity and with decrease in the electrophilicity of the sulphur. The participation of sulphur as an electron acceptor in the reaction with a metal ion involves considerable expenditures

on reconstruction of the electronic structure of both the hetero-atom itself and of its partner in the bond. This explains the subsequent decrease in the thermal effect of extraction.

The entropy of the co-ordination bond in the solvate and the entropy of extraction are functionally related. It is interesting to note that ΔS_e correlates with the electrophilicity of the sulphides (fig. 2).
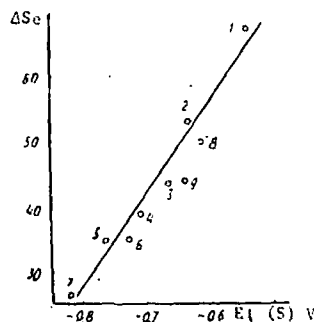

Fig.2
The dependence of the change in entropy of extraction for $PtCl_6^{2-}$ on $E_{\frac{1}{2}}$ for the reduction of the sulphides: 1) $(C_2H_5)_2S$; 2) $(C_7H_7)_2S$; 3) $(C_4H_9)_2S$; 4) $(C_5H_{11})_2S$; 5) $(C_6H_{13})_2S$; 6) $(C_7H_{15})_2S$; 7) $(C_6H_5)_2S$; 8) fraction 1; 9) fraction 2.

If the formation of the σ bonds in the solvate is secured by the donating characteristics of the sulphur atom, its accepting abilities can be attributed to participation in a π bond, especially as the hetero-atom has vacancies at the 3d sub-level. The idea of the realisation of a π bond in the case of soft partners was put forward by Chatt[17]) in a development of the Pearson concept[18]). In the works of Mazalov et alia[19]), however, it was the subject of doubt. We do not intend to confirm that a π bond is in fact formed in the investigated systems, but the electron accepting characteristics of sulphides have a substantial effect both on the stability of the solvants which form and on the extraction process as a whole.

Conclusion

The effectiveness of the extraction of $[PtCl_6]^{2-}$ increases with increase in the electrophilic characteristics of the extractants, i.e. with decrease in the chain length of the hydrocarbon radical and with decrease in

the number of rings in sulphides of the aliphatic series and industrial fractions.

References

1) E M Arnett in Modern problems of physical organic chemistry: Mir, Moscow 1967, p. 195.
2) E N Gur'yanova et alia: Donor-acceptor bond: Khimiya Moscow 1973.
3) E N Karaulova: The chemistry of petroleum sulphides: Nauka, Moscow 1973.
4) K P Mishchenko and A A Ravdel' (editors): Practical work in physical chemistry: Goskhimizdat 1961.
5) V V Ioffe: Refractometric methods of chemistry: Khimiya, Leningrad 1974.
6) Dissociation energy of the chemical bond. Ionisation potentials and electron affinity: Nauka, Moscow 1974.
7) D Stull et alia: Chemical thermodynamics of organic compounds: Mir, Moscow 1971.
8) V S Chekushin and I E Nikonova: Reports of 13th scientific session on the chemistry and technology of organic sulphur compounds and sulphur petroleums: Dushanbe 1974, p. 274.
9) L Pauling: Nature of the chemical bond: Goskhimizdat, Moscow 1947.
10) I Bell et alia: Amer. Chem. Soc. 1954, 76, 1585.
11) A Allred and E Rochew: J. Anorg. and Nucl. Chem. 1958, 5, 264.
12) S S Batsanov: Electronegativity of the elements and the chemical bond: Nauka, Novosibirsk 1962.
13) K Mortimer: Heats of reactions and strength of bonds: Mir, Moscow 1964.
14) L J Bellamy: New data on the IR spectra of complex molecules: Mir, Moscow 1971.
15) R L Obolentsev et alia: Chemistry of organosulphur compounds contained in petroleum and petroleum products: Vysshaya Shkola, Moscow, 1972, 9, III.
16) A I Shatenshtein and E A Gvozdeva: Teoreticheskaya i Eksperimental'naya Khimiya 1965, 1, 352.
17) J Chatt: Nature 1950, 165, 859; 1956, 177, 852; J Chatt et alia: J. Chem. Soc. 1955, 4456; J Chatt, Inorg. and Nucl. Chem. 1958, 8, 515.
18) R G Pearson: J. Amer. Chem. Soc. 1963, 85, 3533.
19) E A Gal'tsova et alia: Izv Sibirsk Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk. 1975, (9), 4, 41.

UDC 669.2

Characteristics of the thermal operation of tuyeres in top blast treatment of melts (by way of discussion)

Yu B Shmonin, Yu D Dekopov, and B V Lepikhin (Leningrad Mining Institute)

The cooled tuyeres used in the top blast treatment of mattes, cast irons, and ferronickel operate for a limited time on account of gradual disintegration of the copper heads[1-3]). The disintegration is due to the considerable heat fluxes on the local section of the head, which gave rise to an abrupt increase of temperature in the wall of the head and subsequent fusion or dissolution in the melt. Thermal stresses in the wall material which arise here also play a specific role[3]). Heat is transmitted from the bath to the tuyere by convection when the head is flushed by melt ejected from the seat of the blast.

Detailed investigations into the thermal operation of tuyeres during top blast treatment of copper-nickel mattes were undertaken during trials on continuous converting at the Pechenganikel' Mining-Metallurgical Combine[1][4]). They showed that cooled tuyeres mostly operate with a crust at the head is periodically removed or melted, after which the tuyere undergoes a unique kind of thermal shock, and this is the direct cause of disintegration. The length of service of the tuyere between repairs depends on the number and intensity of the thermal shocks to which it has been subjected.

In the present article the characteristics of the thermal operation of the tuyere are examined from the standpoint of

its possible mathematical simulation. According to experimental data, the thermal operation of the tuyeres consists of periods of nonstationary increase of the temperatures in the wall of the head (thermal shock), subsequent stabilisation of the temperature field in the head, and finally conditions close to a steady state. It is of greatest interest to model the thermal shock, since this gives rise to disintegration of the tuyere.

The experimental temperature diagrams, recorded on the section of the wall at greatest risk in respect of burning, showed that the thermal shock is characterised by a stepwise increase of temperature at a rate of 20-40°C/sec for 5-15 sec. The maximum temperatures (300-1000°C) are maintained for tens of seconds and then gradually decrease to steady values after a few minutes. The decrease in the temperature during such decay of the thermal shock can be described sufficiently accurately by an empirical formula of the following type:

$$t_\tau = \frac{t_{max}}{1 + m_\tau} \tag{1}$$

where: t_{max} = the maximum temperature reached at a given point on the wall during the thermal shock °C

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SOCIETY OF MINING ENGINEERS of AIME

540 ARAPEEN DRIVE — SALT LAKE CITY, UTAH 84108

ENVIRONMENTAL CONSIDERATIONS IN
URANIUM SOLUTION MINING

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Environmental Protection Department

Atlantic Richfield Company
Los Angeles, California

INTRODUCTION

Atlantic Richfield Company began operating a commercial uranium solution mining project in April, 1975 in Live Oak County, Texas, 10 miles southwest of the town of George West (Figure 1). The operation is designed to produce 250,000 pounds of U_3O_8 per year and is jointly owned by Atlantic Richfield Company, Dalco and U. S. Steel.

The proprietary process employed in this operation consists of injecting an alkaline leaching solution into the ore-bearing formation through a pattern of injection wells. The uranium-bearing solution is then removed through producing wells using submersible pumps in central production wells. The produced solution is pumped through a pipeline to the plant area where the uranium is extracted. The barren solution is refurbished and returned to the pattern area for reinjection.

The injection field and plant site are located in the drainage of Spring Creek, a small intermittent stream tributary to the Nueces River. Land use in the area is primarily agricultural -- cattle ranching and farming -- but several producing gas fields are present in the areas as well.

A nine month environmental baseline study was conducted on the property beginning in February, 1975. Plants and animals of the Clay West area were identified and representative terrestrial and aquatic communities were analyzed. Physical and chemical .

2

parameters of the soils were described and analyzed. The surface
and underground waters were analyzed chemically; radionuclides,
heavy metals, nutrients, and pesticide concentrations were
measured in the creek sediments; bacteriological measurements were
made in creek water and sediments; radionuclide and chemical levels
in plants and animals, both terrestial and aquatic, were measured.
These studies, though not required by existing state or federal
laws, were considered necessary to assess the existing conditions
before operations began on site.

The in-place leaching technique for uranium mining eliminates the
environmental disturbances associated with open pit or underground
mining. No grinding and crushing of ore is needed, nor are large
tonnages of waste tailings produced. Surface subsidence is not
expected since less than 5 pounds of uranium is present per ton of
rock and even complete removal of such small amounts should not
cause subsidence.

Solution mining has fewer environmental problems than conventional
mining. Members of the Texas Water Quality Board recognized the
differences which exist and have recently formulated new environ-
mental control procedures which apply specifically to solution
mining. Some of the solution mining activities which are of parti-
cular concern are discussed in the following pages.

PROCESS DESCRIPTION

The produced uranium-bearing solution is pumped through a pipeline
from the pattern area to the plant area. The first pattern area

consists of a nest of 12
wells (Figure 2). Injec
spaced 50 feet apart on
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A block flow sheet of th
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consists of a nest of 125 fluid injection, production and monitor
wells (Figure 2). Injection wells have four inch casings and are
spaced 50 feet apart on a square grid. Production wells have a
6 inch casing and are located in the center of each square.

A block flow sheet of the plant is given in Figure 3. The produced
solution goes through parallel trains, each consisting of a carbon
column and an ion exchange column in series. The carbon column
removes any sand present in the produced solution and the ion ex-
change column extracts the uranium. The depleted solution is
treated with chemicals and returned to the field for reinjection.
The uranium retained in the ion exchange column is removed periodi-
cally with a sodium chloride solution. Uranium-bearing solution
from the ion exchange column is passed through a charcoal column
for removal of impurities and then to a precipitation tank where the
uranium is precipitated as yellowcake slurry. The yellowcake
slurry is clarified, filtered and dried to produce a granular
yellowcake product.

ENVIRONMENTAL CONSIDERATIONS

Sources of waste solutions to storage reservoirs, the backwash
reservoir and atmospheric discharges are shown in the block flow
sheet (Figure 3). These waste solutions pose a relatively small
problem and are adequately controlled by conventional means. There
is one area, however, that deserves special attention and that is
the effect of the uranium solution mining process on the chemical
nature of water present in the ore body.

4

Waste Storage Reservoirs

The chemical wastes from the plant are pumped into surface reser-
voirs lined with heavy chlorinated polyethylene. The reservoirs
are designed so that the net annual evaporation rate is equal to
the maximum volume of chemical wastes generated every year. Ade-
quate freeboard is provided to accommodate periods of high rainfall
and low evaporation. Waste solutions from these reservoirs are
disposed of in deep disposal wells on site as discussed later in
this paper.

Backwash Reservoir

The carbon columns used to trap sand from the produced solution are
backwashed periodically, requiring a source of clean water. A
backwash reservoir provides this clean water and is also used as a
settling pond. This reservoir is made of reinforced concrete.
The water is recirculated and evaporation losses made up by using
water from a fresh water well. The chemical assay of the pond water
changes little from the original fresh water.

Air Quality

Air quality problems are minimal in uranium solution mining since
no grinding or crushing is involved and insignificant emissions
occur. The yellowcake drying system is the only source of air
emissions in this plant. The exhaust gases from the dryer pass
through two stages of scrubbing before being discharged to the
atmosphere. Texas Air Control Board has examined the operating
plans for these facilities and has issued a letter of exemption
from the requirement of a permit.

Leaching Zone

The leaching operation
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There are two primary
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2. Restoration of
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Leaching Zone

The leaching operation will modify the chemical nature of water
present in the ore body. This zone was not originally a source of
potable water due to naturally occurring high levels of radium. An
extensive water well sampling and analysis program was formulated
in consultation with the Texas Water Quality Board, the Department
of Health and the Water Development Board. The details are shown
in Table 1. The sampling and analysis program prior to the start of
circulation of leaching solutions, constitutes a necessary data base
and clearly defines the aquifer composition at the start of the
leaching operation.

There are two primary environmental considerations related to the
leaching process:

1. Prevention of leakage of contaminants out of the ore body.
2. Restoration of the water in the ore body after conclusion
   of leaching.

1. Prevention of Leakage of Leaching Solution

   Initially the leaching operation will be controlled by balan-
   cing the injection and production rates and adopting other
   reservoir management techniques. Each of the injection and
   production lines is equipped with direct reading flow meters
   and a daily check is made to balance the total production
   against total injection. Monitor wells (Figure 2) around the
   leach area are sampled regularly to detect any migration of
   injected solutions. If migration is detected, injected and
   produced volumes are adjusted to counteract such migration.
   All injection and production wells in the pattern area are

cased and cemented to the surface, preventing upward migration
of injected solution. Four shallow monitor wells drilled in
the pattern area are sampled and analyzed routinely to detect
any upward leakage of leach solution.

2. Ore Body Restoration

Present plans for ore body restoration are to pump solutions
out of the ore body and into deep disposal wells until ion
concentrations are reduced to acceptable levels. Pilot tests
demonstrate that chemical solutions are readily displaced by
native ground water when the solutions are pumped from the
ore body. Other alternatives to pumping the solutions from
the ore body will also be studied.

Disposal Wells

Two deep disposal wells, one of which has been completed, will be
used for the present operation (Figure 4). These two wells will be
drilled to a total depth of about 4500 feet. The upper water and
ore-bearing sand (Oakville) will be isolated by 600 feet of steel
casing cemented over the full length. A second string of steel
casing is set through the upper casing from the surface to the
total depth of the well and cemented from the bottom up to the
surface. The waste material will be injected down steel tubing
through perforations opposite the injection zone. The injection
zone will be isolated by a packer and a non-corrosive fluid will be
placed in the annulus between the tubing and casing. Calculations
of the pressure gradient resulting from twenty years of injection
at an average rate of 150 gallons per minute into 100 feet of the
500 feet of net available sand show that the differential pressure

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This provides a safety facto
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at the well bore would be 194 pounds per square inch (psi) and at
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CONCLUSION

The commercial uranium leaching process has received and will con-
tinue to receive considerable technical monitoring related to its
environmental impact. An environmental task force has been organ-
ized by Atlantic Richfield to define and act on the environmental
needs of the present operation. An environmental baseline study of
the area has been completed. It is believed that with proper
monitoring and controls, solution mining of uranium can be conducted
with a minimal impact on the environment.

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TABLE 1

CLAY WEST URANIUM OPERATION

SURFACE AND GROUNDWATER SAMPLING PROGRAM

No.	Timing	Sample Source	Analyses*
1	Prior to any injection	All water wells within a 2 mile radius of the patterns	(1)
2.	Prior to any injection	28 operational wells in the patterns	(1)
		10 operational wells	(2), (3)
3.	Prior to any injection	Spring Creek - (upstream of plant site and downstream of pattern area) Nueces River - (above and below its confluence with Spring Creek).	(1), (2)
4.	Each 3 months	1/8 of all water wells within a 2 mile radius	(1), (2)
5.	Each 6 months	Six nearest domestic supply wells	(1), (2)
6.	Each 6 months	Spring Creek and Nueces River	(1), (2)

*

(1) List A Ions - Ca, Na, Fe, Mo, HCO_3, SO_4, Cl, NO_3, NO_2, NO_4, pH and TDS (Total Dissolved Solids)

(2) Gross Alpha, Gross Beta - if Gross Alpha is over 3 picocuries per liter a barium coprecipitation for Radium 226 will be done. If Gross Alpha is over 50 picocuries per liter a lead - 210 determination will be done.

(3) List B Ions - Mg, F, As, Ba, B, Cd, Cu, Cr, Pb, Mn, Hg, Ni, Se, Ag, U, simple cyanide, P - alkalinity as $CaCO_3$ and total alkalinity as $CaCO_3$.

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Figure 1
Plant Location
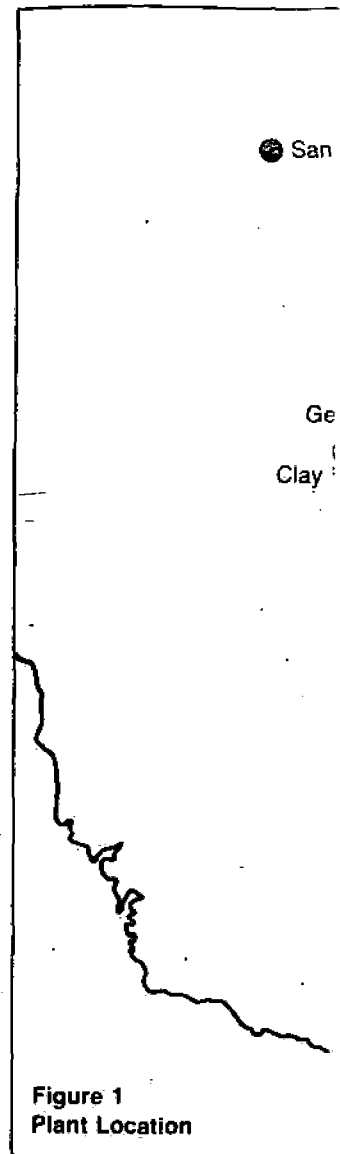
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Figure 1
Plant Location

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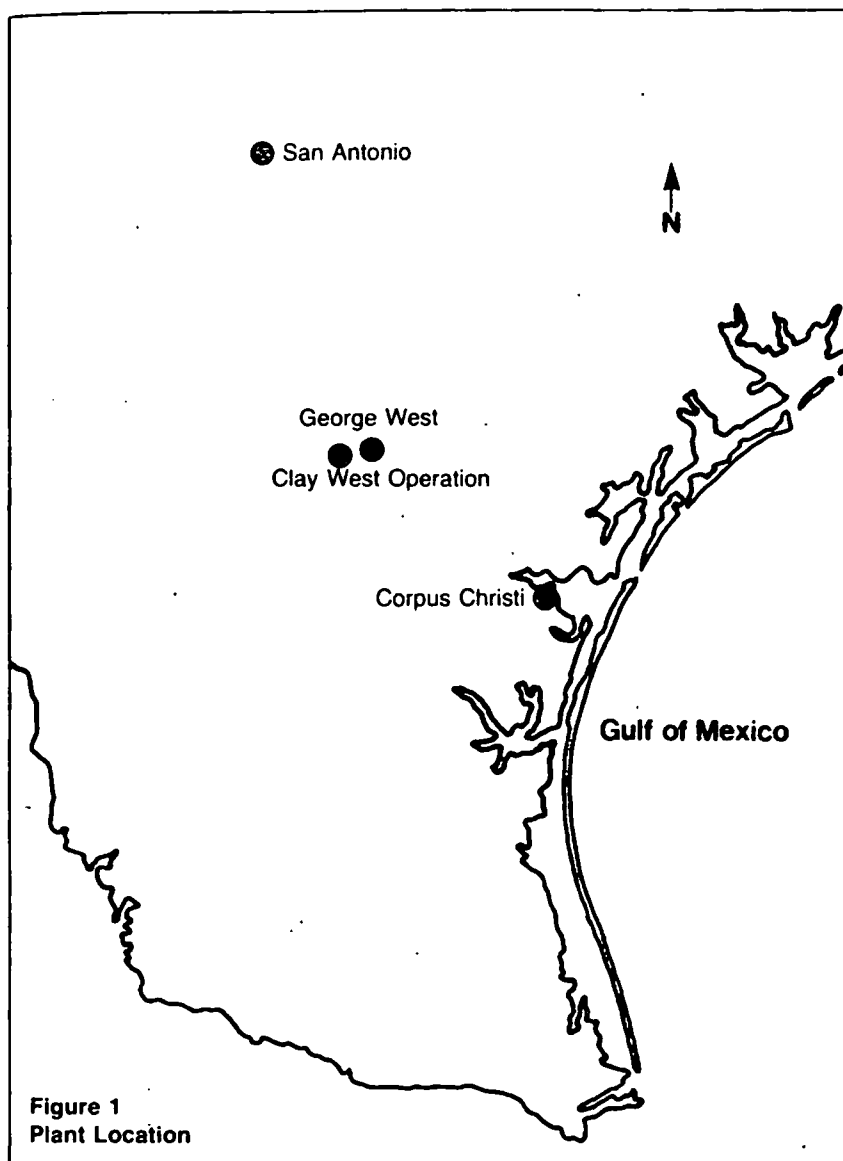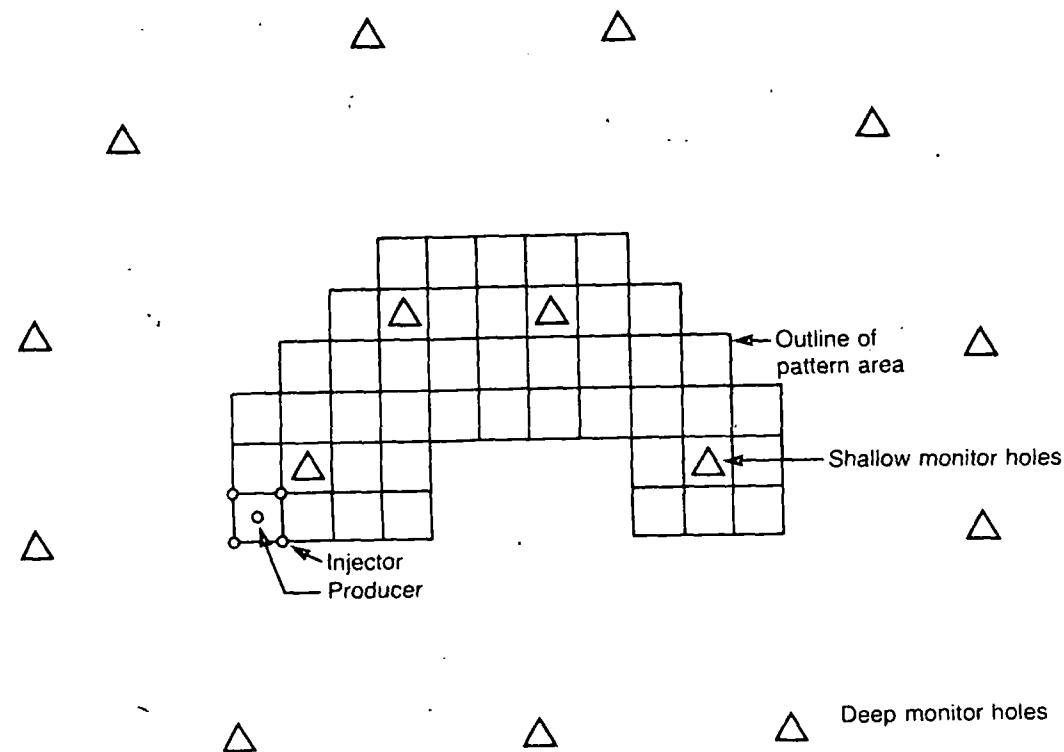
Figure 2
Pattern Area
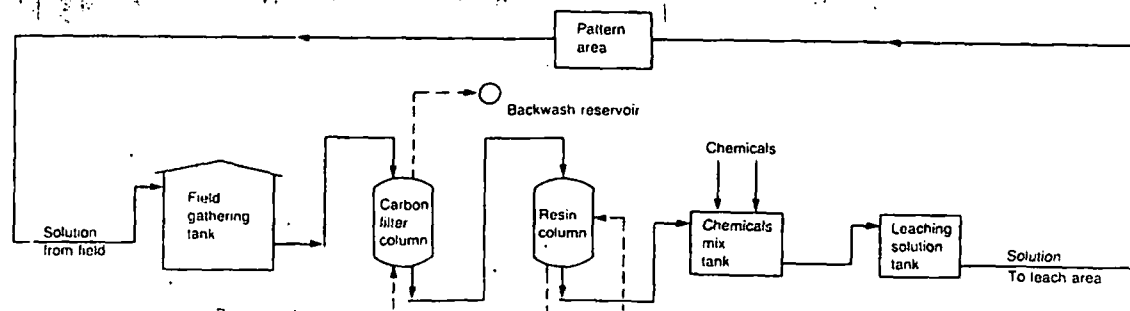
Figure 2
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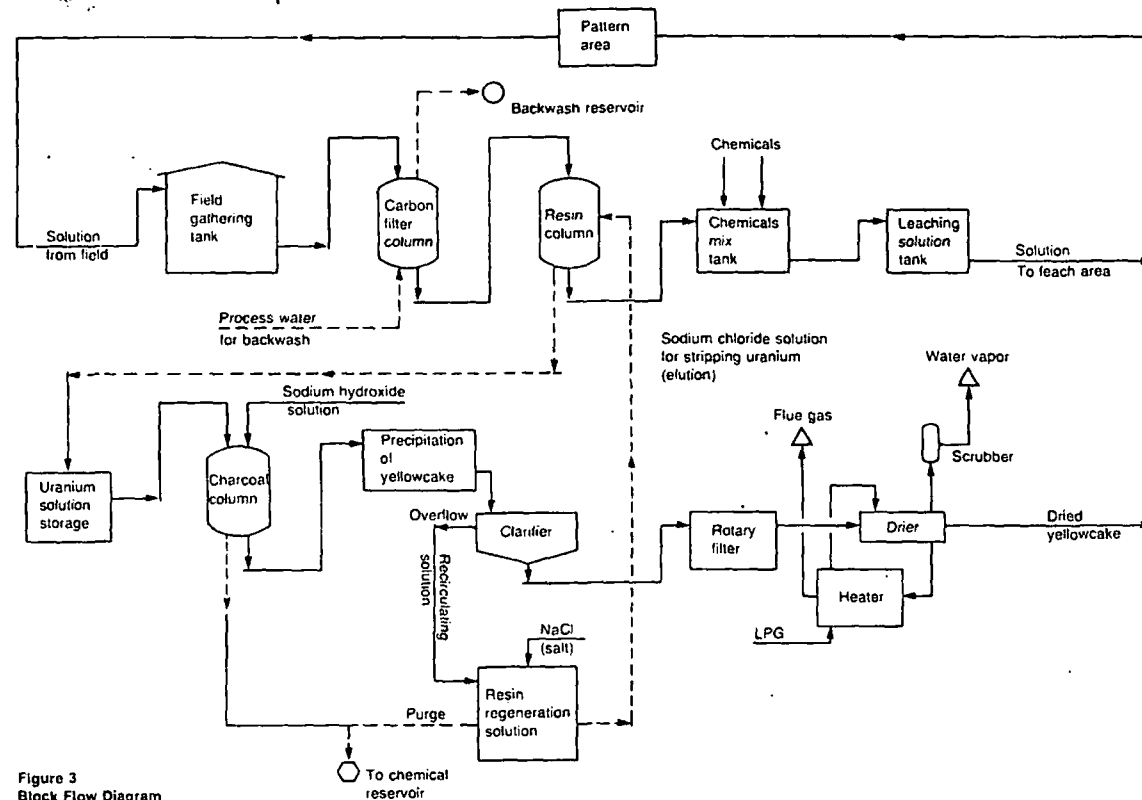
Figure 3
Block Flow Diagram
Uranium Leaching Plant

Atlantic Richfield Company
Clay West Texas
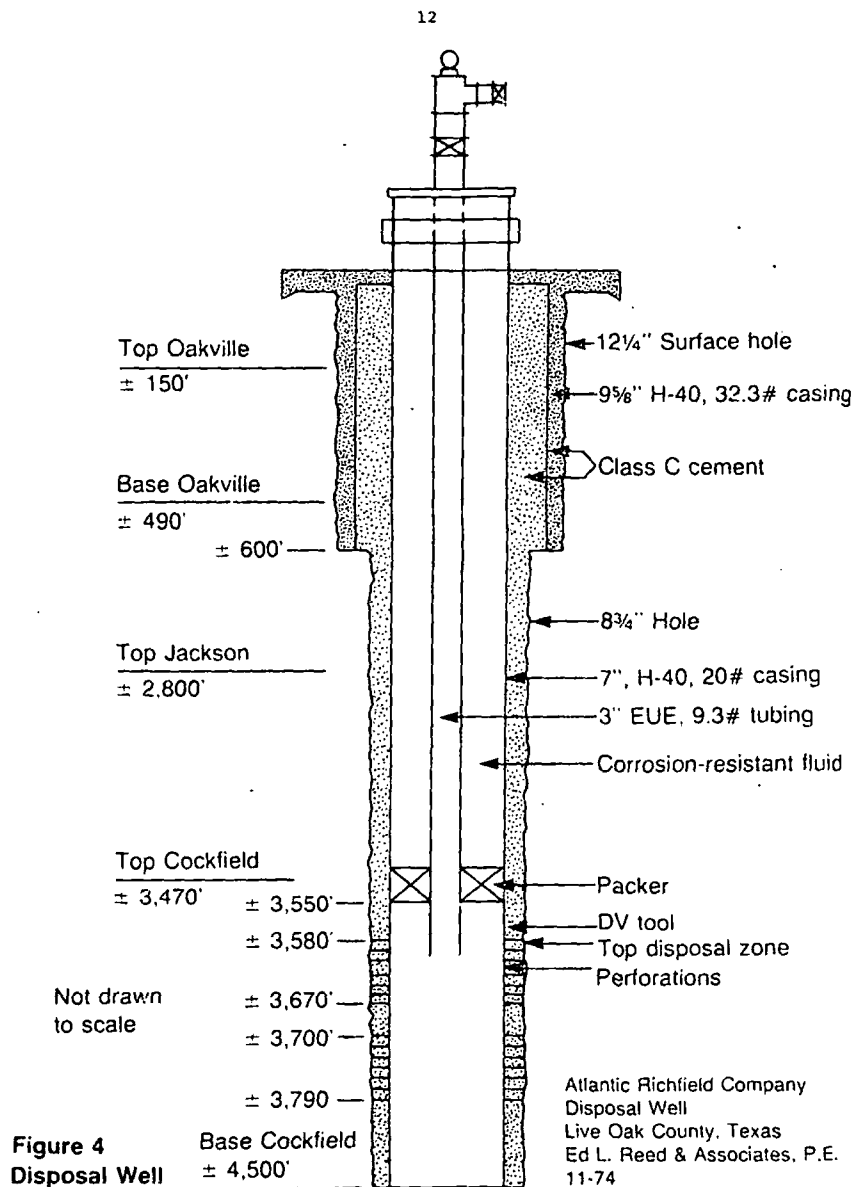
12

Top Oakville
± 150'

Base Oakville
± 490'
± 600'

Top Jackson
± 2,800'

Top Cockfield
± 3,470'   ± 3,550'
± 3,580'

Not drawn   ± 3,670'
to scale   ± 3,700'

± 3,790'

Figure 4   Base Cockfield
Disposal Well   ± 4,500'

12¼" Surface hole

9⅝" H-40, 32.3# casing

Class C cement

8¾" Hole

7", H-40, 20# casing

3" EUE, 9.3# tubing

Corrosion-resistant fluid

Packer

DV tool

Top disposal zone

Perforations

Atlantic Richfield Company
Disposal Well
Live Oak County, Texas
Ed L. Reed & Associates, P.E.
11-74

Chapter 21

ECONOMIC EVALUATION OF IN SITU
EXTRACTION FOR COPPER, GOLD, AND URANIUM

by F. Milton Lewis, Clement K. Chase and Roshan B. Bhappu

1976
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AIME

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ABSTRACT

In situ extraction for copper, gold and uranium, generally involves
several common alternative processes and techniques. These include
dump leaching, heap leaching, leaching of fractured ore in-place or
bore hole mining and unit operations such as cementation, solvent
extraction, ion-exchange or carbon-in-pulp. Since the metallurgical
effectiveness and economics of such processes and unit operations
are well established, it would be possible to select the optimum al-
ternative for extracting either copper, gold or uranium from their
ores using in situ extraction technology. In this paper, efforts
have been made to provide metallurgical evaluation as well as capital
and operating costs for the various processes and unit operations.
Attempts have also been made to utilize the above costs in preparing
feasibility studies for in situ extraction of these metals.

INTRODUCTION

The ever increasing demand for today's metals, the necessity for
treating complex and lower grade ores, with higher operating costs,
the need for conserving our dwindling minerals resources, and the
public awareness of environmental pollution factors make it manda-
tory to develop new techniques for extracting metals. In this
endeavor, it is inevitable that in situ mining and in-place extraction
technologies will be increasingly employed in metal production.

In situ mining is the in-place extraction of metals from ores located within the confines of a mine or in dumps, ore heaps, slag piles, and tailing ponds. These materials represent an enormous, untapped, potential source of all types of metals. The field of in situ mining encompasses the preparation of ore for subsequent in-place leaching, the flow of solutions through rock masses and within rock pores, the leaching of minerals with inexpensive and regenerable leaching reagents under conditions prevailing in-place, the generation and regeneration of such solutions, and the recovery of metals or metal compounds from the metal-bearing solutions. Accordingly, the overall scope of this potential mining method embraces interdisciplinary science and technology requiring application of the principles of basic sciences, mineral technology, hydrology, and economics.

It is not inconceivable that eventually our ore reserves will consist largely of low-grade, refractory and inaccessible new deposits and low-grade zones near previously worked deposits, caved ore and stopes filled with submarginal ore, waste dumps, tailing ponds, and slag heaps. In situ mining promises economic recovery of metals from such types of deposits and sources.

Heretofore, this kind of mining has been more or less limited to the extraction of copper from low-grade materials; however, it has a mcuh greater potential than this. Practically all metals are susceptiable to leaching in the in situ environment. Processes will soon be developed for the in-place extraction and recovery of metals such as lead, zinc, nickel, manganese, uranium, silver, gold, molybdenum, and mercury.

Advantages of in situ mining include environmental attractiveness due to less land disturbance, improved mineral utilization due to working on lower and submarginal ores, and favorable economics due to earlier return on investment. Some of the disadvantages of the process are: possible contamination of ground water, potential land subsidence, and lack of field and operational experience.

A detailed bibliography on in situ leaching technology has been compiled by Twin Cities Mining Research Center of the United States Bureau of Mines (1).

Recent laboratory studies, pilot plant operations, and several plant practices have conclusively demonstrated the effectiveness of in situ extraction of copper, uranium and gold. Heap leaching, leaching of fractured ore in-place and bore-hole mining technology have all been applied in practice and have been found to be economically viable. Although in the above operations different metals are extracted, the unit operations involved in all the practices are more or less common. These include drilling, blasting, hauling, primary crushing, ore handling, pad preparation, leaching, cementation, solvent extraction, carbon adsorption ion-exchange, electrowinning,

and the like. Moreover, these unit operations, especially those pertaining to extraction, are interchangeable and any new developments in extraction technology of one metal, say gold, may be applicable to uranium and copper. Accordingly, the in situ extraction technology and economics for copper, gold and uranium have much in common and since the metallurgical effectiveness and economics of unit processes and operations are well established, it should be feasible to select the optimum flowsheet for extracting either copper, gold or uranium form their ores.

In this paper efforts have been made to illustrate the common technology and economics of in situ extraction for copper, gold and uranium by providing examples of plant practices, by citing capital and operating costs for various unit operations, and submitting appropriate feasibility studies.

IN SITU MINING TECHNIQUES

There are basically three distinct applications and associated leaching systems encountered in the field of in situ leaching, depending mainly in the physical location of the ore deposit. These situations are illustrated in Figure I.

Typical examples of Type I are the numerous dump leaching operations practiced by the open pit copper mines in the Southwestern United States (2). Dump leaching, in general, is a convenience for open pit mining operations to dispose of lower grade (submarginal) stripped material in a remote area with the intention of recovering the valuable metals contained therein. Because of limited available area and placement consideration, such dumps are built to a substantial depth. The leaching of such piles, either through spraying or ponding of solution, is relatively slow and inefficient. Nevertheless, the production of copper from such dump leaching operations at the present amounts to about 200,000 tons of copper per year in the United States or approximately 15 percent of the total production. It should be noted that the effectiveness of copper extraction in these dump leaching operations has been partially attributed to bacterial oxidation of sulfide minerals.

Several successful heap leaching operations for extraction of copper, gold, and uranium as carried out in the United States (Arizona, Nevada, Texas, New Mexico, and Wyoming) also belong to Type I. Heap leaching is a system in which low grade or mixed oxide-sulfide ores are leached in relatively small heaps on prepared pads or surfaces with positive drainage over a shorter leaching period under controlled conditions. In some cases the ore is brought to a designated site for treatment and removal, followed by piling of fresh ore on the same site for treatment.
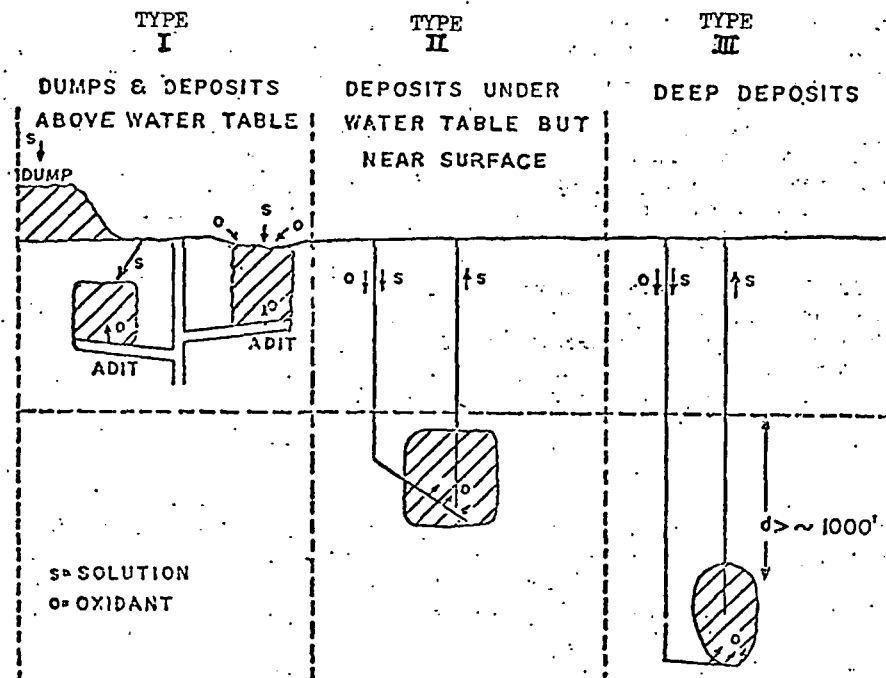
Figure 1

THREE TYPES OF IN SITU LEACHING SITUATIONS

(According to Dr. Milton Wadsworth)

Other viable in-place leaching examples of Type I are the truly in situ leaching systems in which the ore is broken in-place by some type of blasting technique followed by percolation leaching of the fragmented ore mass. Appropriate collection galleries are provided to collect the leach solution for subsequent recovery of metal and re-circulation of the barren solution for additional leaching. Since the ore is broken and left in place, such leaching systems are economically attractive. Ranchers Exploration and Development Corporation's Old Reliable Mine operation in Arizona and the Big Mike Mine in Nevada are fine examples of this in situ leaching method (3, 4).

Also included in Type I are the classic in situ leaching operations of the Miami and Ray Mines, Arizona, in which the leaching has been carried out on fractured submarginal ore zones resulting from block caving operations. In the case of the Miami Mine operation, it has been estimated that 85,000 tons of copper metal have been produced over a 15 year period since completion of the underground mining operation in 1959, with an estimated recovery of about 60 to 70 percent of

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Type II incl
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Type III inv
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the metal left in place. The leaching operation continues with no de-
crease in recovery rate and no immediate end in sight (5).

Type II includes the leaching of relatively shallow deposits located
less than 300 meters from the surface and which are under the water
table. Such deposits may need to be fractured in-place and the solu-
tion drained in order to commence the alternate leaching and drying
cycles. On the other hand, metal values from such deposits may be
extracted by utilizing the bore hole mining technology as is currently
practiced by at least one uranium mining operation in the United States.
The bore hole mining technique usually consists of a properly designed
pattern of wells suitable for injection of the leaching solution and
recovery of metal-bearing liquors. The wells are like water wells ex-
cept that the casings are perforated for optimum leaching conditions
(6, 7, 8).

Type III involves relatively deep-seated deposits in excess of 300
meters and under the water table. Leaching of such deposits through
chemical mining has been proposed by Lawrence Livermore Laboratory,
University of California, after fracturing the ore body by conventional
or nuclear devices. Leaching at such depths is enhanced by direct
oxidation of sulfide minerals due to increased solubility of oxygen
resulting from hydrostatic head (9, 10).

A listing of various U.S.A. commercial and pilot plant operations
employing the above three types of in-place leaching techniques in
the extraction of copper, gold and uranium are given in Table 1.
These examples of practical and economic operations clearly indicate
that the in situ extraction technology has developed into a matured
and a viable metal extraction process.

ECONOMIC CONSIDERATIONS

Feasibility Studies

A well organized and realistic feasiblity study should include:
confirmation of ore reserves and grades, an effective mine plan,
leaching and metal recovery flowsheet, preliminary capital and oper-
ating cost estimates, determination of rate and cost of production
and selling price of end products, and a cash flow analysis and return
on investment (ROI) study. The profit potential and the viability of
the project can then be accurately assessed by all the parties con-
cerned with the development of the mine. Such a feasibility study
also assists in screening and evaluating various choices and options
involved in mining and processing. This is especially true for the
development of lower grade deposits, since the paramount question here
is the selection of the best method of extracting the metal values
from a particular deposit.

In the case of in situ leaching, especially, the feasiblity study
plays a very significant role since the percentage recovery of metal

TABLE 1
IN SITU LEACHING PRACTICES IN USA

Dump Leaching

    1. Several copper operations in Southwest U.S.A.

Heap Leaching

    1. Bluebird Mine, Arizona (copper)
    2. Inspiration Mine, Arizona (copper)
    3. Johnson Camp Mine, Arizona (copper)
    4. San Juan Mine, Arizona (copper)
    5. Carlin and Cortez Gold Mines, Nevada (gold)
    6. Round Mountain Mine, Nevada (gold)

In Situ Leaching (Copper)

    1. Miami, Arizona (block caving operation)
    2. Ray, Arizona (block caving operation)
    3. Mountain City, Nevada (block caving operation)
    4. Old Reliable, Arizona (coyote blast)
    5. Big Mike, Nevada (pit wall blast)
    6. Zonia, Arizona (coyote blasts)
    7. Nuclear Blast (AEC - Kennecott concept for deep-seated deposits)
    8. Kennecott's Experiment (near Safford, Arizona)

In Situ Leaching (Uranium)

    1. Utah Mining and Construction Company, Shirley Basin, Wyoming
    2. Mine Water Leaching at Grants, New Mexico
    3. Bacterial Leaching at Elliot Lake, Canada
    4. Wyoming Minerals, Bruni, Texas
    5. Wyoming Minerals, Ray Point, Texas
    6. Arco-US Steel-Dalco, George West, Texas
    7. Union Carbide, Duval County, Texas
    8. Exxon, Powder River Basin, Wyoming
    9. Mobil Oil Corporation, Webb County, Texas

under in situ leaching environment is very difficult to predict.
Even though the laboratory or pilot plant tests indicate a certain
recovery, say 60 or 70 percent, there is no guarantee that in actual
practice it would be possible to attain the specified recoveries. In
such cases, it behooves the mine management to carry out the above
feasibility study and cash flow analyses at 60, 50, 40, 30, 20, and 10
percent recovery levels. If the cash flow and thus the economic via-
bility of the project does not appear to be favorable for 50 or 40
percent recovery levels, then it would be preferable to cancel the
project or undertake additional laboratory and field studies in order
to increase the confidence level of the economically acceptable recov-
ery figure. On the other hand, if the feasibility study appears fav-
orable for 30 to 20 percent recovery levels, all efforts should be
made to initiate the in situ leaching operation as soon as possible.

As a matter of fact, the economic viability of in situ leaching operations through realistic feasibility studies have been confirmed by recent in situ leaching experiences at Old Reliable Mine, Arizona and Big Mike Mine, Nevada (by Ranchers Exploration and Development Company), both of which proved economically successful at 15 to 20 percent overall copper extractions.

Since the cash flows and thus the overall economic feasibility of an in situ leaching venture may be influenced significantly by the price of metal, it is customary to carry out the above feasibility studies at selected metal prices below and above the prevailing price. In this way, the mine management is in a better position to assess the economics of the venture under different economic climates.

TABLE 2
ESTIMATED CAPITAL COSTS FOR UNIT PROCESSES

Unit Processes	Basis	Estimated Cost
Copper (40,000 lbs/D; 4,000 gpm at 1.0 gpl Cu)		
Cementation	$35-40/lb Cu/D	$1,400,000 to 1,600,000
Solvent Extraction	$150-200/ft set. area	$3,000,000 to 4,000,000
Electrowinning	$60 to 70/lb cathode Cu	$2,400,000 to 2,800,000
Total SX-EW	$135 to 170/lb Cu/D	$5,400,000 to 6,800,000
Gold (200 oz/D; 2,000 gpm; 0.016 oz Au/T solution)		
Carbon Adsorption	$250-300/gpm	$500,000 to 600,000
Desorption-Electrowinning	$1,750-1,800/oz Au	$350,000 to 360,000
Total ADS-DES-EW		$850,000 to 960,000
Uranium (2,750 lbs/D; 2,000 gpm at 0.125 gpl U_3O_8)		
Ion Exchange	$1,750-2,000/gpm	$3,500,000 to 4,000,000
Precipitation	$450-500/lb U_3O_8/D	$1,237,500 to 1,375,000
Total IX-PPT		$4,737,500 to 5,375,000

Finally, in the case of extracting uranium by "bore hole mining" technology, the overall operating costs vary from $5.00 to $17.00 per pound U_3O_8 produced. Since the current price of uranium in the U.S.A. is in excess of $25 per pound U_3O_8, it may be possible to treat uranium ores containing grades as low as 0.02 percent U_3O_8.

Case Histories

In order to demonstrate the economic viability of the in situ leaching systems and to demonstrate the usefulness of preliminary feasibility studies, two case histories, one of in situ leaching of

copper and the other pertaining to bore hole mining of uranium, will be reviewed. The economic evaluation for in situ extraction of gold has already been presented in a previous paper by the authors (16).

(1) In Situ Leaching for Copper

The hydrometallurgical processes currently available for treating oxide copper ore include dump leaching, heap leaching, vat leaching, agitation leaching, and in situ leaching in combination with the conventional cementation (with scrap iron) or the newly developed solvent extraction-electrowinning system for copper production.

Capital and Operating Cost Estimates

From the viewpoint of economics, the net return from a mining venture using a specific process, such as in situ leaching, will depend upon the quantity and quality of metal extracted from the ore. The overall economics will also be influenced by the capital cost of unit processes (cementation, solvent extraction, electrowinning, etc.), the operating cost of unit operations (drilling, blasting, leaching, etc.), the cost of reagents, supplies, and utilities, and the prevailing prices of metals and by-products. For these reasons, the economic feasibility of any new venture and process must be considered in light of all these and many more potential factors.

Table 2 shows the estimated capital costs for unit processes encountered in typical in situ leaching operations for extraction of specified quantities of copper, gold and uranium. It should be noted that in some cases the capital cost is based on quantity of metal produced per day while for others, it is possible to estimate the capital cost of similar processes for other production schemdules (pounds or ounces per day) and leach solution volumes (gpm).

Tables 3 and 4 show the estimated costs for various unit operations encountered in in situ and heap leaching extraction of copper, gold and uranium. As can be seen, the cost of solvent extraction-electrowinning of copper is considerably less than for cementation. The primary reason for this difference is the additional cost of smelting and refining ($0.20 to $0.28 per pound) required for impure copper in comparison to high purity cathode copper produced in the solvent extraction-electrowinning process.

It is also interesting to note that in the processing of gold ores either by in situ or heap leaching, the overall operating costs vary from $1.48 to $1.89 per ton. These figures indicate that, using these leaching techniques, it may be profitable to extract gold values from ores averaging 0.03 to 0.05 ounces per ton when the price of gold is above $100 per ounce gold.

UN
Fracturing in plac
Mining (drilling,
Crushing (primary,

CO
Leaching (heap; pa
Leaching (in situ,
Cementation
Smelting, refining
Solvent extraction
Cost/lb. Cu (in si
Cost/lb. Cu (in si
Cost/lb. Cu (heap-
Cost/lb. Cu (heap

GOI
Leaching (in situ;
Leaching (heap wit
  NaCN; 3.0 lbs
Carbon adsorption,
  winning
Cost/T (in situ-ca
Cost/T (heap with

URAN
Bore hole drilling
Leaching (drilling
Cost/lb. U_3O_8 (in

*Cumulative at eac

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TABLE 3

ESTIMATED DIRECT OPERATING
COSTS FOR IN-PLACE EXTRACTION

UNIT OPERATION	ESTIMATED COST
Fracturing in place (with development)	$0.30 to 0.40/T
Mining (drilling, blasting, hauling and dumping)	0.40 to 0.50/T
Crushing (primary, secondary, tertiary)	0.11-0.22*-0.33/T

COPPER ORE(AVERAGING 0.5 TO 1.0% Cu)

Leaching (heap; pads; 4.0 lbs. H_2SO_4/lb. Cu)	$0.35 to 0.45/T
Leaching (in situ, 4.0 lbs. H_2SO_4/lb. Cu)	0.22 to 0.32/T
Cementation	0.10 to 0.12/lb.
Smelting, refining, and transportation	0.20 to 0.28/lb.
Solvent extraction-electrowinning	0.07 to 0.09/lb.
Cost/lb. Cu (in situ-cementation)	0.39 to 0.46
Cost/lb. Cu (in situ -SX - EW)	0.15 to 0.22
Cost/lb. Cu (heap-cementation)	0.50 to 0.66
Cost/lb. Cu (heap - SX - EW)	0.26 to 0.42

GOLD ORE(AVERAGING 0.03 TO 0.06 OZ./T)

Leaching (in situ; 1.0 lb. NaCN; 3.0 lbs. CaO)	$0.45 to 0.55/T
Leaching (heap with pads; 1.5 lbs. NaCN; 3.0 lbs. CaO)	0.55 to 0.65/T
Carbon adsorption, desorption & electro-winning	0.16 to 0.20/T
Cost/T (in situ-carbon adsorption-EW)	1.48 to 1.58
Cost/T (heap with pads-carbon adsorption-EW)	1.79 to 1.89

URANIUM ORE (AVERAGING 0.05 to 0.10% U_3O_8)

Bore hole drilling (with casing)	$13.00 to 18.00/ft.
Leaching (drilling and carbonate leaching)	2.00 to 3.00/lb.
Cost/lb. U_3O_8 (in situ leach-IX-PPT)	5.00 to 7.00

*Cumulative at each stage.

In the case history illustrated here, we are concerned with a 5 million ton oxide copper deposit with a grade of 0.66 percent copper. The in situ leaching system employed will consist of blasting ore in-place and leaching the broken ore with sulfuric acid under the in situ environment followed by recovery of copper from leach solution by solvent extraction and electrowinning. The leach system and recovery plants are designed to produce 16,000 pounds of copper per day over a 7-year mine life.

The capital and operating costs as shown in Table 5 are taken from the pertinent data provided in previous tables. Table 6 shows the preliminary cash flow analysis for this particular in

TABLE 4

COST COMPARISON (0.66% Cu = 8.0 lbs./ton recovered)
DIRECT OPERATING COSTS PER TON ORE

Unit Operations	Conventional	In Situ
	(strip ratio = 1:1)	
Drilling ⎫		Drilling⎫ $0.35-0.45
Blasting ⎪		Blasting⎭
Hauling ⎬	$0.70-0.90	
Dumping ⎭		
Crushing	0.15-0.30	
Ore Handling	0.10-0.15	
Leaching	0.40-0.50 (with pad)	0.20-0.30
Metal Recovery (SX-EW)	0.56-0.64	0.56-0.64
Supervision and		
Administration	0.35-0.40	0.25-0.30
	------------------	------------------
Total	$2.26-2.89	$1.36-1.69
Cost/lb.	$0.28-0.36	$0.17-0.21

situ leaching operation. As can be seen, the payout time (time
required to pay back the capital expenditure) is about two to
three years with a return on investment of 30 percent. (ROI is
the average compound interest rate at which the expected net
cash flow, discounted to present worth, would return cash outlay
in full.) Obviously, this study indicates an economically
attractive venture.

(2) Bore Hole Mining for Uranium

The in situ mining of lower grade uranium ores has received
increasing attention in recent years due to the favorable price
of uranium in the free market. An in-place extraction technique
of considerable promise is so-called "bore hole" mining in which
the uranium is recovered by drilling into the ore body, circu-
lating a lixiviant fluid to dissolve the mineral, extracting the
uranium values from the pregnant solution, regenerating and re-
cycling the lixiviant. Such a technique is economically and
environmentally attractive in extracting uranium values from
deeper, lower grade reserves.

PARAMETERS

  Ore Reserve
  Grade
  Mine Life
  Estimated Recov
  Daily Productio

CAPITAL COST

  Leaching facili
  SX-EW (with LIX
  Supporting faci
  Cost for proces
  Cost for fractu
  Total capital c

OPERATING COST FO

Capital (3,300,00
Sales (5,760,000

Operating (715,00
Depletion (15% of
Depreciation (str
Local tax and ins
Total operating c

Operating income

Income tax (48%)

Net operating inc
Investment credit
Net Income
Working capital (
Cash flow
Payout time
ROI (discounted t

TABLE 5

PRELIMINARY FEASIBILITY STUDY
IN SITU LEACHING FOR COPPER

PARAMETERS

Ore Reserve	5,000,000 tons
Grade	0.66% Cu
Mine Life	7 years at 715,000 TPY
Estimated Recovery	60% or 8.0 lbs/ton
Daily Production	16,000 lbs.

CAPITAL COST

Leaching facilities	$ 200,000	
SX-EW (with LIX inventory)	3,300,000	
Supporting facilities	100,000	
Cost for processing		$3,600,000
Cost for fracturing (5MM tons at 0.40/T)		2,000,000
Total capital cost		$5,600,000

OPERATING COST FOR PROCESSING	$1.06 per ton

TABLE 6

PRELIMINARY CASH FLOW ANALYSIS
(IN THOUSANDS OF DOLLARS PER YEAR)

Capital (3,300,000 + 2,000,000)	$5,600
Sales (5,760,000 lbs. at $0.60)	3,456
Operating (715,000 at $1.06/ton)	758
Depletion (15% of sales)	518
Depreciation (straight line)	757
Local tax and insurance (5% of capital)	276
Total operating cost	2,309
Operating income	1,147
Income tax (48%)	551
Net operating income	596
Investment credit (10% capital or ½ net income)	298
Net Income	894
Working capital (20% of total operating cost)	462
Cash flow	1,707
Payout time	3.1 years
ROI (discounted to present worth)	30%

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In the evaluation of a uranium-mineralized block as a potential producer by in-place leaching using the bore hole mining technique, it is first necessary to establish a grade-thickness product which will cover development costs and operating costs with something left over for recovery of investment in plant and equipment and for profit. This grade-thickness product is then a cutoff parameter for determining whether another hole is included in reserves or excluded.

Once the holes have been classified as potential ore or waste, the reserves in each potential block can be estimated, for example, by the ore outline method.

Development costs for determination of whether a hole is or is not a potential contributor to ore include:

1. Costs of drilling and casing injection and production wells.
2. Pumps.
3. Surface piping and electrical requirements to bring an ore block into production.

Operating costs in the field include:

1. Operating and repair costs of injection of solvent and of reagents required to convert uranium minerals to soluble form.
2. Operating and repair costs of pumping the pregnant solution from collecting point to the ion exchange plant and costs for recovering the uranium minerals.

Now an injection and production well pattern can be finalized and any necessary adjustments to development costs can be made. The capital cost for the piping to carry the solution from the ore blocks to the ion exchange plant, the capital cost of the ion exchange and precipitation plant, and other ancillary equipment can be estimated.

A cash flow analysis is now made to determine whether the project has satisfactory profit potential. At this stage, it is necessary to be sure that a realistic estimate of the true thickness of strata which will be penetrated by solution has been made. Large amounts of reagents will often be consumed in reactions in sub-ore grade zones above and below the "ore interval." Also, there will often be one or more sub-ore zones within an ore interval which will consume reagents.

TABLE 7
IN SITU URANIUM LEACHING OPERATION

Type of Operation	Bore Hole Mining
Deposit	30 Ft Ore Zone at 400 Ft Depth
Reserves	4,000,000 Ton Deposit at 0.1 Percent U_3O_8
Contained U_3O_8	8,000,000 Pounds
Recoverable U_3O_8	5,600,000 Pounds U_3O_8 at 70 Percent Recovery
Plant Capacity	1,000,000 Pounds U_3O_8 Per Year
	2,750 Pounds Per Day
Production Life	5-6 Years
Type Process	Ion Exchange-Precipitation
Type Leaching	Acid at 100 Pounds H_2SO_4 Per Ton of Ore
Leaching Rate	2,000 GPM
Solution Grade	0.125 gpl U_3O_8
Capital Cost, Leaching	$3,400,000
Capital Cost, IX-PPT	$5,000,000 (IX=$4,000,000; PPT=$1,000,000)
Total Capital Cost	$8,400,000
Operating Cost, Leaching	$3.00 Per Pound U_3O_8
Operating Cost, IX-PPT	$4.00 Per Pound U_3O_8
Total Operating Cost	$7.00 Per Pound U_3O_8

Cut-off Grade Based On:
Operating Cost at $8.00 Per Pound - 0.062 Percent U_3O_8
Operating Cost at $16.00 Per Pound - 0.032 Percent U_3O_8
Operating Cost at $24.00 Per Pound - 0.020 Percent U_3O_8

TABLE 8
IN SITU URANIUM LEACHING ECONOMICS
(Bore Hole Mining IX-PPT)

Cash Flow (In Thousands of Dollars per Year)

	Price of U_3O_8		
	$8/lb	$16/lb	$24/lb
Capital Cost	$ 8,400	$ 8,400	$ 8,400	$ 8,400
Net Sales (at 70% Extraction)	8,000		16,000	24,000
(at 35% Extraction)		8,000		
Costs and Expenses:				
Total Operating	7,000	7,000	7,000	7,000
Depreciation (1)	1,500	1,500	1,500	1,500
Depletion (2)	–	–	3,520	5,280
Indirect Cost (3)	350	350	350	350
Total	8,850	8,850	12,370	14,130
Operating Income	(850)	(850)	3,630	9,870
Income Tax (4)	–	–	1,742	4,738
Net Operating Income	(850)	(850)	1,888	5,132
Investment Credit (5)	–	–	840	840
Net Income	(850)	(850)	2,728	5,972
Cash Flow	650	650	7,748	12,752
Pay-Out in Years	13.0	13.0	1.1	0.7
Return on Investment (6)			86%	117%

Notes: (1) Depreciation – straight-line, 5.6 years
(2) Depletion – Lesser of 22% of net sales or 50% of operating income without depletion
(3) Indirect Cost – 5% of total operating cost
(4) Income Tax – 48%
(5) Investment Credit – 10% of capital cost for the first year, not to exceed 50% of net operating income in one year
(6) Rate of Return Discounted to Present Worth

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Table 7 gives the details of the capital and operating costs for the second case-history involving the feasibility of extracting uranium values from a given sandstone deposit. Table 8 shows the financial analysis for the project under consideration.

As can be noted, the bore hole mining technique appears to be a very attractive method for extracting uranium from lower grade ores. At the old price of $8.00 per pound U_3O_8 the project is not economically favorable. However, at uranium price of over $16.00 per pound, the project appears to be very attractive with ROI in excess of 85 percent.

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24,000

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9,870
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REFERENCES

1. Larson, W.C. and Dandrea D.V., In Situ Leaching Bibliography, Parts 1 and 2, U.S.B.M., February 1976.

2. Sheffer, H.W. and Evans, L.G., Copper Leaching Practices in the Western United States. U.S.B.M. IC 8341, 1968, 57 pp.

3. Rudershausen, C.G., Copper Solution Mining at Old Reliable. Pres. at National Meeting of American Inst. of Chemical Eng., Salt Lake City, Nev., August 18-21, 1974, 11pp.

4. Ward, M.H., Surface Blasting Followed by In Situ Leaching the Big Mike Mine. Proc. Solution Mining Symp., AIME Annual Meeting, Callas, Texas, February 25-27, 1974, 243-251 pp.

5. Fletcher, J.B., In Place Leaching-Miami Mine, Miami, Arizona. Pres. at AIME Centennial Annual Meeting, Soc. of Min. Eng., AIME, New York, N.Y., March 1971, AIME Preprint 71-AS-40; Trans. Soc. of Min. Eng., AIME, V. 250, No. 4, December 1971, 324-337 pp.

6. Crawford, E., Developers Eye Texas Potential for In Situ Uranium Leaching, Eng. and Min. J., V. 176, No. 7, July 1975. 81-82 pp.

7. Shock, D.A., and Conley, F.R., Solution Mining - Its Promise and Its Problems. Proc. Solution Mining Symp., AIME Annual Meeting, Dallas, Texas, February 25-27, 1974, 79-97 pp.

8. Steckley, R.C., Larson, W.C. and Dandrea, D.V., Blasting Tests in a Porphyry Copper Deposit -- In Preparation for In Situ Extraction. U.S.B.M. RI 8070, 1975, 57 pp.

9. Lewis, A.E., Chemical Mining of Primary Copper Ores by Use of Nuclear Technology. Proc. Symp. of Engineering with Nuclear Explosives, Las Vegas, Nev., January 14-16, 1970, Conf. 700101, V. 21, 907-917 pp.

10. Lewis, A.E. "et al.", Nuclear Solution Mining - Breaking and
    Leaching Considerations. Proc. Solution Mining Symp., AIME
    Annual Meeting, Dallas, Texas, February 25-27, 1974 56-75 pp.

11. Heinen, H., and Porter, B., Experimental Leaching of Gold from
    Mine Waste. U.S.B.M. RI 7250, April 1969, 5 pp.

12. Dandrea, D.V. "et al.", A Fragmentation Experiment for In Situ
    Extraction, Proc. Solution Mining Symp., AIME Annual Meeting,
    Dallas, Texas, February 25-27, 1974, 148-161 pp.

13. Dick R.A., In Situ Fragmentation for Solution Mining - A Research
    Need. Pres. at the Second Internat. Symp. on Drilling and Blast-
    ing, Phoenix, Arizona, February 21-16, 1973.; Available for con-
    sultation at U.S.B.M., Twin Cities Mining Research Center,
    Minneapolis, Minnesota.

14. Porter, D.D., Blast Design for In Situ Leaching. Pres. At South-
    west Mineral Industry Conf., Phoenix, Arizona., April 27, 1973,
    7 pp.; Available from E.I. duPont de Nemours and Co., Inc.,
    Wilmington, Del. 19898.

15. Porter, D.D., and Carlevato, H.G. In Situ Leaching: A New
    Blasting Challenge. Proc. Solution Mining Symp., AIME Annual
    Meeting, Dallas, Texas, February 25-27, 1974, 33-43 pp.

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Introduction

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by MILTON H. WARD
Vice President
Ranchers Exploration and Development Corp.

Ranchers selected in situ leaching of a four-million ton copper ore body as an alternative to conventional mining because of the favorable return projected. The deposit offers the possibility of turning to conventional methods if in-place leaching does not proceed as planned

THE NEED FOR additional metal and mineral production will continue its upward spiral as the population and standard of living of the world increase. The scarcity that forecasters predict could become a reality unless technology rises to meet the challenge. Historically, the need begets the solution, and while there is a limit to what technology can accomplish, it is clear that we have not approached all the available possibilities in the mineral industry.

The next few decades should offer mankind an abundant opportunity to apply new thinking and technical capability to fulfill our ever expanding needs. An increasing portion of the requirements for mineral resources will come from an old but little-used method, in situ leaching.

The term "in situ leaching" as used here designates a method for exploiting a mineral deposit that remains in its original position or one which may have been fractured or shattered but otherwise has not been removed from its geological setting. Solution mining, which involves the removal of the valuable mineral without af-

fecting the host rock, involves a number of the same techniques and conditions as in situ leaching. Neither method is new, and the removal of metal by in-place leaching dates from ancient times. Its use in extracting copper from mined-out properties is not uncommon on this continent, but in recent years the technique has been used more often in extracting uranium, undoubtedly because there are more uranium properties available for such treatment.

Advantages of in situ leaching are several

The method will without question be applied more frequently and on a greater variety of metals in the future, since it offers the following advantages:

1) Low capital and operating costs
2) Minimum disturbance of the environment
3) Reduction of development time
4) Preservation of natural resources

Elimination of conventional mining and processing results in a lower capital and operating cost. Steps eliminated or reduced may include mining, transporting, crushing, grinding, waste and tailings disposal, and land reclamation. Benefits gained by eliminating these steps depend on the mineralization of the deposit, its configuration and the processing method used.

Need and cost of protecting the environment have been made all too clear to the mineral industry. This painful experience, caused by external forces, has recently shown a slight change toward reasonableness, but it will continue to plague an industry which now recognizes that environmental standards are on-going concerns. In situ leaching can aid in alleviating this problem in a number of ways, including elimination or reduction of surface disturbance. There is a possibility that ground water in the leach area may be contaminated, but it is more likely that overall water pollution will be reduced. This reduction results from elimination of tailings and spoil seepage.
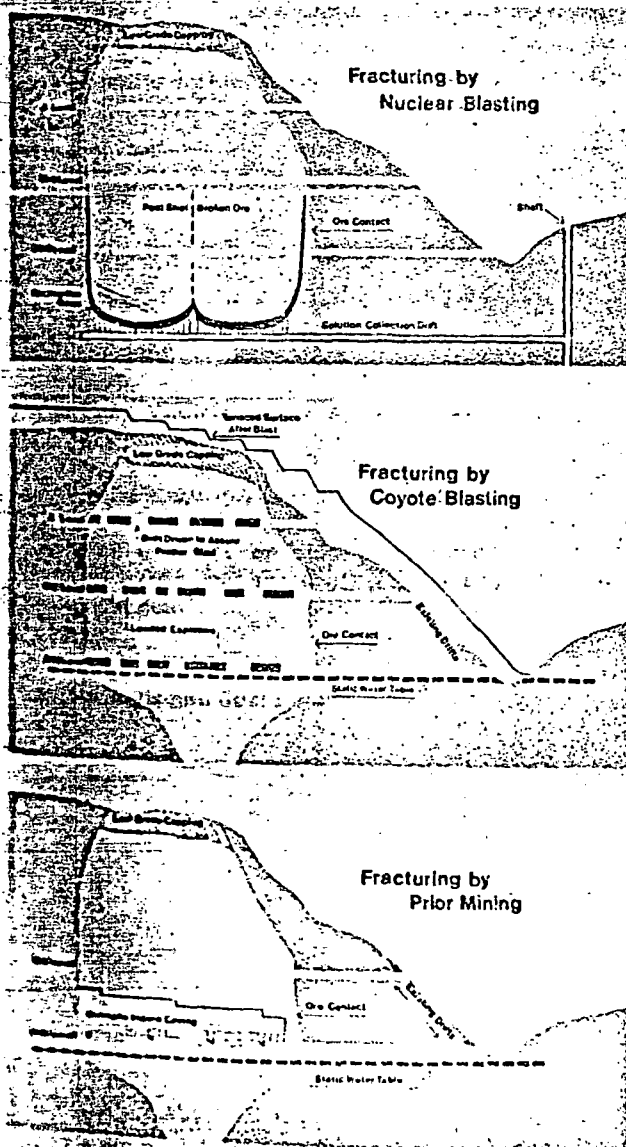
Engineering for In Situ Leaching

Practice can expand mineral reserves

Mineral resources and reserves can be increased and expanded as a direct result of in situ leaching. Low-grade ore and protore may be exploited by this practice, automatically creating additional reserves in an operating area. Stoped-out, caved, and gob-filled stopes can also be leached in place following conventional mining. Mineralized properties that are uneconomical to work by standard methods may be reclassified as ore. Since in situ leaching does not require personal access to the working place, exceptionally deep ore bodies, ore underlying a surface that cannot be disturbed and ore in weak country rock may be exploited.

Factors required for successful production from in situ leaching are:

1) A mineral or metal that can be satisfactorily dissolved when contacted by the leaching solution,

2) A deposit that is naturally permeable or one which can be made permeable so that flow and contact occur,

Fig. 1. Alternative methods for breaking an ore body for in place leaching

Fracturing by Nuclear Blasting

Fracturing by Coyote Blasting

Fracturing by Prior Mining

3) An impervious or nearly impervious barrier that confines or restricts pregnant solutions so that they may be directed to a recovery point,

4) A hydrometallurgical method for extracting the valuable metals from the pregnant solutions.

Metal must be amenable to leaching. Copper and uranium are two metals that are now successfully leached from gangue material. Additionally, sulfur, potash and salt are being recovered by being either dissolved or transported in suspension to the processing plant. While these two methods are different, they have a number of similarities: mineral contacted with a media, dissolved or melted, transported as fluid and recovered in a marketable form.

When considering a particular deposit, the method for extracting the valuable material must be researched and tested to determine the optimal recovery that can be anticipated. Such work can be undertaken using drill core or bulk samples. Metallurgical tests should include column leach tests (drip or flood), roll tests, or small vat tests to determine the extraction, reagent consumption, and characteristics of the pregnant solution.

Permeable deposit. Permeability of the deposit is a necessity since the percolating solutions must contact the ore. Therefore, early in the investigation, porosity and permeability determinations should be undertaken on representative samples. The ore body may be naturally permeable due to the nature of its formation, or fractures may be created artificially. Thus, the deposit may be broken by nuclear or conventional blasting (see fig. 1), caving following previous mining, breakage created by undercutting the ore body and inducing caving, drilling and blasting from surface, and fluid or pressure fracturing of some type.

There has been a great deal of planning and test work on nuclear blasting, but little field application has been undertaken on a commercial ore body. It requires a relatively thick ore body in order to capitalize on the chimney collapse. Several such ore deposits are available and extensive planning was undertaken on Project Sloop, but the actual blast never materialized.

In using explosives to shatter an ore body, consideration must be given to the size and distribution of broken ore following the blast. If the broken material is too fine, there is a possibility of blinding or forming a crust which could disrupt flow of the leach solution. If the ore breaks too large, adequate surface area would not be exposed and recovery would suffer. Additionally, it is more likely that short-circuiting and channeling will occur if the ore breaks coarsely. Size of the broken rock will depend on the characteristics and frequency of natural fractures in the ore area, as well as the rock crushing and shearing strength. Size distribution will not be uniform throughout the ore body because of proximity to the explosion and the amount of confining weight, but this problem can be minimized by proper distribution of the blasting agent.

If possible, a stress response program should be undertaken to aid in designing the blast. Seismic velocity and pressure measurements should be determined during stress wave propagation studies because these characteristics are significant in evaluating potential blast performance. Such a study can indicate whether the

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rock will absorb the energy of the blast rather than transfer fractures.

Solution control. After leaching and permeability requirements are met, the problem of containing the on-flow solutions must be considered. Ideally, the ore body would be enclosed on the sides and bottom by an impervious barrier (fig. 2). Solutions would migrate through the ore body, dissolve the valuable material and flow into a solution-collecting system. Unfortunately, there are few, if any, ore bodies which fit this ideal. It is not too unusual to have an impervious stratum above or below the deposit, but an ideal leach pad is rare. However, it may be possible to create such a pad by injecting cement or chemical grout (fig. 3) to form curtain walls and a floor under the leachable deposit.

A static water table immediately below the ore body (fig. 2) may also act as a barrier, and if one does not exist, it may be possible to create one by injection. The flow and collection of solutions may also be controlled by establishing a negative pressure zone in the collection area. This zone can be created by drilling wells and continually draining the percolating liquors, or by driving a collection drift under the ore body. The pregnant solutions migrate to the sump or drift and are transported to the processing plant.

If an ore body must be shattered prior to leaching, it is possible that a barrier would be formed by the blast itself, as in the case of nuclear blasting where radio-active glass is formed below the detonation point. Conventional blasting may also form a barrier below the lowest point of the explosion by compacting rock directly below the blast.

Project recovery. Methods for extracting the metal in solution will vary depending on the type of metal, the location and size of the deposit, and risk factors involved. Copper may be precipitated to form cement copper, or solvent extraction and electrowinning may be used to produce cathode copper. Recently, extensive design work has been undertaken on portable solvent extraction-electrowinning units, and such modular components will no doubt be used in the future. Portability of these plants allows them to be considered for smaller ore bodies and shorter-term operations. Uranium leaching is currently utilizing a number of ion exchange units, and more will be applied as lower-cost plants are developed.

Feasibility of hydrometallurgical methods is greatly affected by the grade of the collected solutions. In time, the grade of the incoming solution decreases, creating economic and technical problems if the plant was designed for a higher grade of solution. The metallurgist will have to cope with the problem of solution purification, separation in multi-metal solutions, and regeneration of the on-flow solutions. New thinking will be required to apply technology that has been developed in sophisticated chemical and metallurgical plants to the in situ leaching situation.

Ideas applied on Old Reliable project

Many of the ideas presented above have been applied by Ranchers Exploration and Development Corp. at the Old Reliable property. Old Reliable, *located* in the Copper Creek Mining Area of the Galiuro mountains, is about nine miles east of Mammoth, Ariz. (fig. 4).

This project is thought to be the first application of explosives to shatter an entire ore body for in situ leaching. The portion of the deposit considered for leaching contained approximately 4-million tons of 0.80 percent copper with mineralization occurring as chalcocite, chalcopyrite, malachite, chalcanthite and chrysocolla. It occurred in and peripheral to a near-vertical breccia pipe with host rocks being extrusive lavas of Cretaceous
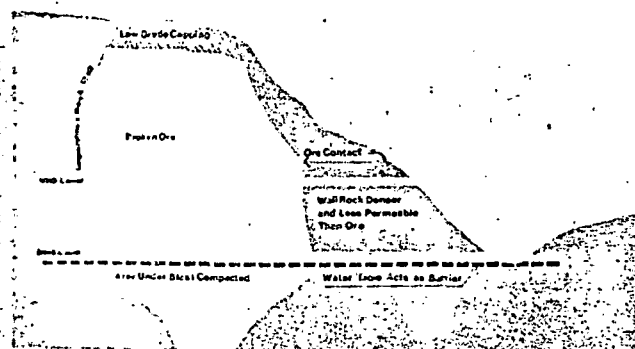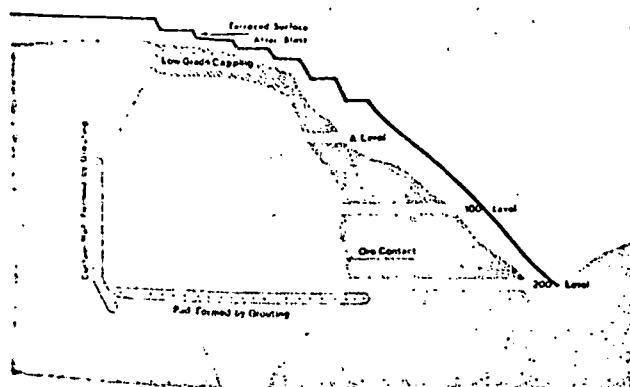

Fig. 2. Solution control barriers. Ideally, the ore body would be enclosed on sides and bottom by an impervious barrier but there are few, if any, ore bodies fitting this deal

Fig. 3. Solution control barrier using grout to form curtain walls and floor under leachable deposit

Fig. 4. Location of Old Reliable property

age. The host material was intruded and mineralized by the Copper Creek granodiorite, which is Laramide in age.

The ore body was exposed by erosion and contained the typical leached cap, oxide copper zone, chalcocite enrichment and chalcopyrite-pyrite zone. The major ore area was almost 400 ft in diameter, and the bulk of the deposit extended from the surface to a depth of about 500 ft. That portion nearest the surface contained less than 0.40 percent copper, but the grade increased with depth, reaching an average of about 2.0 percent in the enriched or supergene zone.

The property had been mined on a limited basis by conventional methods, but was inactive from 1954 until October 1970, when Ranchers leased it from Occidental Minerals Corp. and Siskon Corp. Earlier the deposit had been developed on two levels. These levels were extended and a new level driven about 150 ft below the peak of the mountain by Kop-Ran Development Corp., a Ranchers subsidiary. Both diamond drill and bulk samples were taken from the different levels for metallurgical testing. The metallurgical laboratory at Ranchers' Bluebird mine, Miami, Ariz., along with an independent research laboratory, performed column leach tests on representative samples.

Lab tests gave favorable results in leaching

Results of the tests appeared satisfactory, but since there was a question about how the laboratory tests would compare with actual leaching, an additional comparison was desired. Fortunately, a history of leaching

experience had been accumulated at the Bluebird mine, with numerous comparisons of leach testing to actual practice having been recorded. It was decided to run tests on the Bluebird ore parallel with that of Old Reliable so that comparisons of recovery could be obtained. The results of this study indicated that the Old Reliable ore was amenable to in situ leaching. Both the independent laboratory and the Bluebird metallurgical laboratory had given favorable results.

Permeability and porosity tests were undertaken on the samples to analyze the fracture and flow characteristics of the ore, and it was soon apparent that the ore body would have to be shattered in order 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 discarded, primarily because of the cost of safety and blast monitoring. Use of conventional explosives loaded for coyote blasting was the method selected. The deposit was well suited for a large blast, being remotely located and situated in the side of a hill so that leaching solutions could be drawn off by gravity at the base.

Test blasts made in finalizing blast design

Seismic and sample blast tests were initiated to guide the planning for the blast. It was imperative that damage to surrounding structures and water sources be minimized. Three test blasts, ranging from 100 to 4,000 lb of explosive, were made prior to finalizing the design. It was determined from the tests that no significant struc-

Fig. 5. Blast sequence. Viewers at an observation point three miles away from blast felt only a minor rolling tremor

tural damage would be encountered, and this was the actual case. Skeptics felt that structures a number of miles away would be damaged by ground motion during the blast, but in fact, only a cloud of dust could be seen from Mammoth nine miles away. Viewers at the observation point three miles from the blast felt only a minor rolling tremor. (fig. 5)

The shattered ore appears to be broken at least as well as planned and averages less than 11 in. in size. The bulk of the capping over the ore body was to be thrown off, exposing the low-grade ore, and this was accomplished. The broken ore expanded as anticipated, and control of the blast resulted in a minimum amount of clean-up work and terracing. Approximately 6-1/2 million tons of material was broken, and the fractured zone and resulting surface area is practically identical with that projected.

Explosives placed in 6000 ft of workings

The final blast design developed by E. I. du Pont & Co., which provided engineering and technical assistance for the project, called for four million lb of ammonium nitrate explosives to be loaded throughout 6,000 ft of 6 x 6 ft coyote tunnels on three levels. The 50-lb bags of ammonium nitrate were packed in a predetermined pattern at specified points in the drifts and crosscuts. Millisecond delays were attached, with an instantaneous delay on the top level, followed by 100 ms delays on the middle level and 150 ms delays on the lower level.

The blast was detonated from a firing bunker one

Milton H. Ward has been employed as vice president of operations for Ranchers Exploration and Development Corp. for three years. Before that he worked for Homestake Mining Co. as general manager of Homestake-Sapin Partners from 1966 to 1969. He spent the prior five years with Kerr-McGee Corp., serving successively as mine superintendent, division superintendent, general superintendent and mineral division engineer. Ward worked as a miner and in various engineering and supervisory positions for Magma Copper Co. in the period 1955 to 1960.

mile from the mine. The 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 utilized to reduce the possibility of a misfire.

As the ammonium nitrate was loaded, approximately 80,000 cu ft of sand stemming was blown in place by utilizing a stowing machine and by hand-stacking sacks of sand. Three days prior to blast time, the area was cleared of all livestock and personnel except for the arming crew and others directly involved with the blast. Safety check points were established and security was maintained by ground patrols and helicopter surveillance. In addition to Ranchers and du Pont personnel, the following agencies and companies participated in the blast:

Fig. 6. Blasted area has been terraced in benches about 20 ft high and 15 ft wide. Acid leach solution is distributed over ore body by spraying

- Lawrence Livermore Laboratory—seismic recording
- Sandia Laboratories—air blast measuring
- E. G. & G.—remote photography
- Earth Sciences Laboratory—seismic recording
- J. A. Blume & Associates—seismic and water study
- J. A. Blume & Associates Research Division—seismic recording
- Explosives Excavation Research Division (Corps of Engineers)—seismic recording

The explosives were detonated as scheduled and it appears that the blast was a complete success. Cracks and fractures outside the ore body appear to be at a minimum, and structures and water flow in the area were unaffected. Surface disturbance, as anticipated, was minimal with only an area of 450 to 500 ft in diameter being affected. If conventional open pit mining techniques had been used, an area 10 to 15 times the size of this area would have been disturbed because of pit backsloping and waste and tailings disposal areas.

Unbroken ore more permeable than country rock

Methods for containing and controlling the on-flow solution as it percolates through the shattered ore deserve special attention. Prior to blasting, tests on the country rock surrounding the ore body indicated that the ore was considerably more permeable than the rock. This situation still exists, as an inspection after the blast indicated that the permeability of the broken rock was at least several orders of magnitude greater than the host rock. The density of the perimeter rock was also greater than the ore, and it is anticipated that this rock

will further act as a barrier to any outward flow of solution.

Prior to the blast, holes were drilled immediately below the area to be broken and a static water table was encountered. It appears that the water remained at the same level following the blast. The plan called for introducing leach solutions on the surface and collecting the pregnant liquors in a sump at the toe of the broken ore near the top of the static water table. The static water table is to act as a leach pad and limit the downward flow of pregnant liquors.

Leach solution applied as spray on terraces

The method for extracting copper from pregnant liquors follows standard iron precipitation practice. The blasted area has been *terraced in benches* about 20 ft high and 15 ft wide (see fig. 6). Water required for saturating the ore area is supplied from a 17-1/2-in. diam well drilled on the eastern flank of the San Pedro valley and is pumped through a 6-in. steel pipeline for over six miles. Sulphuric acid is added to the water at the leach plant, and a solution containing one gram per liter H_2SO_4 is prepared in the barren solution pond.

This on-flow solution is gravity-fed to two 200-hp centrifugal pumps, which pump through twin 6-in. plastic lines 2,000 ft to the terraced area. The solution is then distributed through 2 in. plastic pipes connected to rainbirds. The entire surface area of the benches overlying ore is being sprayed.

Pregnant solution will be collected at the toe of the blast and routed by gravity to pregnant storage ponds. A six-cell precipitation plant capable of producing 20,000 lb of cement copper per day has been con-
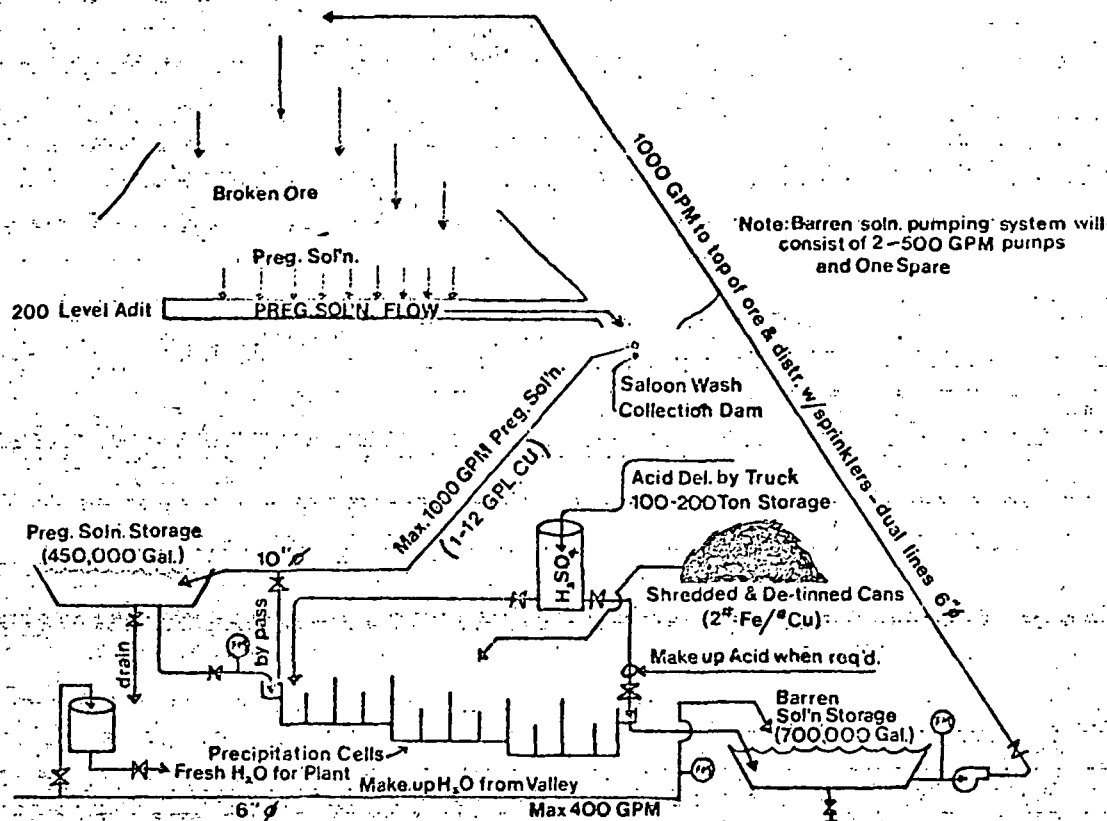
Fig. 7. Old Reliable project flow sheet. Plant is capable of producing 20,000 lb of cement copper daily

structed. Copper in solution will be precipitated on iron, periodically flushed from the cells and spread on concrete pads for drying. Solutions from the precipitation cells will be directed to the barren solution pond where the pH will be adjusted and the solution recirculated to the terraced area (fig. 7).

Risk higher than with conventional mine

The subject method offers a number of advantages and savings but involves more risk than a conventional mine. Some caveats:

1) There is no guarantee that metallurgical results obtained in the laboratory simulate results that will be obtained in practice.

2) Proper fracturing of the ore body is difficult and requires special expertise.

3) The blast must be properly explained to the public so that support for the project can be obtained.

4) Solution control may be a problem because it is extremely difficult to assure that the barriers will be effective and that most solutions will be recovered.

5) Plant solution grade may drop to the point that it cannot sustain a viable operation. Methods for increasing such grades must be developed.

Success of the Old Reliable project is yet to be proven. The amount of copper recovered will depend on factors mentioned earlier; however, it has been forecast that the venture will break even with less than a 15 percent recovery of the metal values. The risk is high, but the potential gain is also high. The following offers a comparison of typical capital costs that might be incurred in a project of this magnitude:

Capital Cost:		
Item	Coyote Blast In Situ Leaching	Open Pit Mining Heap Leaching
Blasting & terracing	$ 950,000	$ -0-
Mining, hauling, heap building*	-0-	6,500,000
Water, power, roads, other utilities	350,000	350,000
Precipitation plant, mobile equipt.	200,000	200,000
Solution collection & storage	100,000	100,000
Total capital**	$ 1,600,000	$ 7,150,000
Estimated recovery	35%	45%
Copper recovery, pounds	22,400,000	28,800,000
Capital cost per pound	S.0715	S.250

*Assume a stripping ratio of 1.25:1, mining contracted.
**Does not include royalties, acquisitions, or property payments.

This particular ore body is situated such that it could have been mined by conventional methods, but the in situ method was selected because of the favorable return that could be projected. Further, the experience gained in this endeavor can be applied to other ore bodies and will offer guidance for future projects. The deposit also offers the possibility of using conventional methods if the results by in-place leaching do not proceed as planned.

Shortly after the blast in March 1972, E. I. du Pont de Nemours purchased an interest of slightly over 20 percent in the project, and it is now functioning as a joint operation with Ranchers acting as manager.

by MILTON H. WARD
Vice President
Ranchers Exploration and Development Corp.

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Elimination of conventional mining and processing results in a lower capital and operating cost. Steps eliminated or reduced may include mining, transporting, crushing, grinding, waste and tailings disposal, and land reclamation. Benefits gained by eliminating these steps depend on the mineralization of the deposit, its configuration and the processing method used.

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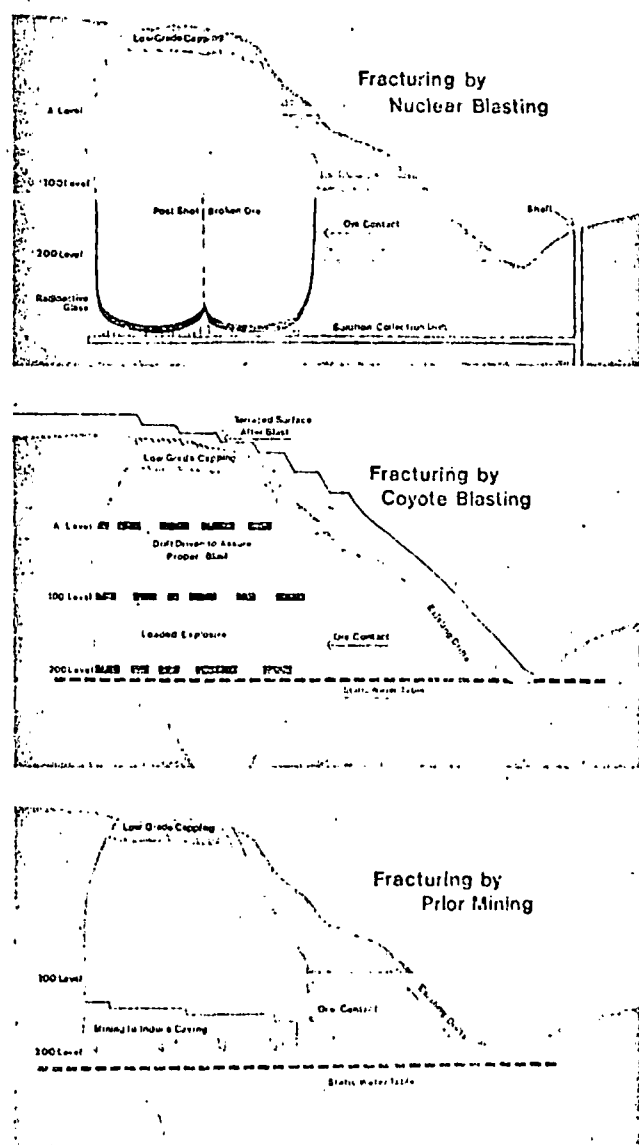
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Factors required for successful production from in situ leaching are:

1) A mineral or metal that can be satisfactorily dissolved when contacted by the leaching solution,
2) A deposit that is naturally permeable or one which can be made permeable so that flow and contact occur,

3) An impervious or nearly impervious barrier that confines or restricts pregnant solutions so that they may be directed to a recovery point,
4) A hydrometallurgical method for extracting the valuable metals from the pregnant solutions.

Metal must be amenable to leaching. Copper and uranium are two metals that are now successfully leached from gangue material. Additionally, sulfur, potash and salt are being recovered by being either dissolved or transported in suspension to the processing plant. While these two methods are different, they have a number of similarities: mineral contacted with a media, dissolved or melted, transported as fluid and recovered in a marketable form.

When considering a particular deposit, the method for extracting the valuable material must be researched and tested to determine the optimal recovery that can be anticipated. Such work can be undertaken using drill core or bulk samples. Metallurgical tests should include column leach tests (drip or flood), roll tests, or small vat tests to determine the extraction, reagent consumption, and characteristics of the pregnant solution.

Permeable deposit. Permeability of the deposit is a necessity since the percolating solutions must contact the ore. Therefore, early in the investigation, porosity and permeability determinations should be undertaken on representative samples. The ore body may be naturally permeable due to the nature of its formation, or fractures may be created artificially. Thus, the deposit may be broken by nuclear or conventional blasting (see fig. 1), caving following previous mining breakage created by undercutting the ore body and inducing caving, drilling and blasting from surface, and fluid or pressure fracturing of some type.

There has been a great deal of planning and test work on nuclear blasting, but little field application has been undertaken on a commercial ore body. It requires a relatively thick ore body in order to capitalize on the chimney collapse. Several such ore deposits are available and extensive planning was undertaken on Project Sloop, but the actual blast never materialized.

In using explosives to shatter an ore body, consideration must be given to the size and distribution of broken ore following the blast. If the broken material is too fine, there is a possibility of blinding or forming a crust which could disrupt flow of the leach solution. If the ore breaks too large, adequate surface area would not be exposed and recovery would suffer. Additionally, it is more likely that short-circuiting and channeling will occur if the ore breaks coarsely. Size of the broken rock will depend on the characteristics and frequency of natural fractures in the ore area, as well as the rock crushing and shearing strength. Size distribution will not be uniform throughout the ore body because of proximity to the explosion and the amount of confining weight, but this problem can be minimized by proper distribution of the blasting agent.

If possible, a stress response program should be undertaken to aid in designing the blast. Seismic velocity and pressure measurements should be determined during stress wave propagation studies because these characteristics are significant in evaluating potential blast performance. Such a study can indicate whether the

Fig. 1. Alternative methods for breaking an ore body for in place leaching

Fracturing by Nuclear Blasting

Fracturing by Coyote Blasting

Fracturing by Prior Mining

rock will absorb the energy of the blast rather than transfer fractures.

Solution control. After leaching and permeability requirements are met, the problem of containing the onflow solutions must be considered. Ideally, the ore body would be enclosed on the sides and bottom by an impervious barrier (fig. 2). Solutions would migrate through the ore body, dissolve the valuable material and flow into a solution-collecting system. Unfortunately, there are few, if any, ore bodies which fit this ideal. It is not too unusual to have an impervious stratum above or below the deposit, but an ideal leach pad is rare. However, it may be possible to create such a pad by injecting cement or chemical grout (fig. 3) to form curtain walls and a floor under the leachable deposit.

A static water table immediately below the ore body (fig. 2) may also act as a barrier, and if one does not exist, it may be possible to create one by injection. The flow and collection of solutions may also be controlled by establishing a negative pressure zone in the collection area. This zone can be created by drilling wells and continually draining the percolating liquors, or by driving a collection drift under the ore body. The pregnant solutions migrate to the sump or drift and are transported to the processing plant.

If an ore body must be shattered prior to leaching, it is possible that a barrier would be formed by the blast itself, as in the case of nuclear blasting where radioactive glass is formed below the detonation point. Conventional blasting may also form a barrier below the
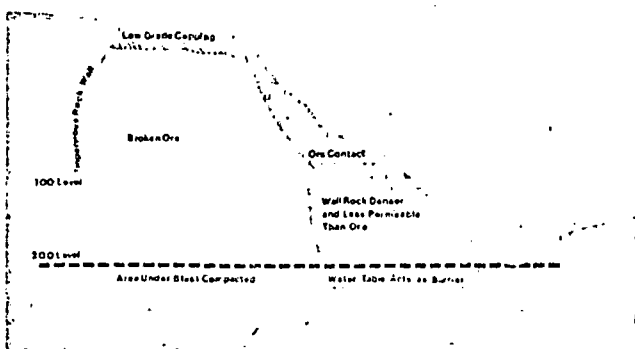

Fig. 2. Solution control barriers. Ideally, the ore body would be enclosed on sides and bottom by an impervious barrier but there are few, if any, ore bodies fitting this deal

Fig. 3. Solution control barrier using grout to form curtain walls and floor under leachable deposit

lowest point of the explosion by compacting rock directly below the blast.

Project recovery. Methods for extracting the metal in solution will vary depending on the type of metal, the location and size of the deposit, and risk factors involved. Copper may be precipitated to form cement copper, or solvent extraction and electrowinning may be used to produce cathode copper. Recently, extensive design work has been undertaken on portable solvent extraction-electrowinning units, and such modular components will no doubt be used in the future. Portability of these plants allows them to be considered for smaller ore bodies and shorter-term operations. Uranium leaching is currently utilizing a number of ion exchange units, and more will be applied as lower-cost plants are developed.

Feasibility of hydrometallurgical methods is greatly affected by the grade of the collected solutions. In time, the grade of the incoming solution decreases, creating economic and technical problems if the plant was designed for a higher grade of solution. The metallurgist will have to cope with the problem of solution purification, separation in multi-metal solutions, and regeneration of the on-flow solutions. New thinking will be required to apply technology that has been developed in sophisticated chemical and metallurgical plants to the in situ leaching situation.

Ideas applied on Old Reliable project

Many of the ideas presented above have been applied by Ranchers Exploration and Development Corp. at the Old Reliable property. Old Reliable, located in the Copper Creek Mining Area of the Galiuro mountains, is about nine miles east of Mammoth, Ariz. (fig. 4).

This project is thought to be the first application of explosives to shatter an entire ore body for in situ leaching. The portion of the deposit considered for leaching contained approximately 4-million tons of 0.80 percent copper with mineralization occurring as chalcocite, chalcopyrite, malachite, chalcanthite and chrysocolla. It occurred in and peripheral to a near-vertical breccia pipe with host rocks being extrusive lavas of Cretaceous

Fig. 4. Location of Old Reliable property

age. The host material was intruded and mineralized by the Copper Creek granodiorite, which is Laramide in age.

The ore body was exposed by erosion and contained the typical leached cap, oxide copper zone, chalcocite enrichment and chalcopyrite-pyrite zone. The major ore area was almost 400 ft in diameter, and the bulk of the deposit extended from the surface to a depth of about 500 ft. That portion nearest the surface contained less than 0.40 percent copper, but the grade increased with depth, reaching an average of about 2.0 percent in the enriched or supergene zone.

The property had been mined on a limited basis by conventional methods, but was inactive from 1954 until October 1970, when Ranchers leased it from Occidental Minerals Corp. and Siskon Corp. Earlier the deposit had been developed on two levels. These levels were extended and a new level driven about 150 ft below the peak of the mountain by Kop-Ran Development Corp., a Ranchers subsidiary. Both diamond drill and bulk samples were taken from the different levels for metallurgical testing. The metallurgical laboratory at Ranchers' Bluebird mine, Miami, Ariz., along with an independent research laboratory, performed column leach tests on representative samples.

Lab tests gave favorable results in leaching

Results of the tests appeared satisfactory, but since there was a question about how the laboratory tests would compare with actual leaching, an additional comparison was desired. Fortunately, a history of leaching experience had been accumulated at the Bluebird mine, with numerous comparisons of leach testing to actual practice having been recorded. It was decided to run tests on the Bluebird ore parallel with that of Old Reliable so that comparisons of recovery could be obtained. The results of this study indicated that the Old Reliable ore was amenable to in situ leaching. Both the independent laboratory and the Bluebird metallurgical laboratory had given favorable results.

Permeability and porosity tests were undertaken on the samples to analyze the fracture and flow characteristics of the ore, and it was soon apparent that the ore body would have to be shattered in order 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 discarded, primarily because of the cost of safety and blast monitoring. Use of conventional explosives loaded for coyote blasting was the method selected. The deposit was well suited for a large blast, being remotely located and situated in the side of a hill so that leaching solutions could be drawn off by gravity at the base.

Test blasts made in finalizing blast design

Seismic and sample blast tests were initiated to guide the planning for the blast. It was imperative that damage to surrounding structures and water sources be minimized. Three test blasts, ranging from 100 to 4,000 lb of explosive, were made prior to finalizing the design. It was determined from the tests that no significant struc-

Fig. 5. Blast sequence. Viewers at an observation point three miles away from blast felt only a minor rolling tremor

tural damage would be encountered, and this was the actual case. Skeptics felt that structures a number of miles away would be damaged by ground motion during the blast, but in fact, only a cloud of dust could be seen from Mammoth nine miles away. Viewers at the observation point three miles from the blast felt only a minor rolling tremor. (fig. 5)

The shattered ore appears to be broken at least as well as planned and averages less than 11 in. in size. The bulk of the capping over the ore body was to be thrown off, exposing the low-grade ore, and this was accomplished. The broken ore expanded as anticipated, and control of the blast resulted in a minimum amount of clean-up work and terracing. Approximately 6-1/2 million tons of material was broken, and the fractured zone and resulting surface area is practically identical with that projected.

Explosives placed in 6000 ft of workings

The final blast design developed by E. I. du Pont & Co., which provided engineering and technical assistance for the project, called for four million lb of ammonium nitrate explosives to be loaded throughout 6,000 ft of 6 x 6 ft coyote tunnels on three levels. The 50-lb bags of ammonium nitrate were packed in a predetermined pattern at specified points in the drifts and crosscuts. Millisecond delays were attached, with an instantaneous delay on the top level, followed by 100 ms delays on the middle level and 150 ms delays on the lower level.

The blast was detonated from a firing bunker one

Milton H. Ward has been employed as vice president of operations for Ranchers Exploration and Development Corp. for three years. Before that he worked for Homestake Mining Co. as general manager of Homestake-Sapin Partners from 1966 to 1969. He spent the prior five years with Kerr-McGee Corp., serving successively as mine superintendent, division superintendent, general superintendent and mineral division engineer. Ward worked as a miner and in various engineering and supervisory positions for Magma Copper Co. in the period 1955 to 1960.

mile from the mine. The 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 utilized to reduce the possibility of a misfire.

As the ammonium nitrate was loaded, approximately 80,000 cu ft of sand stemming was blown in place by utilizing a stowing machine and by hand-stacking sacks of sand. Three days prior to blast time, the area was cleared of all livestock and personnel except for the arming crew and others directly involved with the blast. Safety check points were established and security was maintained by ground patrols and helicopter surveillance. In addition to Ranchers and du Pont personnel, the following agencies and companies participated in the blast:

Fig. 6. Blasted area has been terraced in benches about 20 ft high and 15 ft wide. Acid leach solution is distributed over ore body by spraying

- Lawrence Livermore Laboratory—seismic recording
- Sandia Laboratories—air blast measuring
- E. G. & G.—remote photography
- Earth Sciences Laboratory—seismic recording
- J. A. Blume & Associates—seismic and water study
- J. A. Blume & Associates Research Division—seismic recording
- Explosives Excavation Research Division (Corps of Engineers)—seismic recording

The explosives were detonated as scheduled and it appears that the blast was a complete success. Cracks and fractures outside the ore body appear to be at a minimum, and structures and water flow in the area were unaffected. Surface disturbance, as anticipated, was minimal with only an area of 450 to 500 ft in diameter being affected. If conventional open pit mining techniques had been used, an area 10 to 15 times the size of this area would have been disturbed because of pit backsloping and waste and tailings disposal areas.

Unbroken ore more permeable than country rock

Methods for containing and controlling the on-flow solution as it percolates through the shattered ore deserve special attention. Prior to blasting, tests on the country rock surrounding the ore body indicated that the ore was considerably more permeable than the rock. This situation still exists, as an inspection after the blast indicated that the permeability of the broken rock was at least several orders of magnitude greater than the host rock. The density of the perimeter rock was also greater than the ore, and it is anticipated that this rock

will further act as a barrier to any outward flow of solution.

Prior to the blast, holes were drilled immediately below the area to be broken and a static water table was encountered. It appears that the water remained at the same level following the blast. The plan called for introducing leach solutions on the surface and collecting the pregnant liquors in a sump at the toe of the broken ore near the top of the static water table. The static water table is to act as a leach pad and limit the downward flow of pregnant liquors.

Leach solution applied as spray on terraces

The method for extracting copper from pregnant liquors follows standard iron precipitation practice. The blasted area has been *terraced in benches* about 20 ft high and 15 ft wide (see fig. 6). Water required for saturating the ore area is supplied from a 17-1/2 in. diam well drilled on the eastern flank of the San Pedro valley and is pumped through a 6-in. steel pipeline for over six miles. Sulphuric acid is added to the water at the leach plant, and a solution containing one gram per liter H_2SO_4 is prepared in the barren solution pond.

This on-flow solution is gravity-fed to two 200-hp centrifugal pumps, which pump through twin 6-in. plastic lines 2,000 ft to the terraced area. The solution is then distributed through 2 in. plastic pipes connected to rainbirds. The entire surface area of the benches overlying ore is being sprayed.

Pregnant solution will be collected at the toe of the blast and routed by gravity to pregnant storage ponds. A six-cell precipitation plant capable of producing 20,000 lb of cement copper per day has been con-
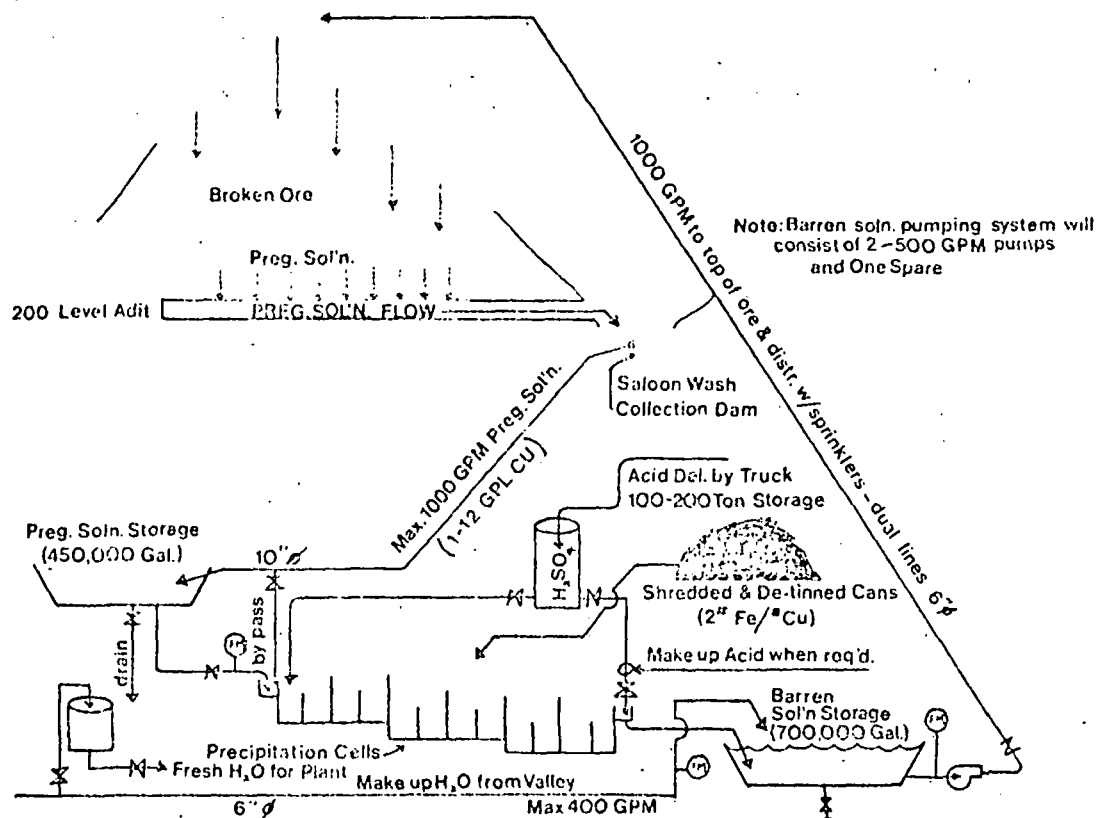
Fig. 7. Old Reliable project flow-sheet. Plant is capable of producing 20,000 lb of cement copper daily

...ructed. Copper in solution will be precipitated on iron, periodically flushed from the cells and spread on concrete pads for drying. Solutions from the precipitation cells will be directed to the barren solution pond where the pH will be adjusted and the solution recirculated to the terraced area (fig. 7).

Risk higher than with conventional mine

The subject method offers a number of advantages and savings but involves more risk than a conventional mine. Some caveats:

1) There is no guarantee that metallurgical results obtained in the laboratory simulate results that will be obtained in practice.
2) Proper fracturing of the ore body is difficult and requires special expertise.
3) The blast must be properly explained to the public so that support for the project can be obtained.
4) Solution control may be a problem because it is extremely difficult to assure that the barriers will be effective and that most solutions will be recovered.
5) Plant solution grade may drop to the point that it cannot sustain a viable operation. Methods for increasing such grades must be developed.

Success of the Old Reliable project is yet to be proven. The amount of copper recovered will depend on factors mentioned earlier; however, it has been forecast that the venture will break even with less than a 15 percent recovery of the metal values. The risk is high, but the potential gain is also high. The following offers a comparison of typical capital costs that might be incurred in a project of this magnitude:

Capital Cost:		
Item	Coyote Blast In Situ Leaching	Open Pit Mining Heap Leaching
Blasting & terracing	$ 950,000	$ -0-
Mining, hauling, heap building*	-0-	6.500,000
Water, power, roads, other utilities	350,000	350,000
Precipitation plant, mobile equipt.	200,000	200,000
Solution collection & storage	100,000	100,000
Total capital**	$ 1,600,000	$ 7,150,000
Estimated recovery	35%	45%
Copper recovery, pounds	22,400,000	28,800,000
Capital cost per pound	S.0715	S.250

*Assume a stripping ratio of 1.25:1, mining contracted.
**Does not include royalties, acquisitions, or property payments.

This particular ore body is situated such that it could have been mined by conventional methods, but the in situ method was selected because of the favorable return that could be projected. Further, the experience gained in this endeavor can be applied to other ore bodies and will offer guidance for future projects. The deposit also offers the possibility of using conventional methods if the results by in-place leaching do not proceed as planned.

Shortly after the blast in March 1972, E. I. du Pont de Nemours purchased an interest of slightly over 20 percent in the project, and it is now functioning as a joint operation with Ranchers acting as manager.

METALLURGY

ALUMINUM, ALUMINA, AND ELECTRODES

EQUATION FOR THE KINETICS OF LEACHING MONOHYDRATE BAUXITES

UDC 669.712.1

L. F. Verbov

Prior research has shown (1) that it is possible to describe the kinetics of leaching monohydrate bauxites with the aid of equations which are correct for those processes occurring with formation of a layer of reaction products inhibiting the reaction rate.

When leaching bauxites with a complex chemical composition, it is unlikely that a nonporous film will form as a consequence of the interaction of the basic bauxite component (aluminum hydroxide) with an alkali-aluminate solution.

An inhibiting film or layer forms as a result of the occurrence -- parallel to the basic process of aluminum hydroxide passage to solution -- of interactions with the solution of macro- and micro-impurities, inevitably present in the natural raw material (Fe, Si, Ti, etc.) (2-4). Further, films containing titanium have the densest structures. There is also the potential of screening the gangue layer, which constitutes over 50% of the starting raw material. This effect is particularly intensive when some time has elapsed after the start of the process, when the aluminum oxide -- found on the open sections of the particles -- has already passed into the solution.

Further, the possibility exists that in some cases a layer of reaction products will form which will dissolve more slowly than the basic component interaction with the solution. For example, when aluminum dissolved in an NaOH solution, at the start of the interaction on the aluminum surface, one finds that a layer of aluminum hydroxide will form on the aluminum surface which will then dissolve -- relatively slowly, but at a constant rate -- in alkali (5).

Thus, the composite relationship between the growth rate for a film or layer of reaction products to the time, which has a direct influence on the leaching rate, is a consequence of the combined effect of many factors. At various stages of the process it is likely that some specific factor will have a more or less dominant effect.

In general, the rate of film growth and the leaching rate, determining the diffusion intensity through a liquid reagent film to the solid particle surface (or of reaction products in the solution) should be in an inverse relationship: the more intensive the film growth the slower the leaching process.

One cannot establish a reliable film thickness with the aid of electron-microscope research (3). In some samples of residues from the leaching of boehmite and diaspore, it is possible to find films which screen the aluminum hydroxide crystals which, according to very approximate evaluations (3), are much less thick than 100 A. Druzhinina (2) has found that films containing titanium compounds are 18 A thick.

Despite the fact that both the composition and the formulas used to calculate film thickness when leaching bauxites are known, the rate of film growth can indirectly be characterized by those process indices most directly affected by the dynamics of film growth. Considering that the heterogeneous leaching process occurs when there is a liquid-phase surplus and that it is limited by the diffusion through a film of varying thicknesses, a change in this thickness can be qualitatively evaluated by the extent of recovery for the basic component. In its turn, extraction is linked with reductions in the linear dimensions of solid particles which take place in time.

If one considers that solid solvent particles are spherical in shape and that an inhibiting film is absent during leaching (or that a porous layer of reaction products form), then when there is a liquid phase surplus with respect to bauxite leaching, the following equation would be correct:

$$A_0^{1/3} - A^{1/3} = \bar{K}\tau \tag{1}$$

where A_0 -- represents the initial weight of the Al_2O_3 in the bauxite; A -- the weight of the Al_2O_3 in the bauxite at a moment in time τ; K -- the constant.

In denoting the reduction in the particle radius in time by y, on the basis of Formula [1], we can write:

$$y = r_0 - r_1 = K''\tau \tag{2}$$

where r_0 -- represents the initial particle radius; r_1 -- the particle radius in a moment of time τ; K'' -- the constant.

On the other hand, reduction of particle radius values in time can be expressed by extraction R:

$$y = r_0[1 - (1 - K)^{1/3}] \qquad [3]$$

Equating the right parts of Equations [2] and [3], we obtain the Roginskii equation (6):

$$1 - (1 - R)^{1/3} = K\tau, \qquad [4]$$

where

$$K = \frac{K''}{r_0}$$

Under actual conditions, the particle forms cannot correspond to a sphere; their surfaces can evidently not only be reduced in time, but can also undergo more complex changes due to the appearance and growth of straight-through openings (7).

The assumptions include the following factors: a) the particles are spherical and have a conditional radius at which their composite surface equals the true active surface of the bauxite; b) changes in the surfaces of these nominal particles with time correspond to the assumed nature of the changes in their radius.

From Fig. 1, it is evident that Equation [4] is correct only at the start of the process, when the diffusion resistance is determined by the resistance at the phase interface; at the same time, the reaction products film is either very small or it is not dense enough to have an inhibiting effect on the process kinetics.

Let us examine a case in which the diffusion resistance of a film is much greater than the diffusion resistance at the phase interface, i.e., the film is non-porous.

Let the film have an inhibiting effect on the process rate as follows, so that:

$$\frac{dy}{d\tau} = \frac{K}{y},$$

after integration, corresponds to:

$$y^2 = 2K\tau$$

where K is the constant.

Replacing the values of y from Formula [3] to Formula [5] leads to the Yander equation (8):

$$[1 - (1 - R)^{1/3}]^2 = K'\tau \qquad [6]$$

where

$$K' = \frac{2K}{r_0^2}$$

For Greek bauxite, at the end of the process the inhibiting effect of the film is greater than is calculated by the Yander equation (Fig. 2). It can be therefore assumed that reductions in the particle radius occur more slowly than is indicated by the parabolic law: $y^2 = 2K\tau$.

Let us assume that changes in "y" with time correspond to the logarithmic law:

$$\frac{dy}{d\tau} = \frac{K}{e^y}.$$

After integration, we get $y = \ln(K\tau)$. $\qquad [7]$

By substituting the value of y from Formula [3] into Formula [7], we obtain

$$\ln\tau - r_0[1 - (1 - R)^{1/3}] = -\ln K. \qquad [8]$$

According to the leaching kinetics in Equation [8], the points plotted at coordinates $[(1 - (1 - R^{1/3})] - \ln\tau$ should lie in a straight line.

A graphic check of Equation [8] (Fig. 3) shows that it corresponds well with the kinetics of the leaching process for the SUBR and the Greek bauxites.

Fig. 2. Leaching kinetics at coordinates of the Yander equation:
1 - SUBR bauxite; 2 - Greek bauxite.
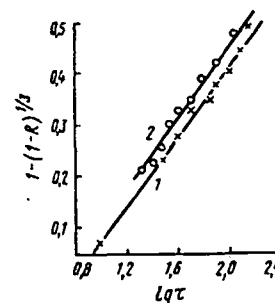
Fig. 3. Leaching kinetics at coordinates of Equation [8]:
1 - SUBR bauxite;
2 - Greek bauxite.

Conclusions

Depending on the duration, the rate of the bauxite-leaching process can correspond to the linear, parabolic, or logarithmic law of decreasing linear dimensions of particles with time. An equation was proposed which more satisfactorily describes the kinetics of the leaching process for monohydrate bauxites.

References

1. N. S. Mal'ts and L. F. Verbov, Tsvetnye Metally, 1972, No. 5, pp. 25-27.
2. N. K. Druzhinina, Alumina Production, Collection No. 39, L., VAMI, 1957, pp. 62-71.
3. V. A. Derevyankin, S. I. Kuznetsov, and O. K. Shabalina, ZhPKh, 1961, vol. 34, No. 7, pp. 1456-1461.

4. M. N. Smirnov, Alumina Production, collection No. 39, L., VAMI, 1957, pp. 1861–1863.
5. A. G. Loshkarev, ZhPKh, 1957, vol. 30, No. 9, pp. 1861–1863.
6. V. V. Blodyrev, Methods of Studying the Kinetics of Thermal Decomposition for Solid
   Substances, Tomsk, Tomsk University, 1958, 332 pp., ill.
7. S. I. Kuznetsov and V. A. Derevyankin, Physical Chemistry of Alumina Production by
   the Bayer Method, M., Metallurgiya, 1964, 352 pp., ill.
8. Fathi Habashi, Chemiker, Ztg. Chem. Apparat., 1969, No. 5, pp. 173–188.

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United States Patent [19]

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[11] 3,902,422

[45] Sept. 2, 1975

SUBJ
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[54] **EXPLOSIVE FRACTURING OF DEEP ROCK**

[75] Inventor: David Linn Coursen, Mercersburg, Pa.

[73] Assignee: E. I. Du Pont de Nemours and Company, Wilmington, Del.

[22] Filed: July 26, 1973

[21] Appl. No.: 382,845

[52] U.S. Cl. 102/23; 299/5; 299/13; 166/63
[51] Int. Cl. F42d 3/04
[58] Field of Search 299/4, 5, 13; 166/63; 102/22, 23

[56] **References Cited**

UNITED STATES PATENTS

2,630,182	3/1953	Klotz, Jr.	166/63
2,630,307	3/1953	Martin	299/4 X
2,952,449	9/1960	Bays	299/4
3,434,757	3/1969	Prats	299/13
3,465,818	9/1969	Dixon	299/13
3,466,094	9/1969	Haworth et al.	299/13
3,650,564	3/1972	Williamson	299/13 X
3,710,718	1/1973	Grant	102/23
3,777,815	12/1973	Boardman et al.	299/13 X

Primary Examiner—Verlin R. Pendegrass

[57] **ABSTRACT**

Producing a fracture network in deep rock, e.g., in an ore body, by detonating explosive charges sequentially in separate cavities therein, the detonations producing a cluster of overlapping fracture zones and each detonation occurring after liquid has entered the fracture zones produced by previous adjacent detonations. High permeability is maintained in an explosively fractured segment of rock by flushing the fractured rock with liquid, i.e., by sweeping liquid through the fracture zones with high-pressure gas, between sequential detonations therein so as to entrain and remove fines therefrom. Ore bodies prepared by the blast/flush process with the blasting carried out in substantially vertical, optionally chambered, drilled shot holes can be leached in situ via a number of holes previously used as injection holes in the flushing procedure and a number of holes which are preserved upper portions of the shot holes used in the detonation process. In the leaching of ore, fines are removed from fractures therein by intermittent or continuous flushing of the ore with lixiviant and high-pressure gas, e.g., air, using, in the case of the in situ leaching of an explosively fractured ore body, a lateral and upward flow of lixiviant from zones that have been less severely, to others that have been most severely, worked by multiple detonations in the ore body.
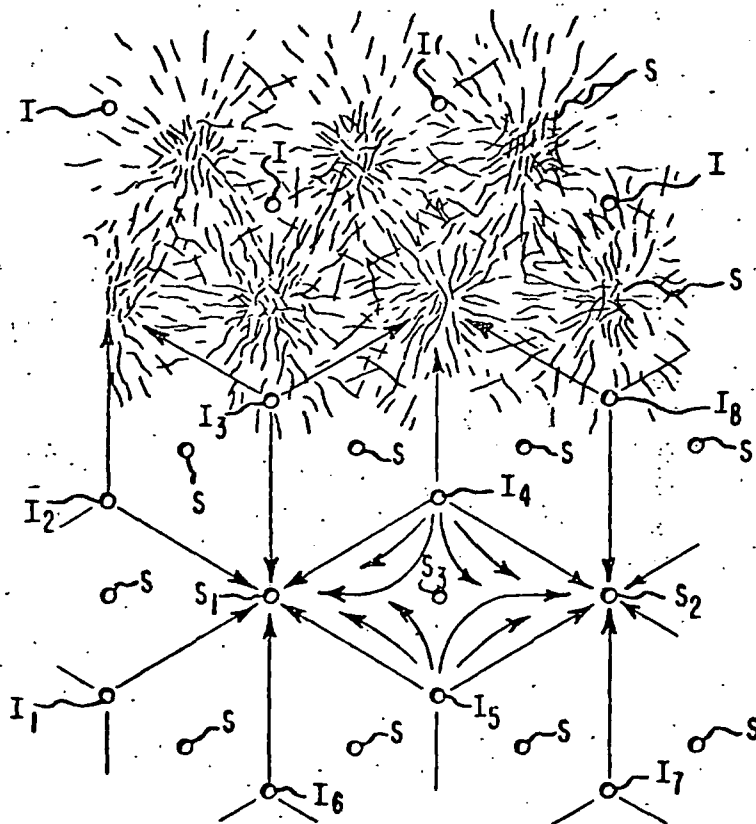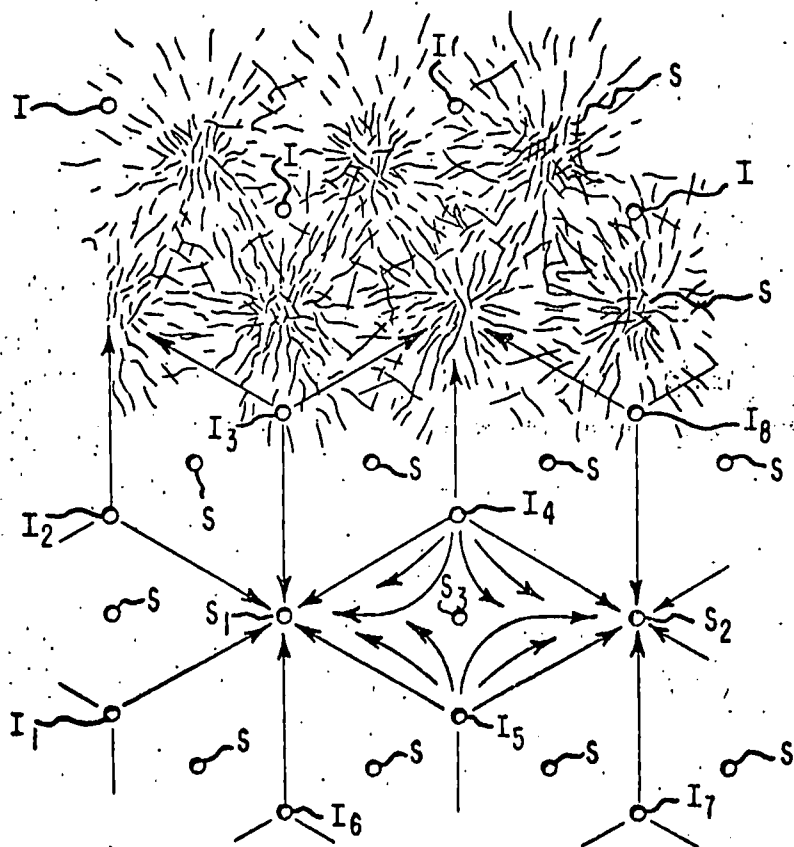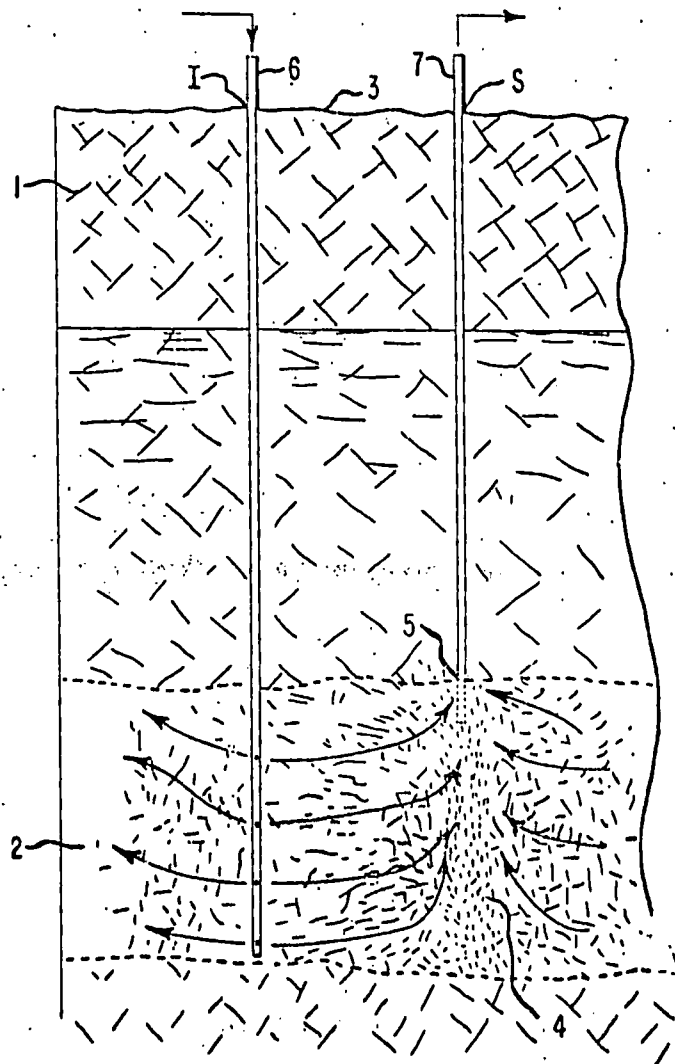
25 Claims, 4 Drawing Figures

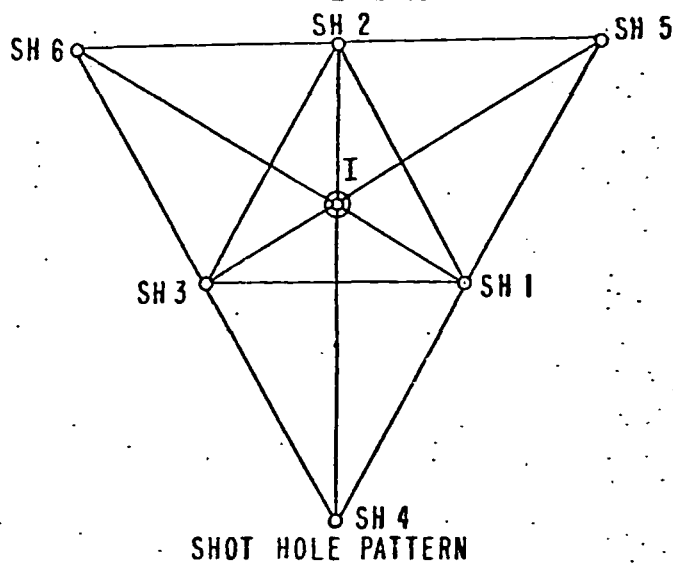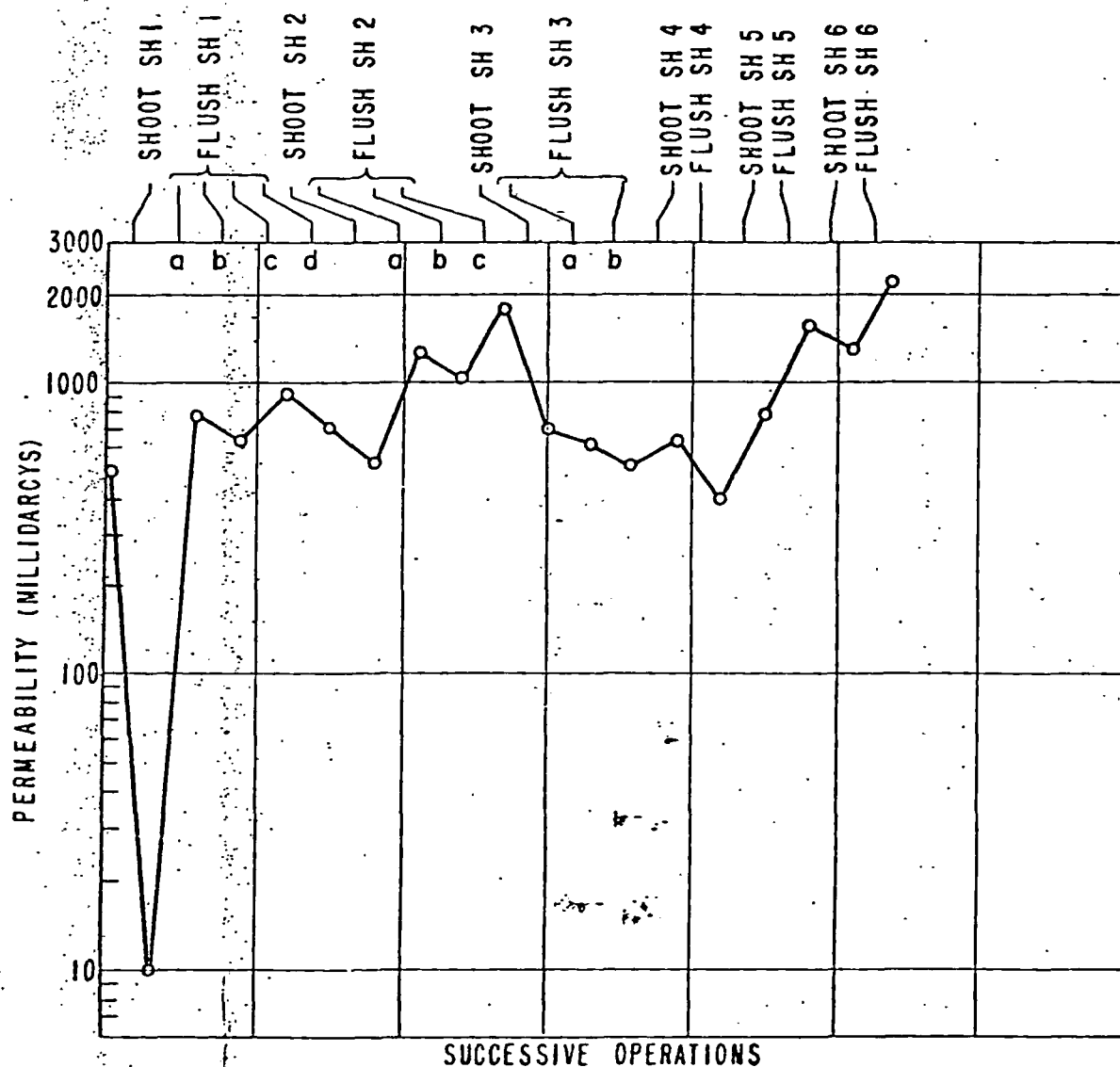# FIG.1

FIG.2

FIG.3

SHOT HOLE PATTERN

FIG.4

1

EXPLOSIVE FRACTURING OF DEEP ROCK

BACKGROUND OF THE INVENTION

The present invention relates to the production of a network of fractures in a deep underground segment of rock by means of explosives, e.g., to prepare deep ore bodies for in situ leaching.

Processes for fracturing deep rock are becoming increasingly important as it becomes necessary to tap deep mineralized rock masses, e.g., ore bodies or oil or gas reservoirs located from about 100 feet to about a few thousand feet beneath the earth's surface, in order to supplement or replace dwindling energy sources and minerals supplies. Numerous deposits of ore, for example ore containing copper, nickel, or silver, lie too deep to mine by openpit methods or are too low in grade to mine by underground methods. Open-pit methods incur both in costs and the environmental impact associated with moving large quantities of earth and rock. Underground methods incur unusually high costs per unit volume of ore mined, as well as difficult safety problems. In contrast, the leaching of ore in place circumvents these difficulties and therefore can be preferred technique for winning values from some ores that are unsuitable, or marginally suitable, for working by traditional mining methods.

Usually however, ore that is favorably situated for leaching in place has such a large fragment size and such low permeability to leach solutions that the leaching rate would be too low to support a commercial leaching operation. In such cases, it becomes necessary to prepare the ore for leaching, by fragmenting it in a manner such as to provide the necessary permeability and leachability. The use of explosives to fracture underground segments of mineralized rock to create areas of high permeability has often been suggested. In an oil- or gas-bearing formation the fracturing is required to increase the overall drainage area exposed to the bore of a well penetrating the formation, and thus increase the rate at which hydrocarbon fluids drain toward the well. In an ore body the fracturing is required to increase the surface area of ore accessible to an injected lixiviant, and thus increase the leachability.

The use of nuclear explosives has been proposed for fracturing large-volume, deep, ore bodies for subsequent in situ leaching. Also, the use of multiple chemical explosive charges in deep reservoir rock has been described in a method for stimulating hydrocarbon-bearing rock, e.g., in U.S. Pat. No. 3,674,089. However, if a deep ore body, i.e., one lying at depths of about from 100 to 3000 feet from the surface, is to be effectively leached in place, and the ore prepared for leaching by blasting, i.e., blasting in the absence of a free face for the ore to swell toward, it becomes necessary to employ special blasting and associated techniques which will provide and maintain the type of fracture network required for efficient leaching.

The leachability of a fractured ore body depends on the size of the ore fragments, and on the permeability of the intact ore as well as of the fracture system separating the fragments. The permeability of the fracture system separating the fragments, which is variable and generally much higher than the permeability of a single fragment, is determined by a network of wider, open fractures (determining the permeability of the ore body as a whole), and a network of narrower, open fractures (determining the irrigability of individual particles to

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be leached). Therefore, in explosively fracturing a segment of an ore body to prepare it properly for in situ leaching, the objective is not simply an indiscriminate reduction in the fragment size of the ore body. Smaller-size, well-irrigated fragments have a higher leaching rate than larger-size fragments, but fragment-size reduction by means of blasting processes heretofore known to the art, when applied to deep ore, tends to leave large unbroken fragments of rock, or to create a network of fractures that are largely closed or plugged with fines. An explosive fracturing process is needed which reduces the larger fragmments to a size that will leach at an economically acceptable rate, and that will result in a network of open fractures throughout the blasted ore that will permit it to be well-irrigated with leach liquid.

SUMMARY OF THE INVENTION

This invention provides a process for producing a fracture network in a deep subsurface segment of rock, e.g., in an ore body, comprising (a) forming an assemblage of cavities, e.g., drill holes or tunnels, in the segment of rock; (b) positioning explosive charges in a plurality of the cavities in the sections thereof located in the segment of rock to be fractured, e.g., in sections of drill holes which have been previously chambered, such as by an explosive springing procedure; (c) providing for the presence of liquid in the segment of rock, e.g., by virtue of the location of the segment of rock below the water table so that water naturally is present in, or flows into, fractures therein, or by introducing liquid into one or more cavities therein; and (d) detonating the charges sequentially in a manner such as to progressively produce a cluster of overlapping fracture zones, the detonation of each charge in the detonation sequence producing a fracture zone which is subject to the cumulative effect of a succession of detonations of explosive charges in a group of adjacent cavities, and the detonation of the charge in each cavity being delayed until liquid is present in fracture zones produced by the previous detonation of charges in cavities adjacent thereto, as determinable by measuring the hydraulic potential, e.g., the liquid level, in the cavity, or in a cavity adjacent thereto.

When the cavities formed are substantially vertical drill holes, some of the holes in the assemblage preferably are left uncharged with explosive, and these holes employed as a set of passageways within the fracture network from the earth's surface, generally to substantially the bottom of the blasted rock, e.g., for the introduction of liquid and/or gas to (or removal thereof from) the fracture network. The uncharged holes preferably are drilled and provided with support casing prior to the detonation of charges in adjacent holes. The sections of substantially vertical shot holes located in the overburden that overlies the rock segment to be fractured preferably survive the blasting process and serve as an additional set of passageways, leading from substantially the top of the blasted rock to the earth's surface, also for liquid and/or gas passage.

In a preferred explosive fracturing process, liquid is driven through the fracture zones produced by the sequential detonation of explosive charges in a plurality of cavities in a segment of rock, in a manner such as to entrain the fines found in the fracture zones, and the fines-laden liquid removed from the rock. This flushing of the blasted rock is achieved by sweeping or driving

liquid at high velocity through the fracture zones by injecting gas into said zones at high pressure, the liquid moving laterally and upwardly through the blasted rock, passing into the fractures, for example, from the passageways formed by uncharged substantially vertical drill holes and out of the fractures into passageways formed by preserved sections of substantially vertical detonated holes located in the overburden. Best results are achieved when substantially each detonation is followed by a flushing step applied to the fracture zone thereby produced, before the next detonation in an adjacent cavity occurs, and this is preferred. In the leaching of a mass of ore, e.g., in the in situ leaching of an explosively fractured ore body or in dump leaching, fines also preferably are flushed out of fractures therein by sweeping the lixiviant therethrough at high velocity by high-pressure gas.

The term "deep" as used herein to describe a subsurface segment of rock denotes a depth at which the detonation causes no significant change in the overlying topography, i.e., the surface does not swell. As a rule, deep rock as described herein lies at a depth of at least 100, and usually not more than 3000, feet. "Fracture zones" and "fractured rock" herein denote zones and rock in which new fractures have been formed, or existing fractures opened up, by the detonations. "Fracturing" denotes herein a treatment which reduces the size of, and/or misaligns, rock fragments.

BRIEF DESCRIPTION OF THE DRAWING

The explosive fracturing process of the invention will be described with reference to the attached drawing in which

FIG. 1 is a schematic representation in plan view of a subsurface segment of rock which has been fragmented by the blast/flush process of the invention, and the liquid circulation pattern between holes therein;

FIG. 2 is a schematic representation in elevation showing the surface-to-surface liquid circulation pattern through the segment of rock shown in FIG. 1;

FIG. 3 is a schematic representation of a shot hole pattern described in the example; and

FIG. 4 is a plot showing the effect of repeated blast/flush operations on the permeability of a fracture zone produced with the shot hole pattern shown in FIG. 3.

DETAILED DESCRIPTION OF THE INVENTION

In the present process, explosive charges are detonated sequentially in separate cavities in a segment of mineralized rock to be fractured, each detonation in the sequence producing a zone of fracture in the rock and being delayed until liquid is present in the fractured rock around the cavity containing the charge to be detonated, especially in fracture zones produced by the previous detonation of charges in cavities adjacent thereto. Thus, the detonations occur while fractures in the surrounding rock are filled with liquid, or the rock is in a flooded, or liquid-soaked, condition. The cavities e.g., drill holes or tunnels, containing the explosive charges are spaced sufficiently close together, and the charges are sufficiently large, that the fracture zones produced by the detonations therein overlap one another. Thus, each fracture zone is within the region of influence of other detonations and is subject to the cumulative effect of a succession of detonations of explosive charges in a group of adjacent cavities. This cumulative effect permits the fragment size-reduction and

disorientation needed to enhance leachability to be obtained readily from the available explosive energy. The degree of overlapping of the fracture zones, which are generally cylindrical in shape, is at least that required to locate all of the rock, in the segment of rock to be fractured, within the fracture zone produced by the detonation of at least one of the charges.

The cavities in the assemblage in which explosive charges are to be detonated (i.e., blast cavities) can be substantially vertical holes (shot or blast holes) drilled into the segment of rock from the surface or from a cavity in the rock, or substantially horizontal cavities such as tunnels, driven in the rock, e.g., from a hillside or shaft. Whether the cavity volume is provided by tunnel driving techniques such as are employed in coyote blasts, for example, or drilling techniques, possibly associated with chambering procedures, will be largely a question of economics, although technical practicability depending on such factors as topography, compressive strength of the rock, etc., will influence the selection of the method. Substantially vertical drill holes are preferred in many cases since the preserved sections of the shot holes can be used subsequently as passageways to or from the fractured rock, reducing the number of holes needed to be drilled solely to provide passageways for liquid injection or ejection.

Although the blast cavities need not form a regular pattern, and regularity of pattern actually may not be desirable or practical, a somewhat regular pattern is indicated in a formation of reasonably uniform contour, structure, and physical strength to assure a high degree of uniformity in the fracture network produced. In some cases, as core tests reveal unpredictable changes in the rock occurring during the sequential blasting process, it may be desirable to deviate from a regular pattern, e.g., to use one or more additional blast cavities where needed to provide the required overlapping of fracture zones. Nevertheless, substantial regularity of pattern generally will be provided in the arrangement of most of the blast cavities. It will be understood, of course, that in the case of substantially vertical drill holes the actual pattern of the holes within the segment of rock to be fractured may approach, rather than match, the hole pattern at the surface, inasmuch as the available drilling equipment may not be counted on to produce parallel holes at depths of the order considered herein.

Regardless of the blast cavity pattern employed, the distance between explosive charges (and, also therefore, between cavities) of a given composition and size is such that a cluster of overlapping fracture zones is produced by the detonation of adjacent charges. Although it may not be possible to delineate the fracture zones with precision, the extent or radius of the fracture zone that can be expected to result from the detonation of an explosive charge of a given composition, density, shape, and size under a given amount of confinement in a given geological mass can be approximated by making some experimental shots and studying the fracture zones surrounding the blast cavities by using one or more geophysical methods. Such methods include (1) coring, (2) measurements in satellite holes of compressional and shear wave propagation, of permeability and of electrical conductivity, and (3) acoustic holography. Based on these studies, the cavities are spaced close enough together to provide the required overlapping of fracture zones.

"Adjacent" blast cavities or explosive charges, as described herein, are blast cavities or explosive charges which, although spaced from one another, are immediate or nearest neighbors to one another, as contrasted to blast cavities or explosive charges which are more distant neighbors or separated from one another by one or more other blast cavities or explosive charges.

Although I do not intend that my invention be limited by theoretical considerations, the delaying of each detonation until liquid is present in the fracture volume surrounding the cavities is believed to have two beneficial effects. First, the liquid can lubricate the fractures so that opposing faces can move suddenly in shear more easily, thereby enhancing fragmentation of the surrounding rock, which is no longer supported by the relatively high resistance of a dry fracture to transient shear. Secondly, liquid-filled fracture volume cannot be rammed shut by the suddenly applied pressure of an explosion. This incompressible behavior, together with the low resistance of the liquid-filled fractures to sudden small displacements in shear, is believed to cause disorientation of individual rock fragments and dilation and swelling of the bed of fragments as a whole. Each detonation creates a misalignment or disarrangement of fragments with an accompanying increase in void volume. Therefore, when the fracture zones produced by the successive detonations in adjacent cavities partially overlap, the fracture zone around each cavity thereby being subject to additional fracturing and/or disorientation produced by the detonations in the adjacent cavities, and previously produced fracture zones are flooded, each fracture zone will be swelled in increments, with each detonation jacking it to larger volume, and higher permeability, against the pressure of the surrounding rock. The present process makes use of the lubricating effect and incompressible behavior of the liquid in the fractures, and does not require the use of high liquid pressures, e.g., of the magnitude needed to lift the overburden and enlarge the fractures before blasting. A liquid pressure in the fractures at the time of blasting equal to the head of liquid above the blast zone is sufficient. Also, any readily available, relatively cheap liquid, e.g., water or water mixtures, can be used to flood the rock. If leaching of ore is performed in the course of the detonation sequence, a lixiviant can be used as the flooding liquid. For reasons of economy as well as because of the safety risks associated with the use of explosives which are sensitive enough to detonate in extremely small diameters, the use of explosive liquids in the fracture zones is not contemplated. Any fluid explosive which may be used in the present process will be gelled to a viscosity that will hinder any appreciable loss thereof from the blast cavities to the surrounding fracture zones, and in any case will not be sufficiently sensitive to be detonated in said zones. Thus, while small amounts of the explosive charges may escape into the fracture zones, such material will behave as a non-explosive liquid therein. Accordingly, the flooding liquid is non-explosive.

A preferred blast cavity pattern for use in the present process is one in which substantially all of the internal cavities, i.e., cavities not located at the edge of the pattern, are surrounded by at least four adjacent blast cavities, e.g., a pattern in which the blast cavities are at the corners of adjacent polygons, which are either quadrangles or triangles and which are as close to equilat-

eral as permitted by wander of the cavities, as shown in FIG. 1.

Although all of the blast holes in a group of adjacent substantially vertical drill holes can be drilled prior to the sequential detonation of the charges, this procedure is not preferred inasmuch as it could be necessary to apply a support casing to the as-yet undetonated holes in the sections thereof located in the segment of rock to be fractured to prevent them from collapsing as a result of detonations in adjacent holes. Casing of the shot holes in these sections usually would be considered economically unsound because the casing would occupy volume that could otherwise be loaded with explosive and because casing in these sections of the holes is not needed in subsequent leaching operations. Therefore, it is preferred that in a group of adjacent drilled shot holes the detonation of each charge takes place before adjacent shot holes are drilled. In practice, one might drill and, if desired, chamber (as described later), one shot hole of a group of adjacent holes, load the hole or chamber with explosive, allow water to enter the formation surrounding the hole or chamber, and detonate the charge, and then repeat the sequence of steps with adjacent holes. In each successive sequence of steps, the entrance of water into the formation can occur prior to, or during, any of the other steps, however. The avoidance of the presence of drilled shot holes during detonations refers to holes in a group of adjacent holes, e.g., a central hole and four to six surrounding holes. However, shot holes farther removed from the detonations can be pre-drilled.

The total amount of drilling needed for vertical-cavity blasting can be reduced by drilling one or more branch or off-set holes by side-tracking from one or more points in the preserved upper portion of a trunk hole which extends to the surface. Each off-set hole is drilled after the charges in the trunk hole and other off-set holes thereof have been detonated. Such holes will be inclined at small angles to one another.

Most of the ore bodies and other mineralized formations to which the present process is expected to be primarily applicable will be located below the water table, and in such a case, unless the section to be blasted rises locally above the water table, or the rock surrounding this section is so impermeable that flooding of the fracture zone does not occur by natural flow, the section will be naturally flooded, or water-soaked, before the sequential blasting begins, and after a certain period of time has elapsed after each detonation to allow the water to flow naturally into the newly formed fractures. If natural flooding is incomplete or absent, water or some other liquid can be pumped into the cavity to be shot after the explosive charge has been emplaced therein, and also into any available nearby uncharged cavities, at a sufficiently high flow rate to cause the rock to be blasted to be in a flooded condition at the time of detonation.

As stated previously, liquid is present in the rock around each cavity prior to the detonation of the charge therein. This means that liquid is present in any pre-existent fractures in the zone which will become a fracture zone as a result of the detonation of the charge in that cavity, and in fractures produced by previous detonations in cavities adjacent thereto. This condition permits the above-described incremental swelling of overlapping fracture zones to take place. In the case of substantially vertical drill holes, the liquid level in the

rock around the hole should be at least as high as the top of the charge in the hole, thereby assuring the presence of liquid throughout the height of the formation where fracturing will occur. With horizontal cavities, the liquid level in the rock around the cavity should be at least as high as the radius of fracture to be produced by the detonation of the charge therein. When the segment of rock to be fractured is located below the water table, the position of the water table above it will conform to the water levels in undisturbed holes, and may be inferred at other locations by interpolation between the elevations of the water levels in undisturbed holes. As a practical matter, the water table will almost always be sufficiently horizontal that the first charge can be detonated when the elevation of the liquid level in any nearby hole is at least as high as the elevation to be reached by the top of the charge (or radius of fracture in the horizontal cavity case). If the liquid level is measured in the cavity in which the charge is to be detonated, the level before loading of the explosive into the cavity should be the level measured. After the detonation, the liquid level in cavities within the resulting fracture zone drops in proportion to the new fracture volume produced, the expulsion of liquid from the immediate vicinity of the charge by the gaseous products of detonation, and the drainage of liquid into the cavity created by the detonation. The detonation of the next charge in the sequence in a cavity adjacent to the first is delayed until the liquid in the formation around the next cavity (including the new fracture volume produced by the previous detonation in an adjacent cavity) returns to its required level. It is understood, however, that explosive charges in blast cavities elsewhere in a section of the formation that is not strongly influenced by a previous detonation (i.e., where the liquid level has not dropped below the required elevation as a result of the previous detonation) can be detonated at any time after the previous detonation. The delay to allow flooding applies to detonations in cavities which are adjacent to previously detonated cavities, where the previously formed fracture zones will be subject to the effect of the next detonation.

As was stated previously, some of the holes in an assemblage of substantially vertical holes preferably are left uncharged with explosive, these holes providing passageways to the fractured rock to allow the introduction of gases and/or liquids thereto, e.g., in a subsequent leaching operation. These holes, which can thus be looked upon as injection holes (although they may serve as ejection or recovery holes depending on the required flow pattern), are also useful in preparing the ore body for leaching, as will be described more fully hereinafter, and it is preferred, on the basis of ease of drilling, that they be drilled prior to the sequential detonation process in holes surrounding them. Pre-drilled injection holes are provided with a support casing, e.g., unperforated pipe grouted to the upper part of the hole wall, at least in the section thereof located in the segment of rock to be fractured, and ungrouted perforated pipe or a wellscreen in the bottom section of the hole, in order to prevent hole collapse as a result of the detonations. Inasmuch as full-length casing will be required for subsequent leaching operations, however, the full length of the injection holes usually will be cased prior to blasting. Damage to the injection piping is minimized in the present blasting process owing to the sequential, long-delay character of the multiple detonations.

The location and pattern of the injection holes are selected on the basis of their intended function during the fracturing and leaching processes, which will be described in detail hereinafter. The overall purpose of these holes usually is to provide a means for introducing gases and/or liquids into the fracture network produced, or being produced, and therefore the injection holes should be distributed throughout the segment of rock among the blast cavities in a manner such that they lie within the fracture zones produced by the detonations. After the detonation of the charge in a substantially vertical shot hole, the resulting fracture zone permits communication between a neighboring injection hole and the portion of the shot hole remaining in the overburden. The shot hole remnants thereby act as passageways to complete the liquid circuit through the fractured rock.

If injection holes are present in the formation during the sequential detonation process, an injection hole lying within the fracture zone produced by a previous detonation in a cavity adjacent to a cavity to be shot can be employed to determine whether the liquid level in the rock surrounding the cavity to be shot has recovered sufficiently to flood the section to be blasted. Whenever an hydraulic potential (e.g., a liquid level) measurement is required after a blast cavity has been loaded with explosive, a nearby injection hole can be used. When the segment of rock to be blasted is at least partly above the water table, liquid is introduced into the rock in the cavity to be shot, in previously detonated cavities adjacent thereto, and/or in nearby injection holes. Flooding via multiple cavities is preferred. Liquid is run into a blast cavity after the explosive charge has been emplaced therein (if the charge is stable in the presence of water), and liquid level measurements, if required, are made in nearby injection holes. It should be understood that, in practice, hydraulic potential measurements, e.g., pressure measurements made with a piezometer, or liquid level measurements, will not be required after each detonation, inasmuch as the experience gained in determining the necessary delay times to permit recovery of hydraulic potential between a few of the early detonations in the sequence will usually allow the practitioner to select with confidence suitable delay times to be used between subsequent detonations

Although the exact delay required depends on the size of each blast, the void volume to be filled, the elevation of the segment to be blasted relative to the water table, and the hydraulic transmissibility of the surrounding rock, delays on the order of hours or days generally will be needed. As a practical matter, the time required for a shot hole to be drilled, or a tunnel to be driven, and loaded with explosive usually will be more than sufficient for the hydraulic potential around the cavity and the previously detonated adjacent cavities to recover to the minimum required level either by natural influx of water from the surrounding rock or by introduction through cavities made in the formation. In general, delay times between detonations of at least about 1 hour, and typically in the range of about from 4 to 24 hours, are sufficient for flooding to take place, although much longer delays, e.g., in the range of about from 4 to 30 days, may be employed in order to prepare the next blast cavity for blasting. It will be understood that these delays refer to the time between detonations of adjacent charges, and that one or more charges

whose zones of fracture are non-adjacent (i.e., whose regions of influence are mutually exclusive) can be detonated at much shorter delay times or even simultaneously.

I have found that when sequential blasting is carried out in less competent, broken, or clayey rock, the permeability of the rock may be decreased, although the fracture volume is increased, by the blasting. Lost permeability can be restored by flushing of the fractured rock, i.e., by sweeping or driving liquid through the fractures at high velocity and removing the fines-laden liquid from the rock, preferably after each detonation. The flushing procedure appears to remove from the fractures the clogging fines that prevent free irrigation around the rock fragments. Such fines are present in the form of existing clays and rock crushed or abraded during blasting.

The flushing can be accomplished by the pressure injection of liquid and gas into the fractured rock through one or more injection holes, and removal of the fines-laden liquid from the fractured rock by bringing it to the surface through one or more detonated shot holes, in the preserved sections of the latter which pass through the overburden to the surface. Liquid and gas, e.g., water or other aqueous liquid and air or oxygen, can both be injected; or gas alone can be injected so as to sweep ahead the liquid already present in the fractures. Alternatively, a liquefied gas, such as air, nitrogen, oxygen, can be introduced into the injection holes and allowed to vaporize therein and thereafter drive the liquid through the fractures. Inasmuch as there is a two-phase flow in a generally upward direction and laterally in the direction of the detonated shot holes, the circulation of the liquid is powered by gas lift such that the gas chases the liquid upward and outward through the broken formation, and fines are driven toward the zones of severest fracture, where their concentration is heaviest, from which zones they are ejected with the liquid. This direction of sweep is preferred inasmuch as the reverse direction drives the fines more deeply into the less severely worked zones of the formation away from their point of heaviest concentration and can cause an intensified clogging of the fractures. The surging high-velocity flow which develops with the upward two-phase flushing system removes fines that prevent free irrigation around the fragments. If necessary to achieve the required lateral circulation of liquid between injection hole and ejection hole throughout the length of the fracture zones being flushed, two or more vertically separated injection zones in a given injection hole can be employed, one substantially at the bottom of the fractured rock and one or more others above it.

The buoyancy of the pressurized gas alone can be sufficient to raise the fines-laden liquid to the surface of the ground when the water table is relatively close to the surface. When the water table is so deep that the buoyancy is insufficient, the liquid can be pumped up the collar of the shot hole.

At the start of flushing, the gas injection pressure should be higher than the ambient hydrostatic pressure at the position in the injection hole where injection occurs, and preferably higher than the lithostatic pressure at this position. The minimum gas pressure required for flushing is highest at the start of the operation and falls as gas injection proceeds.

Although there can be much variation in the number of fracture zones being flushed out at any given time,

and the nature and number of other operations which can be performed during flushing, it is preferred that a detonation in any given cavity be followed by detonations in no more than two or three adjacent cavities, and most preferably by a detonation in no adjacent cavity, before the fracture zone produced by the detonation in the given cavity has been flushed out as described. In some formations, if a given fracture zone is subjected to a number of subsequent detonations without the intervention of flushing, restoration of permeability by a later flushing becomes difficult because the fractures may have become plugged up too tightly with fines. Therefore, a cyclic blast/flush/blast/flush, etc. process is preferred. One or more fracture zones can be flushed at the same time, and flushing of the same zone can be repeated, if desired. An already flushed zone can be left untreated during the flushing of adjacent zones by plugging the ejection hole in that zone. Flushing of one or more zones can be carried out while adjacent blast cavities are being drilled and loaded.

In the present process, the detonation of the charges in sequence permits the preservation of the sections of substantially vertical shot holes that pass through the overburden (the strata overlying the rock segment being worked), and these sections of the shot holes can serve as ejection holes in the flushing process, as described above. The reduced fragment size and unclogged fracture network achieved after all of the charges have been detonated, and the detonations followed by a flushing procedure, produce, in the case of an ore body, an ore which is well-prepared for in situ leaching.

The present invention also provides a leaching process wherein fines are flushed out of a mass of ore by driving lixiviant through the mass by means of high-pressure gas, e.g., in a specific circulation pattern. According to one embodiment of the present leaching process, an ore body which has been prepared for leaching by detonating explosive charges in separate cavities therein, e.g., according to a process of this invention, is leached in situ by introducing lixiviant for the ore into the prepared ore body through a plurality of injection holes therein and intermittently or continuously driving the lixiviant through the ore body to a plurality of recovery holes by means of high-pressure oxidizing gas, the lixiviant moving laterally and upwardly from zones that have been less severely worked, to others that have been most severely worked, by the detonations, whereby fines are removed from the ore body. When the ore body has been prepared for leaching by means of the above-described blast/flush process the lixiviant for the ore can be injected into the ore body through injection holes which have previously been used in the flushing steps, and fines-laden pregnant leach solution recovered from the ore body through the preserved upper portions of shot holes, piping having been grouted into all holes used to circulate lixiviants and pumps provided as necessary to inject lixiviants in one set of holes and remove pregnant liquor from another set of holes. The bottom ends of the pipes and any other positions along the pipes where lixiviants are to be injected or collected are provided with perforations or wellscreens.

The lixiviant (e.g., sulfuric acid/water or sulfuric acid/nitric acid/water for ores whose acid consumption is within tolerable levels, or NH_4OH/water for ores having a high acid consumption), which is a liquid, and a

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gas, usually an oxidizing gas, preferably oxygen, air, NO$_x$, or mixtures thereof, are injected into the base of the prepared ore body at high pressure. As in the case of flushing between blasts, this type of injection gives a circulation powered by gas lift such that the gas chases the liquid through the broken rock. Even with constant flow rates of gas and liquid at the injection holes, a surging, high-velocity flow develops in the rock which is believed to be beneficial in (1) removing fines around the ore fragments (such fines being created during the leaching process in forms as decrepitated ore slimes and precipitated iron salts), (2) increasing the leaching rate as a result of the cyclic squeezing of the ore fragments from the pressure fluctuations associated with the surging flow, and (3) working the ore gently so as to collapse wide openings among the fragments that may develop during the leaching process and can cause channelling of leaching solution. Sweeping the lixiviant laterally toward collection points in the more severely worked fracture regions of the ore body, and from injection points in the less severely worked regions reduces the chances that a more intense clogging of the ore body with fines will occur.

The circulation pattern employed in the leaching process as well as in the flushing steps of the fracturing process may be understood more clearly by reference to the accompanying drawing. In FIG. 1, the holes designated by the letter S are substantially vertical shot holes. Within the blasted segment of rock, these holes are destroyed by the detonations which have taken place therein in the fracturing process and are replaced by the adjacent, overlapping fracture zones shown in the upper half of the figure, and also denoted by the letter S, to indicate a previous shot hole. The shot holes rather than the fracture zones are shown in the lower half of the figure so that liquid circulation lines can be indicated clearly. It should be understood, however, that upon completion of the entire blast sequence all shot holes are surrounded by fracture zones (as depicted in the upper half of the figure) in the sections thereof located in the rock segment that was blasted. In the sections overlying the blasted segment, the shot holes remain substantially intact and in these sections all shot holes appear as they are shown in the lower half of the figure. The preserved upper sections of the shot holes are ejection holes in the flushing steps of the blasting process, and recovery holes in the leaching process. In the hole arrangement illustrated in FIG. 1, the shot holes are arranged in a trigonal pattern wherein lines between adjacent holes form substantially equilateral triangles.

The holes designated I are injection holes. These holes are uniformly distributed among the shot holes as shown. The arrows indicate the direction of flow of liquid from injection holes I$_1$, I$_2$, I$_3$, I$_4$, I$_5$ and I$_6$ to the preserved upper section of shot hole S$_1$; and from injection holes I$_4$, I$_5$, I$_7$, I$_u$, and two other undepicted injection holes to the preserved upper section of shot hole S$_2$. The preserved upper section of shot hole S$_3$ is plugged off while shot holes S$_1$ and S$_2$ are being used for flushing or as recovery holes for pregnant leach solution. At the same time, liquid injected into these injection holes is being driven to other open shot holes.

In FIG. 2, piping in injection hole I and shot hole S is shown as it passes through overburden I to the fractured rock segment 2. Piping 6 in injection hole I leads from the earth's surface 3 to substantially the bottom

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of rock segment 2. Piping 7 in shot hole S leads from the earth's surface 3 to the top of rock segment 2. Fracture zone 4 has been produced by the detonation of an explosive charge in shot hole S, which before the detonation led to substantially the bottom of rock segment 2. Piping 7 terminates in well screen 5, and piping 6 is provided with perforations vertically spaced along the length thereof located in rock segment 2. In the flushing steps of the fracturing process, and in the leaching process, liquid is injected into fractured rock segment 2 through the perforations in piping 6, then is driven by pressurized gas through the fractured rock as indicated by the arrows, and leaves the top of the rock segment through piping 7. Lateral as well as upward flow occurs from the less severely worked zone around hole I to the most severely worked zone, i.e., fracture zone 4.

Regulation of the rate at which gas and liquid lixiviant are injected and collected at the various injection and collection holes allows a high degree of control of the in situ leaching process. By the operation of control valves, the injection and collection pressures can be regulated to obtain a relatively uniform flow through the ore body in spite of variations in permeability from place to place. Shifting the injection or collection from one set of holes to another will change the direction of flow through the ore and can be used to frustrate channelling. The regulation of pressures and flow rates at the various holes can be used to maintain a net flow of ground water toward the operation under conditions that might otherwise result in the escape of leach solution. Leakage of the leach solution is also reduced in the present process as a result of the carriage of some of the fines away from the area of gas agitation where they settle out and plug the leak. In leaching, the gas-liquid pressure injection can be intermittent or continuous, depending upon the degree to which the ore tends to plug up, and the frequency with which flow patterns are changed to obtain uniform and complete leaching throughout the ore.

When lixiviant is introduced into an injection hole simultaneously with gas, its injection pressure should be equal to that of the gas, i.e., higher than the ambient hydrostatic pressure at the injection point, and preferably higher than the lithostatic pressure at this point. In some cases, especially at greater depths, the injection of lixiviant and oxidizing gas at sufficient pressure to exceed the lithostatic pressure may be necessary in order to get sufficient flow rate through the ore. If, in some or all of the injection holes, there are periods of time when lixiviant alone is introduced into the ore, this introduction preferably is done at a pressure at least as high as the lithostatic pressure at the injection position. That is, the pumping pressure preferably is at least as high as the lithostatic pressure minus the heads of fluid in the piping leading from the pump to the injection position.

According to the present invention, permeability can be increased also in ore masses such as mine waste dumps by driving lixiviant through fractures therein by means of gas at sufficiently high pressure that the lixiviant is swept through at a rate sufficiently high to entrain fines present in the fractures, and removing the fines-laden lixiviant from the ore mass.

In a preferred embodiment of the present process, the sections of substantially vertical shot holes which are located in the segment of rock to be fractured are first chambered to larger diameter, and the explosive

charges positioned in the chambered portions. In this procedure, drilling costs are reduced by drilling widely spaced-apart   t holes of smaller diameter than is required to accommodate the size of explosive charges to be employed, and enlarging or "springing" the lower parts of the shot holes to produce chambers having the volume required to hold the explosive charge. The sections of the holes in the rock segment are chambered either by drilling them out, e.g., with an expansion bit, or by detonating explosive charges therein. The chambering method is not critical, the preferred method generally being the one that results in the lowest overall cost per unit of chamber volume for the particular rock segment in question. In the present process, explosive charges used for springing may be 20 feet or more in length. If rock fragments tend to fall from the walls of an explosively sprung hole and thus to occupy some of the volume required for the explosive charge subsequently to be used in producing the fracture zone, the hole to be sprung can be drilled deeper so that the bottom of the hole is located below the bottom of the formation. In this manner, any loss in volume that is to be available for explosive loading is minimized since a portion of the chamber volume below the segment of rock to be fractured can hole the fallen rock fragments.

The advantage of chambering the shot holes before loading them with the charges which will be detonated to produce the fracture network becomes evident when it is considered that an explosively sprung hole typically will hold about ten times as much explosive as an unsprung hole. Thus, for example, a pattern of 30-inch-diameter charges on 100-foot spacings (center-to-center) typically can be achieved by drilling 9-inch-diameter holes on 100-foot spacings.

Although the blast/flush process has utility in deep underground blasting with explosives of all types, the use of chemical explosive charges is much preferred for several reasons. The many technical as well as civil (legal, political, public relations) problems associated with the undertaking of nuclear blasting are self-evident. Vibration effects and radioactivity are the two major roots of these problems. A nuclear blast which is large enough to be economically feasible must be set off at sufficient depth, e.g., preferably appreciably deeper than 1000 feet, in order to be safely contained and not release radioactivity to the atmosphere. Many potentially workable ore bodies will not be located as deep as the safe containment depth. Furthermore, the extreme magnitude and concentration of the energy produced in a nuclear blast imply that it will be difficult, if not impossible, to achieve (a) a high degree of uniformity in explosion-energy distribution and ore breakage, (b) close hydraulic control of the flow of lixiviants without an appreciable amount of additional drilling to increase the number of injection and extraction points, and (c) a close match of the broken volume with the outline of the ore body, particularly for small or irregular ore bodies, such a match resulting in economics in the use of the available explosive energy and in the consumption of lixiviants.

While single explosive charges generally will be detonated in sequence to produce the fracture zones, the charges also can be multi-component charges positioned in separate cavities and detonated substantially simultaneously as a group to produce each fracture zone, each detonation in the sequence of detonations in such a case being a group of detonations.

The following example illustrates specific embodiments of the process of the invention.

The formation to be fractured was a bedded series of shales and silt stones, dipping about 45°, located at a depth of 70 to 90 feet below the surface and therefore subjected to a lithostatic pressure of about 70 to 90 p.s.i. The water table was at a depth of about 15 feet below the surface. A 3-inch-diameter hole was drilled into the formation to a depth of 100 feet. This hole was used as a coresampling and permeability-testing hole, and also as an injection hole for purposes of flushing surrounding shot holes. A core test revealed a competent silty shale at the 70–90 foot depth. A well screen was installed in the hole at the 70–90 foot level, and piping to the well screen was grouted to the hole. Cement filled the hole below the well screen.

The pattern of shot holes used is shown in FIG. 3. Three shot holes (SH 1, SH 2, and SH 3) were located 16.25 feet from the injection hole I, their centers lying on 120° radii from the center of hole I and the lines joining them forming an equilateral triangle. The distance between these shot holes was 28 feet. Three shot holes (SH 4, SH 5, and SH 6) were located 32.5 feet from hole I, their centers also lying on 120° radii from the center of hole I, and the lines joining them (also forming an equilateral triangle) being bisected by the centers of holes SH 1, SH 2, and SH 3. The distance between holes SH 4, SH 5, and SH 6 was 56 feet. It is seen that in this arrangement the lines joining adjacent (i.e., nearest neighbor) shot holes formed equilateral triangles. SH 1, SH 2, and SH 3 each had four shot holes adjacent thereto (SH 2, SH 3, SH 4, and SH 5 for SH 1; SH 1, SH 3, SH 5, and SH 6 for SH 2; and SH 1, SH 2, SH 4, and SH 6 for SH 3), and SH 4, SH 5, and SH 6 each had two shot holes adjacent thereto (SH 1 and SH 3 for SH 4; SH 1 and SH 2 for SH 5; and SH 2 and SH 3 for SH 6).

Shot hole SH 1 was drilled first. The hole was 5 inches in diameter and 91 feet deep and was loaded with 255 pounds of an aluminized water gel explosive having the following composition: 18.9% ammonium nitrate, 10.5% sodium nitrate, 29.6% methylamine nitrate, 30% aluminum, and 11% water. The explosive column was 21.7 feet high, and was covered by a layer of water which naturally flowed into and filled the remainder of the hole and stemmed the explosive charge. The water level in the injection hole was above the level of the top of the explosive charge in the shot hole, indicating that the rock surrounding the shot hole was properly flooded. Before the explosive charge was initiated, the permeability and sound velocity of the rock surrounding the injection hole were measured. The permeability was determined by slug tests, in which the permeability is inferred from the rate at which the head of liquid subsides toward the ambient level in a hole after the rapid introduction of a slug of liquid therein (see Ferris, J. G., et al., "Theory of Aquifer Tests", U.S. Geological Survey, Water-Supply Paper 1536-E, 1962). The sound velocity, measured at depths of 74.5 feet to 85 feet between the injection hole, shot hole SH 1, and a test hole collared 13 feet on the opposite side of the injection hole, was 3970 meters per second.

The explosive charge in shot hole SH 1 in the flooded formation was detonated, whereupon the water level in the injection hole dropped to below its pre-detonation level, as a result of the formation of a new fracture volume around shot hole SH 1, the chasing of water from

the rock fractures by the gaseous detonation products, and the flow of water into the cavity created by the explosive charge. After partial recovery of the water level in the injection hole, the second shot hole (shot hole SH 2) was drilled to the same size as shot hole SH 1, and the rock surrounding shot hole SH 1 was then flushed with water by (a) blowing compressed air into the bottom of the open injection hole (b) injecting water through a packer in the injection hole, and (c) three long air injections, and then (d) 18 short air injections through a packer in the injection hole. The total flushing time was about 4 hours. Silt-laden water was ejected from shot hole SH 1 (but not shot hole SH 2) during the flushing, indicating the preservation of the top of shot hole SH 1, the circulation of the water from the bottom of the rock segment (bottom of the injection hole) laterally and upward through the fracture network to the top of the rock segment (bottom of shot hole SH 1), and the removal of fines from the fractures. The permeability was measured in the injection hole (as described above) before and after the flushing operations.

Shot hole SH 2 and subsequently drilled shot hole SH 3 were loaded and the charges therein detonated as described for shot hole SH 1.

The water level in the injection hole returned to its pre-detonation level, above the level of the top of the explosive charge in shot hole SH 1 before detonation, in about 18 hours. Thereafter, the charge in shot hole SH 2 was detonated, whereupon the water level in the injection hole again dropped to below its pre-detonation level. The rock surrounding shot hole SH 2 was flushed with water, and siltladen water ejected from shot hole SH 2, by sealing off shot hole SH 1 and (a) injecting air through a packer in the injection hole. (b) blowing compressed air into the bottom of the open injection hole, and (c) injecting air through a packer while blowing compressed air into the bottom of shot hole SH 3. The total flushing time was about 11 hours. The permeability was again measured before and after the flushing operations.

After the water level in the injection hole had returned to its pre-detonation level, the charge in shot hole SH 3 was detonated, and the surrounding rock flushed by (a) air injection through a packer in the injection hole, followed by sealing off shot hole SH 1 and blowing air down shot hole SH 2 and shot hole SH 3 to drive water to each slot hole in turn until water was exhausted from the broken rock; and (b) two air injection flushings, each followed by water injection. The total flushing time was about 7 hours. The permeability was again measured before and after the flushing operations.

The remaining shot holes SH 4, SH 5, and SH 5, were drilled, loaded, and detonated in the same manner as holes SH 1, SH 2, and SH 3, with the detonations occurring after the return of the water level in the injection hole to its predonation level. Between the shooting of shot holes SH 4 and SH 5, the rock surrounding hole SH 4 was flushed by three air injections in the injection hole, each followed by water injection; between the shooting of shot holes SH 5 and SH 6, the rock surrounding hole SH 5 was flushed by injecting air into the injection hole, and blowing air down hole SH 6 (unshot), separately and simultaneously; and after hole SH 6 was shot, the rock surrounding it was flushed by alter-

nately injecting air into the injection hole and blowing air down the surviving section of hole SH 6.

The permeabilities measured by slug tests in the injection hole before the blast/flush process began and after each blast and flush operation at each of the six holes are plotted in FIG. 4 as a function of the operation performed, the permeabilities being presented in millidarcys on a logarithmic scale as the ordinate. Nineteen points are shown, including those obtained after the four flushing procedures (a, b, c, and d) described above after the shooting of hole SH 1; three flushing procedures (a, b, and c) after the shooting of hole SH 2; and two flushing procedures (a and b) after the shooting of hole SH 3. Each point denotes the average permeability measured after a given operation.

The plot shows that the permeability of the rock was increased considerably (from 500 to over 2000 millidarcys) by the total six-cycle blast/flush process, and that variations in permeability occurring during the cyclical shooting and flushing tend to decrease as the rock is broken and swelled. The plotted experimental values also show that the rapid flow of water to the remnant of a shot hole achieved by means of air injection through another hole or by strong pumping from a shot hole (by blowing air into the bottom of an open shot hole, for example) increases the permeability after blasting, best results having been achieved when both air injection at the injection hole and strong pumping at a nearby shot hole was used. While blasting was found generally to decrease the permeability, permeability which had previously been reduced by the injection of water (alone or as a final flushing step after blasting) was increased by blasting.

The degree of dilation produced in the rock by the first three of the above-described detonations in flooded rock was estimated from calculations of porosity based on sound velocity measurements. The sound velocity around the injection hole after the three blasts was 3650 meters per second at a 12 foot radius from the hole, and 2530 meters per second through paths in the blasted rock running from the shot holes in to the injection hole (compared with 3970 meters per second in the same prism of rock before blasting). The total porosity in the rock (ψ) was calculated from the following empirical equation for the sound velocity (α, in m/sec) as a function of porosity, for flooded ocean sediments having various degrees of lithification:

$$\psi = -50.748 \ln\alpha + 432.23.$$

Total porosity before blasting: 11.7%
Total porosity after blasting: (12-ft. radiu) 16.0%
Total porosity after blasting: (center to shot holes) 34.6%.

These porosities imply that the fracture volumes caused by the blasting were 4.3% (12-ft. radius) and 22.9% (center to shot holes).

I claim:

1. A process for producing a network of fractures in a deep segment of mineralized rock to prepare said segment for the in situ recovery of mineral values therefrom comprising

a. forming an assemblage of cavities in said rock segment;

b. positioning chemical explosive charges in a plurality of said cavities in the sections thereof located in said rock segment;

c. allowing liquid to fill the fractures existing in the rock around the cavities in the sections thereof located in said rock segment as can be evidenced by

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a liquid level which is at least as high as the top of said rock segment; and

d. detonating said explosive charges sequentially, each detonation in the sequence producing a zone of fracture in said segment and a drop in the level of said liquid, as measurable in the cavity which contained the detonated charge or in a cavity adjacent thereto, said charges being sufficiently large and spaced sufficiently close together that the fracture zones produced in said segment by the detonations of charges in adjacent cavities overlap, the detonation of the charge in each cavity being delayed until after the level of the liquid, as measurable in the cavity containing the charge to be detonated or in a cavity lying within the zone of fracture produced by a previous detonation in a cavity adjacent thereto, has ceased to drop and is at least as high as the top of said rock segment.

2. A process of claim 1 wherein said liquid is water.

3. A process of claim 2 wherein said water is naturally occurring in said rock.

4. A process of claim 1 wherein, in groups of adjacent cavities in which explosive charges are to be detonated, the detonation of the charge in each cavity takes place before charges are positioned in cavities adjacent thereto.

5. A process of claim 1 where in the time elapsing between any two consecutive detonations in a group of adjacent cavities is at least one hour.

6. A process of claim 5 wherein said liquid is introduced into at least one of said cavities and enters said rock by permeating the cavity walls.

7. A process of claim 1 wherein the cavities in which explosive charges are to be detonated form a pattern in which each internal cavity of the pattern is surrounded by at least four adjacent cavities.

8. A process of claim 1 wherein said cavities are substantially vertical drill holes.

9. A process of claim 8 wherein the sections of the holes which are located in said rock segment to be are chambered to larger diameter, and the explosive charges are positioned in the chambered sections.

10. A process of claim 9 wherein said chambered sections are produced by the previous detonation of springing explosive charges in the holes.

11. A process of claim 10 wherein the springing explosive charges employed to produce the chambered sections of said holes are at least about 20 feet long and the bottoms thereof are located below the bottom of said segment of rock.

12. A process of claim 8 wherein a pluraity of holes of said assemblage are drilled from the earth's surface, and are left uncharged with explosive, said holes forming passageways within the fracture network from the earth's surface to substantially the bottom of said segment of rock.

13. A process of claim 12 wherein said plurality of uncharged holes are drilled and their walls provided with support casing, at least in the portions thereof located in the said segment of rock, prior to the detonation of the explosive charges in holes adjacent thereto.

14. A process of claim 13 wherein liquid is injected into said segment of rock through said uncharged holes.

15. A process of claim 8 wherein, in groups of adjacent holes in which explosive charges are to be deto-

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nated, the detonation of the charge in each hole takes place before adjacent holes are drilled.

16. A process of claim 8 wherein said substantially vertical holes are drilled into the segment of rock from the surface, and branch holes are drilled into the segment of rock from said substantially vertical holes at small angles thereto starting at locations overlying said segment of rock.

17. A process for producing a network of fractures in a deep segment of mineralized rock to prepare said segment for the in situ recovery of mineral values therefrom comprising

a. forming an assemblage of cavities in said rock segment;

b. positioning explosive charges in a plurality of said cavities in the section thereof located in said rock segment;

c. detonating said explosive charges sequentially to produce a plurality of fracture zones;

d. driving liquid through said fracture zones by injecting gas therein at sufficiently high pressure that fines present in said fracture zones as a result of the crushing or abrading of existing clays or rocks are entrained by said liquid; and

e. removing fines-laden liquid from said rock whereby the permeability of said rock segment is restored.

18. A process of claim 15 wherein liquid is driven through, and fines-laden liquid removed from, the fracture zone produced by the detonation of an explosive charge in a given cavity prior to the detonation of explosive charges in cavities adjacent thereto.

19. A process of claim 15 wherein an assemblage of substantially vertical holes is drilled into said rock from the earth's surface; explosive charges are detonated in the sections of a plurality of said holes in said segment of rock in a manner such that the sections of said detonated holes located in the overburden that overlies said segment of rock survive the detonations and form a first set of passageways from the earth's surface to said segment of rock, said first set of passageways leading substantially to the top of said segment of rock; a remaining plurality of holes of said assemblage are left uncharged with explosive and form a second set of passageways from the earth's surface to said segment of rock, said second set of passageways leading substantially to the bottom of said segment of rock; and liquid is driven through said fracture zones laterally and upwardly from said second set of passageways to said first set of passageways and is brought to the surface through said first set of passageways.

20. A process of claim 17 wherein said uncharged holes are drilled prior to the detonation of said charges, and have their walls provided with support casing at least in the sections thereof located in said segment of rock.

21. A process of claim 19 wherein liquid present in the fracture zones is driven therethrough by gas injected therein through said holes which form said second set of passageways.

22. A process of claim 21 wherein said liquid is water, and said gas is selected from the group consisting of air, oxygen, and nitrogen.

23. A process of claim 19 wherein said segment of rock is an ore body, and, after the detonation of said explosive charges, a lixiviant for said ore is driven through the fracture zones in said ore body from said

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holes which form said second set of passageways to said holes which form said first set of passageways, and is brought to the surface through said first set of passageways.

24. A process for producing a network of fractures in a deep segment of mineralized rock to prepare said segment for the in situ recovery of mineral values therefrom comprising

a. forming an assemblage of cavities in said rock segment;

b. positioning chemical explosive charges in a plurality of said cavities in the sections thereof located in said rock segment;

c. allowing liquid to fill the fractures existing in the rock around the cavities in the sections thereof located in said rock segment as can be evidenced by a liquid level which is at least as high as the top of said rock segment;

d. detonating said explosive charges sequentially, each detonation in the sequence producing a zone of fracture in said segment and a drop in the level of said liquid, as measurable in the cavity which contained the detonated charge or in a cavity adjacent thereto, said charges being sufficiently large

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and spaced sufficiently close together that the fracture zones produced in said segment by the detonations of charges in adjacent cavities overlap, the detonation of the charge in each cavity being delayed until after the level of the liquid, as measurable in the cavity containing the charge to be detonated or in a cavity lying within the zone of fracture produced by a previous detonation in a cavity adjacent thereto, has ceased to drop and is at least as high as the top of said rock segment;

e. driving liquid through said fracture zones by injecting gas therein at sufficiently high pressure that fines present in said fracture zones as a result of the crushing or abrading of existing clays or rocks are entrained by said liquid; and

f. removing fines-laden liquid from said rock whereby the permeability of said rock segment is restored.

25. A process of claim 24 wherein liquid is driven through, and fines-laden liquid removed from, the fracture zone produced by the detonation of an explosive charge in a given cavity prior to the detonation of explosive charges in cavities adjacent thereto.

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