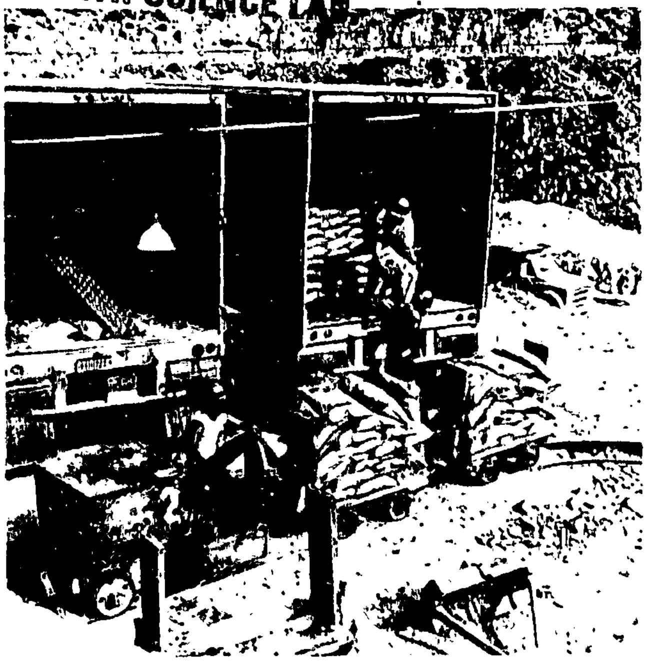
Scene of shot is the Old Reliable mine. Lower adit is barely visible speck between two trailers at bottom of hill.



Workers load 50-lb bags of ammonium nitrate on mine cars for the shot designed to crush 4 million tons of ore.

Ranchers' big blast shatters copper orebody for in-situ leaching

THE BIGGEST PRE-PRODUCTION SHOT in the history of mining was triggered on the 9th of last month by Ranchers Exploration & Development Co. in an aggressive bid to unlock a pipe-like deposit of oxidized and secondarily enriched copper in Arizona for low cost recovery.

In work on the Old Reliable project, 2,000 tons of explosive were detonated in man's first attempt to fracture an entire orebody for a percolation leach of the matrix. This will be followed with cement precipitation of copper from collected, pregnant off-solutions. The project is another prime example of applied creative technology which is rapidly becoming a trademark of Ranchers — a modern maverick operating in an industry known more for its conservatism.

The Old Reliable deposit is almost ideally suited for such treatment. It is compact — some 4 million tons of 0.80% copper ore are located in an area 400 ft in diameter and 350 ft deep — and it is remotely located, so that damage from the blast was nonexistent. In addition, the orebody is situated in the side of a hill, permitting leaching solutions to be drawn off by gravity at the base of the mine.

It is estimated that about 30 million lb of copper can be recovered over a period of five years, making the property a short-term producer of cement copper. Production is expected to get underway in three to four months, when construction of the new precipitation plant is completed.

A running start at development

Located in the Copper Creek area of the Galiuro Mountains, the Old Reliable is on ground first claimed during the Civil War. The mine was worked sporadically from 1890 to 1919 and again in 1953 and 1954, with a total of about 30,000 tons of ore removed. Ranchers acquired a lease on the property from Siskon Corp. and Occidental Minerals Corp. in October 1970.

The deposit occurs in andesite, a lava that is the principal rock in the Glory Hole Volcanic Formation. In the area of the orebody, the rock was broken as the result of pressure from underlying molten granite, which intruded the general area some 68 million years ago. Copper-bearing solutions, apparently carried along by the granite, flowed into cracks and voids of the brecciated andesite. Ground water later redistributed the copper values, dissolving copper near the surface and redepositing it in an enriched zone deeper in the orebody.

The deposit extends from the surface to a depth of 500 ft. That portion near the surface is almost barren, containing less than 0.40% copper. Mineralization increases with depth, however, reaching an average of about 2% near the bottom of the orebody. High grade areas within the deposit sometimes reach 9-10% copper. Principal minerals are chalcocite, chalcopyrite, malachite, chalcanthite, and chrysocolla.

The peak of the hill containing the ore is about 4,200 ft above sea level, and the deposit begins some 100 ft below this point. Three adits and a raise in the hillside tap the orebody (see sectional views on the third page of this article). The bottom level, some 3,750 ft above sea level, is 840 ft long; the middle level, 100 ft above the lower level, is 760 ft long. The upper adit is 165 ft above the middle level and is 660 ft long.

The upper workings — known as the "A" level — and approximately 1,000 ft of crosscuts at right angles to the entry were driven by Kop-Ran De-

2,000 tons of explosive were placed underground on three levels in network of headings, some old and some new.

Primers and Primacord® being attached to the 50-lb bags of ANFO. Fragmentation after blast was better than expected.

velopment Corp., a Ranchers subsidiary. The two lower levels were opened during earlier mining, although Kop-Ran extended both adits and crosscuts. The lower level contains about 2,100 ft of crosscuts, while the middle level contains 3,100 ft.

Planning a production program

The deposit was shattered by the 4 million lb of explosive emplaced according to a plan devised by E. I. Du Pont de Nemours & Co., which is providing the explosive and technical assistance on the project. (Following the blast, Du Pont de Nemours acquired approximately 20% of Ranchers' interest in the Old Reliable for $500,000, including $100,000 in explosives.) The ammonium nitrate, contained in 50-lb bags, was packed at selected points in the tunnels and crosscuts. Sand was placed [illegible] points behind the charges to contain the energy of detonation. About 1,294,550 lb of explosive were placed in the bottom level; 2,103,400 lb were stacked in the middle level and 595,800 lb were used on the upper level.

Millisecond delays were so attached to permit instantaneous explosion of the uppermost level, followed by a 100-ms delay in the detonation of the middle level, and a further 50-ms delay on the bottom 200-ft level. While early measurements indicate that the surface was actually lifted some 40-50 ft in the air, there was substantially less flyrock developed and less surface damage incurred than expected by the engineers on the job.

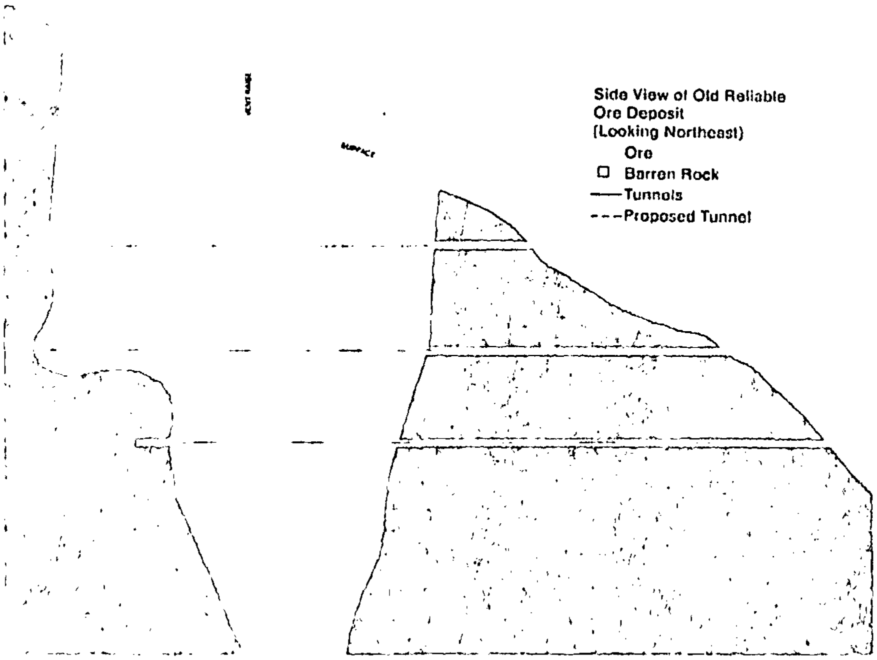
The blast, five seconds after detonation, was recorded at 2,500 ft from ground zero by camera with a 70 mm lens.

Extensive safety tests were conducted in connection with the project, including detonation of three test blasts ranging from 100 to 4,000 lb of explosive. Conducted under the direction of John A. Blume & Associates, Engineers, San Francisco — experts in the study of seismic blast effects — the tests were staged to gain data on ground movement. On the basis of data from these tests, Blume & Associates concluded that structural damage from the blast at the mine would be essentially nil — a fact borne out by experience.

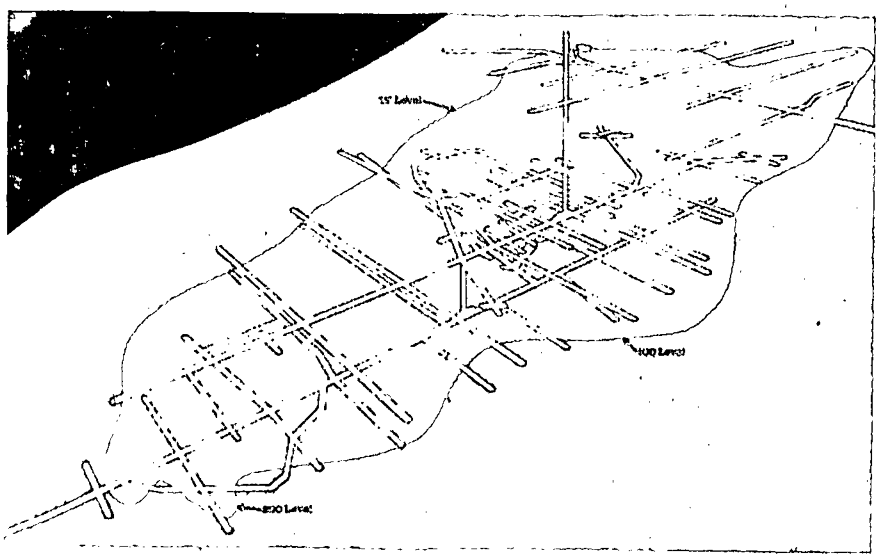
The blast site is ¾ mile from the nearest ranch house; 9.2 miles from Mammoth; 12 miles from the San Manuel mine; and 13.6 miles from the San Manuel smelter. The shot was detonated at a point 1 mile from the mine. An electrical circuit, connected by wires to blasting caps, Primacord®, and high explosive primers placed among the bags of fertilizer, was used to initiate the blast.

Observers were stationed about 3 miles from the site on an unpaved road leading from the mine to Mammoth. A large area around the mine was cleared of humans, livestock, and aircraft to prevent damage or injury from flying rock.

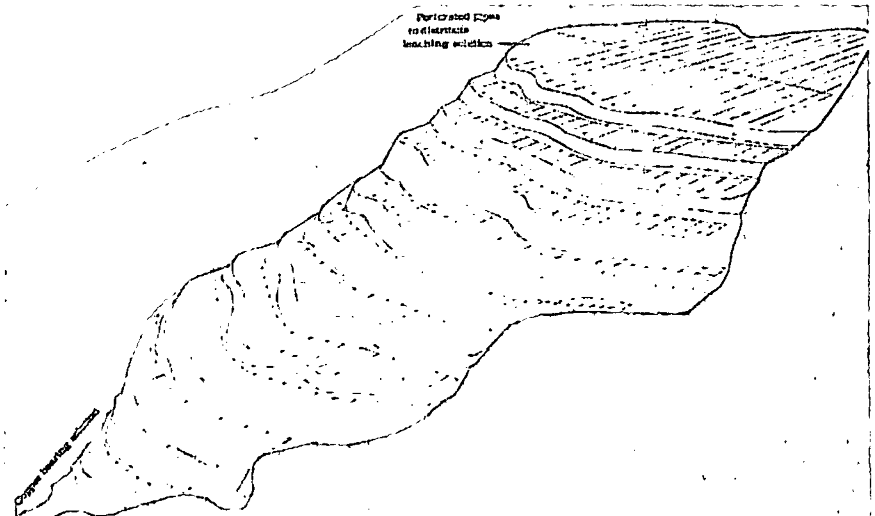
Preliminary measurement of the effects of the blast indicates that the



Two-dimensional view of the pipe-like orebody shows a section that looks to the northeast. The upper level was opened by Ranchers for the project.



Three-dimensional view of the mine workings indicates the development work contained in the mine. Past operators opened the two lower levels.



Terracing of the surface will be necessary for establishment of the leach pipework which introduces the acidified solutions to rock broken by the shot.

primary goals were achieved. Of these, the most important was the adequate degree of shattering of the orebody, and results in this area may have exceeded expectations, according to early reports. Initial measurements indicate that, throughout the orebody, breakage of the rock resulted in fragments measuring 9 in. or less — substantially better than the 11-in. size hoped for when the blast was being designed.

The next step in the program is to terrace the area above the deposit and lay perforated pipes on the terraces for irrigation of the orebody. Recovered solution from percolation will be led to a storage area for pumping to a precipitation plant.

The cost of bringing the property into production is expected to be $1.7 million.

Pioneering a new technology

Successful implementation of the Ranchers' approach to extraction of ore from the Old Reliable has two advantages which could make the method attractive for similar orebodies in the future. These include: 1) low cost, and 2) minimal disturbance of the environment. The low cost results from the fact that ore is never removed from the deposit. For this reason, it is estimated that the cost of producing copper from the mine will be 30-50% lower than if a more conventional method were used.

In terms of environmental damage, the savings are expected to be just as impressive. The blast affected an area 400-500 ft in diameter above the orebody. Vegetation, which was sparse, was completely removed from the area, while a small amount of overlying rock and dirt was scattered around the hill.

It is estimated that if conventional open pit mining techniques were used at the Old Reliable, an area 10-15 times the size of the projected area would be affected. In addition a large pit would remain after the deposit was mined out, and a large tailing area would be required to stock the gangue. It would be difficult to re-establish native vegetation on the tailing pond. Because of the low grade nature of the disseminated sulphides, the leaching program will result in no subsidence.

While the success of the project is yet to be demonstrated, it could lead to a useful new concept of metal recovery from low grade ore deposits. The information gained from operating experience can likely be applied to other mineral extraction projects, although use of the methods will probably be limited to deposits where more conventional techniques are not considered economically feasible.

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RADIATION FROM A CYLINDRICAL SOURCE OF FINITE LENGTH*

PATRICK AIDAN HEELAN, S.J.,†

ABSTRACT

This paper presents the results of a theoretical study of radiation from a cylindrical source of finite length, the walls of which are subjected to symmetric lateral and tangential stresses. Three divergent wave systems are generated, *P*, *SV*, and *SH*, and their amplitudes are calculated in terms of the stresses operative on the walls of the "equivalent cavity." The zonal distribution of amplitude in the three wave systems is calculated, and the total amount of energy in each is estimated. It is shown that under the action of a lateral pressure only, an *SV* wave of amplitude 1.6 times the maximum amplitude of the associated *P*-wave is beamed from the source in directions making angles of 45° with the axis of the source.

This paper is the first of a series embodying the results of a study of the nature and origin of elastic head waves.[1] It was thought well to begin this study by attempting to reproduce in mathematical form the main features of the type of disturbance most frequently employed in seismic prospecting, namely, that generated by the detonation of a charge in a cylindrical shot hole. The problem we were led to consider was the effect of transitory forces acting upon the walls of a cylindrical cavity of finite length embedded in an infinite solid medium. The results of this part of the enquiry are presented in this paper.

When energy is imparted to the ground by an explosion, some is converted into a radiating stress-strain field and some is utilized in producing local deformations of a permanent character. The precise mechanism by which energy is transmitted to the ground is not clear. Considerable research has been done on this type of problem by United States Army and Navy engineers, but the results of the research are not yet available to the public. The energy carrier, however, seems to be a shock wave which travels through the medium with supersonic speed, exepending its energy in breaking and crushing the surrounding rock, and gradually diminishing in intensity through diffusion over an ever broadening wave front. When the stresses in the expanding wave no longer exceed the strength of the medium, the shock wave has become an elastic wave and from there on is propagated according to the well-known laws of elastic wave theory. How the total energy imparted to the medium by a purely elastic disturbance is partitioned between a field of permanent deformation and a radiating field of force has been investigated for certain simple sources by Kawasumi and Yoshiyama, Sezawa, and Kanai. Sezawa[2] concluded that not more than half of the

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* Manuscript received by the Editor October 3, 1952.

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[1] This study was part of a doctoral program undertaken by the author under the direction of the Reverend James B. Macelwane, S.J., at Saint Louis University in 1952.

[2] K. Sezawa, "Elastic Waves Produced by Applying a Statical Force to a Body or by Releasing It from a Body," *Bull. Earth. Res. Inst., Tokyo*, 13, (1935), 740–748; "On the Relation between Seismic Origins and Radiated Waves," *ibid.*, 14, (1936), 149–154; K. Sezawa and K. Kanai, "Elastic Waves Formed by Local Stress Changes of Different Rapidities," *ibid.*, 10–17.

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total energy is ever present in the radiating field, and this much only when the disturbing force is applied or released with great rapidity.

Theoretical studies of the radiation from different types of sources have been made by Sezawa, Kanai, Nishimura and Takayama.[3] In this paper, with a view to simulating conditions in the neighborhood of a shot hole, the source chosen is a cylinder of length $2l$ and radius a, centered at the origin of co-ordinates and embedded in an infinite medium. The vertical walls of this cylinder are subjected to stresses which are symmetric about the vertical axis, uniform in the sense that they have the same instantaneous value at all points, and finite in duration.

Expressing the conditions mathematically in cylindrical co-ordinates (r, θ, z), the conditions at the source become (see Fig. 1):

$$[-\widehat{rr}] = p(t) \quad \text{or 0, according as } |z| < l \text{ or } > l, \tag{1a}$$

$$[-\widehat{rz}] = q(t) \quad \text{or 0, according as } |z| < l \text{ or } > l, \tag{1b}$$

$$[-\widehat{r\theta}] = s(t) \quad \text{or 0, according as } |z| < l \text{ or } > l. \tag{1c}$$

It can be assumed that $p(t)$, $q(t)$ and $s(t)$ are proportional to one another.

Since the deformation is, by hypothesis, symmetrical about the z-axis at all times, the displacement (u, v, w) can be expressed in terms of three wave-functions Φ_0, Θ_0, and χ_0 which satisfy the following wave equations,

$$\begin{aligned} \Phi_0'' - V^2\nabla^2\Phi_0 &= 0, \\ \Theta_0'' - v^2\nabla^2\Theta_0 &= 0, \\ \chi_0'' - v^2\nabla^2\chi_0 &= 0, \end{aligned} \tag{2}$$

where $V=(\lambda+2\mu)^{1/2}/\rho^{1/2}$, $v=\mu^{1/2}/\rho^{1/2}$. The quantities (u, v, w)[4] are the components of particle displacement in the directions of (r, θ, z) increasing respectively. These displacements, when expressed in terms of the auxiliary wave functions, are

$$u = \frac{\partial\Phi_0}{\partial r} - \frac{\partial^2\Theta_0}{\partial r\partial z}, \tag{3a}$$

$$v = \frac{\partial\chi_0}{\partial r}, \tag{3b}$$

$$w = \frac{\partial\Phi_0}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\Theta_0}{\partial r}\right). \tag{3c}$$

The stresses, likewise expressed in terms of the auxiliary functions, take the form,

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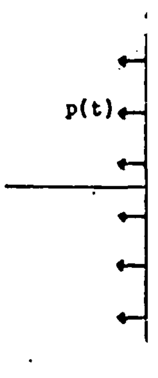
[3] Cf. *Bull. Earth. Res. Inst., Tokyo*, volumes 2 (1927), 14 (1936) and 16 (1938).

[4] The author employs the symbol v both for tangential displacement and shear velocity. The context will make clear which meaning is intended—The Editor.



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$\widehat{rr} = \lambda\nabla^2\Phi$

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It is now assumed that Φ
the following integrals,

$\Phi_0 = \int_0^\infty e^{ikV}$

$\Theta_0 = \int_0^\infty e^{ikV}$

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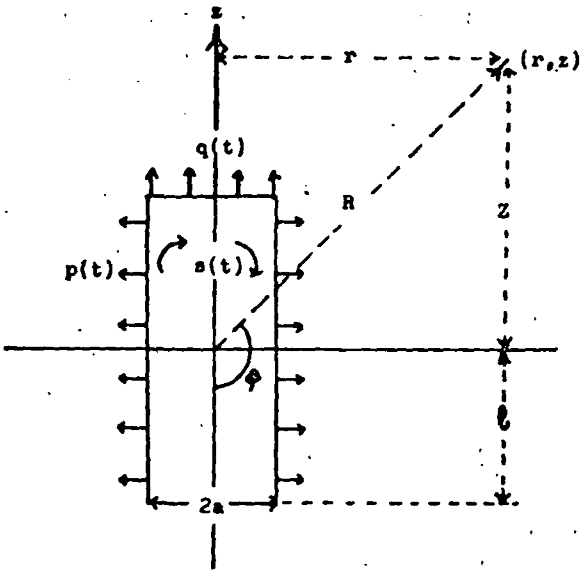

FIG. 1. Source of disturbance.

$$\widehat{rr} = \lambda\nabla^2\Phi_0 + 2\mu\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0}{\partial r} - \frac{\partial^2\Theta_0}{\partial r\partial z}\right),$$

$$\widehat{rz} = \mu\frac{\partial}{\partial r}\left(2\frac{\partial\Phi_0}{\partial z} + \nabla^2\Theta_0 - 2\frac{\partial^2\Theta_0}{\partial z^2}\right),$$

$$\widehat{zz} = \lambda\nabla^2\Phi_0 + 2\mu\frac{\partial}{\partial z}\left(\frac{\partial\Phi_0}{\partial z} + \nabla^2\Theta_0 - \frac{\partial^2\Theta_0}{\partial z^2}\right), \qquad (4)$$

$$\widehat{r\theta} = \mu\left(\frac{\partial^2\chi_0}{\partial r^2} - \frac{1}{r}\frac{\partial\chi_0}{\partial r}\right),$$

$$\widehat{z\theta} = \mu\frac{\partial^2\chi_0}{\partial r\partial z}.$$

It is now assumed that Φ_0, Θ_0 and χ_0 can be expressed as the *real parts* of the following integrals,

$$\Phi_0 = \int_0^\infty e^{ikVt}dk\int_C f_0(\sigma, k)H_0^{(1)}(\sigma r)e^{z(\sigma^2-k^2)^{\frac{1}{2}}}d\sigma,$$

$$\Theta_0 = \int_0^\infty e^{ikVt}dk\int_C g_0(\sigma, k)H_0^{(1)}(\sigma r)e^{z(\sigma^2-k^2)^{\frac{1}{2}}}d\sigma, \qquad (5)$$

$$\chi_0 = \int_0^\infty e^{ikVt}dk\int_C h_0(\sigma, k)H_0^{(1)}(\sigma r)e^{z(\sigma^2-k^2)^{\frac{1}{2}}}d\sigma,$$

where $kV = h\nu$, $H_0^{(1)}$ is the Hankel function of the first kind and zeroth order,[5] and C is a loop from ∞i about $-h$ and $-k$, excluding the origin and such that $\arg.\sigma = \arg.(\sigma^2 - k^2)^{1/2} = \arg.(\sigma^2 - h^2)^{1/2} = \pi/2$ initially.[6] The integrands in equations 5 are determined by the conditions at the source and by Sommerfeld's conditions[7] which require that Φ_0, Θ_0 and χ_0 represent divergent wave systems which are bounded at infinity.

Determination of $f_0(\sigma, r)$, $g_0(\sigma, r)$ and $\eta_0(\sigma, r)$.—The boundary conditions (1) at the source can be expressed in another way, utilizing the contour integral,

$$\frac{i}{\pi}\int_C \frac{\sigma \sinh l(\sigma^2 - k^2)^{1/2}}{\sigma^2 - k^2} e^{z(\sigma^2 - k^2)^{1/2}} d\sigma,$$

which is a transformation of the Fourier integral,

$$\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\sin l\tau}{\tau} e^{iz\tau} d\tau \begin{array}{l} = 1, \text{ when } |z| < l, \\ = 0, \text{ when } |z| > l, \end{array}$$

under the mapping $(\sigma^2 - k^2)^{1/2} = i\tau, -\pi \leqq \arg.\tau \leqq 0$.

Thus, an equivalent way of expressing the condition (1a), at the source, is,

$$[-\widehat{rr}] = p(t)\,\frac{i}{\pi}\int_C \frac{\sigma \sinh l(\sigma^2 - k^2)^{1/2}}{\sigma^2 - k^2} e^{z(\sigma^2 - k^2)^{1/2}} d\sigma.$$

Let the time factor $p(t)$ be expressible as the *real part* of the Fourier integral,

$$\int_0^\infty p_1(k) e^{ikVt} dk.$$

Thus the conditions (1) at the source are equivalent to the following;

$$\begin{bmatrix} -\widehat{rr} \\ -\widehat{rz} \\ -\widehat{r\theta} \end{bmatrix} = \frac{i}{\pi}\int_0^\infty \begin{bmatrix} p_1(k) \\ q_1(k) \\ s_1(k) \end{bmatrix} e^{ikVt} dk \int_C \frac{\sigma \sinh l(\sigma^2 - k^2)^{1/2}}{\sigma^2 - k^2} e^{z(\sigma^2 - k^2)^{1/2}} d\sigma, \tag{6}$$

where $p_1(k)$, $q_1(k)$, and $s_1(k)$ are proportional to one another.

The stresses at the source can be represented by means of equations (4), in terms of the potentials Φ_0, Θ_0, and χ_0. The set of expressions so obtained must be exactly equivalent to the set (6). Equating the integrands, and solving for f_0, g_0 and n_0, the following results are obtained:

$$f_0 = -\frac{i\sigma \sinh l(\sigma^2 - k^2)^{1/2}}{\pi(\sigma^2 - k^2)} \cdot \frac{M_1}{N_1}, \tag{7a}$$

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[5] Cf. E. Jahnke and F. Emde, *Tables of Functions* (4th ed.); New York: Dover, (1945), pp. 133 ff.

[6] If $f_0 = -\sigma/2(\sigma^2 - k^2)^{1/2}$, the contour C can be deformed into the real axis and the integration with respect to σ yields Sommerfeld's classic representation of the Hertzian oscillator $\exp.(ikR)/R$.

[7] A. Sommerfeld, "Die Greensche Funktion der Schwingungsgleichung," *Jahresb. Deut. Math. Verein.*, 21, 309–353 (1912).

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where

$$\begin{aligned} M_1 = {} & p_1(k)\mu\sigma(2\sigma^2 + h^2 - 2k^2)H_1^{(1)}(\zeta a) \\ & - 2q_1(k)\mu\sigma(\sigma^2 - k^2)^{1/2}\zeta\left[H_0^{(1)}(\zeta a) - H_1^{(1)}(\zeta a)/\zeta a\right], \end{aligned}$$

and

$$\begin{aligned} N_1 = {} & -\mu\sigma(2\sigma^2 + h^2 - 2k^2)(2\mu\sigma^2 + \lambda k^2)H_1^{(1)}(\zeta a)H_0^{(1)}(\sigma a) \\ & + 4\mu^2\sigma^2(\sigma^2 - k^2)\zeta H_1^{(1)}(\sigma a)H_0^{(1)}(\zeta a) \\ & + 2\mu^2h^2\sigma^2H_1^{(1)}(\zeta a)H_1^{(1)}(\sigma a)/a, \end{aligned}$$

with

$$\zeta = (\sigma^2 + h^2 - k^2)^{1/2}.$$

$$g_0 = \frac{i\sigma \sinh l(\sigma^2 - h^2)^{1/2}}{\pi(\sigma^2 - h^2)} \cdot \frac{M_2}{N_2}, \tag{7b}$$

where

$$\begin{aligned} M_2 = {} & -2p_1(k)\mu\sigma(\sigma^2 - h^2)^{1/2}H_1^{(1)}(\eta a) \\ & + q_1(h)\mu\sigma(2\sigma^2 - h^2)H_0^{(1)}(\eta a)/\eta - 2q_1(k)\mu\sigma H_1^{(1)}(\eta a)/a, \end{aligned}$$

and

$$\begin{aligned} N_2 = {} & -\mu^2\sigma^2(2\sigma^2 - h^2)^2H_1^{(1)}(\sigma a)H_0^{(1)}(\eta a) \\ & + 4\mu^2\sigma^3(\sigma^2 - h^2)H_1^{(1)}(\eta a)H_0^{(1)}(\sigma a) \\ & + 2\mu^2\sigma^2h^2H_1^{(1)}(\sigma a)H_1^{(1)}(\eta a)/a, \end{aligned}$$

with

$$\eta = (\sigma^2 - h^2 + k^2)^{1/2},$$

$$n_0 = \frac{-is_1(k) \sinh l(\sigma^2 - h^2)^{1/2}}{\pi\mu\sigma(\sigma^2 - h^2)H_2^{(1)}(\sigma a)}. \tag{7c}$$

Equations (7) with (2), (3), (4) and (5), comprise the exact solution of the problem of a cylindrical source of finite length with prescribed forces acting on the walls.

At distances from the source large compared with the dimensions of the source, f_0, g_0 and n_0 can be expanded in terms of the parameters a and l. Retaining only the predominant terms in the expansions, we get,

$$f_0 \simeq \frac{p_1(k)\Delta\sigma}{8\pi\mu(\sigma^2 - k^2)^{1/2}}\left(\frac{2\sigma^2}{h^2} + 1 - \frac{2v^2}{V^2}\right) + \frac{q_1(k)\Delta\sigma}{8\pi\mu h^2}, \tag{8a}$$

$$g_0 \simeq \frac{p_1(k)\Delta\sigma}{4\pi\mu h^2} + \frac{q_1(k)\Delta\sigma}{8\pi\mu h^2(\sigma^2 - h^2)^{1/2}}, \tag{8b}$$

$$n_0 \simeq \frac{s_1(k)\Delta\sigma}{8\pi\mu(\sigma^2 - h^2)^{1/2}}, \tag{8c}$$

where $\Delta =$ volume of the source $= 2\pi a^2 l$, and $A =$ area of vertical walls of source $= 4\pi a l$.

The actual particle displacements in the radiated field are obtained by inserting (5) into (3) and substituting the values of f_0, g_0 and n_0 from (7) or, at large distances from the source, from (8). Thus the radial component becomes

$$u = -\int_C \sigma f_0 H_1^{(1)}(\sigma r) e^{z(\sigma^2-k^2)^{1/2}} d\sigma + \int_C \sigma(\sigma^2 - h^2)^{1/2} g_0 H_1^{(1)}(\sigma r) e^{z(\sigma^2-h^2)^{1/2}} d\sigma,$$

where the integration with respect to k has been omitted. If r is so large that $|\sigma r| \gg 0$ at all points of the contour C, $H_1^{(1)}(\sigma r)$ can be replaced by its asymptotic expansion. Retaining only the first term of the expansion, it is found that

$$u = -e^{-3\pi i/4}\mu(\pi r)^{-1/2}\int_C (2\sigma)^{-1/2} f_0 e^{z(\sigma^2-k^2)^{1/2}+i\sigma r} d\sigma$$

$$+ e^{-3\pi i/4}\mu(\pi r)^{-1/2}\int_C (2\sigma)^{-1/2}(\sigma^2 - h^2)^{1/2} g_0 e^{z(\sigma^2-k^2)^{1/2}+i\sigma r} d\sigma.$$

Debye's Method of Steepest Descent[8] yields for the asymptotic expansion of these integrals,

$$-\frac{2k\cos\phi}{R} f_0(\sigma_1)e^{-ikR} - \frac{2ih^2\cos^2\phi}{R} g_0(\sigma_2)e^{-ihR}, \tag{9}$$

where R is the radial distance of the point (r, z) from the source, and ϕ is the angle made by the radius vector to this point with the negative z-axis (Figure 1), i.e., $R^2 = r^2 + z^2$, $\tan\phi = r/z$; σ_1 is the saddle point $-k\sin\phi$ (with $(\sigma^2-k^2)^{1/2} = +k\cos\phi$), and σ_2, the saddle point $-h\sin\phi$ (with $(\sigma^2-h^2)^{1/2} = +h\cos\phi$). At large distances from the source, f_0 and g_0 take the forms defined by equations (8). Substituting these values into (9) and applying the operator $\int_0^\infty \cdots e^{ikVt}dk$ (real part), the following expression valid at large distances from the source is obtained,

$$u = \frac{\Delta\sin\phi}{4\pi\mu VR}\left(1 - \frac{2v^2\cos^2\phi}{V^2}\right)\frac{d}{dt}\left[p\left(t - \frac{R}{V}\right)\right]$$

$$-\frac{Av^2\sin\phi\cos\phi}{4\pi\mu V^2R}\, q\left(t - \frac{R}{V}\right)$$

$$+\frac{\Delta\sin\phi\cos^2\phi}{2\pi\mu vR}\,\frac{d}{dt}\left[p\left(t - \frac{R}{v}\right)\right] + \frac{A\sin\phi\cos\phi}{4\pi\mu R}\, q\left(t - \frac{R}{v}\right), \tag{10}$$

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[8] *Cf.* E. T. Copson, *Introduction to the Theory of Functions of a Complex Variable* (London: Oxf. Univ. Press, 1935), pp. 330 ff.

where

$$q\left(t-\frac{R}{v}\right)=\mathrm{Rl.}\int_0^\infty q_1(k)e^{ikV(t-R/v)}dk, \tag{11}$$

and

$$\frac{d}{dt}\left[p\left(t-\frac{R}{V}\right)\right]=\mathrm{Rl.}\int_0^\infty p_1(k)ikVe^{ikV(t-R/V)}dk.$$

In a similar manner, the corresponding expressions for v and w are obtained. On inspection, these expressions are seen to be composed of three separate wave systems, a P-wave (u_P, 0, w_P) propagated with phase velocity V, a vertically polarized shear wave (u_{SV}, 0, w_{SV}) and a horizontally polarized shear wave (0, v_{SH}, 0), both of which are propagated with phase velocity v. Thus,

$$u = u_P + u_{SV},$$
$$w = w_P + w_{SV},$$
$$v = v_{SH}.$$

Putting

$$F_1(\phi) = \Delta(1 - 2v^2\cos^2\phi/V^2)/4\pi\mu V, \tag{12a}$$
$$G_1(\phi) = -Av^2\cos\phi/4\pi\mu V^2, \tag{12b}$$
$$F_2(\phi) = \Delta\sin 2\phi/4\pi\mu v, \tag{12c}$$
$$G_2(\phi) = A\sin\phi/4\pi\mu, \tag{12d}$$
$$K(\phi) = \Delta\sin\phi/4\pi\mu v, \tag{12e}$$

the P-wave becomes,

$$\begin{bmatrix} u_P \\ w_P \end{bmatrix} = \left[\frac{F_1(\phi)}{R}\frac{d}{dt}\{p(t-R/V)\} + \frac{G_1(\phi)}{R}q(t-R/V)\right]\begin{bmatrix} \sin\phi \\ -\cos\phi \end{bmatrix}, \tag{13a}$$

the SV-wave,

$$\begin{bmatrix} u_{SV} \\ w_{SV} \end{bmatrix} = \left[\frac{F_2(\phi)}{R}\frac{d}{dt}\{p(t-R/v)\} + \frac{G_2(\phi)}{R}q(t-R/v)\right]\begin{bmatrix} \cos\phi \\ \sin\phi \end{bmatrix}, \tag{13b}$$

the SH-wave,

$$v_{SH} = \frac{K(\phi)}{R}\frac{d}{dt}\{s(t-R/v)\}. \tag{13c}$$

The coefficients (12) which enter into equations (13) and describe the angular variation of the amplitude of the radiated P, SV, and SH waves with the angle ϕ, are graphed in Figures 2–4.

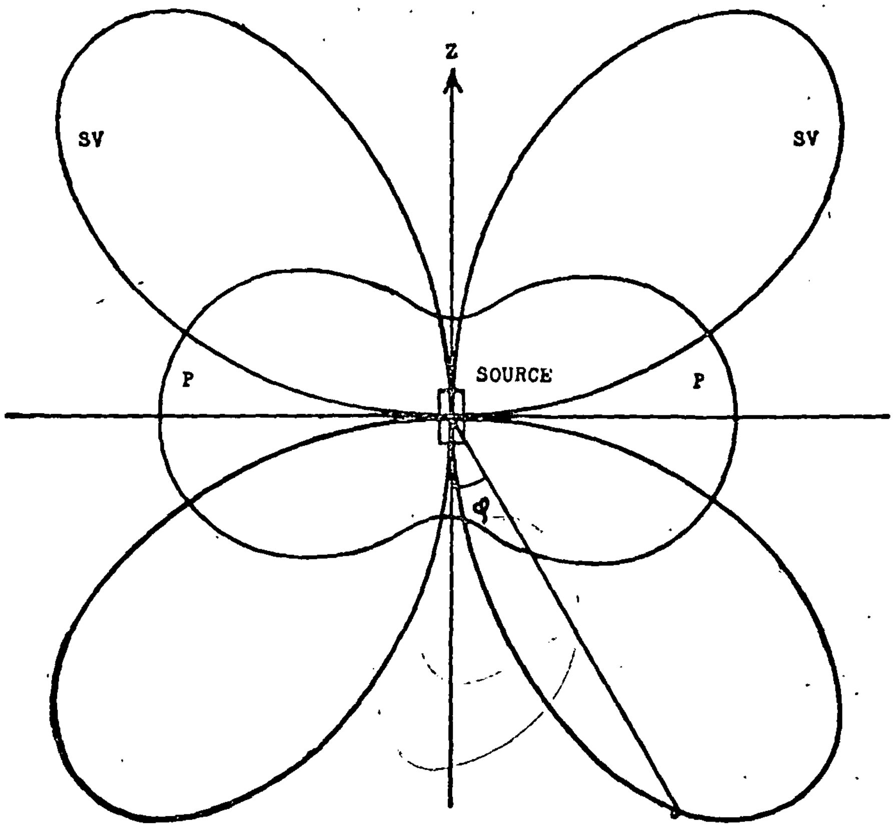

FIG. 2. Variation of P and SV amplitudes with ϕ, when the source is subjected to a pressure $p(t)$ only. Radii in the figure are proportional to $F_1(\phi)$ (in the case of P), and to $F_2(\phi)$ (in the case of SV) *cf.* equations 12a, 12c, 13a and 13b.

Energy radiated from the source in P, SV, and SH.—If Φ_{ij} is the stress tensor of the radiating field, u_j the components of the particle displacement, then, the rate of flow of energy per unit area in the direction of the unit vector n_i is

$$-\sum_j n_i \Phi_{ij} \frac{d\mu_j}{dt}.$$

Integrating this formula over the infinite sphere and also throughout the duration of the disturbance, the total energy of the different waves is obtained. For the P-wave, the total energy E_P is the sum of two parts, E_P' due to the lateral pressure $p(t)$ acting on the source, and E_P'' due to the shearing stress $q(t)$. Thus,

$$E_P = E_P' + E_P''$$

where

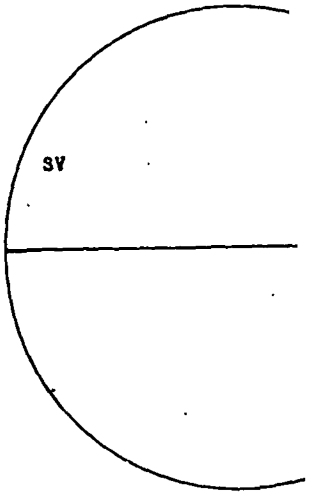

FIG. 3. Variation of P and S
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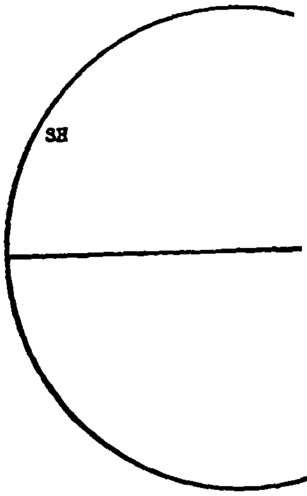

FIG. 4. Variation of SH amplit
stress $s(t)$ only. Ra

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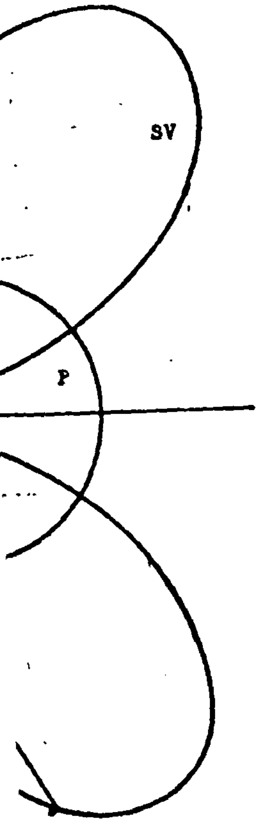

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Φ$_{ij}$ is the stress tensor
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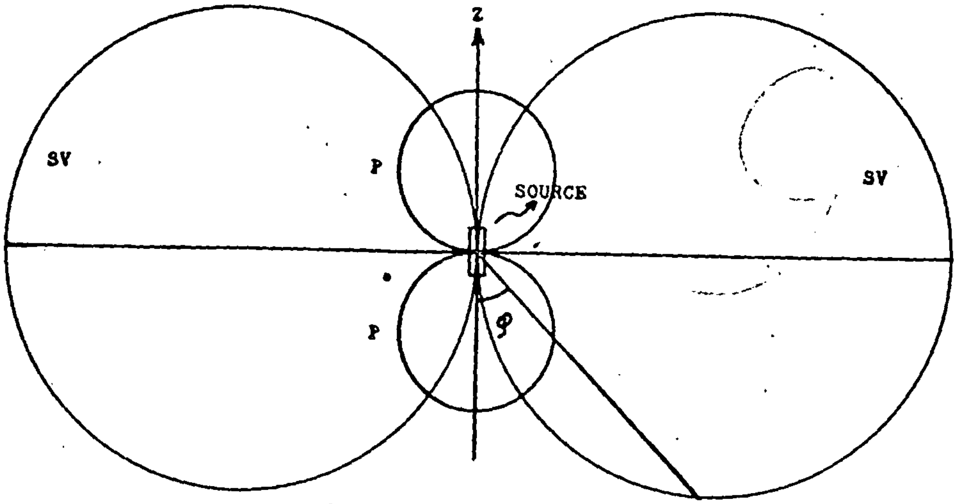

FIG. 3. Variation of *P* and *SV* amplitudes with ϕ, when the source is subjected to shearing stress $q(t)$ only. Radii are proportional to $G_1(\phi)$ (in the case of *P*), and to $G_2(\phi)$ (in the case of *SV*); *cf.* equations 12b, 12d, 13a, and 13b.

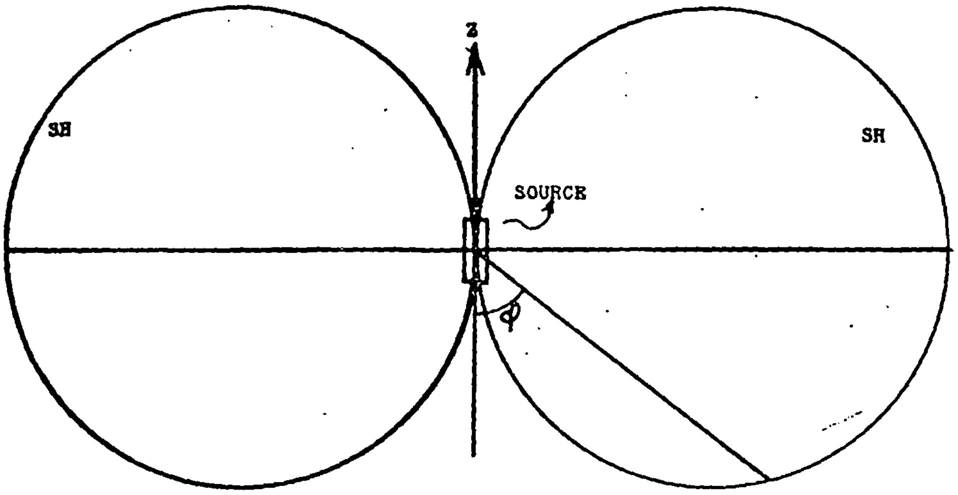

FIG. 4. Variation of *SH* amplitude with ϕ, when the source is subjected to a horizontal shearing stress $s(t)$ only. Radii are proportional to $K(\phi)$; *cf.* equations 12e and 13c.

$$E_P' = \frac{\Delta^2 P^2}{4\pi\mu V^3}\left(\frac{2v^2}{5V^2} + \frac{V^2}{2v^2} - \frac{2}{3}\right),$$

$$E_P'' = A^2Q^2v^2/12\pi\mu V^3,$$

and

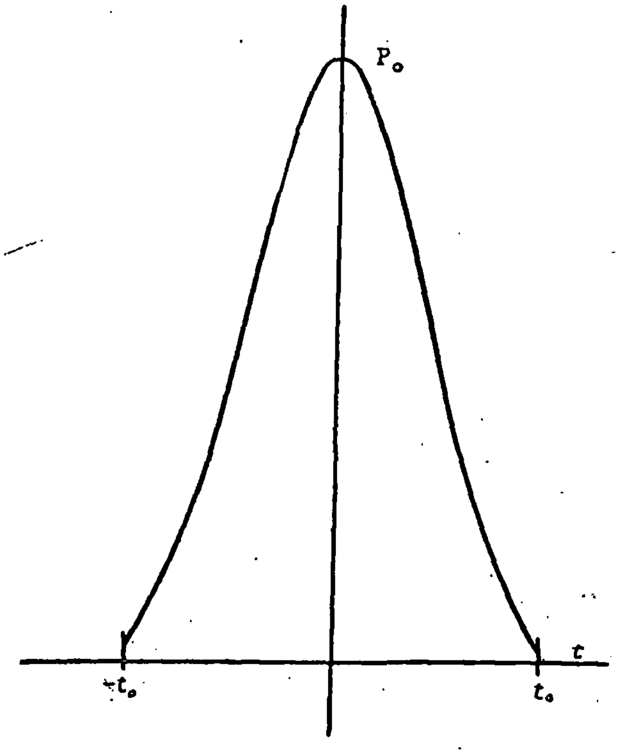

FIG. 5. $p(t) = P_0 \exp.(-\pi t^2/t_0^2)$.

$$P = \int_{-\infty}^{+\infty} [p''(t)]^2 dt,$$

$$Q = \int_{-\infty}^{+\infty} [q'(t)]^2 dt.$$

For SV, the total energy E_{SV} is similarly constituted, E_{SV}' being due to the lateral pressure $p(t)$ at the source, and E_{SV}'' to the shearing stress $q(t)$. Thus,

$$E_{SV} = E_{SV}' + E_{SV}''$$

where

$$E_{SV}' = 2\Delta^2 P^2/15\pi\mu v^5,$$

and

$$E_{SV}'' = A^2 Q^2/6\pi\mu v.$$

The energy of SH is due entirely to the horizontal shearing stress $s(t)$ acting at the source, and is,

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[11] *Cf.* H. Jeffreys, *Report*

E_{SV}' being due to the
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$$E_{SH} = \Delta^2 S^2 / 6\pi\mu v^3,$$

where

$$S = \int_{-\infty}^{+\infty} [s''(t)]^2 dt.$$

DISCUSSION OF RESULTS

We have tried to reproduce, in mathematical form, the disturbance generated by the detonation of a charge in a cylindrical shot hole. The quantities a and l are not the physical dimensions of the bore hole in which the charge is detonated. Conditions in the immediate neighborhood of the shot hole are such that the assumptions upon which our work is founded, in particular the assumption of infinitesimal strain, are not verified in this domain. These quantities correspond rather to the dimensions of Sharpe's "equivalent cavity."[9] This is the smallest surface about the shot hole beyond which the medium is "perfectly elastic" to the disturbance. Morris[10] says that it is "determined by the position at which no further work is done on the medium by the shock wave." The form of the "equivalent cavity" determines to a large extent the characteristics of the elastic waves generated by the source.

The partition of energy between the dilatational and shear waves generated by the application of a lateral pressure $p(t)$ to the walls of a cylindrical source is a problem of special interest as it represents the ideal case of a charge detonated in a shot hole. In this case,

$$\frac{E_P'}{E_{SV}'} = \frac{v^3}{V^3}\left(\frac{3v^2}{2V^2} + \frac{15V^2}{8v^2} - \frac{5}{2}\right). \tag{14}$$

For a Poisson solid, (14) implies that approximately 60 percent of the energy goes into SV and only 40 percent into P. Moreover SV is beamed in directions making angles of 45° with the axis of the source (see Fig. 2), with maximum amplitude 1.6 times the maximum amplitude of P.

These results at first sight cause some surprise. It has often been said that artificial disturbances generate little shear energy.[11] Actually this is not always the case. Wiechert, Brockamp, Wölcken, Jeffreys and others have reported shear waves of large amplitude present in the seismograms of large explosions. Seismograms of local blasts occurring within, say, 20 km of Florissant often contain a powerful SV phase. Whether this phase is of primary origin, originating at the actual source, or of secondary origin, due to a change in type somewhere along

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[9] J. A. Sharpe, "The Production of Elastic Waves by Explosion Pressures: 1. Theory and Empirical Field Observations," *Geophysics* VII (1942), 144–154.

[10] G. Morris, "Some Considerations of the Mechanism of the Generation of Seismic Waves by Explosives," *Geophysics*, XV (1950), 61–69.

[11] *Cf.* H. Jeffreys, *Reports on Progress in Physics*, 10 (1944–1945), 79.

the trajectory of the ray, is still not clear. The theory given in this paper indicates, at any rate, that this SV phase is actually of primary origin. Moreover the theory shows that a characteristic of this wave is that it is channelled in certain directions. The low intensity of shear waves on some blast records may be merely indicative that the seismometer is located outside the range at which the SV-cone of energy reaches the surface. Little use so far has been made of shear waves in seismic prospecting, as their late arrivals are usually obscured by much background noise. Should it be practicable, however, to use these waves, the existence of the beamed SV-wave might prove to be of some importance.

The absolute magnitude of the total energy radiated by the action of the pressure $p(t)$ is, as we have seen, proportional to

$$P = \int_{-\infty}^{+\infty} [p''(t)]^2 dt.$$

The total amount of radiated energy depends in this case upon the double rate of change of the applied stress. Assuming that

$$p(t) = P_0 \exp(-\pi t^2/t_0^2) \text{ (see Fig. 5)},$$

then

$$P = 3P_0\pi^2 2^{-\frac{1}{2}} t_0^{-3};$$

and thus,

$$E_P' = \frac{3\pi\Delta^2 P_0^2}{2^{1/2}\mu V^3 t_0^3}\left(\frac{v^2}{5V^2} + \frac{V^2}{4v^2} - \frac{1}{3}\right),$$

where Δ = volume of the "equivalent cavity," P_0 = maximum pressure at the source.

E_P', E_{SV}' and E_{SH}, being proportional to t_0^{-3} increase very rapidly with decrease in the duration of the impulse. Moreover, the total energy radiated by such a source is proportional to the product ΔP_0. The observations of Sharpe[12] and Morris[12] help to confirm these conclusions.

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[12] *Op. cit.*

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Methods of recovering low-cost copper by precipitation from dilute solutions is lucidly reviewed. Alternatives to cementing on scrap, a high-cost practice, are studied. The author also examines work which has been performed in other chemical methods of precipitating copper from solutions. Certain health hazards are pointed out and a system of automatic control is proposed.

THE RECOVERY OF COPPER FROM DILUTE

Treating copper ores by heap-leaching and similar hydrometallurgical means is a time-honored practice,[1] which was well known even in the 19th century. Later the method lost ground to better ore dressing processes, particularly selective flotation. More recently there has been a distinct reversion to leaching techniques, particularly for scavenging operations in old mining stopes, in connection with LPF systems, irrigation of tailings dumps and similar situations. These hydrometallurgical techniques will gain further ground because processing is simple and permits better extraction of copper, particularly from low-grade or partly oxidized ores.

In the lixiviation of primary ores at some major operations, copper- bearing liquors may undergo recirculation in heap-leaching arrangements or the ores may be subjected to systematic percolation treatment. The liquors resulting from this source usually are quite strong (above 10 gpl copper) and copper would normally be reclaimed by electrowinning or cementation. These processes fall outside the scope of this paper which is concerned with recovery of copper from weak liquors containing from 0.1 to about 3 gpl copper.

Total production from such dilute process streams is probably less than 100,000 tons of copper per year and so it is not a major factor in world copper supplies. On the other hand, this source of the red metal is more important to the copper mining industry than production statistics would indicate because it is low cost copper with a high profit margin.

All weak cupriferous streams whether from natural mine waters, artificial irrigation of old workings or run-offs from tailings dumps, have common characteristics. They are usually quite acid and contain little copper but much iron. Despite such unprepossessing appearances they can be reclaimed for less than 10¢ per lb. The reason is that residual copper in old stopes, tailings, etc., carries no book value and any metal thus available, more or less fortuitously, is to be had cheaply. In consequence, the copper mining industry obtains a gross return from such scavenging operations which, on a worldwide basis, must be of the order $20 million annually. This figure is subject to the usual deductions for refining and realization charges, overheads, taxes, etc. Approximately, each gallon per minute of an effluent carrying 1 gpl Cu is worth $1000 per year.

PRECIPITATION ON SCRAP IRON

This is the most common method of treating mine waters. The main parameters governing plant design are: contact time, water velocity and launder volume per unit of copper reclaimed. These of course are interdependent with the copper content of the process stream. Table 1 indicates how the design factors vary considerably from plant to plant, as does the copper content of the head and tailing waters. Within certain limits, the prime consideration is volume of launder space in relation to cement copper production, or the size of a given plant is governed less by the water volume to be handled than by the copper content of these waters. From the point of view of turbulence and adequate diffusion, a relatively high water velocity is preferable, provided that contact time does not suffer.

Centralized precipitation plants on surface fall into two groups, the zig-zag launder and the straight

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J. S. JACOBI, Member of AIME, is Director of Research, Cerro de Pasco Corp., La Oroya, Peru. Article is abridged version of paper presented at AIME Annual Meeting, Dallas, 1963. Entire paper will be published in *Proceedings of International Symposium on Unit Processes in Hydrometallurgy* to be issued in early 1964.

by J. S. JACOBI

PROCESS STREAMS

line arrangement. The zig-zag arrangement is more compact and somewhat cheaper to operate but is less flexible for adding to the water volume. In this case contact time may be maintained by adding zig-zag launders to the system, but velocity will be raised in proportion and may lead to difficulty with suitable falls. Inadequate slopes are difficult to correct in an existing plant. The straight line launder lends itself to the addition of parallel units, if scrap iron is fed by mobile cranes with clam shells or electromagnets instead of overhead gantrys formerly in vogue.

At Cerro de Pasco, copper reclamation from mine water is still underground in a channel along a main drift on the 1400 ft level. All pregnant waters are pumped from lower levels or gravitate from higher levels to this ditch which is about 1200 ft long. By centralizing activities, considerable labor savings have resulted and operations have been streamlined at practically no capital cost. Scrap iron still has to be taken underground but is easily dumped into position from ore cars. Mine waters are segregated and the water volume treated cut from 1800 gpm to 500 gpm. However, segregation is not perfect and "barren" waters are recombined with the tailing water and pumped to the surface by a single system for scavenging treatment in surface launders. This arrangement, although satisfactory, is not the final answer and a new surface precipitation plant is under study.

Another system which has been studied but not put into practice is the use of an old mine shaft into which scrap iron is dumped. Laboratory testing showed that adequate stripping of the mine waters can be achieved by a single pass through a packed depth of 65 ft which was calculated to give a contact time of 45-50 min. Percolating mine water at 10 gpm per sq ft of cross-sectional area, the copper content was reduced from 2.4 to 0.01 gpl. Surprisingly no ill effects were observed from aeration which of course cannot be avoided under these conditions. A vertical column is good in theory but compaction of the scrap iron could lead to inadequate liquor distribution.

SCRAP IRON CONSUMPTION

Although scrap iron is almost universally used for cementing copper, it is expensive, particularly in isolated localities. Most light sheet metal off-cuts are lacquered and have to be burned, shredded or otherwise prepared which adds to the expense. In the future light scrap supplies may be contaminated with aluminum cans, satisfactory for cementation but a serious toxic risk. Mine scrap, such as old castings or rail, have small surface or high carbon content and are not effective precipitants; they can be used gradually in the first launder sections where the acidity is high. The best scrap must go to the final or scavenging sections. Even so, scrap iron alone cannot reduce the copper content of the tailing to less than 60 mgpl Cu without resorting to artificial agitation.

Scrap iron consumption varies mostly with ferric iron content of the pregnant waters because it must be reduced to the ferrous state and much free acid must be killed before precipitation of copper can take place. In practice a good working figure for effluents containing ferric iron is 2 lb scrap per lb Cu precipitated. Pyrrhotite has been found to be an effective reducing agent for ferric iron, and pilot tests have confirmed this. By leaving pregnant mine waters in contact with lump pyrrhotite ore for three hours all iron was reduced to the bivalent condition and scrap iron consumption was cut down to 1.25 lb scrap per lb of copper precipitate.[1] The reaction is:

$$Fe_7S_8 + 32\,H_2O + 31\,Fe_2(SO_4)_3 \rightarrow 69\,FeSO_4 + 32\,H_2SO_4$$

According to the above reaction 1 lb of pyrrhotite would have the same reducing power as 2.68 lb of scrap iron. In actual fact it was found that 1 lb of pyrrhotite will replace from 1.5 to 2.2 lb of scrap depending on the grade of pyrrhotite used.

Pyrite did not have the same reducing effect as pyrrhotite, even with air rigidly excluded. Yet from time to time a curious phenomenon has occurred whereby *metallic* copper seems to have precipitated on truly pyritic mineral in the mine but such occurrences are rare and it has been impossible to reproduce them in the laboratory. Nor is such a reaction thermodynamically probable. The coating of pyrite or sphalerite by copper *sulfide* is a contingency that one must always bear in mind when irrigating old stopes with near neutral waters containing dissolved copper.

Roaster gases containing sulfur dioxide can be used for conditioning mine waters. This can be done for instance in a normal gas scrubber system. Incidentally the irrigation of roaster gases with oxidized mine waters may help to overcome, at least partially, a nuisance from sulfur dioxide emissions. Small scale experiments,[2] contacting actual mine waters and roaster gases containing about 9% SO_2 in stoichiometric proportions, showed that most of the sulfur dioxide can be absorbed and most of the ferric iron reduced in a simple scrubber system of modest proportions. Again the net effect in mine

Table 1. Comparison of Several Copper Precipitation Plants

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H
Launder system	Zigzag	Straight ine	Straight line	Zigzag	Zigzag	Zigzag	Zigzag	Zigzag
Mine water flow, gpm	2,500	840	5,000	590	1,360	276	2,000	1,000
Copper content, gpl Cu head waters	0.85	2.04	0.31	2.41	3.30	1.2	1.2-2.4	2.0
Tailings waters	0.022	0.06	0.016	0.067	0.36	0.09	0.012(?)	0.10
Copper recovered in launders, %	97.4	97.3	95	97.2	89.1	92.5	99—	90 (estd)
Daily production, lb fine copper	24,600	20,000	18,000	17,100	48,000	3,600	57,000	22,900 (calc)
Number of launders	16 double	200 single	20 single	3 6 comp.	40 single	8 single	24 double	12 double
Length per launder, ft	40	16	100	64	40	34	25	12
Cross-section above grid								
Width, ft	1 2/3	2 2/3	10	10	5	6	8	8
Depth, ft	5	2 2/3	3	6	3	4	4	4
Total effect launder vol, cu ft	64,000	21,362	54,000	69,120	16,000	6,530	28,500	9,216
Launder vol to Cu produced, cu ft per lb per day	2.6	1.1	3.0	4.0	0.33	1.81	0.5	0.42
Velocity of mine water, fpm	6.7	32.0	6.5	1.3	7.3	1.5	10	4.2 (8.4 after expansion)
Contact time, min	192	50	78	875	88	181	61	69

A: Inspiration Copper.[7]
B: Ohio Copper[2] (Bingham Canyon).
C: Anaconda, Butte.[3]
D: Andes Copper.[1]
E: Cananea.[4]
F: Small instn in South America.
G: Large instn in North America.
H: Proposed surface plant at Cerro de Pasco.

waters treatment is a marked lowering in scrap iron consumption.

$$Fe_2(SO_4)_3(aq) + SO_2(g) + 2\,H_2O(l) \rightarrow 2\,FeSO_4(aq) + 2\,H_2SO_4(aq)$$

F — 28.9 kcal per Mol

A relatively low acidity assists the reaction, while low oxygen concentration is essential; otherwise the "autoxidation" reaction takes over:

$$SO_2(g) + 2\,FeSO_4(aq) + O_2(g) \rightarrow Fe_2(SO_4)_3(aq)$$

F — 68.9 kcal per Mol

The latter reaction can, of course, be helpful for leaching but it is quite detrimental in the cementation stage.

SPONGE IRON AND SIMILAR PRECIPITANTS

Indications are that use of scrap iron will gradually decline in favor of sponge iron. Sponge iron is being used on an increasing scale for leach-precipitation-flotation systems and its use has contributed markedly to the extraction of copper from partly oxidized ores. In LPF plants the sponge is used in the finely divided state, often after magnetic up-grading. A similar technique could be applied to mine waters but it would mean contacting in agitation vats which is relatively costly. Assume an effluent containing 1 gpl Cu at a rate of 2000 gpm. With a contacting time of 30 min a total agitator volume of 60,000 gal is necessary. Counter current contacting being impractical, precipitant must be added to each agitator in series; there should be some excess sponge in the system in the final agitator to avoid any re-solution of copper.

A pelletized sponge can be made by roasting pyrite pellets in a fluidized bed (the roaster gases can be used for pre-conditioning mine waters) after which the pyrite cinders, still in the pelletized form, are converted to sponge iron by gaseous reduction, also in a fluidized bed.[3] In this way a particulate product can be obtained which contains 80% metallic iron and has an approximate particle size of ¼ in. diam. While normal cementation launders are not suitable for this type of precipitant, the material can be readily handled in jigs. For a prolonged test run a converted coal jig of the fixed-bed type is used and the results obtained are distinctly encouraging regarding contact time and copper content in final tailing. Sponge consumption was similar to that of scrap, based on the content of metallic iron in both materials. Incidentally, jig agitation was also found to be useful when practicing cementation on scrap iron. For a scavenging operation involving partly decopperized waters a retention time of only 10 min is recommended to strip the water down to less than 30 mgpl Cu (see Table 2).

The economics of preparing sponge iron pellets depends on the raw material at hand. At Cerro, available pyrite contained 10 oz per ton Ag, plus a small amount of copper; the silver, recovered in the copper refining circuit, defrayed the sponge costs.

Table II. Copper Recovery in Pilot Jig with Different Types of Scrap Iron

	Feed Water Strength—mgpl Cu			
	852	230	212	120
Lacquered offcuts—burned	92.9% (25)	90.9% (21)	87.5% (27)	79.1% (25)
Galvanized iron and clean tinned scrap	90% (35)	86.5% (31)	85.3% (31)	79.1% (25)
Old tin cans (used)	91.8% (29)	85.6% (33)	84.1% (34)	72.7% (33)
Black steel	86.1% (49)	82.2% (41)	87.5% (27)	75.9% (29)
Lacquered offcuts—unburned	87.4% (44)	67.5% (75)	67.5% (69)	

Figures in ( ) denote copper content of jig discharge in mgpl Cu; contact time 10 min in all tests.

An interesting scheme, which Cerro has studied and piloted rather extensively, is the preparation of sponge iron from zinc leach residues.[4] These zinc leach residues arise from the treatment of marmatitic (high-iron) zinc concentrates in the electrolytic zinc refinery. They are in essence a crude zinc ferrite carrying all the silver and lead present in the original concentrates. The leach residue slurry is thickened and filtered; after partial drying the filter cake is pelletized with anthracite or similar low volatile fuel. A rotary kiln treatment volatilizes all the zinc, lead, indium and cadmium plus a minor portion of the silver. This zinc fume is recycled to the zinc refining circuit and all the metals are recovered. The kiln residue consists of a crude sponge carrying the iron, copper and most of the silver. When withdrawn from the kiln it has a metallic content of around 40% Fe. It remains in the pelletized state throughout and thus effectively prevents accretions in the kiln.

This crude sponge can be used for the cementation of copper from mine waters, etc., directly; alternatively it may be up-graded by retorting or by crushing and magnetic separation. In the former case the resulting cement copper will be of relatively low grade, particularly if the original zinc concentrates carry more than 1% of insoluble gangue all of which will report in the kiln product. Although contaminated by various inert fillers, the sponge is an active precipitant for copper. Unlike scrap iron the sponge also will precipitate metallic lead from chloride solutions.[5]

While pelletized crude sponge acts extremely well when contacted with mine waters in a jig of the plunger type, for industrial operation a moving bed jig is preferable. Jig agitation promotes a continual cleaning of the active iron surfaces and achieves close contact of fresh sponge with copper-bearing liquors, hence the favorable retention time. This very fact entails a certain disadvantage: while much of the cement copper collects in the jig hutches, some is carried over into the effluent stream where it has to be separated either by thickeners of the conventional type or by hydroclones. Inasmuch as some of the cement copper is of fairly fine particle size (5μ or less) cyclone separation at modest pressures seems not too effective; sedimentation, however, is rapid when assisted by the addition of some proprietary coagulant.

Nevertheless it must be stressed that re-solution of some copper during thickening can and does occur, particularly when jig overflow has been stripped to a point where it carries less than 50 mgpl dissolved copper. Speed is of the essence in this clarification step and final tailing losses should always be calculated on dissolved plus suspended copper. In some cases it may be advantageous to add a little ground sponge iron to the thickener for added protection; this may be separated later by a magnet for re-use. In other situations where the final tailing waters are recycled over leach dumps etc., the problem may not be significant. One thing is certain; a mechanically agitated cementation device will produce a cement copper of finer grain than a more or less stagnant launder system filled with scrap iron. The grain size of the cement copper is also much affected by the strength of mine water and by final acidity; at a high pH a much coarser cement product results.

Other forms of iron may become available for purposes of copper cementation: recently there appeared on the market a granulated pig iron which would be handled equally well in launders or in jigs but, being a chilled iron, the carbide content makes it rather unreactive. By contrast Cerro's sponge iron contains much carbon but little carbide, having been produced in a kiln at relatively low temperatures. An interesting type of iron intended for cementation of copper is under development by one of the big copper producers. It is made from a special copper converter slag exceptionally low in silica; this is subsequently granulated and reduced to the metallic state. This material may contain up to 5% Cu which, of course, would be recoverable when the product is used for cementation purposes.

CEMENTATION OF COPPER BY REDUCING GASES

Cementation of copper powder by hydrogen, particularly from ammoniacal solutions, has received much publicity recently but no attempts are reported to apply these relatively costly pressure processes to dilute effluents such as mine waters.

CATHODIC PRECIPITATION OF METALLIC COPPER

There appears to be little scope for reclaiming copper by direct electrowinning from solutions containing concentrations below 5 gpl. Metallurgists have reported copper refining at high current densities using a system of so-called channel electrolysis, whereby the copper electrolyte is swept past the cathodes at high velocity. Research workers at the USBM have gone even further in effecting electrodeposition at extremely high current densities with the aid of ultrasonic vibrations. In neither case have there been reports of applying such methods to dilute electrolytes, but it is easy to extend the principle in this direction. The only impediment is the limiting factor of diffusion rates which in turn leads to polarization and excessive hydrogen evolution at the cathode. If thickness of diffusion layer can be reduced sufficiently through violent agitation of the electrolyte, electrowinning of copper may become quite commonplace from mine waters containing copper in the mgpl range. The copper would be in the form of a fairly pure metallic sponge, to be refined without further smelting treatment or even, to follow a more recent development, to be compacted directly into commercial shapes. Depending on the composition of the electrolyte, acid and/or ferric sulfate would be regenerated at the anode; this could be useful in cases where the de-copperized waters are to be recycled over leach dumps.

Indirect electrowinning of copper from mine waters is, of course, perfectly feasible, after preconcentration by one of the methods described below.

PRECIPITATION OF COPPER COMPOUNDS

Ground limestone or burnt lime has been used as a "simple" way to precipitate copper from low-grade effluents. It has been claimed that iron can be separated from dissolved copper by neutralizing the liquors with ground limestone. This approach may be quite suitable where the ratio of iron to copper in solution is low (a rare case indeed) or where the principal object of the treatment is to prevent an effluent nuisance from acid or from soluble sulfates. This situation confronted a major copper mining operation in Chile and neutralizing the noxious discharge waters with limestone proved to be the answer. On the other hand, if it is desired to reclaim the most copper at the lowest cost, then this kind of procedure has little to recommend it. The precipitate will consist mainly of basic iron salts and calcium sulfate and will be awkward to handle; since the copper content of the precipitate will be quite low, the amount to be treated will be prohibitive.

Precipitation of copper sulfide has been mentioned in the literature; it may have its place in certain special situations, e.g. if crude natural gas happens to be on hand. Another proposal of interest is the precipitation of cuprous thiocyanate, which is decomposed to cuprous oxide with simultaneous regeneration of the expensive thiocyanate radicle. This scheme calls for the addition of sulfur dioxide gas to the mine waters. Some pilot tests were carried out but it was found that the cuprous compound was not nearly as readily filtrable as its inventors claimed. Also the consumption of caustic soda, which is used to regenerate an alkali thiocyanate, seemed a little costly. Lime may be used in place of caustic soda but this entails a secondary flotation step to separate the insoluble salt from cuprous oxide.

PRECONCENTRATION OF DILUTE PROCESS STREAMS

A clean separation of copper-rich streams from *barren* water, before processing is difficult. First, in the case of mine waters collected underground it is quite difficult to separate water streams which are absolutely barren. Second, cement copper is low-cost copper and the aim is maximum metal recovery even though it may mean processing larger volumes of liquor. Even labor productivity may be sacrificed to obtain maximum metallurgical efficiency. In a typical case, labor cost for a cementation operation would be about one tenth of the value of recoverable copper. Measures which reduce labor cost by a third must not lead to a lowering of metal recovery in excess of 3%, otherwise a loss in contribution results.

Also the capital cost and operating expense of most precipitation plants tend to be governed by the amount of copper produced, not by the water volume handled. A typical cost pattern would be expressed by a formula such as:

$$\text{Operating cost per pound of copper} = A + \frac{B}{q}$$

where A and B are constants and q denotes the concentration of copper in the mine water. A numerical example given in Table III demonstrates that it would be unsound to reject weak liquors unless they contain less than 79 mgpl Cu, while the actual cut-off point for waters without separation is a little lower still at 57 mgpl Cu.

It is often thought that, by splitting off water streams which carry next to no copper, a strong but barren lixiviant may be obtained for surface heap leaching. This surmise seems reasonable if one deals with water percolating through a pyritic orebody where it should pick up no copper but plenty of ferric iron. At the Cerro de Pasco mine results were disappointing in this respect: extensive sampling has proved beyond doubt that the Fe:Cu ratio in all water streams for various parts of the mine remains more or less constant.

Subject to the limitations outlined above it is agreed then that the mining engineer should avoid indiscriminate mixing of effluents which nature has kept apart. More often the problem is that of splitting up a dilute and truly homogeneous solution into a concentrated electrolyte and into fresh water. In this field there are distinct opportunities for technical development. The principle of separating sea water into potable water and residual brine is exactly analogous to that of enriching dilute sulphate liquors by abstracting fresh water from the system.

There are various processes to provide fresh water suitable, if not for human consumption, at least for irrigation purposes, at a cost of around $0.50 per 1000 gal. When dealing with mine drainage waters the first consideration would be to recover the heavy metals, particularly copper, but there may be many situations where the co-produced fresh water would be a distinct asset for use in concentrators etc. The problems of cost may not be insuperable. Assume fresh water can be separated at the figure mentioned; for a mine effluent containing 1 gpl Cu this would be equivalent to 6¢ per lb of copper. It could be worth that much to obtain the copper in a concentrated electrolyte from which the metal can be obtained by electrowinning. Free acid and zinc would also be recoverable and on the credit side there would be fresh water.

Table III. Effect of Splitting Mine Water into Processing and Discard Streams

Assumptions: Original water contains 0.25 gpl Cu. Cost of cement copper $= 3.0 \pm \frac{1.25}{q}$ ¢ per lb fine copper, where q = copper content of water in gpl

Mine water strength, gpl Cu	(0.057)	(0.10)	0.25	0.50	1.00	2.00	5.00
Cost, ¢ per lb fine copper recovered	(25.0)	(15.5)	8.0	5.5	4.25	3.625	3.25
Gross return, ¢ per lb fine copper recovered	(0)	(9.5)	17.0	19.5	20.75	21.375	21.75
Recovery, % (based on constant tallings value of 0.030 gpl Cu)		(70)	88	94	97	98.5	99.4
Gross return, ¢ per lb copper in mine water at different ratings of discard stream:				→ Segregation sound ←			
Discard stream: 0.00 gpl Cu			14.96	18.33	20.13	21.05	21.62
0.03 gpl Cu				17.16	18.26	18.81	19.14
0.05 gpl Cu				16.29	16.95	17.27	17.47
0.08 gpl Cu				14.84	14.88	14.91	14.94
0.10 gpl Cu				13.75	13.42	13.30	13.24
0.15 gpl Cu				10.47	9.47	9.10	8.92
				→ Segregation unsound ←			

Example: Mine water containing 0.25 gpl Cu will give a gross return of 14.96¢ per lb of copper contained. If this is split into a processing stream (2.00 gpl Cu) and a discard stream (0.10 gpl Cu) the monetary return is reduced by 14.96¢-13.30¢ or 1.66¢, equivalent to a loss of 11.1%.

Table IV. Ion Exchange Pilot Plant. Summary of Operating Results

	Single Column	Two Columns in Series
Overall testing period, mon	11	7
Net operating time, hr	6,363	3,492
Operating time, % of total	80.3	89.8
Total mine water treated, gal	3,099,100	1,819,200
Mine water fed per hour, gal	487	521
Copper in raw mine water, gpl	0.277	0.264
Copper in feed to I.E. columns, gpl	0.243	0.220
Copper in discharge from I.E. columns, gpl	0.006	0.012
Copper intake to plant, lb	7,163	4,013
Copper recovery (columns only), %	95.9	91
Copper recovery (whole plant), %	83.5	74.3
Copper lost during conditioning, %	12.4	16.7
Copper lost in column discharge, %	2.0	4.4
Copper lost in spent electrolyte, %	2.1	4.6
	100.0	100.0
Copper in eluate, gpl	9.80	10.49
Concentration ratio, eluate: feed	38:1	36.8:1
Iron in raw mine water, gpl	4.38	5.12
Iron in feed to I.E. columns, gpl	3.43	4.27
Iron in eluate, gpl	8.62	14.37
Copper:iron ratio in column feed	1:14.1	1:19.4
Copper: iron ratio in eluate	1:0.88	1:1.37
Iron rejection, %	92.4	95.3
Reagent consumption per pound copper		
Limestone (74.5% $CaCO_3$), lb	21.54	16.26
Burnt lime (61.9% av. CaO), lb	10.89	10.70
Sulfuric acid (66°Bé), lb	11.74	7.45
Resin, cu ft	0.0010	0.0021
Power consumption DC—kwh per pound copper	3.80	2.79
Current efficiency, %	33.2	50.8

One technique of this kind which deserves special mention is that of electrodialysis. It is heartening to report that this was pioneered by one of the big mining groups, not so much for recovery of metal values but to combat a fresh water shortage.[6] Many dissertations on the possibilities of using this method—both for generating fresh water and for chemical processing—continue to appear in the technical press.[7-10]

Bench scale tests are being conducted by Cerro on the concentration of mine waters by electrodialysis. The objective is a limited one which fits into the local picture at the Cerro de Pasco mine: a lead-zinc mill is situated close to the minehead which uses copper sulfate for zinc activation. Money could be saved if instead of shipping cement copper to the smelter at La Oroya and returning copper sulfate to the concentrator, a fairly concentrated copper sulfate liquor was piped directly from the mine to the mill. This would also make available a corresponding quantity of copper sulfate for outside sale. In this case, the goal is enriched mine water containing at least 10 gpl Cu. Only about one tenth of the copper arising in the total mine water flow would be needed for this particular scheme. Therefore since it is not necessary to make a good copper recovery in the electrodialytic system, the tailing stream would simply be added to the cementation launders or jigs. So far the copper has been upgraded 2 gpl in the feed stream to about 8 gpl in the transfer stream. Ferric iron in the feed gives rise to various difficulties with the membranes and electrodes, but after reducing most of the iron to the bivalent condition, little trouble is experienced.

ION EXCHANGE AND RELATED PROCESSES

The application of ion exchange techniques has been extensively studied in Cerro research laboratories,[11,12]. This work established that cationic resins of the carboxylic type were the most promising, with regard both to selectivity and absorption capacity, for the particular mine waters treated. The raw waters, partly de-copperized in cementation launders underground, were passed through tanks filled with limestone to raise the pH to 3.5 which was found to be the highest permissible acidity consistent with good performance of the resins in the calcium form. During this pre-conditioning some ferric hydroxide was removed from the feed liquors. After clarification in sand filters the mine waters were passed through a three-column resin bed system as follows: two columns were connected in series, the resin in the first being loaded to capacity and that in the second column to the breakthrough point for copper. Meanwhile, the third column was eluted, treated with saturated lime water for resin regeneration and flushed out with fresh water to remove minor amounts of calcium sulfate formed during regeneration. This cycle permitted continuous operation and was quite satisfactory. The eluate contained about 10 gpl Cu and was subjected to cathodic stripping of copper, the acid electrolyte being returned to the system for resin elution.

Metallurgical results for this system are summarized in Table IV. The data quoted are not the optimum conditions established during this work but are the mean values covering the whole test period. A fair amount of resin degradation was encountered which was mechanical rather than chemical; this undesirable feature would put a distinct limitation on the ion exchange method as applied to a relatively low-value process stream. Work on this project was terminated in 1958 and it may be that better and cheaper resins are now available.

Solvent extraction has been advocated for stripping copper from mine effluents, but so far the method has not found industrial acceptance for this purpose, although, the simplicity of liquid-liquid exchange could surpass the usefulness of solid resins. Cost and limited selectivity of solvents have had a discouraging effect on development work so far. Naphthenic acid has been recommended as an inexpensive solvent; unfortunately it will work for copper only at pH 6 which seems to rule it out for acid waters with high iron content. On the credit side it is claimed that solvents of the alkyl hydrogen phosphate type are useful for sequestering zinc as well as copper, quite an important consideration in some mine effluents. Also when handling clear effluents, solvent losses would be limited to the true solubility of the organic phase in water; whereas in pulp treatment, losses by mechanical dragout preponderate.

Similarly the Sebba process of ion flotation[13,14], could have distinct possibilities for mine water treatment if only it can be made to pull the copper and zinc preferentially while keeping the iron depressed in solution. Certainly in cases where mine waters and similar effluents should happen to have a favorable copper to iron ratio, both liquid-liquid extraction and ion flotation deserve close scrutiny.

Ideally, the hydrometallurgist needs exchange media of maximum absorption capacity and selectivity; in most cases he would wish to operate under slightly acid conditions. Solid media should be resistant to mechanical abrasion, while liquid solvents should have a low viscosity, high specific gravity and next to no solubility in water. In addition the price must be right. Admittedly this is asking for quite a lot, but the growth of ion extraction techniques for dilute process streams will depend entirely upon the degree of success with which the organic chemist can approach such ideal specifications.

RISK OF EVOLVING ARSINE GAS

In cementation or cathodic reduction methods applied to acid process streams carrying small amounts of dissolved copper, there is a serious potential health hazard from the evolution of arsine gas.

In the Cerro de Pasco mine where the chief copper mineral is enargite, arsenic is always detectable in the mine effluents. Concentration normally ranges from 0.05 to 0.2 gpl As but on occasions samples have up to 1 gpl As. By introducing metallic iron it is perfectly possible to liberate arsine gas from this kind of water. Fortunately, no trouble has been experienced in underground cementation launders, which may be ascribed to the fact that they are usually placed along main drifts with adequate ventilation.

If sponge iron containing small amounts of arsenides is used for cementation of copper, arsine gas may also be generated. In Cerro's laboratory tests arsenic generated from sponge iron has not been detected.

A more potent hazard could arise in cases where aluminium cans enter the cementation system with scrap iron. This is a possibility and aluminium will liberate the deadly gas with considerable vigor.

The same problem crops up in intensified form during scavenging operations on copper refinery effluents where arsenic is always present in significant concentrations.

PROCESS CONTROL

It is of utmost importance that a copper recovery plant treating drainage waters and similar effluents be designed to work steadily and without interruptions. These waters will flow inexorably, regardless of plant breakdowns, labor disputes or slumps. Unless the mine is abandoned and flooded, there will always be drainage waters that cannot be stored or stockpiled for future treatment. Whatever process is adopted for reclamation of copper, reliability is the prime requirement for any plant design.

By the same token, analytical control of tailings waters must be given careful consideration, especially in cases where there is no effluent recirculation. This is an ideal case for automatic sampling and analysis coupled with recording of analytical results. Therefore, Cerro decided to develop a prototype automatic analyzer for copper effluents, more particularly for determinations in the range below 50 mgpl Cu.

A polarographic technique was first investigated but here a major difficulty was encountered because of the residual current caused by the high iron content of the tailings waters. It must be remembered that the Fe:Cu ratio in these tailings waters may be as high as 500:1. A colorimetric technique was then adopted which works as follows: the sample is diluted and EDTA is added to complex the iron in the mine water; a characteristic copper color is next developed by using diethyldiocarbamate stabilized with a colloid. These reagent additions are in liquid form and readily controlled by a small proportioning pump system. Next the sample is fed continuously through a colorimetric cell and the results are read directly from a commercial colorimeter, the scale being graduated in mgpl Cu. Actually this prototype is not truly continuous, but gives a sample reading automatically every five minutes.

A robust production model suitable for permanent installation at the mine head or tailing discharge point could be made up from commercially available components at a total cost of around $10,000 to $15,000. This would include the sampling system, reagent dosing, colorimeter, automatic readout and chart record of the results, coupled to an alarm system which comes into action if the copper content of the tailing water rises above a predetermined limit. This, of course, is much cheaper than the automatic X-ray fluorescence analytical control for mill pumps, and will be entirely adequate to prevent valuable copper being lost, quite literally, over the dam.

CONCLUSIONS

While copper in dilute mine effluents is not a major contributing factor to world production of the metal, it can be reclaimed at an attractive cost; the gross return from such scavenging operations to the mining industry is not negligible. Copper precipitation processes merit close metallurgical control and extraction efficiency must take precedence over other operating factors such as labor cost. Scrap iron is still universally used for the purpose of stripping copper from such dilute process streams but one may predict a tendency towards other precipitants, particularly argentiferous or cupriferous sponge iron. It is possible that recently developed techniques for sweetening sea water will find an application in the treatment of mine effluents. Ion exchange or liquid-liquid extraction will make little progress until such time as the cost of reagents can be lowered or degradation in use be reduced.

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Ranchers Detonates Large Blast at Big Mike Mine in Nevada

Total of 550,000 tons blasted to start unique copper leaching operation

About 550,000 tons of copper ore and rock were blasted into the Big Mike open pit mine in Nevada on July 10 with 400,000 lb. of explosive to initiate a unique copper leaching operation. The blast was detonated at Ranchers Exploration and Development Corp.'s copper mine 30 miles south of Winnemucca. Personnel from the du Pont company were in charge of emplacing and detonating the explosive.

The explosive was used to shatter about 325,000 tons of copper ore in the walls of the open pit and about 75,000 tons of ore in the bottom of the pit. In addition to the ore, which contains about 2% copper, 150,000 tons of waste rock were shattered by the blast. The ore and waste, reduced to pieces averaging about 9-in. diameter, landed in the bottom of the 300-ft. deep pit. The pit is about 600 ft. in diameter.

Most of the explosive used in the blast was emplaced in about 175 drill holes situated at various points around the perimeter of the pit. Some of the holes were as far as 50 ft. from the edge of the pit and had a maximum depth of 300 ft. The remaining explosive was emplaced in about 75 holes in the bottom of the pit. Maximum depth of these holes was 100 ft. The explosive consisted of ammonium nitrate pellets and waterproof slurry gel. The shattered ore and rock will be leveled and terraced in preparation for leaching, expected to begin late in August. Leaching will be accomplished by sprinkling a solution of sulfuric acid and water on the ore at the rate of about 200 gal. per minute from ordinary lawn sprinklers.

This solution, which contains about 1% acid, will percolate through the crushed ore, gradually leaching the copper. The copper-bearing liquid will be drawn from the bottom of the ore heaps by a pump situated in a pipe-encased hole sunk about 150 ft. below the top of the ore heap. The leaching solutions will drain into the hole through a perforated casing at the rate of about 200 gal. per minute and will be pumped to a precipitation plant on the surface.

The unique operation, the first of its kind to produce copper by blasting ore into an open pit for heap leaching, is expected to produce about 5,000 lb. of copper per day for three years. The mine currently is producing about 5,000 lb. of copper cement daily from ore heaps that were created when some 95,000 tons of high grade ore were removed from the open pit in 1970 and shipped abroad. About 275,000 tons of lower grade ore were placed in heaps near the pit and have been under leach during the past several years.

Freeport Minerals Co. Names James H. McLean to Position

Joins Freeport as assistant to the executive vice president, J. G. Hall

JAMES H. McLEAN

James H. McLean has joined Freeport Minerals Co., New York City, as assistant to executive vice president, according to an announcement by John G. Hall, executive vice president. Mr. McLean came to Freeport from American Metal Climax Inc., for which he had been most recently manager of financial planning for the copper division. He has had more than 14 years of financial management experience in mining and related fields.

A native of Yonkers, N. Y., Mr. McLean received a bachelor of business administration degree in finance accounting and economics from Iona College in 1962. He is vice chairman of the New York section of the A.I.M.E. and is a member of the Mining Club.

JAPANESE STEEL OUTPUT

Production of raw steel in Japan during the first five months of 1973 amounted to 47,938,000 metric tons, up 27.8% from the like period of 1972 when 37,523,000 tons were produced.

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Rate of dissolution of vanadium(V) oxide in soda and ammonia solutions

Vl I Lutsik and Yu M Potashnikov (Kalinin Polytechnical Institute - Department of General Chemistry)

Vanadium(V) oxide is the most important vanadium compound, and its behaviour in dissolution processes is of interest for the chemistry and technology of vanadium. The literature devoted to the study of the equilibria of V_2O_5 in aqueous solutions of bases and acids is fairly extensive[1]). However, the information on the dissolution rates of V_2O_5 is very incomplete and is mainly qualitative in character[2]). There have so far been no researches into the kinetics of the dissolution of vanadium(V) oxide in compact form.

In the present work the kinetics of the dissolution of vanadium(V) oxide in aqueous solutions of sodium carbonate and bicarbonate and ammonia were investigated by the method of a rotating disc with equally accessible surface[3]) with orthogonal factorial experimental design[4]). The discs were prepared by cutting a cylindrical polycrystal 20mm in diameter obtained by directed crystallisation of molten V_2O_5 of specially pure grade (general porosity 2.5%). The effects of four factors on the dissolution rate of V_2O_5 were studied: the concentrations of the solvent v (g-eq/l), temperature T (°K), disc rotation rate n (rps), and the length of the experiment τ (sec). By representation of the operating factors in the form log c, 1/T, log n and log τ and with the logarithm of the amount of vanadium Q passing into solution from 1cm² of the disc surface as response function it was possible to transform the polynominal models of the V_2O_5 dissolution processes to the corresponding kinetic equations by involution and differentiation with respect to time. (In view of the shortness of the article we have omitted the details concerned with the production of the polynomial models and the verification of their adequacy; the relative error in the determination of Q did not exceed 10%). The boundaries of the regions of variation of the factors and their corresponding equations for the dissolution rates of V_2O_5 in the investigated V_2O_5-Na_2CO_3-H_2O (regions I, II), V_2O_5-$NaHCO_3$-H_2O (region III), and V_2O_5-NH_3-H_2O (regions IV, V) systems are given in table 1, and the kinetic parameters of the respective processes are given in table 2. For cases where the mutual effect of the factors characteristic of mixed regimes proved significant, to represent the dependence of one or the other kinetic parameter on the experimental conditions more clearly two or three identity equations are given in table 1. As seen from the tables, the dissolution of V_2O_5 occurs in a mixed regime in region I. This is demonstrated by the increase of the activation energy with increase of c and n and by the increase in the order of the rate in the concentration and the rotation rate with increase in T.

Table 1: The conditions and kinetic equations for the V_2O_5 dissolution processes

Boundaries of experimental region		Equations
I	c10⁻³-10⁻¹ T278-348 n4-25 τ300-1200	$V = 1.08 \cdot c^{2.17-\frac{484}{T}} \cdot n^{1.37-\frac{487}{T}} \cdot 10^{-\frac{2154}{T}}$ $V = 1.08 \cdot c^{2.17} \cdot n^{1.37} \cdot 10^{-\frac{2154+484\ \lg c+487\ \lg n}{T}}$
II, III	c10⁻¹-1 T278-298 n10-25 τ300-600	$V = 12.4 \cdot c^{0.58} \cdot 10^{-\frac{2417}{T}}$ (II) $V = 28.5 \cdot c^{0.63} \cdot 10^{-\frac{2643}{T}}$ (III)
IV	c10⁻³-10⁻¹ T278-323 n4-25 τ300-1200	$V = 3.48 \cdot 10^{-3} \cdot c^{1.47-\frac{151}{T}-0.04\ \lg n} \cdot n^{1.95-\frac{510}{T}} \cdot 10^{-\frac{1068}{T}}$ $V = 3.48 \cdot 10^{-3} \cdot c^{1.47-\frac{151}{T}} \cdot n^{1.95-\frac{510}{T}-0.04\ \lg c} \cdot 10^{-\frac{1068}{T}}$ $V = 3.48 \cdot 10^{-3} \cdot c^{1.47-0.04\ \lg n} \cdot n^{1.95} \cdot 10^{-\frac{1068+151\ \lg c+510\ \lg n}{T}}$
V	c10⁻¹-5 T278-298 n10-25 τ300-600	$V = 1.08 \cdot 10^{-1} \cdot c^{0.40-0.11\ \lg n} \cdot n^{0.09} \cdot 10^{-\frac{1633}{T}}$ $V = 3.48 \cdot 10^{-1} \cdot c^{0.40} \cdot n^{0.09-0.11\ \lg c} \cdot 10^{-\frac{1633}{T}}$

Table 2: The kinetic parameters of the V_2O_5 dissolution processes *)

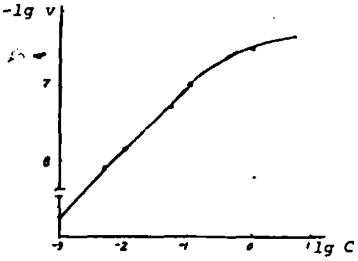
Experimental region	Order of dissolution rate		E_{act} kcal mole	$k_{a.e.}$
	c	n		
I	0.43→0.78 for T↑	0→0.33 for T↑	4.6→10.6 for c↑, n↑	$6.4 \cdot 10^{-[illegible]}$
II	0.58	0	11.1	$9.6 \cdot 10^{-5}$
III	0.63	0	12.1	$3.8 \cdot 10^{-5}$
IV	0.87→0.98 for T↑, n↓	0.16→0.49 for c↓, T↑	4.2→7.5 for c↑, n↑	$9.0 \cdot 10^{-7}$
V	0.25→0.29 for n↓	0.01→0.20 for c↓	7.5	$3.6 \cdot 10^{-7}$

*) The arrows denote the direction of the variation in the factors of the kinetic parameters: dimensions of $k_{a.e.}$ values in region I - g-ion[illegible] · l[illegible] · rev[illegible] · cm⁻² · sec[illegible], region II - g-ion[illegible] · l[illegible] · cm⁻² · sec⁻¹, region III - g-ion[illegible] · l[illegible] · cm⁻², region IV - g-ion[illegible] · l[illegible] · rev[illegible] · cm⁻² · sec[illegible], and region V - g-ion[illegible] · l[illegible] · rev[illegible] · cm⁻² · sec[illegible].

Further increase in c and restriction of the region of investigation to lower temperatures and high values of n (region II) transfers the dissolution process into the kinetic regime, where the rate constant is $9.6 \cdot 10^{-5}$ g-ion$^{0.42}$ l$^{0.58}$ cm^{-2} sec^{-1}; for the same conditions in sodium hydroxide solutions we obtained 21.10^{-5} g-ion$^{0.60}$ l$^{0.40}$ cm^{-2} sec^{-1}. If it is supposed that the dissolution of V_2O_5 in soda solutions, as in alkali solutions, takes place on account of OH ions, the decrease of the dissolution rate constant in soda is much lower than expected in view of the very low concentration of hydroxide ions in solutions of sodium carbonate compared with equimolar solutions of sodium hydroxide. Thus, for 0.1N solutions of NaOH and Na_2CO_3 the ratio of the concentrations of OH^- groups is equal to 40. (The pH values are 13.1 and 11.5 respectively and the rate constant is 2.2). Hydroxide ions formed on account of hydrolysis of Na_2CO_3 in the volume of the solution evidently do not play a significant part in the dissolution of V_2O_5. The reaction is realised on account of OH^- groups formed in a thin layer adjacent to the surface of the disc, where interaction takes place in the field of influence of adsorption forces and hydrolysis can go to completion. The reaction of OH^- ions with V_2O_3 is possibly the controlling stage of the dissolution process. To check these suggestions we carried out experiments on the dissolution of V_2O_5 in sodium bicarbonate (region III). The order of the reaction in the concentration of the reagent and the activation energy of the dissolution processes are very similar in regions II and III. In both cases the reaction occurs under kinetic control. The rate constant for the dissolution of vanadium(V) oxide in sodium bicarbonate is only 2.5 times lower than in sodium carbonate, whereas the ratio of the concentrations of OH^- ions in 0.1N solutions of Na_2CO_3 and $NaHCO_3$ is 1300 (pH values 11.5 and 8.4 respectively). As during comparison of sodium hydroxide and sodium carbonate, this difference is not significant. The determining role is again played by hydrolysis in the surface layer and not in the volume of the solution. The lower value of the rate constant obtained in region I can be explained by thermal dissociation of carbonic acid and by the blockage of the surface of the disc by bubbles of carbon dioxide (detected by microscopic investigation of the discs in special experiments). Moreover, the high temperature and the low concentration of the solvent in this region lead to stronger hydrolysis.

During investigation of the V_2O_5-NH_3-H_2O system we first carried out tests to determine the effect of the ammonia concentration on the dissolution rate of V_2O_5 and we obtained the V = f(c) relation over a wide range of NH_3 concentrations (fig.). Owing to the change in this relationship at C ≈ 10^{-1}, two regions of variation in the factors (IV and V) were selected.

In region IV mixed control close to diffusion is observed.



The dependence of the dissolution rate of V_2O_5 on the concentration of ammonia at 298°K and 4 rps.

This is demonstrated by the strong dependence of the dissolution rate on the disc rotation rate, close to first order in the concentration, and also by the high value of the rate constant. Increase in the ammonia concentration to 5g-eq/l and restriction of region V to low temperatures and high values of n do not lead to complete conversion of the process to kinetic control. It probably occurs when $c > 5$, but the strong evaporation of the ammonia and the intensive consumption of the disc material did not make it possible to extend the region of investigation.

Attention is drawn to the high value of the rate constant for the dissolution of V_2O_5 in ammonia solutions (1.7 times the corresponding value for NaOH). The reason for this may be differences in the mechanism of the processes. If it is supposed that OH^- groups are adsorbed on the surface of the V_2O_5 during dissolution in NaOH[6]), $NH_3 \cdot H_2O$ molecules may play an analogous role in ammonia solutions. Molecules of hydrated ammonia adsorbed on the surface of the V_2O_5 can probably undergo a rapid change, resulting in the release of active OH^- ion, which reacts with the vanadium(V) oxide, whereas the activity of the OH^- ions diffusing from the NaOH solution to the surface of the disc can be reduced by the screening action of the hydrate shell. There is another possible explanation; since the dissolving agent in sodium hydroxide solutions can only be OH^- groups, the increase of the dissolution rate in ammonia solutions can be explained by hydrolysis of the NH_4^+ ion, formed during the reaction of V_2O_5 with ammonia, and as a result the equilibrium of the dissociation of water is displaced in the layer of solution adjacent to the disc, and a certain amount of hydroxide ions above that supplied by the $NH_3 \cdot H_2O$ molecules is formed. Here the excess protons can take part in the formation of $H_2VO_4^-$ ions, since the processes at the surface of the disc are not equilibrium processes.

We conclude with a few words about the change in the dimensions of the rate constants, which casts some doubt on the validity of the comparison of their absolute values. In the transition from one region to another this change is related regularly to the variation of the process mechanism. If, however, the factors c and n have a mutual effect as, for example, in regions IV and V, the dimensions of the 'constant' change within the limits of one region, which can be considered a region of mixed control. In this case the dimensions of the 'constant' can only be determined for fixed values of c or n. Thus, while making it possible to describe the kinetics of the dissolution processes in the rotating discs more fully and precisely, mathematical design reveals the inadequacy of the ideas about the physical meaning of the dissolution rate constant. This aspect requires special investigation.

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UDC 541.661.621.039.59

Chlorination of uranium and plutonium oxides in the molten NaCl-KCl-$MgCl_2$ eutectic

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Summary

The use of ionic melts in the production and refining of uranium and plutonium and also of their oxides requires investigation of the processes involved in the production of the oxides and their chlorination. The chlorination of the oxides was investigated with a mixture of gaseous chlorine and carbon tetrachloride in quartz tubes. Agitation was realised by bubbling the chlorinating agent through the melt.

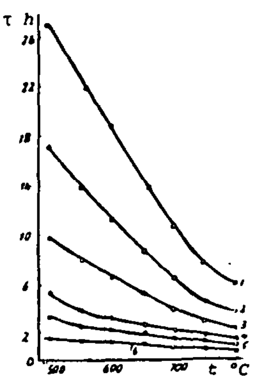

Fig.1

The dependence of the chlorination rate of UO_2 (curves 1,2 and 3) and U_3O_8 (curves 4,5 and 6) on temperature and on the content of the oxide in the system wt.%: 15 (1,4) 25 (2,5), 35 (3,6).

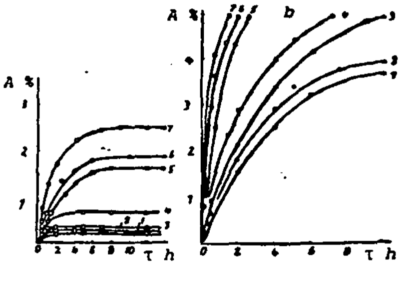

Fig.2 The dependence of the solubility of PuO_2 (A) on temperature and on the length of chlorination with chlorine (a) and carbon tetrachloride vapour (b), t °C: 1 - 500, 2 - 550, 3 - 600, 4 - 650, 5 - 700, 6 - 750, 7 - 800.

TSVETNYE METALLY / NON-FERROUS METALS N8, 1975

RHENIUM EXTRACTION FROM ZINC-CADMIUM SOLUTIONS IN THE CHIMKENT LEAD PLANT HYDROMETALLURGY SHOP

UDC 669.849:(669.5 + 669.73)

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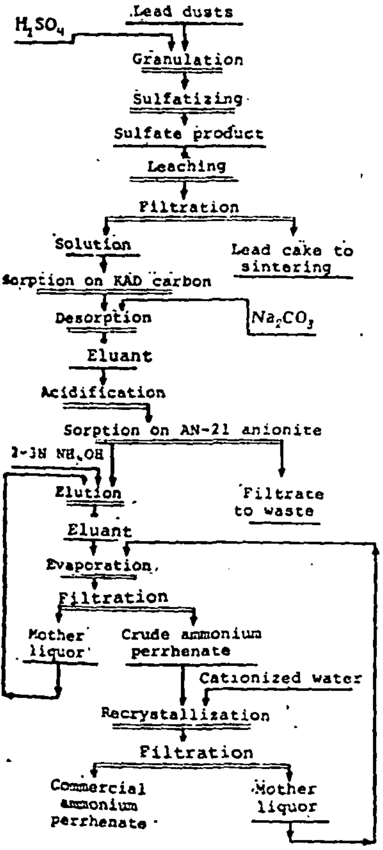
In processing a lead charge, rhenium passes mostly into the sinter shop dusts (bag filter dusts contain 0.05-0.087% Re, electrostatic precipitator dusts 0.058-0.1% Re) and partly into the smelting shop dusts, which contain ∼ 0.004-0.007% Re.

For multiple extraction of valuable constituents (Zn, Cd, In, Tl) from lead dusts, these dusts are given a sulfatizing roast and then processed hydrometallurgically; during the latter process most of the rhenium passes into zinc-cadmium sulfate solutions.

An ion-exchange technology using AN-21 anion exchanger has been developed to extract rhenium from the solutions, and has been tested on a pilot-plant scale.

Following the results obtained, an installation consisting of five columns was designed and built, each column having a capacity of 20 liters. Filters permitting solution feed downward from above and vice versa were fitted to the upper and lower parts of the columns. Temporarily sorption was carried out using KAD grade carbon.



Adsorption/ion-exchange Scheme for Rhenium Extraction from Zinc-Cadmium Sulfate Solutions.

The solutions contained (g/liter): 65.0 Zn, 31.6 Cd, 0.083 In, 0.025 Tl, 0.035 Te, 0.025 Sn, 2.3 Fe, 3.5 As, 0.02 Cu, 100.7 sulfates, 20.0 H_2SO_4, 0.0125-0.019 Re. The filtrate leaving the carbon columns was returned to the main process for extraction of In, Cd, Tl, and Zn.

Sorption extraction of rhenium on KAD carbon was carried out in two parallel columns, each of which was charged with 4.5 kg of KAD carbon; 2495 liters, 207.6 specific volumes, of solution was passed through each column, the capacity of the carbon for rhenium being 0.635%.

The tests confirmed the results of the laboratory studies and demonstrated the possibility of rhenium extraction from hydrometallurgy shop solutions on KAD carbon.

An industrial installation was brought into operation in 1973. The columns, which had previously been filled with water to 2/3 of their volume, were each charged with 150-160 kg of carbon (converted to dry weight). The water was run out as the columns were filled, and sulfuric acid solution (10-20 g/liter H_2SO_4) was fed in from the top at a speed of 5 specific volumes. Flushing with sulfuric acid solution is to prevent precipitation of hydrates on the carbon. After leaching of the sulfate product, the solutions were vacuum filtered and passed to one of the settling tanks (settling time 6-8 hr) for supplementary purification; the solutions were then decanted and fed to the carbon column.

Other metals were also extracted from filtrates containing up to 2 mg/liter Re. Solutions containing > 5 mg/liter Re passed to another column. As the filtrate rhenium content increased (up to 80% of the initial solution content), the solution feed to the column was cut off and it was flushed out, another column containing carbon being brought into the circuit. The rhenium-saturated carbon was flushed in two stages: first with five volumes of solution containing 20 g/liter H_2SO_4, then to pH 3-4 with 7-9 volumes of industrial water. The flushing water was sent to the head end of the sulfate product leaching process. The column was dried out and the rhenium-saturated carbon was sent to the customer.

During the industrial test period, 1500 m^3 of zinc-cadmium sulfate solutions from the hydrometallurgy shop were passed through the columns.

The rhenium concentration in the solutions fluctuated in the 20-55 mg/liter range. The initial capacity of the carbon for rhenium was 2%, falling to 1.5% in the course of operation (eight sorption-elution cycles). The following elements were sorbed on the carbon together with rhenium, %: 0.01 Cd, 0.01 Zn, 0.1 As, 0.003 Tl, 0.1 Sb, and 0.1 Fe. These elements are separated from rhenium in the process of ammonium perrhenate production. Total rhenium extraction into the carbon from solution is 90%.

The sorption extraction of rhenium on KAD carbon was introduced at the Plant at the beginning of 1974, and the second stage of an installation producing commercial ammonium perrhenate will be put into permanent operation soon.

ROCK FRACTURE AND FRAGMENTATION

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Proceedings of the 22nd U.S. Symposium on Rock Mechanics: Rock Mechanics from Research to Application held at Mass. Inst. of Tech., June 28-July 2, 1981 compiled by H.H. Einstein

SUMMARY

The mechanics and physics of fracture are briefly reviewed, with special attention to their applicability to problems of rock fracture and fragmentation. The desirability of analyzing energy changes associated with fracture directly, rather than following the more restrictive procedures of linearly elastic fracture mechanics, is stressed. Application of the direct approach to hydraulic fracturing, rock bursts and coal bumps in mining, laboratory investigations of rock fracture, blasting and drilling are mentioned. The report concludes with some recommendations for future research.

INTRODUCTION

Fractures, or essentially linear discontinuities, are pervasive in rock masses and can be observed at any scale, be it from high altitude aerial photography or through a microscope. They represent a deformational response to forces imposed on the rock at some time in its geological history. Active tectonism or engineering activities may change the current equilibrium sufficiently to reactivate movements along the existing fractures and may also generate new fractures. Consequences include such effects as devastating earthquakes, rock bursts in mines, failure of slopes or dam abutments. New fractures are also generated intentionally in such processes as hydraulic fracturing, drilling, blasting, comminution and grinding. Understanding of the mechanics of rock fracture is thus of broad general importance.

The mechanics of fracture initiation and propagation have been most intensively studied in relation to fabricated materials, usually metals. As in other branches of rock mechanics, the theoretical basis of rock fracture draws heavily on the research and approaches followed for these materials. Although this work has been of considerable value in explaining rock fracture, there remains a tendency, also evident to varying degrees in other branches of rock mechanics, to adopt uncritically the approaches and procedures of the studies on fabricated materials. Some of the questions of most significance in the problems of fabricated materials may be of relatively little import in problems of rock engineering. It is important if maximum benefit is to be gained in rock mechanics from developments in other fields to recognise these differences. Some of the more important differences are the following:

1) Forces in geological situations are generally compressive, either gravitational or tectonic in origin, and may vary in magnitude and orientation. Non-planar extension of fractures is not uncommon.

2) Outer "boundaries" in the earth are essentially infinite so that forces may always be redistributed away from a fracture, which can then stabilize after some extension. Stable fracturing is a common occurrence in mining and tunnelling.

3) Fractures abound in rock, formed at various times over many millions of years. Amelioration of the potentially damaging effects of continued movement along fractures is important, as in earthquake control on one scale and in rock-bolt reinforcement of jointed rock on another. Generation of new fractures is a frequent goal, as in hydraulic fracturing, blasting, and comminution. Prevention of fracture, the main interest in fracture mechanics applied to fabricated materials, is of smaller concern in rock mechanics.

4) The ultimate tensile resistance of most rocks is very small compared to the compressive resistance, so that tensile fractures are frequently observed in rocks.

5) Rocks are heterogeneous on both the small and large scale. Variations in crystal structure and strength locally ahead of an extending fracture can affect the stability and continuity of fracture growth. Discontinuities such as faults, boundaries between different rock types, or variation in the magnitude and orientation of

in situ stress fields can all affect overall fracture propagation.

6) Rocks are often markedly anisotropic. This may be regarded as a variation in the "work of fracture" (required to generate new surfaces), as a function of fracture orientation.

7) Rocks are usually permeable and contain water under pressure. This can have a major influence on the deformation behaviour of the rock.

8) Application of laboratory results to field problems is often made difficult due to the very large differences in scale between the two. Full-scale field experiments, although costly, are essential. There is also a need for larger-scale experiments in laboratory studies of rock fracture.

These characteristics change the emphasis of rock fracture studies compared to those in other branches of fracture mechanics. For example, determination and study of the factors that influence the rate and direction of fracture path growth and the sensitivity of path growth to variations in these factors are fundamentally more valuable than precise determination of fracture toughness in the laboratory. The mechanics of simultaneous growth of multiple cracks, as in blasting, is an important problem.

It is not possible to cover all aspects of rock fracture and fragmentation in one brief review. We have therefore concentrated on the underlying general principles, drawing on specific examples to illustrate how the principles can aid understanding in practical application. The review concludes with some suggestions for further research.

1. THE MECHANICS OF FRACTURE

Let us consider a given solid, which contains an initial imperfection, subjected to a system of time-dependent external loads defined by surface tractions, surface displacements and body forces as well as a time dependent heat flux. If the loads are increased beyond a critical level and (or) if the heat flux transferred to (or from) the solid reaches a critical value, fracture propagation will ensue. The problem to be solved is two-fold:

a) determine the critical levels necessary for fracture to occur;

b) determine the size and the shape of the fracture area as a function of time.

Given the material characteristics and environmental conditions at any time, the first law of thermodynamics implies that

$$\dot{U} + \dot{Q}_o = \dot{V} + \dot{T} + \dot{D} + \dot{Q}_1 \qquad (1)$$

Where

$\dot{U}$ is the rate of work done by the applied loads,

$\dot{Q}_o$ is the rate of heat transferred to (or from) the solid,

$\dot{V}$ is the recoverable stored mechanical energy,

$\dot{T}$ is the rate of change of kinetic energy,

$\dot{D}$ is the sum of the rates of irreversible variations of internal energies,

$\dot{Q}$ is the rate of variation of stored heat.

Generally $\dot{U}$ and $\dot{Q}_o$ are known and the problem addressed by fracture mechanics is the determination of $\dot{V}$, $\dot{T}$, $\dot{D}$ and $\dot{Q}$. This very general problem has not yet been solved; attention has been centred rather on the three following sub-problems:

Sub-problem 1 : quasistatic, adiabatic fracture processes

$$\dot{Q}_o = \dot{T} = \dot{Q}_1 = 0$$

$$\dot{U} = \dot{V} + \dot{D}$$

$\dot{Q}_o$ and $\dot{Q}_1$ are considered to be sufficiently small so as to be included as a component of D;

Sub-problem 2 : dynamic, adiabatic fracture process

$$\dot{Q}_o = \dot{Q}_1 = 0$$

$$\dot{U} = \dot{V} + \dot{D} + \dot{T}$$

as in sub-problem 1, $\dot{A}_o$ and $\dot{A}_1$ are considered sufficiently small to be included as a component of $\dot{D}$;

Sub-problem 3 : quasistatic thermal cracking

$$\dot{T} = 0$$

$$\dot{U} + \dot{Q}_o = \dot{V} + \dot{D} + \dot{Q}_1$$

This report will be focussed primarily on the first case, i.e., quasi-static adiabatic fracture, with a brief mention of dynamic, adiabatic fracture. Quasi-static thermal cracking will not be discussed although it is becoming of central interest to such rock mechanics problems as extraction of geothermal energy or nuclear waste storage.

1.1 Quasi-static Adiabatic Fracture Processes

The term quasi-static implies that either the fracture propagates by a continuously stable process, or that fracture configurations exist for which, after a short unstable phase, the fracture again becomes stable.

1.1.1 Fracture criteria

Griffith's Theory Assuming that the formation of a new surface absorbs a quantity of energy proportional to the area of this surface, Griffith (1921) derived a fracture criterion from the theorem of minimum potential energy.

$$\Delta U\ (\underline{ds}) - \Delta V\ (\underline{ds}) - \Delta D\ (\underline{ds}) < 0 \qquad (2)$$

where

ΔU ($\underline{ds}$) is the variation of energy associated with the work done by external forces when the fracture extends by $\underline{ds}$;

ΔV ($\underline{ds}$) is the variation of energy associated with the material deformation caused by fracture extension $\underline{ds}$;

ΔD ($\underline{ds}$) is the irreversible variation of internal energy caused by the formation of the surface $\underline{ds}$;

In other words, fracture will occur if the final state of the solid is one for which the potential energy is smaller than that which results when there is no fracture propagation.

In his original paper, Griffith considered isotropic homogeneous solids only so that:

$$\Delta D\ (\underline{ds}) = \gamma\ da \qquad (3)$$

where γ is the free surface energy of the material and da is the areal increment caused by fracture extension $\underline{ds}$. This concept of free surface energy is readily generalised to homogeneous anisotropic solids:

$$\Delta D\ (\underline{ds}) = \gamma\ (\underline{n})\ da \qquad (4)$$

where γ ($\underline{n}$) is a function of the orientation of $\underline{ds}$ ($\underline{ds} = \underline{n}$ da).

Equations (3) and (4) imply that the formation of new surfaces constitute the only energy dissipation process involved by fracture propagation, i.e., that the fracturing process is perfectly brittle. For many materials, like metals, some plasticity may occur near the crack tip so that the quantity ΔD (ds) in Equation (2) is:

$$\Delta D\ (\underline{ds}) = \gamma\ (\underline{n})\ da + \Gamma p \qquad (5)$$

where Γp is the energy dissipated through plastic deformation. Further, in heterogeneous materials such as rocks, macroscopic fracture extension is associated with microcracking of the material in the vicinity of the fracture tip. As a consequence, the quantity γ ($\underline{n}$), defined as the quantity of energy associated with the formation of a new surface of unit area for homogeneous materials includes, for heterogeneous solids, all the energy absorbed by microcracking in the formation of a unit macroscopic surface area. Clearly, for such materials γ ($\underline{n}$) is not a material property since it depends in part on the stress gradient near the fracture tip. This point will be further discussed in the next section (Physics of Fracture); in this section γ ($\underline{n}$) will always refer to the energy necessary to create a unit area of macroscopic fracture, the latter being regarded as a discontinuity in the displacement field of the continuum.

Bui and Dang (1979) have recently discussed the problem of three-dimensional crack propagation. They observe that, for a fracture in an infinite medium, the tip of the fracture defines a closed curve Γ as opposed to a single point for a two-dimensional problem. Extension of the fracture corresponds to an increment of surface, which implies first an increment of area and, secondly, an increment in the length of the fracture tip curve (see Figure 1). Accordingly, they propose to add to Griffith's free surface energy two additional terms : the first term is associated with the increment of length of the fracture tip curve Γ, the second term is associated with changes of the radius of curvature for the curve Γ (not that of the fracture tip which remains infinitely small). Without discussing any further the topological problem of fracture extension geometry, we simply note that, in our opinion, the changes of fracture geometry affect only the strain energy in the solid [ΔV ($\underline{ds}$) in equation 2]. Griffith's free surface energy, which refers to the energy required to break the bonds between atoms lying on both sides of the fracture surface, is a three-dimensional concept : any length increment in the fracture tip curve implies an increment of surface area and therefore requires only that the bonds between the atoms that lie within this surface be broken.

With Griffith's theory, the configuration of a stable crack growth in a purely brittle material can be determined by solving for the following equation (Palaniswamy and Knauss, 1974).

$$[\Delta U(X) - \Delta V(X) - \Delta D(X)] - [\Delta U(X_o) - \Delta U(X_o) - \Delta U(X_o)] < 0 \qquad (6)$$

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[*] Griffith's criterion includes, in addition to this energy condition, the requirement that the applied forces must be high enough at some point(s) locally in the material to overcome the interatomic cohesive forces acting across the (potential) plane of separation. For him, stress concentrations at the tips of narrow elliptical cracks provided a suitable mechanism for increasing the applied load to the required much higher interatomic force level. Heterogeneous materials such as rocks contain many sources of intense stress concentration (e.g., triple points at grain boundaries) that can serve the role of the crack tips. It is tacitly assumed in the paper that it will always be possible to initiate crack growth, and attention is turned exclusively to consideration of the energy condition which governs crack propagation.

where X is any virtual crack growth configuration and X_o is the initial crack configuration. Equation (6) expresses the fact that the release of energy associated with crack growth must be a *maximum*. For materials which are isotropic with respect to their "strength" property, equation (6) becomes:

$$[\Delta U(X) - \Delta V(X)] - [\Delta U(X_o) - \Delta V(X_o)] < 0 \quad (7)$$

Note that equation (7) is independent of the "strength" characteristics of the material.

For general load conditions and crack geometries, solving equation (2), (i.e., determining the critical loading conditions for which fracture starts) or equation (6) (determination of the crack path) is extremely intricate and is possible only by using approximate numerical methods. However, in many situations of practical interest involving simpler loading conditions, it is possible to obtain closed form or semi-analytical solutions.

Irwin's Proposition

As mentioned above, fractures may be regarded as surfaces of discontinuity for the displacement field in the solid. In general, the three components of the displacement vector suffer a discontinuity through the fracture surface. Irwin (1957) suggested that the relative displacements between points on the two faces of the fracture could be described completely in terms of three independent kinematic movements:

Consider the frame of reference shown in Figure 1.

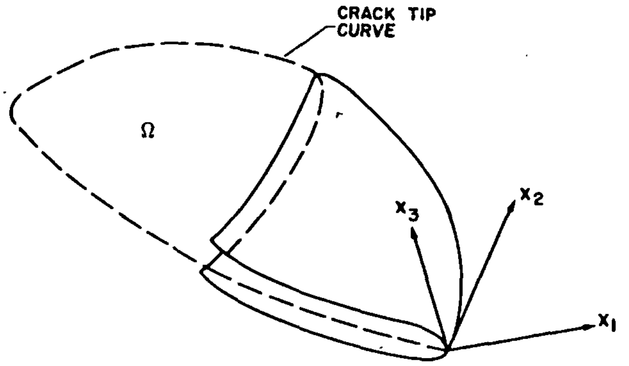

Figure 1

Ox_1, Ox_2 lie in the plane Π tangent to the fracture surface Ω at the fracture tip; Ox_1 is perpendicular to the crack tip curve Γ; Ox_2 is tangent to Γ. Ox_3 is orthogonal to both Ox_1 and Ox_2.

The surface of the fracture Ω is supposed to be smooth with no singularity point.

The three fracture modes defined by Irwin are:

- mode I or opening mode: $\hat{U}_3 \neq 0$; $\hat{U}_2 = \hat{U}_1 = 0$
- mode II or sliding mode: $\hat{U}_1 \neq 0$; $\hat{U}_2 = \hat{U}_3 = 0$
- mode III or tearing mode: $\hat{U}_2 \neq 0$; $\hat{U}_1 = \hat{U}_3 = 0$

where $\underline{\hat{U}}$ is the displacement discontinuity near the fracture tip curve.

These three basis fracture modes are necessary and sufficient to describe all the possible crack propagation schemes in the most general state of stress. Each of the three crack movements is associated with a particular stress field in the immediate vicinity of the crack edge. For linearly elastic material, the three stress components σ_{33}, σ_{12} and σ_{13} at points on the x_1 axis close to the origin, take the following simple forms (assuming that the radius of curvature at the crack tip is infinitely small):

$$\sigma_{33} = (2x_1)^{-1/2} K_I + O(1)$$
$$\sigma_{13} = (2x_1)^{-1/2} K_{II} + O(1)$$
$$\sigma_{12} = (2x_1)^{-1/2} K_{III} + O(1)$$

where the higher order terms, in the variable x_1 have been neglected. Irwin defined the three parameters K_I, K_{II} and K_{III} as the stress intensity factors corresponding to the opening, sliding and tearing modes of fracture. Determination of these stress intensity factors and, as a consequence, the near crack tip stress field is a problem in the mathematical theory of elasticity. Solutions for many problems, 99 per cent of which refer to two-dimensional flat cracks, have been published [see e.g. Sih and Liebowitz (1968), Sih (1973)]. The important implications of these stress intensity factors stems from the fact that the region for which Griffith's energy balance must be satisfied for a crack to grow can be any portion of the body enclosed within a simple closed surface L surrounding the crack tip where the energy is being dissipated. Thus, following Sanders (1960), the Griffith's criterion may be stated as: "The rate at which work is being done by forces acting across L equals the rate of increase of strain energy stored in the material inside L plus the rate at which energy is dissipated by the growing crack". Accordingly, only the stress field in the immediate vicinity of the crack tip needs to be examined.

Following Irwin, let us consider a through crack of length 2a in an infinite plate of unit thickness submitted to a uniaxial tensile stress at infinity. Suppose that the crack is extended by Δa at both ends; the area of the new surface is 4Δa. According to the Griffith criterion of fracture, the crack will propagate if the change of strain energy is such that:

$$W_1(a) - W_1(a + \Delta a) > 4\Delta U\gamma \qquad (9)$$

(There is no displacement at infinity so that no work is performed by the external forces). The function $W_1(a + da)$ may be expanded in terms of Taylor's series:

$$W_1(a + \Delta a) = W_1(a) + \frac{\partial W_1}{\partial a} \Delta U + \frac{1}{2!} \frac{\partial^2 W_1}{\partial a_2} \partial U^2 + \ldots \qquad (10)$$

A strain energy release rate can be defined so that the crack propagates if:

$$G > 2\gamma \qquad (11)$$

accordingly $G = \frac{1}{2} \frac{\partial W_1}{\partial a}$ (12)

For the opening mode encountered here, Irwin showed that:

$$G_I = \frac{1-\nu^2}{E} K_I^2 \qquad (13)$$

for plane stress conditions $(1-\nu^2)$ should be removed from equation (13); E is the modulus of elasticity and K_I is the stress intensity factor for mode I. Accordingly the crack will propagate if K_I reaches a critical value K_{IC} (called the fracture toughness) defined in such a way that $G_I = G_{IC} = 2\gamma$

Since K_I depends on the applied load, equation (13) can be used to calculate the critical load for which the crack of length 2a will extend, provided γ or K_{IC} are known. In his original paper, Irwin followed similar lines of *reasoning for modes II and III* so that, if it is assumed that a crack does propagate in its own plane when submitted to mode II and III fracturing, critical stress intensity factors K_{IIC} and K_{IIIC} could be defined. Accordingly replacement of the concept of free surface energy by that of fracture *toughness for modes I, II and III* has been proposed.

In reality, it has been found (e.g., Palaniswamy and Knauss, 1974) that a fracture submitted *to modes II or III conditions* extends in a direction other than that of its own plane. Thus, equivalence between the Griffith's fracture criterion and the fracture toughness theory has not been proved for crack propagation configurations other than pure mode I.

At this point it may be of interest to note that the stress singularity near the tip of a crack lying at the interface between two different materials is not of the order $r^{-1/2}$ (where r is the distance between the point for which stresses are computed and the fracture tip). Thus, at least for these specific crack propagation problems, the classical concept of fracture toughness does not apply (K.Y. Lin, 1973; Comninou and Dundurs, 1979).

Rice's J Integral

Consider a homogeneous body of linear, or non-linear, elastic material free of body forces and subjected to a two-dimensional deformation field. Suppose the body contains a notch having flat surfaces parallel to the x_1 axis and a rounded tip denoted by the arc Γ_t (see Figure 2).

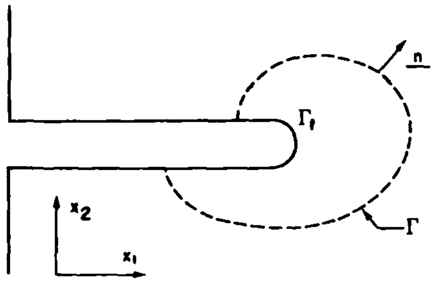

Figure 2

consider the integral:

$$J = \int_\Gamma (W dx_2 - \underline{T} \frac{\partial U}{\partial x_1} ds) \qquad (14)$$

in which Γ is a curve surrounding the notch tip, W is the strain energy density, $\underline{T}$ is the traction vector defined according to the outward normal ($T_i = \sigma_{ij} . n_j$ where $\underline{\sigma}$ is the stress tensor), $\underline{U}$ is the displacement vector and ds is an element of arc length along Γ. *Rice (1968) showed that the integral J is* independent of the path Γ if the notch is free of surface traction and if the crack is linear (dx_2 must be zero along the notch flat surface of the notch).

By taking Γ close to the notch tip, the J integral can be made to depend only on the local field; in particular the path may be shrunk to Γ so that, since $\underline{T} = 0$ equation 14 reduces to:

$$J = \int_\Gamma W dx_2 = -\frac{dP}{da} \qquad (15)$$

where $\frac{dP}{da}$ is the energy release rate associated with crack extension da. This limit is not meaningful for sharp cracks; however since an arbitrarily small curve Γ may be chosen surrounding the crack tip, the J integral may be made to depend only on the crack tip singularity deformation field. The utility of the method rests in the fact that, firstly, the material near the crack tip can be nonlinearly elastic and, secondly, that alternate choices of integral path often permit a direct evaluation of J. For example, if it is assumed that the crack propagates in its own direction for combined modes I, II and III, Rice (1968) has shown that:

$$J = G = \frac{1-\nu^2}{E}\left[K_I^2 + K_{II}^2\right] + \frac{1}{2\mu} K_{III}^2 \tag{16}$$

where G is the strain energy release rate defined by equation (12), and μ is the elastic shear modulus.

The Maximum Hoop Stress Theory

This theory was proposed by Erdogan and Sih (1963) for the investigation of two dimensional crack growth in mixed mode loading conditions for which tensile stresses develop near the crack tip. They proposed that the crack will propagate perpendicularly to the direction of maximum tension, i.e., on a plane along which the shear stress vanishes, when this maximum tension reaches a critical value.

Since, for cracks with infinitely small radius of curvature at the crack tip, a stress singularity exists, Williams and Ewing (1974) proposed to modify this fracture criterion so that fracture occurs when the hoop stress reaches a critical value at a critical distance from the crack tip; this critical distance is assumed to be a material property. Accordingly, because the stress state must now be evaluated at a certain distance from the crack tip, terms in r (where r is the distance between the point under consideration and the crack tip) higher than that of order −1/2 must be included in the series expansion derived by Irwin (1957).

The Critical Strain Energy Density Factor

This theory was developed by Sih (1973) for three dimensional crack growth.

Consider a three-dimensional crack (with infinitely small radius of curvature at the tip) for which a coordinate system similar to that described in Figure 1 is defined (x_1 axis normal to the crack tip in the crack plane; x_2 axis tangent to the axis crack tip in the crack plane; x_3 normal to the crack plane origin O on the crack periphery). As shown by Irwin (1975) for linearly elastic solids, the functional form of the stress components in polar coordinates is as follows:

$$\sigma_{11} = \frac{K_I}{(2r)^{1/2}} \cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) - \frac{K_{II}}{(2r)^{1/2}} \sin\frac{\theta}{2}\left(2 + \cos\frac{\theta}{2} + \cos\frac{3\theta}{2}\right) + \ldots..$$

$$\sigma_{22} = \frac{K_I}{(2r)^{1/2}} \cos\frac{\theta}{2}\left(1 + \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) - \frac{K_{II}}{(2r)^{1/2}} \sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{3\theta}{2} + \ldots..$$

$$\sigma_{33} = 2\nu \frac{K_I}{(2r)^{1/2}} \cos\frac{\theta}{2} - 2\nu \cdot \frac{K_{II}}{(2r)^{1/2}} \sin\frac{\theta}{2} + \ldots..$$

$$\sigma_{12} = \frac{K_I}{(2r)^{1/2}} \cos\frac{\theta}{2}\sin\frac{\theta}{2}\cos\frac{3\theta}{2} + K_{II}\cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) + \ldots..$$

$$\sigma_{13} = \frac{-K_{III}}{(2r)^{1/2}} \sin\frac{\theta}{2} + \ldots..$$

$$\sigma_{23} = \frac{K_{III}}{(2r)^{1/2}} \cos\frac{\theta}{2} + \ldots.. \tag{17}$$

(r is the distance between the origin v and the point under consideration (A); θ is the angle between the x_1 axis and the OA direction; modes I, II and III are defined in the Ox_1, OA plane):

The strain energy density is:

$$\frac{dW}{dV} = \frac{1}{2E}\left(\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2\right) - \frac{\nu}{E}\left(\sigma_{11}\sigma_{22} + \sigma_{22}\sigma_{33} + \sigma_{33}\sigma_{11}\right) + \frac{1}{2\mu}\left(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{13}^2\right) \tag{18}$$

Near the crack tip, the strain energy density is:

$$\frac{dW}{dV} = \frac{1}{r}\left(a_{11} k_I^2 + 2\, a_{12} k_I k_{II} + a_{22} K_{II}^2 + a_{33} K_{III}^2\right) \tag{19}$$

where a_{11}, a_{12}, a_{22} and a_{33} depend upon the elastic material properties as well as on the angle θ. Thus $\frac{dW}{dV}$ is singular in 1/r.

The quantity

$$S = a_{11} K_I^2 + 2\, a_{12} K_I K_{II} + a_{22} K_{II}^2 + a_{33} k_{III}^2 \tag{20}$$

represents the intensity of the strain energy density near the crack tip.

Sih proposed that the crack would extend in the direction of maximum potential energy density, and that the critical intensity of this potential field governs the onset of crack propagation. Since a direct correlation exists between the potential energy density and the strain energy density, Sih expressed his fracture criterion as follows:

$$\left.\begin{aligned} \frac{\partial S}{\partial \theta} &= o \\ S &= S_{cr} \end{aligned}\right\} \qquad (21)$$

Equation (21) expresses the idea that the crack spreads in a direction along which the strain energy density is minimum, when the strain energy density factor S reaches a critical value. Accordingly the path followed by crack extension is that for which S reaches it largest minimum value.

1.1.2 A Case Example: The Angled Crack Problem

The problem is illustrated in Figure 3: a small crack or notch in the middle of an isotropic, homogeneous, linearly elastic plate is subjected to uniformly distributed edge loads. The load magnitude at which the crack grows and the path of crack extension are to be determined. This problem has received extensive attention from investigators in the field of linear elastic fracture mechanics. As pointed out by Swedlow (1976), for uniaxial tensile loading conditions, each approach derived from one of the above mentioned fracture criteria gives its own distinctive result, but the differences between them are small. Further, all such results are qualitatively in agreement with experimental observations and there is little operational basis for preferring any one approach over the others. Such an agreement is not found for compressive, or biaxial, loading conditions and some of the solutions proposed for this problem will now be discussed.

Griffith (1924) applied his energy criterion to determine the compressive strength of brittle material by considering a solid under uniaxial compression. Assuming that in a solid, flaws exist which can be approximated as to elliptical cracks that act as stress intensifiers, he computed the tensile stress which develops near the tip of an inclined "open" ellipse submitted to a uniaxial compressive stress field. He concluded from his investigation that the "compressive strength" of a brittle material should be eight times larger than the "tensile strength". However it was known that for rocks, for example, the "compressive strength" can be as high as a hundred times the "tensile strength". In order to explain this discrepancy McClintock and Walsh (1962), following Griffith's approach, conducted a similar analysis with the additional assumption that cracks in compression are closed so that friction develops. Friction coefficients larger than unity were necessary to reconcile experimental data obtained for both compressive and tensile rock strength, a value which is much too high for most rocks. Subsequent computation of compressive strength from fracture mechanics concepts has failed to resolve the problem and attention has been focussed on understanding of rock propagation in compressive stress fields.

Brace and Bombolakis (1963) and Hoek and Bienoiawski (1965) conducted experimental tests on rock propagation in a uniaxial compressive stress field. The latter, for example, conducted exprer iments on thin rock plates into which an inclined notch had been introduced; the plate was placed under a uniaxial compressive load. They observed that cracks started to extend-initiated from the ends of the notch, propagated so as to become parallel to that of the applied load, and then stabilized.

Ingraffea (1977) conducted similar tests but, in addition, applied the critical strain energy density factor (S_{min}) the maximum hoop stress ($\sigma_{\theta\theta\ max}$) and the maximum energy release rate (G_{max}) to predict both the load for which fracture should initiate and the path followed by the fractures. For this purpose a finite element program was developed to model incremental fracture propagation. Accurate work-tip singularity elements were employed along with a new techniques for efficient, discrete crack propagation through the finite element mesh. Salem (Indiana) limestone and St Cloud charcoal granodiorite were used as material. Ingraffea's main conclusions are:

1. Stress, strain energy density, toughness and characteristic distance parameters obtained from independent tests, different test configurations and different test samples led to substantially similar fracture predictions.

2. Within the range of the K_I-K_{II} values encountered in the model structural analysis, primary crack paths predicted by the $\sigma_{\theta\theta\ max}$ and G_{max} theories were nearly identical.

3. The discrepancy observed between the $\sigma_{\theta\theta\ max}$ or G_{max} predictions and that derived from the modified S min theory was attributed to the dependence of the latter on Poisson's ratio (the modified S min theory states that fracture propagation should occur along the path for which the strain energy density factor is miminum and the tangential stress component is tensile (Swedlow, 1976; polar coordinates are used to describe the near crack tip stress field).

4. Accurate prediction of primary crack length is highly dependent on accurate values for fracture toughness.

5. Failure of the model rock structure tested always resulted from unstable propagation of secondary cracks.

6. Vertical splitting typically observed in the failure of uniaxially loaded rock specimens is probably not the result of the coalescence of a large number of primary cracks. Rather such failure is probably the result of unstable, vertically propagating secondary cracks.

7. The effect on crack propagation of inhomogeneity, porosity and the presence of intergranular microcracks in rocks are not apparently as severe as feared.

Cornet (1979), using Crouch's displacement discontinuity numerical technique (Crouch 1976), investigated the problem of path determination for a fracture extending in a triaxial compressive stress field. Analysis was conducted under plane strain conditions for a crack inclined at various angles with respect to the major far-field principal stress (σ_1) (the intermediate pincipal stress (σ_2) is defined by the plane strain condition). Two fracture criteria were considered, namely the maximum energy release rate (G) and the critical strain energy density factor (S). Indeed, for large enough far-field compressive stress no tensile stress is noticed near the crack tip so that the maximum hoop stress theory does not apply. In this model, the crack can close so that its surfaces come into contact and slide against one another giving rise to a frictional force, which was taken to be directly proportional to the normal load. It was found that, for both criteria, the crack path depends on the σ_3/σ_1 ratio. With the G criterion, increasing the value of the ratio results in a preference for shear mode propagation over tensile mode (see Figure 4). For non zero values for σ_3, the crack path tends toward a direction which is inclined with respect to the major principal stress (σ_1) direction, at an angle of the same sign as that of the original crack orientation. For low values of σ_3, the initial crack increments occurred in combined tensile and shear modes so that crack opening occurs; this propagation phase is stable in the sense that for constant σ_1 and σ_3 values, the magnitude of G decreases as the crack extends. Once the fracture has reached a given orientation, crack growth was found to be unstable in a purely shearing mode. Except for the crack path angle, similar results are obtained with the S criterion if it is modified so as to consider the relative minimum for S for which the stress concentration factor for the least principal stress is smallest (tensile stresses are considered to be positive).

To our knowledge, the three dimensional problem of determining the geometry of extension of a penny-shaped crack submitted to triaxial compressive stress has not been tackled. We simply note here the fact that the kinematics of crack propagation is not uniform at all points of the crack periphery. Whilst combined mode I and II conditions prevail at those ends of the crack which are aligned with the slippage direction, combined mode I and III conditions are encountered for the points lying on the axis perpendicular to slip motion. In between, points lying off the crack front are submitted to combined modes I, II and III. It thus appears that a topological problem is enountered if non-planar continuous rock growth is assumed.

1.2 Dynamic Adiabatic Fracture Processes

In a purely brittle material, rupture becomes dynamic when the potential energy released by this process is larger that the quantity of energy dissipated through formation of new surfaces, or heat, so that kinetic energy is generated. The stability of the fracturing process, i.e., the onset of dynamic propagation conditions, will be discussed by considering the Griffith locus defined by Berry (1960).

Consider a linearly elastic brittle material in which exists a fracture of length, l. When a load Q is applied on the solid surface, the corresponding displacement q, observed at the point of application of the load, is proportional to Q related by a factor m; the longer the fracture, the smaller m. For a given fracture length l, the load Q can be increased until the fracture propagates; this critical load defines a point A in the Q - q plane. The locus of all such points A of incipient fracture propagation for various initial fracture lengths is called the Griffith locus; it will be referred to, hereafter, as the curve Σ. Clearly this curve has two asymoptotes: in the absence of any fracture the load can be infinitely increased and the ratio $Q/q = m_o$ is simply the elastic response of the unbroken material; if the body is completely traversed by the fracture, any small load Q will generate an infinite displacement a (in the absence of body forces). Thus the domain limited by the straight line of slope m_o, the horizontal axis, and the Griffith locus defines the loading conditions for which fracture is stable; for a given material, the shape of the curve Σ depends on the geometry of the body. Assume the curve is as indicated in Figure 5. [Cook (1965) has derived a similar curve for fracture in compression.]

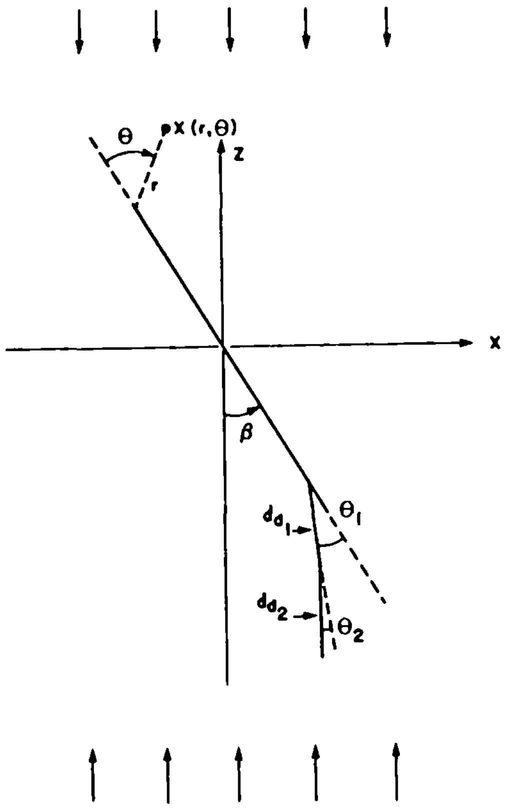

FIGURE 3

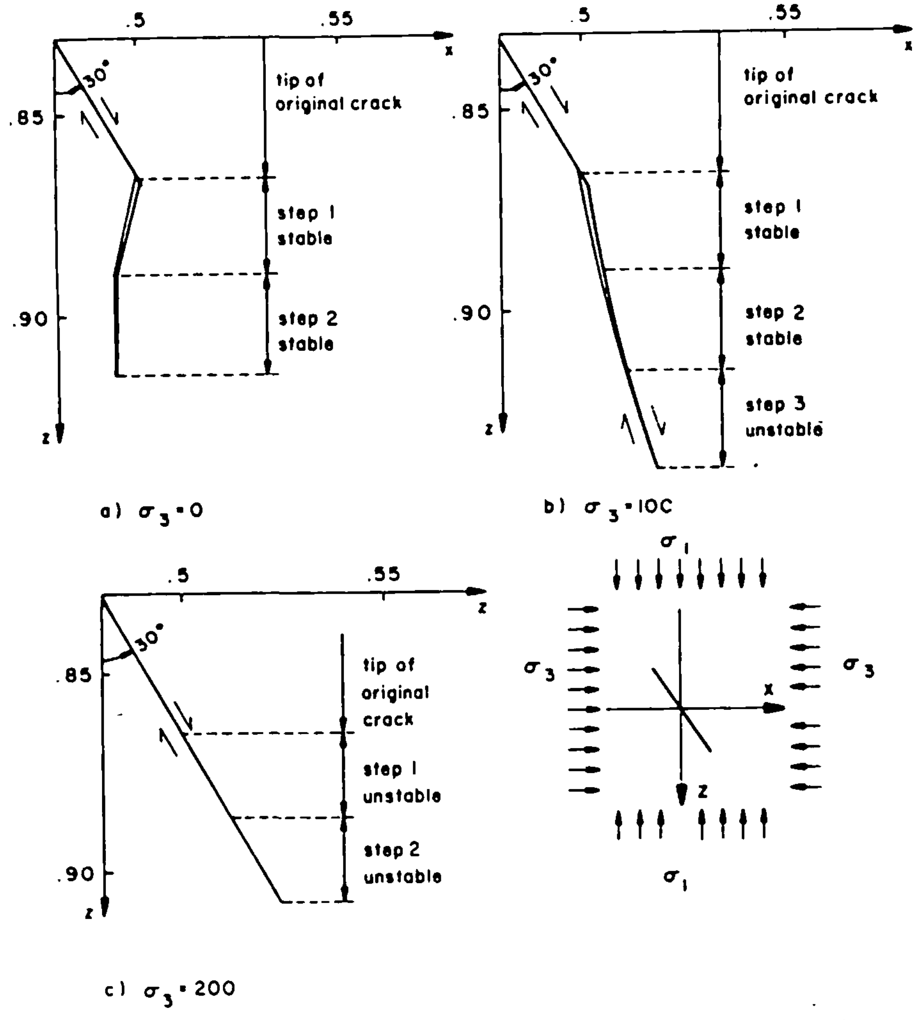

FIGURE 4

a) $\sigma_3 = 0$

b) $\sigma_3 = 100$

c) $\sigma_3 = 200$

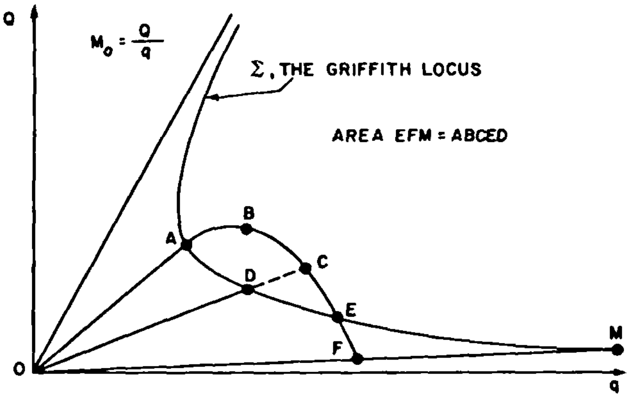

Figure 5

Let us consider the loading path OAD in which fracture extension remains stable: no kinetic energy is generated. It is readily seen that the area of the triangle OAD is exactly equal to the energy dissipated through creation of new surfaces if no heat is generated. This provides one way of measuring the free surface energy of the material, if the corresponding area increment is known.

Let us now consider the loading path OABCEF. At point A the loading path (Q, q) crosses the curve Σ so that the fracture starts to propagate, when the point (Q, q) is at C, the crack length is that which is attained at D. Indeed, virtually instantaneous unloading of the body would result in returning to a stable configuration along the path CDO, the slope of which (m) is a single valued function of the crack length). Thus the area ABCD represents the difference between the variation of potential energy and the quantity of energy dissipated through formation of new area: it corresponds to kinetic energy. A small part of the kinetic energy is dissipated through vibrating energy (be it an acoustic emission or an earthquake). If all this energy can be dissipated through the creation of new surfaces and heat, a new equilibrium state will be reached. This is precisely what occurs in all field situations whether the fracture process is a rock burst, an earthquake or an underground explosion. For such situations if the kinetic energy is large enough the fracture extension velocity varies with time and may reach a constant value which is close to the Rayleigh wave velocity (Erdogan 1968)*.

Consider the two fracture lengths l_1 and l_2 so that for fracture length l_1, the point (Q,q) for which the fracture extends is at J whilst for l_2 it is at J_1 (see Figure 6).

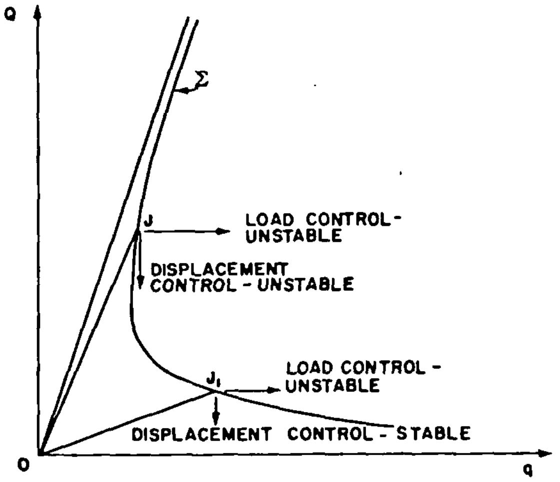

Figure 6

If the loading process is such that the load increases monotonically with time, for both crack lengths, once the points J_1 or J_2 have been reached the fracturing process becomes unstable since the point (Q,q) moves above the locus Σ (see Figure 6). If instead, the loading process is such that the displacement rate q increases monotonically with time, fracture propagation for the body with the crack of initial length l_1 is stable (the point (Q,q) follows the line Σ) whilst for the body with initial crack length l_2, fracture propagation is unstable (some kinetic energy is released even if the load is decreased without displacement).

For compressive loading conditions, these two last situations are similar to those described by Wawersik (1968) as class I (stable fracture development for monotonic displacement rates) and class II (unstable fracture development for monotonic displacement rate): The instability observed for the body with crack length l_2 occurs because the energy stored in the specimen is larger than that which can be dissipated through formation of new surfaces so that kinetic energy is generated. (This will be discussed further in the section on laboratory investigations.) Clearly, with a loading process in which the stored energy can be decreased whilst the crack grows by an amount equal to the difference between stored enegry and free surface energy, it may be possible to develop stable fracture propagation, This is precisely the concept which governs experimentation with servo-controlled testing machines: a parameter that varies monotonically with time as fracture develops is chosen as a feed-back parameter, so that the fracturing process is rendered stable (e.g. Rummel and Fairhurst 1970, Hudson et al.

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*Many research workers have addressed the problem of dynamic fracture propagation (e.g. Freud 1976, Das and Aki 1977, Madariaga 1979); however this very important question will not be discussed further here.

1971). This shows that fracture stability can be defined only with respect to the loading conditions: constant load increment rate; constant displacement rate; constant input energy rate, etc. For the class II problem described by Wawersik for example, control of fracture propagation was obtained by programming, on a servo-controlled testing system, a monotonic, non-accelerating, increase of specimen diameter.

Most rock masses are filled with some pressurised fluid, be it water, oil or gas so that the stability of fracture processes in such rock masses depends not only on the boundary conditions for the soild but also on that for the fluid phase. Fracture development in materials which exhibit pore pressure is governed by the effective stress law (Terzaghi 1945, Hubbert and Rubey 1958, Handin et al. 1963) which is expressed by the relation:

$$\underline{\sigma}' = \underline{\sigma} - \alpha P \tag{22}$$

where $\underline{\sigma}'$ is the effective stress tensor, $\underline{\sigma}$ is the stress tensor defined in the bulk material (solid + fluid) P is the pressure in the fluid, and α is a numerical coefficient, $0 < \alpha < 1$. For some time, discussions arose as to what value should be chosen for α (Terzaghi 1945, Robinson 1959, Serafim 1972, Cornet 1974); it is now generally accepted that, for fracture development, α must be taken equal to unity.

The variation of pore pressure with time (p) is governed by two factors: the rate of change of pore volume and the fluid flow rate, which itself depends on permeability and fluid viscosity. If the rate of change of pore volume (this is related to dilatancy: see Brace et al. 1968, Stuart and Dietrich 1974) is larger than the rate of fluid flow whilst fracture develops, the pressurized fluid acts as a stabilizing factor (e.g. Martin and Brace 1968, Rudniki and Rice 1975, Rice and Cleary 1976). Rice and Simmons (1976) conducted a mathematical analysis of the steady rate, plane strain problem of a quasi-statically advancing shear fault in a porous elastic solid. They showed that coupled deformation-diffusion effects lead to a speed dependent stress concentration at the fault tip so that the stress necessary to drive the fault increases with fault propagation speed up to a maximum value. When this maximum value has been reached, the nominal crack extension force required for fault spreading has increased by a factor between β and β^2 times its value for low speed (drained) conditions ($\beta = (1-\nu)/(1-\nu_u) > 1$, where ν and ν_u are the Poisson's ratio values of the bulk material in the drained and undrained conditions).

While, for slow spreading faults, pore fluid diffusion at a fault tip acts as a stabilizing factor, for fast slipping faults the presence of fluid under pressure along the fault surface may act as an additional cause of instability (Cornet and Fairhurst 1974). Usually faults are dilatant before slippage occurs (Ohnishi and Goodman 1974); this dilatancy may be developed in the gouge material that fils the fault but may also involve the slight opening of all the fractures which intersect the fault (Hoek and Bieniawski 1965). If locally a small local slip occurs along the fault so that the tangential stress is decreased locally, a corresponding slight pore volume decrease will ensue which will generate in turn a slight pore pressure increase. If the fault loading is close to slippage conditions, this slight increase in pore pressure may trigger additional slip which eventually will lead to complete failure along the fault. If, in the process (within less than 15 seconds for large earthquakes) the overall pore volume along the fault decreases with slippage, significant pore pressure increase will result giving rise to an apparently very low friction coefficient. Such a mechanism could help explain why so little heat is generated during earthquakes and therefore why the regional heat flux in active fault regions is lower that that expected from purely dry friction models (Lackenbruck 1980). It may be worth mentioning that in laboratory experiments, overall pore pressure increases were noticed when fracture of saturated specimens occurred in an unstable manner.

This problem of the effect of pore pressure on fault stability is one of central importance for dam foundation engineering and induced seismicity caused by the filling of large reservoirs acres tectonically active faults (see e.g. Simpson et al., 1981).

2 THE PHYSICS OF FRACTURE

In Section 1, it was found that even though fracture was assumed to develop in an ideal homogeneous linearly elastic solid, several questions remain unanswered concerning the mechanics of fracture propagation. It is particularly valuable in this situation to consider information provided by study of the actual physics of fracture. We will first consider the applicability of the results from Section 1 to simple laboratory experiments on rock samples. This will be followed be some tests conducted to investigate experimentally some of the unanswered problems. Finally a new theory on fracture development in compressive stress fields will be proposed.

2.1 Mode I Fracture Propagation

In many structural engineering situations, fracture propagates following the opening mode, and extensive experimental work has been conducted in this regard for metals. In particular, it is now generally accepted that for this type of material, "fracture toughness" (i.e., the critical stress intensity factor for mode 1 deformation) is a material property and standards have been defined for conducting accurate and reproducible measurements. (Standard E399 of the American Society for Testing and Materials). Accordingly, it is now common practice to determine precisely the maximum load which can be supported by a cracked structural element.

For rock type materials, it is well known that determination of the so called "tensile strength" is heavily dependent on the type of test used for the determination, and the advent of Linear Fracture Mechanics Theory has helped understand this discrepancy (see e.g. Hardy 1973). Presently, numerous testing procedures are followed to determine the "true" material property which controls the crack growth in pure mode I. This work is under study by ASTM subcommittee E24-07 so that standard testing techniques for rock may soon be proposed; an over-all review of common practices in fracture toughness testing of rock has recently been given by Ouchterlony (1980). The only main results are briefly presented below.

When attempting to measure fracture toughness in rock samples, Hoagland et al. (1973) observed that microcracking develops in the material neighbouring the crack tip. At first the microfracture zone increases in size with growth of the macroscopic crack but this growth levels off after a certain crack length has been reached so that fracture toughness measurements become independent of crack length. Similar results had been observed previously by Friedman et al. (1972) who invoked this microcracking phenomemon to reconcile measurements of free surface energy in rocks with those obtained for minerals. Since then, most of the work has been oriented toward careful definition of specimen geometry and test type so that reproducible measurements of either "free surface energy", fracture toughness, critical value of the J integral or critical strain energy density factor can be obtained. Presently the most popular type of test is the single-edge notch beam with three point loading or its equivalent, the single edge crack round beam, which can be prepared directly from cores recovered in the field (Bush 1976). Among other test types one may cite the double cantilever beam, the compact tension specimen, the ring test of the double torsion specimen. Specimen geometry is usually derived from metal testing practice, where the main concern is to minimize the plastic zone at the crack tip. In rocks, plasticity for mode I fracture propagation is usually considered to be negligible but the microcracking zone is similar to plastic deformation as far as the energy dissipation process is concerned. Thus it is assumed that specimen geometries that minimize the plastic zone in metals should also minimize the extent of the microfracture zone in rocks. Although no formal proof of this similitude has been given, it is interesting to note that results from various test types and specimen sizes which satisfy the shape standards defined for metals do tend to be quite comparable (see e.g. Ingraffea 1977). Further results by Costin (1980) and Rummel and Winter (1979) seem to indicate that loading rate does not significantly affect fracture toughness measurements.

Important factors affecting the results are environment (Westwood and Mcmillan 1973, Henry et al. 1977) and hydrostatic pressure (Schmidt and Huddle 1977). In the former case Westwood and Mcmillan proposed to use drilling fluids which enhance the "brittleness" of rock for improved drilling efficiency. In the latter case, Schmidt and Huddle found that a hydrostatic pressure equal to 7 MPa enhanced the fracture toughness of Indiana limestone by about 6% whilst a 62 MPa hydrostatic pressure led to a fracture toughness increase as high as 340%. This latter result tends to show that fracture toughness is not an intrinsic material property for rocks but depends on the local stress field.

2.2 Mixed Mode Fracture Propogation

Palaniswamy and Knauss (1974) investigated experimentally, on polyurethane material, the propagation of a planar crack, with a straight crack front, under antiplane shear (mode III). They observed that, along the crack front, small, somewhat lenticular shaped cracks extended on one of the original crack surfaces, spiralled through the formerly uncut portion of the solid, and terminated on the other surface of the original crack. They described the shape of these crack extensions as "parahelical". The individual crack extensions seemed to follow, on the average, some regular spacing along the crack front. Once these multiple cracks grew they began to interact, the larger ones overtaking the smaller ones by coalescing with each other. Similar results have been described for glass (Sommer 1969).

This indicates that not only may crack extension not be coplanar with the original crack surface, as previously descussed in the case of a motch inclined with respect to a uniaxial compressive stress field, but also that fracture extension may involve discontinuous cracking processes.

A somewhat similar discontinuous fracturing process has also been described in rocks by Taponnier and Brace (1975). They observed, in controlled fracture development in rock specimens submitted to triaxial compressive stresses, numerous "en echelon" microcracks starting either at the contact between the constitutive minerals or within the minerals themselves. On a broader scale this discontinuous fracturing process is well known by structural geologists, who describe "en echelon" fractures along fault zones (e.g. discussion by Segall and Pollard 1980). Thus a general fracture theory should allow for the possibility of discontinuous fracture extension. This suggests that fracture theories based only on critical values that a given parameter must reach in the neighbourhood of the crack tip may be too restrictive; however, the Griffith theory, which involves all ofthe energy dissipation processes, might still be applicable if some additional concepts are added to it.

2.3 Proposed Generalization of Griffith's Theory

As discussed at the beginning of the paper, the first law of thermo-dynamics implies that, during fracture:

$$\dot{U} + \dot{Q}_o = \dot{V} + \dot{T} + \dot{D} + \dot{Q}_1 \qquad (23)$$

where

$\dot{U}$ is the rate or work done by the applied loads,
$\dot{Q}_o$ is the rate of heat transferred to (or from) the solid,
$\dot{V}$ is the recoverable stored mechanical energy,
$\dot{T}$ is the rate of change of kinetic energy,
$\dot{D}$ is the sum of the rates of irreversible variations of internal energies,
$\dot{Q}_1$ is the rate of variation of stored heat.

For purely brittle materials, Griffiths proposed that D is directly proportional to the rate of area increment caused by surface extension. He then postulated that this quantity can be expressed, for quasistatic adiabatic conditions, by:

$$\Delta D = \gamma \Delta U \qquad (24)$$

where γ is the free surface energy per unit area. It has already been said that a more general expression for (24) is:

$$\Delta D = \gamma(\underline{n}) \; \Delta U \qquad (25)$$

where $\gamma(\underline{n})$ depends on the orientation of the newly created surface ("strength" anisotropy of the material).

Now let us propose that the free surface energy depends not only on the orientation of the newly created surface but also on the kinematics of the displacement discontinuity so that generaly:

$$\gamma_I(\underline{n}) < \gamma_{II}(\underline{n}) = ?\gamma_{III}(\underline{n}) \qquad (26)$$

Indeed in mode I propagation only, if two atoms have been separated in the development of a new surface, there is no further interaction between them once the crack tip has advanced sufficiently. On the contrary, in pure mode II or mode III, once the atoms have moved by a certain amount so that the atomic force which existed between them has been cancelled, they may come under the influence of other atoms so that new links may develop which will have to be broken if the displacement discontinuity is to reach a given finite quantity. Accordingly it would seem that in pure mode II or mode III propagation the surface energy should be much larger than for mode I. In fact this question should probably be approached following classical dislocation theory (see e.g., Friedel, 1956). For a homogeneous material, one may expect the $\gamma_{II}(\underline{n}) = \gamma_{III}(\underline{n})$ since the breaking of atomic bonds is the same for the two modes. However for heterogeneous materials, one shear mode motion may involve atoms of the same mineralogical constituent, while the other shear mode motion may involve atoms of two different constituents, so that the free surface energy may not be the same for both modes.

Is this postulate is accepted, then an energy balance involving the global system and another involving only a small domain near the crack tip, are no longer equivalent: the stress field generated by the displacement discontinuity along the crack may generate high enough stress some distance away from the crack tip so that dominant mode I cracks may develop in a discontinuous manner. If the distance from the crack tip at which microcrack extension occurs remains small, this effect may be included in the microcracking process that accompanies macroscopic fracture growth and local energy balance may give correct results. However for large enough distances of significant discontinuous crack growth, the microcracking model may no longer be valid and only an overall energy balance will yield the correct answer. An example of the latter is the problem of fracture development in rocks under triaxial compression. Prior to the appearance of a macroscopic shear plane, small scale splitting, oriented parallel to the direction of the major principal stress, occurs in such a manner that the microcracks become aligned along directions of maximum shear; this direction is governed by the specimen geometry as well as the boundary conditions. When the density of microcracking (the microcrack length may be of the order of a few millimetres or even centimetres) reaches a critical value, some instability caused by local buckling of the material contained between these fissures occurs, giving rise to the well-known macroscopic shear planes which lead to total collapse of the rock sample.

The following problem was examined in order to get orders of magnitude estimates for the difference that must exist between γ_I and γ_{II} or γ_{III}, in order for discontinuous crack growth to occur.

We consider an inclined fracture in a triaxial stress field and determine the strain energy released either by a finite surface increment, continuous with the preexisting fracture, or by small discrete en echelon cracks located along the fracture direction. Using Cornet's numerical model (Cornet, 1979), it was found that for a given en echelon crack density (all the discontinuous cracks had the same length) the energy released was about four times as high as that released by the optimum continuous path. The stress field conditions for this analysis were chosen such that the crack in the continuous extension configuration would be closed (the energy dissipated is thus proportional to γ_{II}). The corresponding en echelon crack configuration was found to leave the individual cracks open (the energy dissipated is proportional to γ_I). Accordingly if $\gamma_I < 4\ \gamma_{II}$ the en echelon configuration will result. In this model the pre-existing fracture is introduced only to generate high shear stresses, and should not be assumed to be the same as the shear fracture observed at the end of a real triaxial test.

This indicates that differences between γ_I and γ_{II} do not have to be very large for discontinuous crack growth to occur.

3 ROCK FRACTURE AND FRAGMENTATION

This section will discuss a number of practical applications of the principles of fracture mechanics outlined above. Although "fracture" and "fragmentation" both involve consideration of fracture processes, discussion of rock fracture concerns situations where behaviour along individual fractures is of major interest, whereas rock fragmentation involves the generation of a multiplicity of fractures which intersect in a solid so as to divide it into smaller pieces. As such, it is a natural topic for the application of fracture mechanics.

Rocks may be fragmented to a size suitable for convenient handling and transportation, as in drilling, tunnelling and mining; in other cases it may be necessary to reduce below a certain size to liberate ore particles or facilitate chemical reactions, as in crushing and grinding. In all cases a product of approximately uniform size is the ideal. Most fragmentation techniques produce a range of sizes, due in large part to the fact that energy is transmitted to the solid to be broken by compression, through essentially point or line loading. This implies non-uniform stress and energy distribution*, non-uniform size and inefficiencies in the fragmentation process. This fundamental problem will be seen in several of the fragmentation processes described below.

3.1 Hydraulic Fracturing

Hydraulic fracturing is a good illustration of the benefits which can be gained by applying fracture mechanics principles to rock mechanics problems. New design formulae have been derived for the development of large hydraulic fractures in homogeneous (Abe et al., 1976) or layered (Cleary, 1980) rock masses. Development of conection between boreholes by hydraulic fractures for geothermal energy recovery (Aamodt et al, 1979; Cornet, 1980) or in situ coal gaseification is now possible. A more accurate interpretation of the pressure curves obtained during small injection tests conducted for in situ stress measurements has resulted from a better understanding of crack propagation in anisotropic, discontinuous rock masses (Zoback and Pollard, 1979; Cornet, 1980); models developed to analyze magma intrusion in the upper lithosphere follow similar lines of reasoning (Pollard and Holzhausen, 1979).

Attention will be centred here on the influence of "strength" anisotropy, pre-existing fractures, and material inhomogeneity (interface between two different materials) on hydraulic fracture propagation.

Hydraulic fracture propagation is a fairly stable mechanism for the liquid flow-rate controlled situations encountered in the field (gas expansion caused by blasting is not discussed in this section). As mentioned in Section 1, the path followed by a fracture which propagates in quasi-static fashion is governed by the expression:

$$\Delta U(X) - \Delta V(X) - \Delta D(X) - \Delta U(X_o) - \Delta V(X_o) - \Delta D(X_o) < 0 \quad (G) \qquad (6)$$

where symbols have the meanings assigned to them in Section 1.

For isotropic materials, $\Delta D(X) = \Delta D(X_o)$, so that only the work done by external forces and the change in strain energy have to be considered. This is the well-known situation in which fracture propagates perpendicularly to the least principal stress. However, in materials for which the free surface energy is not isotropic, fractures may develop at an angle to the direction of the major principal stress. This has been observed in granite rock masses at depths up to 200 metres (Cornet, 1980). For such conditions, when hydraulic fractures are developed for stress measurement purposes, the shut-in pressure (P_F) is simply equal to the normal stress exerted on the fracture plane.

$$P_F = \underline{\sigma}\ \underline{n}.\underline{n} \qquad (28)$$

where $\underline{n}$ is the normal to the fracture:

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*Examples of naturally occurring uniform fragmentation are provided in the more or less hexagonal cracking of columnar basalts, due to fracture under a uniform biaxial tension induced during rock cooling, and mud-cracking where the tensions are induced by drying of the mud. These are interesting examples of Griffith theory. Hexagonal "crazing" is the most efficient way (i.e., requires the least surface per unit volume) in which to divide a thin plate into uniformly sized pieces. The size of the hexagons will be determined by the applied stresses and the specific energy required to form the cracks.

For such conditions, six different fracture orientations are theoretically needed to determine the local stress field. However, if one of the principal stresses is vertical and if injections are all conducted at levels that are not too far apart, the local stress field may be taken to be approximately:

$$(\underline{\sigma}) = \begin{matrix} \sigma_1 + \alpha\rho g z & 0 & 0 \\ 0 & \sigma_2 + \alpha\rho g z & 0 \\ 0 & 0 & \rho g z \end{matrix}$$

where $\rho g z$ is the vertical stress at depth z, σ_1 and σ_2 are "tectonic" stresses and α is an unknown proportionallity coefficient. With this simplification, three different fracture orientations only, at various depths, are necessary for the determination of the four unknown (σ_1, σ_2, α and λ, the orientation of $\underline{\sigma}_1$ with respect to North).

Questions may arise with respect to shut-in pressure measurements: the fracture orientation may not be the same at the wellbore and away from it (Daneshy, 1971). This can lead to erroneous conclusions concerning principal stress magnitudes and direction if the direction of the fracture at the borehole only is used in the interpretation of hydraaulic fracture pressure records (Mizuta and Kobayashi, 1980). If it is assumed that the rock mass is homogeneous and isotropic, this change of orientation can be correlated to a change in relative principal stress magnitudes (Zoback and Pollard, 1979) or principal stress directions (Mizuta and Kobayashi, 1980). However, if the rock is discontinuous (because of the existence of pre-existing cracks) these changes of orientations may simply be caused by these discontinuities.

The influence of a pre-existing fracture on the path followed by a hydraulic fracture extending in the σ_1 direction has been investigation numerically. The pre-existing discontinuity and the hydraulic fracture were both assumed to be parallel to the intermediate principal stress direction (the vertical direction in many practical cases). It has been found that if the discontinuity is inclined at less than 45 degrees to the maximum principal stress direction, the hydraulic fracture stops when it encounters the pre-existing fracture and flow occurs along this new plane. For angles larger than 45 degrees, both the magnitude of principal stresses and the friction coefficient along the pre-existing discontinuity must be known is the exact path of hydraulic fracture extension is to be determined.

Another important problem is that of three-dimensional hydraulic fracture propagation in a two-layered material; the interface between the two materials is assumed to be horizontal, and one of the principal stresses is assumed to be vertical (see Figure 7).

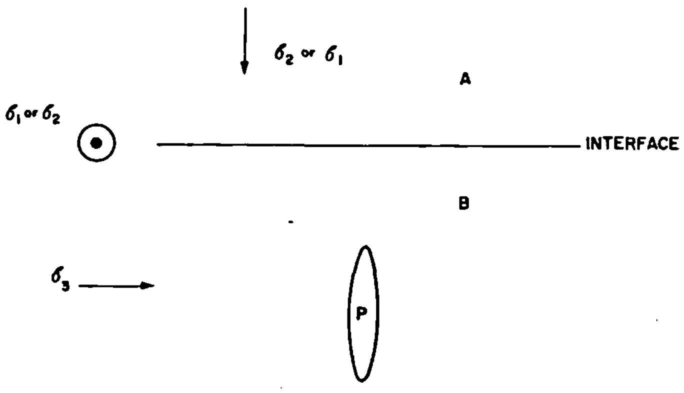


Figure 7

This specific question has been discussed recently by Cleary (1980); solutions to the more general problem of a crack reaching an interface between two different materials have been presented in the literature (see e.g. Lin, 1973; Comninou and Dundurs, 1979). The concept of fracture toughness cannot be applied in this case, since the stresses are not singular in $r^{-1/2}$ (where r is the distance between the point at which stresses are being computed and the tip of the crack); fracture analysis using energy balance criteria directly must be used. Studies are underway (by Cornet) to obtain numerical solutions for the computation of maximum energy release when the fracture extends vertically in material A, or horizontally along the interface C. These numerical solutions can, of course, yield specific solutions only if the free surface energy (work of fracture) values are known for mode 1 crack propagation in materials A and B; and the corresponding value for mode II crack propagation along the interface between A and B must be determined to investigate the possibility of shear fracture propagation along the interface. Although this is an important parameter, necessary for analysis of a practically important problem (i.e., whether fractures will be confined to a particular stratum or whether they will extend across an interface into another stratum), no standard testing technique exists for its deformation.

3.2 Rock Bursts and Coal Bumps

Rock "burst" is the term used to describe the sudden, violent collapse of rock in the vicinity of an underground mining operation. Coal "bump" describes a similar phenomenon in underground coal mines. They can occur in mines of any depth, but are most prevalent in deeper mines. Since they unsually happen in the immediate vicinity of the working area, where miners and mining equipment are concentrated, a burst or bump can be a very serious event. Important advances in understanding, and mitigation of their dangerous consequences have been made in recent years, due primarily to studies at the Mining Research Laboratory of the South African Chamber of Mines (see Jaeger and Cook, 1979, Chapter 18). The brief comments below are intended to illustrate a very fruitfull practical application of fracture mechanics principles.

Many mines in which bursts or bumps occur are thin, vein-like ore bodies, and excavation can be approximated as narrow almost horizontal slits in an elastic medium (South African gold mines, for example, may approach 4,000 metres in depth, with the workings often only 1.50 to 2.00 metres in height). The change in strain energy (W_1) in an isotropic elastic plate due to introduction of a narrow slit length 2a, normal to the compressive principal stress σ is (Jaeger and Cook, 1979, pp 327-329).

$$W_1 = (1 - \nu^2)\frac{\Pi\sigma^2C^2}{E} \quad \text{per unit thickness (plane strain)} \qquad (29)$$

Assuming that the rock excavated can absorb energy γ_m per unit increase in length, in quasi-static crushing. Then, following Griffith theory, the change in potential energy (P) of the extraction system, due to introduction of the slit is

$$P = C\gamma_m - \frac{\Pi\sigma^2C^2}{E} \qquad (30)$$

this system will be unstable, i.e., rapid violent crushing, or rock bursts, will occur if

$$\frac{\partial P}{\partial C} = \gamma_m - \frac{2\Pi\sigma^2C}{E} < 0 \qquad (31)$$

Few, if any, measurements have been made of the value of γ_m, so that inequality 31 cannot be evaluated exactly. Even so, it is clear that the instability or rock burst potential, will increase as the second term increases. This, the spatial rate of energy release, has been termed the Energy Release Rate, or "ERR" by mining engineers, and is now used in analysis of mining layouts. Although actual mining extraction patterns are more complex than the simple extension of a slit, the same principle holds. In plan view, extraction of an aerial section of the mine will release a certain amount of energy. Assuming the rock mass above and below the mining horizon behaves elastically, the total energy released is independent of the sequence of incremental steps by which the section is extracted. However, the rate at which the total release is achieved will vary, and will depend on the position of the section geometrically with respect to other mining operations. In Figure 8, for example, the total energy release E_m, could be approached along path 1 for one extraction sequence, and path 2 for another. In each case the ERR varies over the extraction, and may reach dangerously high values (at the start in path 1, towards the end in path 2). Ideally, path 3, which produces a constant ERR may be the ideal - it may also be concluded that the maximum E_m should be reduced, in which case "backfilling" (introduction of waste material into the excavated portions), may be used to limit the total deformation. Analog and digital computer programs are now available which allow computation of ERR values for complex excavation patterns (Jaeger and Cook, 1979, Chapter 18). Correlation between the damage produced by a rock burst and the ERR show a close correlation. There have been substantial improvements in the design of roof support systems to withstand bursts and, overall, a better appreciation of practical measures that can be taken to reduce the frequency, severity and danger of bursts. US Bureau of Mines research on modifications in mining method and use of "destressing" (heavy blasting of rock ahead of the region to be mined to release energy when no mining is underway), to reduce rock bursts in the Coeur d'Alenes mining area, also based on ERR analysis, appears to be leading to improvements (Board, 1981, personal communication).

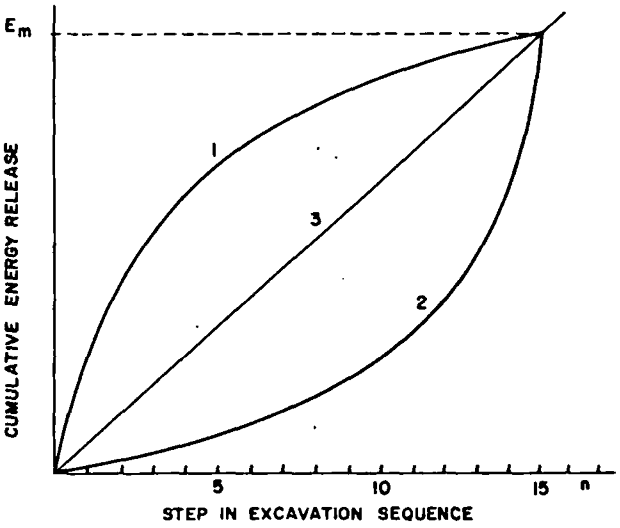


Figure 8

Application of ERR analysis to the problem of coal bumps has revealed that the nonlinear inelastic deformation behaviour of the coal seam in the vicinity of the excavation is an important factor that has a very significant effect on the pattern of energy-release rate. In effect, the peak stress concentration, assumed to develop at the face of the mining excavation in ERR applied to brittle rock (such as the quartzites in South Africa gold mines), are developed behind the face. It is thus necessary to recognize this in inequality 31 by incorporating the force-deformation behaviour of the seam for the γ_m generalization. Even though this complicates the analysis, application of ERR principles is very informative in developing understanding of coal bump phenomena (Fairhurst, 197?).

It appears that analysis of energy changes is a potentially very fruitful avenue of practical research development in mining rock mechanics. It is also evident that the most important need is for more information on the deformation behaviour, full-scale, of the rock affected by the mining activity, especially in the vicinity of the mining level(s). Put another way, the mine itself must be the laboratory. Given the variability of rock, it is necessary to have information on many locations in the mine. Given the expense, and usually the impracticability, of installing detailed instrumentation in more than one or two locations, the most rewarding approach would seem to be that of combining overall qualitative observation (e.g. involving dialogue with practically experienced engineers and miners; simple measurements of convergence etc.) iterative numerical modelling, "informed" by relevant laboratory experiments, to bring prediction into reasonable correspondence with observation, and "a posteriori" analysis of bursts and bumps. Studies such as these require painstaking efforts and success does not appear quickly. Nevertheless it is only from good engineering application that the missing design information can be obtained, and hence this is the direction in which future applied rock mechanics should be headed.

3.3 Laboratory Investigations of Rock Fracture

Laboratory studies of rock fracture have evolved considerably in recent years. The advent of stiff and servo-controlled testing machines indicate recognition of the energetic basis of fracture, and provide good experimental tools for further studies of rock fracture phenomena. The use of fracture toughness concepts to characterise "rock strength" is further evidence of this recognition. It is still necessary to emphasise that the main value, and a very important one, of laboratory studies in rock fracture is phenomelogical, i.e., to understand the processes and mechanisms involved. Numerical values provide useful indices in some cases, but problems of heterogeneity, scale, and inability to simulate field conditions are often severe constraints in attempts to apply laboratory-derived values directly to actual problems.

Complete load-deformation curves, for example, depict heterogeneous processes, especially in the post-peak deformation range. It can be very misleading to report these data as stress-strain curves. Figure 9 shows a type of compressive load-deformation curve (referred to in Section 2.1 as class II behaviour). In appearance it is similar to the Griffith locus shown in Figure 6. Study of specimen deformation in such tests usually reveals the development of a zone of intense deformation (B) between two intact wedges (A).

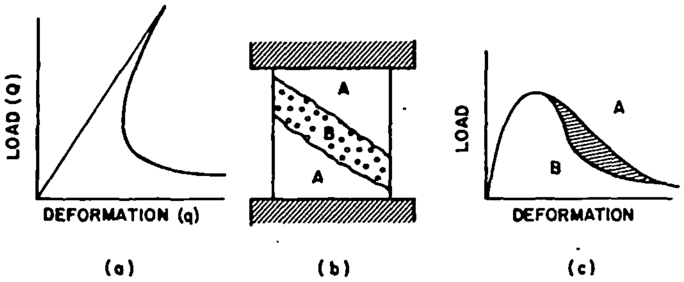


Figure 9

Once the peak load resistance of region B is exceeded, the elastic energy stored within the specimen in region A, exceeds that which can be absorbed by B. The excess energy [shaded in Figure 2 (C)] will be transformed, even with a rigid loading machine, into kinetic energy, causing rapid collapse of the specimen - unless the excess is extracted via another path, i.e., by reversal of the testing machine platens. Certainly we could expect different shapes of the unloading curve if the specimen dimensions are changed - the curve is in no way representative of a homogeneous stress-strain behaviour of the rock. There is a similarity to the Griffith locus in that one crack (or zone of fracture growth) is developing due to energy being released from a large (but finite) elastic region. As the crack (or dissipative zone) increases in relation to the elastic energy "reservoir" the overall system becomes progressively more stable.

A further example of the complexity of rock deformation processes is provided by the comparison of tension and compression strength data on the basis of Griffith theory. Using Cook's (1965) version of the Griffith criterion for fracture in compression, viz.

$$\tau - \mu\sigma_n = \frac{E\gamma_2}{\Pi C} \qquad \text{...compression}$$

analagous to $\sigma_t = \frac{E\gamma_2}{\Pi C}$ ...tension

where τ = shear stress along the "plane of shear failure".

σ_n = normal stress acting across the "plane of shear failure".

σ_t = uniaxial tensile strength.

E = modulus of elasticity in tension and compression (assumed equal).

C = critical Griffith crack.

γ_1 = specific work of fracture in tension (referred to earlier in this report as "free surface energy").

γ_2 = specific work of fracture in shear (referred to as "free surface energy" earlier).

we see that

$$\frac{\gamma_2}{\gamma_1} = {\frac{\tau - \mu\sigma_n}{\sigma_t}}^{2} \qquad (29)$$

Substituting typical values of tension and compression or shear strengths of rock into equation 29 we find that $\gamma 2/\alpha$ can vary considerably and is usually in excess of 10. This illustrates, as is well recognized, that the work of fracture (or free surface energy) concept is far more complicated than the surface energy envisaged by Griffith. Also, the sequence of processes in shear (compression) differ from those in tension, as has already been alluded to in Section 2.3. Study of these phenomena can be very valuable; they are operative also in larger scale deformation, and analogous features (e.g., en echelon fracturing in the vicinity of faults) can be seen in the field.

Although the problem of scale cannot be solved entirely in the laboratory (i.e., field tests are an essential part of rock fracture research) there is much to be learned from tests on larger specimens under the controlled conditions of a laboratory. Studies of fracture propagation where the effects of crystal scale heterogeneity are minimized, where detailed observations can be made of fracture extension (e.g., out of plane propagation) without serious interference from specimen boundaries, where the origins of microseismic emissions associated with fracturing could be accurately located etc., would all provide valuable information for use in resolving currently inportant questions. These studies imply specimens of the order of 1 metre length scale, high loads and special equipment. Although too costly to justify in all laboratories, a few such installations nationally (developed under programs analagous to the geotechnical centrifuge testing facility established by the National Science Foundation at the University of California - Davis, and NASA - Ames Laboratory could do much to advance understanding of rock fracture phenomena - an understanding that is vital to many of the resource-related applications of rock fracture technology.

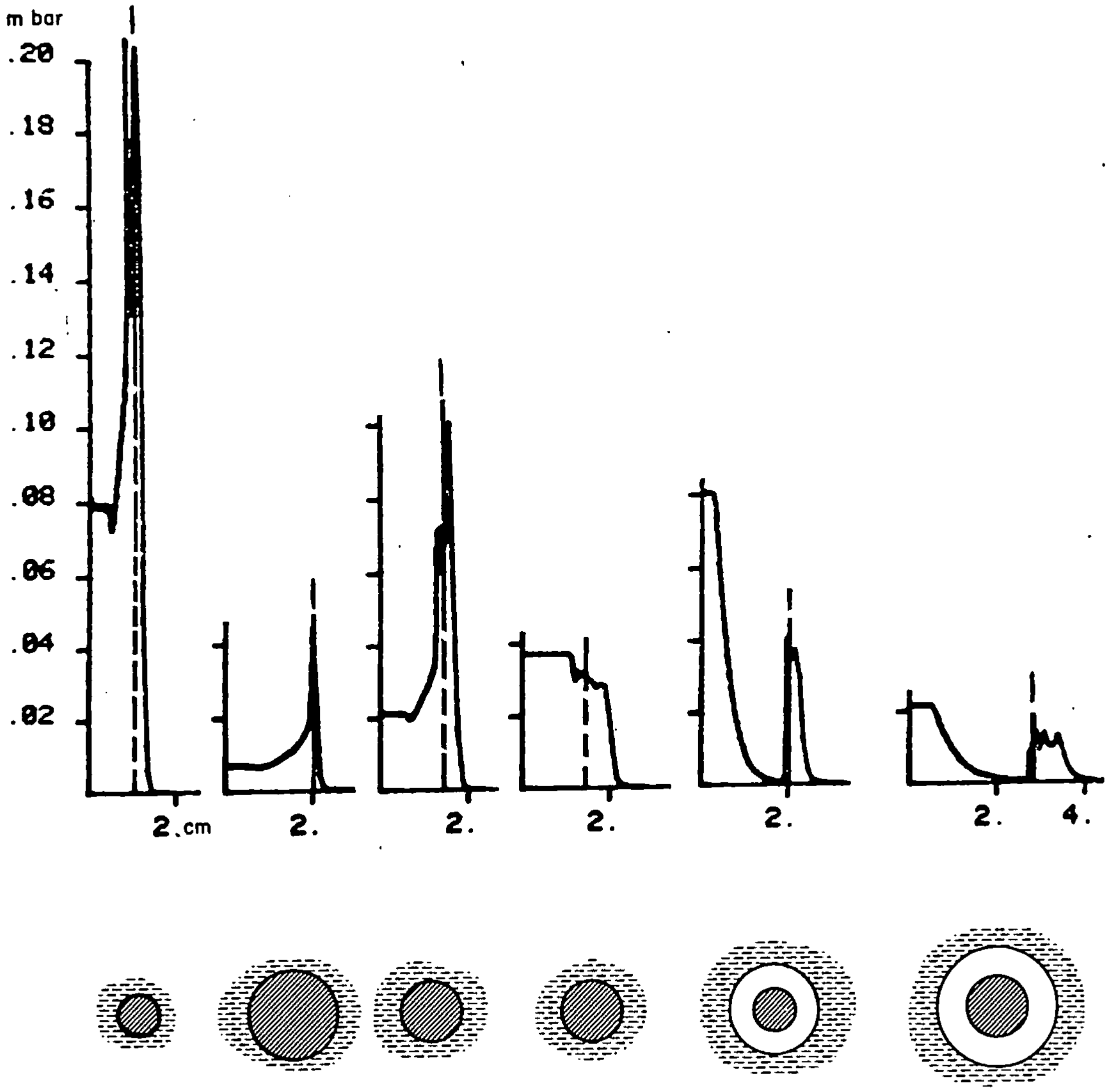
3.4 Blasting

Chemical explosives are a very convenient form of energy for breaking of rock in situ. Although explosives have been used for many years, the mechanics by which they break rock are still poorly understood, largely because of difficulties in making experimental observations. High explosives detonated in a borehole generate gases at pressures of the order of 100,000 bars, and temperatures of several thousand degrees centigrade, these conditions being reached in 1 to 2 microseconds; and in the interior of an opaque solid! Nuclear explosives generate considerably higher pressures and temperature.

Explosive detonation in a cylindrical borehole produces a very rapid exothermic chemical reaction which propagates through the explosive column as a shock wave, generating the above-mentioned high pressure gases, which in turn impact the borehole wall and propagate a strain wave into the rock. The velocity of explosive detonation and strain wave velocity are of comparable magnitude so that the wave front in the rock assumes a conical form spreading from the detonation front moving along the explosive column. Variation in point(s) of detonation is used to direct the wave front to advantage in the rock mass. Although "simultaneous" detonation in several boreholes is intended to produce concurrent and sequential explosive action over an extended region of rock, variations in standard commercial detonators do not give the needed degree of coincidence or intervals between detonation. Considerable improvement is obtained by use of precise electrical timing of detonation (Winzer, 1980; personal communication).

Recognising that explosive fragmentation in practice is a complex three-dimensional process involving interactions between several explosions, anisotropic rock, etc., it is still instructive to consider the simplified case of an explosion in a long cylindrical borehole, detonated simultaneously along its entire length. In this case the conical wave front spreading into the rock degenerates into a cylinder concentric with the borehole. The very rapid radial pressurisation of the borehole produces an associated tangential stress which is initially compressive (see Bligh, 1974) and combines with the radial pressure to produce an annulus of intensely pulverised rock around the borehole. This is a highly dissipative process. The shock wave travels radially outward into the rock producing further crushing, progressively less intensive, and being heavily attenuated in the process. Eventually the wave decays to the point where it is "essentially elastic", travelling at sonic velocity with a tangential tension associated with the radial compression. Cracks begin to extend from flaws that are temporarily overstressed as the wave passes over them but, since they cannot travel as fast as the wave (see Section 1.2) they are soon unloaded and cease to propagate.

Efforts are being made to develop numerical models to describe the intense damage region produced around the borehole during passage of the initial strain wave.



	CJ176	CJ44	CJ88	CV88	ACJ 176	ACJ 88
Type	C-J deton.	C-J deton.	C-J deton.	Const. vol. expl.	C-J deton. air gap	C-J deton. air gap
Borehole Radius (cm)	1	2	$\sqrt{2}$	$\sqrt{2}$	2	$2\sqrt{2}$
Charge Radius (cm)	1	2	$\sqrt{2}$	$\sqrt{2}$	1	$\sqrt{2}$
Charge Density (g/cm^3)	1.76	0.44	0.88	0.88	1.76	0.88
Average Charge Density Calc. on the Borehole (g/cm^3	1.76	0.44	0.88	0.88	0.44	0.22

(Note all cases have the same charge weight/length unit, namely: 5.529 g/cm)

FIGURE 10

Johnson (1979), has used a numerical model in which the rock (in this case, oil shale) is considered to behave as a plastic continuum, and incorporates a "damage" parameter to characterise the intensity of fracturing away from the borehole. Dienes (1979) is developing a model for the constitutive behaviour of the rock in this region based on a Griffith criterion, generalised to include anisotropy.

Additional rock fractures may also result from reflection of the compressional strain wave at a free surface. Fourney el al., (1978) have conducted numerous experiments using photoelastic models to examine the interaction of elastic stress waves generated in explosions. Although the energy contained in the strain wave emanating from the intense damage zone is a small proportion of the total explosive energy, it does appear that this wave may contribute significantly to the overall fragmentation process by conditioning (i.e., weakening through crack lengthening) the rock mass. If precise timing of detonation can be achieved it may be feasible to further augment this conditioning role of the strain wave by appropriate selection of the points of explosive detonation.

The gas pressure in the borehole remains high for considerably longer than the period of detonation and produces behind the strain wave a quasi-static stress distribution (radial compression, tangential tension) in the rock. This stress state tends to open up and extend the cracks initiated by the stress wave, but flow of the gas into the cracks is impeded by the relatively impervious zone of crushed rock around the wall (the extent of the zone will depend very much on the rock type and explosive, and may be a few centimetres thick only in hard rock). Ultimately, however, as cracks reach the free surface, the fragments become detached and are ejected rapidly by the escaping gases.

Bligh (1974) has noted that development of the pulverised zone is a consequence of the very rapid rise in borehole pressure, and can be reduced or even eliminated if the rise-time is increased. This can be accomplished in several ways: use of lower velocity of detonation explosives (e.g., Ammonium Nitrate-Fuel Oil - ANFO), by decoupling of the explosive column from the rock wall (i.e., leaving an air gap around the explosive, reducing the explosive density with inert filler, or by developing special explosive devices that allow controlled pressures and rise-times (Bligh, 1974). Cooper (1980) has modelled the effect of explosive type and decoupling for several cases, and demonstrates that the pressure on the borehole wall can be changes substantially (Figure 10).

It appears, therefore, that increasing the rise-time to eliminate the pulverised zone also involves reduction of the peak pressure. However, since gases may more readily enter the fractures this may lead to more effective rock fragmentation. Hardy (1974) and Ouchterloney (1974) have derived the curves shown in Figure 11 which illustrate that the pressure required to extend radial fractures from a borehole is very much reduced when gases (fully) enter the fractures compared to the case where the gases are restricted to the borehole - as in approximately the case where the pulverised zone is well developed.

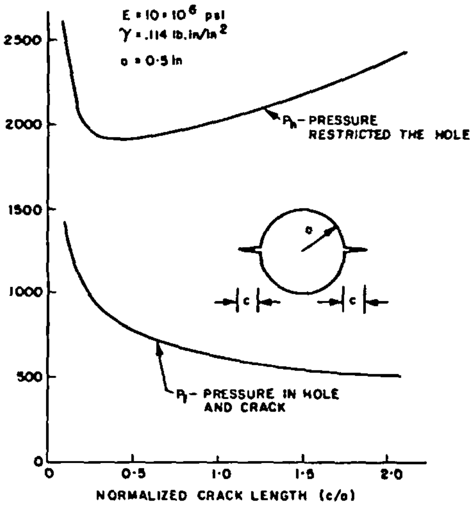


Figure 11

Increased rise-time involves a related effect which should be noted. As a crack AA' in Figure 12 begins to extend from the borehole due to the tangential tension developed by the (slowly rising) gas pressure, strain energy is released in the region A'CC' on each side of the crack. (It is assumed for the present that no gas enters the extending crack.) The rate of growth of the unloading region along the borehole wall (CC') is of the order of the Rayleigh surface wave velocity for the medium. A crack (BB') adjacent to the first crack could grow simultaneously, independently of the latter as long as the two unloading regions (A'CC and B'DD') do not overlap. Cracks in the region between CC' and DD' will not extend since the requisite strain energy is not available. The more rapid the rise in the gas pressure (and hence the tangential tension that initiates the cracks), the greater the number of cracks that can be initiated and extended radially. Thus, it is desirable to reduce the rate of pressure rise to ensure immediate tensile cracking of the borehole wall, but to increase the rate of pressure rise to maximize the number of radial cracks that are generated. This implies optimization of explosive conditions in the borehole. (A similar argument can be used for the case where gases enter the fractures.)

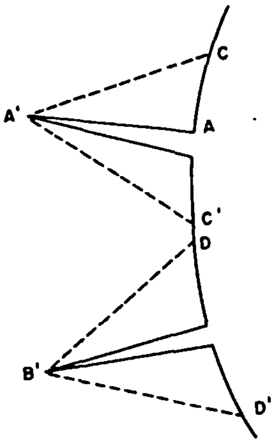


Figure 12

The volume of the fractures is initially small compared to the volume of the borehole, so that, although some cooling will occur, gas pressure will remain relatively high compared to the rock stresses in situ, and the tips of the uniformly extending cracks may be considered to define a circular region of hydrostatic pressure (Kutter and Fairhurst, 1970) equal in magnitude to the explosive gas pressure in the cracks. This pressure will drop with crack extension and, eventually, further growth will be affected by:

(i) the in situ stress field;

(ii) any changes in the stress field produced by the proximity of surfaces;

(iii) by any anisotropic characteristics of the rock.

Extension of fractures by gas pressure may therefore be considered approximately in terms of expansion from a circular cavity, effectively several times larger than the borehole. The pressure in the cavity is sufficiently low that the point of maximum tension stress on the "wall" of the effective cavity is significantly influenced by the in situ stresses in the rock. Following the numerical method of analysis for inclined crack propagation described above (see Section __) and invoking the requirement that the path of fracture extension be that for which the rate of decrease of potential energy of the system be a maximum (see equation 6) it is found that two adjacent boreholes, when pressurised simultaneously in the vicinity of a free surface, will form two independent craters or a single interconnected crater depending on the spacing between the two boreholes, the distance to the free surface (burden) and the stress acting parallel to the surface (Figure 13).

The allowable spacing between the two in order to ensure inter-connection increases with the radius of the effective circle which, in turn, depends on the rate and extent of gas penetration. It is assumed that propagation of cracks in other directions will tend to decelerate quickly as the most unstable cracks, i.e., those defining the contours of the excavation, begin to extend beyond the effective circle and gas pressure tends to flow preferentially into the contour cracks.

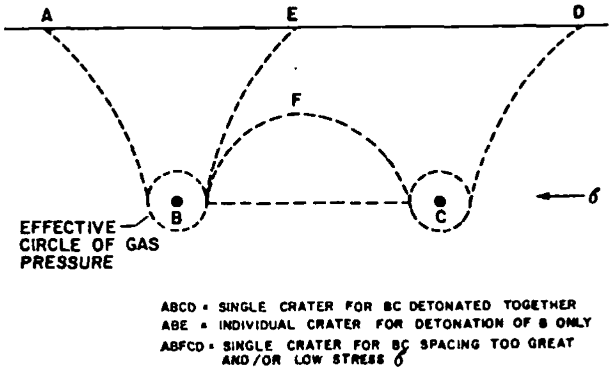


Figure 13

Explosive fracturing is finding application in the development of fractures at relatively great depth, e.g., for geothermal energy recovery, and in situ mining. It is important in such cases to recognise a fundamental difference from conventional blasting - the absence of a free surface. This implies that there will be no reflection of the strain wave and that the pattern of fracture propagation due to gas pressure will be controlled by the in situ stress state and any anisotropic features of the rock mass. It is likely that the cracked region would be elliptical in plan view with the long axis parallel to the direction of maximum compression, modified somewhat by anisotropy. Ideally, it could be expected that fractures would open initially under gas pressure, but close again when the pressure was released, either by cooling or by expansion up the borehole. However, the tearing and rotation of grains associated with fracture propagation in rock will probably allow a path of relatively high permeability to be created along the fracture path. Subsequent quasi-static pressurization, e.g., by hydraulic pressure, is likely to re-open only the crack normal to the minimum compression. Creation of an array of open (i.e., high permeability) fractures at depth poses difficulties and may require novel techniques (e.g., the use of dynamic propping where a fracture propping agent is introduced explosively).

3.5 Drilling

Most rock drilling processes involve the use of mechanical indenters (bits) forced into the rock surface. The high forces under the bit-rock contact area produce intense, biaxially or triaxially compressive stresses which lead to the formation of a wedge of pulverised material immediately below the surface. This wedge allows the development of lateral stresses on the solid rock outside the wedge and ultimately the formation of discrete fractures which propagate to intersect the surface, forming chips. Although the geometry and angle of attack of the indentor vary with the hardness of the rock the basic mechanics of penetration in drilling remain the same, and improvement in penetration rates have been determined in large part by the development of tools able to impart and sustain higher compressive forces on the rock. Prompt separation of the chip from the intact rock can be a serious problem, and it is important to avoid "overcrushing", for example, in petroleum exploitation, when drilling under high hydrostatic head in a deep vertical hole. Although the scales are much different, there appears to be a similarity in drilling and blasting in that fracture extension may be inhibited due to the difficulty of developing, within the fractures radiating from the point of load application, pressures that tend to open the fractures Drilling rates may be substantially increased when the mechanical bit indentation process is supplemented by fluid pressure directed at the bit tip in order to enter the fracture. Similarly, the use of high pressure water jets in place of the mechanical indenters appears to result in more effective drilling. As noted by Jaeger and Cook (1979) the key to successful drilling appears to lie in maximizing the volume of rock detached by the extension of discrete fractures (i.e., the chipping process in drilling) for a given amount of energy used in the preceding (pre-chipping) phase necessary for the application of forces beneath the rock surface*.

The direct approach, i.e., of increasing the depth of penetration (and excavation rate) by mechanical indentation implies high penetration forces, deep cuts per indentation, and rapid repetition of the chipping process. Assuming effective removal of chips (e.g., by water jets), the principal limitation to increased performance in this direction, as noted above, is the ability of bit materials to sustain the required high, repeated forces. The alternative of reducing forces and energy required to fracture the rock has been examined by several investigators, usually in terms of adding chemical "softening" agents to drilling fluids, (Westwood and McMillan, 197_) but no significant practical improvements have yet appeared.

4 CONCLUSIONS AND RECOMMENDATIONS

The authors have been aware from the start that it would be impossible within the constraints of time, limited availability of some material, and knowledge of the subject, to prepare a comprehensive state-of-the-art review of the broad topic of rock fracture and fragmentation. It is clear that there are many actual and potential applications of rock fracture mechanics and that the subject is increasing in practical importance. Our more limited objective has been to suggest general approaches that seem promising, illustrated through discussion of several applications. We would be pleased if colleagues who recognise important points or developments that have been overlooked are stimulated to contribute to the discussion of this important subject.

Specific observations and recommendations are as follows:

1) The growing interest in the application of developments in fracture mechanics to problems of rock mechanics is to be welcomed in that it indicates an appreciation of the fundamental significance of energetics and stability to analysis in rock mechanics.

2) It is important to recognise that the type of problems encountered in rock mechanics and those in fields which have stimulated fracture mechanics' development to date are different and that, correspondingly, rock fracture mechanics may need to develop differently.

3) It is recommended that rock fracture mechanics emphasises the global energy change approach as described, for example, by Palaniswamy and Knauss (1974). Although linear elastic fracture mechanics, which is essentially a derivative of the global approach, is valuable and convenient in some applications, there are important rock mechanics' problems for which it is not well suited.

4) Boundary element methods of numerical analysis provide a modest cost tool for analysis of fracture problems and the energy changes associated with fracture.

5) Laboratory studies can provide valuable insights into the overall mechanics of

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*It is interesting, for example, that the rock excavation efficiency of rock blasting is considerably higher than that of drilling (Jaeger and Cook, op. cit.). In blasting, the drilling of boreholes corresponds, in effect, to the inefficient indentation (pre-chipping) phase in drilling; but the boreholes are a smaller proportion of the total excavated volume. This suggests the desirability of research to develop a more continuous form of drilling and blasting excavation.

rock fracture, but facilities to test larger specimens are needed, especially for studies of planar and non-planar fracture extension and fracture interaction. Such tests can also serve as a check on the validity of numerical models of fracture, and provide guidance for field testing programs.

6) Full scale in situ tests of rock fracture initiation and extension are essential to incorporate scale and other effects that cannot be modelled in the laboratory. Considering the experience of field programs, international co-operation is recommended.

7) Research is needed to better estabish the relationships between in situ rock stresses and the orientation of fractures induced at the borehole during hydraulic fracturing.

8) Strength anistoropy and discontinuities such as pre-existing fractures and interfaces between two rock types significantly influence fracture propagation and orientation. Research is needed to better define ways of controlling the direction of fracture propagation in the presence of such features.

9) Research is clearly needed to improve understanding of the mechanical action of chemical explosives on rock, especially in the neighbourhood of the borehole. This research will be especially valuable in understanding both near surface bla+ting and blasting for fracture generation in deep boreholes.

10) The advances in underground mine design due to the introduction of the Energy Release Rate notion illustrate how rock mechanics principles can be applied to practical advantage even though some factors in an analysis may be understood only qualitatively. Similar developments are possible in other applications of rock mechanics.

11) Effective rock fracture and fragmentation is a key element of many currently important problems such as improved liquid and solid fuel resourse recovery, geothermal energy, controlled blasting etc. Realisation of these applications will require a substantially greater, long range, continuing committment to rock mechanics research than hitherto.

5 ACKNOWLEDGEMENTS

The senior author wishes to thank the Institute de Physique du Globe, Universite Paris VI, the Delegation Generale a la Recherche Scientifique et Technique, Paris, the Mineral Resources Research Center and the Institute of Technology of Minnesota for providing the opportunity to undertake the preparation of this report. We wish also to thank especially Miss Sylvia Nicholson for her outstanding efforts, forbearance and excellent co-operation in typing the manuscript under severe time constraints.

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Economic Geology
Vol. 67, 1972, pp. 198–213

Regional Fracturing in Laramide Stocks of Arizona and its Relationship to Porphyry Copper Mineralization

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Abstract

Joint sets, veins, dikes, and faults were examined in eight nonproductive Laramide stocks and three porphyry copper deposits scattered throughout the Basin and Range Province of Arizona. A structural analysis of these features, employing Schmidt equal-area plots and strike histograms, demonstrates that comagmatic dike swarms and consanguineous mineralized fractures are systematically oriented in a simple pattern. This pattern consists of a near-vertical system of orthogonal fractures striking ENE ± 20° and NNW ± 20°. Only one other fracture set striking WNW is recognized as a reproducible element on a regional scale.

In nonproductive stocks of various size, shape and structural setting, NNW-striking joint sets are typically unmineralized, irregular, curviplanar and discontinuous; whereas ENE-striking sets are continuous, planar, and often mineralized. All stocks show a marked preference for dikes, veins, fault-veins and mineralized joint sets to strike ENE. This repetitious orthogonal fracture system is clearly regional and tectonic in origin and is not restricted to specific Laramide stocks.

In contrast, a similar structural analysis in productive stocks demonstrates that *both* NNW and ENE sets of the regional system are preferentially mineralized in the three porphyry copper deposits studied. A more haphazard orientation of mesoscopic fractures suggests that areas of ore-grade mineralization may be accompanied by the development of radial and concentric fracture patterns or other kinds of local fracturing. This compounding of directions and types of mineralized elements coupled with the ubiquitous appearance of crosscutting microveinlets, microfractures and hairline cracks produces a mineralized fracture pattern reminiscent of the familiar "crackle breccia" or porphyry copper stockwork. Nevertheless, within this complex, mesoscopic structures are systematized with the regional, orthogonal pattern predominating.

The Laramide structural relationships delineated by this analysis are accounted for by accepting the presence of a major upwarp and subdued local arches elongated NNW throughout most of Arizona. Differential vertical uplift of these crustal blocks occurred under the influence of weak ENE-directed horizontal compression. This stress fixed the axis of maximum compression (P_1) within a vertical plane striking ENE during much of the orogeny. With this orientation, P_1 was either vertical during periods of pronounced differential rise or horizontal during periods of ENE-directed lateral compression. Maximum NNW expansion of the rising Laramide blocks was accomplished by transverse extensional fractures striking ENE, while expansion toward the ENE was restricted by the weak regional compression (either P_1 or the intermediate principal stress axis, P_2).

The mineralized NNW and ENE fracture sets delineated in porphyry copper deposits are also interpreted as extensional in nature. This system, however, was probably generated in areas of abnormal tectonic elevation which enhanced horizontal de-stressing adequate to form NNW fractures together with the more pervasive and continuous ENE fractures. Repeated activation of this fracture system played an important role in mechanically preparing ground to allow porphyry copper mineralization to attain ore grade.

Introduction

For many years there has existed a wide divergence of opinion as to the structural control of porphyry copper deposits, particularly regarding the nature and orientation of the fractures which contain the mineralization. Structural preparation of the rock for low-grade mineralization has been attributed to a variety of causes ranging from cooling and shrinkage of the intrusion to tectonic forces (McKinstry, 1955). To emphasize our present lack of understanding on this problem, Anderson (1968, p. 1180) recently concluded with McKinstry's statements of more than a decade ago: "Meanwhile, until some generally applicable mechanism is established we may have to live with the rather unsatisfactory compromise-conclusion that mineralizing solutions were not choosy about the origin of the fractures that they utilized and that the causes of fracturing were different in different districts."

The present study is an attempt to resolve part of the ambiguity regarding the significance of fracturing by placing the porphyry copper deposits and attendant intrusive bodies into a regional tectonic framework. The authors systematically investigated steeply dipping fault, vein, dike and joint patterns in eleven Laramide plutons in Arizona to see if regional fracture trends could be found which might have formed important structural controls for mineralization within the porphyry orebodies.

Method of Study

The effects of a regional stress field can be recognized by similarly oriented structures of like origin over wide areas. Scattered plutonic bodies would be particularly well suited for recording these regional structures, because: (1) their isotropic character precludes structural complexities due to anisotropic factors such as bedding or schistosity (2) the effects of all stresses prior to crystallization of the pluton are eliminated and (3) mineralized structures in the pluton, if co-genetic with intrusion may reflect the stress environment at the time of emplacement.

To test for regional structure, we therefore chose to study eight nonproductive stocks and three porphyry copper orebodies scattered throughout the Basin and Range Province of Arizona. As used here, the term nonproductive or barren merely refers to the absence of ore-grade mineralization in the intrusive rock studied. These items do not imply that the referred to stocks have no associated ore. The ages of the plutons ranged from 75 to 58 ± 2–8 m.y. thus limiting our investigation to the well documented Laramide magmatic pulse (Creasey and Kistler, 1962; Damon and Mauger, 1966).

The initial phase of the study involved a detail fracture (joint, fault and vein) and dike analysis of the eight nonproductive stocks whose locations and names are shown on Figure 3. Later, the structural study was extended to include the intrusive rocks of the Sierrita, Bagdad and Ithaca Peak porphyry copper deposits.

Stock Selection

Selection of stocks suitable for rapid structural analysis was determined by such requisites as geologic setting, accessibility, degree of outcrop and established Laramide radiogenic age dates. Stocks were chosen which invaded country rocks varying in anisotropic character and representing geologic terrains of Precambrian, Paleozoic and Mesozoic ages.

In an effort to approach random sampling and to meet time restrictions, plutonic structure was recorded at arbitrarily assigned sample sites in each pluton. These sites were large enough (up to 1 square mile) to test a significant portion of the intrusion and verify the continuity of any trends found. The number of sites varied from four in the smaller stocks to ten or more in the larger ones.

Sampling Technique

Aspects related to rock mechanics and earlier work on regional fracturing (Spencer, 1959; Harrison and Moench, 1961; Wise, 1964; Rehrig, 1969) indicated that only high-angle structures needed be considered for the study. Therefore, measurement was confined only to planer elements dipping greater than about 50°. The disregard for low-angle elements was also defended on practical grounds because in typical desert outcrops of low relief, these features were relatively difficult to see. Utimately, the existence of low-angle fracturing and aplite diking was established in the stocks, however, it had no effect on the distribution of systematic, near-vertical structure. Presumably, low-angle features represented independent structural elements possibly of local origin.

The planar elements which were treated consisted of mesoscopic structures such as joints (mineralized and unmineralized), veins, faults and dikes. Joints were measured in sets (at least three parallel to subparallel surfaces) at approximately 25 foot intervals along irregular traverses through each sample site. Single joints without parallel counterparts were rarely encountered. At each exposure, particular attention was paid to the physical nature of all fracture surfaces. A number of strike and dip readings were taken on high-angle joint sets before a single average was recorded. Subparallel joint sets with strike differentials in excess of 5° were recorded individually. This sampling technique recorded representative structural elements which grouped in plotting, served as an appropriate means of defining statistical trends involving large populations. The technique also allowed for a considerable expansion of the area sampled.

Mineralized joints were coated with thin films (<0.1 in.) of late magmatic, hydrothermal and supergene minerals. Epidote, magnetite, chlorite, hornblende, biotite, orthoclase, sericite, tourmaline, quartz and an assortment of metal sulfides and oxides were the minerals frequently encountered.

Most exposures did not show multiple veins, dikes or faults; consequently, these elements were recorded individually where encountered along each traverse. Sampled veins consisted of two kinds: simple fissure fillings and structurally complex fault-veins recognized by multiple anastomosing-crosscutting vein strands and minor shear zones. Unbroken fissure veins consisted most commonly of quartz or orthoclase with minor metal sulfides (usually pyrite). Fault veins typically contained mixtures of sheared gangue minerals (quartz or carbonate), metal sulfides and argillic-sericitic alteration products. Dike compositions varied from intermediate to felsic but granitic aplite was by far the predominant type. Dike widths ranged from an inch to greater than 50 feet, with the 1–6 inch class of aplites showing the maximum frequency.

Fig. 1 illustrates the types of structures recorded and their physical character. These photographs present visual evidence of the systematic nature of recorded fractures and dikes, a point which will be demonstrated by means of equal-area net analysis.

Field measurements were recorded directly on IBM mark-sense data cards. Items such as strike, dip, identification (joint, vein, etc), frequency, strike length, dike-vein composition and thickness, and type of mineralization were identified by numbers in columns on each data card. One hundred measurements were considered a minimum for each sample site and approximately 200 or more readings were usually taken.

The method of study within the porphyry copper

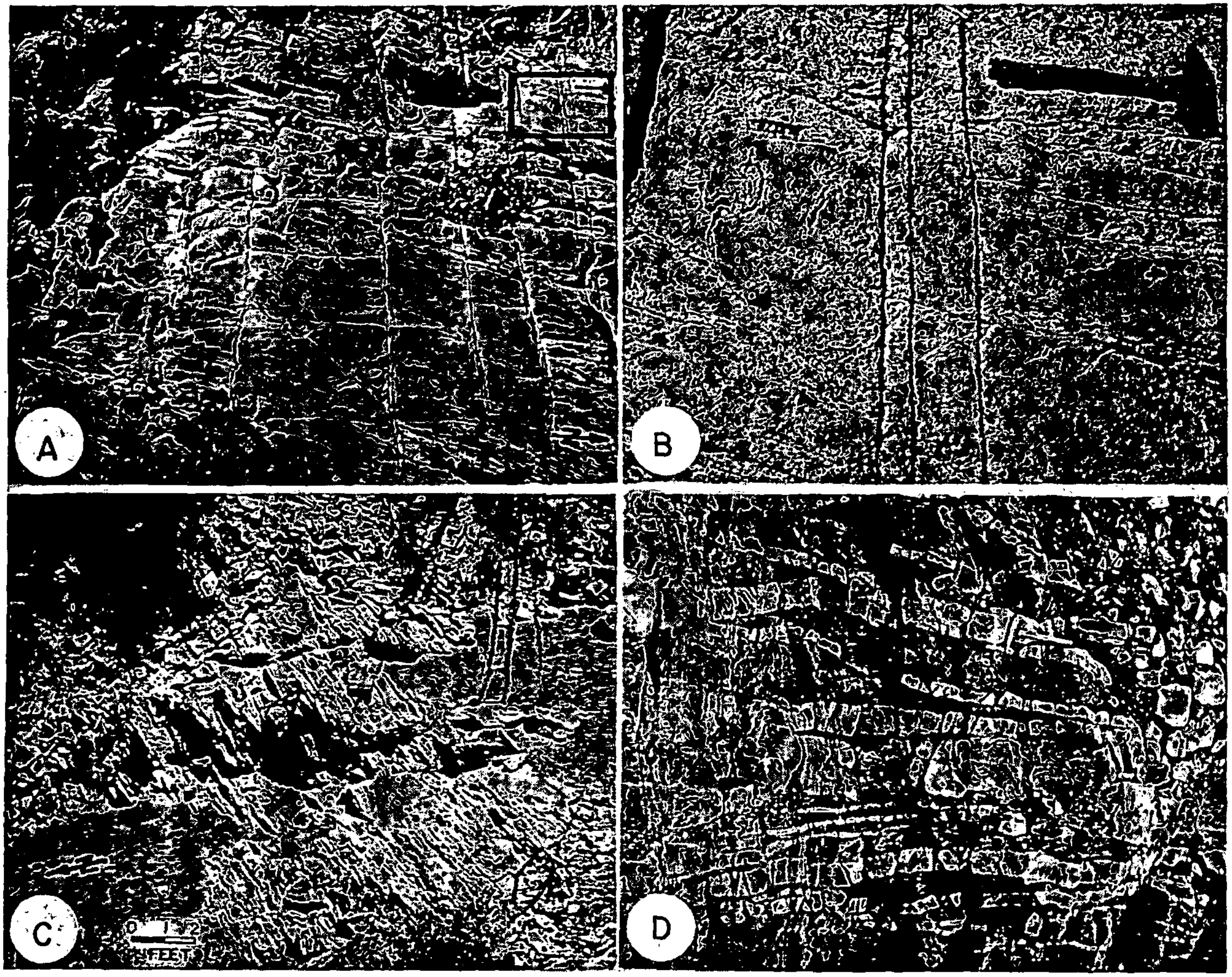


Fig. 1. Representative mesoscopic structural elements in the Copper Creek (A,B) and Amole (C,D) stocks. Figures A and B contrast the marked dissimilarity between the systematic, continuous, and planar tourmaline-filled joints striking easterly with the unmineralized, discontinuous, curviplanar joint set striking northerly. The rectangular inset containing the hammer (upper right corner of Fig. 1A) is enlarged in order to show in detail the relationship between mineralized and unmineralized joint sets (Fig. 1B). Although largely obscured by the joint set of Fig. 1C, the orthogonal relationship shown in Figs. 1A and 1B is still present. Fig. 1D looks ENE parallel to the strike of an aplite dike swarm cutting the Amole stock. Fig. 1D is turned 90° and up is to the right.

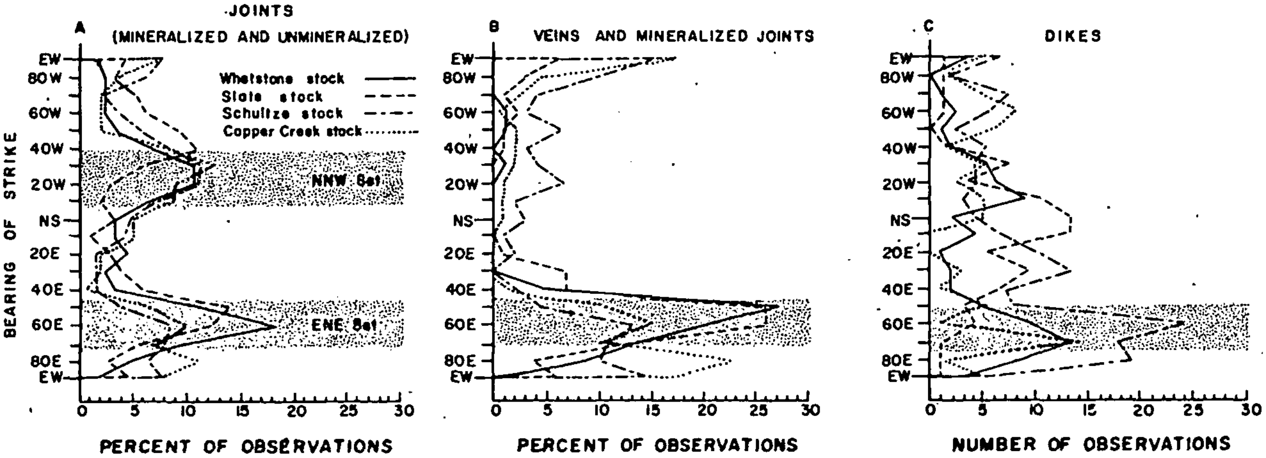


FIG. 2. Strike histograms for steeply dipping (>50°) structure from four Larmide stocks of Arizona. Grouped frequency data for joints (Fig. 2A) defines a simple orthogonal system (ENE and NNW) plus a secondary east-striking set. Figure 2B shows that only the ENE to E sets are significantly mineralized. In Figure 2C, dike trends are more erratic than trends for joints; however, the ENE fracture direction is especially well represented by dikes. Frequency distributions are based on the number of poles to planes used in the corresponding nets of Figures 3, 4, and 5.

deposits was similar to that described above for the nonproductive intrusions except that bench faces in the open pit mines were examined. Sample sites were established on different benches and along faces of variable trend.

Compilation and Analysis

Following the field survey, the mark-sense cards were machine punched and sorted for equal-area net plotting. Data were computer processed to give lower hemisphere, Schmidt equal-area plots showing raw data distributions based on a 1 percent counting circle (Spencer and Clabaugh, 1967). A subroutine was programmed on the computer to yield a strike histogram for each equal-area plot. On this type of diagram, the number or percent of total measurements was grouped in 10° increments of strike.

Structural Data from Nonproductive Stocks

The results of the structural analysis of the eight Laramide stocks are here presented. These stocks are distributed geographically throughout the Basin and Range Province of Arizona, and are characterized by some remarkable similarities in the orientation of mineralized and unmineralized joints, veins and dikes.

Joints

The term joint as used in this paper pertains primarily to a discrete plane of discontinuity along which the rock mass has fractured but discernible displacement of one face relative to the other is absent or quite small. Three or more such parallel or subparallel fracture surfaces constitute a joint set. During the course of the study, systematic joint sets were subdivided into major classes based on their spatial, geometrical and physical development.

The most conspicuous type of joint set is planar, straight and continuous with spacing between individual joints averaging 1–2 feet and strike lengths measuring in tens or even hundreds of feet (Fig. 1, A, B). One common variant of this fracturing is the relatively narrow zone of complex close-spaced joints depicted in Figure 1C. The second most prominent joint set strikes approximately normal to the continuous-planar joint set. Joints of this set are markedly curviplanar and irregular in trace. They are discontinuous in extent with vertical and horizontal dimensions commonly less than a few feet. Typically, this set is unmineralized and demonstrably younger than the mineralized continuous-planar set upon which it may terminate (Fig. 1, A, B). We will return to the significance of these distinct joint classes when the origin of the fracturing is considered.

The strike histograms of Figure 2A which summarize joint attitudes from four of the eight nonproductive stocks clearly show a similarity in joint set orientation. The locations of these intrusive bodies—Whetstone, Slate, Schultze, and Copper Creek—is shown in Figure 3. The joint sets are represented by two major frequency peaks on the strike histogram of Figure 2A. These sets strike approximately N50-70°E (ENE) and N10-40°W (NNW) forming a simple, perpendicular joint system. In the Slate stock, corresponding maxima are displaced from the other maxima by 5–10° of strike; however, the orthogonal relationship is main-

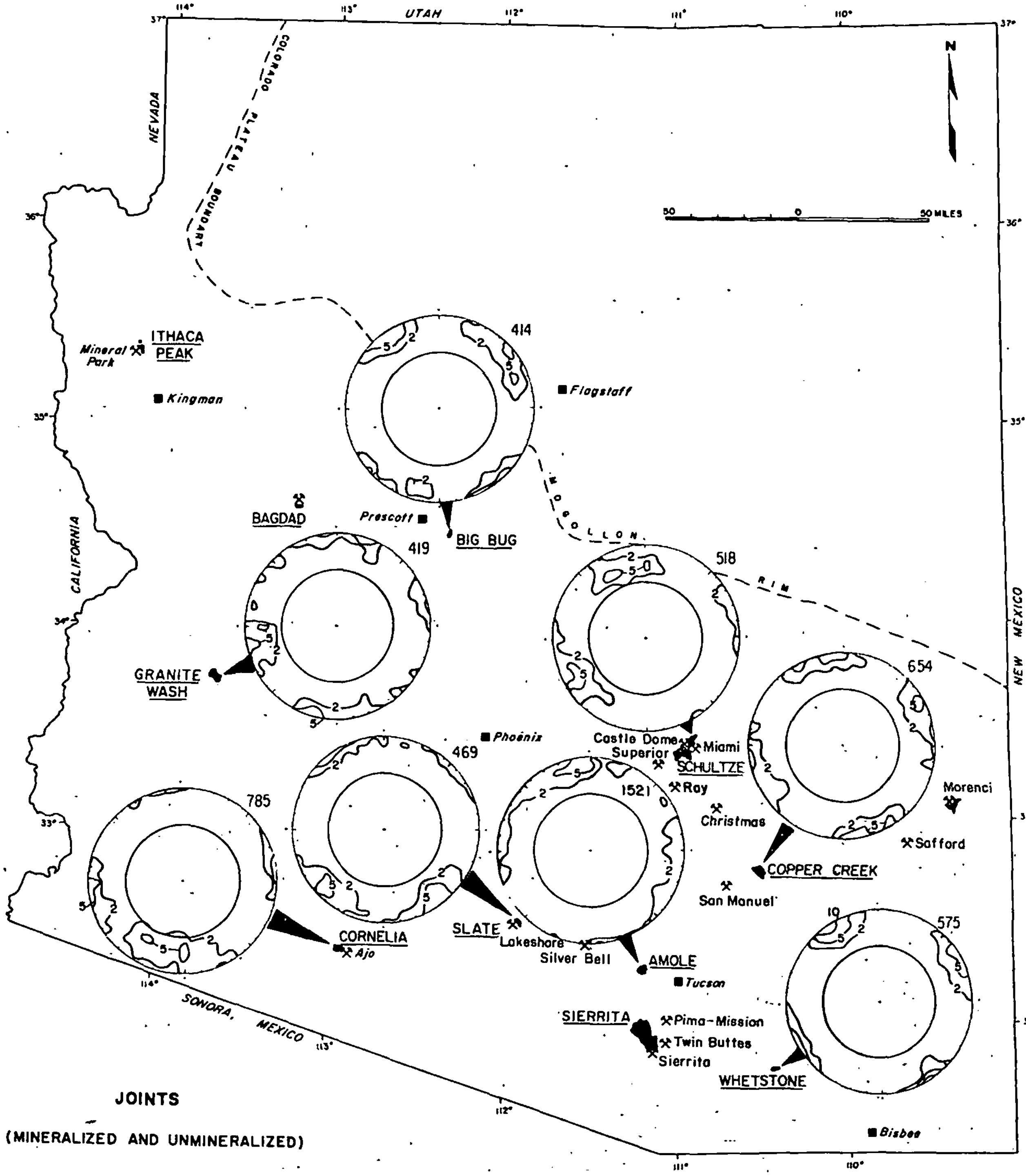


FIG. 3. Poles to mineralized and unmineralized, steeply dipping joints from eight nonproductive Laramide stocks of Arizona. Poles are plotted on lower hemisphere, Schmidt equal-area nets. Stocks are located by arrows from each net. Porphyry copper deposits are shown by mine symbols. The number of poles is shown on the upper right of each plot. Diagram contours are in percent.

tained. A third joint maximum closely related to and possibly gradational with the ENE joint set strikes approximately east. This set is not recognizable in the Whetstone intrusion.

Figure 3 shows the stock locations and equal-area plots for joint sets in the preceding four stocks as well as data from four other Laramide intrusive bodies in Arizona. The orthogonal ENE and NNW joint system is retained in all eight stocks. In the three westermost stocks and possibly in the Slate and Amole bodies, a WNW-striking joint set can also be delineated.

Joints corresponding to the WNW and W-striking double maxima for the Cornelia stock at Ajo, dip approximately 60° north and represent a marked deviation from the norm. In the majority of the stocks, joint sets have dips which approach the vertical. Only in the Schultze and Cornelia stocks are the ENE and W-WNW joint sets dipping appreciably less than vertical. This deviation is interpreted to be the effect of major tilting of large crustal blocks which house the stocks. For example, the north-dipping joints at Ajo suggest some 20–30° counter-clockwise rotation of the Cornelia structure block south of the Little Ajo Mountain fault about a WNW-trending axis. This interpretation is similar to that proposed by Gilluly (1946).

Veins and Mineralized Fractures

Figure 2B shows the summation histogram for veins and mineralized joints in the Whetstone, Slate, Schultze and Copper Creek stocks. The frequency distribution clearly indicates that the ENE set of fractures has been most substantially mineralized. Equal-area nets for the remaining four stocks likewise reveal a near-perfect NE to E unidirectional strike for most veins and mineralized joints (Fig. 4).

Besides the above distribution of mineralized structures, the Cornelia, Big Bug, and Granite Wash intrusions possess well-developed WNW joint sets that are mineralized. The ill-defined NNW to NW farcture set in the Big Bug, Granite Wash and Schultze stocks occasionally contains fractures that are mineralized.

Dikes

Figure 2C summarizes the grouped strike frequency for measured dikes in the Copper Creek, Whetstone, Slate and Schultze stocks. In comparison with Figures 2A and 2B, dikes are less systematically oriented than are the unmineralized joints and mineralized fractures. Despite the variations in dike orientation, all intrusions except the Slate stock show strong frequency maxima for dikes striking ENE, a direction which coincides with the maxima for mineralized joints and veins. This characteristic is further illustrated in Figure 5, which shows the equal-area plots for dikes in all eight stocks. All plots, except those for the Slate and Big Bug stocks, show the existence of pervasive ENE dike swarms like that shown in Figure 1D. More recent research in the Big Bug stock reveals the presence of many ENE-striking dikes not recorded in the initial survey.

Dike trends of lesser importance are present in all but one of the stocks studied. Dikes which approximate a northerly strike are reflected in all stocks except the Cornelia pluton. Maxima with NNE strikes are found in five of the eight stocks while six of the eight have N to NNW maxima. If these two slightly divergent maxima (NNE and N-NNW sets) are viewed as a single maximum of northerly strike, then the northerly and ENE dike system corresponds somewhat to that of the vein and joint plots (Fig. 2, 3, and 4).

Published Structural Data from Porphyry Copper Deposits

Literature concerned with the geology of Arizona mineral deposits abounds with references to a regional system of ENE-trending structures characterized by subparallel to parallel fault-veins, joints, dike swarms and elongated stocks and batholiths. Typically, structures with NE to E strikes are preferentially mineralized and are believed by many authors to have localized Laramide ore deposits throughout Arizona. This relationship was pointed out in general terms by Butler and Wilson (1938), Wilson (1962), Schmitt (1966) and Landwehr (1967). Documentation of structural ore controls is sufficient in several Laramide porphyry copper deposits to indicate that low-grade mineralization is also largely controlled by NE to E and, to a lesser degree, N to NW trending structures.

At Morenci, the work of Lindgren (1905) and Moolick and Durek (1966) defined a prevalent NE orientation for porphyry dikes, major veins and the principal intrusive mass of the district. Butler and Wilson (1938) suggested that a similar systematic orientation would be found for mineralized fractures of the low-grade orebody.

In the Lone Star district at Safford, structural preparation for porphyry copper mineralization is closely comparable to that at Morenci. Robinson and Cook (1966) describe the Lone Star copper deposit as having been localized in a wide sheared and sheeted zone striking N50–65°E. Acid to intermediate dike swarms, small elongate stocks and intrusive breccias thought to be associated with the mineralization are contained within the NE structural zone.

At the Silver Bell deposits, a "major structure" of WNW trend has profoundly influenced the overall distribution of Laramide intrusion and hypogene alteration (Richard and Courtright, 1966, p. 157). It is, however, the intrusion of monzonite and quartz monzonite dikes and the development of close-spaced parallel fractures trending NE to E across the structural zone which most closely relate to the copper metallization. Furthermore, Watson (1964) in his

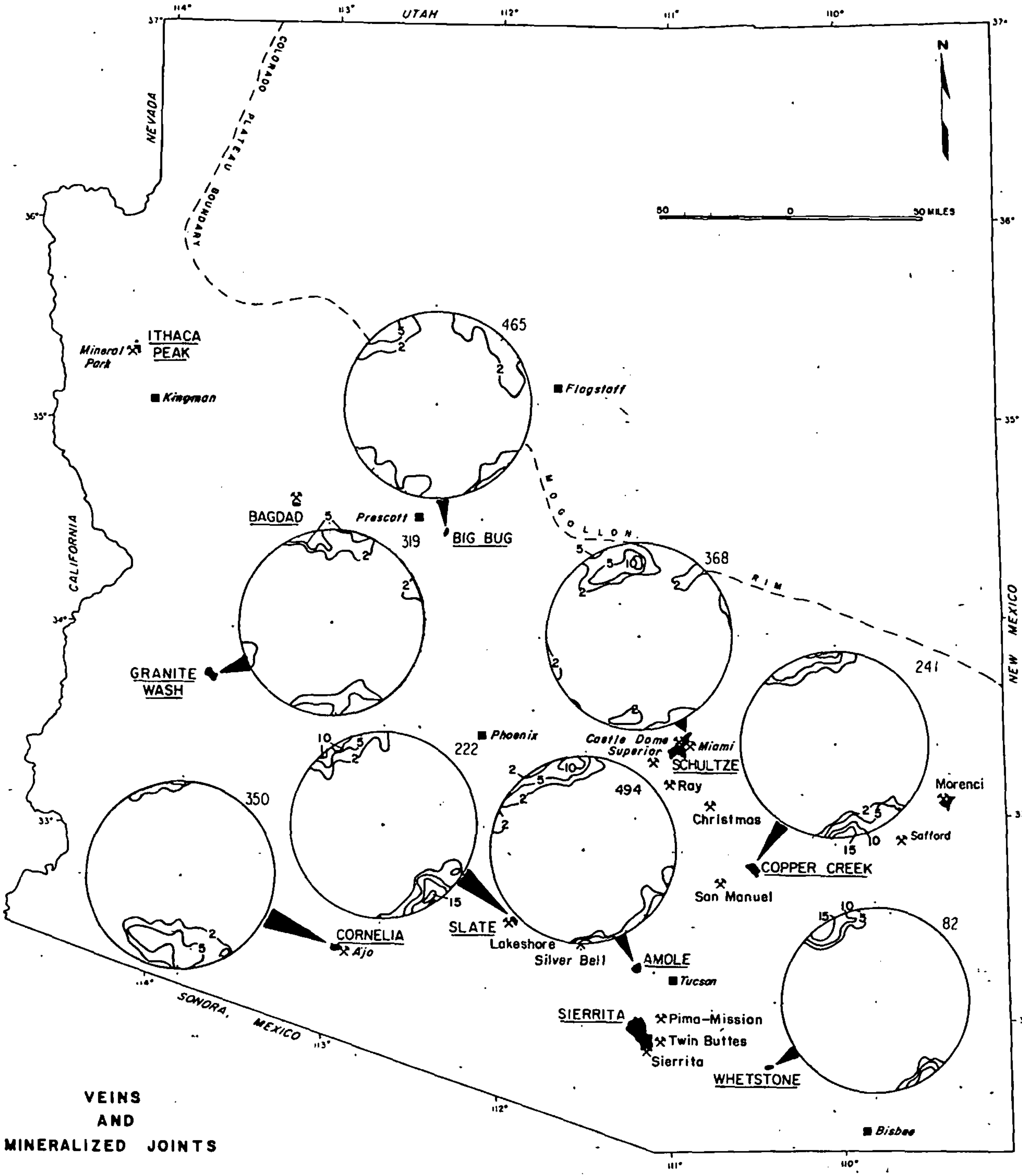


FIG. 4. Poles to high-angle veins and mineralized joints from eight nonproductive Laramide stocks of Arizona. Poles are plotted on lower hemisphere, Schmidt equal-area nets. Stocks are located by arrows from each net. The number of poles shown on the upper right of each plot. Diagram contours are in percent.

mapping of the area, discovered two NE and ENE dike swarms which project into the oxide and El Tiro pits and, where they intersect the "major structure," appear to localize the two orebodies.

The NE to ENE structural trends influencing Laramide intrusion and mineralization in the Globe-Miami-Superior district have been graphically described by Peterson (1962) and Hammar and Peterson (1968). Major copper veins and three porphyry copper deposits (Castle Dome, Copper Cities and Miami-Inspiration) exhibit NE to ENE orientations presumably reflecting a fundamental structural control.

At Bagdad, Anderson et al. (1955) concluded that the intersection of a major N60–70°E intrusive belt with a N20–40°W dike swarm was of a major importance in localizing the porphyry copper orebody. Certainly the great abundance of N60–70°E veins

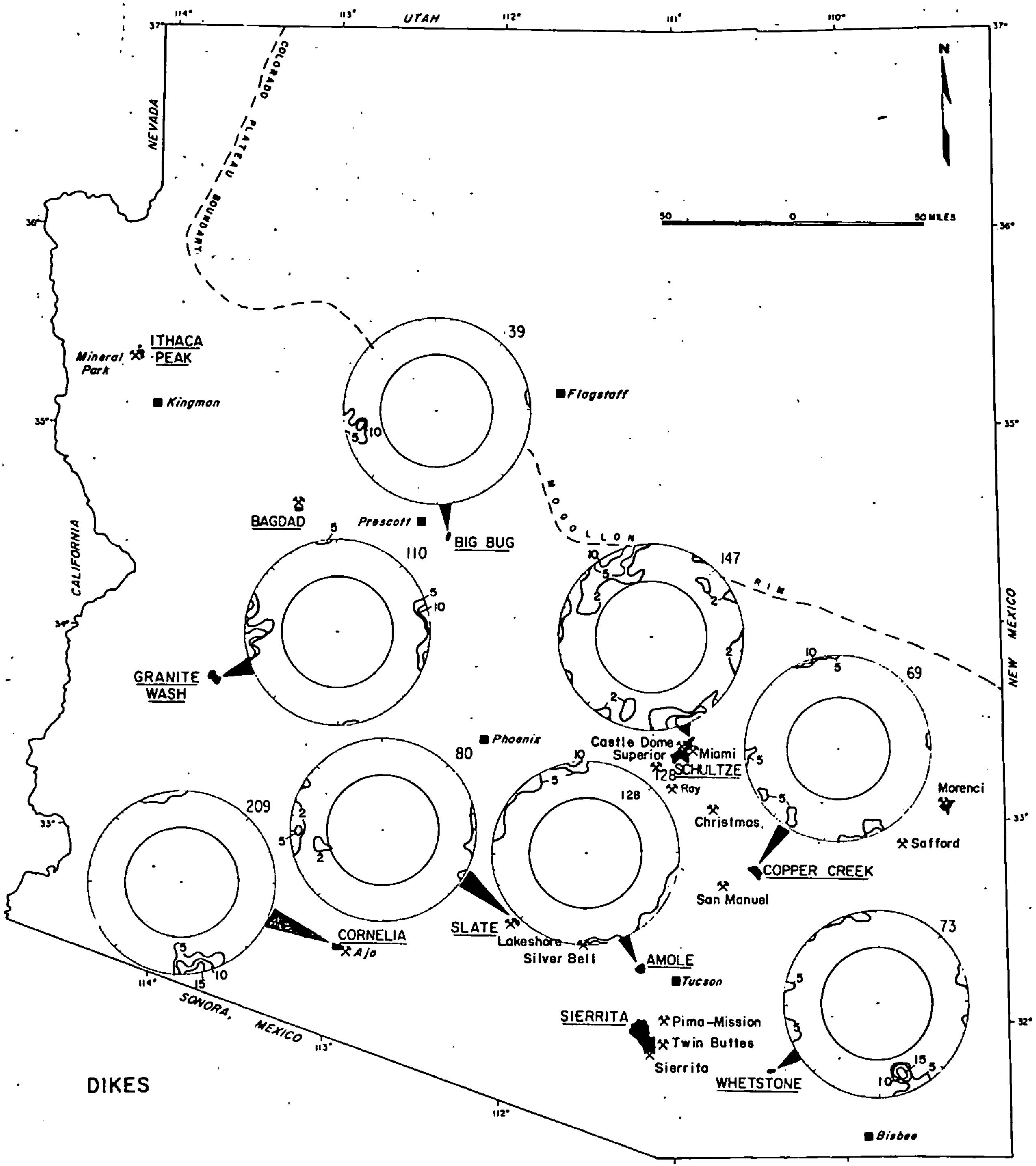


FIG. 5. Poles to steeply dipping dikes from eight nonproductive Laramide stocks of Arizona. Poles are plotted on lower hemisphere, Schmidt equal-area nets. Stocks are are located by arrows extending from each net. The number of poles is shown on the upper right of each plot. Diagram contours are in percent.

and mineralized fractures recorded in the orebody emphasizes the preference of gangue and sulfide mineralization for ENE-oriented structures.

In addition to the seven deposits mentioned above, other examples of NE to E-oriented intrusive and mineralization control include the "porphyry break" at Ray (Metz and Rose, 1966), the elongation of stocks and dike swarms at Christmas (Eastlick, 1968), intrusion and vein orientation in the Twin Buttes-Sierrita area (Lacy and Titley, 1962; Lynch, 1966; Cooper, 1970; Metz, oral communication), and vein trends at Johnson Camp and Tombstone (Cooper, 1950; Butler and Wilson, 1938). Only at Mineral Park (Ithaca Peak orebody) does a different structural trend (NNW to NW) appear to dominate (Thomas, 1949; Dings, 1951; Eidel and others, 1968).

In summary, available published accounts lead to a conclusion analogous to that reached from the study of eight nonproductive stocks; namely that intrusive and mineral fluids were selectively and preferentially emplaced into NE to E, or less frequently; NNW- to NW-trending structures. The resulting elongate stocks, dike swarms, veins and mineralized fractures combined to exert primary structural controls in a majority of Laramide ore deposits in Arizona. This structural control was active prior to, during and after intrusive emplacement.

Structural Data from Productive Stocks

In the final stages of this research project, the study procedure developed for nonproductive stocks was repeated at the Sierrita, Bagdad and Ithaca Peak porphyry copper deposits. The geographic locations of these orebodies are shown on Figure 3.

Data collection in the open pit mines was complicated by conditions of exposure and structural complexity far different from those encountered in the nonproductive stocks. An important factor to contend with in the orebodies was the continuous lateral and vertical rock exposure present in bench faces.

Because of the exposed vertical relief, low dipping (<50°) structures were more apparent in the orebodies than in the barren stocks. However, because our study was primarily concerned with steeply dipping regional fracturing and to maintain a parallel with the work in the nonproductive stocks; low-angle structure was disregarded. In this context we also assumed that post-ore tilting was insufficient to have rotated high-angle structures 40° or more into low-angle positions. As it later turned out, low-angle mineralized structures were only locally prominent and their overall presence did not detract from the significance of high-angle elements.

The nearly continuous lateral rock exposure in the deposits revealed such a concentration and variety of mineralized structures that sampling became somewhat difficult. Mineralized structures ranged from complex, multiple shear zones several feet in width to hairline sulfide-coated microfractures. Measurement of these features closely approximated the technique used in the barren stocks where mineralized joints or veinlets less than 0.1 in. thick were recorded in sets while larger structures were measured individually. Veins consisted either of unbroken fissure fillings of gangue and/or metal sulfide or mineralized fault or shear zones with gangue mixtures of sheared sulfides and alteration products. The veins were sorted into size categories of <1 inch (∽0.1 to 1 inch) and >1 inch (1 inch to several feet) widths. In most cases, mineralized shears or faults were included as veins greater than one inch.

Considerable care went into assuring that structural measurement was sufficiently rigorous in each sample site to constitute a statistically representative mesoscopic sampling, even though every mineralized fracture could not be measured. Admittedly, single joints were left unrecorded as were hairline microstructures. However, uniquely oriented single joints were not common and we have attempted to limit our interpretation only to features of mesoscopic scale.

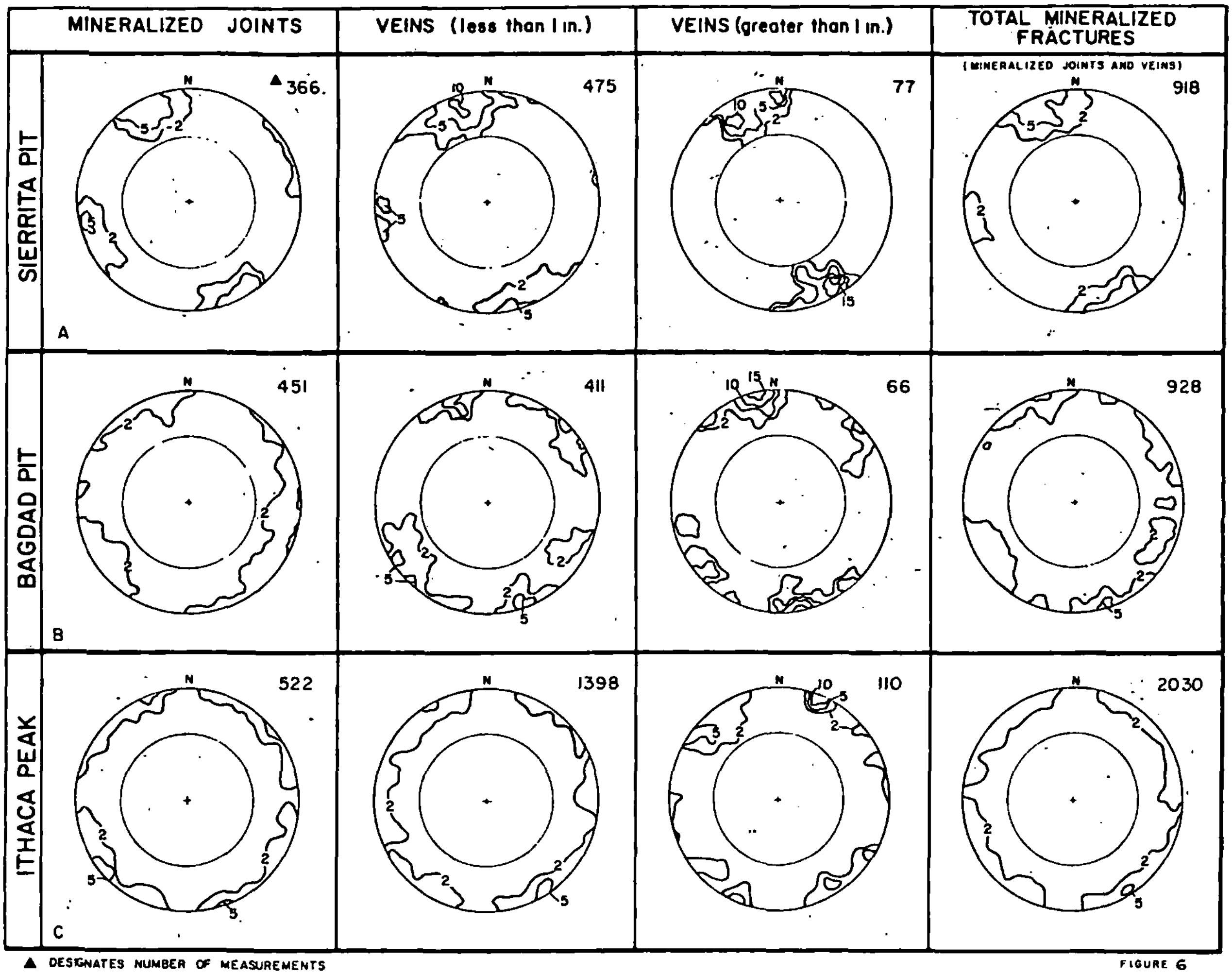
Sierrita Orebody, Pima County

The diagrams for structures recorded in Duval's Sierrita pit reveal a recurring orthogonal system of ENE- and NNW-trending mineralized fractures (Figs. 6 and 7). Part or all of this simple pattern is repeated for joints and veins (large or small) in all equal-area plots. Each summation plot emphasizes the preference of mineralization along ENE-striking fractures; while the overall importance of the NNW-striking fractures is not realized until one considers the less obvious small-scale joints and veinlets.

Our structural analysis and equal-area net maxima for mineralized fractures are in general compatible with structural observations made by other workers (Lynch, 1966; Lootens, 1966). In particular, they agree with those recognized by Metz and associates at Sierrita where the dominant structural trend parallels that of Esperanza, which is NE to ENE (oral communication).

Bagdad Orebody, Yavapai County

Figure 6B represents the synopsis of mineralized structures recorded in Bagdad Copper Company's open pit mine. In comparison with the Sierrita plots (Figs. 6A and 7) several important deviations are apparent.



STRUCTURE IN THREE PORPHYRY COPPER DEPOSITS OF ARIZONA

FIG. 6. Synoptic Schmidt equal-area plots for high angle structures in three porphyry copper deposits in Arizona. Poles to mineralized joints and veins are plotted on lower hemisphere nets. Locations of ore deposits are shown on Figure 3. Diagram contours are in percent.

The strikes of joints are essentially haphazard and "box the compass" except for a general lack of joints which strike approximately WNW and just east of N. The orientation of veins of all sizes, however, falls within two reproducible maxima of ENE and NW strike. The large veins (>1 inch) show a strong preference for ENE strikes. When the more randomly oriented mineralized joints are combined with veins in the summation plot, it is not surprising that the resulting maxima are diffuse and ill-defined; nevertheless, the maximum of ENE-striking structures still dominates.

The Schmidt plot for total mineralized fractures coupled with the corresponding strike histogram show two recurring fracture maxima in the Bagdad open pit. The broader maximum which incorporates the greater number of poles, strikes N20–40°W, the other strikes N70–80°E.

This fundamental fracture system is in general identical to that of the faults, veins and minor mineralized fractures delineated in the Bagdad Mine by Anderson et al. (1955). The trends also parallel the N70°E belt of porphyry stocks and associated N40°W and N60–70°E-striking dike swarms. Other minor directions of mineralized fractures (NNE and WNW) can also be correlated between the two structural analyses.

The fact that our data for mineralized joints approach a random distribution is at variance with the distinct pattern for similar structures over the underground Bagdad mine (Anderson et al., 1955, Fig. 4). The complexities of our plot are probably in part due to the expanded sample area of the open pit orebody, which was not accessible to Anderson and his colleagues.

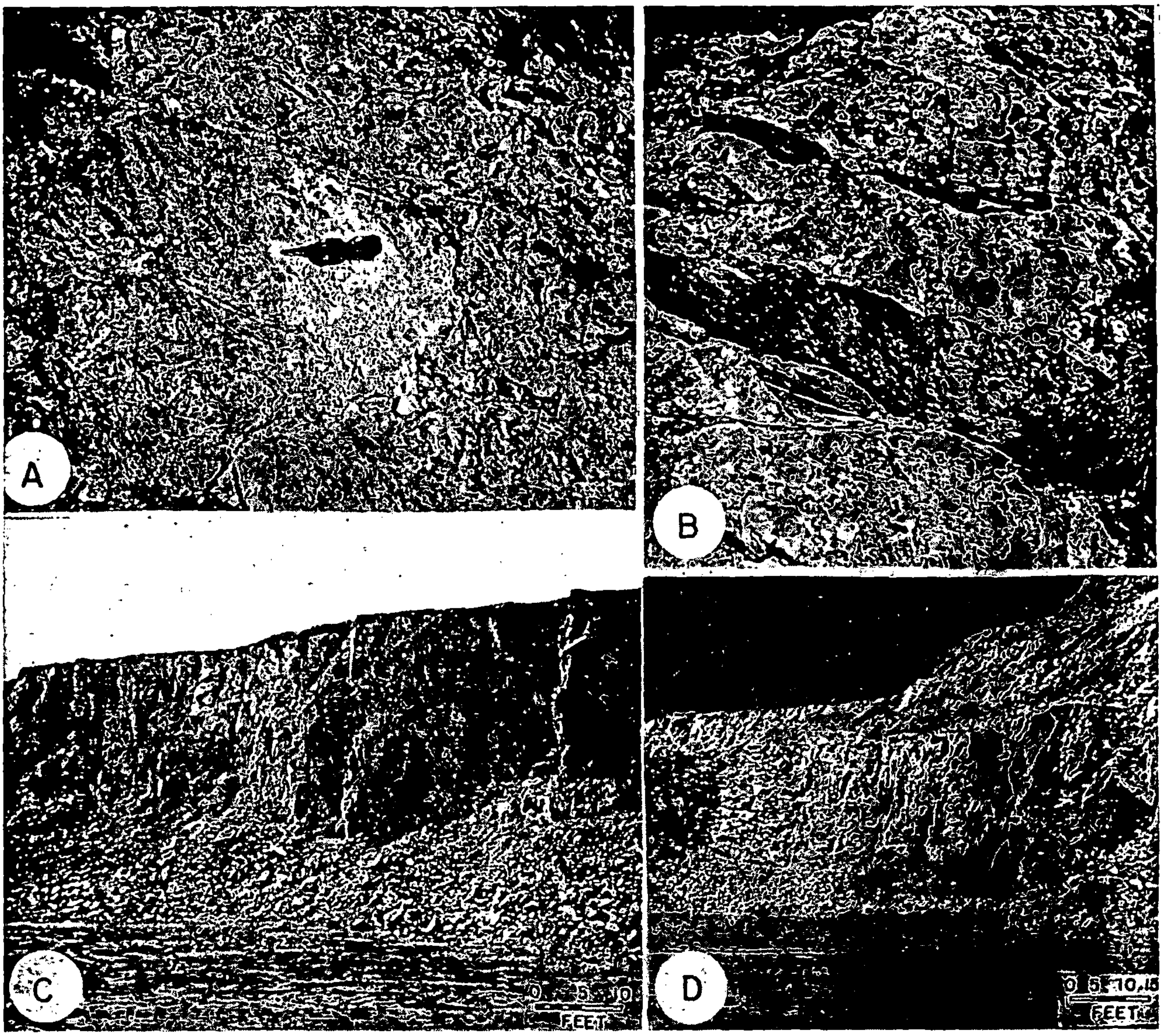


FIG. 8. Mineralized "crackle breccia" at Ithaca Peak (A and B) consisting of a myriad of small veinlets and mineralized joints that are crosscut by larger throughgoing composite quartz pyrite veins (compass points north). Our analysis demonstrates that both A and B actually represent quasi-stockworks comprised of superimposed local and regional fracture sets. Figure 8C looks S70°W parallel to the most prevalent mineralized joint and vein set at Sierrita. The mineralized orthogonal set striking NNW is represented by the smooth joint surfaces normal to the line of sight. Figure 8D shows prominent ENE-striking quartz-sericite fault-veins (in sunlight) cutting several benches in the Bagdad pit.

under vertical stresses first produces high-angle longitudinal fractures parallel to the long axis of the uplift followed by steeply dipping transverse fractures (Beloussov, 1960, Fig. 2; 1961, p. 102). Theoretical considerations of the uplift process were considered by Price (1959, 1966). He predicted that when crustal blocks rise vertically, horizontal components of stress decay in response to the deterioration of gravitational load with attendant uplift and erosion. Consequently, extension fractures form perpendicular to the axis of least principal stress. This multiple, longitudinal fracturing relieves the tensile stresses and the least and intermediate principal stresses interchange. Continued uplift under this new stress orientation causes a set of transverse tensional joints to develop normal to the longitudinal set.

Although the results of Price and Beloussov are in close agreement, they show a marked inconsistency with our structural data for Arizona. The principal disagreements are:

1. Our analysis demonstrates that often the earliest and most prominent set of fractures trend ENE ± 20°, or transverse to the assumed NNW elongate uplifts containing the stocks. Transverse elements

according to Beloussov should be subordinate to and form later than the well-developed longitudinal fractures striking NNW.

2. Beloussov has demonstrated that failure along the transverse direction is temporally restricted and occurs after the longitudinal fractures. Our data, together with published accounts, indicate that no temporal restriction existed for activation of the ENE-trending structures (c.f. Bagdad, Anderson et al., 1955 and Sierrita-Esperanza, Lootens, 1966).

3. Although in general rare, small amounts of strike-slip differential movement along mineralized and unmineralized continuous-planar joints (Figs. 1A and 8C), joint zones (Fig. 1C), and mineralized shear zones (Fig. 8D) was evident in every stock studied.

Other workers have noted similar strike-slip displacements along mineralized structures striking ENE (Anderson et al., 1955; Lootens, 1966; and Schmitt, 1966). Neither the theoretical analysis by Price nor the experimental results reported by Beloussov predict or demonstrate high-angle shear fractures with strike-slip motion.

4. Failure experiments in rock submitted to compression (Griggs, 1936; Brace, 1964; and Muller and Pacher, 1965) have produced multiple extension fractures which are oriented parallel to the axis of maximum compression (P_1). Anderson (1951) and Griggs and Handin (1960) reason that high pore pressures enhance the initiation and propagation of extension fractures normal to the axis of minimum compressional stress (P_3). The majority of mineralized and unmineralized structures striking ENE are similar in character and appearance to the extension fractures produced experimentally in compressional tests.

5. Several of the synoptic equal-areas plots and strike histograms (Figs. 2 to 5) show maxima separated by small dihedral angles corresponding to fracture sets trending generally east-west. The distribution of double maxima for structures striking NNW to NNE are sparse and ill-defined (Fig. 3).

Because of these observations, it is necessary to modify the differential vertical uplift hypothesis as presented by Price and Beloussov. We believe that an axis of maximum regional compression (P_1) was consistently oriented within a vertical plane striking ENE ± 20° throughout much of the Laramide orogeny and vertically uplifted crustal blocks rose under the influence of weak horizontal compression. This stress state allowed P_1 to be either vertical during periods of pronounced differential uplift or horizontal during periods of ENE-directed lateral compression.

Under conditions of uplift, P_1 was applied vertically. In the horizontal plane, P_2 was directed ENE because of the weak regional compression, and P_3 was oriented NNW-SSE. Maximum expansion occurred in the direction of P_3 resulting in pervasive extension fractures (continuous-planar joints) commonly filled by magmatic and hydrothermal fluids. An extension origin for the majority of the ENE-striking fractures is compatible with available empirical data, since they normally do not show evidence of lateral displacement, slickensides or cataclasis.

When P_1 was horizontal and directed ENE, vertical ENE-trending extension fractures were also formed provided the differential stress was small and P_3 remained oriented NNW-SSE. With increasing lateral compression (P_1), eventually the differential stress was adequate to produce failure along conjugate shear sets subtended by a small dihedral angle (Muehlberger, 1961). The resulting shear fractures were vertical, subparallel to parallel with preexisting extension joints, and are represented on the Schmidt equal-area plot by two maxima separated by only a few degrees. In order to explain the occasional distribution of double maxima and the lateral displacements along some stuctures of ENE trend, this orientation of the Laramide stress field is required.

The origin of the occasionally found WNW mineralized fractures set is not clear. This set may have developed in the proximity of only a few selected stocks, as a response to activation of older zones of structural weakness. Fracturing parallel or subparallel to such major anisotropic features would be expected and could for example, explain the WNW mineralized-unmineralized joints noted in the Cornelia stock (Fig. 3), which parallel the Little Ajo Mountain fault zone.

Upon relaxation of the ENE-directed compression, concomitant differential expansion resulted in failure as curviplanar-discontinuous release joints striking perpendicular to the previous axis of compression (Fig. 1, A-C). This interpretation is justified since our data show structures of NNW strike as essentially unmineralized in nonproductive stocks (Fig. 2). Conversely, data from porphyry copper deposits show that both the ENE and NNW fracture directions were active during Laramide mineralization and available to ingress by hydrothermal fluids (Figs. 6 and 7). We view both of these mineralized fracture sets as mutually perpendicular extension or combination extension-conjugate shear fractures of small dihedral angle. Conceivably, this bi-directional fracture system formed concurrently only at sites of porphyry copper mineralization. Clay model studies by Grzovsky and Price's theoretical considerations predict that bi-directional extension fractures are most likely to occur in areas experiencing abnormal amounts of tectonic elevation. Augmentation of regional uplift and stretching by vertically directed magmatic pressure might cause horizontal de-stressing adequate to form NNW longitudinal fractures concurrent with the more pervasive and continuous transverse set. Such local, intrusive-generated stress could also account for the complexity of mineralized microfractures and explain local fracturing of importance as implied at Ithaca Peak (this paper) and described elsewhere (Rehrig, 1969).

Quantitative studies focusing on the partitioning of sulfides between regional tectonic and local fractures, hairline microveinlets, and granular disseminations are needed since we did not deal specifically with the small-scale features. Presented data indirectly shed light on this problem by pointing out the existence of a continuum involving the intensity and complexity of observed fractures. At Sierrita, the ore zone is characterized by a relatively simple system of mineralized joints, faults and veins (Figs. 6, 7, and 8C). It seems certain that without the presence of the regional ENE and NNW fracture system, rock preparation represented by other directions of mesoscopic and microscopic fractures would not have been sufficient to allow mineralization to reach ore grade. In more complexly fractured ore zones characterized by multidirectional patterns (Mineral Park), the importance of regional tectonic farcturing is largely obscured by mesoscopic fractures of local derivation and the myriad of interlaced microveinlets and microjoints of the stockwork. But even in this complex setting, the stockwork may mirror a statistical ordering reminiscent of that defined by this regional analysis.

A complete explanation as to why the structural environment of the porphyry deposits is more complex than that of the barren stock cannot be ascertained by this study. What can be said, however, is that regional stresses were responsible for a large portion of rock breakage which contains ore mineralization. In this context, Laramide metallizing solutions were indeed choosy about the origin and orientation of the fractures mineralized.

Acknowledgments

We would like to acknowledge the helpful counsel and direction of Professors Evans B. Mayo and Spencer R. Titley, University of Arizona who acted as research advisors and critically reviewed the final manuscript. Drs. C. A. Anderson (U. S. Geological Survey), Jacques B. Wertz (Placer Development Limited), Peter C. Badgley (Office of Naval Research), and Joseph W. Mills (Washington State University) reviewed early versions of the manuscript and offered many helpful suggestions for improvement. The hospitality extended by company geologists in the districts studied was also greatly appreciated, especially the help of Robert A. Metz and A. Harvey James (Duval Sierrita Corporation), Ronna Medhi (Bagdad Copper Company), and Shurm Goulding (Duval Mineral Park Corporation).

Appreciation is due the Department of Geology, University of Arizona for access to computer facilities, American Metals Climax Corporation and ASARCO Research Foundation for funds provided the University which were used at various stages during the research, and Holt, Inc. for clerical and drafting services. Advice from Richard Call proved invaluable in solving initial problems related to computer processing of field data.

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April 15; December 13, 1971

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69-AS-74

ROCK FRACTURING TECHNIQUES FOR IN-PLACE LEACHING

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This paper is to be presented at the Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers, Washington, D. C., February 16-20, 1969.

ROCK FRACTURING TECHNIQUES FOR IN PLACE LEACHING

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The two most stringent parameters for in place fracturing of rock are the lack of any initial void space in the rock which to expand into and the ability to gain access only through drill holes. These two restrictions have proven so severe that as of today the only proven techniques for efficient fracturing are the contained nuclear detonation and hydrofracing. Both of these methods have highly developed technologies for their application. Hydrofracing has been a standard oil field practice for two decades, and the experience gained from a couple hundred underground nuclear detonations has resulted in a thorough understanding of the phenomenology of cavity and chimney formation.

What is still lacking is a practical method to create a suitable degree of fracturing for those ore bodies which do not meet the application criteria for either the nuclear explosion or hydrofracing. Nuclear applications must be restricted to thick ore deposits so as to take advantage of chimney collapse height--preferable in excess of 200 feet thick. Other requirements such as ground shock, containment, and radioactive contamination further reduce the number of sites that prudently can be selected.

On the other hand, none of the above restrictions apply to hydrofracing. It can be applied to thin as well as thick ore bodies, and rarely is there any worry about environmental hazards. The essential drawback is that only a very few thin, although extensive, fractures are formed. These cracks are beneficial only if the particular media possesses a relatively high matrix permeability (as is the case in oil and gas reservoirs), or they can be enlarged by solution (in the case of solution mining of potash).

During the past two years we have conducted a modest research program aimed at trying to fill the gap between nuclear fragmentation and hydrofracing. If successful, the method would be useful in generating fracturing suitable for in place leaching of moderate-sized ore zones which must depend on these fractures for adequate contact area for solutions. In order to appreciate the specific aim of the research it is necessary to briefly review the fracture mechanisms associated with both nuclear explosions and hydrofracing.

The vast amount of fracturing which accompanies a nuclear detonation is contained within the collapse chimney. The pressures at the moment of detonation are so high that gross material failure occurs in the vicinity of the detonation causing the cavity to be self-sealing during most of its growth period. This prevents the high pressure gases contained within the cavity to escape out into the surrounding rock to propagate extensive radial fractures. This phenomena results in the loss of considerable energy in the form of simple translation of the surrounding rock. To a lesser degree the identical phenomena happens with any conventional high explosive detonated under conditions of complete containment. Gas pressures are released too suddenly to propagate cracks and most of the explosive energy is released as a shock wave which pulverizes the rock. The shock wave quickly dampens back to the elastic regime within a few diameters outward from the borehole.

In contrast to the high pressure explosions, hydrofrac pressures are only equal the static overburden stress. The cracks are formed either by overcoming the tensile strength of the rock or by fluid penetrating along on a pre-existing break. Cracks continue to propagate as long as fluid pressure is maintained above overburden. Fracture connections between wells spaced as much as one half mile apart have been reported. The prime drawbacks to hydrofracing from the standpoint of in situ leaching is that only a very few of these wide ranging cracks are formed, and insufficient surface area is available for efficient leaching. Multicracking cannot be accomplished because of the inability to pass large volumes of high pressure fluid down the tubing or casing.

Thus, the ideal fracturing mechanism appears to be a system of high volume but reasonably low pressure fluid injection. Two schemes for accomplishing this are under investigation by myself and others at New Mexico Tech. The simplest concept is a simple liquid oxygen and kerosene burner, the fuel and oxidant being transported down the borehole in liquid form and ignited on bottom. A first estimate of desirable down the hole pressures is 10 times overburden stress, and the gas volume should be proportional to the cube of time. Theoretical calculations and preliminary tests indicate that several cubic meters of liquid must be injected underground within a few seconds. The cost of the elaborate hardware required to accomplish this rate of injection is beyond our present funds and we have delayed further development. We are hoping to eventually circumvent this problem by obtaining essential components from liquid fuel rockets through governmental surplus.

The other approach to accomplish the same high volume injection is the concept of a volume lit propellant. Such a substance would ignite the entire volume of propellant by having admixed a small proportion of a detonating agent with the remainder being, a propellant with high gas energy. The entire surface of the grains of propellant would be ignited during the shock traversal of the explosive thus initiating a relatively long gas emission phase from the burning propellant. Currently we are experimenting with two different types of solid propellants, and the major problem we have yet to overcome is getting full ignition without raising the temperature and pressure so high that the propellant itself does not detonate. Our best means of control to prevent total detonation is to keep the mix heterogenous and use large sizes of propellant grains.

Leaching of the fracture zone by this system should be accomplished by repeated injections and withdrawals through the implacement drill hole. Such a procedure would insure that all fractures which are in communication with the hole are leached. Hole spacings should be less than 100 feet apart.

$FeCl_3$ on the thermogram. The chlorination of the oxychloride in reaction (2) only develops after volatilisation of the water. The results from the experiments on the chlorination of Fe_2O_3 in the range of 350-750°C are given in fig.1g. The reaction of ferric oxide with hydrogen chloride takes place fairly rapidly (20-30 min) with almost complete conversion into the chloride. It should be noted that the process is characterised by a weak temperature dependence. The small value of the apparent activation energy (1.4 kcal/mole) shows that the chlorination of Fe_2O_3 takes place under diffusion control, and the limiting stage of the process is evidently the formation of the iron oxychloride.

Conclusions

1. The temperatures corresponding to the beginning of appreciable reaction of nickel and iron oxides with gaseous hydrogen chloride were established by DTA and TGA methods.
2. Investigation of the kinetics of the processes showed that the chlorination of nickel oxide in the ranges of 400-600°C and of ferrous oxide (700-800°C) takes place under kinetic control while the chlorination of ferric oxide (350-750°C) takes place under diffusion control.
3. The results from the investigations show that hydrogen chloride can be successfully used for the chlorination of nickel and iron oxides and, consequently, for their chloride sublimation from complex raw material. Iron can be volatilised at 500-600°C, while nickel requires an increase in temperature to 850-900°C.

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1977 v.5 N2

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UDC 669.28.053.4.068

Relationships governing the extraction of molybdenum from nitric acid and sulphuric acid solutions with polyalkylphosphonitrilic acid

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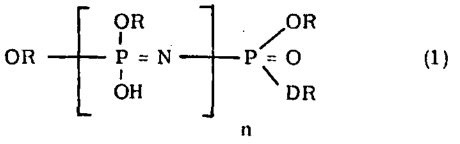
Organic polyalkylphosphonitrilic acids (PAPNA) have been proposed for the extraction of nonferrous metals (Co, Ni, Cu, etc.) from carbonate solutions and from mineral acid solutions[1][2]. The results from laboratory investigations into the extraction of molybdenum by PAPNA from mineral acid solutions have been given in the literature[3][4]. In the present work, in addition to a study of the relationships governing extraction, the results from an investigation into the mechanism of the extraction of molybdenum by PAPNA are given.

Poly-2-ethylhexylphosphoric acid with a phosphorus content of 10.5%, an average molecular weight of 1000-1200, and a polymer number (n) of 2-3 in the formula (1) was used for the work.



$$OR - \left[\overset{\displaystyle OR}{\underset{\displaystyle OH}{P}} = N \right]_n - P\!\begin{smallmatrix} OR \\ = O \\ DR \end{smallmatrix} \qquad (1)$$

Salts of analytical grade were used to prepare the solutions. The acids were of chemically pure grade. For extraction we used a solution of the PAPNA in clarified kerosene, which had first been treated with sodium carbonate solution (10%) and then with the respective acid. The concentration of the PAPNA in the organic phase was determined by two-phase potentiometric titration. Extraction was realised in separating funnels with the organic-aqueous phases in ratio of 1:1. The phases were brought into contact by a mechanical shaker at room temperature (20 ± 2°C) for 5 min. The hydrogen ion concentration in the weakly acidic solutions was determined on a laboratory pH-meter of the LPU-0.1 type. For acids were determined by titration with alkali against methyl orange. Molybdenum and tungsten were determined by a colorimetric method for small contents in the solutions and by a gravimetric method for large contents. The content of nitrates in the organic phase was determined by analysis of the alkaline re-extracts for nitrogen by the Devarda method. The IR spectra of the organic solutions were recorded on a spektromom-2000 spectrophotometer with a sodium chloride prism.

Extraction of molybdenum by PAPNA from weakly acidic solutions. At pH = 0-5 PAPNA behaves as a cation-exchange extractant. The distribution coefficient of molybdenum during extraction from weakly acidic solutions reaches a maximum at pH = 0.5-1 and then decreases with increase in pH. Decrease in the acidity of the equilibrium aqueous phases to pH = 4, in contrast to di-2-ethylhexylphosphoric acid (D_2EHPA) (fig.1), does not lead to a sharp decrease in the distribution coefficient of molybdenum, and the values of the latter are still fairly high (D_{Mo} ≈ 90). Although tungsten is hardly extracted at all by PAPNA, its presence in the solutions reduces the extraction of molybdenum considerably on account of the formation of joint polyanions of molybdenum with tungsten, which are not extracted by PAPNA. In the presence of tungsten it is not possible to extract molybdenum completely even after four extraction cycles in cross flow with the use of the fresh extractant at each cycle (table 1).

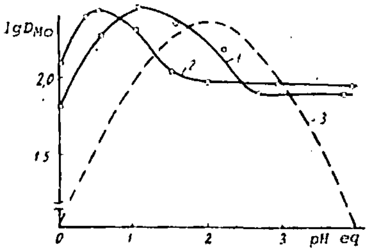


Fig.1 The dependence of the distribution coefficient of molybdenum on the pH of the equilibrium aqueous phase. Organic phase, 01N solution of PAPNA; aqueous phase, 1g/l Mo + acid H_2SO_4 (1); HNO_3 (2); H_2SO_4 + organic phase, 0.136M solution of D_2EHPA (3).

Table 1: The extraction of molybdenum in the presence of tungsten. Initial concentration, g/l: 0.91 Mo, 10W, extractant 0.152N solution of PAPNA in kerosene, organic-aqueous = 1:1 in each cycle

Cycle	pH_{in}	pH_{eq}	C_{Mo} in ref. g/l	Mo extr., %	Σextr. from initial, %
1	4.3	3.16	0.471	53	53
2	3.16	2.45	0.396	16	56.5
3	2.45	2.2	0.333	16	63.5
4	2.2	2.02	0.280	16	69.4

These results are similar to those obtained by previous authors[5])[6]) during the extraction of molybdenum from tungstate solutions with D_2EHPA.

The behaviour of molybdenum during extraction with PAPNA from solutions with a high concentration of nitric and sulphuric acids. Fig.2 shows the dependence of the distribution coefficient of molybdenum on the concentration of nitric and sulphuric acids. The initial concentration of molybdenum amounted to 5 and 1 g/l. The concentrations of PAPNA were 0.25 g-eq/l and 0.152 g-eq/l respectively. In sulphuric acid solutions the distribution coefficient decreases with increase in the concentration of the acid, and this is typical of the extraction of metals taking place by a cation-exchange mechanism. In nitric acid solutions up to a concentration of 2-4 g-eq/l HNO_3 the distribution coefficient of molybdenum decreases with increase in the concentration of the acid, and it then begins to increase. This indicates a change in the mechanism of extraction and, in all probability, a transition from cationic exchange to a solvate or mixed mechanism. During extraction of molybdenum from mixed nitric-sulphuric acid solutions (fig.3) the distribution coefficient increases with increase in the proportion of nitric acid in the isonormal (5 g-eq/l) mixture of acids. Thus, during extraction with PAPNA from mixed nitric-sulphuric acid solutions the values of the distribution coefficient of molybdenum lie between the maximum (in nitric acid) and minimum (in sulphuric acid) values and can be calculated if the ratio of nitric and sulphuric acids is known.

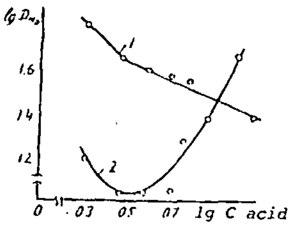


Fig.2 The dependence of the distribution coefficient of molybdenum on the acidity of the solution g-eq/litre 1 - H_2SO_4; 2 - HNO_3.

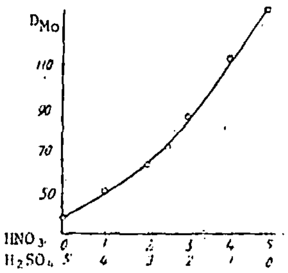


Fig.3 The dependence of the distribution coefficient of molybdenum on the ratio of nitric and sulphuric acids in the isonormal mixture. Organic phase 0.25N PAPNA; aqueous phase 1g/l Mo + H_2SO_4 + HNO_3 (c_{acid} = 5g-eq/l).

The mechanism of the extraction of molybdenum. The form of the variation of the distribution coefficient of molybdenum during extraction from sulphuric acid solutions indicates a catio-exchange mechanism for the extraction of molybdenum both in the strongly acidic and in the weakly acidic regions. The complex character of the dependence of the distribution coefficient of molybdenum on the nitric acid concentration does not make it possible to solve the problem of the extraction mechanism unambiguously. Investigations were therefore conducted into the composition of the compound which is formed in the organic phase during the extraction of molybdenum from solutions with various nitric acid contents. The effect of the hydrogen ion concentration for a constant concentration of nitrate ions in the solution and of the nitrate ion concentration for a constant concentration for a constant concentration of hydrogen ions on the distribution coefficient of molybdenum was also investigated. The Mo-PAPNA ratio in the extracted compound was determined by saturation, isomolar series, and equilibrium displacement (dilution) methods. The first two methods made it possible to establish that the extracted compound contains 3 g-eq of PAPNA for 1 g-atom of molybdenum, i.e., the Mo:PAPNA molar ratio is 1:1.5 (with allowance for the fact that a gram-mole of PAPNA contains 2 gram-equivalents). The same ratio was obtained from the dependence of the distribution coefficient of molybdenum on the concentration of the extractant. (The tangent of the gradient of the straight line against the coordinates log D_{Mo} and log [PAPNA] $\cdot_e$ is 1.5). For comparison the Mo:PAPNA ratio in the compound extracted from weakly acidic solutions (pH = 3.8) was determined by the saturation method. It was found that in this case the Mo:PAPNA molar ratio is 1:2. Thus, additional evidence was obtained for the difference in the mechanism of the extraction of molybdenum by PAPNA from solutions with low and high concentrations of nitric acid.

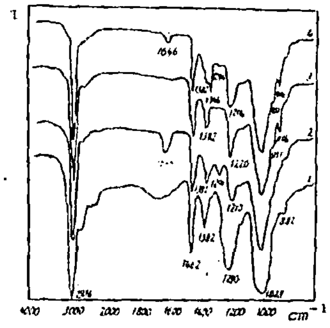


Fig.4 The IR adsorption spectra of the organic solutions: 1 - Pure PAPNA; 2 -PAPNA after contact with 5N HNO_3; 3 - PAPNA after contact with a weakly acidic nitrate solution (pH = 3.8; Mo 20g/l); 4 - PAPNA after contact with 5N HNO_3 + 20g/l Mo.

In the IR spectra of the organic solutions (fig.4) obtained by extraction from 5N HNO_3 the presence of a band at 1296 cm⁻¹, which is absent in the extracts from the weakly acidic region (pH 3.8) and from the spectrum of the pure extractant, and the results from chemical analysis show that nitric acid is extracted by PAPNA. The doublet at 916 and 951 cm⁻¹, which appears in the spectra of the organic solvents containing molybdenum (irrespective of the extraction conditions), corresponds to the absorption of Mo = O. Analysis of the dependence of the concentration of NO_3^- ions on the molybdenum content in the organic solutions (fig.5) shows that nitric acid is displaced from the extract as the molybdenum is extracted, but a certain amount of NO_3^- corresponding to the ratio Mo:NO_3^- = 1:0.5 remains even in the organic phase saturated with molybdenum. This fact and also the appearance of an additional band at 1346 cm⁻¹ in the organic solutions obtained during

Fig.5 The dependence of the concentration of nitrate ions in the organic phase (c_1) on the concentration of molybdenum (c_2). Organic phase 0.5N PAPNA; aqueous phase 5N HNO_3 + Mo.

the extraction of molybdenum from strong nitric acid solutions make it possible to conclude that the nitrate ion enters into the composition of the extracted molybdenum compound. Thus, a purely cation-exchange mechanism for the extraction of molybdenum by PAPNA is ruled out for solutions with nitric acid concentrations of 5 g-eq/l or more, since the nitrate ion enters into the composition of the extracted molybdenum compound. This is also confirmed by the character of the dependence of D_{Mo} on the concentration of NO_3^- ions (fig.6). The increase in the concentration of nitrates in this series of experiments was achieved by the addition of the calculated amount of lithium and sodium nitrates (in the ratio of 7:5) to a 2N solution of nitric acid. This made it possible to maintain in the solution a level of hydration characteristic of nitric acid with the respective concentration of nitrate ions[7]. For a concentration of NO_3^- ions below 4N D_{Mo} does not depend on their concentration (fig.6), and this corresponds to the cation-exchange mechanism. For higher concentrations of NO_3^- D_{Mo} is directly proportional to the NO_3^- concentration, and this corresponds to the extraction of the $MoO_2NO_3^+$ cation by an exchange-solvate mechanism.

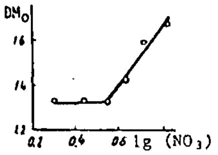


Fig.6 The dependence of the distribution coefficient of molybdenum on the concentration of NO_3^- ions in the solution. Organic phase 0.25N PAPNA; aqueous phase 2N HNO_3 + 4.4g/l + $LiNO_3$ + $NaNO_3$.

In the exchange-solvate mechanism the distribution coefficient should be inversely proportional to the hydrogen ion concentration. We studied the dependence of the distribution coefficient of molybdenum on the hydrogen ion concentration. A constant ionic strength in the solutions and constant mean ionic activity coefficients corresponding to 7.7 NHNO_3 were maintained by the addition of lithium and sodium nitrates to the solution in a ratio of 7:5. From fig.7 it is seen that the D_{Mo} value is inversely proportional to the hydrogen ion concentration. Thus, an exchange-solvate mechanism has been established for the extraction of molybdenum from solutions with concentrations of 4g-eq/l or higher. As already mentioned, during the extraction of molybdenum nitric acid is displaced from the extractant, and increase in the acidity should consequently reduce the extraction of molybdenum. At first glance this contradicts the results given in fig.2, where D_{Mo} clearly increases with increase in the concentration of HNO_3. It should, however, be noted that an increase in the concentration of HNO_3 in the solution leads to the combination of water and to an increase in the activity coefficients of the ions, including the MoO_2^{2+} ions, and the increase in the activity coefficient can have a predominating effect on the extraction. To check this suggestion the relation between log (D_{Mo}/γ) and log a_{HNO_3} was plotted. Since γ_{Mo} in nitrate solutions is unknown, it was assumed that γ_{Mo} varies in the same way as $\gamma_\pm$ for nitric acid solutions, and the mean ionic activity coefficient was used instead of γ_{Mo}. From fig.8 it is seen that D_{Mo}/γ' does in fact decrease with increase in a_{HNO_3}, as should occur if nitric acid is displaced during the passage of molybdenum into the organic phase.

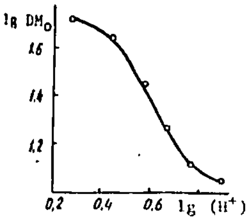


Fig.7

The dependence of the distribution coefficient of molybdenum on the concentration of hydrogen ions. Organic phase 0.25N PAPNA; aqueous phase HNO_3 + 3.56g/l Mo + $LiNO_3$ + $NaNO_3$; $[NO_3^-]$ = 7.7g-ion/l.

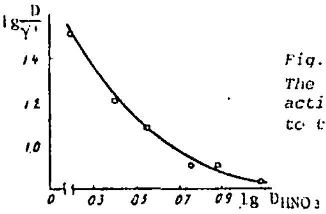


Fig.8

The dependence of log $(D/\gamma_\pm)$ on the activity of nitric acid according to the data in fig.2 (curve 2).

Conclusions

1. The extraction of molybdenum by PAPNA in weakly acidic nitric and sulphuric acid solutions takes place by a cation-exchange mechanism with a maximum distribution coefficient D_{Mo} at pH = 0.5-1. The presence of tungsten in the solution reduces the extraction of molybdenum on account of the formation of joint polyanions of molybdenum and tungsten, which are not extracted by PAPNA.
2. In sulphuric acid solutions the mechanism of the extraction of molybdenum is cation exchange up to a sulphuric acid concentration of 12 g-eq/l.
3. In solutions with a high concentration of HNO_3 (4-10 g-eq/l) molybdenum is extracted by an exchange-solvate mechanism.

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UDC 546.659

Reaction of lanthanum sesquioxide with a mixture of chlorine and carbon monoxide

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Summary

The paper gives the results from an investigation into the reactivity of lanthanum oxide obtained by decomposition of freshly prepared lanthanum oxalate at 700 and 900°C. Xray analysis of the products showed the presence only of the hexagonal form of La_2O_3. The reaction of lanthanum oxide with a 1:1 mixture of chlorine and carbon monoxide was

RECOVERY OF GOLD FROM ORE PULPS BY MEANS OF "PORE-CARRIER" FLUID (SOLVENT) EXTRACTION

UDC 669.213.6:66.061

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A novel method of fluid extraction of metals from solutions and pulps, first advanced in 1967 [1], following successful tests turned out to be a very promising approach to the extraction of gold from cyanide media and synthetic pulps [2].

This paper represents a development of the above research and deals with a very interesting practical problem -- "fluid "pore-carrier" extraction of gold from complex cyanide pulps.

It should be noted that previous studies dealt with the modeling (simulation) not only of the solid phase of the pulp (purified quartz), but also with the liquid (water) phase, which was prepared by adding appropriate amounts of complex cyanides, free cyanide, and protective alkalies.

The tests (the results of which are reported in this paper) called for use of the novel extractive-leaching method, along with cyanide leaching of ore followed by extraction in porous media.

As with the well-known sorptive leaching, this method calls for leaching, combined with pore-carrier fluid extraction in which the granules and the extractant together are in a solution which performs integral leaching of the metal to be recovered. The new method ensures additional recovery of metal (gold, in our case) from the cyanidation tailings and reduction of the cyanidation time since in this case, equilibrium shifts toward formation of low-dissociation gold compounds in the organic phase.

Earlier papers [2, 3] offer a general description of the method and the process parameters, with the exception of data presented later in this text.

Extraction from ore pulps was tested by two techniques, using ore samples from several ore deposits:

a) without preliminary cyanidation -- extractive leaching for ore samples No.1 and 2 of gold-bearing concentrates;

b) after preliminary partial cyanidation for sample No. 2, and complete cyanidation for flotation tailings from the ore-dressing plant.

Extractive leaching of sample No. 1. The chemical composition of the sample is: 71.4% SiO_2, 13% Al_2O_3, 0.5% CaO, 0.7% MgO, 0.2% TiO_2, 1.3% Na_2O, 6.5% K_2O, 0.03% Cu, 0.1% Zn 0.08% Pb, 3.4% Fe, 2.1 % As, 0.002% Sb, 1.03% S, and 7.7 g/t Au, with no Ag.

The percentage analysis of gold from the ore sample (for a 100% comminution degree) ground to a particle size of 0.0074 mm showed the following results, in %:

Free gold with a clean surface................	53.2
Partially broken-up (in concretions)...........	35.7
Combined with sulfides (fine-dispersed)........	11.1
Compounds with quartz..........................	None

The tests were performed according to the following schedule: weight sample of ore 100 g; gold content in weight sample, 0.77 mg; grinding degree, 100%; particle size, -0.074 mm; solid-to-liquid ratio = 2.1; a 0.04% concentration of KCN, and 0.02% of CaO; organic phase 3 ml of 10%; organic phase - 3 ml of a 10% solution of trialkylbenzyl-ammonia chloride (TABAC) mixed with kerosene plus 40% of decyl alcohol; the pore-carrier was porous polyethylene [2].

One hour after starting the tests, we fed an additional 0.018% KCN to restore the initial amount and 0.018% CaO to restore it from traces to 0.02%. During the following hours, the concentration of these reagents remained almost constant.

Extraction tests were conducted with extraction bottles.

As is evident from Table 1, gold extraction proceeds satisfactorily; in the first half hour, over half the amount of gold passes into the organic phase. However, the insufficiently-complete final extraction of gold is due to the fact that substantial amounts of gold in the given ore are found in the films and are intimately associated with sulfides.

Extractive leaching of sample No. 2. The chemical composition of the sample is: 73.02% SiO_2, 7.89% Al_2O_3, 8.51% Fe_2O_3, 0.55% FeO, 0.45% CaO, 0.56% MgO, 0.37% TiO_2, 0.08% Na_2O, 2.93% K_2O, 0.14% S_{tot}, 0.09% MnO, 0.11% Cu, and 0.02% Pb.

The gold content in the ore sample was 0.62 mg.

During the leaching stage, the KCN concentration was 0.045% and the CaO concentra-

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Translator's note: The original Russian term "poroplast'" stands for porous-plastic slabs, obtained by pressing and subsequent heat treatment of synthetic resins.

Table 1
Extraction Rate and Au Distribution in Sample No. 1, by Phases

Time, hr	Organic phase		Aqueous phase		Solid phase		Au balance	
	mg	%	mg	%	mg	%	mg	%
0,5	0.40	52.4	0.09	11.7	0.29	36.0	0.78	101.3
1	0.53	68.8	0.06	7.8	0.17	22.1	0.76	98.7
2	0.60	77.9	0.04	5.2	0.11	14.3	0.75	97.4
4	0.66	85.7	0.02	2.6	0.08	10.4	0.76	98.7
6	0.69	89.7	0.01	1.3	0.07	9.1	0.77	100.1

tion of 0.02%. After the second hour of leaching, the solution was supplied with an additional 0.024% KCN to restore the initial amount; during the first and third hour, some CaO was added to restore the amount to o.02% from traces.

The tests were conducted in a glass reaction vessel at a mixing rate of 30 rpm. The other conditions were the same as for sample No. 1.

Gold extraction from sample No. 2 holds particular interest because the pulps obtained after cyanidation of the starting ore lend themselves to filtration with difficulty because of the presence of clayey material.

The results (Table 2) indicate the possibility of successful metal extraction. Use of three sequential extractive-leaching stages, lasting 1 hour in each stage, made it possible to reduce the gold content to 0.2-0.3 g/ton in the solid phase and to traces in the liquid phase of the tailings.

Extractive-leaching of gold-bearing concentrate. The concentrate was obtained by flotation of quartz-sulfide ores. The chemical composition of the concentrate is: 0.8% As, 35.98% SiO_2, 1.48% SiO_2, 9.38% Al_2O_3, 24.09% Fe_2O_3, 3.57% CaO, 2.30% MgO, 22.28% S_{tot}, 0.33% $S_{sulfate}$, 0.065 Cu, 0.18% Zn, 0.115 Pb, 0.33% Sb, and 186.4 g/t Au.

Analysis of the mineralogical composition showed that in the starting ore, antimony is present as antimonite -- which is extremely reactive with alkalies, cyanides, and the mineral oxidizer. Therefore, the concentrate was subjected to preliminary oxidation roasting for three hours at t = = 450-550°C, intended to transform antimony sulfide into a pentavalent oxide form.

The tests were conducted under the following conditions: weight sample of calcine - 50 g; to 70% grinding of calcine particle size -0.074 mm; solid-to-liquid ratio 4:1; KCN concentration 0.11%; CaO concentration 0.03%; organic phase content - 4 ml of 10% TABAC. Leaching was performed in a glass reacting vessel at a mixing rate of 300 rpm. The gold content of the weight sample was 9.32 mg. After one hour, the pulp was additionally fed with 2 ml of KCN at a 72% concentration; after 1, 2.5, 3 and 4 hours it was additionally fed with 40 mg CaO.

Table 2
Extraction Rate and Au Distribution in Sample No. 2, by Phases

Time, hr	Organic phase		Aqueous phase		Solid phase		Au balance	
	mg	%	mg	%	mg	%	mg	%
0,5	0,37	59,5	0,05	8,1	0,20	32,3	0,62	100,0
1	0,44	71,0	0,07	11,3	0,12	19,3	0,68	101,6
2	0,48	77,5	0,036	5,8	0,09	14,5	0,606	97,8
3	0,52	84,0	0,026	4,2	0,08	12,9	0,626	101,1
5	0,56	90,4	0,004	0,65	0,05	8,0	0,61	99,05

Table 3
Distribution of Au by Phases During the Leaching of Concentrate

Time, hr	Organic phase		Aqueous phase		Solid phase		Au balance	
	mg	%	mg	%	mg	%	mg	%
1	4,50	48,5	1,94	20,8	2,68	28,8	9,12	98,1
2	6,39	68,7	1,34	14,4	1,55	16,6	9,28	99,7
4	7,61	81,5	0,42	4,5	1,35	14,5	9,38	100,5
6	7,80	84,0	0,38	4,1	1,24	13,3	9,42	101,4
2*	7,68	82,5	0,17	1,82	1,27	13,6	9,12	98,0

* When using 40% TABAC.

As is evident from Table 3, during the first four hours of the tests, one notes a considerable rate of gold extraction and passage into the organic phase. During the following two hours, there is no substantial change in the gold content of all the phases. This is probably due to the lack of excess amounts of extractant. This assumption is confirmed by the high figures for gold extraction, when using a 40% extractant. In this case, the results obtained after two hours are close to corresponding figures obtained after 6 hours with 10% TABAC. In terms of metal recovered in the liquid phase, the results are far superior.

When using three successive extraction stages and a 10% extractant (6 hours extraction time), gold recovery reached 90% with a residual content of 0.03 mg/l gold in the liquid phase of the tailings.

Attempts to further increase the degree of gold recovery brought little success since according to ultimate analysis results, the residual part of the gold is combined with pyrite and arsenopyrite.

Table 4

Results of Countercurrent Extraction of Gold

Time and place of selection of analytical sample	Content of determined components		
	Au, mg/l (in liquid phase)	Au, g/t (in solid phase)	KCN, %
Pulp from cyanidation of sample No. 2			
Starting pulp	2,6	0,89	0,02
After 1st hour of extraction	0,17	0,6	0,008
After 2nd hour of extraction	0,12	0,48	0,008
After 3rd hour of extraction	0,07	0,4	0,008
After 4th hour of extraction	0,05	0,4	0,004
1st Pachuca after shutdown	0,2	0,7	0,01
2nd Pachuca after shutdown	0,11	0,5	0,012
3rd Pachuca after shutdown	0,04	0,4	0,008
4th Pachuca after shutdown	0,04	0,5	0,008
Pulp from ore-dressing plant			
Starting pulp	0,6	0,7	0,038
1st-2nd hour of extraction	0,14	0,6	—
3rd-4th hour of extractior	0,10	0,5	0,013
5th hour of extraction	0,05	0,5	—
1st Pachuca after shutdown	0,48	0,6	—
2nd Pachuca after shutdown	0,40	0,55	—
" " "	0,23	0,5	—
4th Pachuca after shutdown	0,06	0,5	—

Countercurrent Extraction of Gold from an Ore-Pulp Pore-Carrier

The tests were conducted on a large-scale laboratory unit made up of four series-connected Pachuca tanks each with a 1.2-liter holding capacity, with a countercurrent phase motion, while the pulp was mixed with a pneumatic agitator. The pulp used in the tests was obtained by preliminary cyanidation of ore sample No. 2; the industrial pulps were obtained by cyanidation of flotation tailings from the ore-dressing plant.

Table 5

Content of Extractant in the Aqueous Phase of Tailings from Ore Pulps Subjected to Countercurrent Extraction

Sampling place and time	TABAC content, mg/l
Sample No. 2	
1st hour of extraction	5,3
2nd hour of extraction	5,3
3rd hour of extraction	5,8
4th hour of extraction	5,0
1st Pachuca after shutdown	5.8
2nd Pachuca after shutdown	6,6
3rd Pachuca after shutdown	5,6
4th Pachuca after shutdown	5,2
Ore-dressing plant tailings	
1st hour of extraction	5,2
2nd hour of extraction	3,2
3rd hour of extraction	3,6
4th hour of extraction	3,2
1st Pachuca after shutdown	3,8
2nd Pachuca after shutdown	4,1
3rd Pachuca after shutdown	3,6
4th Pachuca after shutdown	3,4

Sample No. 2 underwent preliminary cyanidation in a pressure Pachuca tank for 4 hours with a solid-to-liquid ratio of 2:1. After 1.5 hours of leaching, the solution was fed with up to 0.026% additional KCN to restore the starting amount; after 1.5, 2.5, and 4 hours, the solution was restored to 0.02% of CaO from traces. On completion of cyaniding, the pulp was subjected to chemical analysis in order to determine the cyanide content as well as the gold content in the solid and liquid phases of the pulp.

Industrial pulp from the ore-dressing plant had a solid-to-liquid ratio of 2:1 and the following content (in mg/l): 0.6 Au, 0.2 Ag, 25 Zn, 6 Cu, 5.5 Fe, and 0.0385 cyanide and 0.01% CaO; the solid phase contained 0.7 g/ton Au and 0.55 g/ton Ag.

Extraction of gold from pulps, obtained by cyanidation of sample No. 2, was performed with 10% TABAC mixed with kerosene and 20% decyl alcohol; gold extraction from industrial pulps was effected with 5% TABAC mixed with 30% alcohol. In either test, the volume of the organic phases was 10 ml per Pachuca tank. The output capacity of the extraction unit was 1 liter of pulp per hour. Recording the countercurrent results began after preliminary filling of the installation with pulp for 4 hours. The component content was determined on samples taken from tailings at the outlet from the fourth Pachuca tank as well as from every tank following shutdown of the procsss.

As is evident from Table 4, gold extraction in the countercurrent schedule is rather efficient since, along with direct extraction, gold is additionally leached from the pulp solids with no supplementary cyanide feed into the system. In our opinion, the slightly higher gold content in the liquid phase of the tailings can be avoided if we increase the number of Pachuca tanks to 6-8.

The method permits the extraction of large quantities of free cyanide, thus sufficiently decontaminating the process tailings; at the same time, following regeneration, part of the cyanides may be recycled to the process. In our tests, during the processing of industrial pulp from the ore-dressing plant, we extracted -- along with the gold -- almost all of the zinc, 80% of the silver, and 30% of the copper. Analytical results showed that no iron was recovered.

Losses of Extractant with Effluent from the Pulp

The TABAC content in decanted aqueous solutions from countercurrent extraction was determined using a method which had been proposed for octylamines, permitting the use of complex amines with methyl orange for colorimetric analysis [4]. Chloroform was used as the extractant. The content of the latter was determined from extraction tailings at their discharge from the fourth Pachuca tank, as well as from the aqueous phase of each tank following shutdown of the process.

As is evident from Table 5, all of the samples showed only slight variations in their contents of extractants for single ore types; it is within 5 to 6 mg/l for ore samples No. 2 and 3, and 4 mg/l for pulps from the ore-dressing plant.

CONCLUSIONS

1. In the countercurrent "ore-carrier" extraction of leached ore pulps on a large-scale laboratory installation, it is possible to obtain additional gold recovery from the solid phase as well as the removal of cyanides from the tailings.
2. Extractant losses vary within 3 to 6 mg/l of the aqueous part of the tailings.

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SPE 9494

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RESTORATION OF GROUNDWATER QUALITY FOLLOWING PILOT-SCALE ACIDIC IN SITU URANIUM LEACHING AT NINE-MILE LAKE SITE NEAR CASPER, WYOMING

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

ABSTRACT

The results of the first restoration of a pilot-scale acidic leaching of an uranium ore body in the United States are given. The project was done under a cooperative agreement between the Bureau of Mines and a joint venture consisting of the following companies: Rocky Mountain Energy, Mono Power, and Halliburton. The leaching phase is only briefly described, since it was reported earlier by Tweeton et al (4)[6]. Leaching was done with H_2SO_4 (pH range of 1.6 to 3.9) and H_2O_2 (80 to 1,000 ppm) over an 11-month period.

The restoration phase began in November 1978 and was completed in 9 months. Water samples were taken from observation wells located between injection and production wells as the leaching solution was decreased in strength. Groundwater quality in the leached ore zone was restored by the diluting and neutralizing effects of injecting native groundwater and treated water produced from recovered solution. Recovered water was purified by a combination of chemical precipitation and reverse osmosis. In situ measurements of pH, Eh, dissolved oxygen, conductivity, and temperature were made by a downhole probe in one of the wells. Water samples were taken and analyzed for U, V, Na, K, Ca, Mg, SO_4, S, P, Cl, F, Fe, Mn, Al, Si, Ti, Zr, Zn, As, and Se.

INTRODUCTION

The Bureau of Mines and a joint venture consisting of Rocky Mountain Energy, Halliburton, and Mono Power Co. entered into a cooperative agreement aimed at modeling in situ leaching of uranium with sulfuric acid at the venture's Nine-Mile Lake test site near Casper, Wyo. (fig. 1). Acidic leaching of uraniferous ores is very new, as most earlier leaching systems used alkaline leachants. This report describes the first restoration of a pilot-scale acidic-leached ore body in the United States. The results of an 11-month leaching phase conducted on a five-spot pilot test area (pattern No. 2, see fig. 2), were previously reported by the Bureau (4). The present study consisted of weekly in situ determinations of water quality parameters within the ore zone being restored, coupled with additional water analysis in the laboratory.

GEOLOGY

The uranium mineralization occurs in the Teapot sandstone members of the Upper Cretaceous Mesaverde formation. The project site is located approximately 15 km (9 miles) north of Casper, Wyo., in Natrona County. The leached uranium ore (and aquifer) restored to baseline in this study was a bedded deposit ranging from 155 to 165 m (508 to 541 ft) deep. The sandstone contains quartz, feldspar, and minor amounts of mica, black (organic-containing) minerals, glauconite, carbonaceous fragments, blue to earthy clay inclusions, and disseminated argillaceous materials. The deposit is amenable to acidic leaching because of the relatively low carbonate content.

The mineralization is of the roll-front type. The principal uranium mineral is uraninite (UO_2), with minor amounts of coffinite $U(SiO_4)_{1-x}(OH)_{4x}$. Further details are found in The Operators' Environmental Report to the U.S. Nuclear Regulatory Commission. (1).

HYDROLOGY

The Teapot sandstone is an artesian aquifer in the project area, being confined by the overlying Lewis shale and the underlying Pumpkin Buttes shale. The formation dips to the east-northeast at about 7 degrees with groundwater movement in that direction at about 4 m/yr (14 ft/yr). The aquifer is recharged at the outcrop approximately 3 km (2 miles) west of the test area. Groundwater in the project area is generally acceptable for livestock watering. Because of the naturally high total dissolved solids (TDS) in the water within the Teapot Sandstone of the project area, the water cannot be used for irrigation, industrial, or residential use without extensive pretreatment. The groundwater is a sodium sulfate type with a (TDS) quite variable in concentration (800 to 12,000 ppm) over the project area.

Leaching with sulfuric acid obviously changes a number of water quality parameters very significantly

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

References and illustrations at end of paper.

in the leached area, especially the pH, Eh, SO_4, Ca, V, Ti, and Fe. In situ leaching operations are now required by the Wyoming Department of Environmental Quality (DEQ) to restore the groundwater to its original use category. Earlier the DEQ required that the water quality must not only be returned to its original use, but that all parameters must be also returned to their original range. The study of groundwater restoration is an integral part of designing a successful in situ leaching operation. The industry is not yet mature, and as new information arises, regulations change to reflect what is most important and achievable in environmental protection. Today, the DEQ requires restoration to levels "consistent with" the baselines and to the same use category.

LEACHING PHASE

Wellfield Description

The pilot-scale leaching operation used a wellfield (designated as pattern No. 2) positioned in a 15-m (50-ft)-radius five-spot pattern. Sulfuric acid solution and oxidizer were injected into the four corner wells of the pattern (see fig. 3 and 4). The center well served as a production well. Within this pattern, the Bureau drilled three observation (sampling) wells (labeled OB1, OB2, and OB3). A plan view of all the wells at the depth of the ore zone is shown in fig. 3. Note in fig. 3 that the commonly encountered deviation of the drill string has produced a rhomboidal configuration of the four injection-wellbore locations at the 165-m average depth of the ore zone. All wells were cased with 13-cm (5-in)-inside-diameter polyvinylchloride (PVC) plastic pipe. The injection and production well casings were cemented down through all the sandstone formation layers and were then perforated in situ within the Teapot Sandstone Member of the Mesaverde Formation with the Bureau of Mines' water-jet perforator (2). Horizontal slots of about 0.5-mm (02-inch) width were cut in the injection and production well casings over a 2.8 to 4.9 m (9 to 16 ft) interval at approximately a 160-m (525-ft) depth, (the midpoint depth of the ore zone). OB1, OB2, and OB3 each had 10-m (33-ft) horizontal slot openings at the 160-m (525-ft) midpoint depth. Further detail is given by Tweeton et al (4).

The primary sampling wells were OB1 and OB3. OB2 did not perform satisfactorily because of a failure in well completion and was not sampled. Water samples from this well were radically different in quality and pumpable quantity from the rest of the pattern wells. These sampling wells were located to allow sample taking at points intermediate between the injection and production wells for the following two reasons: 1) A downhole water-quality-sensing and data-gathering probe (described in a later section) placed in a production well below the pump could not be pulled up for periodic calibration without interfering with production. 2) Taking samples only from production and injection wells would not provide all the information needed for geochemical modeling. For example, a case wherein uranium was being dissolved but reprecipitated before reaching a production well would be indistinguishable from a case wherein uranium was not being dissolved. In this way an intermediate sampling point avoids any ambiguity in interpretation.

The pattern No. 2 well field was generally operated at about 158 ℓ/min (42 gpm) production from the center with 38 ℓ/min (10 gpm) input per injection well. This resulted in an overproduction of about 6 ℓ/min (1.6 gpm), which maintained hydrologic control. Water sampling from OB1 and OB3 was done with 34-ℓ/min (9-gpm) pumps several meters above the slotted section.

LIXIVIANT CIRCULATION

Content vs. Time

While many Texas and Wyoming in situ leaching operators heretofore have used an ammonium bicarbonate-carbonate leachate, this is the only operator currently using dilute H_2SO_4 solution. Here the lime mineralization is low and acid is applicable without high consumptive losses. Injection began December 1, 1977, with dilute H_2SO_4 (0.15 g/l) added. The H_2SO_4 strength was increased to about 1.5 g/l on December 30, 3 g/l on January 10, 1978, and 5 g/l on April 3. If strong acid were added initially, uranium and other elements could be mobilized at high concentration near the injection well only to be reprecipitated near the production well as groundwater diluted the H_2SO_4 further and $CaCO_3$ neutralized the H_2SO_4. Additional effects, such as CO_2 liberation, which could cause loss in permeability, could also occur. The rate at which acid strength was increased was intended to be conservative.

Hydrogen peroxide (H_2O_2) was added as a 35 pct solution starting January 21, 1978, to give a concentration of 80 ppm. The concentration was slowly raised to 1,000 ppm over a 1-month period. During the remainder of the leaching phase, the H_2O_2 concentration in the injection well was held in the range of 80 to 1,000 ppm by adding as a 35 or 50-pct solution.

FLOWRATES AND VOLUMES

The production solution was stripped of uranium by ion exchange, and additional H_2SO_4 and H_2O_2 were then added to the raffinate to fortify the lixiviant for reinjection. This total "circulating" solution has been estimated by Rocky Mountain Energy at 4.57×10^6 liters (1.21×10^6 gal) for this pilot-scale leaching operation. This recirculation of leachant and extraction of uranium continued until September 5, 1978. After that time, no additional H_2SO_4 was added to fortify the reinjected solution.

On September 8, 1978, a partial flow of the raffinate was directed to the evaporation pond since higher quality water produced from treated raffinate and native groundwater were being injected into the ore zone to start restoration. By November 11, 1978, the total stream of barren liquor (raffinate) was routed to the evaporation pond, and only native groundwater (from a well about 400 m away) was injected into the ore zone. By this sequence the leaching phase made the transition to the restoration phase. Leaching was curtailed by a need to investigate restoration for NRC's environmental review, not because uranium was necessarily depleted to the economic limit. Uranium concentration of the production solution was about 50 ppm when acid addition ceased.

SURFACE RECOVERY PROCESS

During the leaching phase of pattern No. 2, uranium in the production solution was in the range of 60 to about 300 ppm, with average values of about

about 100 ppm.

The recovery of uranium from the production wells (pregnant solution) was accomplished by a series of hydrometallurgical unit processes. The pregnant solution was pumped through an ion exchange (IX) system, which selectively adsorbed the anionic uranyl-sulfate complexes.

The uranium-depleted solution (raffinate) was refortified with H_2SO_4 to raise concentration to the 3,000 to 5,000-ppm range. More H_2O_2 was added to maintain an oxidation-reduction potential (Eh) range of +450 to +700 mv.[7] This refortified lixiviant was then returned to the injection wells.

Uranium adsorbed on the IX resin was stripped off with a strong H_2SO_4 solution (over 100 g/l). Yellowcake was precipitated as U_3O_8 (yellowcake) with ammonia and thickened with the aid of a flocculant. The thickened yellowcake was filtered on a 90 by 30-cm (3 by 1-ft) drum filter and then dissolved in HNO_3 for shipment in solution form. This method of yellowcake handling was used for pilot plant purposes only.

EXCURSION MONITORING

During the pilot-scale leaching of pattern No. 2, six monitor wells located outside the radius of this five-spot pattern were sampled biweekly, to provide a continuing record of baseline water conditions. These wells encircled the pattern, approximately 49 m (160 ft) from the center production well. Sampling indicated that no excursion occurred during leaching or restoration. Both monitor and leaching wells will be sampled periodically after the leaching zone restoration to determine if water quality has remained high and is not fluctuating.

WASTE MANAGEMENT

Since production of solution exceeded injection by about 5 pct to maintain a hydraulic gradient toward the production well, an equal volume of the barren solution was sent to the evaporation pond (figure 2 - background). This bleedstream was drawn from the raffinate surge tank.

Other wastes routed to the evaporation pond include brine and precipitates (as slurry) from the water treatment plant operated during the restoration phase (described under Restoration phase section).

RESTORATION PHASE

The restoration operations spanned the period from November 1978 through July 1979. Pilot plant treatment of raffinate by reverse osmosis (RO) purified it for reinjection. Passage through the ore zone diluted the residual leaching solution. Additionally, native groundwater from a well about 400 m away was blended with the RO-purified raffinate for injection. The groundwater carried neutralizing species principally Ca ions, into the ore zone, which reacted with the SO_4 radicals to precipitate as calcium sulfate. The following listing of major events in the nearby pilot plant that controlled the conditioning and flow of restoration fluids is given as a brief chronology and overview.

RESTORATION CHRONOLOGY OF PILOT PLANT OPERATIONS

Sept. 5, 1978 Acid injection was terminated. Native groundwater was added to the injection stream as a portion of the untreated raffinate was directed to the evaporation pond.

Nov. 21, 1978 Restoration circuit (raffinate purification system) was completed with an initial capacity of 19 ℓ/min (5 gpm). Unit has cellulose acetate spiral-wound membrane.

Dec. 5, 1978 Restoration circuit run at 19 ℓ/m (5 gpm) during December on a partial basis owing to capacity and sealing problems with pan filters.

Dec. 18, 1978 Thickener component was added to the restoration circuit to alleviate a flow "bottlenect" at the lime pan filters. Flocculant addition system was employed in thickener to provide a needed surge capability and a clear overflow for subsequent reinjection.

Dec. 21, 1978 Uranium in production stream was down to 16 ppm. IX unit for uranium recovery was shut down.

Jan. 8, 1979 Installation and testing of additional, second RO unit (125 ℓ/min, polyamide type) was completed. Changes in design were made to the thickener unit to approach 98- ℓ/min (30-gpm) flowrate.

Jan. 15, 1979 Both RO units were run briefly with both restoration circuit and groundwater. Thickener flowrate capacity still inadequate. The production solution pH was at 2.8.

Jan. 22, 1979 All chemical variables were in baseline region, except for pH level. Groundwater continues to be injected.

Feb. 5, 1979 Large RO unit was brought on line.

Feb. 12, 1979 Operation of RO unit is hampered by inadequate thickener performance. Higher pH water containing calcium salts was injected for only 3 days to aid removal of H^+. This was stopped since $CaSO_4$ precipitated heavily on the injection solution filter. The pH was at 3.4

Feb. 26, 1979 Restoration solution injection and production was discontinued because evaporation pond was full. Sprayers were installed to promote evaporation.

March 2, 1979 Seeding of thickener unit with gypsum to increase the amount of solids in the underflow was started, but discontinued when no appreciable gain in thickener performance was noted. Ice (75 m^3 20,000 gallons) was cut and removed from pond. Operations were discontinued when it was discovered that

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[7] Oxidation-reduction (Eh) measurements mentioned in this paper use the convention of + oxidation and - reduction, and are vs. S.C.E.

the ice was impure. Operations then began to truck the pond solution from Nine-Mile Lake to an alternate company site where adequate capacity was available.

Mar. 8, 1979 Restoration circulation resumed. Pond solution was continued to be hauled to an alternate evaporation pond.

Mar. 19, 1979 Restoration continued to be complete, except for pH. However, SO_4 levels have started to rise. pH was now at 3.7.

Mar. 28, 1979 Sodium carbonate was used to maintain an injection solution pH of 10.6. This addition probably was responsible for the rise in SO_4 levels. Pumping was impaired by fungus. Use of flocculant in thickener increased the underflow solids to 20 pct. Gypsum seeding of thickener terminated.

Apr. 2, 1979 Sodium carbonate addition halted.

Apr. 9, 1979 Localized precipitation of gypsum, vanadic complexes, and fungus near production well reduced flow to 57 to 76 ℓ/min (15 to 20 gpm). pH was up in the production well. Second set of evaporation sprayers was installed. Fungus died as pH was increased to 4.3. Decantation tanks added to provide surge capacity needed for higher RO flowrate.

Apr. 24, 1979 Small RO restarted at a feed rate of 17 ℓ/min (4.5 gpm). Sodium hydroxide addition was started to control pH of injection solution. pH was now at 4.7.

Apr. 30, 1979 Flow reversal was initiated to ease plugging around the production well; wells OB1 and OB3 were used for production while the production well was injected. RO units tested for series use. Circuit ran at 68 to 95 ℓ/min (18 to 25 gpm) for the last week in April.

May 4, 1979 Injection initiated into OB1 to aid in raising the pH in the internal part of the pattern. Injection of 1 well-bore volume of acidic solutions, intended to enhance well performance, decreased the pH to around 3.8.

May 7, 1979 Flow reversal was completed. Production well was now unplugged. High bicarbonate levels (200 ppm) were detected. pH was donw to 4.3.

May 10, 1979 Failure of the spiral-wound membranes in the small RO unit occurred, and the unit was disconnected.

May 17, 1979 RO units were taken out of service for cleaning. Injection solution pH was adjusted to around 9.5 with NaOH.

May 21, 1979 3.8-cm (1-1/2-in) line installed for discharge of thickener underflow to evaporation pond to avoid lime plugging in the main line. pH was now at 4.8.

May 31, 1979 Large RO was taken out of service and cleaned. Production problems reduced flow to 9 ℓ/min (24 gpm) at the end of May.

June 1, 1979 Pump was replaced in the production well, restoring production flow to 132 ℓ/min (35 gpm).

June 4, 1979 Injection rate was decreased to cause a greater hydraulic gradient which should aid the flow of solution through areas of low permeability.

June 7, 1979 Flow reversal initiated with wells OB1 and OB3 used for production and the production well used for injection.

June 19, 1979 Flow reversal was completed. Production solution pH was around 5.6, with several days of deviation as low as 5.2.

June 26, 1979 Only two injection wells used for injection and OB1, OB3, and the production well producing, to provide the best sweep of the minor transmissive axis. One of the permeators in the large RO failed. Tests indicated that the membrane was defective.

June 30, 1979 pH was now at 5.6, after dropping to 5.3 when OB1, OB3, and the production well started to produce.

July 9, 1979 Full restoration appears to be approaching completion. pH was now around 6.0. Restoration circuit operating smoothly at 114 ℓ/min (30 gpm).

July 16, 1979 Injection was run at 76 ℓ/min (20 gpm) vs. production of 114 ℓ/min (30 gpm) employed to provide gradient needed to restore remaining areas of low permeability.

GROUNDWATER QUALITY DATA GATHERING

In Situ Measurements With Downhole Probe

In observation well OB3, five water quality parameters were measured in situ. Oxidation-reduction potential (Eh), hydrogen ion concentration (pH), dissolved oxygen (D.O), conductivity (cond.), and temperature were measured using a Hydrolab System 8000[8] downhole probe, manufactured by Hydrolabs, Inc., Austin, Tex.

The probe consisted of two parts: A downhole sending unit with sensors, and a battery-powered surface data-control unit. The transmitter or sending unit is about 7.6 cm (3 in) in diameter and 46 cm (18 in) long.

The probe is capable of measuring the following parameters:

1. Temperature, using a linear thermistor. Range: -5 to +45° C (23° to 113° F).
2. Depth of water in well using a strain-gage transducer. Range: 0 to 200 m (0 to 656 ft.).
3. Dissolved oxygen, using a semipermeable Teflon membrane-covered gold-silver polarographic cell. Range: 0 to 14 ppm.
4. Conductivity, using a platinum four-electrode cell. Range: 0 to 200 millimhos/cm.
5. pH, using a glass electrode and silver-silver chloride reference. Range: 0 to 14 pH.

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[8] References to specific products does not imply endorsement by the Bureau of Mines, but are mentioned only for identification.

6. Oxidation-reduction potential (Eh), using a platinum electrode and silver-silver chloride reference electrode. Range: -2,000 to +2,000 mV.

Field usage indicated that all parameters of the probe required recalibration within 30 days. The depth sensor was quite sensitive to barometric pressure changes and required calibration several times per day. It was not used in this study. The pH calibration drifted upward after approximately 2 weeks' immersion in the well. For this reason, surface measurements of pH with another meter were taken as the most accurate. All other parameters showed insignificant calibration changes and required only small corrections at the 30-day recalibration interval.

The downhole probe was placed in well OB3 145 m (476 ft) from the surface. This is approximately 3 m (10 ft) above the perforated zone and 10 m (36 ft) below the pump.

It was found in previous work (4) that groundwater quality parameters, especially Eh and D.O., need to be measured as near to the screened or perforated casing zones in the well as possible. In water from OB3, where both in-situ (probe) and surface measurements were taken, significant differences between the Eh measurements can be noted (see appendix). This behavior is not unexpected: ionic specie in groundwater taken to the surface rapidly oxidizes and also the water commonly dissolves additional oxygen.

EFFECT OF HYDROLOGY ON SAMPLING

Fig. 4 shows a simulated streamline pattern for the leaching site using average values of injection and production flowrate. Injection rates of 20 ℓ/min (5.3 gpm) for each injection well and production rates of 80 ℓ/min (21 gpm) were used. Injection of restoration water took place at the four corner wells, and production was from the center well, as shown in fig. 4.

The streamline pattern was generated and drawn by a computer and plotter. The program designated ISL-50, was developed at the Bureau's Twin Cities Center by Schmidt (3). The shape of the pattern is determined by a number of factors which include injection and production rates, directional permeability, aquifer vertical dimension, and well-perforation placement. The shape of the pattern and the direction of major permeability in the aquifer have an important effect on the changes in water quality taken from the observation wells.

Observation well OB3 is located almost directly between the injection and production wells along the major axis of permeability. Accordingly, the velocity profile in the vicinity of OB3 is nearly constant. This allows geochemical changes noted in OB3 to be rapid and well defined. Also, geochemical changes between the injection well and OB3 are easier to identify. When calculations using average restoration flow rates are used, the program indicates that it takes 1 to 2 days for water to travel from the injection well to OB3.

Well OB1 lies within a wider range of streamlines. The velocity profile across OB1 exhibits considerable variation due to the lower directional permeability between the closest injection and production wells. Travel times for water leaving the injection well and arriving at OB1 vary from 2 to 19 days. Average restoration-phase flow rates were again used in this calculation, taking into account the changes due to varying lengths of streamlines. If the composition of the injection solution changes, the water in OB1 begins to change after 4 days and continues to change for approximately 2 weeks more.

WATER SAMPLING PROCEDURE

The quality and reliability of geochemical analyses depend heavily on the sampling procedure followed. Samples from OB1 and OB3 were taken at the well head. Samples of the injection solution were taken from the plant (fig. 1). Injection samples were collected at hourly intervals, composited daily, and averaged weekly. The following sampling procedure for the observation wells has evolved from earlier similar company projects and seems to give the most consistent results:

1. Each well is pumped out for a minimum of 45 min at 15 ℓ/min (4.6 gpm) to fill the well bore with fresh water from the surrounding aquifer. The water is routed to a production well.

2. Downhole water parameter readings are taken in OB3 with the downhole probe.

3. Four-liter (1-gal) samples are taken from each well for analysis.

4. Samples are filtered with 0.45-μm filters to remove sediment. Filter media were inert to the reagents or dissolved ions.

5. Half of each sample is acidified with HCl to keep all cations in solution.

6. Field laboratory measurements (in building in fig. 1) of pH, Eh, conductivity, and temperature are taken on an unacidified portion.

7. Samples are stored in clean polyethylene bottles and shipped to the Bureau's Twin Cities Research Center for further chemical analysis.

CATION AND ANION ANALYSES

In addition to the field measurements, cation and anion analyses were performed on the weekly samples. Specific elements and the analytical methods are listed in Table 1. The time lag from sampling to analyses ranged from 1 to 6 weeks and averaged about 2 to 3 weeks.

COMPUTER DATA STORAGE

All the chemical analyses taken for the project have been stored on the computer file at the Bureau's Twin Cities Research Center. This file is available in printout or plotted format and is also included in the appendix of this paper.

ANALYSES OF GROUNDWATER DATA

Water Quality vs. Time Plots

Based on weekly chemical analyses, the water quality parameters that had the largest change in value starting from baseline (1) through the leaching phase, and returning toward original value as restoration progressed (150-day restoration study period) were U, V, Ca, SO_4, pH, Fe, As, Se, Eh, conductivity, and dissolved oxygen (fig. 5-15). Other parameters that were analyzed periodically but not graphed here because of the relatively small concentration changes were Na, K, Al, Zn, Mg, Zr, Ti, Si, P, Mn, Fl, Cl, S, and groundwater temperature. These values, along with data used for the above noted figures, are given in the appendix.

Note in the graphs (fig. 5-15), the baseline concentration region, derived from an averaging of three to six independent groundwater analyses (depending on element), run prior to the leaching operation.

Examination of the figures shows that most groundwater quality parameters returned to the baseline region, or very near, over the 220-day restoration period.

GEOCHEMICAL TRENDS TOWARD RESTORATION

In general, at the start of restoration, uranium values remaining in the ore zone were economical to extract by ion exchange techniques. However, in the case of pattern No. 2, leaching operations were terminated because of the need to examine restoration rather than because of economic considerations. As restoration proceeded, the aquifer acidity levels moved from pH 1.6 to about 2.6 in the first 40 days (see Restoration Chronology Section). The uranium levels in the production solution dropped even further (to 16 ppm in the same 40 days) because of decreased solubility at the higher pH levels.

It is worthwhile to view several geochemical changes that occurred during the restoration phase of the groundwater within the leached portion of the orebody. The following water quality changes are not unexpected from geochemical principles but are given here since this is the first restoration of an acid-leached uranium-bearing orebody in the United States. Even though this was a pilot-scale operation, its successful completion opens the way for commercial acidic in situ leaching ventures for deposits with relatively low calcium and clay content.

CO-OCCURRENCE OF SOME ELEMENTS AND PARALLEL CHANGES OF CONCENTRATION LEVELS

Certain pairs of elements exhibit similar trends in concentration changes. A good example was found in Figures 5 and 6, in which shifts in uranium levels in solution were mirrored by vanadium levels.

Similarly, iron and aluminum ions exhibited roughly parallel decreases as pH levels rose toward neutrality as restoration progressed (not graphed, see appendix).

Sodium and potassium ion concentration changes in groundwater are commonly inversely linked. Sodium levels moved slightly upward from 333 to 470 ppm in an early 100-day restoration period, while potassium trended downward from 11 to 8 ppm in the same time period. This data was not plotted (found in appendix for dates Dec. 6, 1978, to Mar. 20, 1979). Calcium from the native groundwater and from the treated water pumped into the ore zone is expected to exchange sodium ions from the clay in the ore zone, thereby accounting for the increased sodium levels. Sodium carbonate was added as pH control to the reinjected water for a week in March 1978, contributing to the rise in sodium.

ENVIRONMENTALLY SENSITIVE ELEMENTS

Arsenic and selenium levels (fig. 11 and 12), which are of environmental importance because of their high toxicity, are easily mobilized in acidic media. These elements were analyzed on an approximately monthly basis. During the first 150 days of restoration, arsenic values ranged from 14 to 75 ppb, while selenium ranged from 20 to 82 ppb. Arsenic concentration values were close to the National Primary Drinking Water Standards of 50 ppb (5). Selenium was above the primary standard of 10 ppb (5). However, the aquifer within the ore zone was never intended to supply drinking water for human consumption. No public water supply wells are recorded within 5 km (3 mi) of the test site (1).

RELATIONSHIPS OF RESTORED ORE ZONE GROUNDWATER QUALITY TO OTHER BASELINE CRITERIA

The restoration of the cooperators' well field pattern No. 2, which began in November 1978, was now essentially complete after nine months. Table 2 compares the groundwater of pattern No. 2 after leaching and restoration operations with pattern No. 2 preleach groundwater and with native groundwater outside the ore zone. The native groundwater outside the ore zone shows significant variation in quality. Almost none of the values shown in table 2 are within the National Secondary Drinking Water Standards of 500 ppm total TDS; however, water of this quality is generally satisfactory for livestock (5).

A comparison of water quality before and after the leaching and restoration operations indicates that the restored groundwater is close to preleached quality and is also close to the water quality range outside the ore zone. Graphs showing the change in water quality during restoration are shown in fig. 16. This figure highlights the gradual rise in pH which has occurred. The pH appears to be a function of the total amount of solution swept through the leached ore zone during restoration. The pH should return to preleached value after sufficient ions have been moved through the ore zone.

COMPARISON OF PILOT-SCALE RESTORATION TO LABORATORY EXPERIMENTS

Laboratory studies of restoration were conducted at the University of Texas at Austin as a part of Bureau of Mines Contract No. H0282016. The Principal Investigators were Dr. W. Michael Breland and Prof. Robert S. Schechtor. Experiments simulating both leaching and restoration were performed, but only restoration will be discussed in this report.

EXPERIMENTAL PROCEDURE

The laboratory studies were performed with a blended sandstone core material from the Nine-Mile Lake Site. The core material had been stored unfrozen in plastic bags for several months, so it was probably partially oxidized during storage. This oxidation would not affect the restoration simulation, but could make uranium dissolve more readily during the leaching simulation.

Four different types of restoration experiments were performed with plastic columns containing core material which had been previously leached with 28 to 32 pore volumes of H_2SO_4 solution. The first experiment used a 120 by 7.6-cm column, and the "restoration" solution consisted of 3 pore volumes of 25 pct groundwater and 75 pct distilled water, followed by 100 pct groundwater to restoration completion. The porosity of the sandstone packed in the column was 37 pct, making 1 pore volume about 2.0 liters.

The second experiment used a smaller (60 by 2.5-cm) column of ore. This was also restored, using the same method.

The third experiment was another smaller column using only 25 pct groundwater plus 75 pct distilled water for the complete restoration.

The fourth experiment used two of the smaller sized columns, which were restored using a saturated $Ca(OH)_2$ solution (450 ppm).

The term "restoration" as used in describing the laboratory studies means that time at which the H^+ ion effluent concentration matched the feed concentration, within 0.5 pH unit.

The flow rate in all of these experiments was about 3 m (10 ft.)/ day. This rate was about three times the field flow rate near well OB3 during restoration. The laboratory restoration experiments were conducted before the field restoration, so the laboratory flow rate had to be chosen before the field flow rate was established. The restoring solution was passed through the column only once.

All of the experiments, except those using Ca $(OH)_2$, were with ore that had been leached with sulfuric acid at the University of Texas during laboratory simulation of the leaching phase at the Nine-Mile Lake Site. The studies of the leaching phase were done with H_2SO_4, increased in several steps, as had been used in the field. The final step in the laboratory leaching involved 4 pore volumes of 4.0 g/l H_2SO_4 plus 1.3 g/l H_2O_2. This step followed 28 pore volumes at lower concentrations. Each pore volume required about half a day to flow through the column. After the final step of each series of leach studies, the feed solution was changed to the restoration solution (25 pct groundwater plus 75 pct distilled water or 100 pct groundwater). The effluent was collected at least four times per pore volume of fluid flushed through.

The 25 pct groundwater - 75 pct distilled water combination was used because the operator was considering recirculating a combination of 25 pct groundwater and 75 pct water that had been purified by reverse osmosis. It was recognized that water from a reverse osmosis unit contains more dissolved solids than distilled water, but for standardization, comparison, and interpretation, distilled water was preferred over reverse osmosis product water. The groundwater was from the Nine-Mile Lake Site.

In the $Ca(OH)_2$ restoration experiments, the ore was first saturated with H^+ ions by running a 3-g/l solution of H_2SO_4 through the column until the effluent pH was less than 0.3 pH unit different from the feed pH. Then the influent was switched to the $Ca(OH)_2$ solution.

COMPARISON OF RESULTS

Restoring the ore in the larger column was complete within 3 to 5 pore volumes, with respect to most of the ions, as shown in fig. 17-25. However, the restoration required considerably more pore volumes to restore the pH to baseline levels.

The hydrogen ions have a greater affinity for montmorillonite clay than even triply charged Al cations do. This tenacity, which results in a slow pH rise, could be caused by hydrogen bonding to the oxygen of the clays. The pH, as shown in fig. 17, displayed a gradual climb for 11 pore volumes, followed by a rapid ascent from pH 3.5 to 7.5 within about 2 pore volumes.

One approach to comparing field and laboratory results is on the basis of relative volumes required for leaching and restoration. The laboratory restoration required about 50 pct of the solution volume for leaching. A comparison with the field data indicates that similar results were obtained. The restoration of pH was nearly complete after 45 pct as much solution had been pumped out during restoration as had been injected during leaching.

Another approach for comparison is on the basis of pore volumes. A factor for correlating days of field operation to pore volumes was calculated with the Bureau's hydrologic computer program termed ISL-50 (3). The calculations indicated that 10.5 days of field operation corresponded to 1 pore volume for solution moving through well OB3 to the production well from the vicinity of the nearest injection well. The site had been well characterized, so such factors as the differences in down-hole well spacings and transmissivities could be taken into account. Nevertheless, the result should be considered an estimate, subject to considerable error.

As indicated in a previous section, the streamlines flowing near well OB1 correspond to widely varying flow rates, so assigning a specific correspondence between days of field operation and a pore volume of solution moving to OB1 from the nearest injection well could not be done. Therefore, the field results compared with laboratory results do not include OB1

Using the pore volume basis for comparison, restoration of pH levels in the field was more gradual than in the laboratory. As shown in fig. 9, the pH in the production well had risen to 2.5 by the 40th day of restoration, corresponding to 3.8 pore volumes. The pH in the production well rose gradually and erratically after that, reaching 6.4 by the 220th day of restoration, corresponding to over 20 pore volumes.

The more gradual change in field pH may have been caused by the higher clay content in the uranium-bearing aquifer immediately above and below the actual uranium-bearing zone. The laboratory core material was from the uranium-bearing zone only. In the field, part of the leach solution would contact the clayey layers, and the release of H ions from that clayey material could be quite slow. It should be noted that the effects of the widely varying lengths of streamlines extending from the injection wells to the production wells were avoided by using well OB 3 as a sampling point. Accordingly, the gradualness of changes in OB3 should not be attributed only to hydrologic considerations. Handling of the core material prior to laboratory leaching is another factor to be considered.

The behavior of Eh in the laboratory was governed only partly by the change in pH. At 12 to 13 pore volumes, the pH had increased by 3.7 units. A corresponding theoretical change in Eh would be (3.7) (60 mV) = 220 mV. As shown in fig. 18, the observed decrease was only 100 mV, indicating that the solution became oxidizing. This, together with the fact that during leaching studies the Eh increased more than could be attributed to decreases in pH while H_2O_2 was not being added, suggests that the solution could be transporting O_2 from the air.

The behavior of Eh in the field was quite different. As shown in fig. 13, the Eh in OB3 (surface measurement) dropped from 380 mV at the 29th day of restoration to 60 mV at the 39th day. In situ field conditions became more reducing before the pH rose, judging from the fact that the Eh dropped significantly by the 39th day, whereas the pH did not rise significantly until after 40 days.

Conductivity dropped quickly in both the field and laboratory, as shown in fig. 14 and 19, respectively. In the field, the conductivity became lower than the preleach value owing to the injection of process water (groundwater from another location) of lower conductivity than the leach field baseline. In the laboratory, it dropped to about the same value as before leaching.

Sodium in the laboratory reached a fairly constant value after only a few pore volumes of 100 pct groundwater (see fig. 20). The data in the appendix shows that the field sodium concentration was below 350 ppm, about half of the preleach value, by the 29th day of restoration, owing to the lower sodium levels in the process water and the exchange of sodium for calcium on the clays. The concentration rose after that. Sodium concentrations were fairly constant during leaching in both the field and the laboratory.

Calcium concentrations showed more interesting behavior. In the laboratory, the Ca concentration increased as restoration progressed. Apparently calcium was not being adsorbed from the groundwater as rapidly near the end of the simulated restoration as at the beginning. At the beginning of restoration, the clays were mostly saturated with H^+ ions. The groundwater, containing about 120 ppm calcium, was low in H^+ ions but high in calcium with respect to the clay surfaces. Therefore, exchange occurred, removing calcium from the groundwater. Near the end of the restoration phase, there were fewer H^+ ions left on the clay, so less exchange occurred (see fig. 21). In OB3, the Ca concentration was 70 ppm, about half the preleach value, by the 29th day of restoration. It showed a small tendency to rise, going to 100 ppm by the 46th day (fig. 7).

Uranium, V, Fe, and SO_4 in the laboratory were reduced to fairly low levels within just 1 or 2 pore volumes (see fig. 22-25). A sharp peak occurred after the 100 pct groundwater flush was started. For U, V, and Fe, this peak was primarily due to the higher ionic strength water displacing these ions from the clays. The sharp jump in SO_4 and conductivity at that point was expected, as the groundwater had a high concentration of SO_4.

In well OB3, SO_4 was below preleached concentrations by the 29th day of restoration (see fig. 8) as a result of the injected clean process water. However, levels rose subsequently above baseline, adding to the SO_4 contribution to the already high TDS levels of the groundwater. Uranium was very low in OB3 by the 29th day, and only a few ppm persisted in OB1 for about 100 days (see fig. 5). Vanadium concentrations stayed high for about 69 days (see fig. 6), and iron stayed high for about 146 days (see fig. 10). The concentrations of vanadium and iron are sensitive to pH, so the slow decline in these values is explained by the slow rise in pH.

Laboratory restoration studies with the smaller (60 x 2.5 cm) column gave results similar to those with the larger column, indicating that the smaller column can be used to conserve core material and to reduce the cost of test work.

In a second restoration with the smaller column, 25 pct groundwater and 75 pct distilled water was used for the entire restoration, instead of changing to 100 pct groundwater after 3 pore volumes. The restoration required 28 pore volumes, much more than when using 100 pct groundwater. Since reducing the H ion concentration involves cation exchange, the greater effectiveness of 100 pct groundwater is not surprising since it has four times the ionic strength of the 25 pct solution.

A laboratory restoration experiment was also performed using a saturated $Ca(OH)_2$ solution. About 11 pore volumes were required to attain pH restoration (see fig. 26). This is not very different from the amount of flushing required with groundwater. Approximately 14 pore volumes were required with groundwater, but 3 of those pore volumes were with 25 pct groundwater and would be only as effective as about 1 pore volume of 100 pct groundwater. Thus, about 12 pore volumes of 100 pct groundwater would be required versus 11 pore volumes of saturated $Ca(OH)_2$. The $Ca(OH)_2$ solution was not tested in the field.

It is possible that keeping the Ca concentration more carefully controlled near the theoretical maximum of 450 ppm (saturated solution) may increase the effectiveness. The observed concentration varied from 250 to 450 ppm. Most of the variation was probably due to CO_2 in the atmosphere dissolving in the solution and reacting with the $Ca(OH)_2$ to form insoluble $CaCO_3$. Theoretically, the saturated $Ca(OH)_2$ solution could be very effective for pH restoration since the Ca would displace H ions from clay and the H would be neutralized by the OH. It would also hel to neutralize any H ions that are hydrogen bonded t the clays or other minerals.

GROUNDWATER MONITORING AND SITE ABANDONMENT

To monitor the confinement of the leach solutions, four monitor wells were placed around the pattern at a spacing of about 49 m (160 ft) from the production well. Each of these was screened over the entire sandstone level.

The monitor wells were sampled routinely before and during pattern operation to provide a continuing record of baseline water conditions. Monitoring did not indicate any excursions during leaching or restoration. Both monitor and leaching wells will be sampled periodically after restoration to determine if water conditions have stabilized. Those wells not to be utilized during commercial leaching operations will be plugged prior to startup of the commercial operation.

The evaporation pond contains the bleed stream of barren leach solution produced during the leaching phase, as well as the waste produce streams from the restoration phase. After evaporation is complete, the remaining solids from the pilot operation will be placed in an approved tailings disposal site. Assuming a commercial plant is constructed at Nine-Mile Lake, this material will be placed in the evaporation pond constructed for the larger plant. Ultimately the evaporation pond site will be reclaimed either by placing all solids in another existing tailings disposal site, or by covering the material in a clay-lined pit with an impermeable liner and capping material to contain all potential pollutants. Revegetation of the emplaced topsoil will complete the restoration scene.

CONCLUSIONS

Restoration of the Nine-Mile Lake pilot-scale acidic uranium leaching site can be regarded as very informative and successful.

pH appears to be the water quality parameter that returns on the slowest to the preleached baseline region. Nearly all of the other parameters returned to the baseline region within 150 days.

Laboratory experiments conducted by the University of Texas through a Bureau of Mines contract showed that restoration of pH by the use of a calcium hydroxide injection solution provides only a small (under 10 pct) savings in groundwater flush volume over that of using native groundwater.

Accurate establishment of baseline water quality and baseline variability is very important to meaningfully define restoration. Accurate measurements of some parameters like Eh and dissolved oxygen should be made in situ, using one of the commercially available down-hole probes.

Field water sampling procedure has a dramatic effect on the accuracy of laboratory chemical analysis. Standardized techniques, such as those outlined by Wood of the USGS, should be followed (7).

The use of acid as a leachant sidesteps many of the environmental problems associated with ammonium carbonate-bicarbonate leachants, the most notable one being the reluctant release of ammonium ions from the clays under-restoration fluid flushing. The successful restoration of this site adds to the viability of sulfuric acid as an alternative leachant for uranium contained in low-calcium carbonate ores.

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APPENDIX: BUREAU OF MINES CHEMICAL ANALYSES

DATE	NO.OF DAYS	WELL	U	V	SE	AS	SI	ZN	MN	FE	MG	CA	K	NA	P	F	CL	SO4
12/06/78	29	OB-1	5.8	58.			49.	4.4	.29	19.	47.	86.	11.	333.	.52	1.0	38.	1.72
12/16/78	39	OB-1	4.0	55.	.11	.20	47.	4.2	.31	23.	50.	87.	12.	337.	.24	1.2	44.	1.11
12/22/78	45	OB-1	4.5	55.			46.	4.0	.38	22.	53.	101.	11.	349.	.34	1.7	35.	1.65
12/29/79	52	OB-1	7.9	65.			39.	6.0	.40	18.	63.	126.	12.	354.	.33	.73	39.	1.85
1/06/79	60	OB-1	12.0	79.	.16	.25	39.	6.0	.50	25.	67.	124.	13.	391.	.18	.83	36.	1.83
1/13/79	67	OB-1	9.5	58.			34.	5.0	.39	18.	63.	119.	12.	370.	.14	.83	37.	1.68
1/20/79	75	OB-1	9.7	67.			32.	4.0	.28	15.	60.	103.	12.	375.	.11	.79	39.	1.56
1/26/79	81	OB-1	6.5	43.	.15	.24	30.	3.4	.23	12.	58.	106.	8.0	419.	< .05	1.1	36.	1.50
2/03/79	88	OB-1	5.3	29.			28.	3.3	.22	11.	57.	104.	7.8	409.	< .05	.90	47.	1.47
2/09/79	94	OB-1	3.7	24.			29.8	3.1	.20	11.1	57.	103.	8.4	400.	< .05	1.1	40.	1.48
2/17/79	102	OB-1	2.4	24.			30.5	2.9	.20	14.1	54.	99.	8.2	690.	< .05	.81	36.	1.52
2/24/79	109	OB-1	2.1	17.			32.0	2.7	.30	14.6	53.	98.	8.3	420.	< .05	.82	35.	1.53
3/20/79	133	OB-1	2.2	24.			30.4	2.7	.35	15.2	55.	105.	8.0	470.	.05	.68	25.	1.60
3/26/79	139	OB-1	2.2	23.			24.6	2.6	.39	12.7	66.	135.	9.0	790.	< .05	.53	29.	2.45
4/02/79	146	OB-1	.12	2.5			27.3	1.5	.30	.2	51.	111.	9.3	1130.	< .05	1.1	34.	2.80
4/07/79	151	OB-1	.43	16.6			29.5	1.4	.27	1.4	59.	111.	10.3	1310.	.05	1.7	37.	3.20
4/16/79	160	OB-1	.45	8.2			29.	.8	< .20	4.2	49.	35.	11.9	1020.	< .05	1.2	35.6	2.94
4/27/79	171	OB-1	2.0	22.0			35.	4.6	.21	7.8	50.	24.	12.7	1090.	.074	.8	36.4	3.29
5/24/79	198	OB-1	4.2	17.0			29.	5.1	< .20	7.2	42.	20.	12.3	1200.	.086	.77	41.5	3.64
6/09/79	214	OB-1	.31	2.9			11.	.15	< .20	1.3	35.	34.	12.9	1630.	.11	.61	47.2	4.47
12/06/78	29	OB-3	.16	15.			32.	1.4	.22	11.	46.	73.	9.	286.	.07	.66	41.	1.13
12/16/78	39	OB-3	.07	15.	.12	.16	31.	1.6	.18	16.	51.	90.	11.	324.	.05	.68	44.	1.64
12/22/78	45	OB-3	.06	24.			29.	2.1	.35	21.	53.	106.	10.	338.	.12	.62	36.	1.51
12/29/78	52	OB-3	.06	13.			30.	1.4	.25	13.	52.	103.	10.	324.	< .05	.58	37.	1.38
1/06/79	60	OB-3	.13	14.	.16	.23	25.	1.0	.24	13.	53.	99.	10.	356.	< .05	.33	37.	1.33
1/13/79	67	OB-3	.07	< 2.			21.	1.0	.23	11.	52.	98.	10.	359.	< .05	.33	38.	1.32
1/20/79	75	OB-3	< .05	< 2.			19.	1.0	.19	9.	53.	91.	10.	355.	< .05	.38	39.	1.27
1/26/79	81	OB-3	.07	< 2.	.14	.20	18.	1.2	.23	10.	54.	103.	7.2	399.	< .05	.51	39.	1.32
2/03/79	88	OB-3	.05	< 2.			15.	0.9	.21	8.	55.	102.	7.0	397.	< .05	.50	43.	1.29
2/09/79	94	OB-3	< .05	< 2.			15.	0.8	.20	8.7	52.	99.	7.4	370.	< .05	.78	36.	1.29
2/17/79	102	OB-3	< .05	< 2.			18.6	1.2	.30	13.5	50.	98.	7.5	380.	< .05	.75	35.	1.39
2/24/79	109	OB-3	< .05	< 2.			20.7	1.0	.20	12.6	51.	98.	7.7	410.	< .05	.76	35.	1.40
3/20/79	133	OB-3	< .05	< 2.			16.4	.7	.31	11.1	42.	87.	6.6	420.	< .05	.56	25.	1.25
3/26/79	139	OB-3	.06	< 2.			12.7	.4	.45	12.0	70.	145.	8.5	790.	< .05	.38	30.	2.30
4/02/79	146	OB-3	< .05	< 2.			15.1	.5	.46	4.9	60.	136.	10.6	1630.	< .05	.40	31.	4.05
4/07/79	151	OB-3	.06	6.1			17.0	.5	.35	9.7	44.5	106.	10.9	1850.	.20	2.7	32.	4.10
4/16/79	160	OB-3	.21	7.5			18.	.3	< .20	7.4	26.	21.	10.6	1160.	.17	2.2	34.2	3.15
4/27/79	171	OB-3	2.8	27.			38.	8.1	.35	16.5	5.7	26.	13.8	1000.			37.2	
5/24/79	198	OB-3	4.2	17.0			29.	5.1	.20	7.2	42.	20.	12.3	1200.	.086	.77	41.5	3.66
6/09/79	214	OB-3	.22	< 2.			10.	< .1	< .20	0.6	28.	31.	13.0	1830.	.19	1.3	36.1	4.84
12/06/78	29	INJ.	.07	< 2.			< 5.	< .1	.22	< .5	53.	95.	10.	311.	< .05	1.4	39.	1.34
12/16/78	39	INJ.	.05	< 2.	.15	.16	< 5.	< .1	.19	< .5	51.	97.	10.	316.	< .05	1.2	44.	1.39
12/22/78	45	INJ.	.06	< 2.			< 5.	< .1	.26	< .5	51.	103.	9.	306.	< .05	1.4	41.	1.13
12/29/78	52	INJ.	.06	< 2.			< 5.	< .1	.25	< .5	51.	103.	10.	296.	< .05	1.3	38.	1.14
1/06/79	60	INJ.	.08	< 2.	.14	.16	< 5.	< .1	.21	< .5	54.	99.	10.	334.	< .05	.81	36.	1.13
1/13/79	67	INJ.	.09	< 2.			< 5.	< .1	.19	< .5	53.	91.	10.	345.	< .05	.80	36.	1.14
1/20/79	75	INJ.	.13	< 2.			5.	< .1	.18	< .5	53.	95.	10.	347.	< .05	.78	46.	1.15
1/26/79	81	INJ.	.08	< 2.	.11	.18	< 5.	< .1	.15	< .5	46.	84.	5.5	334.	< .05	.93	36.	0.97
2/03/79	88	INJ.	.08	< 2.			< 5.	< .1	.16	< .5	48.	87.	5.8	359.	< .05	.80	39.	1.01
2/09/79	94	INJ.	< .05	< 2.			< 5.	< .1	.20	< .5	55.	100.	7.1	370.	< .05	1.1	40.	1.19
2/17/79	102	INJ.	< .05	< 2.			6.0	< .1	.10	< .5	39.	70.	5.2	320.	< .05	1.2	32.	.95
3/20/79	133	INJ.	.062	< 2.			6.2	< .1	.10	< .5	13.5	31.	15.5	1540.	< .05	.83	40.	3.10
3/26/79	139	INJ.	.087	< 2.			< 5.	< .1	.14	< .5	26.9	61.	8.8	1490.	< .05	1.0	29.	3.10
4/16/79	160	INJ.	.080	< 2.			< 5.	< .1	< .20	.3	30.	33.	12.8	1310.	.05	.76	34.2	3.67
4/27/79	171	INJ.	.060	< 2.			< 5.	< .1	.20	< .2	35.	35.	12.4	1050.	< .05	.63	37.2	2.86
5/24/79	198	INJ.	.080	< 2.			< 5.	< .1	.21	< .2	50.	47.	10.9	640.	< .05	.59	43.3	1.74
6/09/79	214	INJ.	.050	2.3			< 5.	< .1	< .20	< .2	17.	8.	13.0	2330.	< .05	.60	36.1	6.02

APPENDIX: FIELD LABORATORY MEASUREMENTS

	NO.OF			OB-3			OH-1			INJECTION			PRODUCTION		
DATE	DAYS	WELL	TEMP	PH	EH	COND	PH	EH	COND	PH	EH	COND	PH	EH	COND
12/06/78	29			3.30	378	2000	2.70	396	2600	6.68	178	1750	2.31	335	4800
12/16/78	39			3.30	52	2000	3.30	123	2600	6.85	92	1800	2.49	323	4300
12/22/78	45			4.50	148	1800	3.24	49	2100	6.62	154	1800	2.90	273	2700
12/29/78	52			4.95	112	1750	2.95	235	2400	6.48	200	1750	2.82	241	2800
1/06/79	60			5.22	145	2200	4.50	52	3200	6.75	-23	1900	2.88	297	3100
1/13/79	67			5.75	-15	2000	4.70	-4	2300	6.55	150	1800	3.50	181	2200
1/20/79	74			5.65	-20	1800	4.70	42	2200	6.50	-52	2000	2.90	255	2600
1/26/79	80			5.80	-26	1800	4.95	-9	2000	6.65	-40	1900	3.10	81	2300
2/03/79	88			6.10	9	2000	5.15	2	2000	6.50	98	1800	3.35	180	2800
2/09/79	94		14.0	5.95	-107	1600	5.05	-57	1900	6.75	52	1750	3.35	188	1200
2/17/79	102		14.8	5.82	-36	2000	5.98	-30	2000	6.42	72	1750	3.47	192	2200
2/24/79	109		13.4	5.82	48	2000	5.13	53	2000						
3/20/79	133		15.7	5.97	56	2200	5.05	41	2500	6.46	15	4700	3.81	160	2600
3/26/79	139		13.5	5.89	-25	3500	5.15	45	3800	6.87	42	4500	3.73	43	2500
4/02/79	146		13.5	5.93	25	5400	5.91	65	4400	7.26	10	5800	4.15	150	3500
4/06/79	150		16.4	6.69	40	6400	6.23	10	5200	6.90	0	7000	4.29	110	3800
4/16/79	160		17.0				5.98	15	4800	6.57	-60	5800	4.09	-80	4300
4/27/79	171		16.5	5.10	15	4900	4.35	0	5000	6.75	195	5400	5.15	30	5100
5/24/79	198		21.0	4.65	222	5400	4.65	222	5400	1.80	222	17500	4.65	420	5400
6/09/79	214		17.3	7.23	97	7800	6.95	157	7000	8.22	262	8000	6.29	187	6000

APPENDIX: DOWNHOLE PROBE MEASUREMENTS FOR OH-3

DATE	NO.OF DAYS	WELL	TEMP	PH	EH	COND	D.O.
12/06/78	29	PROB	13.1	4.70	425	2030	1.32
12/16/78	39	PROB	12.7	6.50	293	2690	.94
12/22/78	45	PROB	12.5	6.50	258	2710	.34
12/29/78	52	PROB	12.6	6.63	257	2660	.40
1/06/79	60	PROB	12.3	7.27	201	2660	.48
1/13/79	67	PROB	12.3	7.30	108	2630	.44
1/20/79	74	PROB	12.1	7.79	117	2630	.42
1/26/79	80	PROB	12.0	7.24	109	2670	.32
2/03/79	88	PROB	12.3	7.20	106	2650	.24
2/09/79	94	PROB	12.7	7.61	126	2630	.28
2/17/79	102	PROB	12.7	7.32	99	2730	.16
2/24/79	109	PROB	12.7	7.24	100	2790	.06
3/20/79	133	PROB	12.9	7.26	13	2640	.04
3/26/79	139	PROB	13.2	7.00	41	4500	.04
4/02/79	146	PROB	13.3	7.10	32	7400	.08
4/06/79	150	PROB	13.0	7.54	-2	7980	.06
4/16/79	160	PROB	13.6	7.22	3	6260	.06
4/27/79	171	PROB	14.2	5.58	163	5890	.00
6/09/79	214	PROB	16.1	9.92	31	9100	.08

APPENDIX: ROCKY MOUNTAIN ENERGY CHEMICAL ANALYSES

DATE	NO.OF DAYS	WELL	PH	EH	COND	U3O8	V2O5	FE	CA	SO4
11/07/78	0	INJ.	1.56	430.	12700	.002	.146	.044	.109	4.47
11/14/78	7	INJ.	1.99	350.	7100	.001	.002	.011	.086	1.47
11/21/78	14	INJ.	6.76	60.	2800	.001	.001	.001	.082	1.13
11/28/78	21	INJ.	6.75	100.	2750	.001	.001	.001	.082	0.81
12/05/78	28	INJ.	6.93	80.	2400	.001	.001	.001	.087	0.87
12/12/78	35	INJ.	6.90	90.	2500	.001	.001	.001	.085	1.84
12/19/78	42	INJ.	7.26	90.	2700	.001	.001	.001	.089	1.05
12/25/78	49	INJ.	6.74	125.	2800	.001	.001	.001	.089	1.22
1/02/79	56	INJ.	7.09	105.	2100	.001	.001	.001	.085	1.00
1/09/79	63	INJ.	7.81	150.	2500	.001	.001	.001	.086	0.87
1/16/79	70	INJ.	6.88	150.	2700	.001	.001	.001	.086	1.19
1/23/79	77	INJ.	6.73	50.	2800	.001	.001	.001	.083	0.96
1/30/79	84	INJ.	7.79	15.	2700	.001	.001	.001	.085	1.04
2/06/79	91	INJ.	6.66	45.	1470	.001	.001	.001	.079	1.16
2/13/79	98	INJ.	6.67	-30.	2969	.001	.001	.001	.069	1.26
2/17/79	102	INJ.	7.38	15.	5280	.001	.001	.001	.096	1.75
3/07/79	120	INJ.	7.00		2700	.001	.001	.001	.089	1.22
3/14/79	127	INJ.	5.65		2300	.001	.001	.001	.023	1.28
3/21/79	134	INJ.	5.79		4300	.001	.001	.001	.030	2.34
3/28/79	141	INJ.	6.99		4300	.001	.001	.001	.011	1.95
4/11/79	155	INJ.	7.69		4800	.001	.001	.001	.066	3.29
4/18/79	162	INJ.	6.69		7200	.001	.001	.001	.054	3.65
4/25/79	169	INJ.	6.95		8400	.001	.001	.001	.041	3.94
5/02/79	176	INJ.	7.46		5100	.001	.001	.001	.067	2.47
5/09/79	183	INJ.	7.07		10400	.001	.001	.001	.032	5.44
5/16/79	190	INJ.	9.71		8300	.001	.001	.001	.034	4.24
5/23/79	197	INJ.	9.99		9500	.001	.001	.001	.017	5.03
5/30/79	204	INJ.	9.88		7700	.001	.001	.001	.036	4.01
11/07/78	0	PROD	1.59	415.	13300	.051	.413	.121	.177	6.60
11/14/78	7	PROD	1.79	410.	15200	.042	.329	.102	.154	5.95
11/21/78	14	PROD	1.81	390.	10300	.042	.191	.066	.118	4.03
11/28/78	21	PROD	2.24	340.	6800	.029	.119	.044	.089	2.72
12/05/78	28	PROD	2.34	340.	4900	.022	.112	.032	.080	2.30
12/12/78	35	PROD	2.43	350.	4500	.018	.093	.028	.081	2.13
12/19/78	42	PROD	2.65	330.	4300	.015	.077	.024	.086	1.88
12/25/78	49	PROD	2.55	350.	4500	.012	.064	.027	.091	1.96
1/02/79	56	PROD	2.59	330.	4000	.012	.074	.022	.081	1.89
1/09/79	63	PROD	2.74	330.	3700	.013	.068	.021	.082	1.69
1/16/79	70	PROD	2.87	320.	4100	.011	.061	.018	.081	1.82
1/23/79	77	PROD	3.03	350.	4100	.009	.059	.018	.085	1.56
1/30/79	84	PROD	3.13	300.	3800	.007	.052	.015	.084	1.55
2/06/79	91	PROD	3.38	300.	3200	.008	.046	.013	.094	1.62
2/13/79	98	PROD		280.	3500	.007	.046	.013	.078	1.60
2/17/79	102	PROD		270.	3400	.007	.046	.015	.089	1.63
3/07/79	120	PROD	3.58		3400	.0068	.046	.014	.086	1.86
3/14/79	127	PROD	2.66		2600	.0062	.040	.013	.102	1.56
3/21/79	134	PROD	3.66		2500	.0063	.038	.012	.095	1.59
3/28/79	141	PROD	3.70		3300	.0061	.038	.013	.093	1.76
4/11/79	155	PROD	4.24		3900	.0051	.043	.013	.157	2.96
4/18/79	162	PROD	4.29		5000	.0061	.047	.014	.128	2.98
4/25/79	169	PROD	4.16		5400	.0033	.032	.015	.116	2.84
5/02/79	176	PROD	6.35		6900	.0003	.004	.001	.034	3.48
5/09/79	183	PROD	4.45			.0060	.029	.011	.089	3.46
5/16/79	190	PROD	4.24		6500	.0042	.033	.008	.075	3.58
5/23/79	197	PROD	4.96		7300	.0039	.023	.007	.065	3.78
5/30/79	204	PROD	5.50		7700	.0038	.026	.007	.066	3.92

TABLE 1. - List of cations and anions and methods of determination

Ion	Method	Ion	Method
Sodium	1	Silicon	1
Potassium	1	Uranium	2
Calcium	1	Arsenic	3
Magnesium	1	Selenium	3
Zinc	1	Aluminum	1
Iron	1	Sulfate	4
Manganese	1	Chloride	5
Zirconium	1	Fluoride	5
Titanium	1	Phosphorus	6
Vanadium	1	Sulfide	5

[1] Atomic adsorption - direct aspiration.
[2] X-ray fluorescence.
[3] Atomic absorption - graphite furnace.
[4] Gravimetric.
[5] Ion-selective electrode.
[6] Colorimetric.

TABLE 2. - Groundwater quality - Comparing preleach and restored groundwater[1]

	Native groundwater outside ore zone	Preleach pattern groundwater	Restored groundwater
pH	6.8	5.8-7.9	6.0
Free acidity	10	10	20
Calcium	110	20-360	65
Sulfate	1,620	300-3,600	2,200
TDS	2,660	680-5,450	3,000

[1] All values in parts per million (except pH).

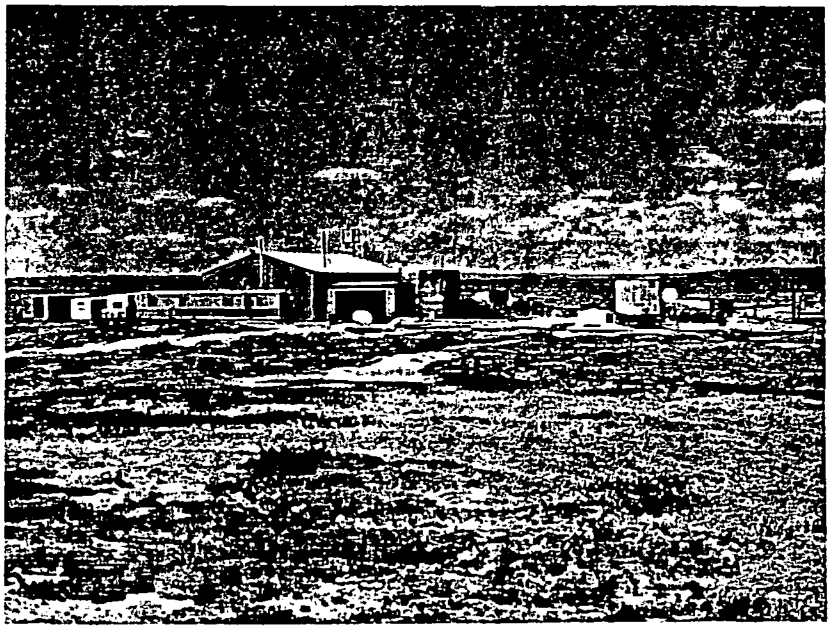

Fig. 1 - View of joint venture in situ pilot leaching facility at Nine-Mile Lake.

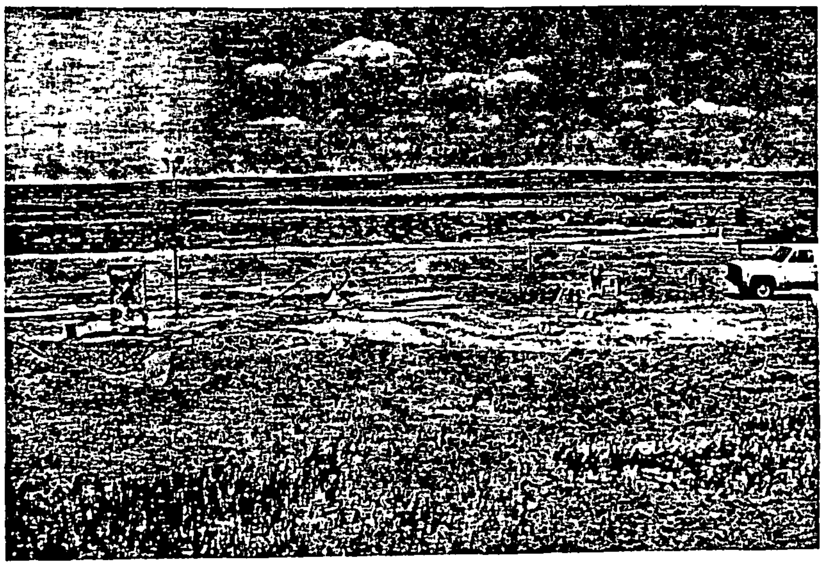

Fig. 2 - View of five-spot pilot test area (pattern No. 2).

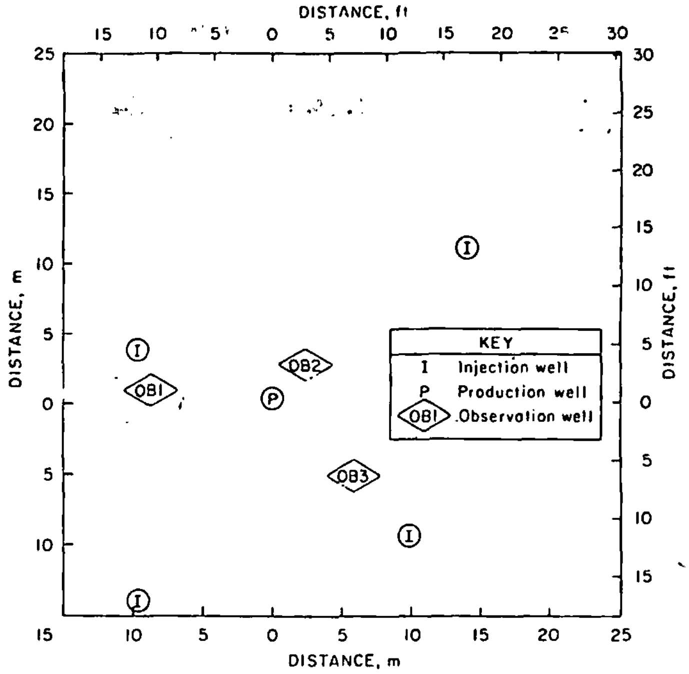

Fig. 3 - Plan view of five-spot pattern and observations wells at 165 = meter depth.

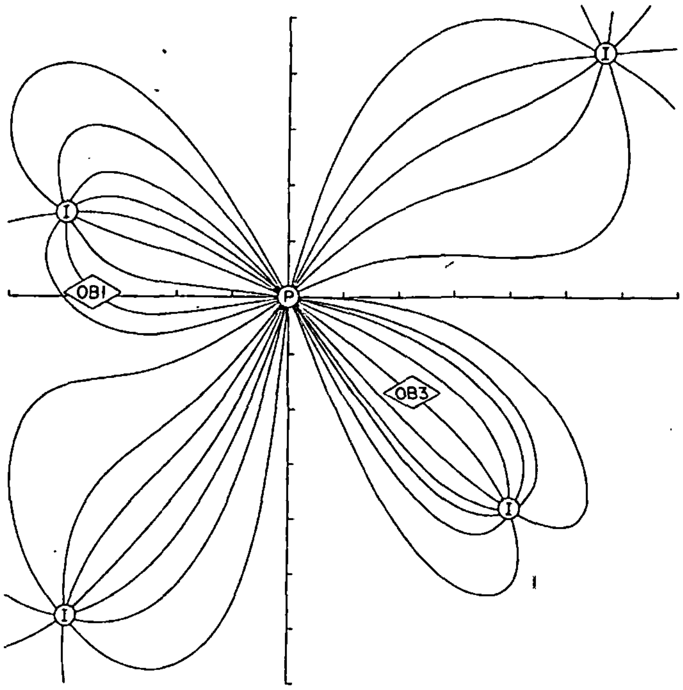

Fig. 4 - Nine-Mile Lake restoration pattern (2months).

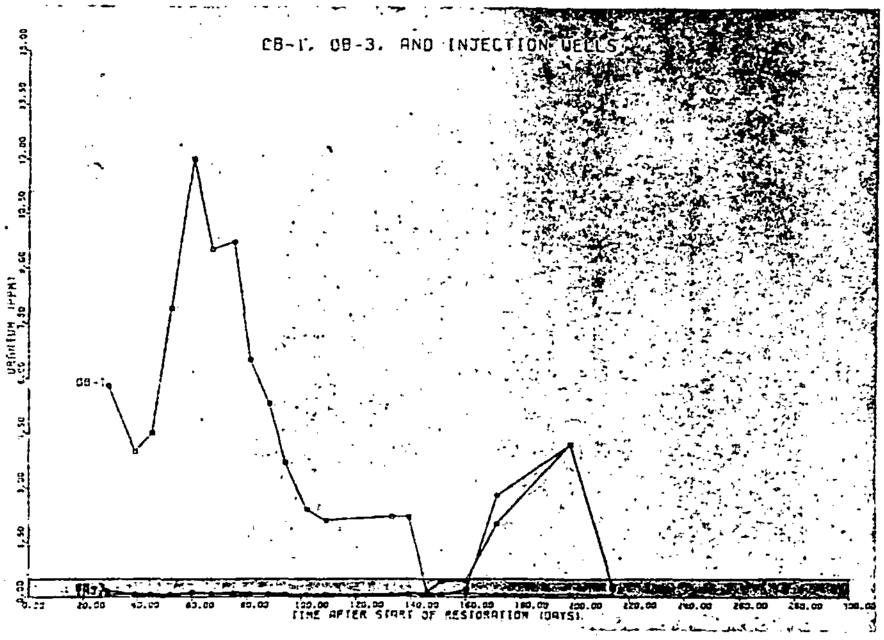

Fig. 5 - Uranium concentration vs. time.

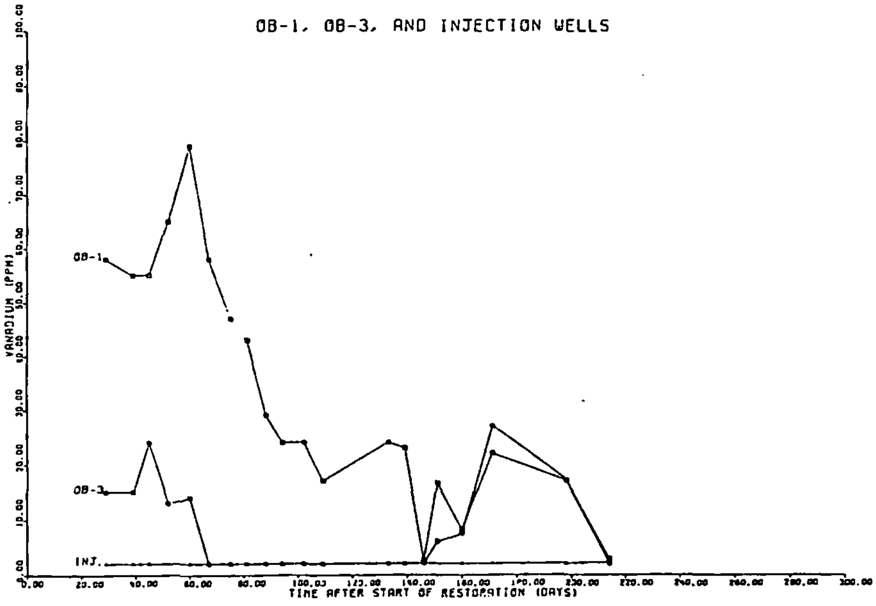

Fig. 6 - Vanadium concentration vs. time.

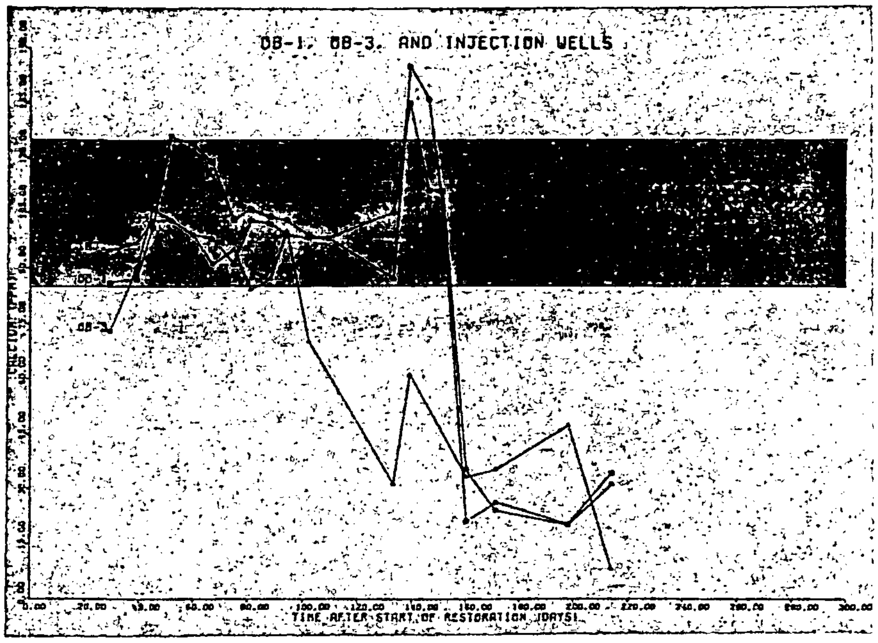

Fig. 7 - Calcium concentration vs. time.

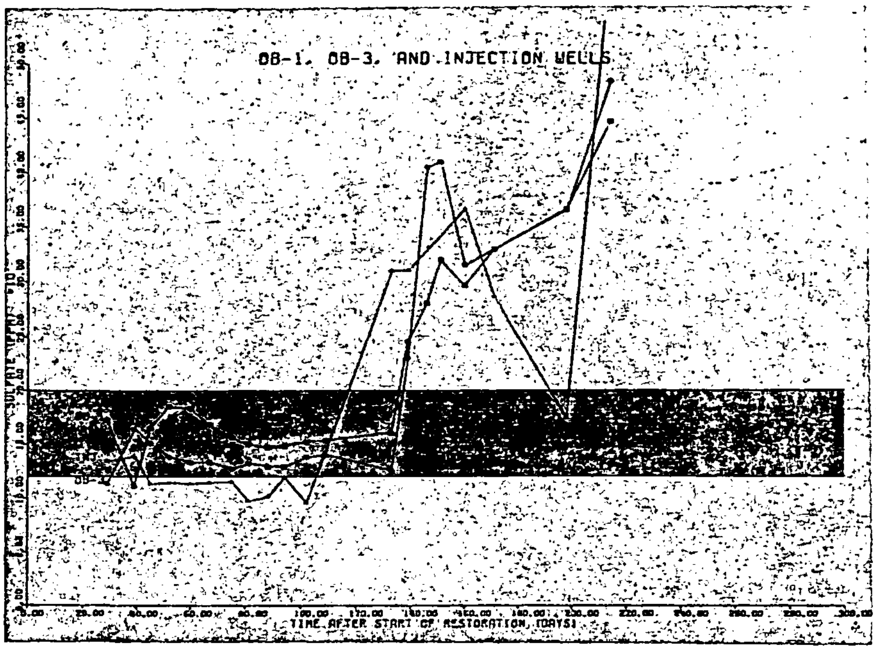

Fig. 8 - Sulfate concentration vs. time.

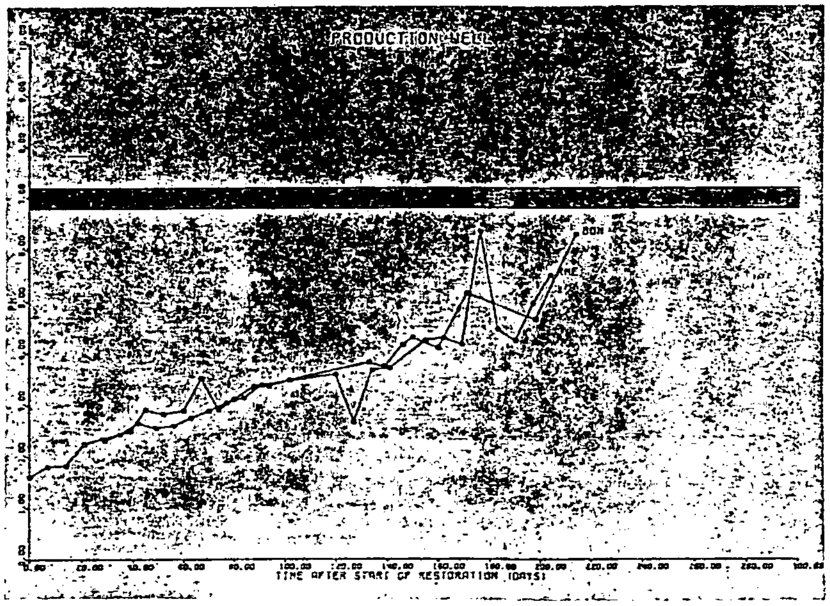

Fig. 9 - pH vs. time.

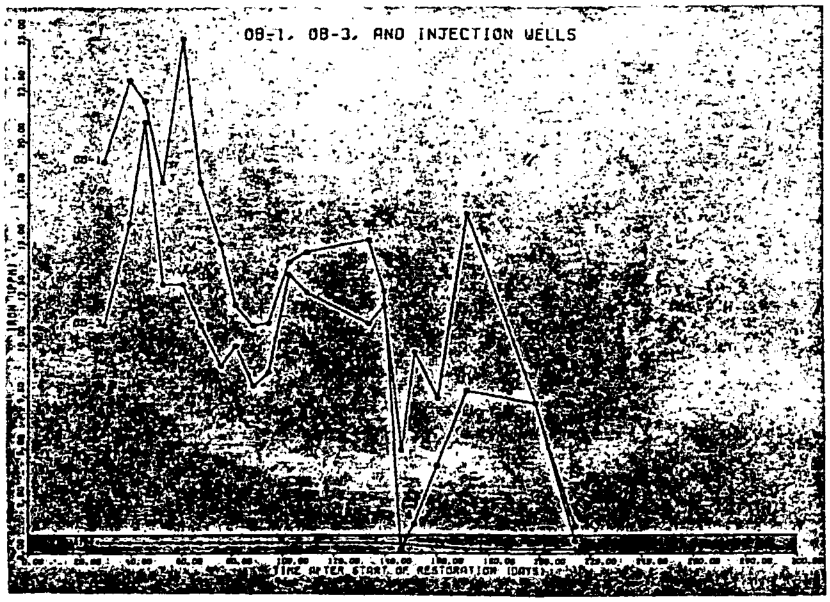

Fig. 10 - Iron concentration vs. time.

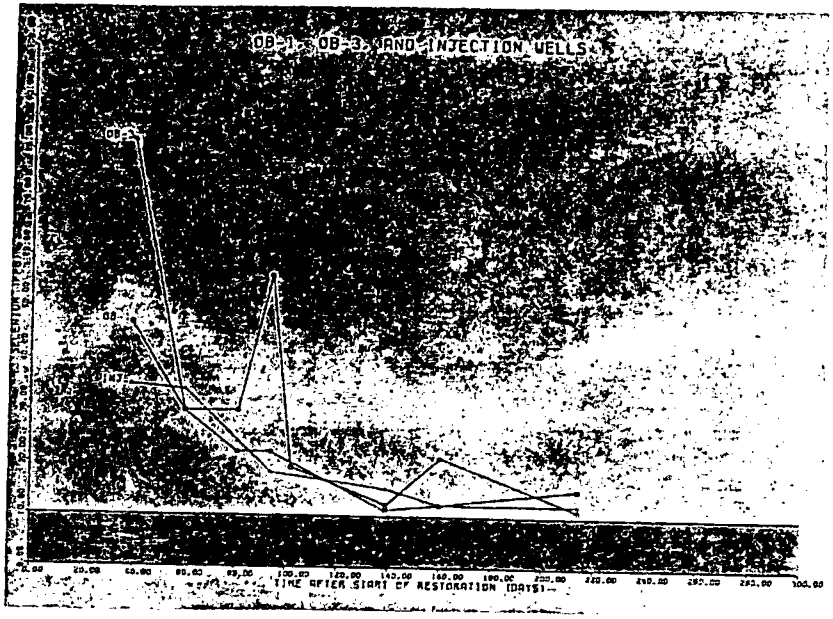

Fig. 11 - Arsenic concentration vs. time.

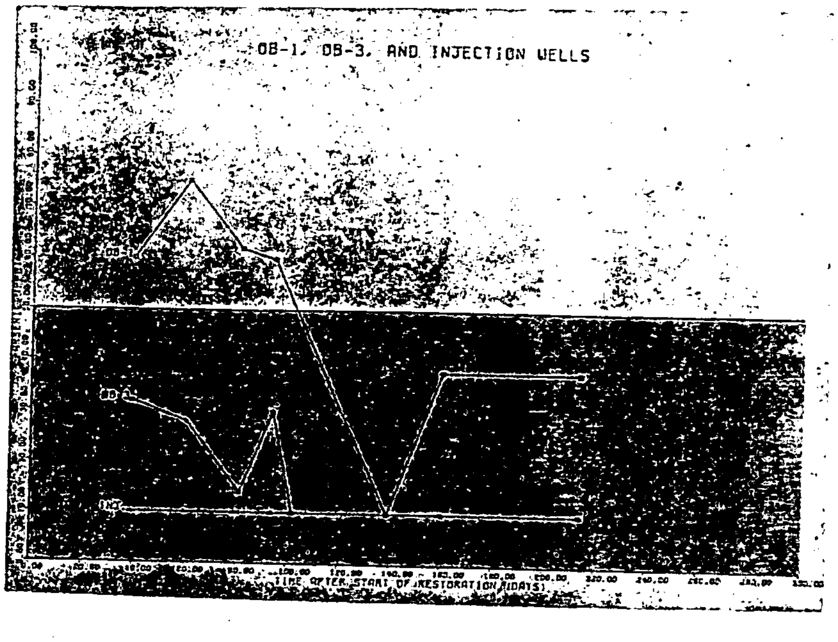

Fig. 12 - Selenium concentration vs. time.

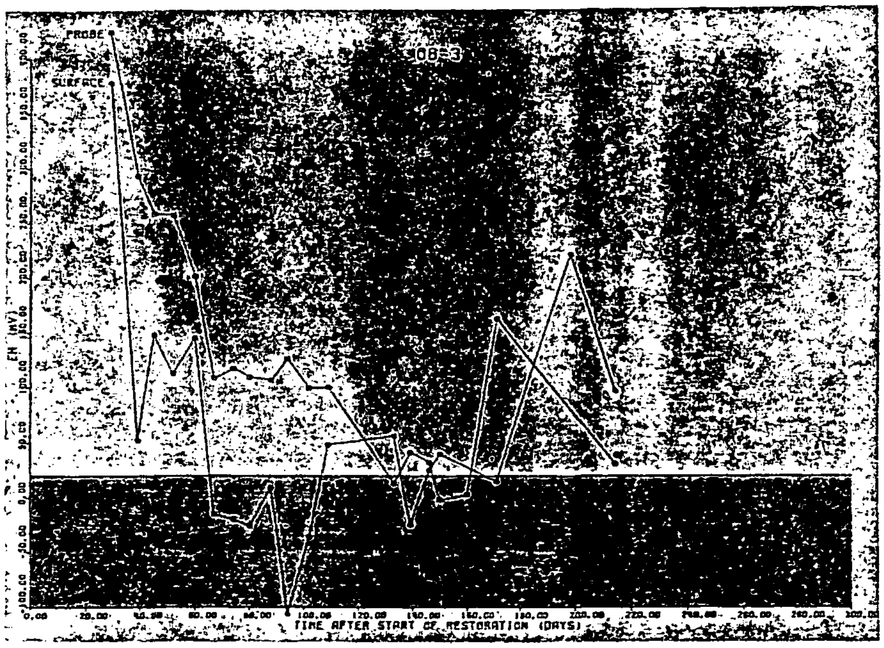

Fig. 13 - Oxidation-reduction potential (Eh) vs. time.

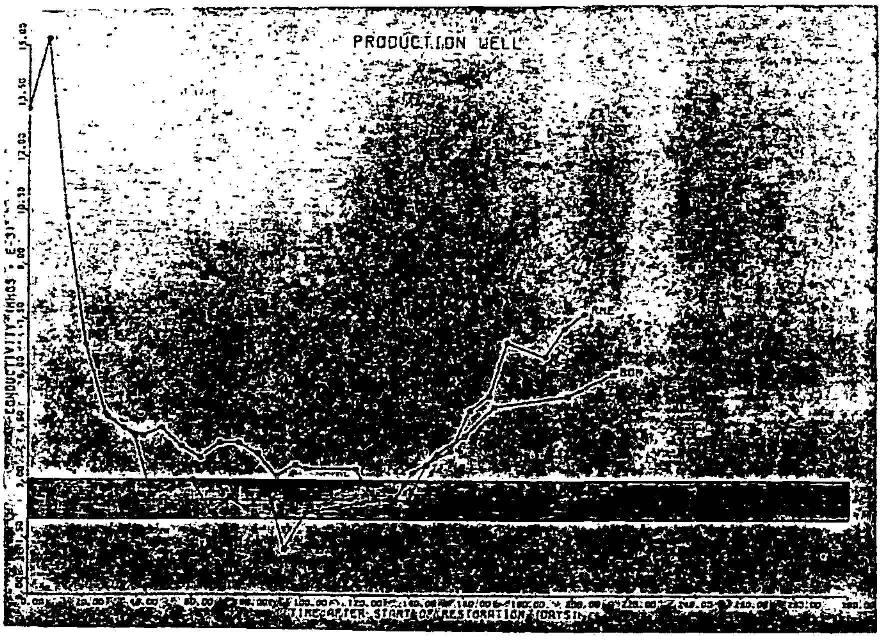

Fig. 14 - Conductivity vs. time.

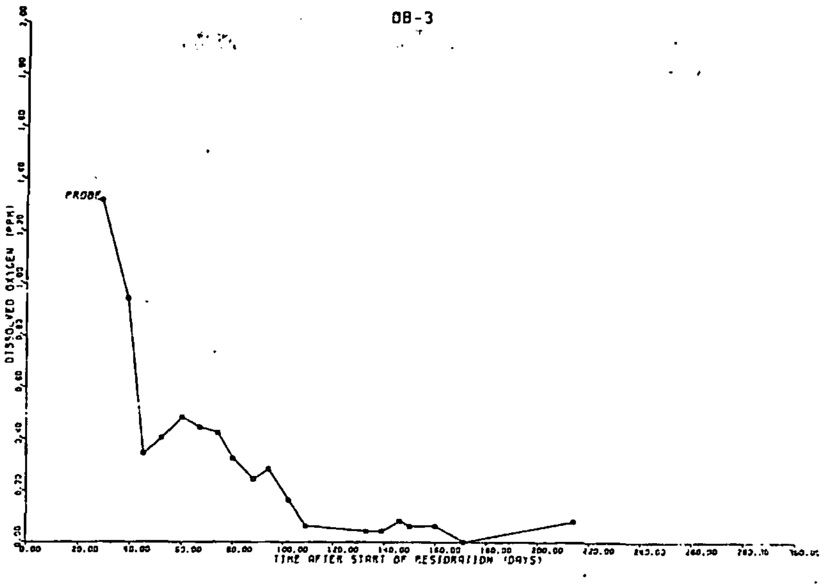

Fig. 15 - Dissolved oxygen vs. time.

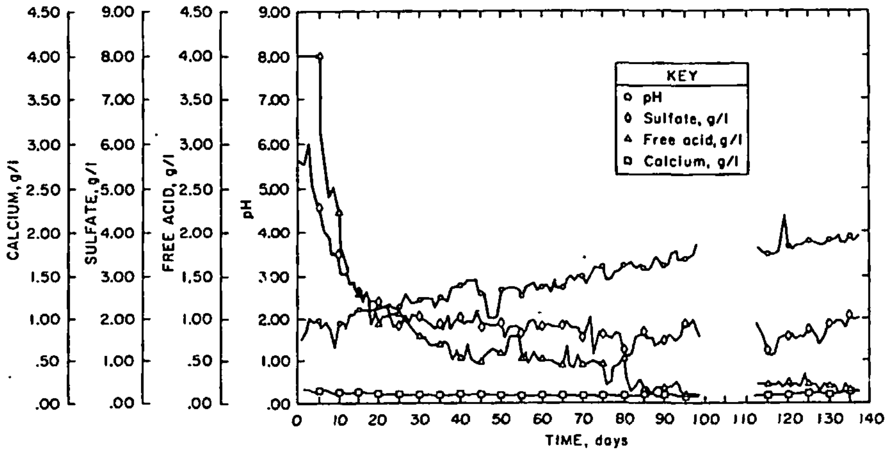

Fig. 16 - Changes in production well water quality with time.

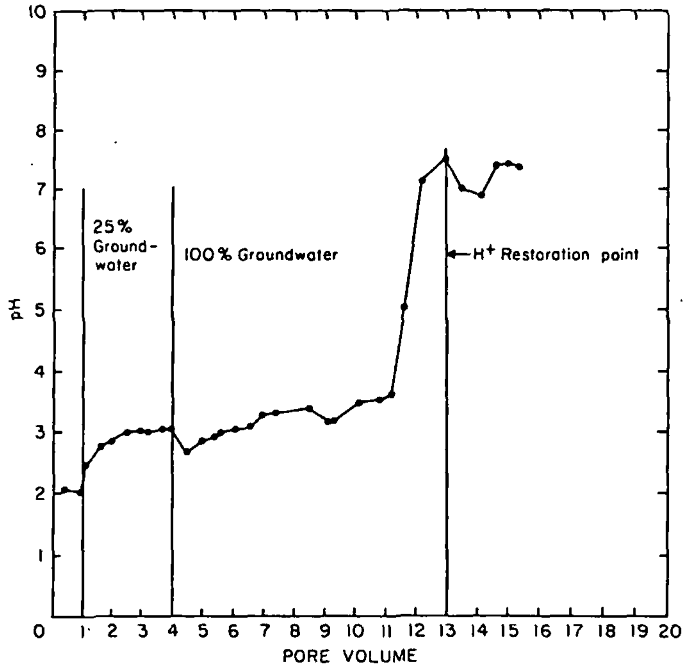

Fig. 17 - pH vs. pore volume during sample restoration in a 120-cm column.

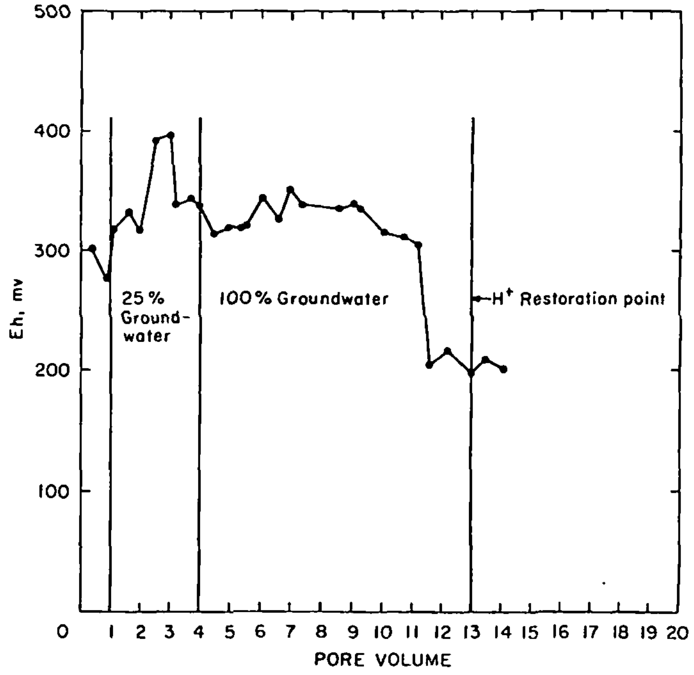

Fig. 18 - Eh vs. pore volume during sample restoration in a 120-cm column.

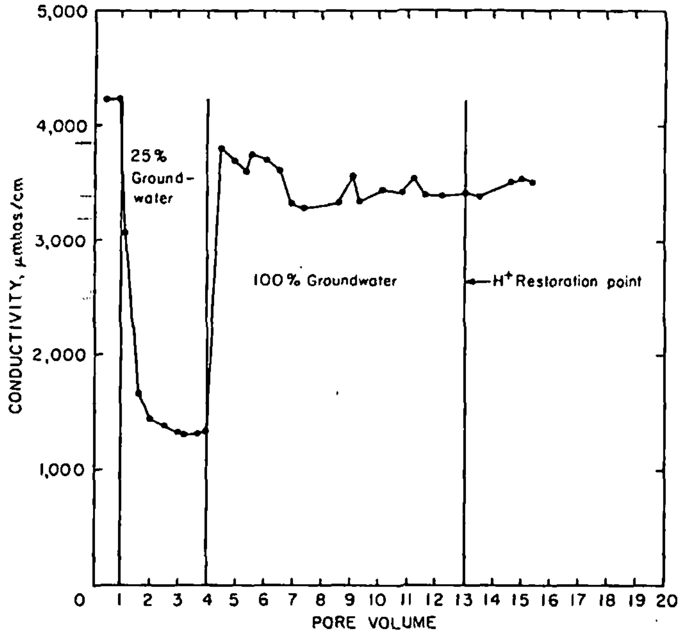

Fig. 19 - Conductivity vs. pore volume during sample restoration in a 120-cm column.

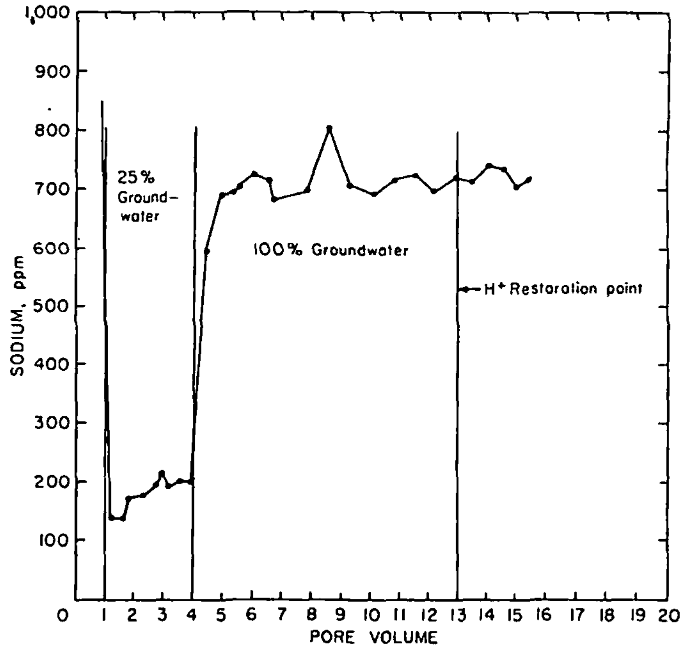

Fig. 20 - Sodium vs. pore volume during sample restoration in a 120-cm column.

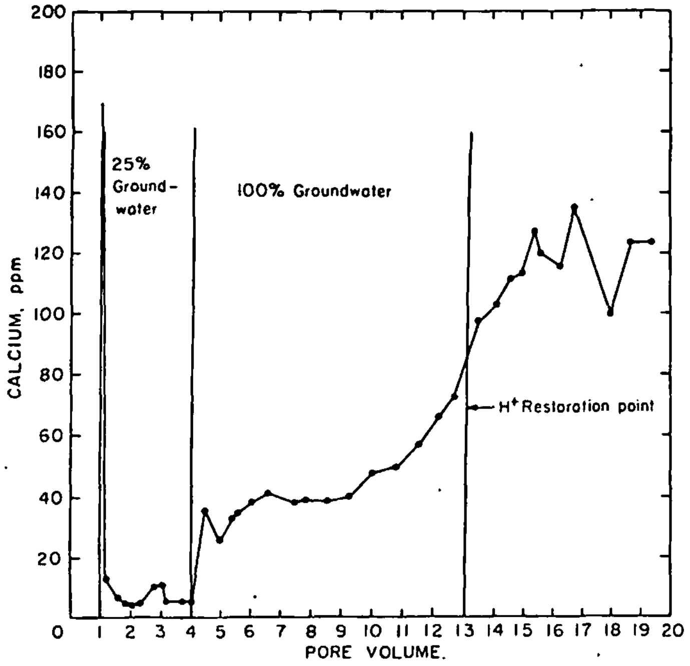

Fig. 21 - Calcium vs. pore volume during sample restoration in a 120-cm column.

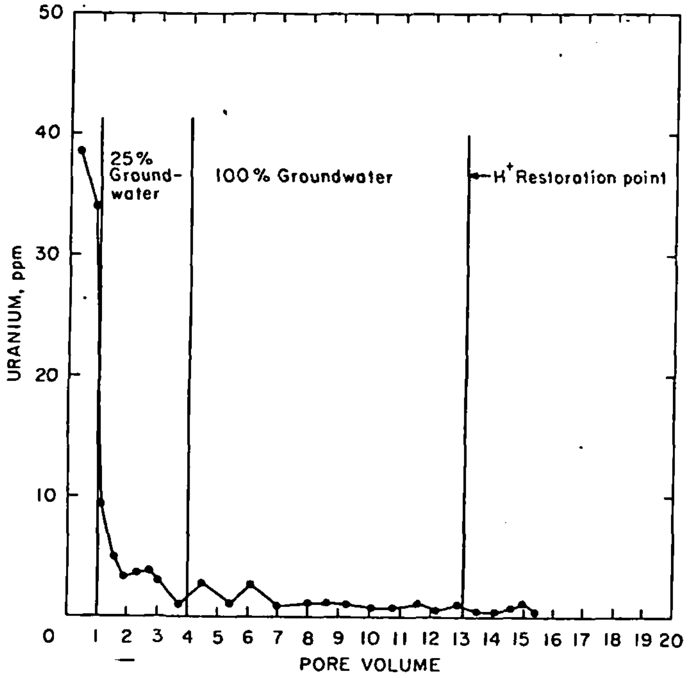

Fig. 23 - Vanadium vs. pore volume during sample restoration in a 120-cm column.

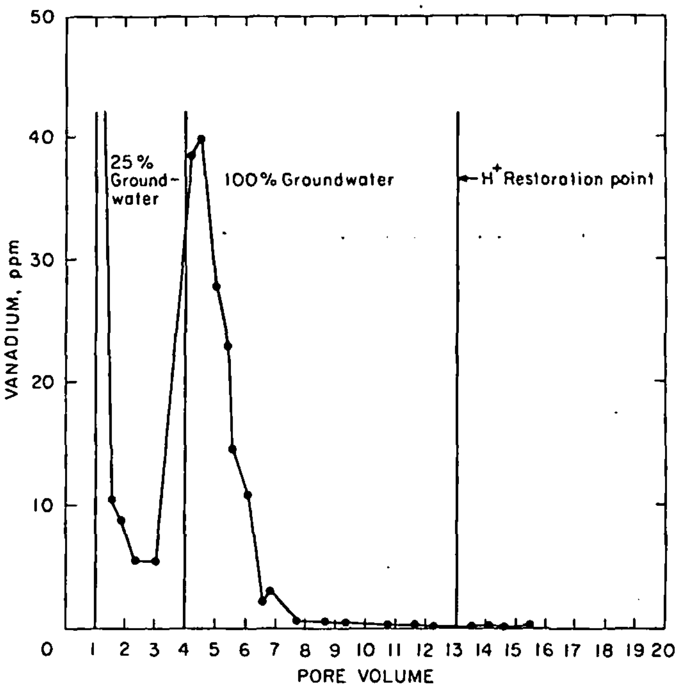

Fig. 22 - Uranium vs. pore volume during sample restoration in a 120-cm column.

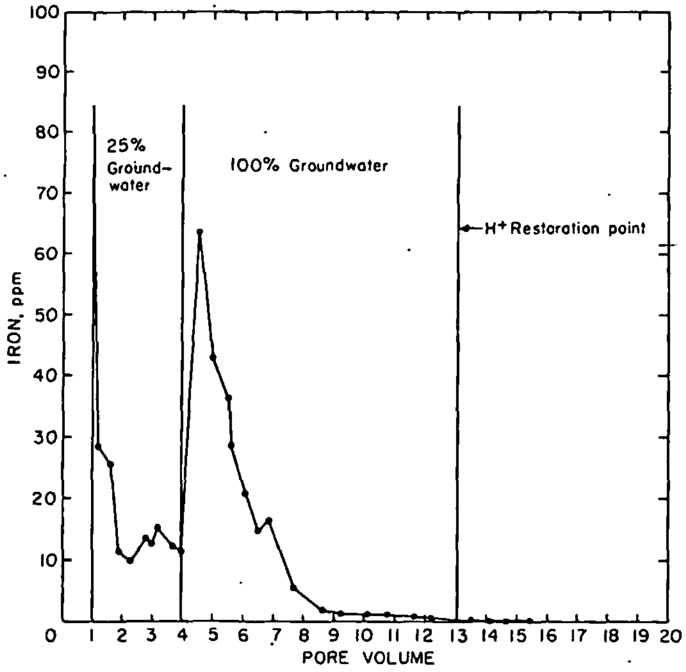

Fig. 24 - Iron vs. pore volume during sample restoration in a 120-cm column.

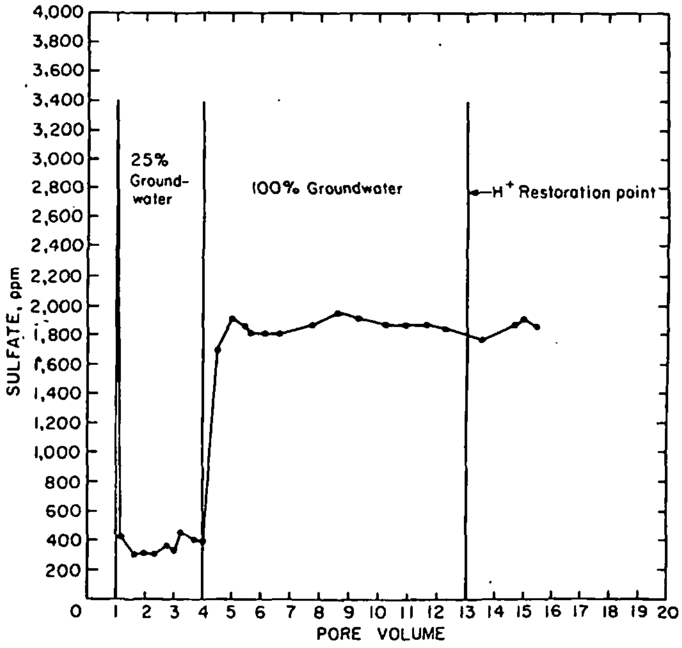

Fig. 25 - Sulfate vs. pore volume during sample restoration in a 120-cm column.

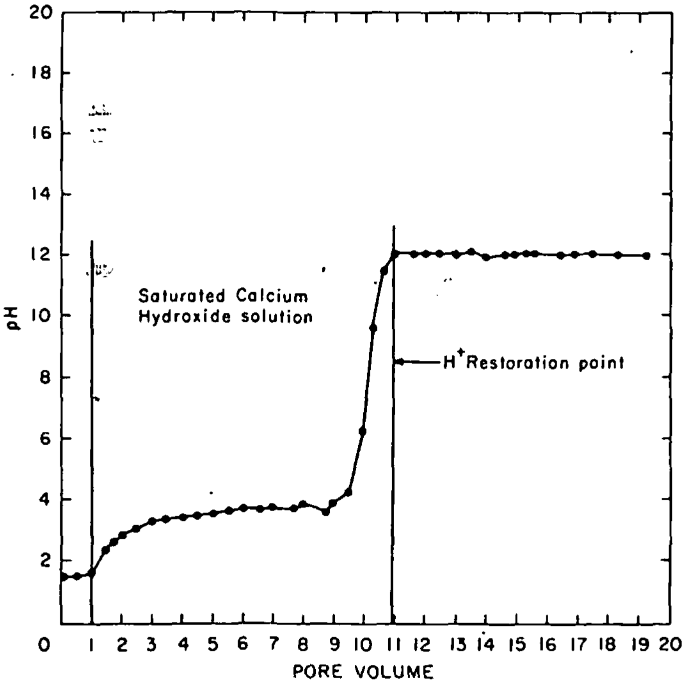

Fig. 26 - pH - vs. pore volume for calcium hydroxide restoration solution in a 60-cm column.

SPE
Society of Petroleum Engineers of AIME

SPE 7536

REGULATION OF IN SITU URANIUM MINING FOR PURPOSES OF PROTECTING GROUND WATER QUALITY

by William R. Taylor, Texas Department of Water Resources

This paper was presented at the 53rd Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, held in Houston, Texas, Oct. 1-3, 1978. The material is subject to correction by the author. Permission to copy is restricted to an abstract of not more than 300 words. Write: 6200 N. Central Expy., Dallas, Texas 75206.

GENERAL

In mid-1974, a representative of ARCO Petroleum Company walked into our Austin offices and asked for a permit for ARCO's first Clay-West mine site. This was the first in situ uranium mining permit issued in the United States. That initial permit, issued in January 1975, was for 3 acres. The four years since have been characterized by growth and change. Briefly, today there are 16 permits approved for approximately 1,540 production acres issued to five companies at eight sites in four counties. There are approximately 7 additional permit applications being processed or on the verge of being submitted for an estimated 2,000 additional acres of production. These permits will involve five more companies in two more counties. Based on the inquiries that we have received and the known exploration, it's certain that still other operators will firm up their plans soon. As a rough gauge of the financial scope of this activity at the typical 40 production wells per acre and a conservative $2,000/well, operators have installed or committed to $122,000,000 for production wells. This does not account for the exploration and development wells installed to delineate the ore or the processing facilities for extracting the uranium. Along with this growth, it continues to be an unavoidable necessity for the operators and ourselves to frequently adjust our approach to problems as we learn or understand various "facts of life". There are signs, however, that in our "old age" we are progressing toward a more formal, somewhat less flexible, posture with the development of rules at the state level and Underground Injection Control Regulations at the Federal level.

HISTORY OF URANIUM MINING IN TEXAS

Open pit mining or uranium began in Texas in the 1950's and is continuing today almost exclusively in the Southwest portion of Texas. A few shaft mining efforts were unsuccessfully attempted during the 1950's and 60's.

Information I have concerning early in situ uranium mining activities is "sketchy" but the apparent first on-site test of in situ uranium mining was conducted between 1967 and 1971 at the Duterstat site north of Yorktown in Gonzales County by City Services.

During the 1970-71 period, a consortium involving Conoco, Pioneer Nuclear, Westinghouse, Union Carbide and Getty conducted an on-site test at the Bruni site in Webb County.

During the 1971-73 period, City Services, Dalco and U. S. Steel conducted a test at the Burns site near George West in Live Oak County.

During the 1972-74 period, Dalco and Arco conducted a test at the Clay-West site also near George West.

During the period, between 1967 and 1974, the Water Quality Board personnel in the central and district offices maintained a general surveillance of these various test activities.

With the advent of ARCO's initial production scale (3 acre) effort in the Clay-West area at the Moser mine site, regulation of in situ uranium mining was formalized with the issuance of a permit in January 1975. This effort by ARCO has been progressively expanded at this location to 650 production acres authorized by 3 permits and has been transferred to operation by U. S. Steel and Niagra Mohawk Uranium. Another permit application is currently pending for a fourth mine to be developed near this cluster.

Mobil's O'Hern permit and Westinghouse's (now Wyoming Mineral) Bruni permit was approved June 1975 and the Wyoming Mineral's Lamprecht permit was issued August 1975. Dalco obtained a permit August 1976 for the Burns site and transferred its operation to U. S. Steel. IEC's Pawnee permit and the Union Carbide's Palangana permit were issued in January 1977. U. S. Steel's Clay-West permit was approved December 1977. This year (1978) permits were issued in May to U. S. Steel for the Boots Mine and an enlarged Burns site and to IEC for its Zamzow Mine. Mobil's Holiday and El Mesquite mine permits were approved in July 1978. Eleven additional permits are currently being processed: 5 for Mobil's Piedre Lumbre-Brelum Mine; one for U. S. Steel's enlarged Moser Mine and one for the

U. S. Steel Brown/Pawlek mine; one for an enlarged Palangana Mine for Union Carbide; and one each for Wold Nuclear, Everest Exploration, Uranium Resources, Inc. and Lomex, Inc.

The accelerating rate of mining activity is noticeable. It is also noticeable that exploration is accelerating. There were 16 rigs operating early in 1977. This year, the rig count is averaging 46; a 287% increase.

HISTORY OF LEGISLATION

Of course, parallel with this mining activity, legislation and regulation was proceeding at the State and Federal level. The following is a brief chronology of this legislation that is directly or indirectly related to uranium mining.

In 1961, the Injection Well Act was passed by the Texas Legislature. This legislation has been revised several times and responsibility for its administration has been shifted from the Texas Water Commission to Texas Water Development Board that was created in 1965 and to the Water Quality Board that was created in 1967 Legislation. The Industrial and Municipal disposal wells are now administered as the Disposal Well Act under the Department of Water Resources created in 1977. The Railroad Commission regulates disposal wells receiving waste resulting from production of oil or gas.

As most of you know, disposal wells are an integral part of most in situ uranium mines installed in Texas. They are used both during production and during aquifer restoration following production. This legislation has also been one of the prime sources for the Underground Injection Control Regulations being formulated at the Federal level.

In 1963, the Texas Radiation Control Act became effective. This legislation has also been revised but has remained under the Texas Department of Health's authority. As you may know, Texas is an "Agreement State" and, as such, issues necessary licenses to operations involved in handling radioactive materials in coordination with Nuclear Regulatory Commission regulations.

In 1967, the Water Quality Act established the Water Quality Board from a nucleus of personnel in the Texas Department of Health. Up to that time, the Department of Health concerned itself with both the safety of drinking water supplies and discharges to these supplies. The Water Quality Board was chartered to concentrate on protecting the State's waters from discharges. In the same year that this legislation was enacted, Water Quality Standards were issued by the Water Quality Board for discharges to all fresh and tidal waters. These standards are based on use of the water (contact, non-contact, propagation of fish and wildlife, domestic water supply). These regulations were adjusted to comply with the Federal Water Pollution Control Act of 1972 and were approved by EPA in 1973. These standards are due to be revised again to reflect the 1983 goals of Public Law 92-500.

In 1969, the Solid Waste Act was enacted by the Texas Legislature. This legislation provided for control of wastes from manufacturing, mining and agriculture. This legislation was used to regulate uranium surface mining activities until 1975 when the Texas Surface and Mining Reclamation Act enacted by the Legislature placed responsibility for uranium open-pit mining with the Railroad Commission along with responsibility for surface mining of coal and lignite.

In 1972, the Federal Pollution Control Act (Public Law 92-500) was passed. This legislation evolved into the NPDES (National Pollutional Discharge Elimination System) and the subsequent Point Source Categories, effluent guidelines and standards for these categories. The Nov. 6, 1975 issue of the Federal Register established interim final rules for Best Practical treatment levels for discharges from ore mining and dressing operations. Sub-part E of these Rules set discharge concentration limits for 8 parameters for discharges from uranium mines. This same Federal Register proposed Rules for Best Available treatments, adding limits for 2 more parameters. Suits were initiated by 11 companies against these proposed rules, and they are currently being reconsidered for issue in 1979.

In 1974, the Federal Safe Drinking Water Act (Public Law 93-523) was passed. Parts of this Act have been implemented in Texas. For example, on July 1, 1977, the Texas Department of Health made effective drinking water standards to comply with this legislation and regulations developed by EPA. A second part of this legislation is the Underground Injection Control Regulations. These Regulations have undergone various hearings procedures and are now being developed. It is expected that proposed regulations will be published in the Federal Register before the end of the year.

In 1975, the Administrative Procedures Act was passed for the general purpose of making permitting and other procedures used by various agencies more uniform and providing for the State Register. Texas Surface Mining and Reclamation Act (Senate Bill 55) providing for the RRC's authority to require reclamation (back-filling) of coal, lignite and uranium surface mines was also passed in 1975. This legislation was initially introduced providing for controlling reclamation of all surface mining to include such resources as gravel, clay, etc.

In 1977, an amendment to Senate Bill 55 was introduced, that proposed to place regulation of in situ mining of coal, lignite and uranium within the RRC authority. This proposed amendment was modified then ratified and made effective January, 1978 to include in situ mining of coal and lignite only, leaving regulation of in situ uranium mining with the Texas Department of Water Resources.

In 1977, the Water Resources Act was passed combining the Water Rights, Water Development Board and the Water Quality Board.

WATER QUALITY ACT AND WATER RESOURCES ACT

In the middle of all of this rapid technical, economic and legislative change, it is fortunate that three concepts have remained constant. One of these constants is the State's "Water Quality Policy".

As mentioned earlier, on September 1, 1977, the "Water Resources Act" became effective. This legislation combined the Water Quality and Water

Development Boards with the Water Rights Commission to form the Department of Water Resources. To oversimplify, the first nine pages of this Act defines organizational structure and responsibility. The other 140 pages are primarily a compilation of past legislation. For example, the Water Quality Act passed in 1967 said that (to paraphrase), "It is the policy of this State...to maintain the quality of water in the State consistent with the public health and enjoyment...the operation of existing industry, the economic development of the State...and to require the use of all reasonable methods to implement this policy". This language has remained constant and is duplicated in the Water Resources Act passed 10 years later.

I personally feel that the Water Quality Act has been sound and effective legislation as administered by the previous Water Quality Board. The poor conditions of several major water courses in the State that prompted the Water Quality Act in 1967 have been substantially improved due to the efforts of both municipalities and industry and despite continued population and industrial growth. The Water Quality Act, as now duplicated in the Water Resources Act, has been the starting point for protection of surface water quality and now provides the authority and basic policy for protection of ground-water quality.

UIC REGULATIONS

At the Federal level, a currently active input that influences our thinking relative to in situ uranium mining is the Safe Drinking Water Act and its sublegislation, the Underground Injection Control Regulations. The most recent rules proposal was published in April 1978.

The stated purpose of the Underground Injection Control Regulations is "to protect the present and potential drinking water sources from contamination". Underground injection endangers drinking water sources "if the injection might make it necessary for a public water supply to use more extensive treatment than would be necessary otherwise". This legislation applies to all water with less than 10,000 mg/l TDS. A public water supply is defined to be one that has more than 15 connections or regularly serves 25 individuals or more.

You may understand that this is not an optional program. The states must assure that underground injection will not endanger drinking water sources. Either the individual states will take the initiative or the program will be imposed at the Federal level.

LEGISLATIVE IMPLEMENTATION - PERMITS

To familiarize those of you that have not been involved with the permit procedure or its requirements, and to set some background for discussion, I would like to review some basic definitions and the current permit procedure. As I mentioned earlier, there are three concepts that have remained constant over the last four years relative to in situ mining. The first, as discussed, is State's water quality policy. The other two constants are the objectives of the in situ uranium mining permits issued by our agency.

Objective #1 - Contain leachates during mining.

Objective #2 - Restore the affected aquifers soon after mining.

In a nut shell, Contain It and Restore It. All of the permit requirements to complete pump tests, restoration demonstration, define Baseline water quality and routine monitoring directed at achieving these objectives. When the situation is distilled down to the two words of "containment" and "restoration" the problem may seem misleadingly simple. Only an experienced, qualified geo-hydrologist can appreciate what is involved in containment under the hydraulic stress of production. Only a geo-chemist can fully appreciate the complexity involved in restoration.

PERMIT DEFINITIONS

Looking briefly at some basic permit definitions, there are five kinds of "Areas" involved in a permit. From largest area to smallest, they are:

a. The Leased Area - defined by the leases.

b. The Permit Area - This area is either the same as the Lease Area or smaller but within the Lease Boundary as defined by the operator.

c. The Mine Areas - These are areas in the Permit Area defined by the ring of Production Zone Monitor Wells around the Production Areas at a maximum distance of 400 feet from the Production Area.

d. The Production Areas - These are the ore producing areas defined by the Injection/Recovery wells.

e. The Buffer Area - This is the area defined as a minimum distance of 100 feet between the Mine Area Production Zone Monitor Wells and the Permit Boundary and possibly other boundaries such as rights of ways and easements.

One of the more significant effects of these definitions is that it requires a total of 500 feet between the production area and the permit boundary if the operator wants to maintain the full 400 feet between the production area and the monitor wells. Of course, the operator may reduce this 400 foot distance but this will increase the risk of an excursion. Briefly, a ten-acre production area will normally require at least a 70-acre permit area.

The purpose of the Buffer Zone is to insure that, in the event of an excursion, the operator will have adequate area in the Buffer Area in which secondary wells may be installed to determine the extent of the leachate's outward movement. This is not a new concept but it is a consideration that an operator should be aware of as lease arrangements are being firmed up.

PERMIT PROCEDURE

Looking briefly at the Permit Process, there are three basic steps involved in getting into Production.

a. Get a permit.

b. 1. Get a Production Area Authorization.

2. Complete a Restoration Demonstration.

To obtain a permit, an operator needs to complete a Permit Application and attach various technical information relating to containment and restoration.

When the application is received, a draft permit is originated and reviewed internally, with other agencies and with the applicant. Following this review process, the draft permit is adjusted if necessary. A public hearing is scheduled by the Commission and a notice of the hearing published in the local paper by the operator at least 21 days before the hearing. The public hearing is held and, based on information presented, the Hearing Commissioner will make a report to the Texas Water Commission recommending approval, denial, or approval with amendments.

While the permit application is being processed or following the permit approval (at the operator's option), an application for the first Production Area Authorization may be compiled and submitted as soon as Baseline and pump test data is available. The Production Area Authorization Application will include more technical information detailing specific conditions of the involved Production Area.

For Production Area Authorization applications submitted after the first application, a restoration progress report is also attached.

There are two reasons for the "double-layered" procedure issuing a permit plus Production Area Authorizations:

Reason #1 - It allows the operator to have a permit in hand before expending large capital on the plant, production wells, monitor wells, pump tests, etc.

Reason #2 - It provides a mechanism for assuring restoration progress. If restoration progress is delayed, approval of the next Production Area Authorization may be delayed.

After approval of the permit and the first Production Area Authorization, the operator will complete a restoration demonstration that simulates, as closely as reasonable, actual Production/Restoration conditions. The objective of this demonstration is to document that the operator has sufficient waste fluid handling capacity to meet or beat the restoration deadlines indicated in the mine plan.

IN SITU URANIUM MINING RULES

Those of you that have been directly involved in obtaining a permit are familiar with various requirements that are currently contained either in the permit application or in the permit itself. It is expected that the standard language in this application and that is redundant from permit to permit will be incorporated to rules in the near future. The permit will then contain only information, exceptions and requirements that apply to the particular site. These rules are being developed with an awareness of the Federal UIC (Underground Injection Control) regulations pursuant to the Safe Drinking Water Act. The rules will be consistent with these UIC regulations to the degree that it is reasonable to do so.

In summary, the Water Quality Act, the permit, the rules and the UIC are currently the primary legislative and regulatory devices.

TECHNICAL

In considering the technical factors involved in an in situ uranium mine, the large number of different conditions are impressive. For example:

TDS; 500 to 6,500 mg/l

Depth; 200' to 1,500'

Transmissivity; 100 to 25,000

Production Pattern; 5-spot to staggered-line-drive

Lexiviant; Acid to Alkaline, Ammonia to Non-Ammonia

Excursion Control; Hydro-Sink to Hydro-Barrier

IX Column; Up Flow to Down Flow, Central to Satellite

Transport; pipe to truck

Fluid Disposal; evaporation to disposal well

Product Shipment; yellow cake to slurry

Production Zones; single to multiple

Overlying and/or Underlying Aquifers; several to none; artesian to water table

Aquicludes; tight to porous

Water Quality; uniform to highly variable

Superimposed on these technical differences are economic differences of grade, formation thickness, reserve, the operators economic and organizational structure, etc. It is because of these variables that care must be taken to avoid rules that are practical and effective at one site but invalid at other sites.

Rather than dwell on the differences, however, I would like to review the similarities of a typical site:

1. As water flows down gradient, and if uranium is in solution in this water, the uranium will precipitate when it arrives in a reducing environment that has the correct pH. Selenium and molybdenum tend to precipitate under the same conditions.

2. The "daughters" of uranium, such as radium tend to be present in the vicinity of the uranium deposits.

3. The reducing agent is H_2S.

4. As a result of the presence of high concentrations of radium, selenium, molybdenum, arsenic and other parameters, the water is toxic to plants, animals and people and rates very low on the taste and odor scale due to the H_2S sulfates, manganese and iron.

5. The in situ mining process introduces agents that shift the pH and/or the redox potential to cause the uranium to solubilize.

6. Currently, the most common pH "adjuster" is ammonium carbonate/bicarbonate. Other alkaline materials are beginning to be used or considered. Where the production zone does not have excess calcium, an acid may be considered.

7. The combination of the ions introduced plus those solubilized may increase the initial concentrations by a factor of ten or more.

8. After circulating these fluids through ion exchange towers to remove the solubilized uranium, the waters are restored by:

   (a) Replacement - replacing the affected water with either natural water (the affected water is disposed of by deep disposal wells, evaporation or transferred to the next area to be mined as a pretreatment) and/or by;

   (b) Surface Treatment - processing the affected water through surface treatment such as RO, ED, precipitation, etc. (The "restored" water is reinjected and the "brine" is disposed of by disposal well or evaporation).

9. The toxic ions tend to return to Baseline levels as Baseline TDS concentrations are reached. Due to physical removal of certain ions, the precipitation of certain metals in a higher pH environment or the oxidation of H_2S by the mining process, the concentration of these ions may be lower than Baseline concentrations in the restored fluids.

10. Experience to date indicates that there is only one ion that does not tend to return to Baseline at the same rate that TDS returns to Baseline; the cation used to adjust the pH, usually ammonia.

11. NH_3 may be at levels between 300 and 500 mg/l when Baseline TDS is approached after extracting 3 to 6 pore volumes using the replacement method. It required 12 pore volumes to reach 15 mg/l even with the assistance of a cation chemical flush in one clay rich aquifer. It would require many more pore volumes to reach Baseline concentrations.

12. One pore volume in a one acre area, ten feet thick, with a 30% porosity, is approximately one million gallons of ground water.

13. Production in a typical area, 10 acres in size, may affect the water in a 28 acre area and production in a 10 foot seam of ore may affect in a 20 foot thickness as a result of horizontal and vertical flow lines and dispersion. The overall result in this situation, is that 5.6 million gallons of ground water are affected for every acre mined. If six pore volumes are required to restore this area, it will require almost 34 million gallons of water per acre.

These technical considerations of the typical site emphasizes the dominant importance of the production procedures in the overall effectiveness of in situ uranium mining. For example, providing a hydraulic gradient toward the production area by means of excess fluid withdrawal from the center of the production area or by excess injection around the perimeter of the production area will reduce the volume of water affected by at least half. Placement of the recovery production wells around the outside of the production area rather than the injection production wells will reduce this volume of water affected even more.

One final point concerning restoration, initially we envisioned restoration progress in a Production Area to be total restoration from one end of the Production Area to the other. However, the phenomena of "Hot Spots" in the Production Area has now been recognized. These are wells that continue to produce uranium long after most others have quit producing. It is not normally economically reasonable to terminate production in these wells. It is technically possible, however, using particular production procedures, to substantially restore the areas around the producing "Hot Spots". If parameter concentrations are substantially reduced over most of the Production Area, favorable consideration may be given to authorizing the next Production Area.

In conclusion~~s~~, I would like to emphasize that the very best advice that I can offer a potential permit applicant, whether it is the first or tenth application, is to please discuss your situation with us before you start gathering information for the permit. The most difficult condition to deal with is one we do not know about. It takes two to three hours to review the permit procedure, requirements and definitions with a person that is not familiar with the subject. It may take longer for a person that is familiar. For example, we spent an entire day here in Corpus with all of the active mine operators discussing the subject of "How to take and analyze a sample". The conclusions reached were not unanimous primarily because each operator had a slightly different set of conditions to content with. Between an operators selected operating procedures and the geologic, hydrologic and chemical facts of the site, the permutation of combinations is almost infinite. This is not to infer that operators have not done a generally professional job of effectively addressing these problems. Some operators have been more effective than others. Some have had more adverse conditions than others. But, the operators have generally been cooperative and have anticipated and avoided problems. Where problems were not anticipated, they have been controlled. In the three and one-half years of production, there have been relatively few excursions of leachates considering the large number of operating injection wells and considering the relative inexperience that all of the operators share in this new industry. There has not been one excursion that has not been contained.

This brings up a point that is probably worth emphasizing. In developing the permit procedure and its requirements, we have received inputs from many sources. Obviously, the primary input is from the operators themselves. They are the experts although their experience is limited compared to other industries. Other technical and legal inputs come from our agency staff and other agencies at both the State and Federal levels. Additionally, we get inputs from precedent, preconceived ideas and emotion. The word "uranium" has emotional connotations. Possibly the major input is experience, particularly poor experience. This is a fact of life as much as is gravity. You can fight, but you can't avoid its effects. There is a strong tendency by any individual, group or organization to hunt rats with an elephant gun and to impose methods to prevent an adverse situation even if it cannot occur more than one time in a million. This is the best reason I can think of for operators to screen their procedures for the purpose of preventing problems rather than just correcting the problems after they occur.

Thank you for your time. We will be glad to discuss with you in depth in Austin.

Removal of Iron Oxide From Silicate Minerals

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The presence of iron oxide and other iron-containing minerals in silica and alumino-silicates seriously detracts from their commercial value for some important industrial uses. It is well known for example, that silica sands, for high quality glass making, must contain extremely small amounts of iron (<0.008% Fe).[1] Less widely known is the effect of iron oxide in determining the value of some of the clay silicates, particularly kaolinite $Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$, used extensively as a paper filler and coater. Vast deposits of this mineral occur in Devon and Cornwall in England and in Georgia, Florida, Carolina, and Idaho in the United States.

Since exceptional gloss-imparting properties have been found in clays consisting predominantly of particles less than 2 microns[2] modern paper coating clays are fractionated to this desirable size during production. Chemical analysis of natural kaolin of this particle size may show an iron content of as much as 1% Fe_2O_3. Mineralogical analysis shows however, that only a fraction of this amount of iron is present as iron oxide, the balance occurring either in small amounts of accessory minerals such as biotite, hydrous micas and ilmenite or substituted for aluminum in the clay lattice. The iron oxide appears to occur chiefly as thin coatings on the kaolinite platelets. In this position as little as 0.01% Fe_2O_3 detracts from the visual whiteness of the clay and thus from its commercial value.

Techniques for removing iron oxide from clay and for improving the whiteness of the ultimate product have been developed over the past fifty years. Kaolinite is amongst the least expensive pigments in a strongly competitive field. The economics of colour improvement and the increasing rigidity of standards to be met by clays for paper coating encourage continuing research in new and improved methods.

The purpose of the present discussion is to review the chemistry of the so-called bleaching of clays and to examine the possibility of applying some of the new technologies to the process.

LEACHING OF IRON OXIDE

Gruber[3] in 1910 described the leaching of iron oxide from acidified clay suspensions by the addition of sodium dithionite, $Na_2S_2O_4$. The reactions taking place during this process have formed the basis for a large number of ensuing patents. Bump[4] in 1939 described the use of sulphurous acid in the presence of zinc dust, thus reproducing within the clay slurry the first stage of the commercial process for producing sodium dithionite.[5] Lyons[6] outlined a similar scheme but using electrolytic reduction of bisulphite for the production of the dithionite, again reproducing in part a commercial process for the production of dithionite.[7] The electrical conductivity corresponding to an acidity of pH 2, used for conventional dithionite leaching, is low and thus electrolytic bleaching is poorly efficient with regard to power consumption. Closely spaced stator and rotor electrodes[8] have been proposed in a cell designed to minimize this undesirable feature of the process.

At room temperature the bulk of the iron oxide present in hydrated form as goethite or lepidocrocite, FeO(OH), is solubilized by dithionite in a few minutes. Dehydrated oxides such as haematite are relatively unaffected under this condition. Dithionites are notoriously unstable in aqueous solutions, decomposing rapidly, especially under acid conditions. The stoichiometry of reaction (1) is thus never realized in practice.

$$2\,FeO(OH)_{(s)} + HS_2O^-_{4(aq)} + 3\,H_3O^+ \rightarrow 2\,Fe^{++}_{(aq)} + 2\,HSO^-_{3(aq)} + 5\,H_2O \qquad (1)$$

(s) = solid (aq) = aqueous

In addition to loss by decomposition, initial additions of dithionite to a clay slurry serve only to deoxygenate it due to the excellent oxygen scavenging qualities of the compound (Fig. 1).

Raising of the temperature of the clay slurry to between 50° and 100°C whilst leaching with dithionites has been described.[9] The life of dithionites under this condition is likely to be so brief that leaching is in fact being partially performed by bisulphite. At room temperature the rate of reaction of bisulphite with even hydrated iron oxides is extremely slow; at elevated temperatures it could be sufficiently rapid to be of commercial significance. A patent of 1931 (10) described the use of sulphurous acid at elevated temperatures and pressures.

The use of aldehyde- and ketone-sulphoxylate derivatives of dithionite, considerably more stable than dithionite itself, has been patented.[11]

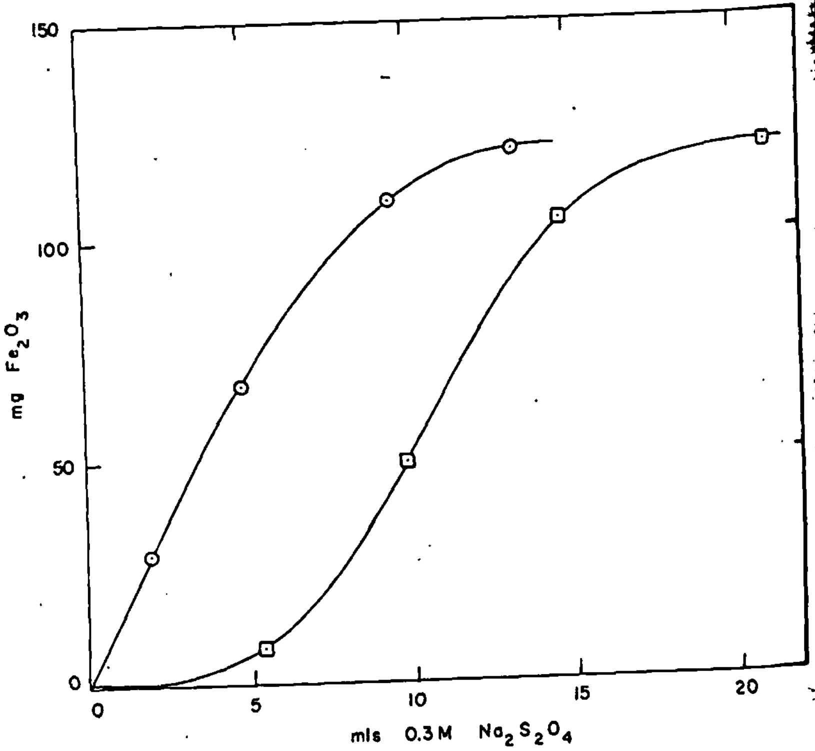

Fig. 1. Effect of dissolved oxygen on leaching of iron oxide with dithionite. □ Dissolved O_2 present. ○ Dissolved oxygen removed prior to $Na_2S_2O_4$

These compounds are stable and inactive reducing agents at room temperature but apparently decompose on heating to yield sulphoxylic acid. The sequence of reactions in an ideal system is probably described by (2) and (3), though as with dithionite stoichiometry is never achieved in practice.

$$CH_2CHSO^-_{2(aq)} \rightleftharpoons CH_2O_{(aq)} + HSO^-_{2(aq)} \tag{2}$$

$$2\,FeO(OH)_{(s)} + CH_2O_{(aq)} + HSO^-_{2(aq)} + 4\,H_3O^+ \rightarrow 2\,Fe^{++}_{(aq)} + CH_2O_{(aq)} + HSO^-_{3(aq)} + 7\,H_2O \tag{3}$$

Powerful cationic reducing agents such as titanous sulphate and vanadous sulphate leach iron only very slowly from even hydrated iron oxides. In this respect the results of Schofield,[12] who showed that hydrous iron oxide has an anion exchange capacity in acid solution may be of significance. In the initial step of the leaching reaction, dithionite ions may be adsorbed on these exchange sites according to (4), (5), and (6).

$$H_2S_2O_{4(aq)} \rightleftharpoons H^+ + HS_2O^-_{4(ap)} \quad K = 0.45\ (13) \tag{4}$$

$$FeO(OH)_{(s)} \rightleftharpoons -\overset{|}{\underset{|}{F}}eO^+_{(s)} + OH^-_{(aq)} \tag{5}$$

$$-\overset{|}{\underset{|}{F}}eO^+_{(s)} + HS_2O^-_{4(aq)} \rightleftharpoons FeO.HS_2O_{4(ads)} \tag{6}$$

Less bisulphite ion may be adsorbed under the same condition due to the lower first dissociation constant K of 1.26 × 10^{-2} for sulphurous acid.[13] Unfortunately no experimental work has been reported in an attempt to establish the rate determining steps in these reactions.

REMOVAL OF IRON FROM THE LEACH SOLUTION

Kaolinite with a cation exchange capacity of the order of 5 meq/100 g is able to retain by adsorption, highly significant amounts of ferrous ion on filtration. Further quantities are retained by occlusion in the thirty per cent of moisture in the filter cake. Without appropriate treatment, oxidation of this iron on drying would largely nullify the effects of the leach. Early attempts to decrease the amount of ferrous ion retained by the clay, depended upon the use of various complexing agents such as tartaric, tannic, and oxalic acids.[14,15,16] Latterly, complexing with hexametaphosphate has been suggested.[17] Parker[18] patented the process of washing the clay filter cake with a multivalent cation such as Al^{3+} which would displace the adsorbed ferrous ion and which itself on being adsorbed by the clay would be non-chromophoric. Due to the low permeability of clay filter cakes large scale washing is likely to prove slow and costly. The proposal in 1950[19] to preferentially adsorb ferrous ion on a high capacity cation exchange resin added to the clay slurry and then to subsequently screen out the loaded resin, predated the now familiar resin-in-pulp procedures of the uranium industry.

The alternative to complete removal of ferrous ion is to ensure that any remaining, is on oxidation converted to a less chromophoric compound than iron oxide. This can be achieved according to Davis[20] by the addition of an orthophosphate prior to filtration. Since ferrous phosphate is soluble in even faintly acid solutions removal of ferrous ion during filtration is not impeded by orthophosphate. However, oxidation of ferrous iron in the presence of orthophosphate leads to the precipitation of a basic iron phosphate, possibly of the formula $Fe(OH)_2H_2PO_4$[21] instead of iron oxide. Precipitation of iron phosphates more complex and even less chromophoric than the simple basic salt may occur under the conditions of the process.[22]

THE PROBLEM OF ULTIMATE WHITENESS

After complete leaching of hydrated iron oxide, major variations are apparent in the visual whiteness and measured brightness with reference to $MgCO_3$ or MgO as standard[23] between clays from different sources. In most instances these variations can be ascribed to the presence of additional iron-containing minerals or iron substitutions in the clay lattice. Not all brightness depression can be ascribed to iron-containing compounds, however. Fine grey silica has been shown to be a major contaminant and brightness depressant in at least one instance, and a flotation procedure devised for its removal.[24] Flotation has also been proposed as a means of separation of kaolinite from titaniferrous iron minerals which impart a grey colour to the clay.[25,26,27]

Drastic chemical procedures, involving attack at high temperatures with chlorine, carbon monoxide or hydrogen sulphide, with or without a subsequent leach, have been devised for the complete removal of iron from clay.[28,29,30,31] Illmenite, for example, is readily converted to iron sulphide and TiO_2, by heating in an atmosphere of carbon monoxide and sulphur at 600–1000°C.[32] Kaolinite is completely dehydrated at 500–600°C under one atmosphere pressure of water, and the product exhibits rheological properties in aqueous suspension which make it entirely unsuited for paper coating. For this reason none of the high temperature processes that have been devised for iron removal from kaolinite appear to be of industrial significance.

APPLICATION OF NEW TECHNOLOGIES

Dithionites (24 cents/lb.) and aldehyde-sulphoxylates (22 cents/lb.) are relatively expensive reducing agents compared with sodium bisulphite (5–7 cents/lb.). With clays requiring 10–20 lbs/ton of dithionite, the cost of iron leaching is considerable. The advances made in recent years in hydrometallurgy, particularly in pressure leaching,[33] may have increased the possibilities of developing an attractive alternative to dithionite leaching.

Due to the shift of reaction (7) towards increased hydrolysis with temperature,[34] direct acid pressure leaching of iron oxide would only be possible at high acid concentrations.

$$2\,Fe^{3+}_{(aq)} + 12\,H_2O \rightleftharpoons 2\,Fe(OH)_{3(s)} + 6\,H_3O^+ \qquad (7)$$

However, use of a cheap reducing agent such as sodium bisulphite might be highly effective in rapidly leaching both hydrated and dehydrated oxides at temperatures of 150–200°C. More refractory iron minerals may also be attacked under this condition. With short retention times and the use of tube or flash heat exchangers,[35] equipment and processing costs might not be unattractive. The use of acid sulphite solutions at high temperatures and pressures in bauxite processing has been reported by Scott.[36] Preliminary experiments (Table I) suggest that the leaching of iron oxide with bisulphite is indeed very rapid under typical pressure leaching conditions. Also more iron may be leached than with dithionites at room temperature. The fundamental chemistry of the leaching of iron oxide with bisulphite, and mixtures of bisulphite and formaldehyde, is now under study. Formaldehyde in the presence of small amounts of bisulphite, as catalyst, has been shown to reduce aqueous suspensions of U_3O_8 to UO_2 at high temperatures.[37] A superior precipitation of highly insoluble colourless iron compounds also may be possible at high temperatures with a consequent decrease in the chances of colour reversion on drying.

TABLE I

Extraction of Iron from Iron Oxide-containing Kaolinite on Pressure Leaching for Ten Minutes with Ammonium Bisulphite at Various Temperatures

Temp. °C	Pressure psia	NH_4HSO_3 g/100 g clay	Iron leached as Fe_2O_3 %
160	90	1	0.05
190	182	1	0.14
230	405	1	0.15
25	—	Dithionite Control	0.06

Efforts to improve the visual whiteness of coated papers have centred during recent years around the use of fluorescent organic pigments.[38,39] These pigments absorb in the near ultraviolet and fluoresce in the visible blue region of the spectrum.[40] Some calcium alumino-silicates, $CaAl_2Si_2O_6$ and $CaAlSi_2O_7$, activated with cerium[41,42] also fluoresce blue. With the availability of very high temperature plasma flames the possibility of forming inorganic fluorescent coatings on clay particles has become possible. By rapid passage of kaolinite containing base exchanged calcium and cerium through a plasma flame a thin surface layer of the mineral may be converted to an inorganic phosphor. Experiments on this possibility are being conducted at the University of British Columbia with a high frequency plasma torch similar to that described by Reed.[43]

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Discussion

T. R. Scott:* A main problem appears to be physical retention and chemical adsorption of iron in clay, even after it has been reduced and dissolved by dithionite. Why then, cannot a strong acid like HCl be used for decomposing the iron minerals present, without resort to reduction at all. Alternatively, if use of HCl is uneconomic, would it be feasible to use more dilute solutions of oxalic acid, which is also a reducing agent and a complexant for iron in either valence state. Oxalic acid is stable to 180°C and faster reaction might thus be obtained if impure clay was subjected to pressure leaching.

I. H. Warren: Strong hydrochloric acid will of course readily remove hydrated, and much of the dehydrated iron oxides. Unfortunately its use is entirely uneconomic for the materials under consideration. Dilute oxalic acid certainly dissolves hydrated iron oxides at room temperature and is proven to be more effective at higher temperatures. Although oxalic acid complexes iron in solution it is ineffective in preventing reoxidation of iron salts occluded at filtration.

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FEATURE

The fact that literally billions of living cells can be found in one milliliter of solution, emphasizes the need for a better understanding of . . .

The Role of Microorganisms in Chemical Mining

E. E. Malouf

Rapid depletion of the world's mineral deposits combined with the expanding demand for metals places great pressure on our ability to provide technologically and economically feasible processes to recover greater amounts of metals from progressively lower grade sources. Chemical mining is one area in which expanding research and development can provide new processes or refinements to existing ones. These new techniques could result in increased production of metals from materials now considered uneconomic to process by current technology.

To mine by chemicals requires the interaction of such disciplines as hydrometallurgy, microbiology, chemistry (both organic and inorganic), fluid flow, mineralogy, geology, and of course, economics. One of the least understood areas but one which may end up being an essential part of any chemical mining process is microbiology, i.e., the role of microorganisms in altering minerals and metals in solution.

The Discipline of Microbiology

Metallurgists and mining engineers, as currently trained, are not exposed to the additional disciplines of microbiology and enzyme chemistry to the degree that they can incorporate this knowledge in the development of new processes for recovering metals. Similarly, microbiologists are completely removed from the chemistry and problems of the metallurgical and mining industry.

The time is rapidly approaching where students in the fields of mineral and mining engineering will have to supplement their education with courses in microbiology, thereby developing an intimate understanding of the interactions of buffered solutions, pH, enzymes, catalysts and organic reagents. They will have to become as versed in the chemical kinetics of microorganisms with minerals as they are with drilling, blasting, mining flotation, and smelting. Also, the mining industry will require the entwining of the disciplines of microbiology and metallurgy, bringing microbiologists into contact with metallurgical problems. This type of interplay will provide a better understanding of such things as the formation of deep sea nodules, the stratification and enrichment of trace

"Microorganisms . . . are new tools to be developed and applied in chemical mining to provide new and economic processes for the recovery of metals."

E. E. Malouf, Chief
Hydrometallurgical Development Section
Kennecott Research Center
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compound has been identified in sea water as well as in the solutions used in leaching mine waste.

energy source and require oxygen. Considerable laboratory work has been done on the Thiobacillus thiooxidans and the

of the thioparus. However, as the pH drops to 4.0 or ower the thiooxidans become well established and ontinue the oxidation of the sulfides. Usually assoiated with the thiooxidans is the species ferrooxidans hich, in the compatible environment of pH 1.5-4.0, eadily oxidizes the ferrous iron in solution to ferric on. The combination of ferric iron and acid solutions esults in a powerful chemical lixiviant that produces n accelerated chemical alteration of the minerals to arallel the activity of the bacteria in releasing mets to solution.

Corrick and Sutton[2] stated that the optimum pH for icrobial oxidation of pyrite is 1.8, although that for

They Are Immune

The toxicity of copper has constituted an objection to syngenesis of copper sulfides. However, the work by K. L. Temple and N. W. Leroux[4] indicated that the sulfate-reducing bacteria were protected from copper toxicity by producing the sulfide. They determined that the anaerobic microorganism Desulfovibrio desulfuricans could survive additions to the solution of 0.25% copper sulfate. The principle that emerges from this study is that a sulfate-reducing organism is protected from heavy metal ion toxicity by the sulfide it produces. This principle would apply to any bio-

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NEW MEXICO ENVIRONMENTAL IMPROVEMENT AGENCY

RADIOACTIVE MATERIALS LICENSE

**UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.**

Pursuant to the New Mexico Radiation Protection Act of 1971, and the Radiation Protection Regulations Part 3, and in reliance on statements and representations heretofore made by the licensee designated below, a license is hereby issued authorizing such licensee to transfer, receive, possess and use the radioactive material(s) designated below; and to use such radioactive materials for the purposes(s) and at the place(s) designated below. This license is subject to all applicable rules, regulations, and orders now or hereafter in effect of the New Mexico Environmental Improvement Agency and to any conditions specified below.

Licensee

1. Name Michael P. Grace

2. Address 1413 Willow Drive,
Milan, NM 87020

3. License number NM-GRA-UL-00

4. Expiration date March 31, 1981

5. Reference number -

6. Radioactive materials (element and mass number)	7. Chemical and/or physical form	8. Maximum quantity licensee may possess at any one time
A. All natural radioisotopes encountered in the production of natural uranium.	A. Any required in the production of U_3O_8.	A. 20,000 pounds of natural uranium.

CONDITIONS

9. Authorized use. (Unless otherwise specified, the authorized place of use is the licensee's address stated in Item 2 above.)

A. For in-situ leaching, heap leaching, processing into uranium concentrate, storage, and distribution to authorized recipients.

10. Radioactive material shall be leached and ion-exchanged on the licensee's leased propert or property otherwise acquired for such use by the licensee* approximately 20 road miles NE from Gallup, New Mexico for an in-situ leaching operation (also known as Site 1, NE¼ NE¼, Section 23, T 16 N, R 17 W, as shown on Exhibit 23-E), approximately 25 road miles NW from Rio Puerco Trading Post on I-40 for an in-situ leaching operation (also known as Site 2, NW¼ Section 13, T 12 N, R 4 W, as shown on Exhibit 13-F), and approximately 20 road miles NW from Magdalena, New Mexico for a heap leaching operation (also known as Site 3, SW corner of Section 13, T 1 N, R 6 W), as specified in his applicatior

11. The licensee shall comply with Part 4, New Mexico Radiation Protection Regulations.

12. Radioactive material shall be used by individuals designated by Michael P. Grace.

* to be read in conjunction with Condition 16

HEALTH
ENVIRONMENT
department

STATE OF NEW MEXICO

Page 1 of 1 page

ENVIRONMENTAL IMPROVEMENT DIVISION

RADIOACTIVE MATERIAL LICENSE

License number NM-GRA-UL-00 is amended to become

License Number NM-GRA-UL-01

Michael P. Grace
c/o William Condren
Attorney at Law
9 West 57th Street
New York, New York 10019

The subject license is amended to add the following:

18. The expiration date of this license is hereby extended from March 31, 1981 to September 30, 1981.

For the New Mexico HED Environmental Improvement Division

Date March 27, 1981

By

for Gerald W. Stewart, Program Manager
Uranium Licensing Section

EID 017A Revised 6/80

A REPORT ON ACIDIZING
- STATUS OF THE ART -

DOWELL

Revised 12/1/70

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A REPORT ON ACIDIZING
- STATUS OF THE ART -

I. INTRODUCTION

The interdependence of the well problem, chemicals and the technique of application are the keys to effective acidizing treatments. The primary purpose of an acid treatment is to dissolve rock. The manner in which the rock is dissolved, the "how" and "where", is the key to effective use of acid. Correlation of the many factors for this effective use makes acidizing one of the scientific arts of well stimulation.

II. ACIDIZING CHEMICALS AND REACTIONS

A general knowledge of the chemicals used along with their reactions provides a better understanding of the correct choice and use of these tools in the acidizing processes. Proper choice of materials and techniques are necessary to complement a complete treatment design.

The use of polymers, surfactants, alcohols, types of acid, etc., has led to the development of many acid formulations. In addition to the basic types of acid, concentration also has played an important part in the development of optimum acid stimulation treatments.

A. Types of Acids

1. Hydrochloric Acid (HCl), or "Regular Acid", is ordinarily supplied in concentrations of 32 to 36%; and is normally diluted to 15% for field use. 1000 gallons of 15% HCl will dissolve 1840 pounds (10.8 cubic feet) of limestone. Approximately 2040 pounds of calcium chloride is produced in the reaction along with 40 gallons of water and 6640 cubic feet (STP) of carbon dioxide. The resulting spent acid is a 20% $CaCl_2$ brine solution. 1000 gallons of 28% HCl will dissolve 3670# (21.6 cu. ft.) of limestone. The resulting spent acid is approximately 35% $CaCl_2$ brine.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$

The use of more concentrated acid solutions has increased greatly. Results with 28% HCl have been exceptionally good, much better than with equivalent volumes of lower concentration, i.e. 15%.

2. Acetic Acid (HAc) and Formic Acid (HCOOH) are weakly ionized, slow reacting, organic acids. These are normally diluted to 10% with water for field use. They have also been mixed with HCl to obtain a blended formulation. 1000 gallons of HAc will dissolve 740 pounds of limestone, whereas HCOOH dissolves 970 pounds. HAc is available in concentrations up to 100% as

glacial acetic acid; or the equivalent of 120% as an acetic anhydride, glacial acetic mixture. HCOOH is available in 70 to 90% concentrations.

$$2HOrg + CaCO_3 \rightarrow CaOrg_2 + H_2O + CO_2$$

Use of organic acids has increased in recent years in stimulation and as perforating fluids. They have inherently retarded (slower) reaction rates, one fifth to one tenth as fast as HCl, and are much easier to inhibit against corrosion at high temperatures (300°-400°F) than HCl formulations.

3. Hydrofluoric Acid (HF) is used in combination with hydrochloric acid, and is often referred to as Mud Acid. It is used primarily in sandstone matrix treatments to remove clay particle damage or increase permeability of clay containing sand formations. 1000 gallons of 3% HF and 12% HCl will dissolve 500 pounds of clay and up to 1450 pounds of $CaCO_3$.

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

$$2HF + SiF_4 \rightarrow H_2SiF_6$$

Cost factors and possible precipitants make HF/HCl combinations undesirable for extensive use in formations containing carbonates (i.e., having more than 20% solubility in HCl). HF is not used without being mixed with HCl. At least an equal concentration of HCl should be used with HF. The Mud Acid formulations currently in use are:

3% HF - 12% HCl, Regular Mud Acid
6% HF - 12% HCl, Super Mud Acid
10% HF - 12% HCl, Ultra Mud Acid
15% HF - 20% HCl, Ultra Mud Acid
20% HF - 25% HCl, Ultra Mud Acid

Recently, Organic Mud Acid has been developed as a substitute for HCl-HF mixtures where required due to temperature limitations and acid sludging problems. The current formulations in use are:

3% HF - 9% Formic Acid
3% HF - 10% Acetic Acid

4. Sulfamic Acid is a granular powdered material, which has had only very limited use. It reacts with carbonates as fast as HCl, but will only dissolve about one-third as much calcium carbonate and is significantly more expensive than HCl. It does have handling and transportation advantages in isolated areas. It is not recommended for formation temperatures above 180°F.

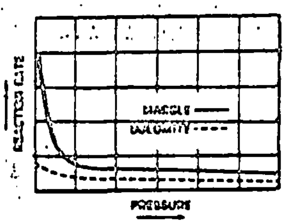
B. Acid Reaction Rate Factors

1. These are major factors that govern the reaction rate of an acid:

Pressure	Acid Type
Temperature	Area Volume Ratio
Flow Velocity	Formation Composition
Acid Concentration	Chemical
Reaction Products	Physical

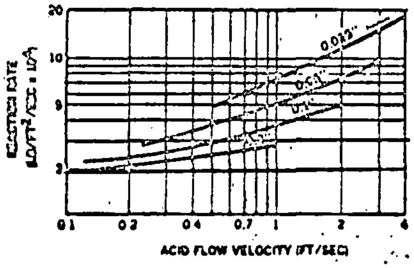
2. Pressure The following curve shows the effect of pressure on reaction rate of 15% HCl acid with limestone and dolomite at 80°F. Above 500 psi, pressure has little effect on reaction rate. At bottom-hole treating pressures, there is only a small difference (a factor of 1.5 to 2.0) in reaction of acid with limestone and dolomite compared to the rather large difference (a factor of about 10) at atmospheric pressure.

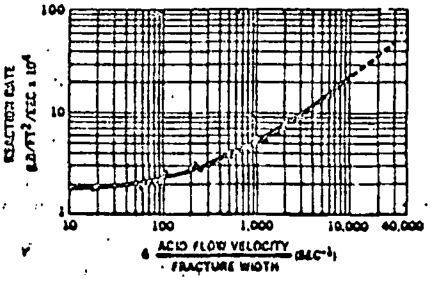
EFFECT OF PRESSURE ON REACTION RATE



3. Temperature Acid reaction rate increases directly with temperature. At 140° to 150°F., the reaction rate of HCl and limestone approximately doubled over that at 80°F. It must be recognized that the temperature controlling the reaction is affected by the injection temperature of the acid (a major factor), and by the heat liberated by the reaction itself (a minor factor). Recently a computerized program to accurately predict the bottom hole injection temperature at various volumes was developed. This will enable us to design more effective acid treatments.

4. Flow Velocity The following curves show that increased flow velocity acts to increase reaction rate of 15% HCl with $CaCO_3$. The velocity effect is more pronounced in narrower fractures. Reaction rate is a function of shear rate, 6 V/W, sec^{-1}:





Reaction rate, $\#/ft^2/sec = (28.5\ (V/W)^{0.8} + 184) \times 10^{-6}$

(The reaction rate is for 15% HCl at 80°F under 1100 psi with marble.)

The flow velocity in fractures and channels is dependent upon injection rate and actual geometry of the flow path.

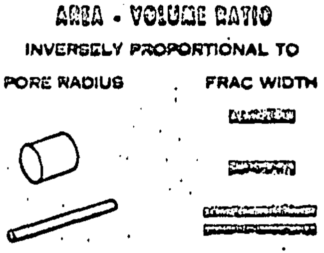
Velocity, ft/sec = $0.18\ Q/nr_fW$ (Radial fracture)

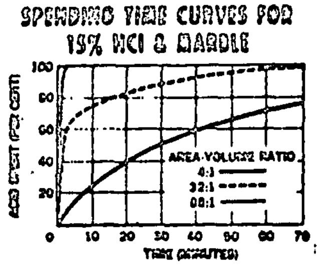
= $1.15\ Q/nhW$ (Linear fracture)

= $17.2\ Q/nd^2$ (Cylindrical channel)

5. Acid Concentration Reaction rate is nearly proportional to acid concentration up to 20% HCl. However, above 20% to 24%, the reaction rate increases to a maximum; above this level, the rate appears to be reduced. As the acid spends, reaction rate decreases, due to reduced acid concentration, and also to the effect of dissolved reaction products such as calcium or magnesium chloride (See section on retardation).

6. Area-Volume Ratio (A/V Ratio) The following curves show acid reaction or spending times, at 80°F and 1100 psi, for three area-volume ratios. Area-volume ratio is one of the major factors affecting spending time and may vary over a wide range. This ratio, the area in contact with a given volume of acid, is inversely proportional to pore radius or fracture width.





The term, spending time, has very little meaning or value by itself. It must be related to flow geometry and thus to the distance acid penetrates before it is spent.

In matrix acidizing, extremely high area-volume ratios may be encountered. For example, a 10 md, 20% porosity limestone may have an area-volume ratio of 28,000 to 1. In such a formation, it would be very difficult to obtain significant penetration before spending. A natural fracture 0.001 inch wide has an area-volume ratio of 3200:1. A 0.1 inch fracture has an area-volume ratio of 32:1. The smaller ratios in wider fractures allow greater penetration of the acid into the reservoir before its reaction is complete.

7. Formation Composition Probably the most important factor in determining spending time, and thus spending distance, is the chemical and physical composition of the formation rock. Acid solubility of a formation, the percent of rock sample that is dissolved by an excess acid, offers a clue to its susceptibility to an acid treatment. Most limestones react at about the same rate with a given acid, all other factors remaining constant. Generally, the reaction rate of limestone is only about 1.5 times that of dolomite. The area-volume ratio is, in part, controlled by the physical structure. Also, the physical structure is of primary importance since the solubility and permeability make-up can exist in several ways. "Where does the acid-soluble portion of the rock exist with respect to the flow patterns in the rock?" is the key to acid response. Two formations having the same acid solubility and permeability may respond differently to acid treatment because of variances in physical structure.

C. Acid Additives

1. Surfactants Many types of surfactants are available to reduce surface tension or interfacial tension of raw acid and spent acid solutions. Typically, the surface tension of 15% HCl is 72 dynes/cm^2. By addition of about 0.1% of an effective surfactant, this can be reduced to 30 dynes/cm^2. Surfactant type and concentration should be selected on the basis of laboratory tests.

Emulsion-prevention is also an important role for a surfactant. In the lab, a high-speed stirrer should be used to mix volumes of crude and spent acid at various rates. Surfactants should be added in concentrations ranging from 0.1% to 1.0%. An effective surfactant should produce 90% separation in ten minutes.

Surfactants also aid by dispersing and suspending fine solids to provide better clean-up of the treatment. The fine solids may be mud solids or natural fines released from the formation. The mud solids that induce damage may be dispersed, suspended and physically removed from the well rather than by the direct acid dissolving action. Some carbonate formations release many fine silica and clay-like solids in their reaction with acid. These should be removed along with the spent acid to improve the overall effectiveness of the acid treatment.

2. Sequestering Agents Sequestering agents act by complexing ions of iron to inhibit precipitation as the hydrochloric acid spends. Of primary concern is ferric iron. Citric, lactic and acetic acids as well as Versene (EDTA) and Nitrillo-Tri-Acetic Acid (NTA) are common sequestering agents. Sequestering

acid has particular application in treating water injection or disposal wells where insoluble iron compounds are deposited. It is not uncommon for acid to pick up as much as 2000-10,000 ppm total iron. Fortunately, of this amount, only 20% is usually ferric iron. Ferrous iron will precipitate at a pH of 7-9 and ferric iron will precipitate at a pH of 2-4. Because the pH of spent acid during clean-up is usually in the 0-6 pH range, only ferric iron precipitation has to be considered. This precipitate is ferric hydroxide which is an insoluble slimy gelatinous mass The sequestering agents mentioned above will prevent the precipitation of ferric iron during acidizing. However if an overtreatment of citric acid is used, there is a good possibility of the excess acid reacting with carbonates in the formation and precipitating insoluble calcium citrate. Conversely, with an overtreatment of NTA, the precipitate is soluble and will dissolve in spent acid.

3. Anti-sludge Agents Some crudes, form an insoluble sludge when contacted with acid. The sludge consists of asphaltenes, resin, paraffin and other high molecular hydrocarbons. The reaction of acid with the crude is initiated at the interface between the oil and acid by the formation of an insoluble film. The coalescence of this film leads to the formation of the sludge particles.

   Addition of certain oil-soluble surfactant blends can prevent this insoluble film from forming. In many instances, these surfactants function well as emulsion preventers, also.

4. Corrosion Inhibitors An acid inhibitor temporarily slows the reaction of acid with metal. The length of time that the inhibitor is effective depends on temperature, type of acid, acid concentration, type of steel and the concentration of inhibitor.

   Organic inhibitors in HCl are effective up to 300°F; but over 200°F, required concentrations are relatively large.

   The inorganic arsenic inhibitor can be used effectively up to 350°F. Arsenic is more effective than organic inhibitors at all temperatures in acid concentrations of 15% HCl or less. At higher concentrations, specially developed organic inhibitors should be used. Arsenic inhibitors are being used less frequently because they not only poison refinery catalysts, but will probably be under severe pollution control in the future. Dowell's policy on pollution control will make this inhibitor unavailable after January 1, 1971.

   The effect of temperature on acid corrosion inhibition is illustrated in the following table.

TYPE INHIBITOR	CONCENTRATION %	TEMP °F	PROTECTIVE TIME *
ORGANIC	0.6	200	24
	1.0	250	10
	2.0	300	2
INORGANIC	0.4	200	40
	1.2	250	24
	2.0	300	18

* TIME REQUIRED TO REMOVE 05 POUNDS METAL PER SQUARE FOOT EXPOSED METAL AREA. 15% HCl.

Mathematical equations have been developed for calculating the bottom hole temperatures during acid treatments. By knowing these temperatures, adequate corrosion protection can be provided even in wells with static bottom hole temperatures in excess of 350°F.

5. Alcohol Normal concentration of methyl or isopropyl alcohol is 5 to 20% by volume of acid. The primary advantages of using alcohol is improvement in rate and degree of clean-up. This is particularly helpful in dry gas wells. High vapor pressures and low surface tensions of alcoholic solutions are the two properties that provide these advantages. Unlike surfactants, alcohol doesn't come adsorbed on the rock surfaces. Thus, low surface tensions are maintained throughout the volume of acid used.

6. Gelling and Fluid-loss Materials These materials are generally made up of natural or synthetic polymers. Their purpose is the same as similar additives for water or brine fracturing. In addition, some degree of acid retardation is afforded. Gelling agents that are in common use today are guar gum, gum karya blends and a wide variety of synthetic polymers.

7. Clay Stabilizers This material is used to prevent permeability damage due to foreign water intrusion in water-sensitive formations. The stabilizer functions by permanently holding clay particles together and preventing their movement or dispersion and subsequent particle plugging. It stabilizes all varieties of clays immediately on contact and does it permanently. Formation fluids will not affect or remove the clay stabilizer. It adsorbs principally on clays, has no temperature limitations and can be used in dilute acids, acidic brine or methyl alcohol. The clay stabilizer can be used to stabilize clays after matrix acidizing, prior to gravel packing and as a spearhead for fracturing with fresh water frac fluids.

8. Scale Inhibitors Liquid organophosphates are used in acid clean-up treatments as scale inhibitors with medium term scale protection (4-8 months). They require no expensive well preparations, are stable at temperatures of 300°F and will not revert to an orthophosphate. They prevent the deposition of calcium

sulfate in formations containing anhydrite or highly sulfated connate waters and the reprecipitation of calcium carbonate from basic highly bicarbonated waters. This could insure a successful treatment which could otherwise be ruined by secondary deposition.

9. Acid Dispersions Solvent-in-acid dispersions are used to remove oil and paraffinic deposits from scales or formations during matrix acidizing. The dispersion is designed to give simultaneous organic solvent-acid contact on the scale or formation being treated in a one-stage treatment. The dispersion can be prepared using various mineral or organic acids and aromatic solvents in varying ratios. The dispersion can also be prepared using Versene and an aromatic solvent to remove sulfate scales.

10. Mutual Solvent Surfactants Ethylene Glycol Mono Butyl Ether is a mutual solvent. It is used in matrix sandstone acidizing to water wet the formation. This prevents particle migration and subsequent particle plugging. It also prevents the stabilization of emulsions with fine particles as a nucleus. This improves clean-up and allows the acid to function as it was designed to function. It is also being used in carbonate acidizing and in water-base frac fluids to improve fluid recovery or clean-up.

11. Formation Cleaners This inhibited oxidizing agent is designed to restore permeability to formations damaged by non-petroleum organic residues. These residues may be naturally occurring bacterial slimes or may be gums or polymers which have been introduced into the well. The agent is used in conjunction with HCl or mud acid formulations.

D. Retardation of Acid

1. To achieve deeper penetration, it may be necessary to use a retarded acid. In matrix flow, most retarded acids spend quickly and have limited penetration. Retardation is most effective in fracture acidizing and can be done by:

   --Using a slower reacting type acid (acetic or formic).

   --Adding chemicals to reduce reaction rate of hydrochloric acid.

   a. Using additives to introduce a barrier on the surface of the rock preventing normal contact with the acid.

   b. Additives such as calcium chloride introduce a common ion effect.

   --Increasing the acid concentration to extend spending time.

2. Slow Reacting Type "Retarded" Acids Acetic and formic acids are sometimes used to obtain longer reaction time. The additional cost of these acids may prohibit extensive use. In certain formations, deeper matrix penetration is obtained by the faster reacting HCl since the channeling or wormhole effect produced by the HCl reduces the area-volume ratio, this prolonging reaction time. In fractures, the acetic and formic acids would obtain deeper penetration than HCl; however, larger volumes would be required to dissolve an equivalent amount of rock.

3. Common Ion Effect, Retardation Calcium chloride can be incorporated into HCl to retard reaction rate. High concentrations of $CaCl_2$ are required, up to 1 to 2 pounds/gallon. Such acid solutions also have higher viscosity when spent. This may aid in keeping insolubles in suspended or dispersed form and aid in clean-up. High concentration HCl has a built-in calcium chloride effect and further extends the inherent longer spending time of the concentrated acid.

4. Barrier Effect Method of Retardation Acid-in-oil emulsions generally have retarded reaction rates. The acid in the emulsion is to some extent prevented from completely contacting the rock surface by the presence of an oil film. This is particularly true for emulsions with at least 20% oil as the outer phase. Also, the viscosity of the emulsion tends to restrict flow into the smaller pores; thus minimizing contact with extremely high area-volume ratios. The "channeling" or "wormhole" effect is increased in matrix flow with this type of formulation.

   Certain surfactants have recently been found to be beneficial in reducing reaction rate, and thus extending spending time and distance. These surfactants, in the presence of oil, provide a hydrophobic or water-repellent, oil-like film on the rock surface which restricts acid-rock contact. Dowell's Retarded Avid V and Halliburton's CRA operate through this type of mechanism.

   Fluid loss materials and gelling agents (acid-thickening additives) also tend to reduce the reaction of HCl to some extent by film development on rocks. Diffusion is restricted to some extent by the viscous acids.

5. High concentrations of an acid will have longer reaction times then lower concentrations. First, there is more acid to react; second, the additional reaction products further retard reaction rates; and, third, the enlarged flow path, with reduced area-volume ratio, would tend to extend the spending time and distance of a high concentration acid. For example, 28% HCl may take four to six times longer to completely react than 15% HCl does. In this case, the extended reaction time results in spite of an initially faster reaction rate of the 28% HCl.

E. Methods of Testing Acid

The wide variety of tests used to study acid reactivity with formations can be put into three major categories:

--Static and dynamic methods
--High and low area-volume ratios
--Reaction rate and spending time

1. Although many tests have been based on static (non-flow) or controlled flow procedures in the past, recent trends are to dynamic, controlled flow procedures. The recognition of the importance of fluid flow velocity on acid reactivity has apparently been responsible for this trend. Realistic conditions can be used in such study to more closely duplicate the actual occurrences in a treatment. Complete duplication on a laboratory scale to account for all of the treating factors is impractical. A static spending time on an acid can be approximated by the following equation.

   $$\underset{\text{(Minutes)}}{\text{Spending Time}} \qquad \underset{\text{(in fractures)}}{10{,}000\ C_xW/{}^\circ F} \qquad \text{OR} \qquad \underset{\text{(in channels)}}{5{,}000\ C_xd/{}^\circ F}$$

   The effect of increased injection rates is to reduce this spending of acid but also affect an increase in penetration before the acid spends.

2. Since the area-volume ratio is so high in a rock matrix, actual core flow tests with acid more closely represent acidizing rocks than chunks or pieces of rock do. Of course, flow distribution in the rock itself is of primary importance, also. Acid slot flow tests representing fracture environments have led to many new and improved concepts in acid fracturing. The chemical and physical characteristics of the fluids along with the hydraulic flow properties play important roles in effecting the treatment results. A limit to the size of the test model, core or fracture lengths, in the laboratory studies has limited more exact duplication of reservoir conditions.

3. The relative reaction rates or spending time tests of acids are used to give a basis for treatment recommendations. Generally, a spending time type of test is quite limited in its value. In such tests, many of the field conditions cannot be taken into account. Relative reaction rates can be used to calculate spending times and spending distances of acid. The calculations take into account many more of the factors involved. Such data are used as a guide to planning better acid treatments.

4. Regardless of the test methods and well data available, the data interpretation furnishes information for guidelines that is of only relative value. The final analysis should be made by careful control of treatments followed by a thorough evaluation of actual field results.

III. ACIDIZING TECHNIQUES - ACID TREATMENT DESIGN

The success of any stimulation treatment depends on the correct analysis of the well problem so that proper materials and technique can be selected. Well problems may be classified into two categories:

--Damaged permeability
--Low natural permeability

Wells with damaged permeability are candidates for matrix treatments. Those with low natural permeability are candidates for fracturing as well as perhaps a complementary matrix treatment. Treatment results may be carefully analyzed to determine how subsequent treatments can be improved or optimized with respect to treatment cost vs. results. The results should be evaluated over a significantly long period of time to determine the true values and not just a flush production result.

It is extremely difficult to say that a formation with a certain composition or solubility will or will not respond to an acid treatment. In carbonate formations having more than 50% acid solubility, both matrix-type and fracture-type acid treatments can be applicable. In formations with solubilities less than 50%, these will generally be a sandstone, matrix-type acid treatment using HF/HCl, HCl, or equivalent; however, these formations with limited acid solubility are stimulated more frequently with water or oil fluid rather than with acid.

Acidizing Techniques

There are three fundamental techniques in acidizing treatments:

Wellbore cleanup - A fill-up and soak of acid in the wellbore. Fluid movement is at a minimum unless some mechanical means of agitation is used.

Matrix acidizing - Injection into the matrix structure of the formation below the hydraulic fracturing pressure. Flow pattern is essentially through the natural permeability structure.

Acid fracturing - Injection into the formation above hydraulic fracturing pressure. Flow pattern is essentially through hydraulic fracture; however, much of the fluid does leak off into the matrix along the fracture faces.

A. The terms "wellbore" and "matrix acid" treatments are often used collectively under the single term "Matrix Acidizing". Actually, principles and purposes of both are very similar. The major difference is the spending time of acid in the two techniques. A wellbore soak may require extensive time for reaction, whereas acid contact in the matrix results in almost immediate, complete reaction of acid. The volume of wellbore clean-up treatments is normally restricted to one or perhaps just a few wellbore volume "fill-ups".

B. Matrix Acidizing may be selected as a proper technique for one or more of the following reasons:

--To remove formation damage either natural or induced.

--To achieve low-pressure breakdown of formation prior to fracturing.

--To achieve uniform breakdown of all perforations.

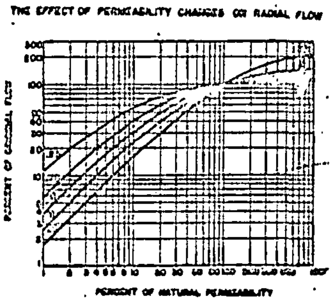
--To leave zone barriers intact.

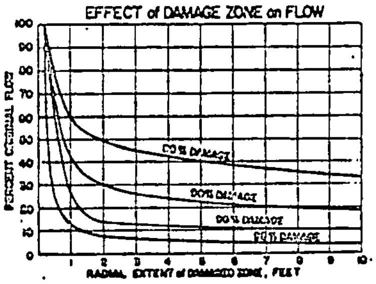
--To achieve reduced treating costs.

Sufficient native permeability should be available to provide desired flow capacity. If the reservoir permeability is limited, then increased productivity must be obtained through a fracturing treatment. The primary purpose of matrix acidizing treatments is to remove and restore natural formation permeability. The type or sources of damage that occurs may be listed as follows:

Mud
Cement
Deposits
Saturation changes
Migration of fines

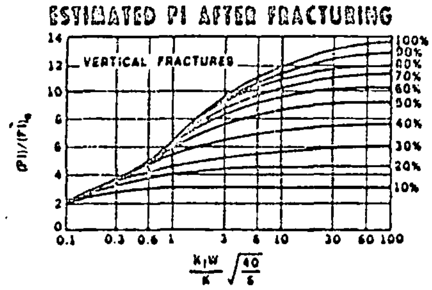
The effect of damage on injectivity or productivity can be illustrated by the following figures. It can be seen that the primary increase in flow occurs by restoring the natural permeability. Increasing natural permeability results in only a limited increase in flow.





C. If sufficient natural permeability is not available from the drainage radius to the well, fracturing should be considered. The primary purpose of fracturing is to achieve injectivity or productivity beyond the natural reservoir capability. An effective fracture may create a new permeability path, interconnect existing permeability streaks, or break into an untapped portion of the reservoir.

The success of any fracture treatment depends on two factors: conductivity and effective penetration, as illustrated in the following figure.



An optimum acidized fracture condictivity exists for an optimum penetration. This, in turn, depends on and is interrelated with the well and reservoir properties, injection rate, type, and volume of acid. Orientation and shape of the fracture are important factors in treatment results, too.

Acid Treatment Design

A. Matrix Acidizing - Carbonate Formations

1. Damage can be removed, and permeability restored, in two ways: First, by dissolving the damaging material itself; or, second, by dissolving part of the rock in which the damage exists. In carbonate rocks with acid solubilities greater than 50%, the latter method is often most effective. The damage, solids or liquids, can then be physically removed in the return of the spent acids to the well.

2. HCl or its equivalent is normally used in carbonates, but should be modified to meet special situations. Acetic or formic acid should be considered for wells with temperatures in excess of 250°F to 300°F. Since the extent of damage is not normally too great, penetration-wise, the volume of acid needed is small. With a formation porosity of 10%, 60 gallons of acid per foot of section are required to fill the porosity to a distance of 5 feet from the wellbore. Usual matrix treatment volumes range from 10 to 300 gallons per foot of section. If damage is deeper than 5 to 10 feet, larger volumes of acid, a means of retarding reaction rate, or perhaps fracturing techniques, may be required. Only a small fraction of rock needs to be dissolved to result in a significant amount of damage repair or permeability increase. To remove only 1% of limestone or dolomite for a distance of about 5 feet of a well requires only 70 gallons of 15% HCl/ft. of vertical interval.

a. Acid inhibitor selection must be based primarily on treating temperature and, to some extent, on the type of acid formulation.

b. Surfactant type and concentration should be selected to prevent emulsion tendencies and perhaps to aid in dispersing fine solids that are not dissolved. These may be mud or cement solids, or natural material released from the formation. Suspension and removal of these materials can play an important part in the overall treatment results.

c. Diverting agents may be used to promote uniform penetration in long sections. Acid-swellable synthetic polymers, controlled-solubility particulate solids, balls, gel slugs, etc., have been used successfully. Assuring the distribution of acid into the entire interval is a critical part of carrying out a matrix treatment. Without uniform distribution, large portions of the interval may get very little if any acid.

3. Preferably, injection rates should be controlled so that the formation is not fractured. The use of as high a rate as possible without exceeding the fracturing pressure is recommended. In certain cases, it may be necessary to create a fracture to open perforations, after which pressure can be reduced below fracturing pressure, thus providing a matrix flow pattern.

   Actually, injection pressure and not rate is a more correct factor to consider. A control of bottom-hole pressures below hydraulic fracturing pressures may restrict injection rates to only fractional barrels/min., but may allow an increasing rate as the treatment progresses.

4. Penetration of acid in a carbonate rock is far from uniform. In most every rock, especially carbonates, the pores are different sizes and shapes. The porous structure may be in the form of vugs, hairline fissures, or tortuous capillary-like pores. Because of these heterogeneities, a "channeling" or "wormholing" occurs with most any acid formulation. The resultant effect is the attainment of much greater acid penetration of matrix than expected.

   The following example illustrates the wide distribution of flow in a rock of varying pore diameters. Acidizing would further accentuate the flow distribution.

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

As discussed in a preceding section, the fast-reacting hydrochloric acid may be much more efficient in regard to penetration of the limestone matrix than the slow-reacting acetic, but not as great as with the emulsified acids. Evidently, the slow reaction of acetic acid does not change the flow distribution rapidly enough to "channel"; but rather results in several small pore enlargements for short distances as opposed to a few large, long channels. The highly restricted penetration thought to exist with various acids may not exist to the extent previously believed.

5. An overflush in the matrix acidizing treatment is recommended. This will assure placement of the acid efficiently into the matrix. A minimum shut-in time is recommended prior to returning the spent acid to the well. Since the spending time of acid is short, a long shut-in time of several hours is not necessary--even for the so-called "retarded" acid. Such practices may lead to an incomplete clean-up and a less effective treatment. The overflush fluid may be brine, water, oil or a weak acid. Enough volume should be used to insure maximum penetration of the last portion of the acid before it is spent.

B. Matrix Acidizing - Sandstone Formations

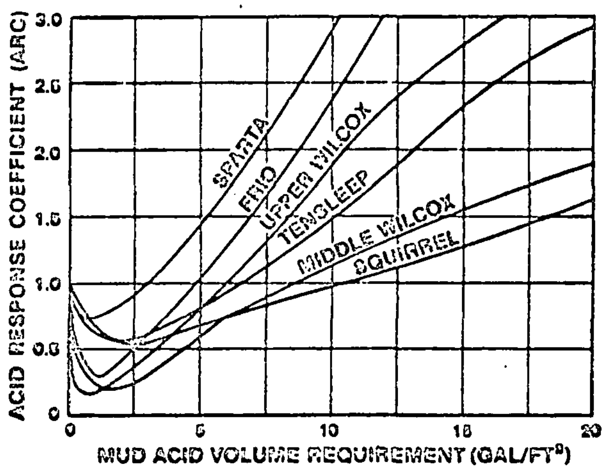
1. The purpose of sandstone acidizing is to restore permeability by dissolving away formation damaging clay-like minerals or other materials. The clay may be inherent in the formation, or may be the result of drilling or workover activities. X-ray analysis can be used to determine the type and amount of clay present. Not only the type and amount are important factors, but the physical rock structure also plays an important role.

2. The type of acid most often used in sandstones is a mixture of HF and HCl (Mud Acid). Concentrations of 2 to 6% hydrofluoric acid (HF), and 8 to 12% hydrochloric acid (HCl) are normally used. If a significant amount of $CaCO_3$ is present in the formation (5 to 10%), a spearhead of HCl should be used to react with it before the HF/HCl is injected. With $CaCO_3$ content above 20%, HF acid is probably not needed except to give entry through a clay damage.

3. As in any matrix-type treatment, injection of the HF/HCl should be below fracturing pressure. Acid fracturing treatments in sandstones are not too applicable. Etching of the fracture faces for development of fracture conductivity normally does not occur in sandstones. In a few soft, unproppable sandstones, large fracturing treatments with HF/HCl formulations have been performed to create a highly permeable matrix lens along the fracture faces.

4. The volume of acid required depends on the depth of damage and degree of damage. 50 to 150 gallons of acid per foot of interval is a normal treatment volume if damage is not extensive. An acid solubility test, made by exposing excess acid to a ground-up core specimen, may not be a realistic evaluation of acid requirements.

A core flow test with the acid gives a more realistic picture of the response the formation will have to acid. The acid response coefficient (ARC) is a measure of the relative change in permeability of a core caused by acid injection. This is illustrated by the following date. Although some of these formations have approximately the same acid (HF/HCl) solubility, permeability and porosity, the response to acid is quite different. Each formation requires a different amount of acid.



The initial reduction in permeability is a common occurrence observed with many formation core flow tests. It is attributed to sloughing particles (clays, silica, fines, etc.) that apparently bridge in the flow channels and restrict flow prior to their further reaction with the acid. An inadequate acid volume treatment could lead to a restricted permeability in a formation if the bridging is severe.

5. Since secondary reactions may occur, resulting in possible precipitation of damaging reaction products, Mud Acid should be returned to the wellbore as soon as the initial spending time has elapsed. These materials have not proved to be of serious concern in most treatments. <u>However, preparing or comingling of HF/HCl acids with brine should be avoided.</u>

6. Inhibitors, surfactants and diverting methods should be selected just as in an HCl acid treatment.

7. As in the case of a matrix acid treatment in carbonates, an overflush is recommended. Type of fluid used may be a weak acid, oil, or water. In the latter cases, tests for compatibility problems should be made. Brine should not be used to overflush HF/HCl. Short shut-in times should be used—a few hours at the most.

C. Fracture Acidizing - Carbonate Formations

1. The primary purpose of a fracturing treatment is to achieve productivity, or injectivity beyond the natural capabilities

of the reservoir. It is most applicable in formations with low and/or ineffective permeability structure. The effectiveness of an induced hydraulic fracture is a function of both its conductivity and penetration of the drainage radius of a well. These two factors are closely interrelated to each other and to the reservoir properties.

2. The purpose of a guide for designing effective acid fracturing treatments is: "To correlate the many factors that can be considered in design factors such as reservoir characteristics, chemical and physical properties of acid formulations, and mechanical techniques of the operation." The ACID GUIDE consists of three basic steps:

   a. Achieve an effective fracture area --

      Parameters include: Folds of increase desired
      Fracture shape
      Fluid coefficient
      Injection rate
      Fluid volume required

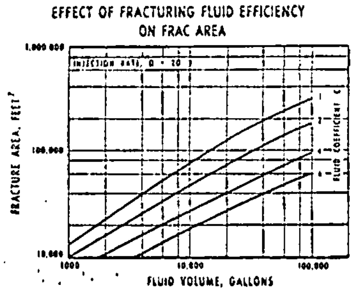
   b. Be sure acid penetrates effectively --

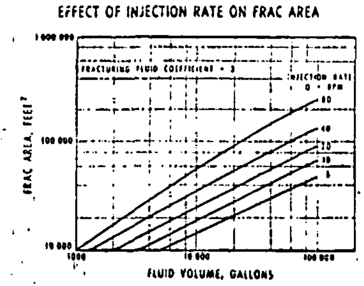
      Parameters include: Fracture shape
      Effective injection rate
      Type of acid required

   c. Create enough conductivity --

      Parameters include: Type acid
      Injection rate
      Acid volume required

3. An effective fracture area is related to an effective penetration of the reservoir through its orientation and shape. Fracture area created is directly proportional to pump rate and inversely proportional to fluid efficiency, as shown by the following figures.





Additives to obtain a high overall efficiency for creating fracture area include friction control materials, fluid-loss additives, diverting agents, etc.

4. The factors governing acid reaction rate with the formation are important in determining the distance acid penetrates before it is spent. Spending distance may be related to injection rate and fracture shape, and width as well as the type of acid and reservoir properties, according to the following equations:

For linear fracture flow --

Spending Distance $= 33.5\ Q_e t/hW$

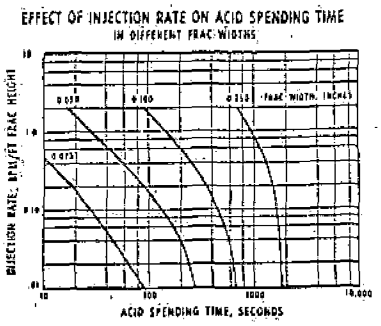
Percent of Acid Reaction Completed $= 100\{1 - e^{-\{1 + (Q/h)^{0.8}/10W^{1.6}\}}\ 1.92 \times 10^{-4} C_A t/W\}$

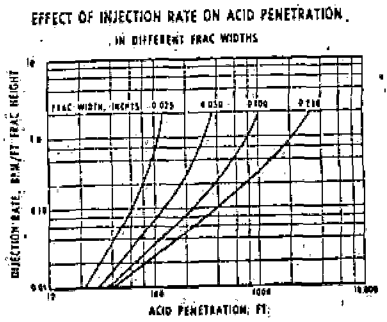
For radial fracture flow --

Spending Distance $= (21.4\ Qt/W)^{1/2}$

Percent of Acid Reaction Completed $= 100\ \{1 - e^{-\{1 + Q^{0.4}/52W^{1.6}t^{0.4}\}}\ 1.92 \times 10^{-4} C_A t/W\ \}$

The data in the following figures were obtained from these equations - A C_A of 1 in a vertical linear fracture was used for illustration.





It can be seen that penetration of acid before it is spent increases at increased injection rates and in wider fractures. It is of interest to note that the spending times at the higher injection rates actually are much shorter than the lower injection rates. Spending time, therefore, is not a direct guide to acid treatment design. Some degree of retardation may be necessary to obtain the desired penetration of the acid before it is spent. To obtain efficient use of acid, an overflush and a minimum shut-in time should be used in most all cases. The amount of overflush (non-acid fluid) will depend upon the spending time of the acid.

5. In an acid fracturing treatment, propping agents are not necessarily used to provide fracture support for conductivity. The reaction of acid with the fracture faces is normally very uneven. This heterogeniety, or etching characteristic, provides roughened surfaces which, in turn, prevents the fracture from fully closing. Thus, after the hydraulic pressures are released, a highly conductive fracture flow capacity may exist. Enough acid strength and volume must be used to produce sufficient dissolving action and provide the required conductivity. The etching reaction rate of acid is illustrated by the following equations:

For linear fracture flow of 1.5% HCl --

$$\text{Etching rate, in/min.} = \{15.2\ (Q/hW^2)^{0.8} + 156\}\ C_A \times 10^{-6}$$

For radial fracture flow of 1.5% HCl --

$$\text{Etching rate, in/min.} = \{6.1\ (Q/r_f W^2)^{0.8} + 156\}\ C_A \times 10^{-6}$$

Fracturing Conductivity --

$$K_F W,\ \text{D. Ft.} = 4.5 \times 10^6 W^3$$

Nomenclature for terms in the equations as they appeared in this outline are listed below:

V,	acid flow velocity, ft./sec.
W,	fracture width, in.
Q,	effective injection rate, BPM
n,	n number of channels or fractures
h,	fracture height, ft.
d,	channel diameter, in.
t,	acid spending time
C_A,	acid coefficient (relative reactivity)
r_f,	fracture penetration

IV. SUGGESTED READING REFERENCES

1. Lehnhard, P. J.: "Mud Acid--Its Theory and Application to Oil and Gas Wells", Petr. Engr. (1943), Annual Issue, pp 82.

   It is the purpose of this paper to show that large increases in the productivity of sand wells treated with mud acid are due to the reduction or elimination of abnormally high pressure drops near the bore hole of the well; and that only small increases in productivity may be obtained in most instances unless such abnormal pressure drops occur. It is shown that some oil sands contain clay or bentonitic material that has the ability to hydrate or swell when in contact with water, and that hydration of such materials in the sand will cause a reduction in its permeability. The paper points out that screens or perforated liners, gun perforations, and hydration of clay materials in the sand near the bore hole may all cause abnormally high pressure drops near the well.

   It is also intended that the paper should be a resume of field experience with mud acid to date, together with conclusions reached as a result of more than two years of the commercial application of mud acid to oil and gas wells.

2. Rowan, G.: "Theory of Acid Treatments of Limestone Formations", Jr. Inst. Petr., 45, No. 431 (1959).

   This paper is devoted to the study of the problem of the increase in permeability of porous limestone formations due to acid treatment and proposes a theory of the process under certain simplifying assumptions. These assumptions are similar to those adopted for the prediction of permeability from pore size distribution data.

   This approach is based on non-uniformity of pore structure, in recognition of the fact that, in general, the effective pore structure may be expected to be composed of a distribution of pore sizes. Calculations based on the proposed theory appear to be in better accord with the results of laboratory investigations.

   The results of this study demonstrate the dominant effect of the larger pores and the rapid increase in permeability obtainable when a distribution of pore size is present. It appears inevitable that the major portion of the acid ultimately passes through only the large pores and, in view of their great contribution to the overall permeability, any attempt to block them off, in the hopes of attaining more uniform acidizing, must result in a lower permeability increase and a less economical employment of the acid.

3. Pollard, P.: "Evaluation of Acid Treatments from Pressure Build-up Analysis", Trans. AIME (1959), 216, 38.

   A method has been developed for evaluating acid treatments in fractured limestone fields by breaking down pressure drawdown into three component parts: (1) pressure differerential across "skin" near the bore hole face; (2) pressure differential due to flow resistance in the coarse communicating fissures; and (3) pressure differential between the fine voids and the coarse fissures.

   It is apparent that in most successful acid treatments the first term, skin resistance, has been reduced or eliminated. Further, it is often possible to estimate the volume of coarse fissures associated with the second term, coarse fissure flow resistance. In cases where this volume is comparable with practical acid volumes, it seems likely that this resistance also may be attacked with a suitably retarded acid.

4. Hendrickson, A. R., Hurst, R. E., and Wieland, D. R.: "Engineered Guide for Planning Acidizing Treatments Based on Specific Reservoir Characteristics", Trans. AIME (1960) 219, 16.

   Analysis of acidizing techniques, in correlation with reservoir data and a backlog of past treatments, has resulted in the development of a valuable engineering guide for planning acidizing treatments. Such treatments fall into three categories: acid injection into the pores of the matrix; acid injection into natural formation fractures at less than parting pressure; and combination acidizing-fracturing treatments in which acid solutions (without propping agents) are injected at treating pressures sufficient to open and extend fractures through which the acid flows.

5. Dunlap, P. M., and Hegwer, J. S.: "An Improved Acid for Calcium Sulfate Bearing Formations", Trans., AIME (1960), 219, 339.

   An improved acid for the treatment of sulfate-containing limestones and dolomites is described. The acid is designed to reduce the reprecipitation of dissolved calcium sulfate and the possibility of plugging permeable flow channels. In addition, this improved acid has a much lower reaction rate than that of regular acid; the advantages of a "retarded" acid are obtainable.

   Field testing of the acid has shown it suitable for use in sulfate-containing formations. Substantial improvements in productivity generally resulted.

6. Harris, F. N.: "Application of Acetic Acid in Well Completion, Stimulation and Reconditioning", Jr. Petr. Tech. (Feb. 1960), 12, No. 2, 16.

The use of acetic acid as a solution in the treatment of wells is not new. However, its applications now are greater than ever before. The chemical properties that can be imparted from this organic acid are remarkably suitable in dealing with many present day problems encountered in well completion and stimulation procedures.

The corrosive action of acetic acid can be greatly minimized, even at temperatures in excess of 240°F. The acid-pipe contact times now can be extended for days with the proper organic inhibitors.

A variety of treating mixtures of this acid have been used successfully many times in the past few months. These uses have been as a (1) perforating fluid, (2) retarded acid without viscosity, (3) treatment for removal of carbonate scale in the presence of chromium plated pump parts, (4) stimulation treatment in the presence of aluminum metal at elevated temperatures, (5) "kill" fluid for wells, (6) weak aqueous solution for carrying surfactants to remove emulsions and waterblocks in the presence of water-sensitive clays, (7) first-stage treating fluid ahead of hydrochloric acid for a greater drainage pattern, and (8) transitory true gel or emulsion for placement of temporary bridging agents.

7. Hendrickson, A. R., Rosene, R. B., and Wieland, D. R.: "The Role of Acid Reaction Rates in Planning Acidizing Treatments", Trans., AIME (1961), 222, 308.

The spending time of acid with carbonate rock is dependent upon many variables. The effect of pressure velocity, acid concentration, area-volume ratio, as well as physical and chemical structure of the rock is reported. Acidizing treatments may be classified into three general categories: acid injection into matrix pores, into natural formation fissures, and into opened and extended fractures at elevated hydraulic pressures.

An important aspect of preplanning an acidizing treatment is to gain an insight into these reaction parameters and possible techniques so that an optimum design can be achieved.

8. Barron, A. N., Hendrickson, A. R., and Wieland, D. R.: "The Effect of Flow on Acid Reactivity in a Carbonate Fracture", Jr. Petr. Tech. (Apr. 1962), 409.

A definite relationship has been found between the reactivity of flowing hydrochloric acid and its shear rate in a carbonate fracture. Both flow velocity and fracture width affect the acid reaction rate. Laboratory studies were conducted on acid reactivity at different flow velocities through horizontal-linear fractures, using 15 percent hydrochloric acid at 80°F. and approximately 1100 psi. Fracture width varied from 0.02 to 0.20 in. These date provide a new basis from which the spending time and penetration of the acid can be estimated. Equations were derived expressing the relationship between injection rate, fracture width, acid concentration, time and fracture height, for linear and radial fracture systems. Because the penetration of the acid before spending is closely related to the extent of productivity increase resulting from an acidizing treatment, these data provide a valuable insight into some of the controlling factors that must be taken into consideration during treatment preplanning.

9. Bleakley, W. B.: "CO_2 - A New Shot in Arm for Acid, Frac Jobs", The Oil & Gas Jr. (Oct. 8, 1962).

Experience gained through some fifty jobs performed to date shows several advantages in the use of CO_2 as an additive in well-stimulation jobs.

Wells are back on production quickly.

Large volumes of CO_2 can be used without danger of screenout during fracture jobs.

Corrosion is no problem.

No shock-absorber effect--full hydraulic horsepower is applied to the formation.

Cost is relatively low.

CO_2 retards formation damage.

10. Lasater, R. M.: "Kinetic Studies of the HCl-$CaCO_3$ Reaction", presented at the 18th Southwest Regional ACS meeting in Dallas, Texas (Dec. 1962).

The experimental data which have been presented show that a first order kinetic is followed for up to one half of the reaction time. A change to about one and one fourth order occurs during the last half of the reaction. This data is compared to the Powell plot method of kinetic reaction data comparison.

11. Grubb, W. E., Martin, F. G.: "A Guide to Chemical Well Treatments", Reprint from Petr. Engr. (1963)

Contents:

Part 1: Know the Well, the Treatment and What to Expect
Part 2: Know More About Formation Damage
Part 3: Handy Guide to Treating Chemicals
Part 4: Some Acids--Their Uses and Mis-Uses
Part 5: Other Acids--Their Uses and Mis-Uses
Part 6: How and When to Use Surfactants
Part 7: How to Interpret Treatment Results

12. Ross, W. M., Pierson, N. O., and Coulter, A. W.: "Matrix Acidizing Corrects Formation Damage in Sandstones", Petr. Engr. (Nov. 1963), 35, No. 12, 36.

Matrix acidizing is a new, field-proven technique to correct producing formation damage incurred while drilling or cementing sandstones. It is the result of two significant modifications in conventional Mud Acid treatments to overcome "skin effects" around the wellbore. Key to the new acidizing method is a recently-developed, granular, synthetic polymer that swells upon contact with acid and serves as an effective fluid loss control additive. The other principal change in mud acidizing is in the application of injection pressures. During treatment, the bottom-hole pressure is maintained below fracture pressure in a manner similar to that applied when performing low-pressure, low-water-loss cement squeezes. The idea is to force acid to enter the formation through individual formation pores to remove damage and restore natural permeability.

13. Knox, J. A., Lasater, R. M., and Dill, W. E.: "A New Concept in Acidizing Utilizing Chemical Retardation", SPE 975 presented at the 39th Annual Fall Meeting SPE-AIME, Houston, Texas (Oct. 1964).

Establishing a technique to compare the reaction times of various types of acid solutions on limestone was the first phase in the development of a new method for retarding acid. With a critical comparison available, the well-known approaches could be more properly evaluated.

The limitations of the available methods of retardation became obvious and pointed out the necessity of finding a better way to retard acid.

Reaction times, using the new system, of up to 3 hours at 200°F on pure limestone formations have been observed. The effect of chemical type, temperature, pressure and surface area to volume ratio was studied.

A possible theory describing the mechanism for this type of retardation is discussed.

14. Smith, C. F., Hendrickson, A. R.: "Hydrofluoric Acid Stimulation of Sandstone Reservoirs", Jr. Petr. Tech.(Feb. 1965, 27, No. 2, 215.

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

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

Extensive deposition of calcium fluoride in acidized cores was not observed. Although some FaF_2 was detected, it was not considered a major source of damage in cores containing moderate amounts of carbonate. Other fluosilicates could be potentially more dangerous than CaF_2 in reducing permeability.

15. Horton, H. L., Hendrickson, A.R., and Crowe, C. W.: "Matrix Acidizing of Limestone Reservoirs", API No. 906-10-F presented at Spring Meeting of API in Dallas, Texas (March, 1965).

Matrix Acidizing is a technique of injecting various acid formulations into a formation at rates low enough to prevent pressures from exceeding the formation failure pressure. This technique of treating provides advantages over fracture treating in that costs are reduced and productive zone boundaries protected.

The factors primarily affecting spending time of acid and the penetration pattern during this type of treatment of a limestone reservoir are the area-volume ratio and the pore space distribution within the rock. With a knowledge of these factors and the reservoir problem, matrix acidizing can often be effectively and economically applied in limestone reservoirs without the inherent dangers of fracturing.

16. Broddus, E. C., and Knox, J. A.: "Influence of Acid Type and Quantity in Limestone Etching", No. 851-39-1 presented at the API Spring Meeting, Wichita, Kansas (March-April, 1965).

The satisfactory stimulation of oil and gas producing wells by "Fracture Acidizing" is dependent upon development of adequate flow capacity in naturally occurring or induced fractures of sufficient areal extent.

The flow capacity is either obtained or improved through the action of the acid on the exposed fracture faces. The type and quantity of acid used in a treatment greatly influence the pattern and degree of etching. Data is presented which illustrate the influence of acid type and quantity on limestone etching. The type of etch consequently affects the fracture flow capacity.

17. Davis, J. J., Mancillas, G., and Melnyk, J. D.: "Improved Acid Treatments by use of the Spearhead Film Techniques", SPE No. 1164, Presented at the Rocky Mountain Regional Meeting in Billings, Montana (June, 1965).

A new treating procedure has been developed which uses additives in a spearhead fluid ahead of the acid treatment to create new fractures and to form an acid-dispersible seal on all exposed formation surfaces. The specially compounded additives are only slowly dispersible in acid and their presence on the exposed formation and fracture surfaces inhibits the chemical reaction until after the entire treatment volume has entered the formation. Additives used with the spearhead technique improve the overall efficiency of an acid treatment.

18. "New 'Beads' Help Acidizing, Fracturing", Oil & Gas Journal, (Aug. 30, 1965), 52.

Wax-based pellets developed by Union Oil improve multiple fracture patterns in single operation and permit better control of acidizing.

Union Oil Company has developed a new and highly effective method of improving fracturing and acidizing operations. Using was-based pellets called "unibeads", Union is achieving multiple fracture patterns in a single operation and is controlling acid so that it works over the entire face of the exposed wellbore.

The beads function as a temporary sealing agent, plugging any opening in the wellbore through which fluid will pass.

In fracturing, they will plug the fracture as soon as it is created and propped open, permitting the operator to fracture a second or third, or even a fifth or sixth time during the same operation.

In acidizing, Unibeads plug any hole created, preventing the acid from being drained off into the formation at a single point and forcing it to attack other areas of the wellbore.

The beads are soluble in oil and, within hours after completion of the fracturing or acidizing operation, they dissolve and reopen all of the passages which have been plugged.

19. Moore, E. W., Crowe, C. W., and Hendrickson, A. R.: "Formation, Effect, and Prevention of Asphaltene Sludges During Stimulation Treatments", Jr. Petr. Tech. (Sept. 1965), 1023.

Formation of asphaltic sludge during acid stimulation has been a serious problem in many areas for several years. Such sludges have had adverse effects on the results of treatments in many reservoirs of the United States, particularly in California and the Rocky Mountain Region. Recent studies have shown that sludge may also affect results in many areas where it has not yet been recognized as such. These studies indicate that: (1) Sludge is a precipitate of colloidal materials present in crude oils; (2) The precipitates occur due to changes in environmental conditions of the crude by addition of materials such as acid; (3) Once formed, sludge is insoluble in most treating chemicals; and (4) Sludge can be prevented or controlled by use of stabilizing agents in treating fluid or by use of certain solvents as the outer phase of acid-in-oil emulsions.

This paper shows how and why sludge is formed and how it can be prevented or controlled. Simple laboratory tests to determine the probability of sludge formation prior to treatment are discussed.

20. Smith, C. F., Ross, W. M., and Hendrickson, A. R.: "Hydrofluoric Acid Stimulation - Developments for Field Application", SPE No. 1284 presented at 40th Annual Fall Meeting of SPE-AIME, Denver, Colorado (Oct. 1965).

Use of hydrofluoric-hydrochloric acid mixtures in matrix treatments of sandstone reservoirs can provide economical and effective stimulation in many areas. Laboratory data of HF-HCl reactivity in many types of formations have been expanded and and applied to actual field tests to obtain a correlation on which to base treatment recommendations. Knowledge gained has led to methods of determining the most efficient acid volume requirement for specific reservoir conditions and development of better techniques for uniform placement of acid in the formation.

21. McLeod, H. O., McGinty, J. E., and Smith, C. F.: "Alcoholic Acid Speeds Clean-Up in Sandstones", Petr. Engr. (Feb. 1966).

Alcoholic Mud Acid, a hydrofluoric-hydrochloric acid mixture containing alcohol is proving highly successful in stimulating production from "problem wells" in sandstone formations. Primary advantage of this acid is the better and more rapid "clean-up" properties provided by the added alcohol. It is particularly useful in gas-producing formations, but has proved effective in oil-producing formations as well.

Many acid treatments in sandstone which would otherwise be quite successful are spoiled by a very slow spent-acid clean-up. This clean-up problem is often the result of waterblock in the critical matrix surrounding the wellbore. The addition of alcohol to the acid can often prevent this water-blocking problem and also can impart other desirable properties to the acid.

22. "Atomized Acid Treats Problem Wells", Oil & Gas Jr. (June 6, 1966).

A new concept in acid treatment is showing good results in problem wells where normal treatment methods can't be used--or where these normal methods fail to stimulate a well.

The new technique, developed by Nitrogen Oil Well Service Company (NOWSCO), involves automation of acid by injecting it into a stream of nitrogen gas through a specially designed high-pressure atomizer. The gas/liquid ratio is adjusted so that at bottom-hole conditions the nitrogen gas is the continuous phase of a two-phase treating fluid entering the formation.

This technique is not claimed as a cure-all, but the results shown in the table indicate that it can be a useful tool when properly applied.

23. McLeod, H. O., McGinty, J. E., and Smith, C. F.: "Deep Well Stimulation with Alcoholic Acid", SPE 1558 presented at the 41st Annual Fall Meeting SPE-AIME, Dallas, Texas (Oct. 1966).

A hydrofluoric-hydrochloric acid mixture containing an alcohol has proven to be highly successful in stimulating production from "problem wells" in sandstone formations. The primary advantage of this acid is the better and more rapid "clean-up" properties provided by the added alcohol. It is particularly useful in gas producing formations, particularly those with a high clay content.

Many acid treatments in sandstone which would otherwise be quite successful are spoiled by a very slow spent acid clean-up. This clean-up problem is often the result of waterblock in the critical matrix surrounding the wellbore. The addition of alcohol to the acid can often prevent this water-blocking problem and also can impart other desirable properties to the acid.

24. Harris, O. E., Hendrickson, A. R., and Coulter, A. W.: "High-Concentration Hydrochloric Acid Aids Stimulation Results in Carbonate Reservoirs", Jr. Petr. Tech. (Oct. 1966), 18, No. 10, 1291.

Use of high concentrations of hydrochloric acid in fracture acidizing treatments has solved the stimulation problems in many stubborn reservoirs and has improved results in many others. Treatments of this type were first designed for injection wells in the Aneth Field in Utah about a year ago.

Their use has now spread to many areas throughout North America. Success of the treatments has led to a re-evaluation of the role of acid concentration in stimulation by acidizing. Extensive laboratory studies and wide-spread field experience have uncovered many new facts concerning acid concentration and have shown that some of the older assumptions are not true at all.

This paper presents the technology of acid concentration and factors involved in using high concentrations. Advantages of the strong acid are discussed, as well as the problems (such as inhibition and additive compatibility) encountered in its use. Actual field examples are used to substantiate the work done to the present time.

25. McLeod, H. O., and Coulter, A. W.: "The Use of Alcohol in Gas Well Stimulation", SPE 1663 presented at the Annual Eastern Regional Meeting SPE-AIME, Columbus, Ohio (Nov. 1966).

Alcohol when added to stimulation fluids will reduce or eliminate waterblocking following these treatments. Although waterblocking can occur in clean, well consolidated sandstone, it is more likely to occur with other forms of damage such as particle blocks or rock wettability changes. Water blocking is most severe in heterogeneous formations particularly where high permeability variations are in series such as in crossbedded sediments. Alcohol has been successfully used in waterblock removal, matrix acidizing, and hydraulic fracturing. Properties of alcoholic fluids and detection of heterogeneity are discussed. Guidelines for selecting the best alcoholic treatment are presented.

26. Kincheloe, R. L.: "Matrix Acidizing Reduces Formation Damage", Petr. Engr. pg 74 (Jan. 1967).

When production from a well is below the desired or expected level, a pressure build-up test should be conducted for determination of formation damage. If this test indicates any significant amount of damage, the matrix acidizing technique may be employed as a remedy. The technique has proven to be very effective in increasing the productivity of a well and can be done at minimum expense and risk. The treatment is not a cure-all; however, it has an application in the Gulf Coast Lower Wilcox sands under certain qualifying conditions.

27. Raymond, L. R., Binder, C. G.: "Productivity of Wells in Vertically Fractured, Damaged Formations", Jr. Petr. Tech. (Jan. 1967), 120.

One primary purpose of hydraulic fracturing as a well stimulation technique is to overcome formation damage. The literature provides ways of designing fracture treatments and evaluating their results but not of incorporating formation damage in vertically fractured wells. Results of an investigation of this problem are presented in this paper . . . An example fracture design and evaluation problem indicates the usefulness of considering formation damage in planning well stimulation jobs. When damage exists, but its extent and the degree of permeability reduction are not estimated from diagnostic tests, the formation permeability used in planning the job may lead to under-designing. As the example shows, too low a target stimulation ratio can lead to much lower production rates (by half) than could be attained otherwise.

Solutions of equations representing several special cases of the mathematical model are presented in graphical form and details of the derivations of the equations are given in the Appendix.

28. Smith, C. L., Ritter, J. E.: "Engineered Formation Cleaning", Paper No. 801-43B presented at the API Spring Meeting, Los Angeles, California (May 1967).

The problem of restricted productivity caused by drilling mud or filtrate invasion can be solved by corrective chemical treatment. By using well and laboratory data and a few simple laboratory tests, an engineered approach can provide custom-made chemical treatments that will help in restoration of damaged productivity or injectivity. Tables of commonly used mud removal chemicals and types of formation damage that respond to chemical action with charts on some formation characteristics help to make engineered formation cleaning a reality.

29. Veley, C. D.: "How Hydrolyzable Metal Ions Stabilize Clays To Prevent Permeability Reduction", SPE No. 2188 presented at the 43rd Annual Fall Meeting SPE-AIME, Houston, Texas (Sept. 1968).

The principal cause of water-sensitivity is dispersion and movement of clay particles. This dispersion is brought about by expansion of tiny cation "atmospheres" around each clay particle.

Hydrolyzed metal ions prevent clay dispersion by displacing the exchangeable cations and becoming firmly attached to clay surfaces. Formations treated with soluble compounds of hydrolyzable metals are highly resistant to permeability damage from clay movement.

Polyvalent metals hydrolyze through formations of multiple hydroxyl bridges (olation polymerization). The actual ions present in hydrolyzable metal solutions may be complex and have a charge of +6, +8 or more, per ion. The high net charge of these ions causes them to be very strongly attracted to clay surfaces.

Soluble compounds of hydrolyzable metals have effectively combated formation water sensitivity both in laboratory and field tests.

30. Smith, C. F., Nolan, T. J., and Crenshaw, P. L.: "Removal and Inhibition of Calcium Sulfate Scale in Waterflood Projects", SPE No. 1957 presented at the 42nd Annual Fall Meeting SPE-AIME, Houston, Texas (Oct. 1967).

The problem of preventing calcium sulfate scale deposition has been gaining prominence in the last few years with the increasing use of waterflood as a means of secondary recovery. Many methods have been proposed for removing and/or preventing scale deposition. A few chemicals and treatment methods have been effective while others of dubious value continue to be used in scale control applications where operators have not tested the effectiveness of the materials and techniques being used. There are many ineffective scale removal agents and inhibitors on the market today. This paper describes the results of the laboratory testing program which evaluated 98 potential scale inhibitors and 20 scale removal agents. The paper also describes a field testing program in which various removal methods and inhibitor placement techniques were evaluated in a 19 well test program. The results of this field program are described and comparative laboratory results are shown.

Liquid scale inhibitors have often failed to gain acceptance because they won't stay in the formation long enough to "pay out" the treatment. Although the inhibitor may be chemically effective in preventing scale, it must be formulated to "stick" in the formation and it must be placed in the zone in such a way that it will stay. Even under optimum conditions, liquid scale inhibitors afford protection for an average 7 - 9 months. Lifetime of the inhibitor depends on water-oil production and varies considerably with well conditions.

31. Smith, C. F., Crowe, C. W., and Nolan, T. J.: "Secondary Deposition of Iron Compounds Following Acid Treatments", SPE No. 2358 presented at the Eastern Regional Meeting SPE-AIME, Charleston, West Virginia (Nov. 1968).

Recent laboratory and field research studies have been conducted to determine the nature of iron precipitation from spent acid and evaluate the sequestering agents commonly used to prevent secondary deposition.

It was found that iron can be put into acid solutions from three sources: (1) corrosion, (2) iron scales, and (3) minerals in the formation. It was shown that total iron in solution was not as important as the Fe^{++}/Fe^{+++} ratio. This ratio dictates precipitation potential in the critical pH range of 2.2 - 6.8. It was further noted that rapid reduction of Fe^{+++} occurs in acid solution contained in N80 steel pipe. The oxidation potential causes a shift in iron ratio and greatly reduces the amount of potentially damaging Fe^{+++} expected to precipitate. Tests were developed to determine the effectiveness of presently marketed iron stabilizing agents to include lactic acid, acetic acid, citric acid and EDTA salts.

Field test data were obtained and showed that iron precipitation is a potential hazard to effective acidizing treatment, but is not routinely as bad as expected from total iron content of spent acid samples. Many stabilizing agents are being overused in well treatments and some of these agents, such as citric acid, will form a calcium citrate precipitate when iron (III) is present in the quantity estimated.

32. Smith, F. C., Crowe, C. W., and Wieland, D. R.: "Fracture Acidizing in High Temperature Limestone", SPE No. 3008 presented at the 45th Annual Fall Meeting SPE-AIME, Houston, Texas. (Oct. 1970).

During the past few years, concentrated hydrochloric acid has proved to be better than less concentrated acid in providing improved etch patterns and deeper live acid penetration. However, adequate inhibition of the acid becomes a problem at BHT above 300°F. Various organic acids and HCl-organic acid mixtures have been used to increase total acidity at high temperature, but acid fracturing results are about the same as those expected from 15 per cent HCl.

Recent laboratory studies have been conducted to determine the properties of the commonly used "retarded" acid systems in treating high-temperature formations. Results indicate the boost in acid concentrations from adding an organic acid to HCl is largely offset by a kinetic limitation of reaction whereby carbon dioxide formed by the primary reaction of the acid with limestone prevents complete reaction of the organic acid. Thus, addition of 5 per cent organic acid will result in a reaction of only 2 per cent to 3 per cent of this acid until the carbon dioxide is removed from solution by pressure release. It was further shown that mixing acids did not affect the individual acid's reaction with limestone.

Concentrated HCl provides the distinct advantage of improved etch pattern and deeper live acid penetration. The world's record producing gas well (Hunton Lime) was acidized with 28 per cent HCl. BHT was in excess of 350°F. The problem with 28 per cent HCl is adequate inhibition. Arsenic inhibitors are ineffective in HCl above 17 per cent concentration. Organic inhibitors give two hours' protection, so their use with concentrated HCl requires the use of a water pad to cool the pipe. No corrosion problems have been encountered with this technique, but the use of concentrated acid with its limited inhibition leaves small room for error.

This paper presents an evaluation of acids commonly used in acidizing high temperature wells and treatment results. Cooling data for the "cool down" technique is also presented.

33. Hendrickson, A. R. and Cameron, R. C.: "New Fracture Acid Technique Provides Efficient Stimulation of Massive Carbonate Sections," 19th Annual Technical Meeting of the Petroleum Society of CIM, Calgary, May, 1968.

A new stimulation technique has been developed and successfully applied to deep massive carbonate completions in several areas. This same technique should prove useful in similar massive carbonate sections in Canada. Basically, the new technique provides deep fracture penetration into the reservoir with low-cost fluids and good fracture conductivity by effectively etching the fracture faces with special acid formulations. It differs from conventional hydraulic fracturing treatment only in that acid replaces conventional propping agents. The treatment is economical in that it uses inexpensive frac fluids to create fracture area and penetration and reduce fluid leak-off. Much smaller quantities of acid may then be used to etch the desired conductivity at the required depth of penetration in the reservoir. If acid alone were used, the volume required would be prohibitively expensive.

The new technique also eliminates many of the hazards of conventional fracturing and acidizing. As no propping agent is used, there is no danger of screen-outs. Corrosion is minimized, because the pad volume of frac fluid cools the well equipment prior to the injection of acid. The technique, thus, is particularly useful in deep, high-temperature reservoirs.

34. Crenshaw, P. L. and Flippen, F. F.: "Stimulation of the Deep Ellenburger in the Delaware Basin," SPE No. 2075 presented at the Deep Drilling and Development Symposium of SPE, Monahans, Texas (March, 1968).

The problems encountered in attempting stimulation of deep, hot wells have been difficult and expensive to solve. These factors, together with the limited number of deep wells drilled in previous years, have caused a long delay in reaching adequate solutions to the problems. The recent deep drilling activity in the Delaware Basin has provided enough wells grouped together in one area to permit the problems to be solved, since research groups can justify long-range, expensive projects, and their theoretical approaches now have an adequate proving ground.

Basically, the problems encountered in these Delaware Basin wells are not vastly different from those present in the shallower wells producing from the same formations, and mainly consist of (1) inability to confine the treatment within the desired interval; (2) lack of frac fluid-loss control; (3) lack of definite knowledge regarding acid reaction parameters and flow mechanisms at these high temperatures and high differential pressures; (4) the inherent limitations dictated by dry gas reservoirs which are not present in oil reservoirs. However, the depth and

Recovery of Copper by Leaching

A summary of present-day methods

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MOST copper is recovered today by flotation, followed by smelting. Considerable tonnages are, however, still produced by leaching operations. It is rarely an economic alternative to smelting; rather is it applied to low-grade oxidised ores or oxidised minerals plus sulphides which do not lend themselves readily to concentration processes. Leaching methods have been used on ores, concentrates, mattes and other copper-bearing materials, but methods now in use are generally confined to the raw ore. It has perhaps achieved its most extensive application in the treatment of oxidised ores in which the copper is soluble in dilute sulphuric acid. By oxidised ores are meant those other than sulphides, such as Malachite, $CuCo_3$, $Cu(OH)_2$, Chrysocolla, $CuO.SiO_2.2H_2O$, Brochantite, $CuSO_4.3Cu(OH)_2$, Atacamite, $CuCl_2.3Cu(OH)_2$, Cuprite, Cu_2O. When sulphide minerals are present some preliminary treatment such as weathering or roasting must be applied.

Dissolving the copper

In general dilute sulphuric acid is the most widely used solvent for oxidised copper minerals; its action on the sulphide minerals is practically nil. A disadvantage of acid leaching is that, in addition to the oxidised copper minerals, the gangue when composed of such compounds as carbonate, silicate and oxide, is also attacked. These dissolved impurities are objectionable not only from the viewpoint of the amount of acid they consume, but also because they tend to accumulate in the solution when recycled. Methods have therefore had to be devised for their elimination, as in some cases their presence is decidedly deleterious and, in fact, if allowed to accumulate, renders the process useless. This aspect will be discussed in more detail further on.

Sulphuric acid plus an oxidising agent will attack and dissolve many copper minerals which are not soluble in acid alone. One of the most convenient agents is ferric sulphate, which is not only an active solvent of most oxidised copper minerals, but also of sulphide minerals. When iron accompanies the copper minerals as, for instance, in Chalcopyrite or Bornite, ferric sulphate can be formed in the nascent condition by suitably controlled conditions.

Ammonia and ammoniacal solutions in the presence of air will also dissolve copper and oxidised copper compounds. The active constituent is cupric ammonium carbonate, which reacts with the copper minerals forming cuprous ammonium carbonate. Ammonia leaching, however, principally as a result of its volatile nature, tends to serious losses, and is only practised in extreme cases. In fact, only one or two plants are at present using the process. Ores containing a carbonate gangue or native copper are practically the only compounds extracted with ammonia, as these are not readily amenable to sulphuric acid leaching.

Leaching methods

There are three principal methods of leaching: (*a*) heap leaching, (*b*) leaching in tanks by percolation, (*c*) leaching by agitation. A fourth method has been applied to exhausted ore-bodies, the leaching being carried out *in situ* without removing any of the ore from mine. These methods will be first touched on briefly, and the details will be further elaborated in specific examples of plants.

Heap leaching. This method of copper recovery is the oldest known and has been practised (at Rio Tinto, in Spain) since the eighteenth century. It assumed large proportions after the property was acquired by British interests in 1870. The Phelps Dodge Corporation at Bisbee, Arizona, have used this method on low-grade ore and Kennecott Copper Corporation, New Mexico, are at present using the process for recovering copper from their waste dumps. The method is generally used on low-grade ores or waste dumps which cannot be profitably treated by conventional ore-dressing and smelting methods. Immense heaps amounting to thousands of tons are built up and the lixiviant consisting of water and/or spent liquor from the precipitating unit is sprinkled over the surface and seeps through to the bottom of the pile and collects in dams, from which it runs to the cementation (scrap iron) precipitating unit. The reaction is largely the resultant of oxidation brought about by air and the ferric salts contained in the lixiviant, the copper being dissolved as copper sulphate. The cement copper is collected, dried and refined in reverberatory furnaces.

Leaching in situ. Leaching in place is used to recover copper from underground workings containing exhausted ore-bodies of too low a grade for profitable mining. The leaching procedure is similar to that in heap leaching, and is carried out by the intermittent circulation of water (or solution) and air through the crevices in the ore. The method has been applied by the Kennecott Copper Corporation in Arizona to a portion of their worked-out mine estimated to contain 50 million lb. of copper in ore averaging 0.6 per cent.

An underground pumping station delivers water to the caved-in ore-body, from whence it is distributed by movable sprinklers. Alternate periods of leaching and oxidation permit the oxidation of the pyrite mineral to ferric sulphate, which dissolves out the copper. The pregnant solution then flows through concrete cells containing scrap iron. The precipitated copper is periodically flushed out through a false bottom into a settling tank from which the water is drained off. In eighteen months the following results were obtained :—

Leach solution	= 0.92% Cu
Tailing	= 0.008% Cu
Recovery	= 99%
Copper produced	= 5,100 tons
Ratio of scrap iron/cu	= 1.2
Copper content of precipitate	= 87.2%

Tank leaching. In this process the ore is confined to tanks. The operation is conducted in either of two ways, depending upon whether the ore must be ground or not, to permit an economic extraction.

(*a*) Percolation. If the ore is porous and readily acted upon by the lixiviant grinding will not be necessary and the ore is charged into large concrete tanks holding up to 10,000 tons and treated by a series of leaching and washing operations. The pregnant (sulphuric acid) leach is submitted to electrolysis for precipitation of copper and the spent electrolyte returned to the leaching department, forming the lixivient for a new batch of ore.

(*b*) Agitation. When the ore is not porous and does not permit of solution percolation, the stationary leaching method obviously breaks down and the ore must be ground and agitated with lixiviant in order to effect solution of the metal. Agitation is carried out in Pachuca tanks provided with compressed air for circulating and aerating the pulp, the separation of solids and solution being effected in thickeners arranged in the counter current decantation system. Recovery of copper from solution is by electrolysis.

Heap leaching

The operations at Rio Tinto, in Spain, occur most readily to mind as a sample of dump or heap leaching. As the ore contains iron pyrite for which there is a considerable demand for sulphuric acid manufacture, the ore after it has been leached of its copper content is shipped abroad to acid manufacturers. The essential in the Rio Tinto leaching process is the alternation of periods of oxidation with those of application of lixiviant during which the copper is extracted as copper sulphate, leaving a residue behind which is mainly pyrite. The ore is composed of iron pyrite, Chalcopyrite, Chalcocite, etc., and assays 1.25 per cent. Cu, 42 per cent. Fe and 47½ per cent. S. It is received for leaching as run-of-mine ore, i.e. without any preliminary crushing. The heaps are formed by dumping forward from a suitable level until the vertical face of the heap is some 7-10 metres. In order to secure the necessary oxygen for converting copper sulphide to soluble sulphate, ventilation has to be provided. False bottoms are therefore constructed as follows. Large lumps are hand picked from the face of the advancing dump and made into parallel walls some 9 in. apart. The walls are bridged by placing flat pieces of ore on top and the dump proper is constructed over this ventilating vent. When the heap is completed, it contains some 100,000-150,000 tons of ore. Leaching solution comprising fresh water and various effluent solutions is applied to the top of the dumps through sprays, each spray delivering 240 cu.m. per day over an area measuring some 20 sq. metres. For service by each spray an area of some 400 sq. metres is earmarked to be wetted over a period averaging 7 days, the spray being regularly moved along so that the area is sprayed in the given time. As a result of the oxidation of the pyrite ($2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4$), which is an exothermic reaction, a heating-up of the mass of ore occurs. The rate of copper extraction is relatively little affected by this rise in temperature, but as oxidation of pyrite accelerates rapidly as temperature increases, temperature control must be rigid if high yields of ore for shipment are required. The temperature is therefore held at 35-50° C. by controlled application of lixiviant.

The composition of the leach liquor before and after leaching is as follows :—

	On	Off
Copper (grms. per cu. metre)	200	2,200
Zinc	500	2,000
Ferric iron	1,000	2,000
Total iron	5,000	20,000
Sulphuric acid	1,000	11,000

The effluent solution from the heaps is caught in dams and from there is sent to the precipitation plant. The dams also take care of any rain increments. Previously the leach was applied through perforated launders, but this was found to lead to channelling and consequent uneven leaching. The total process time for leaching of a heap is about two and a half years, which includes three months to build the heap and twenty-four months for the actual leaching. When the heaps are fully leached, the ore is loaded by electric or steam shovels into trucks and sent to a crushing and screening plant, where it is reduced to ⅜ in. and stored in stock piles for shipment. It assays Cu 0.40 per cent., S. 48 per cent., Fe 41.7 per cent. Zn 0.91 per cent. A total of about 4,000 tons of ore per day is handled by a labour force of 300 men for ore movement and 100 men for controlling the actual leaching operations.

Precipitation. The average copper content of the liquor received from leaching averages 2,000 grm. Cu per cu. metre, the total volume per day averaging 16,500 cu. metres. Cementation (precipitation by scrap iron, $CuSO_4 + Fe = FeSO_4 + Cu$) is the method used for the recovery of the copper and as ferric iron (2,000 grm. per cu. metre) present in the pregnant liquor is a large consumer of iron (without any equivalent precipitation of Cu) this is reduced to the ferrous state by means of sulphur dioxide ($Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$) produced by burning pyrites.

The precipitation is carried out in canals filled with both scrap and pig iron. The volume dealt with is about 1,000 cu.m. per hour, from which 45-60 tons of copper per day is obtained. When the clean-up period comes round, the liquor flow is cut off and the iron lifted out from the canals by a magnetic crane. Men shovel out the precipitate into tubs and when finished the crane replaces the iron, deficiency in iron being made good. Precipitate, when produced on scrap iron, falls off to the bottom of the canal when the iron is removed, but when precipitated on pig iron it remains fast and has to be cleaned off by hand. The average consumption of iron per ton of copper precipitated is 1.44 tons, the two main constituents which consume it being ferric iron and sulphuric acid, the two together accounting for some 40 per cent. of the total iron used.

Two classes of precipitate are separated out by screening, washing and classifying, a low grade assaying 62 per cent. Cu and a higher grade containing 75-80 per cent. Cu.

Leaching in tanks

(*a*) *Percolation method.* Probably one of the best known leaching operators is the Chile Copper Co. at Chuquicamata, Chile. The plant has a capacity of some 40,000 tons of 2 per cent. ore per day. The principal copper-containing mineral is Brochantite ($CuSO_4\,3Cu(OH)_2$), a basic copper sulphate. This mineral is readily soluble in dilute sulphuric acid and introduces copper sulphate into the solution, which on electrolysis liberates sufficient free acid (0.40 kilo H_2SO_4 per kilo of copper leached from the ore) to make the addition of acid from outside sources unnecessary.

The ore is mined on the surface with electric shovels, loaded on cars and transported by rail to the crushers. Here the ore measuring up to 5 ft. in section is brought down to ⅜ in. mesh by four stages of crushing. Belt conveyors deliver the crushed ore to a travelling bridge, from which it is automatically discharged into one of thirteen reinforced concrete leaching tanks lined with mastic to render them acid proof. Each tank is 150 ft. long by 110 ft. wide by 17 ft. deep, and is equipped with a false filter bottom. Each tank holds 11,500 tons of ore.

The method used for leaching is a somewhat complex batch percolation system. In general, the object is to leach fresh ore with solution from another tank, which after a period of soaking goes to the electrolytic plant. Approximately 3,500 cu.m. of solution is required to submerge 10,000 tons of ore. This first treatment solution is then displaced in the tank by a partly enriched solution from another vat, and this after a period of soaking forms the treatment solution for a charge of fresh ore. In all, the ore is subject to five different soakings followed by six washes. Composition and volume of leaching and washing solutions are given in Table I. The complete cycle takes 96 hours, with an extraction of 93 per cent. Electrically-operated buckets of 12 tons capacity, operated from a bridge spanning the tanks, excavate the spent ore and load the tailings in cars for removal to the dump. A charge of 11,000 tons can be discharged in 7½ hours. Relevant leaching plant data is given below :—

LEACHING PLANT DATA (CHUQUICAMATA)

Leaching plant capacity (tons per month) ..	1,400,000
Tons per leach charge	11,500
Extraction (per cent.)	88-94
Acid from ore (kilos per ton)	6-12
Copper recovered (kilos per ton)	14-20
Iron dissolved (kilos per ton)	0.15
Molybdenum dissolved (kilos per ton)	0.01-0.05
Chlorine dissolved (kilos per ton)	0.04
Total available acid in electrolyte (grm. per litre) ..	80-90
Temperature of leaching solution	14-30° C.

During the course of leaching, impurities in the form of chlorides and nitrates enter the solution with the copper, and as they tend to upset the efficiency of electrolytic precipitation, they must be removed before the pregnant solution undergoes electrolysis.

Purification of electrolyte. Chlorine is eliminated from the pregnant solution by agitation with cement copper whereby it is precipitated as cuprous chloride. At the same time ferric iron, which is also invariably present and is also deleterious, is reduced to the ferrous condition. The insoluble cuprous chloride is settled out, collected and dissolved in ferrous chloride and run over scrap iron when the copper in solution is cemented and comes out of solution, is filtered off, dried and melted in a reverberatory furnace. The

TABLE I—LEACH SOLUTION DATA (CHUQUICAMATA)

	First strong sol.	Second strong sol.	Third leach sol.	Fourth leach sol.	Treatment sol.	Spent electrolyte	1st wash	2nd wash	3rd wash	4th wash	5th wash	6th wash	Water
Volume (Cu.m.)	5,000	5,000	3,500	3,500	3,500	8,800	3,000	2,000	2,000	2,000	2,000	3,000	2,350
Copper (grms. p. l.) ..	42	32	22	19	17	15	9	7	5.5	3.4	2.5	1.0	—
Sulphuric acid ..	25	32				58							
Ferric iron ..	1.7	1.0				2.0							
Ferrous iron ..	1.8	1.5				0.5							
Nitric acid ..	1.5	1.5				1.5							

process dechloridises, the solution from 0.50 grm. of chlorine per litre to 0.05 grm. per litre. Immense difficulty was experienced in early plant operations by decomposition of nitrates present in the solution undergoing electrolysis. The trouble took the form of decomposition of the nitrate with accompanying oxidation of ferrous iron and cuprous chloride. Once started, this reaction became self catalysed and spread throughout the entire solution system. The solution fumed strongly, giving off large volumes of nitrogen oxide, chloride values sky-rocketed and copper cathodes were contaminated with large amounts of cuprous chloride. Anodes and fittings were badly corroded and the current efficiency fell from a normal 90 per cent. to 60 per cent.

Research disclosed the fact that molybdenum was responsible. When the ore contained over 0.008 per cent. of this element it catalysed the decomposition in the solution of the nitrate, which in turn set up the series of disastrous reactions. Further research found that sulphurous acid had a stabilising effect and inhibited the decomposition of nitric acid. Accordingly an SO_2 plant was incorporated in the flowsheet so that the electrolyte in the cells contains 0.2-0.5 grm. SO_2 per litre.

Electrolysis. The purified pregnant solution is now ready for precipitation and recovery of its copper. Cells numbering in all 1,100 are of concrete, made acid-proof by lining with mastic. They are arranged in sections so that the solution flows by gravity from one cell to the next, 16 or 17 cells comprising one section. Trouble was originally encountered in finding satisfactory anodes, the nitric acid present in solution corroding the lead sheets which were first in use; finally a copper silicide alloy was developed which proved satisfactory. However, owing to the fact that in recent years the nitrate content of the ore has been decreasing, lead antimony anodes are being successfully used.

ELECTROLYTE DATA (CHUQUICAMATA)

Current density (amps. per sq. ft.)		..	7-18
Electrolyte (entering)	Copper	..	21-26 g.p.l.
	Ferrous iron	..	2.0 ,,
	Total iron	..	2.5 ,,
(exit)	Copper	..	14-16 ,,
	Ferrous iron	..	0.5 ,,
	Total iron	..	2.5 ,,
Current efficiency	.. ..	..	85-92%
Pounds copper per k.W. day	.	..	24-28
Capacity K.W. load	.. ..	..	55,000

Flow of electrolyte is approximately 750 litres per minute, which is very rapid (normal flow is 20-30 l.p.m.), reason being to minimise polarisation and ensure deposition of firm cathodes. Temperature of electrolyte varies from 30°-45° C. and increases as it drops down the cascade as does also the ferric iron, which causes a falling off in the current efficiency. The presence of ferric iron is liable to cause short circuiting and inspection of cathodes becomes an important part in routine operations. Electrolyte in the tanks is covered with a petroleum oil preventing the escape of dissolved sulphur dioxide and spray.

Agitation method

The agitation method of copper recovery is well illustrated by the operations conducted by the Union Minière du Haut Katanga at their plant in the Belgian Congo. The ores are principally oxidised with Malachite ($CuCO_3\,Cu(OH)_2$) predominating, plus minor amounts of Azurite, Chrysocolla and Cuprite, while some of these ores are sufficiently high grade for direct furnace smelting, the average grade of ore undergoing leaching is 6.5 per cent. Cu. The nature of the ore and gangue renders it unfit for percolation methods for large quantities of slime are present which prevent effective percolation by solution, and further, the ore being a carbonate, tremendous gas evolution takes place on contact with an acid lixiviant, which would froth out of any leaching tank, taking the fines with it. The principal points of interest and difference from the percolation method are :—

(*a*) The process is continuous not batch, the leaching being carried out by agitating the ground ore with solution and not by percolation in vats.

(*b*) Separation of pulp into sands and slime is done by classifiers.

(*c*) Washing of slime is carried out in thickeners by counter current decantation methods.

(*d*) Solution is purified and freed from iron and alumina by using ore as the purifying agent.

Agitation plant consists of twenty-eight Pachuca-type agitators built of steel, lined with lead sheet and provided with air at 30 lb. pressure. Twenty of the agitators are arranged in five rows, four to a row, the remaining eight being set aside for purification purposes. The ore is crushed and ground to 20 M., enters the agitators together with spent acid electrolyte from the tank house and passes through four Pachucas in succession when the bulk of the copper is dissolved. Pulp is then classified on one of six 4½-ft. Dorr bowl classifiers, which separates it into sands and slimes (200 M.), the sands being progressively washed in a three-deck washing classifier, the washed sands from the last deck going to the dump. The slimes are washed by counter current decantation in a series of four 70-ft. Dorr thickeners which wash the slime free of entrained copper solution. In all there are twenty-eight thickeners. Twenty are in five sections, four to a section, corresponding with the same division in the agitation sections. Four are allotted to the purification section, and a further four serve as spare and storage tanks. The overflow from the first thickener constitutes the feed to the electrolytic plant. Dorrco pumps progress the slime from one tank to the next, the solution overflowing (in the opposite direction) by gravity from one tank to the next lower. Wash water is added in the last thickener in amount equal to that discarded in the slime tailing from this thickener.

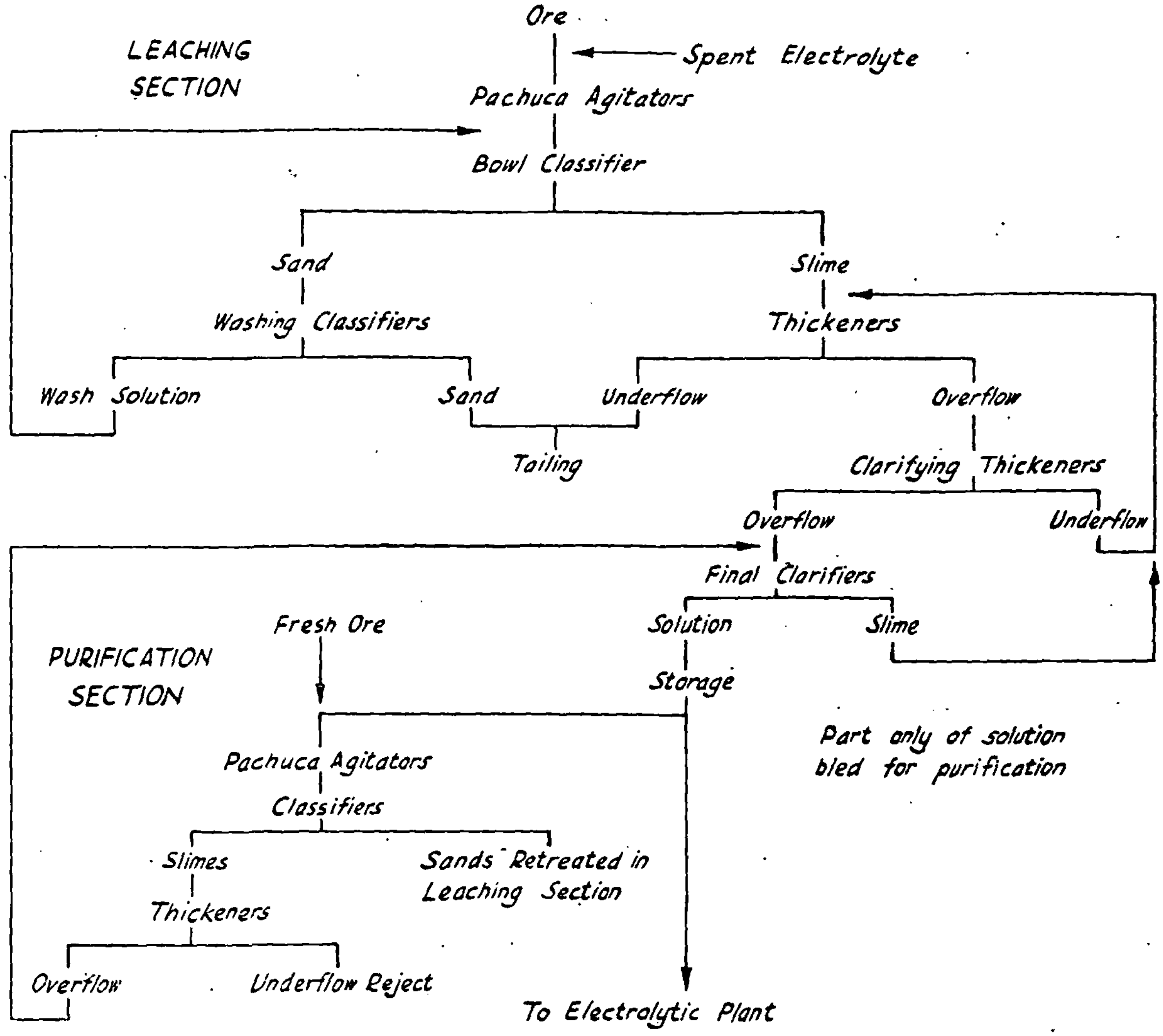

Fig. 1 Union Minière du Haut Katanga, flowsheet for acid leaching and purification of solution

Purification. The presence of ferric iron (5 grm. per litre) in the electrolyte resulted in low ampere efficiency, although where small in amount (below 3 grm. p.l.) the effect is not marked. An original method of purification was worked out employing neutralisation of solution with ore. Tests indicated that agitation for some 17 hours with run of mine ore would give an effective elimination of iron and alumina from the leaching solutions. The method was devised to run parallel with the acid agitation and washing operations. Strong solution from the main section is mixed with excess of ore whereby the free acid is neutralised and the soluble iron and alumina sulphates are hydrolysed and precipitated, at the same time acid set free is consumed by the ore. Summing up, the solution drops most of its iron and alumina, dissolves more copper and has all its free acid neutralised. The neutralised pulp is classified and the sands (containing the excess ore) are sent to the main section to join the new ore, the slimes containing all the precipitate are washed in Dorr thickeners and then finally dumped. Effect of the purification is shown in Table II.

TABLE II

	Cell house		Acid agitation discharge	Purification	
	Feed	Discharge		Feed	Discharge
Copper (grms.) per litre) ..	30.5	16.2	30.5	30.2	45.0
Free sulphuric acid ..	5.5	34.4	12.2	11.2	—
Iron total ..	5.6	5.6	6.6	5.8	2.0
,, ferric ..	5.4	4.0	6.4	5.0	1.4
,, ferrous ..	.0.2	1.7	0.3	0.8	0.6
Alumina ..	11.0	11.0	11.7	10.9	7.5

Since the solution leaves the purification plant at between 1 and 2 per cent. ferric iron and the danger point is 3 per cent. and above, it is not necessary to purify the whole volume; only a portion is bled for this treatment.

Leaching solutions are extremely corrosive. Brass and bronze pumps originally installed were like sieves within two weeks. Copper nails below the solution line in the agitators were completely gone within two days. Ferric iron would not account for it, and it is believed that the cobalt in solution may have something to do with the corrosiveness. All materials that come into contact with the leach have to be lined with lead, duriron, mastic, etc.

Leaching and Purification Data (Katanga)

Ore fed to leach (tons per month)	33,000
Ore and concentrates fed to purification (tons per month)	1,060
Cu in ore fed to leach (per cent.)	6.5
Cu in concentrate	28.7
Cu in slime tails	0.17
Cu in purification slime tails	0.43
Recovery per cent.	88.3
Acid consumed per kilo Cu (kg.)	0.7
Sand tails, percentage of total	40.5
Acid slime tails, percentage of total	56.1
Purification slime tails	3.4

Electrolysis. The tanks are of concrete made acid-proof with mastic and are of unusual length, being 62 ft. by 3 ft. wide by 4 ft. deep. Anodes are of antimonial lead, whilst cathodes are the usual copper starting sheets made in separate electrolytic tanks. Sulphuric acid (supplied by a contact plant nearby) is added in the tank house to the electrolyte to bring it up to the required concentration of 60 g.p.l. Cathodes are complete in 10-14 days and are then pulled from the tanks, washed and sent to the furnace refinery for casting into wire bars. Copper produced per kWh equals 0.47 kilos, whilst ampere efficiency is 78.5 per cent.

Ammonia leaching

About half the copper in the ore of the Kennecott Copper Corp., Alaska, occurs as sulphide, the remainder being Malachite and Azurite. Gravity concentration and flotation remove the bulk of the copper, but 1 per cent. Cu as carbonate persists in the tailings. When the question arose as to the treatment of these tailings for the recovery of copper, two possible methods were considered (*a*) Sulphidising the tailings and then floating off the sulphidised copper, (*b*) Ammonia leaching. Kennecott's isolated position and consequent high freight charges demand that the product must be as high a grade as possible and as flotation would yield only an approximate 25 per cent. concentrate as against an ammonia leach product of 70 per cent., the latter process was adopted.

The leaching tanks are of all steel construction, totally enclosed and vapourtight. They measure 30 ft. in diameter and hold an average of 500 tons each.

The feed, comprising the dewatered tailings from the gravity concentrating plant, is introduced through a manhole at the top of the tank and the first leach solution is pumped through the bottom. This first leach is a second leach from a preceding charge, the ammonia containing about 60 per cent. of its possible copper content. Leaching period for this first leach is twelve hours, when it is enriched to 75 per cent. of its saturation point. A portion of this rich solution is then withdrawn and sent to the evaporation unit for recovery of its copper content. This solution is replaced in the tank by an equal volume of low-grade make-up solution and enough strong ammonia from the evaporators to complete the extraction of the copper. This second leach is then circulated for 36-48 hours through the charge when it is pumped to a new charge on which it becomes the first leach. As the second leach is pumped off it is followed by 30 tons of wash water and steam, washing is continued until the ammonia content of the effluent is practically nil. Steam is then turned off and the tailing is automatically excavated on to conveyor belts which carry it to the dump.

Recovery of copper and ammonia. Originally the recovery unit was patterned after the continuous column stills used in ammonia distillation, but the formation of crusts of copper carbonate and oxide on the walls and tubes of the still led to excessive shut-downs for descaling. The present type consists of 16-ft. steel cylinders, 10 ft. in diameter with dome tops and cone bottoms, the latter connected to filters. The unit is not continuous, but operates as a batch process. Steam is admitted to the strong leach solution in the evaporator ammonia going off, steaming being continued until the distillate shows less than 0.01 per cent. NH_3, by which time all the copper has been precipitated as black copper oxide. The charge is then forced by steam pressure through the filter, and the Cu dried and shipped. Grade of copper is 75 per cent., recoveries ranging from 76-88 per cent.

In actual practice, the evaporators are operated in double, triple or quadruple " effect." Essentially, this means that for, say, triple effect the strong solution (from the first leach) contained in evaporator No. 3 is heated by vapour coming from two preceding evaporators (No. 2 and 1), the first being heated directly with steam. The charge in vaporator No. 1 is now dropped for filtration and fresh solution run in. Steam is turned on evaporator No. 2, the vapour of which passes through evaporator No. 3, which in turn heats up the fresh charge in No. 1. Steam is always turned on the oldest charge which is termed the " first effect," the fresh solution charge being the " third effect." Maximum temperatures range from 265° F. in the first effect to 220° F. in the last. The vapours from the last effect are passed through a preheater in which incoming fresh solution is employed as the cooling medium, and achieve a temperature of 180-190° F. before being charged to the evaporators. The condensed ammonia flows to storage. Fig. 2 will perhaps help to show the method of operation.

Efficient recovery of ammonia is absolutely necessary for the economics of the process, and hence the proper application of the steam wash is highly important. The steam consumption ranges from 210-230 lb. per ton of ore, approximately 55 per cent. of the steam being used in evaporation, and 45 per cent. in the steam wash.

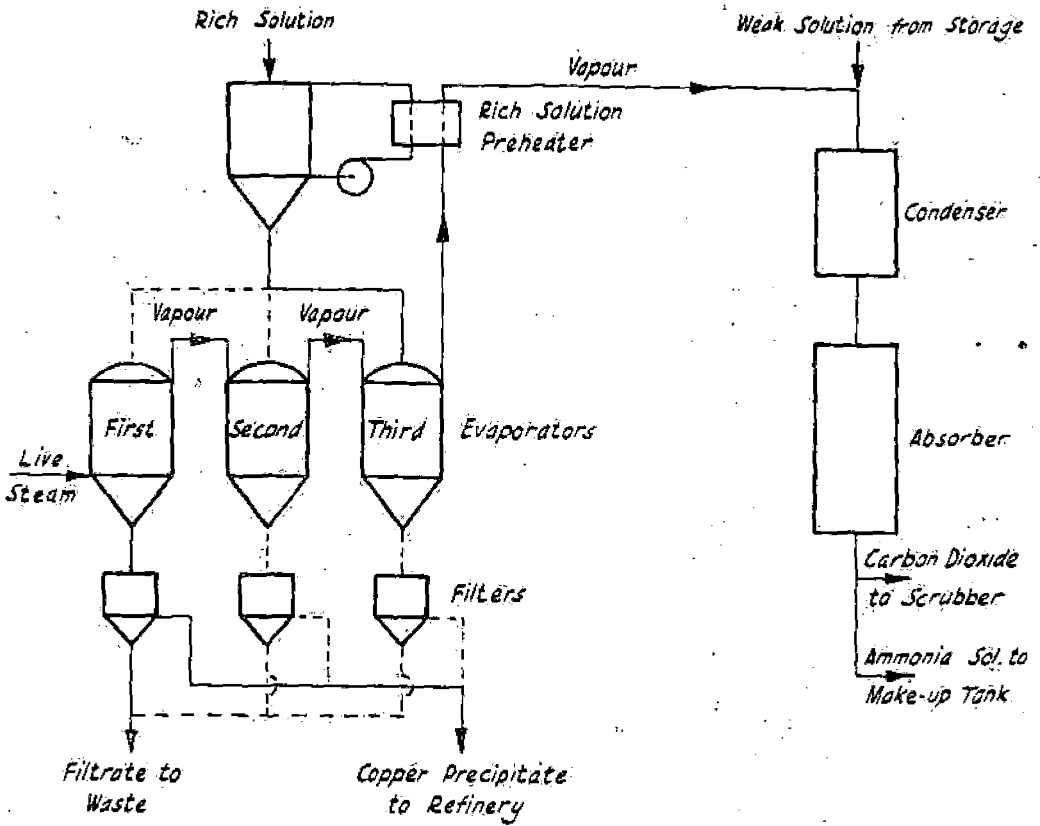

Fig. 2 Kennecott Copper Corporation, Alaska, recovery of copper and ammonia from leach solution

The Calumet and Hecla Copper Co., Michigan, have also applied the ammonia leaching process for recovery of copper in their tailings. The material treated is finely divided metallic copper in sands. The plant treats 3,000 tons daily of 0.51 per cent. Cu tailings in steel leaching tanks 54 ft. diameter by 12 ft. The operations are similar to those practised at Kennecott. The second leach from another charge containing 30 grm. Cu, 60 grm. NH_3 and 40 grm. CO_2 per litre constitutes the leaching solution for a new charge. After allowing to soak for 10-12 hours, it is displaced by ammonia water and finally steamed. A partial vacuum is maintained beneath the filter bottom in the leaching tank to ensure as complete an elimination as possible of ammonia. Copper is recovered as before by evaporation. Final tailing assays 0.10 per cent., making the extraction 80 per cent.

Ammonia leaching was also used during the recent war to reclaim copper from copper-clad steel strip scrap. The process, however, is not economic and was only put into operation as a war-time expedient.

Other leaching processes

There are, of course, many variants in the leaching process. Some firms incorporate both agitation and percolation leaching methods for the recovery of their copper, whilst other concerns embody flotation, roasting, etc., in their leaching circuits.

The Kupferwerke Stadberger, Nieder-Marsberg in Germany treated (up to and during the war) their 1.4 per cent. Cu Chalcopyrite and Malachite ore by crushing to 2 m.m. mesh, adding salt (8 per cent.) and Pyrite, and giving a chloridising roast in Wedge-type mechanical furnaces. The presence of Pyrite is presumably for assisting in the liberation of chlorine from the salt and also to help maintain the heat of the reaction. Chloridisation takes place with the formation of soluble cupric chloride ($2NaCl+CuS+2O_2=Na\ SO_4+CuCl_2$). The calcine is dumped in concrete leaching vats and leached with hot water, when the cupric chloride goes into solution. Leaching period is about 24 hours. The process was not economic, cost per ton of copper being somewhere in the region of £100.

The tailings of the Ohio Copper Co., Utah, contain 0.45 per cent. Cu in the form of sulphides and oxides. Dilute sulphuric acid is added when the oxide copper amounting to about 25 per cent. of the total dissolves. This dissolved copper is then precipitated by cementation, the iron removed by passing the pulp through a trommel and the precipitated copper plus the original sulphides (untouched by the dilute acid) are then recovered by flotation as a bulk concentrate assaying 72 per cent. Cu. Extraction is 73 per cent. of the total copper in the original tailing.

ACKNOWLEDGMENTS
Bulletin 457, I.M.M., 1942. (Rio Tinto Pyrite Leaching.)
Vol. 106, A.I.M.E., 1933. (Copper Metallurgy.)

AIME Transactions
V. 73 1926 p. 31-57

Recovery of Copper by Leaching, Ohio Copper Co. of Utah

By Arvid E. Anderson and Frank K. Cameron, Bingham, Utah

(Salt Lake City Meeting, September, 1925)

The weathering of copper-bearing ores with the formation of a water-soluble salt and the recovery of the metal by leaching and evaporation or precipitation, are processes long known, which have at various times been utilized with more or less commercial success. It is commonly assumed that the technical principles involved are quite simple and their application to a particular case easy. If these assumptions were true, we should anticipate a long list of uniformly successful leaching operations, which is not the case, and one would be justified only in calling attention to either unique or peculiar features of any particular enterprise; whereas, in studying the problems of the recovery of copper from the old workings of the Ohio Copper Co. in the light of available descriptions of other leaching projects, we have not found the assistance hoped for to guide us to the best realization of our own opportunities. It appears desirable, therefore, to call attention to these guiding principles, together with a description of the facts of accomplishment.

Justification lies in the fact that the leaching and precipitation of copper at the Ohio Copper Co. mine in Bingham Canyon, Utah, is successful. This success is measured by an average monthly production of 600,000 lb. of copper at an average operating cost, to date, of 3.85 cents per pound at the company's workings, or 6.32 cents per pound after paying shipping and smelter charges on the finished copper. A total of 17,076,099 lb. of copper had been shipped to the smelter from the beginning of operations, August, 1922, to April 1, 1925. Probably these results can be bettered with further study and realization of the factors involved and the devising of methods of meeting them. It is now an assured fact that the enterprise will have a relatively long and continuously profitable life and that its reserves will not, nor cannot, be suddenly and permanently depleted.

It is particularly noteworthy that the financing of this enterprise has been entirely from its earnings. The few hundred dollars necessary for the first experiments and production were obtained by the sale of used, and no longer needed, equipment from a mill belonging to the company; and all funds since required throughout the growth and development of the enterprise, from a few troughs with a production of 2000 or 3000 lb. per month to the present output, have come from receipts in hand.

It will be pertinent to quote here from a report of the General Manager to the Board of Directors, covering operations for the fiscal year 1924, as follows:

> The total number of gallons of water treated in this period was 672,408,000, which is equivalent to 2,801,700 tons. The average copper content was 4.0302 lb. to the ton of water; and the total copper content, therefore, was 11,639,345 lb. The recovery, based on the daily estimates of the plant, was 11,290,165 lb. which represents 97 per cent. of the copper contained in the heads. In the tailing water was, therefore, 349,180 lb., and of this amount, we recovered, in the outside plant, 206,365 lb. *making a total recovery in pounds of copper of* 11,496,530 lb. *and the amount* lost in the tails was 132,815 lb. These two recoveries, both from the inside and the outside plant, show a recovery of 98.77 per cent. of the copper contained in the heads.
>
> During the same period, our shipments to the smelter consisted of 18,127,200 lb. The average moisture content was 28.67 per cent., which made a deduction of 5,208,088 lb., leaving the dry weight 12,919,132 lb. The average copper content was 88.99 per cent. and the gross copper shipped to the smelter was 11,496,530 lb. The copper deduction made by the smelter was 381,201 lb., leaving the net pounds paid for by the smelter, 11,115,329.
>
> The average price paid by the smelter was 12.876 cents per pound and the amount realized therefrom was $1,431,217.26. The total cost per pound, including smelter charges, was 5.815 cents per pound; the operating profit for the period, per pound, was 7.061 cents; and the total operating profit therefrom, for the year, is $784,759.56.
>
> The total number of pounds of copper extracted from Jan. 1, 1923, to and including Dec. 31, 1924, is 15,546,873; and the total operating profit for this same period is $1,048,840.43.

HISTORY OF OPERATIONS

In August, 1922, pumping was started, distributing 250 gal. per min. of water from Bingham Canyon Creek upon the surface of a large fill of broken rock overlying a portion of the caved zone. The solution reaching the Mascotte tunnel contained 0.45 per cent. copper, demonstrating that recovery of the copper values would be commercially feasible; the following January, the pumping capacity was increased to 400 gal. per min. At that time, the copper was precipitated in a row of boxes, using "country scrap" or whatever iron was available locally. These facilities were inadequate and insufficient, but results were soon sufficient, financially, to permit of a widening of the Mascotte tunnel and the installation therein of two rows of launders of improved design, one on each side of the haulage track; a larger and more efficient precipitation was promptly realized with improved profits. In the spring of 1923, with the installation of a larger pump, the water was increased to 600 gal. per min. In November, 1923, water from the Bingham Mines became available, which, with a reuse of a portion of the tailing solution, gives a supply of 1200–1400 gal. per min. at the surface, delivered by a relay system of pumps.

The leachings reach the Mascotte tunnel through some one or other of the old ore chutes, depending on where it is applied at the surface, and is laundered to the precipitation boxes. In the earlier operations, leakage losses were serious; these losses were stopped by guniting the precipitation launders.

Production in January, 1923, was 120,000 lb.; in October of that year it had reached 351,801 lb., the recovery having increased from 41.9 to 99.2 per cent. For 1924, the production was 11,496,530 lb. of copper, a recovery of 97.3 per cent., and the copper content of the product shipped from Lark averaging 88.99 per cent.

Early in the operations, it was recognized that the "country scrap" was an inefficient precipitant. Since June, 1923, a detinned scrap iron prepared by the Metal & Thermit Corpn. in California has been used; this has proved highly efficient, more than justifying the greater initial cost.

THE OREBODY

The orebody of the Ohio Copper Co. has recently been described in detail in publications of Varley, Oldright, and Wormser.[1] The veins, on which mining operations originally depended were more or less completely worked out and the original stopes and intermediate regions broken down, so that the property now consists of a "caved area," or more properly, a zone of broken rock surrounded on the sides, bottom, and much of the top by consolidated or mainly unbroken rock. The caved zone may be roughly described as a truncated cone, distorted, inverted, and standing at an angle of about 40° from the vertical. It is thought to be quite completely and uniformly filled with broken material of approximately 4 in. diameter on the average. The upper transverse dimensions of the cone are approximately 1400 by 600 ft. The axis of the cone is approximately 1200 ft. and the zone is estimated to contain 38,000,000 tons of rock. The truncation of the cone at the bottom has about one-fourth the area of the top, is horizontal, and from it chutes lead to the Mascotte tunnel, about 700 ft. lower. All this material carries copper, both in the caved zone and the surrounding consolidated rock. A vast number of assay figures on the old maps of the company give 0.88 per cent. as the average; but an inspection of these assay maps suggests a higher figure as more probable. The assay of the heads at the

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[1] Address by Varley and Oldright, Bureau of Mines, before Utah Metal Mining Institute, Salt Lake City, May 5, 1923; Oldright, MINING AND METALLURGY (1923), 4, Pages 1–4; Wormser, *Eng. & Min. Jnl.-Pr.* (Oct. 20, 1923) and (July 26, 1924).

mill formerly operated by the company averaged 0.88 per cent., hence this figure is regarded as the most reliable.

The rock itself is a porous quartzite, or sometimes a monazite, easily crushed or shattered, with sulfides of copper or copper and iron irregularly disseminated, sometimes in streaks or stringers, more often in small particles, always with more or less evidence of copper sulfate on surfaces and frequently malachite and azurite.

The original mineral, which alone concerns us, is chalcocite Cu_2S, as it has been shown by Zies, Allen and Merwin[2] that, at temperatures below 200° C., the reactions between the various sulfides of copper, iron, zinc and lead with copper sulfate yield chalcocite as the final stable phase persisting. These facts may be summarized conveniently, as follows:

Pyrite (FeS_2) → covellite (CuS) → chalcocite (Cu_2S)
Pyrohotite (Fe_7S_8) → chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4)
Bornite (Cu_5FeS_4) → chalcocite (Cu_2S)
Chalcopyrite ($CuFeS_2$) → covellite (CuS) → chalcocite (Cu_2S)
Sphalerite (ZnS) → covellite (CuS) → chalcocite (Cu_2S)
Galena (PbS) → covellite (CuS) → chalcocite (Cu_2S)
Covellite (CuS) → chalcocite (Cu_2S)

It is possible that at some particular time or spot one or more of these other minerals might be present as well as chalcocite, but sooner or later they will disappear with the formation of the last. It is also possible that gold, silver, arsenic, antimony, lead, zinc, nickel, cobalt, bismuth, etc., might be present.[3] We are without confirming evidence as to these, at least in significant amounts, and the only solutes appearing in leachings of this ore are copper, iron, magnesium, calcium, sodium, aluminum (as Al_2O_3), silicon (as SiO_2), sulfur (as sulfuric acid).

Chalcocite, Cu_2S, is quite readily attacked by oxygen at ordinary temperatures in the presence of water, and whatever reactions may intervene, the result may be summarized in the equation:

$$Cu_2S + 5O + H_2O \rightarrow CuSO_4 + Cu\,(OH)_2$$

The reaction is markedly exothermic, hence will proceed with rising temperature and increasing acceleration, provided it is not retarded or checked by: (1) Cooling, (2) exhaustion of the supply of oxygen or water, (3) accumulation of too high a concentration in the resulting solution of the soluble reaction product, $CuSO_4$; (4) mechanical interruption by formation of a protecting film of the insoluble hydrate.

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[2] *Econ. Geol.* (1906), **11**, 407; see summary by Clark, The Data of Geochemistry, U. S. Geol. Sur. (1924) *Bull.* No. 770, 673, 676.

[3] See Analysis of Finished Copper, by Wormser, *loc cit.;* an analysis of the waste liquor from the portal of the tunnel at Lark is in the records of the University of Utah, showing the presence of these same constituents.

Each of these factors is of primary importance and must be given full consideration in determining that procedure in applying water and air to the orebody, which, in the summation of their effects, will make this summation a minimum. They will be discussed in detail later, but are cited here to emphasize the importance of the characteristics of the rock material forming the orebody.

It has been pointed out by Oldright that the quartzite and the quartzite-monazite host, carrying the disseminated sulfides of copper or mixed sulfides of copper and iron in this deposit, are rather readily permeable to water. Not only is this true of cleavage cracks and parting planes, but, to a marked degree, throughout the consolidated rock mass. This is readily proved by soaking a weighed piece of the rock in water. When taken from the water, after the surface is wiped dry, it will be found to have markedly increased in weight (different pieces, however, naturally showing wide variations in the percentage of absorption) and, on drying, there will practically always be more or less of a deposit of copper sulfate on the surface. This procedure can be repeated many times with the same piece of rock, each time bringing copper sulfate to the surface.

The marked absorbent character of this rock material makes it apparent that we are concerned here not only with the copper appearing in appreciable cracks and crevices or surface coatings, but with the entire mass of disseminated copper minerals. The water absorbed so readily must be mainly in very thin layers, or films; whether in layers of molecular dimensions, as held by some authorities, or thicker, need not now concern us. It is of the utmost importance, however, to remember water has a selective power of absorption for gases and will absorb from air relatively much more oxygen than nitrogen. More important yet, in thin layers or adsorption films, the water appears to be, or actually is, under great pressures so that it absorbs many more times the oxygen than it would in ordinary circumstances; that is, today there is a great increase in the solubility of oxygen in film water. We do not suggest that the film water inside a wetted rock mass is saturated with oxygen; probably the mass is far from saturation, but it is very probable that if the individual rock masses are bathed with film water, instead of large masses, a much larger amount of oxygen will be carried into the rock masses than would otherwise be the case, and under the most favorable conditions possible for a continued oxidation of the contained minerals. In other words, a rationally controlled leaching operation in an orebody, such as that of the Ohio Copper Co., will continue to form as well as remove copper sulfate. Two practical consequences are apparent. The life of the enterprise is not determined by the amount of "soluble" copper present at any particular time, and it is not physically possible suddenly and completely to deplete the ore reserve. Should this be attempted, very certainly, and probably quite quickly, the is not, and cannot be from its very nature, a rapid procedure; rather it is a time-consuming one, probably of many years.

The interstices of the orebody in the caved zone, where most of the leaching has been done, are large and irregular, compared with the capillary surfaces in the individual pieces of rock. The percolating waters bathe the surfaces only of the individual masses, whereas most of the soluble copper is within the fine pores of these individual masses, from which it can diffuse but very slowly, compared to the rate of flow of the percolating water. Moreover, copper is continually being converted to soluble sulfate in and upon these masses and at continually varying rates. It is impossible to determine, or predict quantitatively, how these simultaneous phenomena will mutually affect the composition of the solution at any given time or position within the orebody, and hence to make use of a quantitative formula for computing the removal of the copper by leaching. Even more difficult is it to evaluate to the consequences of the differences in rate of solution of the several copper compounds, with the rate of percolation of the water. It is well recognized that a slow percolation in thin water layers is the most efficient use of the given volume of water. However desirable it may be that the percolating waters flow over the individual ore masses in film form only, it can hardly be anticipated that this state of affairs will ever be attained completely, and it certainly has not up to the present, for its importance has not been fully realized. It has been recognized that the distribution of a given amount of water over a large area in small streams is preferable to a concentration in a few large streams, hence the use of perforated launders.

Within the past few months the problem of the best distribution of the water has been closely studied and in the light of large-sized practical experiments. The water has been delivered in large streams into holes on the surface, into cracks, and fissures; upon a rather wide area prepared by deep blasting (20–30 ft.) under the overlying burden of soil and into consolidated rock adjacent to the caved zone, as well as upon the surface overlying the caved area in well-distributed volumes. As well as can be determined, it has been found that there was but little percolation of the water throughout the consolidated rock and, while there was a recovery of some copper, the heads were disappointingly low. Better results were obtained from the water entering by way of holes over the caved zone; but the best results came from a wide distribution over the caved zone. It is now planned to abandon temporarily efforts to leach the consolidated-rock regions pending the inauguration of a systematic procedure for preparing this region for leaching, and to confine the leaching operations to the caved zone for the immediate future. To this end, a tunnel (Dederich on 100-ft. level) is now being driven through the upper part of the caved zone from which laterals and sublaterals will be constructed so that, when completed, practically the whole horizontal cross-section of the region or any desired part of it, can be wetted at once, thus permitting a desirable mobility in alternately leaching and drying. The completion of this tunnel system will make possible the leaching of a much larger part of the caved zone than has been practicable. In fact, it is reasonably certain that a relatively small part only of the broken mass has been leached and that far from thoroughly.

The percolating waters have two dominant duties, as well as several minor ones. They must dissolve copper sulfate and carry it to the precipitating plant; and they must carry oxygen from the surface for the continuing oxidation of the sulfides of copper within the ore mass. Both these functions are dependent on the manner of applying the water; and there is a decided division of opinion on this fundamental operation. It is held that mass percolation, where a large volume of water is applied quickly to a restricted area, by bringing a large volume of water in a given time into contact with the copper-sulfate coatings on the individual rock masses, dissolves them more completely; and that this method of application traps and mechanically drags into the orebody large volumes of air. To these views it can be objected that a relatively large part of the water is passing through the large interstices out of contact with the copper sulfate, and having no appreciable effect upon it; that the rate of solution of crystallized salts is so slow, compared to the rate of passage of the water being forced past it, that the solvent action effected is out of all reasonable proportion to the volume of water required for it; and that it is improbable that any large part of the trapped air is carried very far, being pretty thoroughly scrubbed out by the first few feet of broken rock, and returns to the surface without doing any useful work. Obviously, this method requires the maximum amount of pumping.

Diametrically opposed is the view that the water should be applied in the film form, or as nearly in the film form as can reasonably be attained in a practical operation, which means distributing any given volume over a very wide area slowly but continuously. In this way, the water (for the most part at least) will enter and continue through the orebody in approximately film form, a very much larger area of ore surface will be bathed, and a larger amount of copper sulfate will come into contact with it and a much longer time for solution will be afforded. A much larger amount of oxygen (in distinction to air) will be absorbed by the films at the surfaces and carried in dissolved form far into the interior of the orebody and in the form most useful for oxidation of the minerals.

It should be noted that spreading the water over so large a surface as to attain film form induces a rise in temperature, especially when the surface being wetted is relatively dry. An increased temperature above that of the entering water can be maintained by making the percolation sufficiently slow. It has been pointed out that a high temperature is favorable to the rapid oxidation of the copper sulfides, from this point of view a film percolation is to be preferred.

Copper sulfate in aqueous solution is hydrolized, the solution behaves as though it contained free sulfuric acid and will dissolve copper hydrate. The greater the concentration and the higher the temperature, the greater will be the amount of the hydrolysis and the more copper hydrate will be dissolved. Similar statements hold for the action on copper carbonates. Likewise, the solution will dissolve the hydrates of iron, which are practically always an accompaniment of the oxidation of copper sulfides in nature, and by forming protecting films may retard the action. Obviously, as film percolation rather than mass percolation tends to dissolve and remove more copper and iron hydrates from the sulfides, it is to be preferred.

The film method of percolation is to be preferred to mass percolation from every point of view, especially because it will bring more copper to the precipitating launders daily, or for a given volume of water, and also because it better promotes the conditions in the orebody favorable to the continued and rapid production of soluble copper sulfates.

The time required for penetration of the caved zone by water applied in the mass percolation manner, as measured by its appearance in the launders in the Mascotte tunnel is about 48 hr. If, however, film percolation is followed, this time element will be longer (probably very much longer) depending on how near to the ideal film condition the practice may be. No sufficient knowledge exists of the various factors that particularize this case to justify any attempt at evaluating them; consequently it is useless to attempt any theoretical estimates of what this time will be. It may well be two or three weeks. Probably for a short interval, the first runnings will be pure or nearly pure water, but quickly high "heads" will be attained, which will persist for a relatively long period and then gradually diminish. Obviously, once the flow is established the volume delivered to the precipitating launders for a given interval of time will be the same, no matter what system is followed, and independently of the rate through the ore mass.

Considering, now, an individual piece of the ore, over the surface of which the percolating water is moving, the water with dissolved oxygen penetrates more or less completely the entire mass; reaction with the contained sulfides sets in, and if not checked by too rapid a flow of cold water on the outside, a quick rise in temperature follows; the reaction proceeds at constantly increasing speed for awhile, and then gradually slows down as there is an accumulation of the reaction products. If the soluble products of the reaction be removed as they are formed and the undissolved products do not form a too impenetrable coating, the reaction continues until the sulfide mineral completely disappears—or what is more likely, the supply of oxygen is exhausted. The temperature may rise to the boiling point of water, introducing another factor in percolation with which to contend.

However, diffusion of the reaction products from the interior of the mass through the capillary and film water to the flowing water on the surface of the mass is very slow and cannot add much to the content of the percolating water, at least in any individual case, although the aggregate be appreciable; consequently, the reaction slows down and stops. If the percolation is stopped and the clearly washed surface of the mass dries, evaporation at the surface begins; there is a capillary flow started from the interior to the surface that carries with it the dissolved sulfates, which will be deposited on the surface as evaporation proceeds as a more or less thick and dense film of basic copper and iron sulfates, with less conspicuous amounts of other substances in individual cases. How far, or rather how long, this procedure should be carried, in practice, is purely a matter of judgment of the operator at present. The movement of water, or of a dissolved substance, in a porous medium follows a law expressed by the formula $y^n = kt$ where y is the distance and t the time.[6] The value of n is constant for any given absorbent medium, say an individual piece of rock, but the porosity appears to vary too much in different pieces, as well as the size of the different pieces, to permit any useful application of the formula.

On resumption of leaching, water again penetrates the ore mass, carrying a new supply of oxygen, for the reaction with the remaining sulfides, and sulfuric acid for the solution of protecting films of hydrate. Thus, the cycle of operations can be continued indefinitely, but with slowly diminishing results until that time when it will be of no practical importance. It would be advantageous to know how far the phenomena just described have progressed in our orebody, particularly in the caved zone. The driving of the Dederich tunnel and laterals affords an unusual opportunity to obtain samples to test this matter and accumulate data of great technical value, not alone for the Ohio Copper Co.'s enterprise, but for all copper-leaching projects.

The laboratory problem is to determine not only the total copper in the sample, but that proportion of the total which is now soluble in water and soluble in dilute sulfuric acid. It is proving to be far from a simple problem. As a preliminary step, a column of broken ore was arranged by placing about 4500 gm. of rock from the broken zone in a series of funnels made by cutting off the bottoms of "Winchester quarts," or the ordinary bottles in which acid is sold. The funnels were arranged

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[6] Cameron and Bell: Bur. of Soil, U. S. Dept. of Agriculture *Bull.* No. 30, 50 *et. seq.*, 18.

Bell and Cameron: *Jnl. Phys. Chem.* (1906) **10** 659; Wolfgang Ostwald, *Zeit. Kol. Chem.* 2, Supplementheft, *Zeit. Kol. Chem* (1908). 20.

the town authorities of Bingham and all other interested parties to pump 400 gal. per min. from the open drain through that town, returning an equal volume from its tailings; this is called the creek water. It is always acid in character, contains considerable organic matter, which is objectionable as a consumer of oxygen, and varies in composition from time to time. A typical analysis is given in Table 3. The pumping operations at the Bingham mines are interrupted at 45-min. intervals, however, so the average from this source is about 600 gal. per min. It is anticipated that this source of supply will be largely augmented in the near future. The water at present has an alkaline reaction due to dissolved carbonate of lime. It is quite constant in composition and a typical analysis is shown also in Table 3. We are without adequate information as to its probable composition when the augmented supply becomes available.

To these must be added the tailings from the precipitating launders, which are quite acid in character and carry large amounts of dissolved iron. At present, part of these tailings are discharged through the Mascotte tunnel to Lark, where the small amount of copper they sometimes carry is precipitated on iron scrap in a "scavenger" plant. Another part is mixed with the Bingham mines water. When these waters are brought together, there is a noticeable precipitation of ferrous hydrate or carbonate. Passing through the pumps, through 1600 ft. of piping to the surface, and through the launders, pipes and ditches on the surface, the precipitation continues, accompanied by absorption of oxygen, so that all the conduits are soon lined and the surfaces upon which the water is discharged are soon covered with a deposit of ferric hydrate. On standing, the ferric hydrate settles to a dense mass, which has much merit as a seal in the pipes and launders, but is otherwise a great nuisance.

TABLE 3.—*Analyses of Waters Used for Leaching*

	Creek Water, Per Cent.	Bingham Mines Water, Per Cent.	Recirculated Water, Per Cent.
Fe''	0.016	0.001	0.107
Fe'''	0.012	0.001	0.005
Cu	0.0016	.....	0.0024
CaO	0.033	0.029	0.047
MgO	0.020	0.006	0.021
H_2SO_4	0.006	.....	0.008
$CaCO_3$	.....	0.010	.....

When the tailings and Bingham mines waters are mixed, both the dissolved calcium bicarbonate and the ferrous sulfate are greatly diluted; unfortunately, at high dilutions, the reaction between these salts is very slow, probably because of the very slow disengagement of the carbon dioxide. A laboratory investigation showed that about equal volumes of Bingham mines water and tailings produced a neutral solution, but after pumping air through such a mixture for intervals of about an hour, no apparent precipitation was obtained although it is readily apparent at all times about the mine workings. A precipitation was gradually obtained in the laboratory by heating such mixtures. Very serious consideration is being given to this "iron" problem, as it is undesirable to have the hydrate deposited in the orebody, even if it takes place at very shallow depths only; it adds appreciably to operating costs to replace piping the effective cross-section of which is reduced by the deposit. No chemical treatment seems to be economically justified. Filtration through sand seems to be the practicable and best means of meeting the situation. Not only will the solid precipitates be retained mechanically, but sand is particularly efficient in selectively absorbing iron from its dissolved salts and permitting the freed acid to be carried on by the percolating waters.[7] This remedy, to be fully effective, presupposes complete adoption of the film method of percolation and practical engineering difficulties may prevent this being done in its entirety until the completion of the Dederich tunnel.

If, and when, the sand filtration method cannot be followed, it would be desirable to discard all the tailing waters, for their content of copper (about 0.4 lb. per 1000 gal.) is not sufficient to justify any treatment other than at the company's scavenger plant. Unfortunately, this is not deemed practicable at present, as it appears unwise to leach with the Bingham mines water directly, for it is feared that in the first part of its path through the orebody, it will precipitate copper instead of dissolving it because of its alkaline character. A mixing with the tailings is apparently the cheapest and an effective method of giving the percolating waters an acid reaction from the start of the leaching operation. Further experimental study of the question is under way.

Confusion regarding these "iron" phenomena has developed wherever similar operations are carried on and has led to erroneous concepts of what may be occurring within the orebody. It is assumed that ferrous sulfate is hydrolized in solution, which is true; that oxygen is absorbed and converts the hydrolized ferrous hydrate to ferric hydrate, which is true; and that the ferric hydrate then precipitates, which is not true, as any one may quickly learn by trying the experiment under controlled conditions of the laboratory. The total content of sulfuric acid is not changed on the absorption of oxygen and ferric sulfate is much more

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[7] For a discussion and references see Bureau of Soils, U. S. Department of Agriculture (1905) *Bull.* No. 30.

soluble than ferrous sulfate; consequently, there is no change in the content of dissolved iron. What does happen, if time and oxygen are sufficient, is a complete conversion of the ferrous sulfate to ferric sulfate and this latter is hydrolized to the degree that the solution behaves in its solvent action on metals, oxides, or carbonates, as though it were a solution of free sulfuric acid. If, now, the solution is neutralized by adding some relatively strong basic substance, as the calcium bicarbonate of the Bingham mines water, the weak base ferric hydrate will be formed and, being insoluble, it will precipitate. The descriptive phrase "hydrolizing out of iron" is most unfortunate in concept and expression. The phenomenon of hydrolysis of electrolytes in aqueous solution is entirely different and distinct from the phenomenon of precipitation of an insoluble substance resulting from a reaction and there can be no justification for confusing the two.

Ferric hydrate is an exceedingly weak base, weaker than cupric hydrate which, in turn, is weaker than ferrous hydrate. If, then, to a given solution of ferric sulfate, cupric hydrate or ferrous hydrate is added slowly and continuously, at first there will be solution and disappearance of all solid phases, but in time ferric hydrate will commence to separate as solid phase, just as though any other base were being added, such as magnesium hydrate or sodium hydrate. As pure ferrous hydrate will turn red litmus to blue,[8] one would expect that a complete precipitation of ferric hydrate might be accomplished by adding enough ferrous hydrate, although obviously more than a stoichiometrical equivalent of magnesium or sodium hydrate, because ferrous sulfate itself is appreciably hydrolized with formation of an acid solution. Similarly, ferric iron may be precipitated from a sulfate solution by cupric hydrate. The precipitation of cupric hydrate by ferrous hydrate is a more complicated affair because of the difference in the state of oxidation; it is to be expected that there will be reduction of the cupric to cuprous hydrate with oxidation of the ferrous to ferric hydrate and precipitation of this last.

It has been shown above that cupric hydrate and ferrous hydrate are present in the orebody. It is conceivable that a percolating solution of ferric sulfate, either in traversing a long path or by moving slowly, might ultimately dissolve sufficient cupric or ferrous hydrate to cause precipitation of ferric hydrate, especially if this path had previously been scoured free from cupric sulfate. The probability of such a catastrophe seems remote, but catastrophe it might well be if the precipitation were long continued, hence, the wisdom in not taking the chance and removing the possibility. The only certain and practical way yet suggesting itself is the use of the sand filter.

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[8] Mendelew.

PRECIPITATION

The precipitation plant is located in the Mascotte tunnel about 2 miles from the portal at Lark. It is arranged in two rows of launders on either side of the haulage track, each row aggregating 1600 ft. in length, or 3200 ft. in all. The rows are subdivided into sections of 320 ft. with a siphon at the end of each section to bypass the pregnant solution to the opposite row during washing or loading operations. The individual units are 16 ft. long with a cross section 32 by 32 in. They are gunited to prevent leakage. A false bottom is supported 17 in. above the floor of the launder; this bottom is a wooden lattice with ¼-in. square openings and is built in sections for ease of handling. Immediately above the lattice, in the side of the launder, is a hole that is opened during washing or draining; at other times it is closed with a plug. The rows are set with a grade of 0.5 per cent. The pregnant solution (heads) is brought to the launders from the old ore chutes, where it appears in the tunnel, by a launder system aggregating about 1500 ft. The barren solution (tails) is discharged to a drain through the tunnel to Lark, but with a gate a few feet beyond the precipitating launders, where it is diverted, in part, into a sump from which it is pumped to the surface above the orebody. This sump receives also the Bingham mines water in transit to the surface.

The scrap, or detinned iron, is received in compressed bales weighing about 75 lb. each. The Metal & Thermit Corpn., from whom it is obtained, remove the tin by treatment with caustic soda, leaving a metal with a surface very well adapted to copper precipitation. Usually it reaches the launders in excellent condition, but sometimes there is a little adherent caustic and rust. The bales are torn apart at the launders and the loosened scrap heaped upon the false bottom; it is the duty of the plant operatives to keep a full supply in the launders always. It seems to be necessary that the scrap be piled well above the surface of the solution and apparently offering an excellent opportunity for rusting; twice the equivalent iron is lost as a copper precipitant, and with added contamination of the copper. The experiment was tried of running two series of boxes in parallel; in one series the scrap was kept completely submerged, while in the other it was piled above the surface as usual. After some days the copper precipitated was sampled. They showed no significant difference in grade or iron content but in both cases were somewhat above the grade usually recovered from the same boxes. The latter fact is probably due to the more than usual interest, and therefore care, of the plant operatives in the experimental boxes. It is probable that if solid oxides of iron were formed, they were floated on to succeeding launders. As the weight of scrap used and copper recovered were not recorded, it is yet to be determined if complete submergence is desirable or would justify the additional labor that would be required.

The Mascotte tunnel and all offsets where men are employed are well lighted by electricity. Extra and ample lighting is provided in the precipitation plant. An electric tram provides adequate haulage facilities and the ventilation in the plant is good. At intervals, 2-in. piping with hose attachments are provided for washing the copper and keeping the equipment clean. The equipment is first class and adequate, and the operations well done, due, in great measure, to the small labor turnover. Three shifts of fifteen men each are employed in the plant operations.

The pregnant solutions reaching the head of the launders vary somewhat in volume, from 1200 to 1500 gal. per min. The average rate of flow or advancement down the launder system is about 40 ft. per min., so that the minimum time of contact with metal is not less than 40 min. The gradient being fixed, the rate of flow is determined by the volume of solution handled and the effective cross section of the launders; this last, in turn, is determined by the amount of scrap submerged. The general policy is to crowd the submerged scrap as much as possible without causing overflows. Under any conditions, the velocity of transport is higher than the usual practice elsewhere, but it is thought to be an important factor for the production of a high-grade copper precipitate.

The composition of the pregnant solution also varies somewhat, and probably always will. Naturally we may anticipate much higher heads as development at the surface makes possible a wider area of ore surface to be bathed by the percolating waters; it is thought that this will be advantageous not only in an increased production, but because increases in grade of product and efficiency in iron consumption are promoted by "high" heads. The composition of the solution for the last six months of 1924 is indicated in Table 4, the figures being averages of the daily analyses.

TABLE 4.—*Pregnant Solutions for 6 Month Period*, 1924

Month	Head, Gal. per Min.	Insol., Per Cent.	$CuSO_4$, Per Cent.	$FeSO_4$, Per Cent.	$Fe_2(SO_4)_3$, Per Cent.	$CaSO_4$, Per Cent.	$MgSO_4$, Per Cent.	$Al_2(SO_4)_3$, Per Cent.
July	1352	0.011	0.494	0.052	0.147	0.141	0.102	0.168
August	1402	0.012	0.477	0.035	0.125	0.141	0.087	0.332
September	1343	0.013	0.454	0.060	0.086	0.141	0.097	0.157
October	1260	0.013	0.617	0.095	0.125	0.143	0.135	0.157
November	1324	0.012	0.412	0.049	0.150	0.148	0.197	0.077
December	1407	0.012	0.324	0.033	0.168	0.156	0.281	0.107

These figures appear to show that the use of the smaller volume of water not only brings higher heads to the precipitating launders, but also more copper. For instance, in October, with an average volume of 1260 gal. per min. percolation, about 65 lb. per min. of copper sulfate was treated; while in August, with 1402 gal. and in December, with 1407 gal. per min., 56 and 39 lb. of copper sulfate per minute were treated. The figure for August is associated with, and probably due to, the extraordinary concentration of aluminum sulfate. The figures are practical arguments for film percolation. Further, it appears that while the percentage of total iron in the smaller and larger volumes does not differ significantly, so that the actual mass will be less with less water, a significant difference does exist in the state of oxidation, a larger proportion being ferric iron, when the larger volume of water is employed. This means that more scrap will yield less copper when the larger volume is employed.

The average copper (Cu) content of the pregnant solution for the year 1924 was 0.204 per cent., that of the barren solution 0.0058 per cent.; hence the recovery was somewhat better than 97 per cent. This must be considered a very gratifying result when the iron consumption is also considered. The record of actual shipments confirms the calculated recoveries quite closely and mechanical losses are small.

The principal factors determining the rate of precipitation of the copper, aside from temperature, are the concentration of the solution with respect to copper and sulfuric acid.[9] Consequently, the precipitation regularly decreases as the solution becomes impoverished in copper content, and the acidity is decreased by solution of ferrous iron. These facts are shown in Table 5, which has been computed from the analyses of the solutions entering at the head of the sections indicated.

TABLE 5.—*Percentage Recovery of Copper in Several Sectors; Averages for the Year* 1924

Average volume of pregnant solution, 1276 gal. per min.
Average copper per 1000 gal. pregnant solution, 17.031 lb.

Sections	1–2	3–4	5–6	7–8	9–10	All
Recovery	37.2	29.2	17.9	8.7	4.3	97.3

The relatively high velocity of the solution through the launders, and the agitation thereby produced, prevents occlusion or "sticking" of foreign substances in or upon the copper films as deposited. Moreover, it floats, or carries in mechanical suspension, the smaller and lightest particles from box to box. This flotation is selective, hence there is a marked and progressive segregation of ferric oxide in the lower launders. These facts have been charted, Fig. 1, where "grade" of the product has been plotted against percentage of copper in solution. As a matter of practice it has been found that a high velocity of the solution is more important

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[9] Iron does not precipitate copper from an alkaline solution but zinc does; these facts suggest that the high concentration of acid is desirable because of the more rapid solution of the iron therein.

than long-continued contact of metallic iron and solution. In the earlier operations, when the launders were set so that the movement of the solution was sluggish, poor recoveries were realized; but, the recoveries were promptly brought to their present high efficiency when the launders were brought to their present gradient.

The speed with which the copper is precipitated may be a practical factor in the purity, or grade, obtained, aside from mechanical inclusions in the film. Theoretical and *a priori* considerations would suggest a better copper with slow deposition from dilute solution. Actually, plant results seem to be opposed in that the best grade of copper is obtained with high heads and rapid deposition, the grade always falling below 90 per cent. when the concentration of copper in solution falls below 0.06 per cent. Whether or not slow deposition is undesirable for good plant precipitation and the plant observations are a confusion of other and masking phenomena, is of practicable importance and must be worked out under controlled laboratory conditions.

In its progress through the launders, the solution becomes progressively leaner in copper, but progressively dissolves iron to form ferrous sulfate. Ferrous iron is a fairly strong base, so the hydrogen ion concentration is rapidly reduced. Gaseous hydrogen escapes from the solution and precipitation of metallic copper slows down. There must be some absorption of oxygen as well as evaporation in the passage through the launders; this oxidation is reflected in a higher and higher consumption of iron per unit of copper precipitated. The concentration may reach the point where a basic ferrous sulfate will separate as solid phase; some observations in the plant indicate that this has happened, although the major part of it must have floated off in the tailings. It has been suggested that in the nearly neutralized solutions of the lower launders the relatively "strong" base ferrous hydroxide causes a precipitation of the relatively very "weak" base ferric hydrate formed by the absorption of oxygen and that this accounts for the accumulation of the latter in the copper recovered. In other words, metallic iron in a satuated solution of ferrous sulfate exposed to the air will completely disappear to form ferric hydrate and it is futile to attempt the recovery of a small amount of copper from such a solution. Technically the addition of more water and sulfuric acid is the answer; economically, the problem is whether a very high recovery of copper is justified, considering the iron consumption and equipment necessary. The answer may well vary for different installations and at the same installation with changing conditions in the price for copper, iron or labor.

At the Ohio Copper Co.'s plant, the consumption of iron in the several sectors is to be determined with the precision necessary to justify any modification of the present practice, which has been developed empirically. It is believed that contamination of the copper from precipitated ferric hydrate is not serious, if it occurs at all, the ferric oxide in the lower grades being explained by the rust on the scrap, with selective flotation. In all grades, there is always some iron, usually an insignificant amount, in the form of minute undissolved fragments of scrap, and a decidedly significant amount in occluded and adsorbed sulfates which cannot be removed by washing with water alone.

The iron consumption for the entire operation is about pound for pound; that is, a pound of iron is dissolved for every pound of copper shipped. This result would probably compare favorably with those obtained elsewhere; nevertheless, a margin for improvement exists. It shows that about 88 per cent. of the iron is actually used in precipitating copper. Allowing 2 per cent. for rust and impurities, about 10 per cent. is used in reducing ferric iron to the ferrous condition. No great improvement in the plant practice appears possible, hence any increased efficiency in iron consumption must be sought in an increase in the ratio of copper to iron in the pregnant solution with improved percolation. That this will be realized, is indicated clearly by the history of this enterprise.

The Product

Depending on its position, the concentration of the pregnant solution, and to less extent on other factors, the space below the false bottom of the individual launder becomes filled with copper in from 6 to 30 days. Always several launders are about filled at the same time. The solution is then bypassed, by the siphons at the head of the section, and when the flow has ceased the plugs are drawn in the launders to be emptied, the scrap washed by means of the hose, and moved to a convenient place. The copper is agitated and washed by means of the hose, settled, the supernatant solution of ferrous sulfate drained off, and the copper shoveled into lorries and carried to the loading station at Lark, when it is shipped to its destination. On the whole, the operation is efficient. Washing the scrap recovers copper from it and improves its surface for further use, but entails a certain risk of carrying small fragments of iron and other undesirable components into the copper. Possibly a diaphragm pump could advantageously be employed for loading the lorries. About three-fourths of the product, when dried, will grade 90 per cent. copper or better; the remainder, from the lower launders and containing much iron, grades sometimes to a lower limit of 60 per cent., but usually above 70 per cent. copper.

By the time the product is loaded at Lark, it has settled and much water has drained from it. As shipped, it carries about 30 per cent. water, which has somewhat lessened at destination where sampling for settlement analyses are taken. Meanwhile, oxidation has taken place, the bright characteristic metallic appearance has given way to a dull brown or almost black. On drying, in preparation of the sample for analysis, a further and more extensive oxidation occurs, which may amount to 5 per cent. or more, so that a product which should grade 90 per cent. copper will grade only 86.5 per cent. This difficulty is a serious handicap in the marketing of cement copper and working out an equitable basis for settlements. Two problems are involved. One, the working out of a quick laboratory method of drying the sample, which will preclude further oxidation without reduction of any oxides that may already be present; attempts to dry the sample in an inert gas are promising. The second problem is to free the product from moisture before shipment, without at the same time oxidizing it.

To this end, it has been suggested that the product be dried in a current of stack gases, but it is necessary to use an excessive amount of heat to remove the moisture to the point where oxidation will not promptly set in and continue extensively unless stirring be employed; and with stirring, dust losses are high.

Melting has been proposed. The product is excellent, for no refining is needed, and it appears to be a simple matter to reduce copper oxide to a negligible minimum and slag and skim off the iron, sulfur and silica. But the dust losses are again high in the melting and the product must be dried first.

Recourse to briquetting at high pressures seems to promise a way out of the difficulty. The Salt Lake Iron & Steel Co. has put at our disposal 100-ton hydraulic press and the Salt Lake Shop of the D. & R. G. W. R. R. has permitted certain experiments with its 600-ton press.

The first experiments were made with rejects of the settlement samples, which were stirred up with an excess of water. The results were promising but the bricks were too high, in comparison with their cross-section, and broke or shattered too easily, generally along surfaces in which some foreign substance, usually a silicate mineral fragment, was embedded. On standing 24 hr., apparently due to readjustment of internal stresses, the bricks became much tougher and resistant to breaking tests. Coming from the press, the bricks felt cold, but quickly came to room temperature and appeared to be perfectly dry. The water extruded in the pressing carried notable quantities of ferrous sulfate and some ferric sulfate.

Bricks were then prepared at various pressures, up to 150 tons per square inch. The densities, when plotted against the pressures, fell on a smooth curve; but as subsequent investigation proved them to have no absolute significance, they are not presented. The curve was asymptotic and it appeared that the higher pressures would not be justified by the increase in density attained, considering the added expense of building a press for a quantity production with excessive pressures. At 150 tons per square inch, the plunger was bent and split and the die was distorted.

Special steels from two manufacturers have been secured, new dies and plungers made and tested, and it is no longer a problem to secure suitable material for them.

The brick made at 150-tons pressure, although distorted and, when tested, showing but little greater density than bricks made at half the pressure, nevertheless appeared, generally, to be more desirable and less resistant to abrasion than any yet made. The density, a little more than 6, was far short of the density of melted copper; hence a more detailed study of the bricks was made in various ways, which need not be detailed.

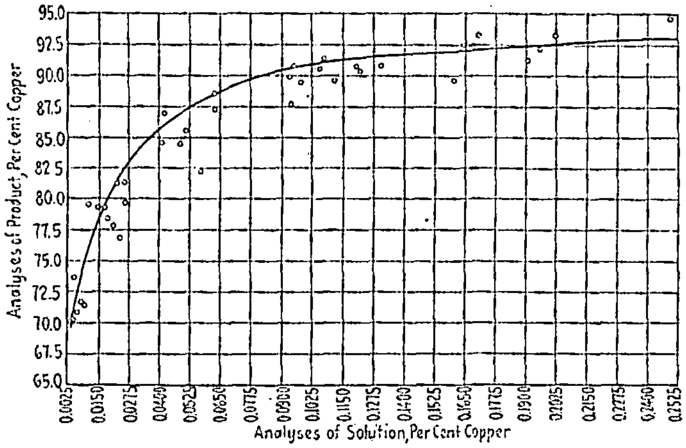

FIG. 1.—CURVE SHOWING GRADE OF PRODUCT OBTAINED USING VARYING CONCENTRATION OF COPPER IN HEADING SOLUTION; ANALYSES OF PRODUCT OBTAINED FROM AVERAGE COPPER CONTENT OF CONTROLS RECEIVED FROM JUNE, 1924, TO APRIL, 1925; ANALYSES OF SOLUTION, AVERAGE ANALYSES DURING THIS PERIOD.

It was found that, for stability, the truncated cone is most desirable and that the height should be less than the diameter; the samples of copper tested so far were unsuited to the purpose, the individual particles being coated with an oxide film. A suitable die having been made, a barrel of the fresh product was shipped directly to the foundry, a brick made for the instruction of one of the laborers, who thereupon, himself, promptly made about 100 of the bricks, at a pressure of 40 tons to the square inch, without slip or mischance of any kind to bricks, die or plunger. This shows that the operation can readily be carried on by intelligent labor without special training; satisfactory steel is available for dies and plungers and excessive pressures are not required, for the bricks made were in every respect satisfactory. They were heaped promiscuously in a nail keg, which was placed in the tonneau of a small motor car and carried over roads and pavements, cartracks, etc., and showed no abrasion. They are very resistant to breakage on being dropped or struck with a hammer. They have been drilled and sawed, showing clear metallic surfaces after the tool. After standing for several weeks, the surfaces are yet bright, showing little or no evidence of oxidation. Placed in a clay crucible in a muffle, they melt cleanly, as would a copper bar, without any suggestion of dusting. In fine, they appear to be in excellent form for shipping.

Analysis of the product shipped to the foundry was made at the plant laboratory, which reported a copper content of 91.4 per cent. Two of the bricks, picked at random, were sent to the laboratory which reported as follows:

	Cu, Per Cent.	Fe_2O_3, Per Cent.	Insol., Per Cent.	S, Per Cent.	Moisture, Per Cent.
Before briquetting........	91.48	1.90	0.70	0.27	43.80
After briquetting..........	94.43	1.64	1.00	.18	.76

Another brick, also picked at random, was sent to Crismon & Nichols, public analysts, who reported 95 per cent. copper. It may thus be said that an appreciable increase in grade is obtained by the briquetting in addition to putting the product into a dry form, resistant to oxidation, and well suited for direct shipment or to melting. Preliminary inquiries indicate that the difference in cost of installation would not be of material import between a suitable press or dryer equipment, while the operating cost would be greatly in favor of the press.

The slight compressibility of water and its extrusion in the restricted space between the plunger and walls of the die, was foreseen; also that a part of the occluded iron would be thus removed. As ferrous sulfate dissolves with contraction of the volume of water, pressure must increase the solubility. It would be interesting to determine the relations between the effect of pressure on the absorbed or adsorbed solute and solvent, but for the present we are obliged to be content with the assurance these experiments have given that it is quite practicable to prepare a cement copper for shipment with an iron content of less than 1 per cent.

COSTS

Up to and including April 30, 1925, there has been shipped by the Ohio Copper Co. 17,076,099 lb. of cement copper at a total operating cost of $656,837.32. The smelting charges during the same period have been $422,919.22, bringing the total cost of making and marketing the product to $1,079,756.54. Consequently, on the pound basis, the figures are 3.847 cents for operating; 2.477 cents for smelting charges, and 6.323 cents for making and marketing.

The figure for operating cost includes all labor and materials in leaching, precipitating, mining and exploration, office, laboratory, and salaries at Bingham, Lark, and Salt Lake City. It varies from time to time with production or with the individual items. The cost of the iron per pound of copper produced is approximately 1.25 cents for the metal. More than half the labor is expended in handling the iron, hence it seems safe to assess half the remaining operating cost to it, bringing the total cost of iron to 2.55 cents, or a little more than 66 per cent. of the total operating cost of making copper under present conditions. Instinctively, the engineer will look here for an opportunity to cut costs. It has been shown that there is possible a small improvement in iron consumption with an increase in the copper content and decrease in the ferric-iron content of the pregnant solution and, doubtless, with the larger mass of scrap that will be required by an increased copper production, there may be a small decrease in the labor item; however, no important change in the present efficient handling of the scrap is foreseen, hence, no important lowering of the cost for iron.

On the other hand, with an increased production of copper and an increased revenue in consequence, it is reasonable to anticipate that a much larger campaign of exploration and development will be inaugurated. All the evidence available, and it is significant in amount and character, is to the effect that there is an enormous territory contiguous to the present caved zone, with a copper content as high, or higher, which can be caved and prepared for leaching. Apparently much of this region can be so prepared economically; experts differ as to the extent to which such operations should be carried. From an engineering point of view, it would be desirable to resume a systematic exploration of the uncaved regions, for it must remain a speculative problem what the life and value of the enterprise may be until a more precise knowledge of the nature of the ore has been obtained, as well as the cost of mining, moving, and crushing it.

Life of the Enterprise

A visit to the Dederich tunnel, now some 590 ft. into the caved zone, will show that there is much copper sulfate to be removed. It is everywhere apparent that the oxidation of sulfides is continuously in progress, for the temperature is uncomfortably high except at the outlet from the blower; particularly, it will be evident that no leaching has been effected in the part of the caved zone now accessible. Attempts to outline, in diagram, the probable paths of water already applied on the surface but add to the conviction that only a restricted portion of the caved zone has been leached and that the greater part is yet to be so treated. It is evident that the recovery of the copper is to be a gradual process throughout many years. If we accept an estimate of 34,000,000 tons of ore in the caved zone and make a conservative estimate of the average content of copper that may economically be removed by leaching, say 0.3 per cent., and that during the period of removal there will be an average production, annually, of 10,000,000 lb., the life of the operation will be 20 years.

Norden and Crane[10] have estimated the caved zone to contain 251,218,248 lb. of copper, of which 136,107,463 lb. can be recovered by leaching. Examination of the details of their estimate in the light of our present experience inclines us to the opinion that these engineers were ultra-conservative. They further estimate "proved" territory adjacent to the present caved zone to contain 322,427,696 lb. of which 214,414,418 lb. can be recovered by leaching, although expressing doubt of the economic feasibility of recovering part of this estimated poundage. To resolve these doubts, further exploration work is necessary. In addition, there is a much larger territory of unproved rock, some of which undoubtedly contains sufficient copper to justify leaching, but it is pure speculation at this writing to state quantities. From an engineering point of view, the prospects amply justify an early and systematic exploration of the possible reserves and preparation of new territory for leaching. Other considerations must have their weight. The rapid development of large sources of copper in South America and Africa will undoubtedly have a marked effect on the market, probably in the direction of lower selling values, at least until the world market has been stabilized, and the selling price must be a factor in determining what can reasonably be expended in preparing new leaching territory. Fortunately the proved operating expenses, together with the economies in sight, assure a continued production by the Ohio Copper Co. against any probable competition and for a period to be measured in decades.

DISCUSSION

T. B. **Brighton**, Salt Lake City, Utah.—There are near Lark 6,000,000 or 7,000,000 tons of tailings from the Ohio Copper concentrators. These tailings contain an average of about 0.4 per cent. copper, partly in an oxidized form. Since leaching of waste rock in the old stopes and fills has proved profitable, the question has been raised as to whether or not a leaching treatment of the tailings would pay. The material in the old ponds is striated and there are lenses of slimes, which are not easily permeable to water, so that any leaching in place in quantity is out of the question. When these claylike slimes are broken up and mixed with the sand tailings, water percolates through the mass quite readily.

At the University of Utah, we have made a few tests to see what recoveries of copper might be expected if the tailings were broken up and leached. The total copper present averages about 8 lb. per ton, but only part of it is water soluble. Long percolation with distilled water dissolves only about 1.5 lb. per ton and a short stirring with three

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[10] Private communications; valuation report, January, 1924.

parts water to one part tailings causes only about 0.7 lb. per ton to dissolve.

The only water now available for leaching is that from the precipitating tanks of the company. This flows from the Mascotte tunnel and is distinctly acid in character. Tests made with dilute sulfuric acid, made up 2 lb. of acid per ton of water, showed that approximately 2.7 lb. could be dissolved in 1 to 3 pulp by short stirring. Under the same conditions, the water from the precipitating boxes dissolves 2.8 lb. per ton. Some of this is held up by the water that will not drain from the tailings, so that only about 2.5 lb. can be obtained in the solution for recovery. Repeated percolation over several hours with fresh precipitation box water removes almost half of the total copper present, but not more than the above 2.5 lb. would be in solutions of such concentrations that it could be recovered at a profit by precipitation.

Whether or not the recovery of 2.5 lb. of copper per ton of tailings will pay will depend on the cost of breaking up the bedded material, moving, leaching and dewatering it, and then precipitating the copper. Simple agitation with water does not produce a solution that settles clear quickly so either some type of filtration would be needed or settlers of considerable extent.

A considerable part of the iron in solution is in the ferric state so that precipitation costs on detinned scrap would be above normal. While careful analysis of costs might show a possible profit, the margin, if any, is extremely small. To us, it appears that under present conditions, leaching of the tailings would not prove a profitable undertaking.

In many places on the tailings beds a considerable part of the soluble copper has been carried, by the capillary rise of water, to near the surface. In some spots, the surface is distinctly blue; from such places copper salts are being steadily removed by wind action. So the recoverable copper present in the beds depends on the rate of oxidation of the sulfides and the rate of removal of copper salts by capillary rise and subsequent wind action. Given sufficient time, natural processes will remove a large part of the copper originally present and, when removal is proceeding more rapidly than oxidation of new sulfides, the possible value of the old deposits will drop. So unless copper prices increase or handling methods considerably improve, the tailings ponds are likely to remain undisturbed.

H. C. Goodrich, Salt Lake City, Utah.—Is there any difference in the amount of iron consumed and copper recovered in these various sections; that is, the first 640 ft. and the second 640 ft.?

A. E. Anderson.—Daily analyses are made of the solutions leaving each respective set of sections. The average analyses of these solutions for several months indicate that the consumption of iron per pound of copper precipitated is about 1 to 1, showing that the consumption of iron throughout the plant is quite uniform and ordinary analytical methods do not detect any greater consumption of iron in any particular set of sections.

H. C. Goodrich.—Is there any difference in the cost on the tailing and upper ends of the operation?

A. E. Anderson.—The labor per pound of copper extracted is practically the same in each section. The unconsumed iron is separated from the copper by washing the precipitated copper through a false bottom into a settling chamber, using a hose placed at regular intervals throughout the plant. The chief iron-consuming constituents of the heading solutions are copper sulfate, ferric sulfate, and some free sulfuric acid. As the ferric iron and the free acid are the only compounds that would produce a high iron consumption per pound of copper precipitated, the lower boxes will contain less of these compounds and consequently the consumption of the iron will theoretically be less. As I have stated, the average analyses of solutions indicate a very uniform consumption of iron throughout the plant. The quantity of ferric iron and acid present in the original heading solution is so small that from a practical standpoint the errors introduced by sampling etc. more than offset this consumption and, therefore, we have the conditions as given. Of course if the ferrous iron were oxidized to ferric during the time the solutions were passing through the sections, one would expect to find the costs of producing copper to be higher in the lower boxes than in the upper but the rate of flow of solutions and the excess quantity of scrap iron prevents the oxidation of the ferrous iron and in very few instances have we found ferric iron in the tailing solutions.

T. P. Billings, Salt Lake City, Utah.—If the iron in the solution containing the copper were increased would the extraction decrease?

A. E. Anderson.—The iron in the heading solutions is very constant, therefore I can give no data pertaining to this effect.

T. P. Billings.—We had some experience using solutions from two sources and found that the solution low in iron gave recoveries of the copper around 99.0 per cent., while the solution high in iron gave very low recoveries. I thought that this low recovery was due to the presence of the iron.

F. K. Cameron.—The fact that all the iron must be reduced before the copper will precipitate will probably account for the low recoveries when using a solution high in iron. The detinned iron added in the upper boxes was being consumed by the ferric iron and was not efficiently precipitating the copper; therefore, to obtain the good recoveries it requires more iron which probably, in your case, would mean more boxes, and not having them your recoveries were low.

SOCIETY OF
MINING ENGINEERS
of
AIME

345 EAST 47TH STREET, NEW YORK, N. Y. 10017

PREPRINT
NUMBER

71-AS-88

A REVIEW OF IN SITU LEACHING

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This paper is to be presented at the AIME CENTENNIAL ANNUAL MEETING
New York, New York - February 26 - March 4, 1971

In situ, or in-place leaching is concerned with the extraction of metals from natural mineral disseminations without removal from their geologic location which, in many cases, amounts to the reversal of the deposition process accompanied by a presumed increase in velocity of the processes, if the project is to be profitable.

Solution mining processes involve removal of minerals such as sulfur, common salt, and potash, generally leaving cavernous voids, in contrast to in situ leaching which term is applied to the selective dissolution of a mineral from its gangue without sensible disturbance of the formation. Where such a process can be operated, the advantages are manifold and have been so recognized by miners from the earliest days of mining.

Recent technological developments have encouraged a reassessment of the status of in situ leaching, and it now appears possible to extend the application of the method from a few isolated special situations to many uranium and copper deposits.

Anaconda's interest in the techniques stems from long experience with vat and heap leaching, dump leaching, and natural leach activities associated with several established mines. Increasing activity throughout the industry has been noted, particularly in leaching low grade pillars and the peripheral zones of operating mines, often by the introduction of leach solutions via boreholes drilled from surface. Reactivation of dormant mines[1] using similar techniques has been successful.

Over the long term, environmental improvement activity will lead to excess sulfuric acid production, even to a disposal problem. The cost of leach solutions and reagents must be reexamined in this light.

The mineral industry now classifies as uneconomic deposits of readily soluble minerals whose potential value, on a per acre basis, may be several times that of many currently profitable oil field reservoirs. Some of these deposits are suitable for in-place leaching. There is evidence that the cost of selected in-place leaching mineral recovery systems and the technical problems to be solved may not be much greater than those of secondary oil recovery operations.

A measure of the current interest in these processes is the level of patent activity. Recent applications have directly referred to:

Borax
Copper
Mercury
Molybdenite
Phosphate
Potash
Salt (NaCl)
Trona
Uranium

Brief notes on several patents are given in Sievert's paper.[2] A comprehensive bibliography of chemical mining references is available.[3]

Leaching agents attracting attention are dilute aqueous solutions of:[4]

Sulfuric acid - ferric sulfate,
Sodium carbonate - sodium bicarbonate,
Sodium chloride, ferric sulfate, ferric chloride,
Thiosulfates,
plus bio-extractive materials[5]

The research effort involves contributions from many engineering and scientific disciplines, bringing a variety of new specialists into the mining field. Anaconda's investigations have been led by the author, a member of the Mining Research Department, and experience at pilot plant scale has shown that the effective research team requires:

1. Geologists to locate, describe and value the mineral deposit.
2. Hydrologists with strong ground water experience to detail the environment in which the process is to operate, forecast the changes likely to occur, and to expose potential pollution problems.

3. Petroleum engineers to contribute knowledge of drilling and well completion techniques.
4. Reservoir engineers for specialized knowledge of water flood techniques, flow net analysis and field experience in permeability-porosity relationships, clay behavior and similar problems.
5. Computer programmers and mathematicians to process and analyze masses of data.
6. Metallurgists to design and control the chemical processes.
7. Bacteriologists to discourage harmful and encourage useful bio-extractive agents.

And, of course, mechanical engineers, drillers, geophysical services, and many others.

Metallurgical processes for leaching ores and low grade materials after mining and transportation to prepared locations are well developed. The annual production of copper is in the many millions of pounds and of uranium in the tens of thousands of pounds by these methods. Recovery efficiency is low in terms of annual recovery as a percentage of total metal content of a dump. Overall recovery estimates currently run around 20%. This low figure is primarily the result of failure to achieve contact between lixiviant and mineral, and losses of pregnant liquor through the dump base. Where conditions are favorable, in-place leaching may offer an improvement over dump performance and maintain extraction efficiency through seasonal temperature changes.

In-place leaching under suitable conditions may exhibit some of the following advantages. Note that the first three are of particular interest in 1971.

1. Minimum capital investment -- by mining standards.

2. Very short preproduction period -- three months is not impossible.
3. Minimum pollution of land, water, air.
4. Very low labor intensity per unit of product.
5. Extremely low safety hazard.
6. Probable application of these methods to inaccessible mineral deposits -- offshore, high rock pressures, high temperatures, under permanent ice, underground conditions unsuitable to exploitation by known techniques.
7. Negligible waste disposal costs.

In certain circumstances, in-place leaching may be a profitable addition to existing production facilities. Low grade or low tonnage peripheral zones may be treated to provide additional metal recovery from a mining lease,[6] or alternately to increase production rate where a conventional concentrator plant is operating at maximum designed rate. In each case, demands for new capital expenditures are reduced significantly, and the economics of leaching requires a special study for each situation.

While some or all of these advantages may be applicable to a given orebody, there are three factors which will play an increasingly important part in the future of the mining industry. These are

1. Pollution,
2. Safety, and
3. Process optimization.

While there are possibilities for chemical and thermal pollution of underground waters with in situ leach systems, the system under development by Anaconda is designed to be pollution free.

By any criterion the hazard rating of an in-place leach operation is low. Equipment is simple, fully developed, and the accessible surface plant works under conditions of low pressure, low temperature and chemical activity.

Even such exotic methods as corrosive gas leaching (chlorine and steam, for example) use equipment that is well developed and very safe to operate. It is a little early to discuss chloride-complex brines, but they offer very attractive alternates to low concentration acid and the end result may be to leave a harmless and chlorinated water supply. It is interesting to note the role played by chloride brines in cases of natural mineral mobilization occurring at the present time.[7]

A systems engineering approach exposes the reduction in the number of process stages required to produce a salable product using in-place methods. It is believed that this is the road to reduction of production costs in the long run.

Each stage in a production process in most instances consumes labor, power and materials, requires plant investment and capital servicing, and frequently involves product losses of some kind. It may, therefore, be attractive to operate a small number of process stages at quite low efficiency rather than strive for high technical efficiency in each of a multiplicity of process stages, thus finally achieving the same end. Along with the reduction of process stages come such fringe benefits as lower administration, supervision and labor costs, lower capital investment and sharply reduced service department expenditures.

In the case of in-place leaching, the reduction of stages compared with conventional mining is likely to be as follows:

Stage eliminated	Significant improvements in
1. Mining	Labor costs Safety Power costs Support costs Rock breaking costs Capital investment
2. Rock Handling	Power costs Hoisting and storage
3. Crushing	Capital costs Power costs Wearing parts cost
4. Grinding	Capital costs Wearing parts cost
5. Tailings dam operation	No chemical neutralization* No radium problem* No land requirement* No effluent problem*
6. Waste dump operation	No land requirement No landscape and pollution problems No conservationist attention

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* Applied to uranium production.

Any mineralized zone exhibiting the following characteristics may be suitable for in situ leaching.

1. Technically amenable to hydrometallurgy (the economics of leaching are rapidly changing, in particular, processes utilizing sulfuric acid).
2. A degree of permeability -- better than 5 millidarcies (as an illustration of this value, a poor-yielding water well running 5 gpm will require a permeability of 500 millidarcies over about 100-ft thickness of aquifer).
3. Ability to confine liquor circulation to the operational zone. (It can be assumed that this is feasible wherever the deposit lies below the natural ground-water table.)

Given the above, the presence of any, or a combination of the following conditions will favor the in situ leaching approach.

1. Subore deposit resulting from
    a. Dissemination of values
    b. Excessive dilution when conventional mining methods used
    c. Low extraction ratio
2. Inaccessible or noneconomic using standard methods
    a. Ultradeep -- high pressures and temperatures
    b. Submergence -- water, ice, permafrost
        -- offshore locations
    c. Fringe areas and remnants of operating or defunct mine.
    d. Vulcanism
3. Environmental, social, and health factors
    a. Effluent disposal problems
    b. Tailings disposal problems
    c. Unacceptable atmospheric pollution -- SO_2 particulates
    d. Radioactivity involving unacceptable levels in
        -- labor exposure
        -- effluent disposal
        -- tailings containment
    e. Land use restrictions -- disfigurement
        -- wildlife preserves
4. Integrated operation utilizing excess sulfuric acid from smelter stack gas pollution control units.

COMPARISON OF IN-PLACE LEACHING AND OIL FIELD WATERFLOOD TECHNIQUES

In general, at the present state of the art, flooded sandstone formations of less than 50-ft thickness, flat lying, and with upper and lower confining and impermeable beds, are by far the easiest to deal with. This discussion will be confined to this type of mineralized deposit.

Oil field waterfloods, or other secondary oil recovery techniques which are used to drive oil towards the production wells, are one-pass systems in which the bulk of the recovery is complete by the time of breakthrough of water as opposed to the multiple-pass, recirculation systems considered advantageous for mineral recovery. While it is conceded that one-pass, "reaction-front" types of mineral leaching methods may be developed in the future, such methods are not available in present day technology.

Secondary oil recovery operations generally encounter differences in physical characteristics of two fluids or of a gas and a fluid, in order to mobilize the crude oil and to drive the oil towards the recovery well. Differences in viscosity, density, and a general low miscibility result in mobility differences between the fluids on each side of the contact front, and such differences in apparent viscosity play a part in operational control. Such differences are not significant in mineral leaching operations.

The movement of the leaching solution away from the injection borehole is extremely irregular. Where rock permeability is high, liquid velocity and, consequently, the volume passing along such preferential direction is high, relative to other lower permeability zones. The higher velocities result in more rapid mixing with the liquid previously occupying the overrun sites; therefore, wide variations in liquor dilution rapidly develop within the rock formation.[8,9] The rock we have to deal with is heterogenous and anisotropic and this is typical of western sandstone uranium deposits.[10] Of economic necessity, liquor velocities are high compared with oil field secondary recovery practice and it is considered that about 90% of the rock volume under treatment will become a transition, or mixture zone, until several pore volumes of liquor have circulated. This is the conditioning time.

The results of these dispersion and dilution effects[11] is to create operational difficulties in the maintenance of a reaction-front zone in which the level of chemical activity is sufficient to perform the job intended. The reaction zone can be likened to the skin of an expanding balloon with deep wrinkles, the troughs extending perhaps only one tenth of the average radius of the reaction-front from the injection borehole. Contrary to waterflood practice, it is not considered that any mineral leach system will approximate this pattern.

The use of large volumes of highly concentrated acids may be feasible where the disposal of reclaimed pollutants is part of the overall scheme. However, preliminary investigations point to serious undesirable side effects, but discussion of this subject is outside the scope of this paper.

A secondary difficulty found in the reaction-front zone dissolution method involves effluent disposal. The high acid concentrations and redox values required to take the mineral into solution during the limited transit time of the reaction zone tends to pick up unwanted radicals, resulting in a surface plant effluent problem, and to change the quality of ground water left in the aquifer at termination of processing, a situation which will seldom be acceptable to the water resource authority, for good reason.

The dissolution of uranium minerals is a complex heterogenous reaction involving many steps over a period of time. Broken down to the simplest form, it involves

1. Contact between mineral and solution
2. Adsorption of reactants at the mineral surface.
3. Reaction
4. Desorption of products
5. Transfer of product from mineral surface to fluid recovery stream.

The mineral particle size ranges over perhaps some 5 orders of magnitude, creating difficulties in system design. The required contact, or residence time, and lixiviant concentration need to be maintained as the circumference of the slug expands from the injection borehole and as the reactants become used up. The variations of the sandstone permeability and, therefore, of liquor velocities increase the severity of the design problems.

It is expected that mineral leaching techniques will rely heavily, at least in the foreseeable future, on low energy chemical systems which differ from the natural ground water by small differences in pH and Eh. A slow conditioning stage precedes a recovery stage, and it is likely that a minimum of five pore volumes, that is, five or more recirculations of leach liquor, will be required for acceptable mineral recovery. For this reason and for reasons shown below, liquid velocities used are likely to be much higher than those common to waterflood practice.

A quick comparison of unit values will emphasize the difference between oil and uranium leach production. The following figures are typical for the Southwest U.S.A. area and are suitable for comparison, but should not be used for estimating.

Mineral (Uranium)		Oil (West Texas, New Mexico)	
Site value	$4.00/lb U_3O_8	Crude oil at well head	
Value of 42 gal. bbl	$0.14	Value of 42 gal. bbl	$2.95
Value of 1 gal.	$0.0033	Value of 1 gal.	$0.07
Value ratio	1	Value ratio (leach soln.=1)	21
Concentration U_3O_8, say	100 ppm	Concentration, crude oil (reduces after waterflood breakthrough)	100%

Mineral (Uranium)		Oil (West Texas, New Mexico)	
Typical Operating Conditions			
Mineral bed thickness, swept	40 ft	Sandstone formation thickness	30 ft
Value per acre, 0.025% U_3O_8	$220,000.00	Value per acre	$100,000.00
Leach patterns per acre	1.5	Acres per well	10
Production rate per unit or 5173 bbl per 24 hrs	150 gpm	Production rate per well or 68 bbl per 24 hours	2.0 gpm
Liquid injected or 5178 bbl per 24 hrs	150 gpm	Liquid injected = liquid produced (until waterflood breakthrough)	
Site value daily production	$730.00	Well head value, daily production	$200.00
Site value per acre of daily production	$1100.00	Well head value per acre daily production	$20.00
Estimated life of unit	200 days	Estimated life	15 years

STAGES IN THE SELECTION OF DEPOSITS FOR IN SITU LEACH OPERATIONS

Initial requirements:

1. An orebody or mineral deposit chemically amenable to leaching techniques.
2. Confinement of orebody by natural or artificial means in such a way that dilution or fluid losses may be restricted to an acceptable level. The present state of the art demands a flooded formation below the piezometric surface.
3. Low ground-water velocity.
4. Compatible environment
   a) with the proposed hydrometallurgical process; no contrary side reactions which cannot be economically controlled; no restriction to the recirculation of stripped liquor.
   b) not located in an aquifer used for domestic water supply.

5. A rate of return on capital invested which appears at this first estimate stage to be satisfactory. (Financial objectives *need to be defined for each situation. No general set* of rules is available at this time.)

Second stage:

Assuming these criteria are satisfied, then detailed field work commences with:

1. Regional hydrology survey including seasonal variation, water usage, and regional ground-water flow.[12]
2. Local hydrology survey, say for 10,000-ft radius around proposed site. Ground-water contours, terrain, geological features (in particular, faults, dikes, and sills which may indicate local variation in permeability), and surface drainage features must be included.
3. Geophysical surveys to substantiate hydrological and geological interpretations. Minimum requirements are gamma log, self-potential, and resistivity logs, spaced with due regard to heterogeneity of formation.
4. Detailed water sampling program covering all seasons to determine quality of water in adjacent aquifers, streams, lakes and springs. This is essential in order to establish contamination levels existing prior to commencement of operations and to set standards for a continuous monitoring system during later operations.
   Differences in water chemistry should corroborate regional hydrology (Item 1 above) and subsurface geology interpretations (Item 4).[13]

Third stage:

The results of the above being favorable, it is now justifiable to commence site work in the following sequence:

1. Bailer tests in all boreholes in the mineralized area. This is an inexpensive series of tests used to give guidance as to permeability. It is valuable in its ability to expose changes in permeability which may occur in directional trends across the area of interest.
2. Core drilling to provide material for laboratory permeability tests and metallurgical investigation. A series of standard API test procedures is available for permeability measurements. Comprehensive laboratory test facilities are maintained by the major oil field service companies and it is recommended that these services be utilized. In the metallurgical testing, care should be taken that the work be done under conditions of temperature and pressure similar to those forecast for subsurface operating conditions and the sample cores should be protected from oxidation until test work is in progress.
3. Pressure injection tests. This is a critical stage of field test work. From estimates of circulating volumes and maximum feasible operating pressure and flow rates, a set of injection well conditions can be projected and the test well layout constructed to suit. A program of injection tests will then provide data from which the dimensions and operating conditions of the final leach array can be derived.

   Care should be taken that changes induced during the test pumping do not create irreversible chemical changes within the mineralized zone or physical changes in clays which may be difficult to reverse.

4. Pilot plant design can now be attempted.

LEGAL AND GOVERNMENT

As with so many new endeavors, in situ leaching brings the mining or petroleum company face-to-face with new controls, some of which are legal, some governmental. The situation will be likely to continue in a state of flux for some time in the future.

It can be reasonably expected that the status of in situ mineral leaching will vary from state to state. If a petroleum company is the first operator of an in situ mineral lease in a petroleum province, it is likely that operations will be governed by existing local petroleum production legislation. In other localities, operations will be carried on under control of mining legislation. It may well be that some operators, for a time, will be able to claim exemption from both mining and petroleum regulations.

Outside the direct industrial control legislation, involvement with environment maintenance, specifically water quality control, aquifer contamination, and with water resources utilization will bring new governmental contacts, both at state and Federal level. Those companies contemplating entry into the in situ mineral leaching field will find it advisable to make informal contact at state level at an early stage. Uninformed or capricious pollution accusations may be circumvented when the technical staff of the state environmental control department are fully cognizant of the controls and safeguards planned to prevent contamination at in situ leach locations.

ANACONDA'S EFFORTS IN THE IN-PLACE LEACHING FIELD

Early in 1968 it appeared the basic knowledge required to operate a uranium in-place leaching project was available.

The Elliot Lake mines in Canada were leaching worked-out mine areas to produce several tens of thousands of lbs U_3O_8 per year. Their bio-extractive methods are particularly interesting.

The Ambrosia Lake mines in New Mexico were treating mine water for the profitable reclamation of uranium.

Pinnacle Exploration was successfully leaching a partly caved mine with a severe support problem.[1] Utah Construction[14] in the Shirley Basin of Wyoming had patented a true in-place leach method suitable for a specific type of mineralized bed and was operating profitably. For them, as with Pinnacle, in-place leaching was an attractive alternate to very expensive support problems involved with conventional underground mining. Both of these mines were above average in ore grade.

It was decided to investigate the general case of a true in-place leaching situation starting with a horizontal sandstone orebody below the water table with impervious lower and upper boundaries. This geometry is typical of Westwater Canyon sandstone tongues (Figure 1). An isolated pod of uranium mineralization located in the lower 40 ft of the Jackpile sandstone, locally 140 ft thick, was selected as being of sufficient grade to sustain a meaningful pilot project. The zone had been drilled at wide spacing some fifteen years ago. Further drilling better defined the mineralization and natural gamma logs permitted detailed evaluation.

The Jackpile sandstone is described in detail by Schlee and Moench.[10] It is a typical braided-stream sandstone, thickness up to 200 ft, known extent about 15 miles wide by 40 miles long, the major axis aligned SW-NE. Although adjacent to the Mount Taylor volcanic complex with the nearest side vent about five miles away and to the Rio Grande depression a short distance east, the Jackpile sandstone in the mine area is undisturbed. It is locally the uppermost sand of the Morrison formation and the youngest Jurassic sediment (Figure 2).

The thickness at the pilot plant site is 140 ft with uranium values concentrated in the lower 40 ft. A high clay zone of low vertical permeability tends to restrict liquor circulation to the mineralized zone, and the well system is designed to take advantage of this. Well defined horizontal bedding with local festoon crossbedding results in anisotropic permeability with a ratio of about 10:1 horizontal to vertical which is in line with oil industry water flood experience of similar sandstone.

The grain size is fairly constant with a modal value of 0.2 mm and maximum ranging from 0.6 mm[10] in the upper 50 ft to 1.0 mm in the lower 20 ft. Calcite cement predominates toward the base and kaolin clay at the top. Montmorillonites, illites, kaolin and bentonite clays are well distributed, with the result that porosities over the range 20% to 32% are associated with permeabilities of some 12 to 350 millidarcies in distilled water. In core samples no correlation was found between porosities and permeabilities using air, distilled water, H_2SO_4 solution at pH 2 and pH 4, and hexane.

As a first stage, three core holes were drilled close together in higher grade center of the mineralized area and detailed core logging, assaying, and probe comparisons made. One hole was reamed to about 7½ in. diameter to accept 4½-in. diameter Birdwell borehole probes. Almost all available probes were run, including experimental probes supplied by the AEC. This portion of the program was conducted in cooperation with Anaconda's Geological and Geophysical Departments. These holes, together with additional drilling, provided extensive information on the 400-ft by 900-ft zone of Jackpile sandstone involved.

After detailed logging, one core was sent to the Anaconda Western Exploration Laboratory for mineralogical study, one to the Anaconda Extractive Metallurgical Research at Tucson, and one was kept for mining reference. Selected sections of this #3 core were the subject of permeability investigations at the Tulsa labs of the Dowell Company. It was considered important to work over these cores using API methods in the expectation that as experience accumulates some basis of comparison with oil field water flooding will emerge.

Extensive outside hydrological assistance was obtained through a research contract with New Mexico Tech Foundation, by employment of the Dowell Company for special site work, from Baroid Division of National Lead, and Stewart Brothers Drilling Company.

As a result it was decided to proceed with a pilot plant (Figure 3) treating two well arrays, each 200 ft diam, at 115 total gpm. Each array contains 1.3 million gallons of pore volume (assuming 70% sweep effectiveness) giving a retention time of about 23 days. Two central injection wells are surrounded by production wells, each array has similar but significantly different geometry.

Pumping commenced in April 1970 with two injection wells and nine production wells operating in the lower 40 ft of the Jackpile sandstone at a depth of 200 to 240 ft below surface. Early problems with higher than predicted caprock leakage were traced to old exploration hole leakages and corrected by cementing, upon which subsequent tests show that the aquifer behaved as a confined aquifer of near-infinite radial extent. This appears to be a valid approach to interpretation of field data and its application over the limited time period and for the special conditions.

Monitor wells, some equipped with continuous water level recorders, are located at strategic locations up to 1000 ft from the site center.

It was soon shown that this layout did not provide the desired degree of control over the piezometric surface outside the test arrays, and the production well spacing was closed in over a 90° segment of one array with good results. This revised spacing has been applied to each array and the present layout provides two injection wells and 29 production wells covering approximately one-half acre.

PRACTICAL ASPECTS--applicable to dilute lixiviants in low energy systems

Permeability Modification

Given metallurgical amenability, the most important factor in the assessment of viability of an in-place leach system is the pattern of rock permeability. On this depends the ability to attain contact between mineral and leach liquor at a rate high enough to offer the prospect of economic operation. Many in-place leach proposals have foundered on this subject. The work which we have done to date indicates very clearly that

1. There is no apparent correlation between lab permeability tests, or pump tests of various kinds, with the permeability as measured during a pressure injection pump or power drive circulation operation.
2. Field tests, in our limited experience, indicate permeabilities far higher than core tests or core logs, or sondes indicate. This phenomenon is not new, but the magnitude of the increase in permeability appears much greater than generally understood.

At the present time we attribute this to physical reorientation of clays resulting from the power drive in a way not fully understood.

Well Capacities

All conventional formulas include factors or constants affecting the permeability of the well bore. A better correlation results from the substitution of calculated sand face areas developed by short fractures. We are actually dealing with a situation similar to a filter bed area. Very large increases in sand face (as filter bed) area result from small radial fractures. Liquid velocities are sharply reduced. The energy of the power drive should be substituted for gravity in each of the relevant equations.

Well Dimensions

We are now able to operate all facilities in two-inch plastic casing cemented into 4½-in. drill holes, put down for less than $1.00 per ft and completed at between $2.50 and $4.00 per ft, depending on pressure requirements and the type of casing used.

Hydro-Fracturing

The most powerful tool at our disposal in mineral leaching will be fracturing, and it can be confidently forecast that a wide variety of techniques will be developed in the coming years, ranging from nuclear energy explosive shattering on a vast scale to fluid fracturing penetrating only a fraction of a borehole diameter.

Basic assumptions:

1. Fracture patterns generated in western sandstone-type uranium deposits will be very similar to patterns generated in shallow braided-stream-type oil formations, and many years' experience is available in this type of fracturing.
2. Mineral deposits in general are closely associated with past ground disturbances. Faults, folds, planes of weakness, cleavages, and joint systems abound. It will be necessary to

develop new techniques to enable induced fractures to be superimposed on existing patterns.

The application of induced fracturing techniques therefore requires a clear understanding of geologic history and structural ore controls. The general rules governing vertical and horizontal fracturing processes in oil fields are unlikely to apply. Each attempt at induced fracturing should be considered on its own merits and it would be prudent to assume that:

1. Fracture direction will be controlled by existing planes of weakness in the rock.
2. Permeability will be sharply reduced at the interfaces of mineral-filled fissures due to blinding by mineralized solutions at the time of ore deposition. If this were not the case, the minerals would be disseminated through the rock. As a result, it can be expected that the lateral extent of an induced fracture will exceed that of an oil field fracture involving similar quantities of fluid.
3. The metamorphosed rocks associated with mineral deposits will not exhibit any self-healing effects, and may even slough off into the fracture and become self-propping.

Fracture propagation can generally be assisted by the use of self-degenerating muds. As the fracture advances,the porous walls are sealed by the action of these muds. The addition of a suitable enzyme to the mud mixture results in breakdown of the mud over a period of three to four days and restoration of natural permeability to the wall of the fracture. This method sharply reduces the quantity of fracture fluid, rate of fluid injection and horsepower required to hydro-frac.

Large increases in effective sand face area through which the liquor must pass result from very short radial fractures. For example, in a 4-5/8-in. diam borehole, sand face area per foot is doubled by a fracture which extends less than 6 in. into the rock. A 100-fold increase in sand face area requires a fracture extending only 9 ft into the rock.

Clarification of the leach liquor, either recirculated or raw feed, is expensive and the extension of the sand face area to compensate for the blinding action of suspended solids may be an economic alternative. The opening up of fresh channels by this method increases swept volume by creating a new dispersion fan. When pump pressure capacity is sufficient, fracture propagation will occur automatically and will compensate for sand face friction increases which occur as the effective area is decreased by blinding off.

BIOLOGICAL LIXIVIANT REGENERATION

A comprehensive review of current status is available in the proceedings of the SME Short Course "Bio-Extractive Mining" 1970.[5]

Contrary to oil field waterflood injection well experience, we have found no difficulty in maintaining injection flow rates without increasing pressures at the pilot plant site. The stock tanks are open-topped, occasional colonies of green algae appear, and the water is biologically active. When this condition became apparent in the early spring of 1970, it was decided to continue without water treatment until a 5% rise in injection pressure occurred. In fact, injection pressures have decreased by about 15% to 160 psi.

The regeneration of lixiviants on or adjacent to the mineral surface has many advantages and the biologically active agents are capable of performing this function at moderate levels of pH and chemical activity. Future test work is planned to investigate feasibility of this approach.

FACTORS DETERMINING LEACH FIELD WELL GEOMETRICS

This discussion is limited to the case of a near horizontal, fully saturated nonleaky confined aquifer, of about 40 ft in vertical thickness but not exceeding 150 ft, and of near infinite horizontal extent. Other formation structures may be suitable, in particular syncline or basin conditions, or reservoir traps of various types; a wide variety of geometric forms may provide the degree of lateral constraint necessary.

The heterogeneity of the aquifer will in practice prevent precise control of the boundary of the leach liquor lateral penetration. It is, therefore, necessary to accept either a degree of dilution by inflowing formation water or a loss of leach liquor into the surrounding formation at the periphery of the operational zone. Thus, it follows that the greater the number of contiguous arrays in operation at a given time in a mineralized zone the lesser the peripheral complications will be.

Both economic and pollution considerations indicate that the peripheral wells should be production units, in order to induce a decrease in the elevation of th piezometric surface at the circumference of the pattern, and thus minimize liquid transfer across the boundary. Production well spacing should be sufficiently close to ensure interference, well to well, resulting in an irregular, trough-like depression around the periphery of the operating area, so that a constant dilution by inward flowing formation water occurs (Figure 4). Disposal of the excess water is not likely to be a problem when dilute lixiviants are used and recovery plants are efficient, as with uranium.

The multiple well, horizontal flow concept (in its simplest form) would, therefore, appear to require a periphery fence of production wells with spacing calculated from drawdown curves, strategically located internal pressure injection wells, a symmetrical distribution of internal production wells designed to minimize irregularities in the piezometric surface and with production capacity to match the injection well rate.

A wide variety of geometric patterns has been developed by reservoir engineers, and any of these standard patterns can be modified to suit the permeability and mass flow patterns and control problems of in situ leaching.

SUMMARY

This paper is an attempt by the author to present an introduction to in situ leaching understandable to engineers and geologists in the mining, petroleum and hydrology fields, despite their differing terminology, measurement systems, and economic yardsticks. Each group has important contributions to offer to this developing technique and it is hoped that this paper will assist interdisciplinary communications.

The changing environmental and economic climate is demanding reevaluation of many accepted production methods and the new values encourage development of in situ leaching. The demands of environmental maintenance alone may provide incentives for the accelerating development of this mining method.

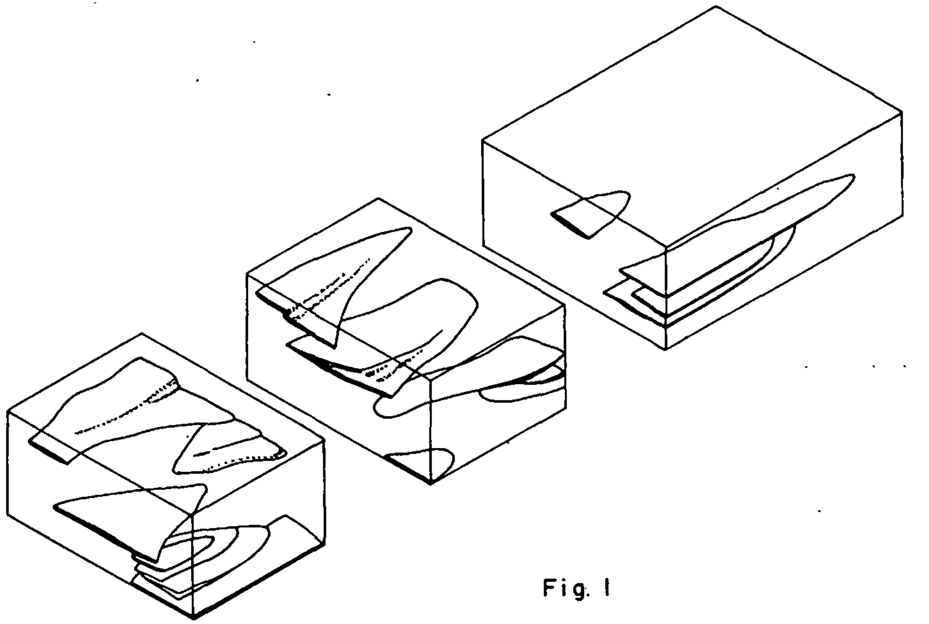

Fig. I

Idealized exploded block diagram showing typical relationships of prefault ore bodies throughout the Westwater Formation. The ore bodies are elongate, lensshaped masses arranged singly or en echelon vertically and horizontally.

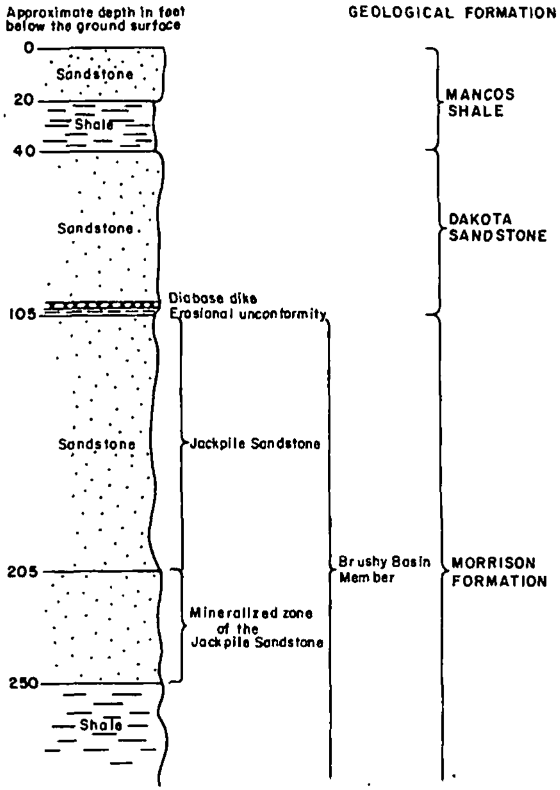

Fig. 2

General stratigraphic column showing thickness and relationship of geological units in the North Windwhip area.

THE ANACONDA COMPANY
PILOT IN-SITU LEACH PROJECT
FLOW DIAGRAM
ACID PROCESS — CHLORIDE ELUTION

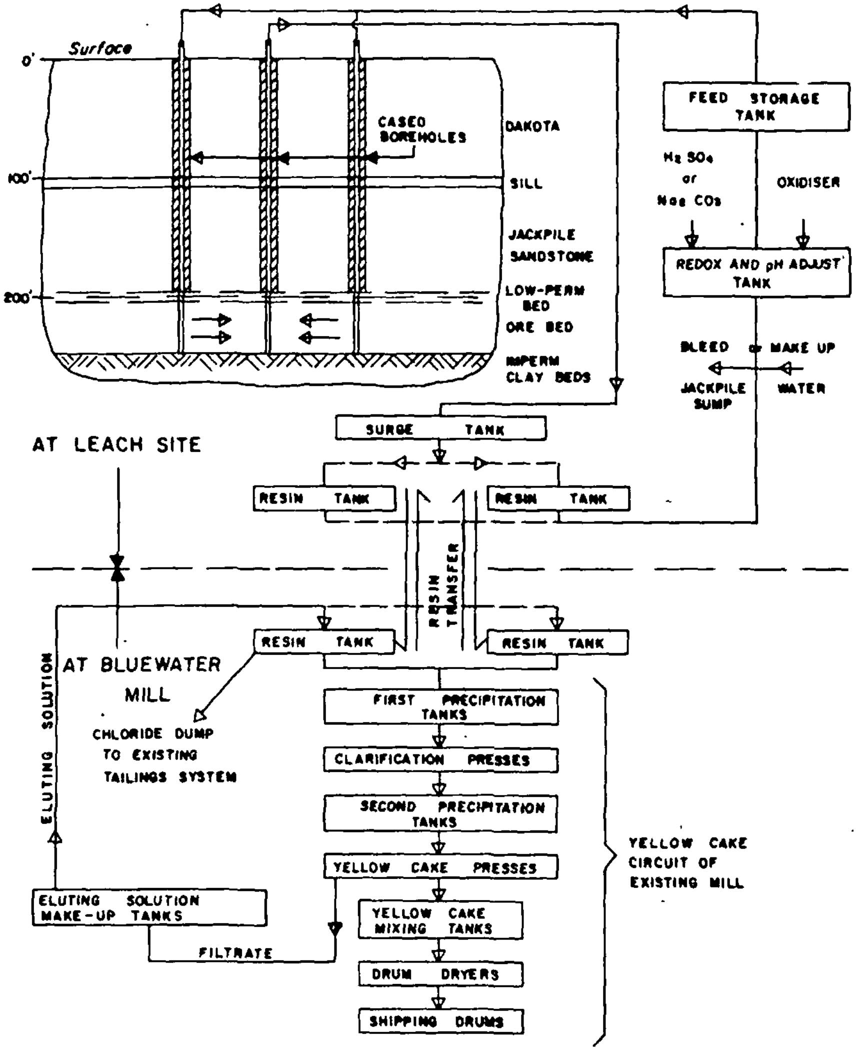

Fig. 3

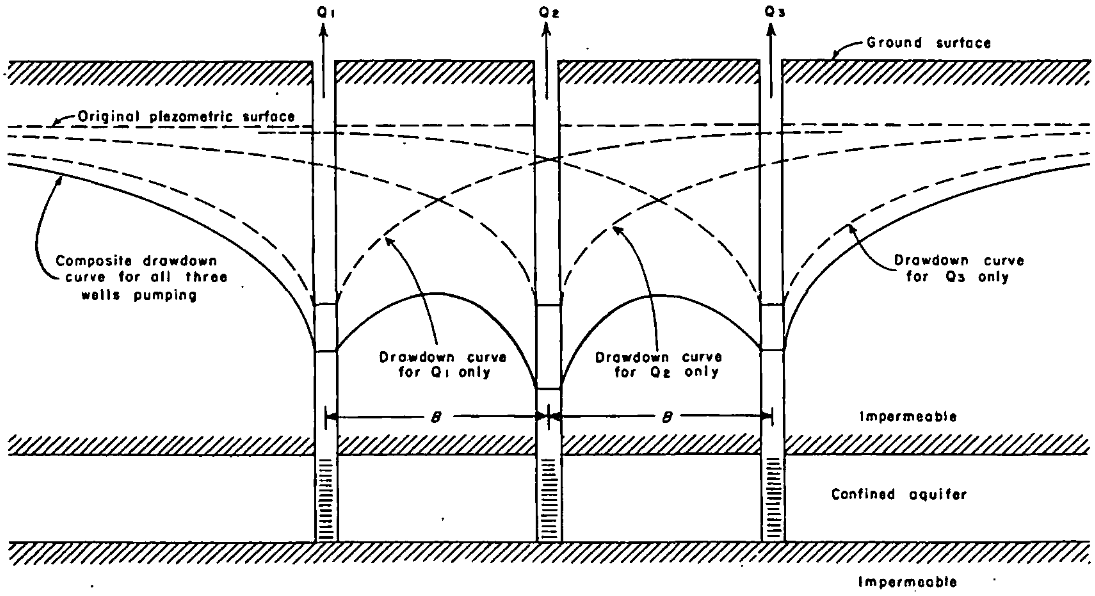

Fig. 4

Individual and composite drawdown curves for three wells in a line.
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Dup.

RECOVERY OF METAL VALUES FROM LOW GRADE COPPER SULFIDE ORES

by

Milton E. Wadsworth‡

ABSTRACT

In the United States approximately 12 percent of the new copper produced comes from dump leaching of low grade waste rock from open pit mining. While this amount of copper is significant it is unusual, even for massive dumps, for steady-state recovery rates to exceed 20 percent. Basic physical and chemical features important in leaching typical copper porphyry waste rock have been determined in laboratory studies in tests involving up to several tons of waste rock. The important findings of such tests including chemistry of extraction, laboratory modeling, energy implications, and recovery from dilute streams are presented. Special emphasis is given to important rate limiting features of waste rock leaching including the role of autotrophic bacteria in the oxidation sequence. Difficulties in scale up from the laboratory to practice are discussed.

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INTRODUCTION

Although copper usually is not thought of as being a critical or strategic metal, the U.S. 1978 net import reliance was 19 percent,[1] a change from zero net import reliance in 1975.[2] In spite of this general trend excess copper production and low prices have periodically plagued the copper industry.[3] Nevertheless, for the future, recovery of copper from ever lower grade sources will be the pattern in the United States, placing increased strain on supply sources.

Copper porphyry deposits form by igneous intrusion of copper bearing magma and upward movement of copper bearing fluids. The copper forms in part as disseminated grains formed during cyrstallization of the magma. Dissolved mineral in water causes movement and deposition of primary minerals in cracks and fissues. On the average some seventy percent of the copper is deposited in the intrusive portion of the deposit and thirty percent in the peripheral country rock. The deposits are typically 3,500 to 6,000 ft. across and up to 10,000 feet in depth.[4] Figure 1 illustrates a polar view of the distribution of copper porphyry deposits world wide. Sillitoe[4,5] has associated the regions of igneous intrusion with a "plate techtonic model" consistent with the distribution of porphyry deposits.

The principal mineral of copper is the sulfide chalcopyrite ($CuFeS_2$). Natural weathering processes occur when the primary (hypogene) chalcopyrite is subjected, by geological activity, to regions of high oxidation potential, producing oxidized minerals and releasing copper to solution. Movement of the copper bearing solutions downward causes supergene enrichment of the primary sulfides forming regions or zones of secondary

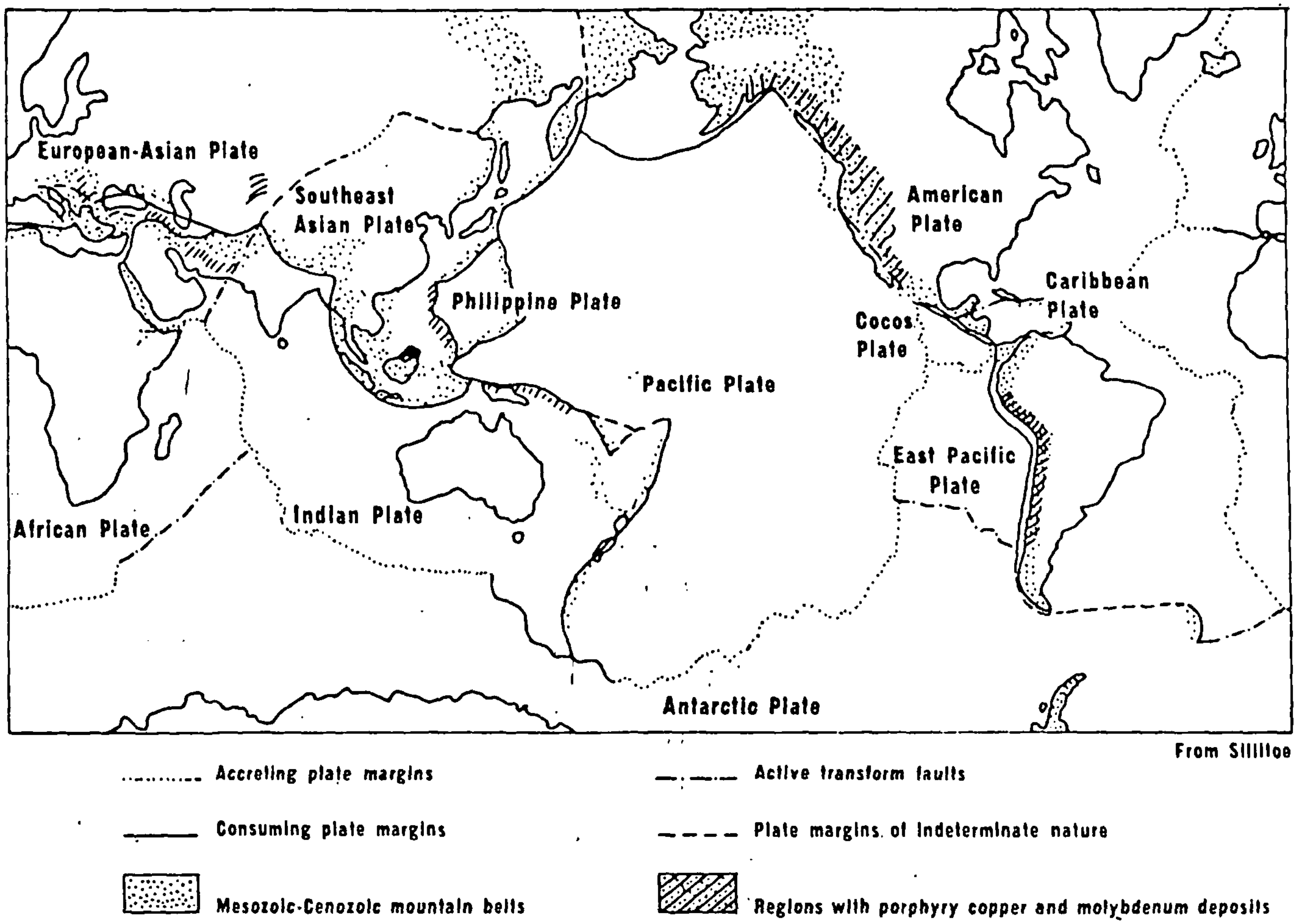


Figure 1. Sillitoe's Plate Tectonic Model for the Origin of Porphyry Copper Deposits.

sulfides. Typically a copper deposit will have an upper zone of oxidized minerals with a zone of secondary enrichment below and primary mineralization at greater depths. Secondary enrichment occurs mainly near the surface of the water table where there is an abrupt decrease in the oxidation potential with depth. Figure 2 illustrates a cross section of a typical copper porphyry showing the oxidized cap, secondary enrichment zone, and the primary zone.[4] Figure 3 illustrates the minerals typically formed in each zone, according to Bateman.[5] In similar fashion consideration of oxidation potential and pH delineates zones of copper mineral formation. Figure 4 is an E_h-pH diagram illustrating regions of mineral formation. Also included is the typical pH range for acid leaching solutions needed to solubilize copper. For dump leaching to continue, adequate aeration and in situ generation of acid, assisted by chemoautotrophic bacteria, must generate solutions with E_h and pH values within the shaded region of Figure 4.

The recovery of copper from low grade sources is classic in the sense that the extraction process is based upon the treatment of unusually great tonnages of low grade copper bearing waste material with large volumes of low grade leach liquors. For example, at Kennecott's Bingham mine approximately 250,000 tons of waste rock (containing 0.15 to 0.20 percent copper) is placed on the leaching dumps each day. Fifty million gallons of leach solution is applied daily, producing effluent solution grades of approximately 0.5 gpl. The copper waste going to leaching dumps is normally near to or less than 0.2 percent copper. In a typical open pit mining operation with a stripping ratio of 3:1, an average head grade of 0.6 percent Cu, and a cut off grade of 0.2 percent, approximately

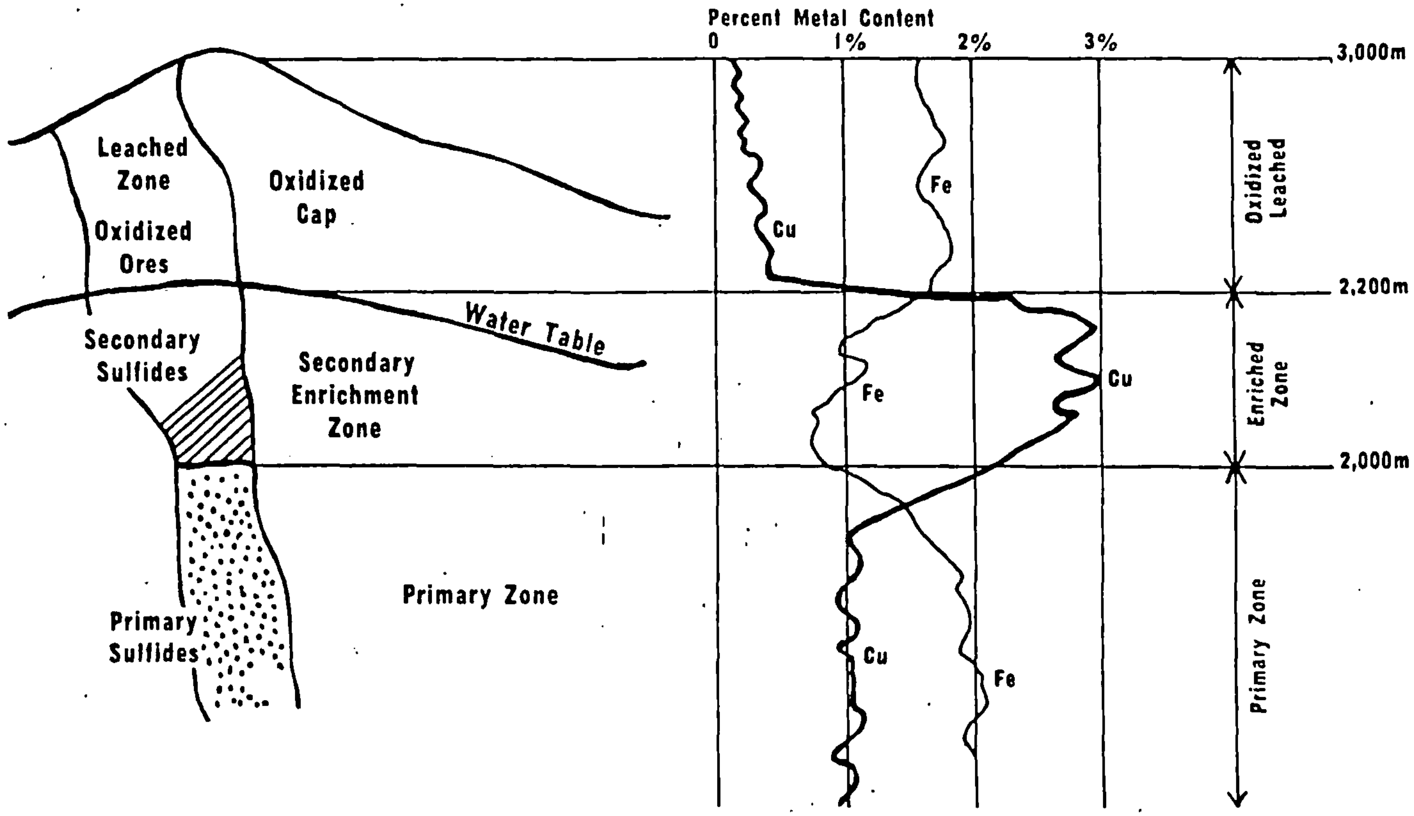
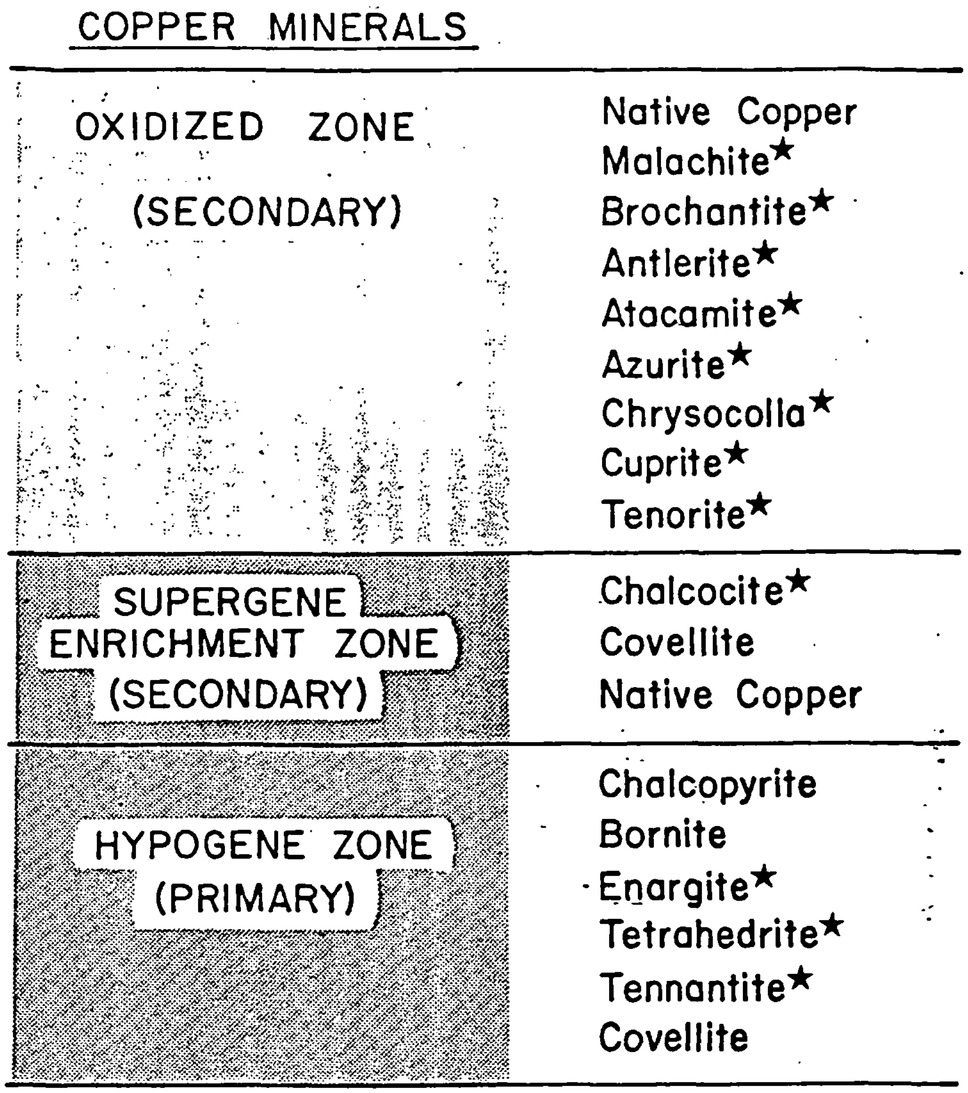


Figure 2. A schematic cross section of a typical copper porphyry.



★always in position indicated

Figure 3. Minerals typically formed in oxidation, supergene enrichment, and hypogene zones.[5]

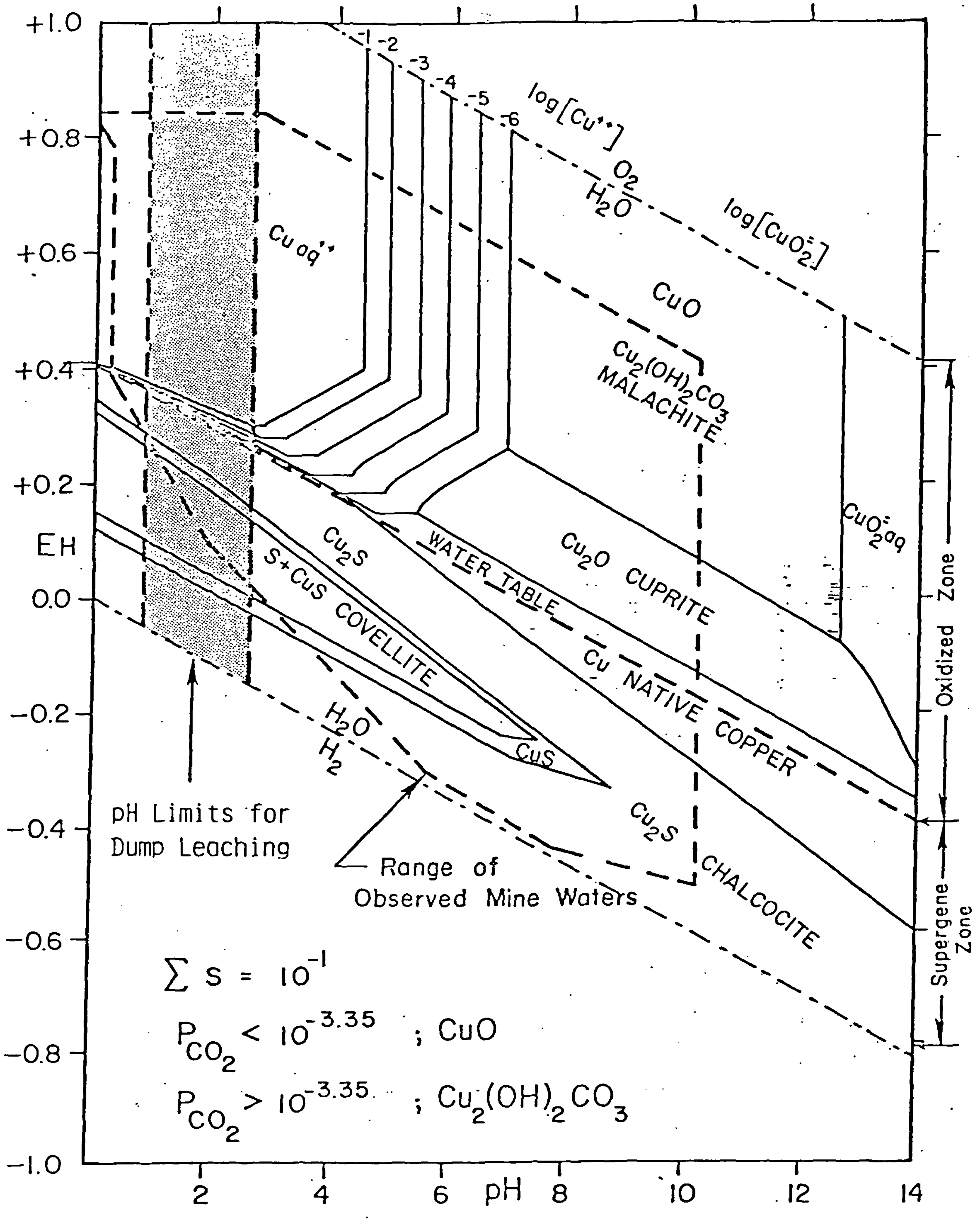


Figure 4. Pourbaix diagram for the Cu-O-S-H_2O-CO_2 system showing the region observed for natural mine waters and the region expected for dump leaching of copper oxide and sulfide ores.

equal quantitites of copper will go to the waste dump and to milling for recovery by conventional flotation technology.[6]

Table I presents yearly copper production by major copper producers in the western United States for 1978.[6] The tonnage produced by dump leaching and the leaching of oxide ores is 18 percent of total yearly tonnage.

TABLE I

1978 COPPER PRODUCTION (Schlitt[6])

Statistics for Western Copper Operations with Significant Leach Output

Company	Copper Production, Tons Concentrating	Leaching	Percent of Total Copper produced by Leaching
Kennecott	287,200	88,200	23.5
Phelps-Dodge	283,600	34,550	10.8
Duval (Pennzoil)	112,300	10,200	8.3
Anamax Mining	67,200	35,810	34.8
Asarco	85,780	10,720	11.1
Cities Services	72,800	7,750	9.6
Cyprus Mines	61,600	12,150	16.5
Inspiration Consolidated	20,700	18,000	46.5
	991,180	217,380	18.0

An estimated two-thirds of this, or approximately 12 percent of the total, may be attributed to dump leaching of low grade predominantly sulfide waste materials.

The percentage of copper produced by leaching will probably increase in the future as the average grade of major deposits decreases. The distinction between ore and waste will require an even more definitive assessment as energy costs for milling increase,[7] probably favoring a greater percentage production of copper by leaching. As an open pit operation continues the stripping ratio will increase to the point that underground mining or some other alternative must be considered if increased recovery is to be achieved. Sutulov[4] has estimated North American reserves of recoverable metallic copper by current methods to be in excess of 86 million tons. As a very rough estimate, approximately an equal amount of copper will remain, after conventional mining, in low to medium grade zones including regions of "halo" mineralization, deep seated medium grade ores, and unleached residues in waste dumps. This amount of copper is a worthy target for extraction by dump leaching and in situ solution mining. These leaching techniques will receive increasing attention in the decades ahead. Current estimates of expected recovery by leaching is in the 30 to 50 percent range.[6] If 30 percent recovery is assumed it is conceivable that an additional 26 million tons of copper may be recovered by leaching low grade porphyry copper deposits in North America during the next century. Also the economic value of precious metals contained in leached residues is so great that these also constitute a worthy target for new, yet to be developed, leaching technology.

DUMP LEACHING PRACTICE

In dump leaching practice, waste rock (usually below 0.2 percent copper) is placed on dumps by truck or rail haulage. These dumps vary greatly in size and shape. Depths extend from a few tens of feet to as much as 1200 ft. It is generally recognized that good aeration is required as well as good permeability. Consequently the stepped surfaces in the dump are usually ripped to provide needed permeability. As-mined ore, newly placed on a dump, will have permeabilities of approximately 1000 darcy's. Weathering of intrusive material can cause dramatic changes in porosity. Weathering plus deposition of salts can also cause significant changes in permeability with time. The impact of such induced weathering is an important consideration in assessing expected recoveries, since leaching may extend for years. The porosity of newly dumped rock will be in the range of 35 to 40 percent but the weight of haulage trucks can cause compaction of as much as 10 ft in 100 ft. Porosities of as low as 25 percent result from compaction and weathering.

Figure 5 illustrates a dump cross-section according to Whiting,[8] showing important hydrological and structural characteristics.

1. Channeling: Channeling of leach liquor occurs as a result of compaction and salt precipitation. Fluid flow down channels essentially by-passes regions of the dump. It is enhanced if solution application is by surface ponding.
2. Seep or Blowout: Compacted zones may cause entrapment of solutions causing the formation of a perched water table within the dump. The build-up of hydrostatic pressure can cause surface seepage and even expulsion of solid material for relatively great distances.
3. Stratification: During the dumping of waste rock, the coarse material travels further down the slope of the dump than the fine material, causing stratification. Without appropriate

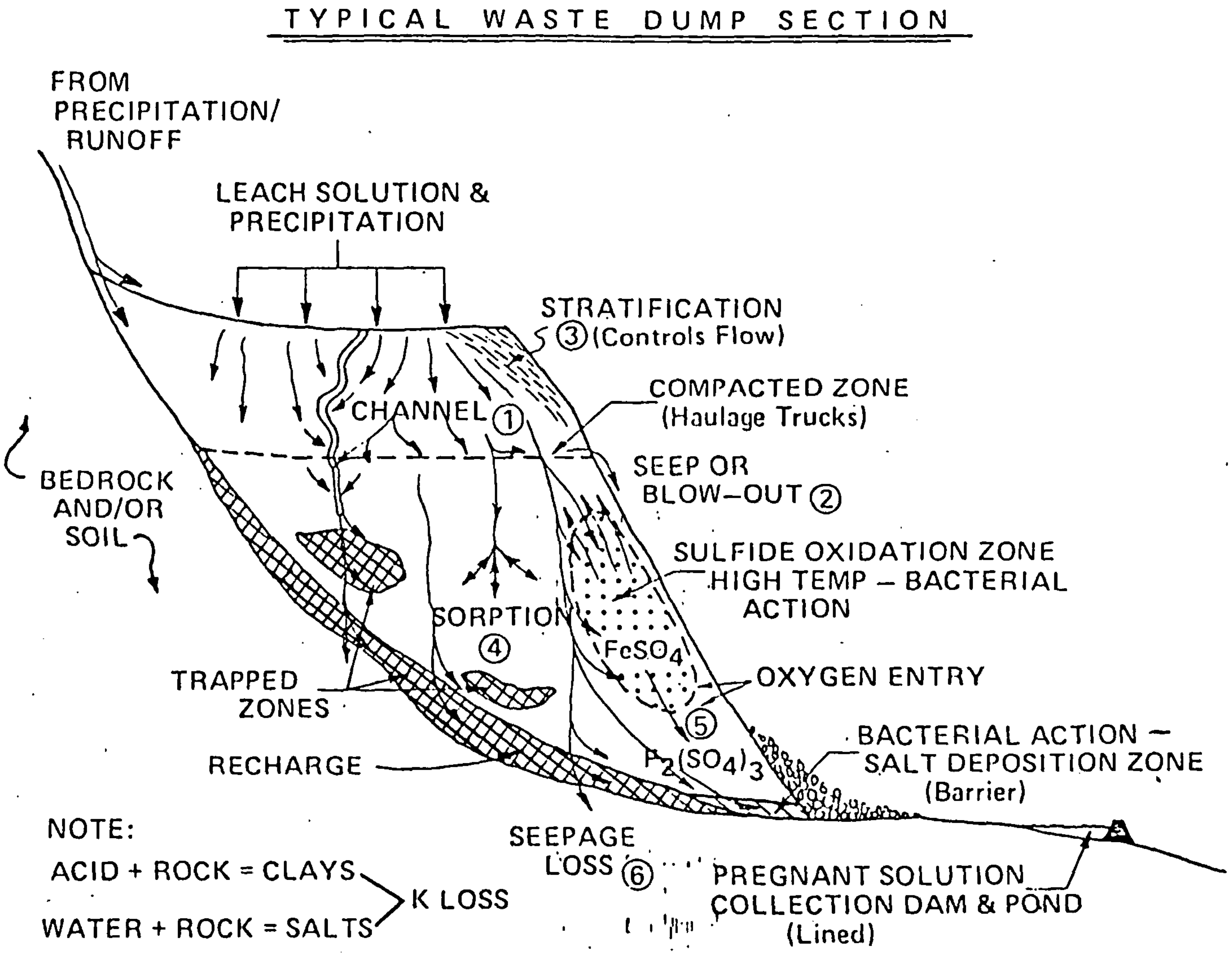


Figure 5. Cross section of dump illustrating hydrodynamic features according to Whiting.[8]

ripping stratification may effect the flow pattern within the dump.

4. Sorption: Solutions bearing dissolved metals may pass through regions containing non-gravitational water at lower concentrations. of metal values will occur by inward diffusion into the pore structure of the rocks and into stagnant aqueous regions, causing loss of metal value.
5. Aeration: Aeration is best near the face of the dump providing optimal conditions of temperature and bacterial activity. Studies have shown that zones of good aeration extends some 200 ft. into the dump from free surfaces. Aeration by convection through the dump is an essential part of the leaching mechanism. In regions of high oxidation potential, iron is oxidized by bacterial activity to the ferric state resulting in the precipitation of ferric oxides and jarosites.
6. Seepage Losses: Seepage can occur through the foundation of the dump although the formation of salts and the presence of fines often keeps this at a surprisingly low level. Run-off waters may also recharge or dilute the percolating liquors through the foundation of the dump.

In practice, dump leaching depends upon a sequence of processes. For an element within a dump system, three conditions are essential for leaching to occur and continue. These are:

- effective air circulation
- good bacterial activity
- uniform solution contact with the particle

The major unknowns in dump leaching for any given dump are:

- a knowledge of air circulation relative to the dump configuration
- the hydrology in terms of channeling and by-pass
- the effect of fines and precipitated salts
- effect of weathering as a function of time.

Sheffer and Evans[9] presented an excellent review of dump leaching practice in 1968. Although the presentation is now 13 years old, the operating data are important since they established actual operating conditions in practice for dumps containing very large inventories of waste rock. Table II summarizes the 1968 data for those dumps containing predominantly copper sulfides. The tonnages listed represent the inventories of leachable waste rock as of 1968. For example, the total tonnage of dump rock at Kennecott, Bingham was estimated to be 2 billion tons. Since 1968 an additional 1 billion tons has been added, bringing the total estimated inventory in the waste dumps at Bingham, Utah to 3 billion tons. The effluent grade values of liquors from dumps containing secondary sulfides are generally in excess of 0.8 grams per liter. Dumps containing predominantly the primary mineral chalcopyrite leach at a lower rate, generally producing solutions in the range of 0.5 to 0.75 grams per liter. Table II lists the total iron in the dump effluent, it's pH, and the ferrous to ferric ion ratio. This latter ratio is an indication of the effectiveness of the bacteria within the dump. Good bacterial activity is essential for the oxidation of ferrous iron to

TABLE II. DUMP LEACHING PRACTICE IN THE WESTERN UNITED STATES (Sheffer and Evans[9])

Dump for Which Copper Minerals are Predominantly Sulfide (Concentration in gpl)

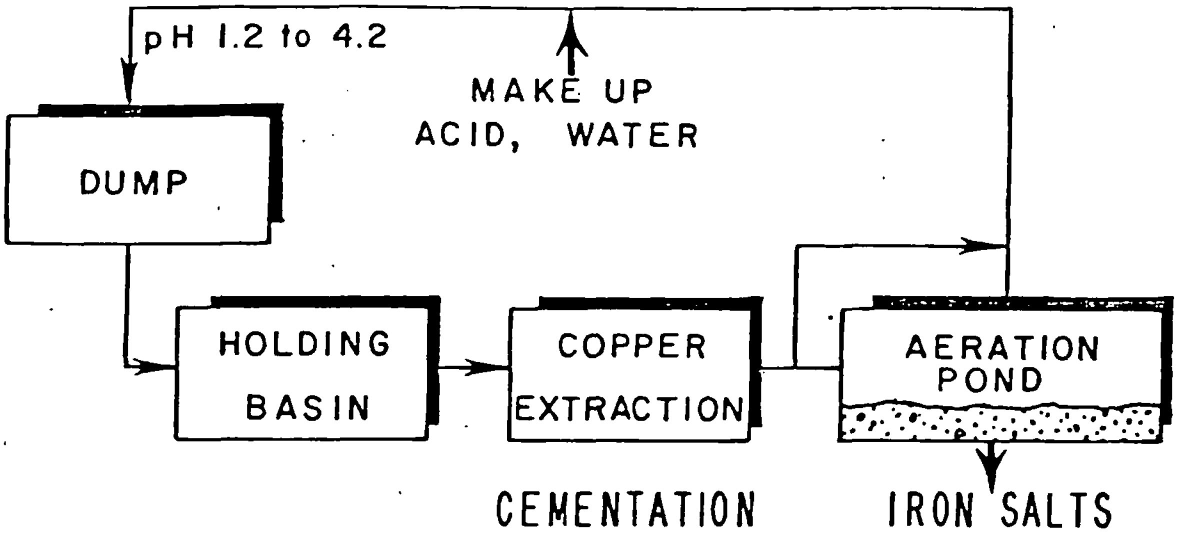
Company	Principle Copper Minerals	Estimated tonnage 1000's tons (1968)	Solution Flow Rate (gpm)	DUMP EFFLUENT				COPPER CEMENTATION EFFLUENT		
				Copper	(Fe)(total)	Fe^{III}/Fe^{II}	pH	(Fe)(total)	Δ(Fe)total	$\Delta(Fe)_T/Cu$
AS & R, Silver Bell, Arizona	Chalcopyrite and chrysocolla	30,000	1,000	1.09	0.58	57.0	2.3	1.71	1.13	1.04
Anaconda, Butte Montana	Chalcocite	33,000	5,000	0.86-1.00	0.50	4.6	2.3	1.55	∼1.05	∼1.21
Duval, Esperanza, Sahuarita, Arizona	Chalcocite and some chalcopyrite	19,000	1,600	1.32-1.56	0.20	<0.2	2.6	1.90	1.60	0.94
Duval, Mineral Park, Arizona	Chalcocite	5,500	750	1.24	0.48	47.0	2.3	2.46	1.98	1.60
Kennecott, Bingham, Utah	Chalcopyrite	2,000,000	44,000	0.80	4.80	0.39	2.5	8.39	3.59	4.49
Kennecott, Ray, Arizona	Chalcocite	186,500	7,000	0.90	0.48	9.6	2.3	2.16	1.68	1.86
Miami Copper, Castle Dome, Arizona	Chalcopyrite and Chalcocite	48,000	--	0.85	1.08	53.0	2.3	1.56	0.48	0.56*
Miami Copper, Miami Unit, Arizona	Chalcocite	NA	2,000	1.75-2.00	2.15	0.9	2.4	4.70	∼2.55	1.82
Miami Copper, Copper Cities Unit, Arizona	Chalcopyrite and Chalcocite	NA	1,800	∼1.5	0.34	16.0	2.5	1.05	0.71	∼0.47
Phelps Dodge, Bisbee Arizona	Chalcocite	47,000	2,300	0.96-1.80	6.60	0.8	2.0	8.77	2.17	1.64
Phelps Dodge, Morenci Arizona	Chalcocite	NA	5,300	1.00-3.60	0.28	27.0	3.0	2.01	1.73	1.33

*Iron removal external to dump.

ferric. The ferric to ferrous ratio is a good relative measure of the bacterial activity. A high ratio does not of itself mean that the bacterial activity is uniform throughout the dump. It may simply mean that, in regions where solutions imerge from the dump, good bacterial activity occurs. Dump solutions emerging from dumps in which adequate bacterial activity occurs have temperatures in the range of 30° to 35°C. Also included in Table II are solution concentrations for effluent from cementation which was used universally for the cases listed in Table II. The total iron difference indicates the amount of iron picked up by cementation of copper on iron. Also listed is the change in iron divided by the copper removal from solution. While the general results presented in Table II are relatively old they are characteristic of dump leaching practice in general. Many changes have occurred including the closing of some properties and major changes in solution management of some of the major leaching operations. For example, at Kennecott, Bingham the solution grade has dropped in the last 5 years from 0.8 gpl to approximately 0.5 gpl. Currently the ferric to ferrous ion ratio is approximately 6, the effluent pH is close to 2.4 and the total solution flow has been reduced to approximately 36,000 gallons per minute.

SOLUTION MANAGEMENT

Figure 6 illustrates the general flow of solution to the dump, to a holding basin, and to copper extraction. Copper extraction is achieved either by cementation on de-tinned scrap iron as indicated or by solvent extraction using one of the LIX reagents for selective removal of cupric ion from sulfate leach liquors. The general trend is toward solvent



$Cu^{+2} + Fe = Cu + Fe^{+2}$

SOLVENT EXTRACTION

$2RH + Cu^{+2} = R_2Cu + 2H^+$

IRON REMOVAL:

$2Fe^{+2} + O_2 + 2H^+ = 2Fe^{+3} + H_2O$ *(Slow)*

$6Fe^{+3} + 4SO_4^{-2} + 14H_2O = 3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O\downarrow + 10H^+$

DUMP EFFLUENT:

pH	1.9 - 3.5
Cu^{+2}	0.2 - 2.0 gpl
Fe^{+3}	0.2 - 3.0 *(Varies with degree of oxidation)*
Fe^{+2}	0.01 - 3.6
Al^{+3}	small - 10
Mg^{+2}	small - 7

Figure 6. Copper dump leaching. Ranges of concentrations were taken from actual dump leaching practice.[9]

extraction due to the high cost of iron scrap. Schlitt has indicated[6] that the operating costs for solvent extraction are less than those for cementation although the capital costs may be higher. Also, solvent extraction-electrowinning produces a marketable copper cathode.

Following extraction, solutions are recycled or enter a containment pond where some aeration occurs. It should be noted, however, that the iron balance for the greater part is achieved by precipitation of iron salts throughout the dump itself. Iron removal occurs as indicated in Figure 6 by hydrolysis and precipitation of salts. The reaction depicted illustrates the formation of hydronium jarosite. Similarly sodium, potassium, ammonium or other metal jarosites may also form. The concentrations listed in Figure 6 for dump effluent represent the ranges observed in actual leach practice.

A feature of special importance is the method of solution application.[8,10] The general methods employed are:

1) Pond irrigation
2) Trickle
3) Multi-low pressure spray
4) Single-high pressure spray
5) Well injection

Ponding is still prevalent in practice but the trend is to trickle leaching or sprays. In ponding, channeling can cause excessive dilution with loss of control over effluent quality. Trickle leaching is carried out by using a network of perforated PVC pipe. This system provides a more gradual application of solutions and more uniform air and solution access to the dump. Spraying, using low pressure multiple sprays or high pressure single sprays, also provides uniform coverage. Spray systems may suffer excessive solution loss by evaporation in areas having high evaporation rates. Both trickle and spray leaching suffer in some areas where excessive ice formation may occur during winter months. In such cases more than one method of solution application may be needed. The last method is injection down wells. This method is the method used in uranium solution mining. Wells are drilled on a grid pattern and lined with perforated pipe. Solution flow is controlled by combined down-well and up-well pumping through a flooded formation. Percolation leaching using this method for copper recovery suffers in that uniform coverage is difficult. Solutions move generally downward under free flow conditions requiring a close network of injection wells for adequate coverage. This method has been used by Anaconda in Butte, Montana where ice formation is a serious problem.

Jackson and Ream[10] recently reviewed the results of an extensive field test study at Kennecott's Bingham Mine. A comparison was made between trickle and spray leaching. In general spray leaching resulted in effluent solutions containing somewhat high concentrations of copper, illustrating the importance of uniform coverage with minimal channeling. In typical dump leaching practice the solution application rate differs from the irrigation rate.[10] The application rate is the leach solution flow rate per unit area of surface to which it is being applied. On the average application rates observed to give best results vary from less than 20 ℓ/m^2-hr (0.5 gal/ft^2-hr) for sprinklers, to 80 ℓ/m^2-hr (2 gal/ft^2-hr). for trickle leaching. For pond leaching, the application rate may be as high as 200 ℓ/m^2-hr (5 gal/ft^2-hr). The irrigation rate is the total dump system solution flow rate divided by the total surface area available for solution application. In general, intermittent leaching with alternate leach and rest cycles is preferred to continuous leaching. Typically the irrigation rate will be 1/4 to 1/5 of the application rate[10] for a given dump area. This practice conserves energy consumed in pumping and is effective since pore leaching continues during the rest period, under conditions of good aeration, building up dissolved metal values in the contained liquid phase. Continuous leaching without the rest cycle, extracts large quantities of heat from the dump (up to one-half of the exothermic heat of reaction) adversely affecting leaching rates.

It is uneconomical to remove salts from leach liquors before recycle. Usual practice is to add make up water as needed and in some cases sulfuric acid. The solutions will build up in metal and sulfate concentration until salt deposition occurs. Iron is soon in equilibrium with a variety of jarosite salts depending upon the general chemistry of the dump system. Aluminum and magnesium can increase to very high values, e.g. 5 to 10 gpl., and sulfate concentrations may approach one molar. In general a successfully operating sulfide leach dump is capable of generating acid internally; that is, a dynamic buffering effect, balancing acid producing and acid consuming reactions, must produce pH values and solution oxidation potentials conducive to the promotion of bacterial activity and solubilization of copper and iron in solution. Acid additions to influent leach liquors do not alter the balance of acid consuming and acid producing reactions of such massive systems, but serve to prevent precipitation of iron salts in the upper strata of the dump, preserving adequate permeability for uniform solution penetration.

DUMP LEACHING CHEMISTRY

A detailed treatment of dump leaching chemistry would be too extensive for this treatise, therefore only the more pertinent features are considered. The steady state generation of ferric iron, in all of its soluble forms (Fe III), and hydrogen ion are of primary importance in an acid leaching system.

At 30^oC the solubility of oxygen in pure water is 2.3×10^{-4} mpl. In the high ionic strength liquors produced in recycled leach liquors the solubility is considerably less. As may be shown the oxygen oxidation of sulfide minerals is kinetically less important than oxidation by complex ferric ions in solution, present in much greater concentration. Oxygen is essential, serving to oxidize ferrous iron to ferric and to provide conditions for the growth of chemoautotrophic bacteria.

Normally the oxidation of ferrous iron to ferric is slow. The bacterium Thiobacillus ferrooxidans, an aerobic chemoautogroph deriving its energy from the oxidation of ferrous iron, greatly accelerates the oxidation of ferrous iron according to the reaction

$$\frac{1}{2} O_2 + 2H^+ + 2Fe^{+2} \overset{bac}{=} 2Fe^{+3} + H_2O \qquad (1)$$

Oxygen is essential since the bacterium respiration cycle terminates by the reduction of oxygen forming water. The bacterium Thiobacillus thiooxidans is also an aerobic chemoautogroph deriving its energy from the oxidation of elemental sulfur, thiosulfate, or sulfide as contined in heavy metal sulfides. Sulfur oxidation produces sulfuric acid in place, an essential feature in maintaining open porosity in dump leaching.

The presence of appreciable quantities of ferric ion in leach dump effluent is evidence of bacterial activity and represents a steady-state ferric ion level resulting from competing oxidation and reduction reactions. Pyrite is a strong acid producer supplying ferrous iron which is subsequently oxidized to the ferric state in the presence of <u>T. ferrooxidans</u>. Pyrite also greatly influences the net consumption of oxygen in the system which often may be as high as 7-20 moles of oxygen per mole of Cu^{+2} produced.

Ferric iron in solution (Fe III) exists in several forms. Thermodynamically, the more important forms are: $Fe(SO_4)_2^-$, $FeSO_4^+$, $Fe_2(OH)_2^{+4}$, $FeHSO_4^{+2}$, and $FeOH^{+2}$. The sulfate complexes are greatly favored over the hydroxyl complexes.[11] To illustrate the importance of iron complex formation, a typical leach solution will be considered in equilibrium with precipitated hydrogen jarosite, having an approximate free sulfate activity of 0.02. The equilibrium is represented by

$$(Fe)_3(SO_4)_2(OH)_5.2H_2O + 5H^+ = 3Fe^{+3} + 2SO_4^= + 7H_2O \qquad (2)$$

for which log K is -2.7. The iron sulfate complex equilibria are

$$Fe^{+3} + SO_4^= = FeSO_4^+ \qquad (3)$$

and

$$Fe^{+3} + 2SO_4^= = Fe(SO_4)_2^- \qquad (4)$$

with log K values of 4.15 and 5.4 respectively. Accordingly, at pH = 2.3 the ferric ion activity would be approximately 8.6 x 10^{-5}. Using activity coefficients of approximately 0.7 the corresponding ferric sulfate complex concentrations of $FeSO_4^+$ and $Fe(SO_4)_2^-$ respectively would be 0.035 and 0.012 molar. This corresponds to a total maximum Fe III concentration of approximately 2.6 gpl at this pH. Under conditions of dump leaching, ferric ion complexes are present with activities much greater than the activity of dissolved oxygen and are kinetically more important than oxygen in the mineral oxidation. In the total dump leaching system the oxidation sequence is:

- aeration by convection, promoting bacterial activity
- oxidation of ferrous iron to ferric
- ferric iron dissolution of sulfides with metal release and acid generation

The presence of even small concentrations of Fe III in dump effluent is indicative of bacterial activity.

The dissolution of sulfide minerals occurs generally by electrochemical processes. Some reactions are acid consuming and some are acid producing while others are neutral. The dissolution of gangue constituents and oxygen reduction (Eq. 1) are acid consuming processes while hydrolysis reactions are acid producing. Many sulfides form elemental sulfur which is metastable under dump leaching conditions. The slow leaching rate of sulfur to sulfate under ambient conditions and in the absence of sulfur oxidizing bacteria results in long term stability of elemental sulfur;

however, the times involved in dump leaching are sufficiently long that little elemental sulfur is found. For this reason only the net overall reactions with sulfate formation are considered.

Typical reactions involving chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), and selected carbonates and silicates are listed illustrating acid consuming, acid generation, and pH independent reactions:

Acid consuming reactions:

(malachite)

$$CuCO_3 \cdot Cu(OH)_2 + 4H^+ = 2Cu^{+2} + CO_2 + 3H_2O \tag{5}$$

(azurite)

$$2CuCO_3 \cdot Cu(OH)_2 + 6H^+ = 3Cu^{+2} + 2CO_2 + 4H_2O \tag{6}$$

(chrysocolla)

$$CuO \cdot SiO_2 \cdot 2H_2O + 2H^+ = Cu^{+2} + SiO_2 + 3H_2O \tag{7}$$

(calcite)

$$CaCO_3 + 2H^+ + SO_4^{-2} + H_2O = CaSO_4 \cdot 2H_2O + CO_2 \tag{8}$$

(chlorites)

$$\begin{aligned} H_4Mg_3Si_2O_9 \cdot y\, H_4\, Mg_2\, Al_2\, Si_2\, O_9 = {} & (6+6y)H^+ + \\ & (2+2y)\, SiO_2 + (3+2y)Mg^{+2} + 2y\, Al^{+3} + (5+5y)H_2O \end{aligned} \tag{9}$$

(biotite)

$$H_2K(Mg)_{3x}(Fe)_{6-3x}\,Al(SiO_4)_3 + 10\,H^+ = K^+ + 3xMg^{+2} + (6-3x)Fe^{+2} + Al^{+3} + 3SiO_2 + 6H_2O \qquad (10)$$

(K-feldspar alteration to K-mica)

$$3KAlSi_3O_8 + 2H^+ + 12H_2O = KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6H_4SiO_4 \qquad (11)$$

(K-mica alteration to Kaolinite)

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ = 3Al_2Si_2O_5(OH)_4 + 2K^+ \qquad (12)$$

(Kaolinite)

$$Al_2Si_2O_5(OH) + 6H^+ = 3Al^{+3} + H_2O + 2H_4SiO_4 \qquad (13)$$

Acid-generatiing reactions:

(chalcopyrite oxidation)

$$CuFeS_2 + 16Fe^{+3} + 8H_2O = Cu^{+2} + 17Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (14)$$

(covellite oxidation)

$$CuS + 4H_2O + 8Fe^{+3} = Cu^{+2} + SO_4^{-2} + 8Fe^{+2} + 8H^+ \qquad (15)$$

(pyrite oxidation)

$$FeS_2 + 8H_2O + 14Fe^{+3} = 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (16)$$

(iron hydrolysis to hydrated hematite)

$$2Fe^{+3} + (3+x)H_2O = 6H^+ + Fe_2O_3 \cdot xH_2O \qquad (17)$$

(iron hydrolysis to hydrogen jarosite)

$$Fe^{+3} + \frac{7}{3}H_2O + \frac{2}{3}SO_4^{-2} = \frac{5}{3}H^+ + \frac{1}{3}Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O \qquad (18)$$

(iron hydrolysis to jarosite salts)

$$Fe^{3+} + \frac{1}{3}M^+ + 2H_2O + \frac{2}{3}SO_4^{=} = \frac{1}{3}MFe_3(SO_4)_2(OH)_6 + 2H^+ \qquad (19)$$

(chalcopyrite alteration to chalcocite)

$$5CuFeS_2 + 11CuSO_4 + 8H_2O = 8Cu_2S + 5FeSO_4 + 8H_2SO_4 \qquad (20)$$

Neutral reactions:

(chalcopyrite alteration to covellite)

$$CuFeS_2 + CuSO_4 = 2CuS + FeSO_4 \qquad (21)$$

(chalcocite)

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4 \qquad (22)$$

The dynamic character of dump leaching in terms of pH is obviously complicated as suggested by the above reactions. Few reactions in dump leaching are pH independent. For this reason a dump must have the ability to produce acid at a rate which is capable of maintaining a pH which will maintain an iron concentration effective for dump leaching. The rates of the above reaction are of basic importance in establishing and maintaining suitable solution chemistry for metal extraction.

In general, reactions involving the silicate minerals are slower than those involving oxides and secondary sulfides. The primary sulfide ($CuFeS_2$) is the most refractory of all of the copper sulfides. The secondary minerals (e.g. CuS and Cu_2S) react readily under oxidizing conditions.

RATE PROCESSES IN COPPER DUMP LEACHING

The body of literature on dump leaching processes and modeling is extensive and has been advanced to explain practice, large scale field tests, and laboratory tests. As early as 1943 Taylor and Whelan[12] described operating practice at the Rio Tinto Spain property. These authors recognized the importance of free flow of air to the dump to provide needed oxidation of sulfide minerals. They explained the extraction of minerals on an empirical basis, discussed the virtue of spraying in comparison to ponding, and emphasized the importance of avoiding the precipitation of salts and plugging as a result of slimes at the surface of dumps. Harris[13] was one of the first to consider mathematical modeling in heap leaching of copper ores on a semi-quantitative basis. Bartlett[14,15] developed a model based upon continuity conditions which provides the general basis for a variety of additional studies in modeling of dump leaching and solution mining systems. Braun, Lewis and Wadsworth[16] developed a model incorporating diffusion control and mineral surface reactions which can be shown to be a special case of the general solution proposed by Bartlett. Other researchers have used similar models to explain the leaching of sulfides and oxides.[17,18,19,20,21] Cathles and Apps[22] developed a model incorporating oxygen and heat balance and convective flow of air through a dump, based upon observed operating data from a dump opoeration. Roman[23] has examined the problems of scaling laboratory tests to actual dumps.

Researchers in general agree that ore fragment rate processes involve diffusion of Fe III through pores, cracks, and fissures. Figure 7 illustrates an ore fragment[a] showing the pore structure and diffusion of ions. A surface film, depicted flowing over the cross-section on the right, is exposed under optimal conditions to convective air flow. Oxygen transfer to the liquid film occurs by diffusion. In well aerated dumps tranfer of oxygen to the liquid phase is not rate limiting because of the large surface areas involved. Ferrous ion in the film is oxidized to the ferric state, a reaction requiring bacterial oxidation to occur at a rate suitable for leaching to proceed. The Fe III produced diffuses through the pore structure reacting with sulfide minerals and releasing cuprous and ferrous ions which in turn must diffuse in directions indicated by the localized concentration gradients. Copper may diffuse to the center of the ore fragment and continue to diffuse if a gradient is established by secondary enrichment reactions. Release of copper and ferrous iron occurs by outward diffusion through the pore structure of the rock fragment joining the flowing film. During rest cycles, leaching continues with a build-up of dissolved metal values in the immobile aqueous phase held by capillary forces. When the rock fragment is first exposed to solution, surface reaction control may occur followed by increased kinetic dependence upon diffusion as the process continues.

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[a] Ore (rock) fragment or particle refers to the composite piece of ore with associated gangue minerals and contained metal oxides and sulfides. A mineral grain refers to a sulfide mineral particle within the ore fragment.

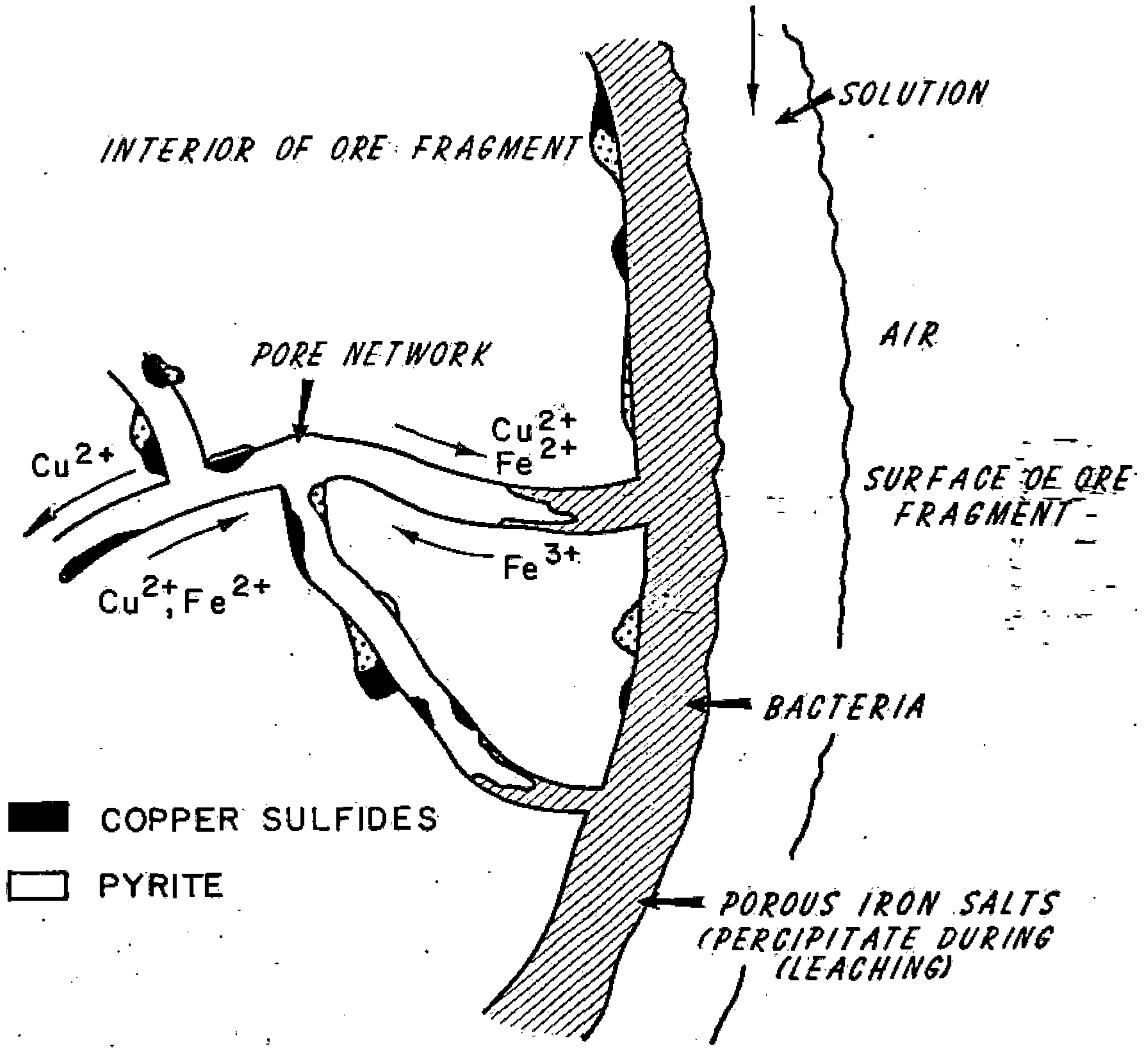


Figure 7. Ore fragment showing pore network and diffusion of ions.

The rate of extraction may thus be the sum of surface convective transfer, surface chemical reaction and diffusion through the pore structure. Figure 8 represents a case where the partially unreacted sulfide particles exist in a relatively narrow reaction zone of thickness Δr with a reacted outer region and an unreacted core, giving rise to the so-called "shrinking core" kinetics. The narrow reaction zone is a special case which, as will be shown, is a satisfactory model for secondary copper sulfides and oxides, but not generally for chalcopyrite ($CuFeS_2$) which often leaches very slowly, and is highly variable with source. For very slow leaching sulfides a non-steady state analysis is required. The secion AA of Figure 8 illustrates the copper content of the fragment and the ferric ion complex concentration within the pores as a function of radius, r, for some time, t. The reaction zone thickness is Δr.

Using the mixed kinetic shrinking core model developed by Braun, et al.[16], Madsen, et al.[18] applied the model to several 7 ton ore samples of secondary copper sulfide ores. The mixed kinetics model in integrated form is

$$1 - 2/3\alpha - (1-\alpha)^{2/3} + \frac{\beta}{r_o}\left[1-(1-\alpha)^{1/3}\right] = \frac{\gamma}{r_o^2}\,t \qquad (23)$$

where α = fraction of copper removed from the ore fragment

r_o = ore fragment radius

t = time

β, γ = constants at constant solution concentration and temperature

The constant β and γ contain ore grade, apparent diffusivity, intrinsic

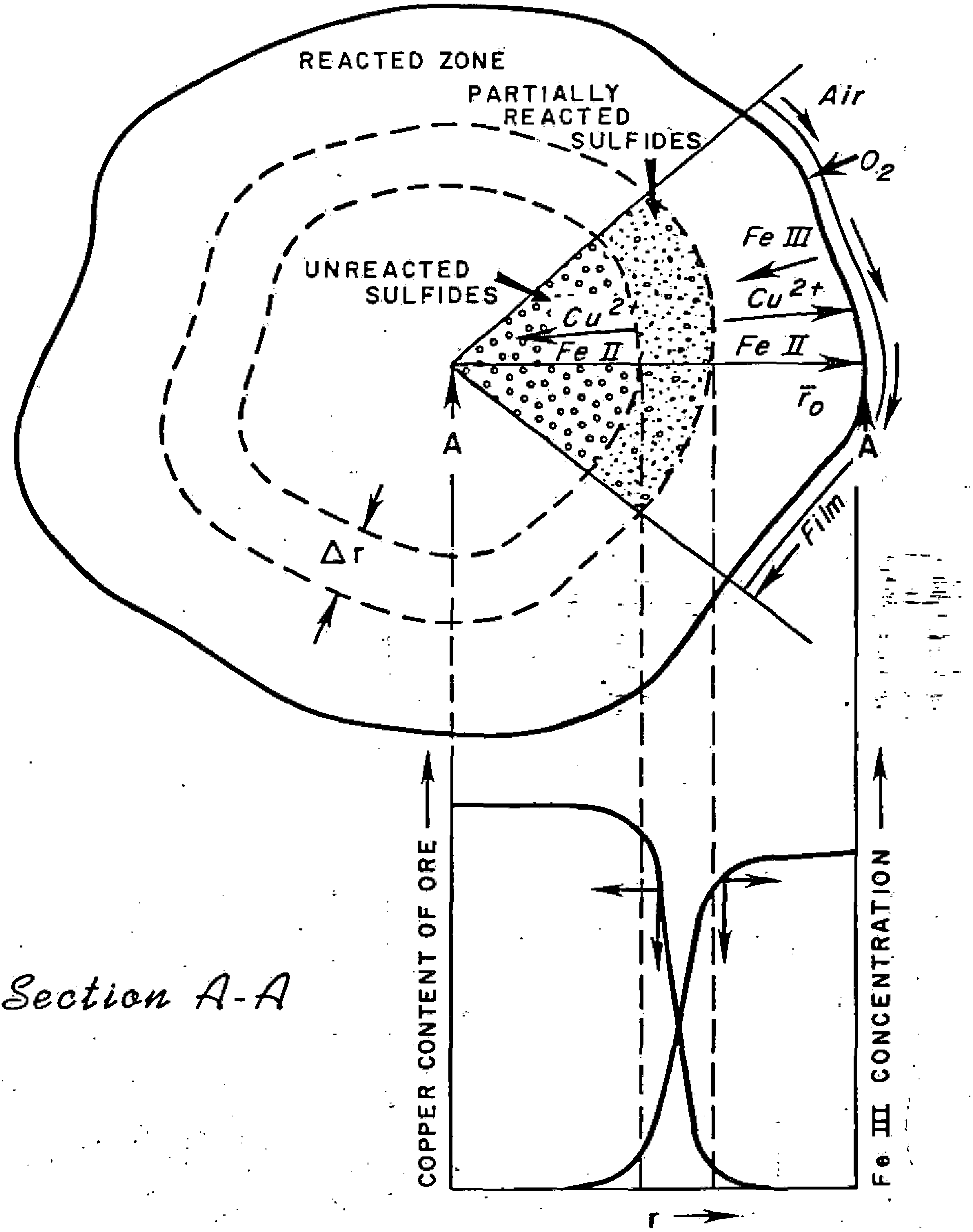


Figure 8. Ore fragment showing reacted and unreacted regions and diffusing ions.

sulfide kinetic parameters and physical values, including ore and contained mineral densities. Figure 9 illustrates the correlation of leaching data for a 7-ton sample of monzonite secondary copper sulfide ore. The diffusivity required were observed to be consistent with expected values for pore diffusion. Madsen, et al.[19] also correlated leach data with a non-steady state particle diffusion model.

Cathles and Apps[22] provided a one-dimensional non-steady state model to the leaching of the Kennecott, Midas test dump containing 93,000 tons of ore. Three equations relating oxygen balance, heat balance, and air convection were used. This study was one of the major developments in modeling of dump leaching, since it incorporated flow, both air and solution, heats of reaction, and shrinking core ore fragment kinetics. Figure 10 illustrates the observed and calculated rates of copper extraction and cumulative recovery using the non-steady state model.

Roman has considered[23] the difficulties inherent in the modeling of massive dumps from small scale tests. Laboratory tests of 5 to 10 tons and even the 93,000 ton Midas Dump test are small compared to typical massive dumps containing millions of tons of waste rock. From drill hole log data taken from large dumps it is evident that an approximate bi-modal or tri-modal density and moisture distribution is present. Figure 11 illustrates well log results from a drill hole in Kennecott's, Chino, New Mexico dump.[23] The fine structure appears to be in intervals of a fraction of a foot to one or two feet. Superimposed is a larger periodicity of several feet. Figure 12 shows the effect of low and high compaction on fluid flow within a dump.[23] Solution by-pass zones or particles clusters may behave like individual ore fragments; i.e.,

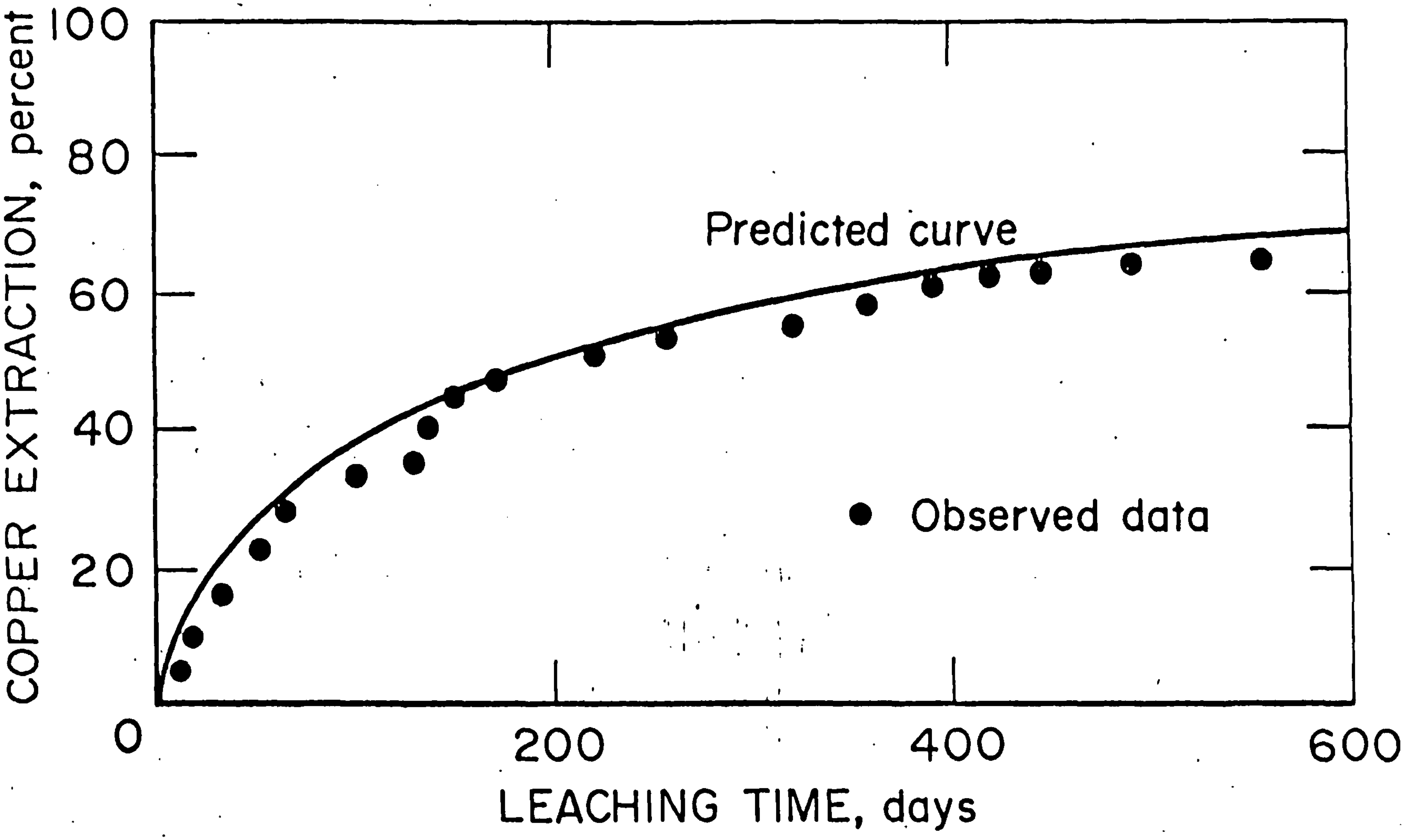


Figure 9. Predicted copper extraction for monzonite ore.

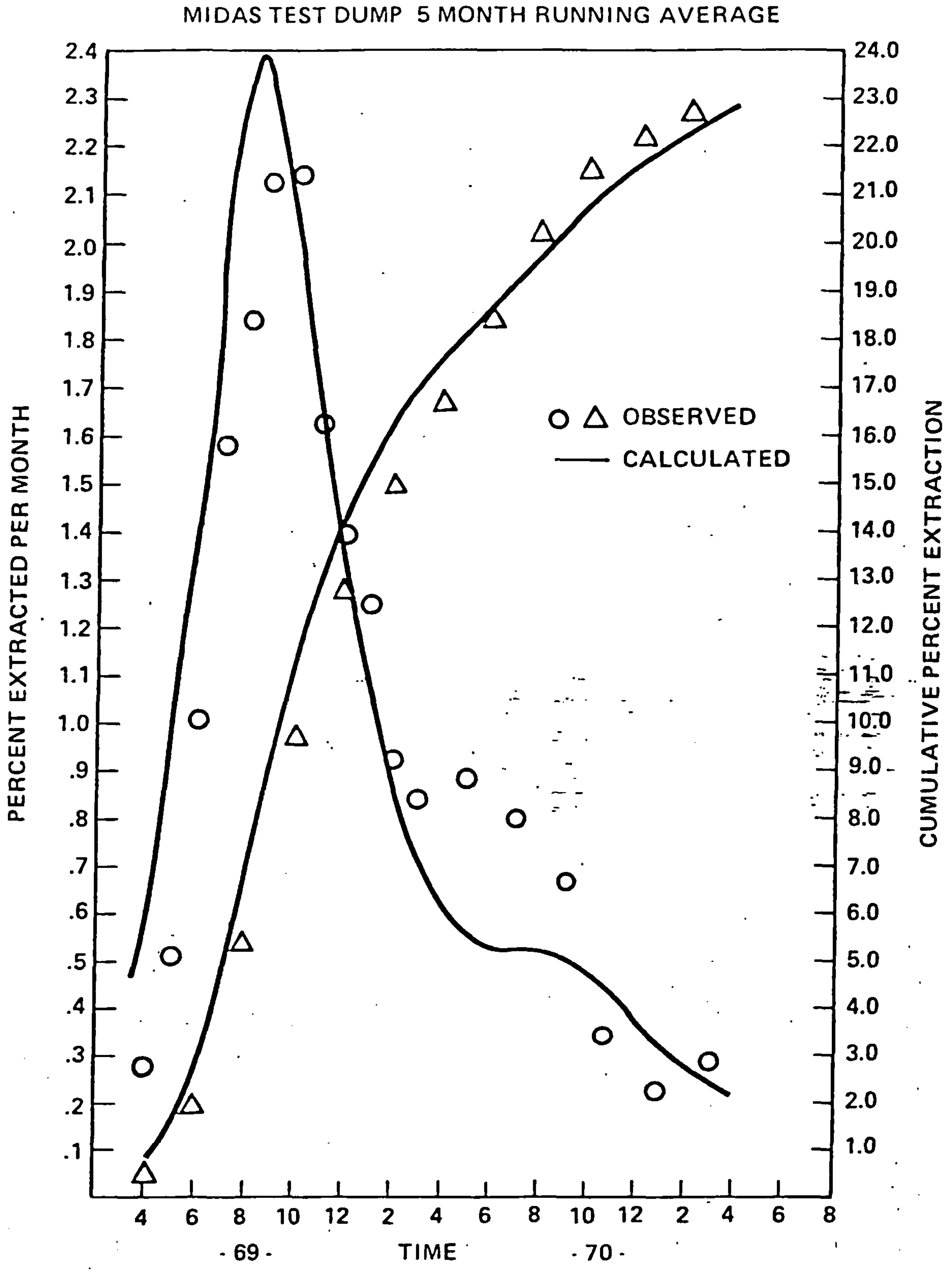


Figure 10. Comparison of observed and calculated dump behavior.

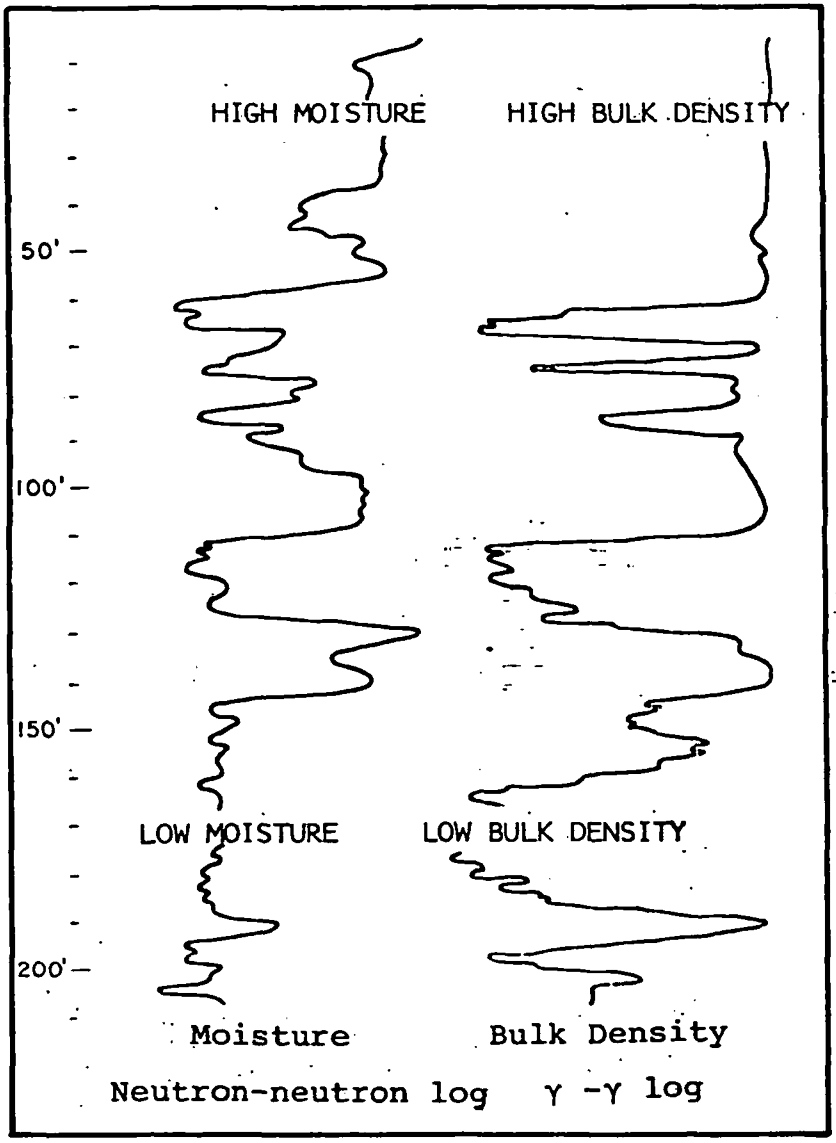
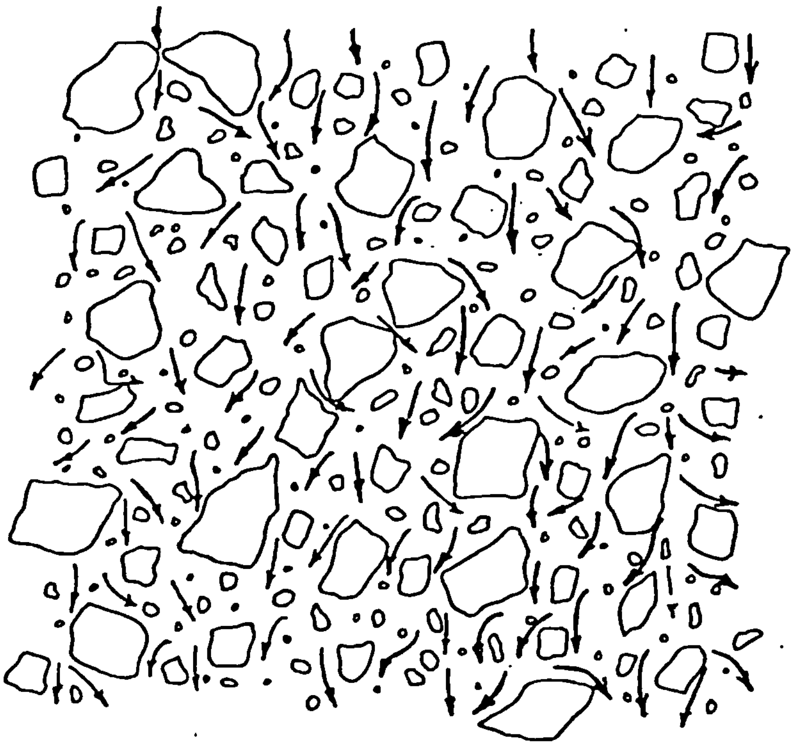
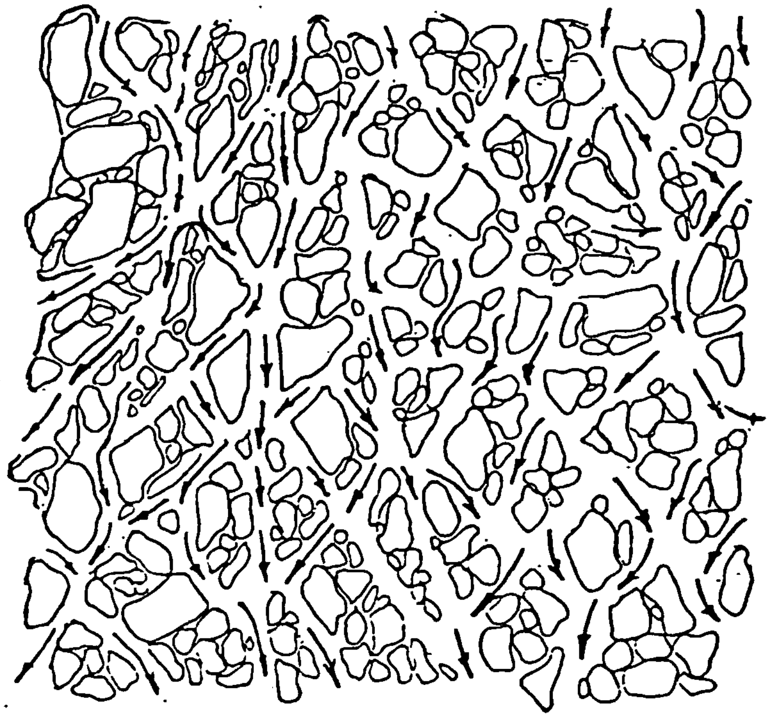


Figure 11. Well log-data from Kennecott's Chino dump, showing variations in moisture and density.



REGION OF LOW COMPACTION



REGION OF HIGH COMPACTION

Figure 12. Illustration showing effect of compaction on fluid flow within a dump, according to Roman.[23]

with free flow around the perimeter and diffusion to the interior. It is interesting to note that leaching data may be well approximated by using for the initial radius, r_0, (Eq. 23) the fifty percent passing size of the initial ore size distribution. Uncertainties relative to two phase flow of liquid and air in dump leaching represent the most difficult aspect in the scaling of test data to the massive dumps being leached in practice. Steady state daily recovery, which is the fraction of the daily tonnage of copper added to a dump which is recovered by leaching generally falls in the range of 15 to 50 percent. For example at Kennecott, Bingham 250,000 tons of ore (∿0.17 percent copper) goes to the waste dump daily. This ore contains approximately 850,000 lb. of copper of which 150,000 lb. or 18 percent is recovered daily.

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Recovery of nickel, copper and precious metal concentrate from high grade precious metal mattes

by L. R. Hougen and H. Zachariasen

Falconbridge Nikkelverk A/S sequentially treats high grade precious metal copper nickel mattes with HCl and chlorine, producing a precious metal concentrate having a bulk no greater than 1% of the original matte.

L. R. HOUGEN

Lief R. Hougen received his degree in Chemical Engineering from The Technical Univ. of Norway in 1946. After being employed with Norwegian Dairies from 1946 to 1952, he became Head of the Dept. of Chemical Engineering. Sintef (i. e. Institute for Industrial Research at the Technical Univ. of Norway). In 1965 he joined Falconbridge Nikkelverk A/S as Research Manager.

In the Falconbridge Matte Leach Process[1,2] nickel is selectively leached with strong hydrochloric acid from finely divided nickel-copper converter matte, leaving copper sulfide and precious metals in the leach residue. The nickel-bearing acid solution is purified by solvent extraction, after which nickel chloride is crystallized. Nickel chloride is converted to nickel oxide granules in a fluid bed hydrolyzer[3] and reduced to metal with hydrogen in a rotary kiln[4] and finally marketed as NICKEL 98.

This process was originally designed for treating Falconbridge matte containing about 20 ppm combined precious metals recoverable by roasting the matte leach residue, leaching copper from the calcine by spent electrolyte from electrowinning of copper and by further upgrading the precious metals from the copper leach residue.

When it became necessary for Falconbridge to treat high grade precious metal mattes of the type produced from the nickel, copper and precious metal bearing ores mined in South Africa, the matte leach process was evaluated for this purpose. However, experience with Falconbridge matte had taught that although there was complete recovery of precious metals in the residue from the nickel leach, losses occurring in the roast-leach operation seriously affect the economics of the process when applied to the relatively high grade matte under consideration. This prompted the development of a hydrometallurgical process for removing copper and sulfur from the hydrochloric acid leach residue.

OXIDIZING LEACH IN SULFURIC ACID

Although the refinery solutions contain both chloride and sulfate ions, the first experiments were directed to leaching the copper from the residues by pressure oxidation in sulfuric acid so as to exploit the known tendency for precious metals to resist dissolution as sulfates.

In order to achieve practical reaction rates, the oxidation leach of copper sulfide in sulfuric acid must be conducted in high pressure equipment in the presence of oxygen.

Test work was done in a 10-liter titanium-lined autoclave. Conditions such as temperature, oxygen partial pressure and acid strength were varied, and the degree of copper leach vs. dissolution of precious metals determined.

The test work showed that pressure leaching could be made a practical process for leaching copper from the matte leach residue, although there was some dissolution of precious metals, particularly of the so-called bymetals (rhodium, ruthenium and iridium), which required additional treatment of the leach liquor for their recovery. But more important, because of impurities introduced into the copper sulfate solution, particularly chlorides and selenium, this solution could not be directly utilized for electrowinning of copper. For these reasons attention was directed to investigation of the chloride leach.

OXIDIZING LEACH IN THE CHLORIDE SYSTEM

The oxidizing leach of copper sulfide in the chloride system is carried out by adding chlorine to a slurry of copper sulfide in a copper-bearing chloride solution. Because monovalent copper ions are present other chlorides, e.g., nickel chloride or hydrochloric acid, have to be present in order to prevent cuprous chloride from precipitating.

Reactions taking place in the chlorine leaching of copper are:

$$2Cu^+ + Cl_2 \text{ —— } 2Cu^{++} + 2Cl^- \quad (1)$$

$$Cu_2S + Cu^{++} \text{ —— } CuS + 2Cu^+ \quad (2)$$

$$CuS + Cu^{++} \text{ —— } 2Cu^+ + S \quad (3)$$

$$S + 2e \text{ —— } S^{--} \quad (4)$$

$$Cu^{++} + S^{--} \text{ —— } CuS \quad (5)$$

The complete leach of copper depends on reaction (3). However, equations (4) and (5) show that it is the oxidation potential of the solution that governs whether copper shall be leached from sulfur into solution or precipitated from solution as copper sulfide.

At high red-ox potentials as measured between platinum and saturated calomel electrodes in the solution, reaction (3) will proceed as shown. At lower red-ox potentials, however, reaction (4) may create sufficient concentrations of sulfide ions for reaction (5) to occur at a given level of copper in the solution, i.e., when the solubility product of CuS is exceeded at a given acidity and temperature, with the result that copper sulfide will precipitate.

The lowest red-ox potential necessary to effect a complete leach of copper is therefore in principle dependent on the concentration of copper in solution, acidity and temperature, but will for most practical purposes be in the region of 350-450 mV. As illustrated in Fig. 1 the precious metals are substantially kept out of solution in this range of red-ox potentials, either because they are not dissolved in the first place or because they are reprecipitated according to reactions (4) and (6) in a similiar manner as earlier described for copper.

$$S + 2e \longrightarrow S^{--} \qquad (4)$$

$$Pt^{++} + S^{--} \longrightarrow PtS \qquad (6)$$

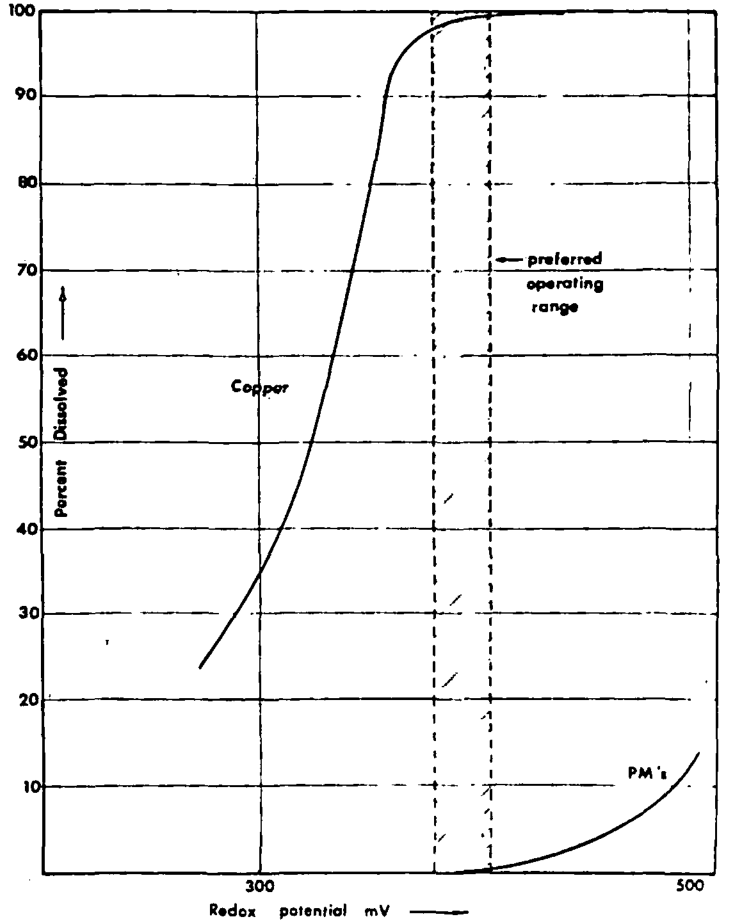
Any selenium liberated during the leach may also react with precious metal ions and form insoluble selenides, possibly in a similar mode as suggested for the sulfides.

From the curve in Fig. 1, it is possible to pre-select a red-ox potential at which to conduct the leach for minimum dissolution of precious metals consistent with high extractions of copper. The dissolution curves for copper and the precious metals as well as the preferred range of red-ox potentials for leaching shift slightly to the left at high acid, high temperature and low copper concentration in the leach solution, and to the right at lower acid, lower temperature and high copper concentration in solution.

The leach residue from the chlorine leach conducted at such a selected red-ox potential consists of precious metal residue and elemental sulfur and selenium if originally present in the matte. After removing sulfur, i.e., by leaching with tetrachloroethylene, a precious metal residue is left which has been upgraded by a factor of approximately 100 from the matte.

After having demonstrated the feasibility of this approach in the laboratory, this all-chloride route was chosen to be developed for commercial operation. The decision was based on the indications from research work that this process would give equal or better recoveries of precious metals as compared to other processes and because it fitted in so well with the company's other chloride metallurgical operations for the production of high quality nickel. This latter feature made it possible to erect facilities for treating high precious metal mattes by adding a side line to the previously existing matte leach plant built for treating Falconbridge matte and utilizing part of its capacity for refining the nickel contained in the high precious metal mattes. When operating the precious metal matte leach, the feed of Falconbridge matte to the main plant is reduced correspondingly. In this way the nickel refining capacity of the matte leach plant can always be fully utilized.

Fig. 1—Dissolution of copper and PM's in chlorine leach. Ni 100g/l, Cu 50g/l, HCl 150g/l, Temperature 80°C, Red-ox electrodes Pt/calomel.



PROCESS DESCRIPTION

As shown in the flowsheet, Fig. 2, the recovery of nickel, copper and precious metal concentrate from high precious metal South African mattes as practiced at Falconbridge Nikkelverk A/S, Kristiansand S., Norway, involves the following process steps:

1) Leaching of nickel in strong hydrochloric acid[5]
2) Further leaching with chlorine at a preselected red-ox potential to dissolve copper
3) Filter off chlorine leach residue
4) Reprecipitate copper with H_2S and filter off copper sulfide for subsequent processing to electrowon copper

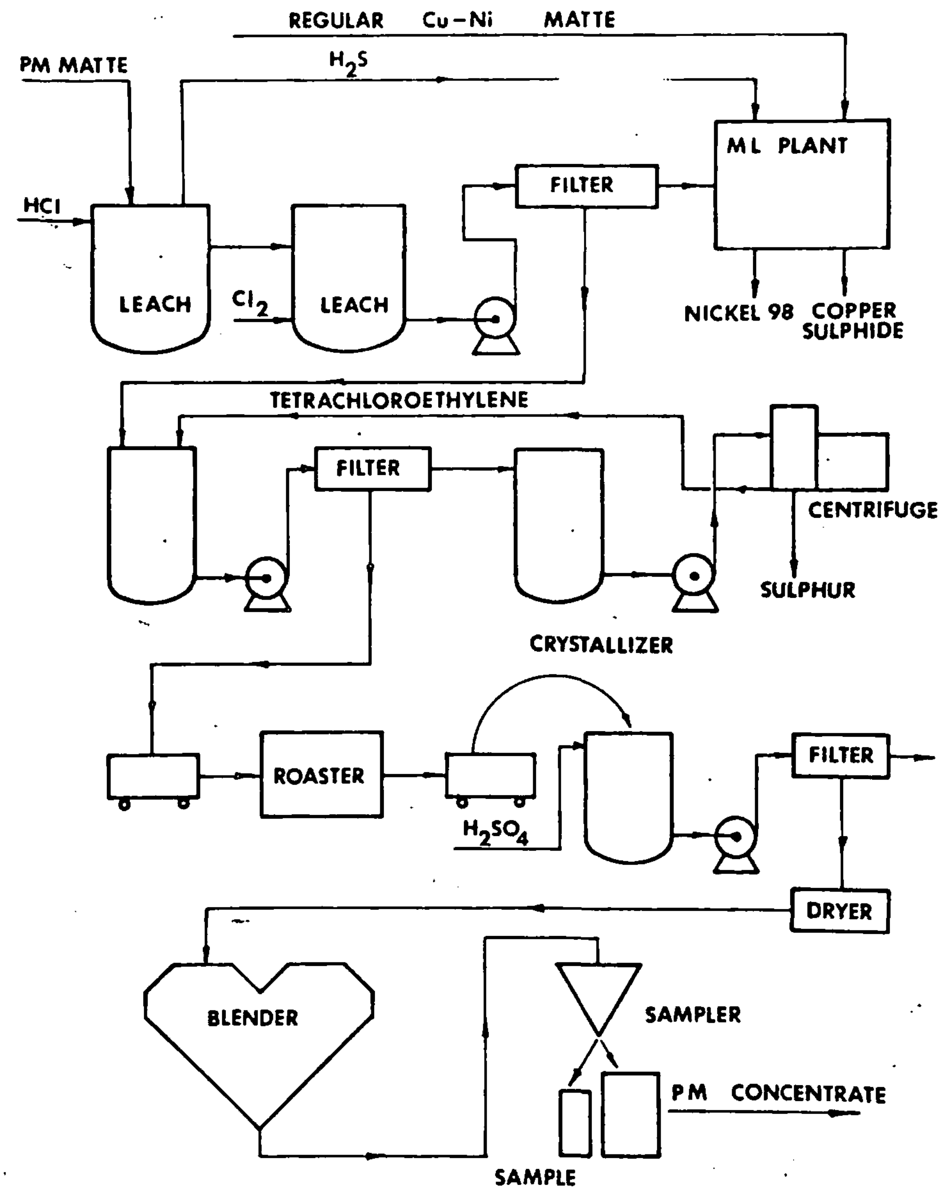


Fig. 2—Schematic flowsheet Falconbridge Nikkelverk A/S plant for treating high grade PM mattes.

5) Treat filtrate according to the Falconbridge Matte Leach Process Flowsheet[1] for recovery as NICKEL 98
6) Leach sulfur with tetrachloroethylene from chlorine leach residue and filter off precious metal residue
7) Recover sulfur and regenerate tetrachloroethylene
8) Further upgrade precious metal residue by a sulfating roast followed by leaching with dilute sulfuric acid.

The HCl and chlorine leach are carried out in rubber-lined agitated tanks. The chlorine leach tank is equipped with submerged platinum and saturated calomel electrodes which measure the red-ox potential in the solution and control the feed of chlorine in proportion to the inflow of copper sulfide residue from the HCl leach tank such as to maintain a preselected red-ox potential. Sulfur and precious metal residue is filtered off in a filter press with polypropylene frames and plates and the filtrate passed to the main plant for nickel and copper recovery.

The precious metal and sulfur filter cake is discharged from the filter press into a feed bin fitted with load cells from which it is continuously fed to a steam-jacketed glass lined agitated tank where sulfur is dissolved in hot tetrachloroethylene. The leach slurry is continuously withdrawn by a stainless steel centrifugal pump, and the precious metal residue is filtered off in steam-jacketed closed pressure filters. The filtrate is passed through a second polishing filter before sulfur is removed by crystallization.

UPGRADING OF RESIDUE

The filter cake from the pressure filters, containing the precious metals and now reduced in weight by a factor of 100 from

Table I—Batch treatment of high grade precious metal matte: assays of matte and precious metal concentrate

Assays	*Au**	*Pt**	*Pd**	*Rh*	*Ru*	*Ir*
Matte, ppm	69.	732.	329.	33.	74.	13.
Concentrate, percent	2.43	26.55	11.77	1.20	2.64	0.43

*Average of assays by independent laboratories

the matte is manually transferred to stainless steel trays which subsequently are placed in a small roasting furnace equipped with gas absorption facilities. The roasting rate is controlled by the rate at which air is admitted to the furnace. This rate is kept low in order to prevent any draft resulting in dust losses. Such losses have indeed not been experienced. Roasting temperature is about 500°C and the resulting base metal sulfates are leached with dilute sulfuric acid after which the precious metal concentrate is filtered, washed, dried and transferred to a V-shaped rotating blender of 1000 kg capacity from which, it is withdrawn, at intervals, weighed and automatically sampled. The grade of the final concentrate is obviously dependent on the quantity of insoluble components originally present in the matte, particularly silica. Normally, the concentrate regularly produced analyzes 15-30% platinum and corresponding quantities of other precious metals when starting with a matte containing 700-800 ppm platinum.

RECOVERY

An accurate determination of the precious metal recovery from the operating plant is a difficult task, because being a continuous operation it always contains inventories whose weights and assays are difficult to ascertain. As a check of the recovery obtainable for metallurgical reasons, and not including possible transportation losses, dust losses, etc., a well-assayed batch of matte was treated according to the described process in the laboratory. Table I shows the assays of the matte and resulting precious metal concentrate and Table II shows the precious metals balance for this batch.

INSTRUMENTATION AND PROCESS CONTROL

As has been previously published[2] the operation of the Falconbridge Matte Leach Plant is controlled by a DDC system involving a PDP8 twelve-bit machine. When adding the leaching equipment for processing high precious metal mattes, this machine did not have sufficient capacity to incorporate some 20 additional control loops required. This lack of capacity was remedied by adding a disc memory to the computer as well as various other hardware in minor amount.

Of outstanding importance in this process is to insure that there is no overfeeding of chlorine into the chlorine leach, resulting in a high red-ox potential and dissolution of precious metals. For the sake of safety, the chlorine leach tank is equipped with two independent sets of red-ox potential electrodes of which one set controls the chlorine feed. The other set will trigger an alarm signal if it at any time should read a red-ox potential higher or lower than a preset range.

These controllers, in combination with the computer, have worked extremely well, and it is interesting to note that modern instrumentation and reliable process control have made it possible to apply novel metallurgical process principles which otherwise could not be used, particularly for this delicate purpose where the recovery of these highly valuable metals might be jeopardized.

The process is now regularly operating at a rate of some 20 tpd of high precious metal matte. It has proven to be efficient, reliable and economic for the production of a high grade precious metal concentrate in combination with high quality nickel and copper.

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H. ZACHARIASEN

H. Zachariasen received his degree in chemistry at the Univ. of Oslo in 1955, and joined Falconbridge Nikkelverk A/S in 1956. On leave from the company he received a M. Sc. degree in analytical chemistry at the Univ. of Toronto in 1958, where he also served as lecturer in chemistry from 1960 to 1962. He returned to Falconbridge and is engaged in analytical and metallurgical research work, particularly in the field of precious metals.

Table II—Batch treatment of high grade precious metal matte: precious metals balance

	Weight grams	*Au mg*	*Pt mg*	*Pd mg*	*Rh mg*	*Ru mg*	*Ir mg*
Matte	9000.0	621	6588	2961	297	666	117
Concentrate	25.01	608	6640	2944	300	660	108
Upgrading Factor	360						

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The response of rocks to large stresses

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Abstract—To predict the dimensions and characteristics of impact- and explosion-induced craters, one must know the equation of state of the rocks in which the crater is formed. Recent experimental data shed light upon inelastic processes that influence the stress/strain behavior of rocks. We examine these data with a view to developing models that could be used in predicting cratering phenomena. New data are presented on the volume behavior of two dissimilar rocks subjected to tensile stresses.

INTRODUCTION

WHEN A BODY IMPACTS or explodes in rock or soil, some of the energy is converted into heat and some into mechanical work on the surrounding material. The relative magnitude of heat and work as well as the form of the work itself (i.e., elastic, inelastic, fracture, compaction) are directly dependent on the mechanical response of the surrounding material to the stress conditions. Thus, knowledge of the nature of the relation between stress and mechanical response (strain) is needed to predict the effect of an impact or explosion. The crater form can be predicted if source parameters are known; the source energy and boundary conditions can be predicted if the crater form is known. Terhune and Stubbs (1970) have given an excellent description of the effect of material parameters (such as strength and compressibility) on crater dimensions. They have also compared calculations and observations of explosion-created craters. The purpose of this paper is to review recent experimental work on the response of rock to stress. We seek constitutive relations that can be incorporated into computer codes whose function is to predict the phenomenology of explosions or impacts. The underlying purpose of these experiments has been to increase understanding of the physical processes responsible for observed behavior, so that models developed can be applicable to a broad range of stress and strain conditions (i.e., so that they can be truly predictive, rather than simply fitted to experimental data).

To develop inelastic constitutive models, we must determine the stress and the strain tensor and the tensor that couples them (Schock, 1970) over the range of conditions encountered. Unlike those for elastic materials, the moduli (or stress/strain coupling coefficients) are not independent of stress state. The range of conditions in rock is commonly described by mean pressure (or the invariants of stress), shear stress (or the invariants of stress deviation), and strain rate. Constitutive relations may be considered in terms of stress and strain or, if strain-rate effects are considered, in terms of stress and strain rates. Experimental arrangements incorporating this range of conditions have become common.

See, for example, the papers by Brace *et al.* (1966), Scholz (1968), Swanson and Brown (1971), Schock and Duba (1972), Schock *et al.* (1973), and Scholz and Kranz (1974). The answers to such questions as, "How complex must the models be to accurately describe the desired behavior?" and "What kinds of approximations must be used to make them usable in a time-limited computer code?" are of interest.

In the discussion that follows, brittle, ductile, and porous rocks will be discussed in order. Then, important effects such as fluid saturation and sample size will be considered. Within each classification, behavior in compression, tension, and at high strain rate will be considered. In almost all of the experimental work considered, there was a stress geometry such that the intermediate principal stress was equal to either the maximum or minimum principal stress. Other experimental conditions are difficult to achieve and will be given only brief mention. However, it should be noted that for point source explosions or impacts, shock waves and resultant stresses closely approximate this geometry over significant times and distances.

BRITTLE ROCKS

For our purposes, the failure of brittle rocks may be characterized by a through-going fracture that propagates at sonic or nearly sonic speeds. Inelastic behavior may be observed in the axial stress/strain relation, but total axial strain before failure is usually less than 1% (Griggs and Handin, 1960). Granite, limestone and dolomite at low confining pressure, and quartz-cemented sandstones and metamorphic rocks exhibit this behavior. Failure stress in these materials is strongly dependent on and increases with confining pressure (Jaeger and Cook, 1969). It is not uncommon to observe changes of an order of magnitude with 0.1 GPa confining pressure. This is due primarily to the strong effect of pressure, which increases friction and thereby inhibits sliding on inter-granular crack surfaces.

One of the most striking characteristics of low-porosity, brittle rocks is that before they fail in compression, there is a pronounced nonlinear behavior in the axial-stress/radial-strain relation. This results from inelastic volume dilatancy (Brace *et al.*, 1966), which characteristically precedes failure in these rocks (Scholz, 1968; Schock *et al.*, 1973). This behavior has been ascribed to the opening and the propagation of cracks whose major axes are oriented parallel to the active principal stress. Such cracks open with a tensile stress in the region of the crack tip, even though all of the macroscopic stresses are compressive. Cracks with other orientations are compressed shut at much lower pressures.

Swanson and Brown (1971) determined that at constant strain rate, the curve that describes compressive failure in granite as a function of confining pressure is independent of loading path. A similar observation was made by Schock *et al.* (1973) for the onset of dilatant behavior as a function of confining pressure. If one considers the success of critical-strain-energy criteria for failure (Griffith, 1921; Sih and MacDonald, 1974), this uniqueness in behavior suggests a uniqueness in strain at a given mean pressure and shear stress. This hypothesis has been tested on several brittle rocks (Schock, 1976; Costantino and Schock, 1976) and has been found to be true for the stress conditions prescribed. This allows the construction of a constitutive relation that expresses dilatant strain in the form,

$$\epsilon_d = \exp\left[\frac{dP}{x(\tau)} - A(\tau)\right],$$

where dP is an increment of mean pressure, τ is shear stress, and x and A are material constants. The production of dilatant volume thus appears to follow an exponential law. This form of constitutive relation is not only simple, but it expresses the rock behavior in terms of experimentally measurable and thermodynamically definable parameters. The relation has the additional advantage of being able to predict failure shear stress accurately (Schock, 1976). The physical meaning of the exponential form is not yet clear.

After loading in compression due to an impact or an explosion, one or more of the principal stresses in the rock medium may become tensile during unloading. Brittle rocks typically fail in tension at stress levels an order of magnitude or more below those in compression, again presumably because of the lack of friction on grain boundary cracks when the active stress is tensile. Thus, significantly larger volumes of rock may be affected by inelastic phenomena resulting from tensile stresses than compressive stresses. Investigation of this stress regime has been carried out by Brace (1964), who monitored the axial strain and, more recently, in our laboratory (Schock and Louis, 1974), where both axial and radial strain were monitored. These latter results on Westerly granite were obtained on "dog-bone-shaped" samples in the apparatus described by Schock and Duba (1972).

The experimental stress paths are shown in Fig. 1. The circles represent failure points and collectively describe failure in tension as a function of confining pressure. The two points on the ordinate are extension data (all principal stresses are compressive), for which the minimum principal stress was atmospheric pressure. The coincident strain data are shown in Fig. 2 in terms of mean pressure and volume strain. Significantly, the amount of dilatant behavior is a function of the ratio of tensile to compressive stress in the particular test. Apparently, oriented cracks that will not open until they propagate through the specimen when no stress is tensile, are pulled open by the tensile stress when the compressive stress is lowest. The rock also becomes substantially weaker in these instances, perhaps because of the presence of open cracks. The dilatant behavior as a function of the tensile-stress/compressive-stress ratio (as shown in Fig. 2) would seem to lend itself to a simple relation useful in a constitutive equation. More work is required to define the exact form of this relation.

Failure in brittle rocks is a strong function of strain rate (Green and Perkins, 1968; Logan and Handin, 1970; Green *et al.*, 1972). Increases of failure stress of about 5% per order-of-magnitude increase in strain rate generally are observed. This is a significant amount, which, when considered over 8 to 10 orders of

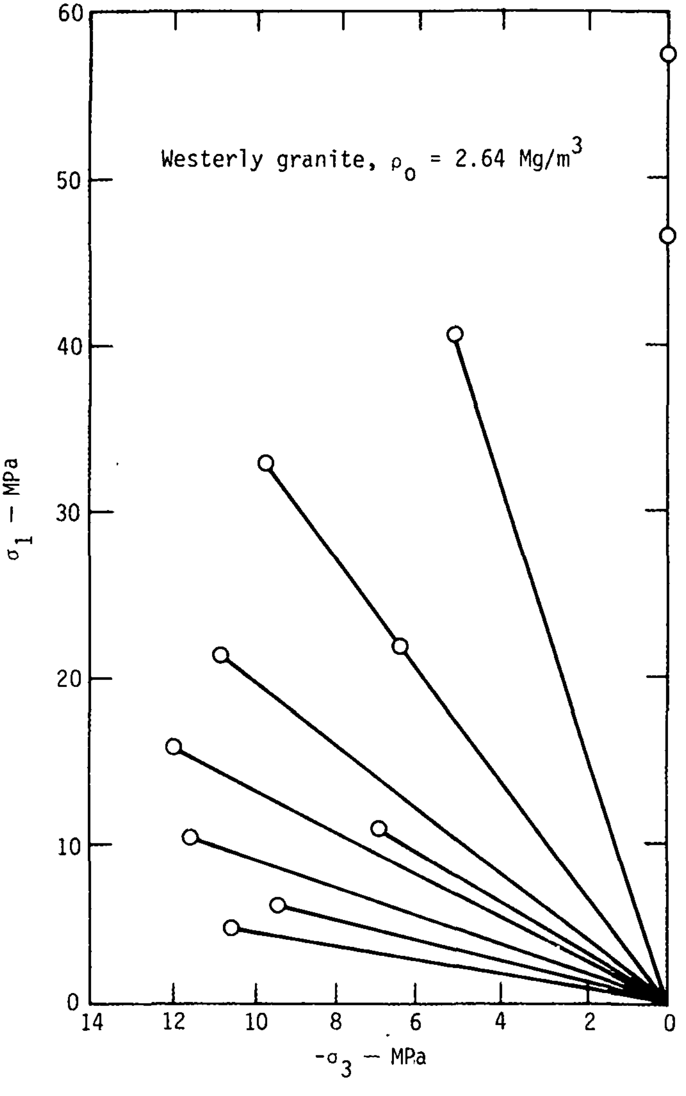

Fig. 1. Stress paths to failure (circles) for a number of samples of Westerly granite (initial density 2.64 Mg/m^3) in terms of the tensile stress (σ_3) and the maximum compressive stress (σ_1). The intermediate principal stress (σ_2) was in all cases equal to σ_1.

magnitude of strain rate, must be accounted for in calculations of the effect of dynamic impulses on rocks. In addition, there is evidence in the combined results of static and shock-wave experiments that the onset of dilatant behavior is suppressed (occurs at higher stress) and that the dilatant strain is reduced as the strain rate increases (Schock and Heard, 1974). This evidence, together with the observation of Scholz (1968) that microfracturing becomes localized only

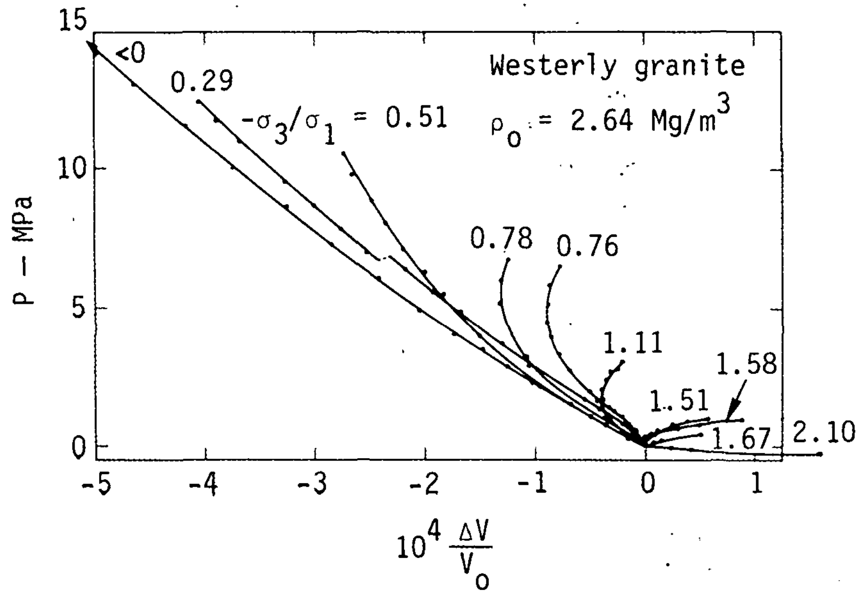

Fig. 2. Behavior of Westerly granite during the loadings shown in Fig. 1 in terms of mean pressure $(2\sigma_1 + \sigma_3)/3$ and sample volume strains.

near the failure stress, suggests that brittle failure at very high strain rates ($>10^4$/s) may be a much more disruptive process involving more of the rock volume than commonly observed visually in the laboratory at low strain rates. At low strain rates, microfractures have time to terminate and relieve local stress concentrations. For example, some brittle rocks are observed to strain for periods of greater than two weeks at constant stress below their fracture strengths (Kranz and Scholz, 1976). Laboratory specimens failed at strain rates of $\sim 10^{-4}$/s commonly show one or two through-going fractures. On the other hand, there is evidence of "pulverized" rock at the edges of nuclear-explosion-induced cavities (Borg, 1972), where extremely high strain rates (perhaps $>10^5$/s) were achieved.

DUCTILE ROCKS

With increased confining pressure, many of the mineral constituents in rock undergo a transition from brittle to ductile behavior (Handin *et al.*, 1967). In addition, some rocks contain minerals that are ductile at normal pressures. The resulting behavior is distinguished from brittle failure in that the rock does not achieve a maximum shear stress at a fixed strain. Many ductile rocks exhibit work-hardening; stress and strain continue to increase in a highly nonlinear manner, with the result that a unique failure surface does not exist.

Since dilatancy is related to the opening of microcracks, it is expected to be an inherent property of brittle rocks and to be absent in ductile materials, where flow and creep reduce stress concentrations at crack tips. Experimental confirmation of this has been found in several graywacke sandstones that exhibit brittle fracture at low confining pressures and flow at high confining pressures (Schock *et al.*, 1973). At high confining pressure, argillaceous and carbonate cements flow, allowing for rearrangement of the brittle quartz and feldspar grains and suppressing the dilatancy characterized by microfracturing.

A diminishing of dilatant behavior also is seen in these rocks when they are subjected to tensile stresses. Graywacke sandstone loaded in a similar manner to the granite in Figs. 1 and 2, exhibits little or no tendency to dilate (Fig. 3). Since at these low confining pressures, the rock fails by brittle fracture, the explanation for this behavior must lie in the nature of the cracks themselves. In order for tensile stress of the order of megapascals (tens of bars) to open cracks in granite, aspect ratios must be very small ($<10^{-5}$) (Walsh, 1965). Thus, the average aspect ratio of the cracks present in this sandstone is large enough so that they do not open before the material fails.

The effect of an increasing strain rate is: (1) to raise the stress level for a given amount of strain (higher deformation modulus), and (2) to raise the pressure at which rocks go from brittle to ductile behavior (Handin *et al.*, 1967; Schock *et al.*, 1973). This decrease in ductility with increasing strain rate amplifies the importance of brittle deformation phenomena in explosive and impact events in rock. Even though there are rocks that behave in a ductile manner at the highest strain rates, most common rock types, if ductile at

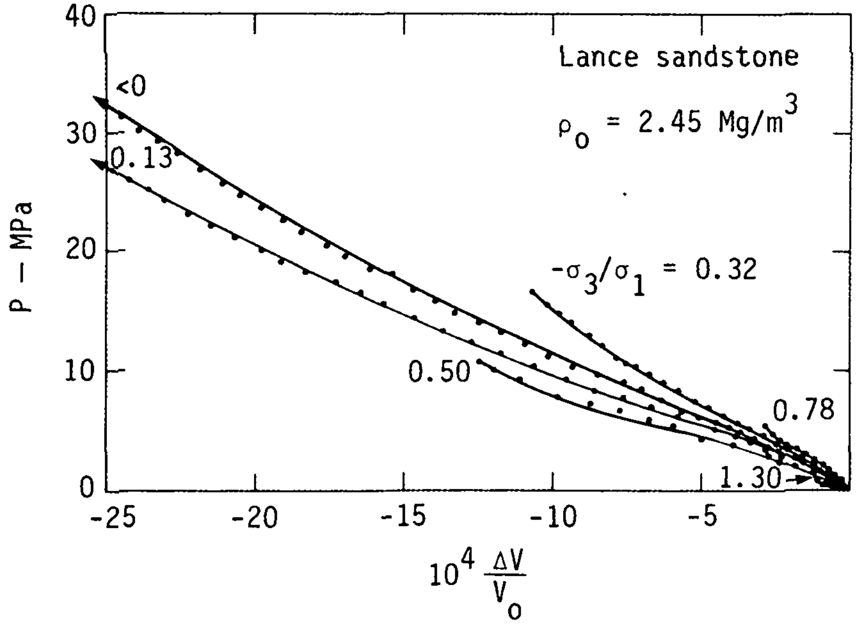

Fig. 3. Behavior of Lance sandstone during loading with one principal stress tensile, in terms of mean pressure and volume strain.

atmospheric confining pressure, show a ductile/brittle transition with increasing strain rate (Handin *et al.*, 1967).

POROSITY

Early observation (Schock *et al.*, 1973; Schock and Heard, 1974) indicated that granites and graywacke sandstones did not fail when compressed quasi-statically in uniaxial strain (constant radial strain) to simulate plane-wave shock-loading conditions. On the other hand, loading to failure did take place in very porous, brittle rocks, such as tuff, subjected to the same conditions (Heard *et al.*, 1971). Furthermore, there appeared to be little or no dilatancy prior to failure when these tuffs were loaded at constant confining pressure. This suggests that at least in some rocks, catastrophic pore collapse rather than a through-going fracture was the dominant failure mode. This idea is supported in part by a curvature of the failure envelope concave to the shear stress axis. The subsequent work of Duba *et al.* (1974a) on a sandstone with 26% gas-filled porosity verified these conclusions by demonstrating that the failure envelope was effectively depressed by pore collapse from that for the matrix material without pores.

Another significant observation is that the compressibility of a material in the pore-collapse region is a function of the shear stress (Schock *et al.*, 1971; Schock *et al.*, 1973; Shipman *et al.*, 1974; Schock *et al.*, 1976). The volume strain in the pore collapse region, unlike that in the dilatant region previously discussed, is stress path dependent. This shear-enhanced compaction is not incorporated in most constitutive relations derived to treat inelastic pore collapse (Herrmann, 1969; Carroll and Holt, 1972a; Carroll and Holt, 1972b; Bhatt *et al.*, 1975). Instead, only properties under the hydrostatic or presumed hydrostatic conditions of most experiments are treated.

One of the more successful forms of constitutive relations is

$$P = 2/3\tau(\ln 1/\eta),$$

where τ is yield stress $(\sigma_1 - \sigma_3)$ η porosity, and P pressure in the yield region. This form results from a consideration of the ideally plastic deformation of a hollow sphere. τ can be made to vary with porosity. For rocks, Bhatt *et al.* (1975) considered τ in terms of a Mohr–Coulomb material.

To date, two methods have been used to treat shear-enhanced pore collapse specifically. Shipman *et al.* (1974) fitted data on porous uranium metal. Data on other porous metals (Johnson *et al.*, 1974; Kuhn and Downey, 1971) and on some porous rocks and soils (Nelson *et al.*, 1971) can be fitted with models using movable failure surfaces and computing strain through "associated" flow rules. These models are complex and require a large number of tests to define an equally large number of parameters.

FLUID SATURATION

When water is allowed into the pore space in a dry rock, it can introduce large departures from the response to stress. The collapse of pore space in water-saturated rocks is controlled, not only by the strength of the pore wall, but by the compressibility of the water. The pressure on the pore fluid controls failure by dictating the effective stress, i.e., the difference between applied stress and pore pressure (Terzaghi, 1943). When rocks remain completely saturated to failure, the failure stress is observed to decrease with increasing fluid pore pressure (Heard, 1960). During dilatant behavior, brittle rock will behave almost as if it were dry, if the total volume of water is fixed so that the rock becomes unsaturated. As the microcracks open, the resulting volume increase is such that the pore pressure drops until the rock becomes undersaturated (Duba *et al.*, 1974b). If that pore space is connected so as to allow the fluid pressure to increase, strength will decrease. This is the mechanism of the suggested dilatancy model of earthquake generation (Scholz *et al.*, 1973). The brittle/ductile transition is also controlled by the effective stress (Heard, 1960).

Wherever movement of fluid is possible, strong strain-rate effects on behavior are expected (Martin, 1972). The movement of fluid through pore space is a strong function of its viscosity. Since viscosity is the relation between stress and strain-rate, it follows that the pressure in the fluid is a function of time, at a given strain.

Water may also introduce complications through its behavior as a thermodynamic fluid during shock loading (Stephens, 1969). Consider a saturated rock that has been adiabatically shocked such that the temperature is above 100°C. On isentropic unloading, the pressure will drop faster than the temperature, and water may convert to steam with a volume increase and a release of energy associated with the latent heat of vaporization. This energy will be added to that from the impact or explosion to enhance crater formation.

SUMMARY

These observations lead to the development of simplified constitutive models that can be used to predict the response of rock to impact loading by identifying the important parameters that determine that response. The importance of shear stress and mean pressure in defining regions of behavior has been demonstrated. It has been shown experimentally that dilatancy is related to failure in low-porosity, brittle rocks. The onset of dilatant behavior can be defined in terms of mean stress and shear stress, and, once begun, it can be described by a simple constitutive relation involving these two system variables. For rocks that exhibit flow instead of fracture, little or no dilatancy is observed.

Compaction of pore space can be an important process in rock behavior in terms of enhanced compression and decreased failure shear strength, both of which absorb energy that might otherwise be used in the cratering process. In addition, compaction is influenced by shear stress. These observations may be summarized in a schematic diagram (Fig. 4). Here, the axes are the two system variables, shear stress and confining pressure (function of mean stress). The failure envelope, which defines the limit of shear stress in terms of mean stress fo low-porosity material, the dilatant and compaction region boundaries, and po

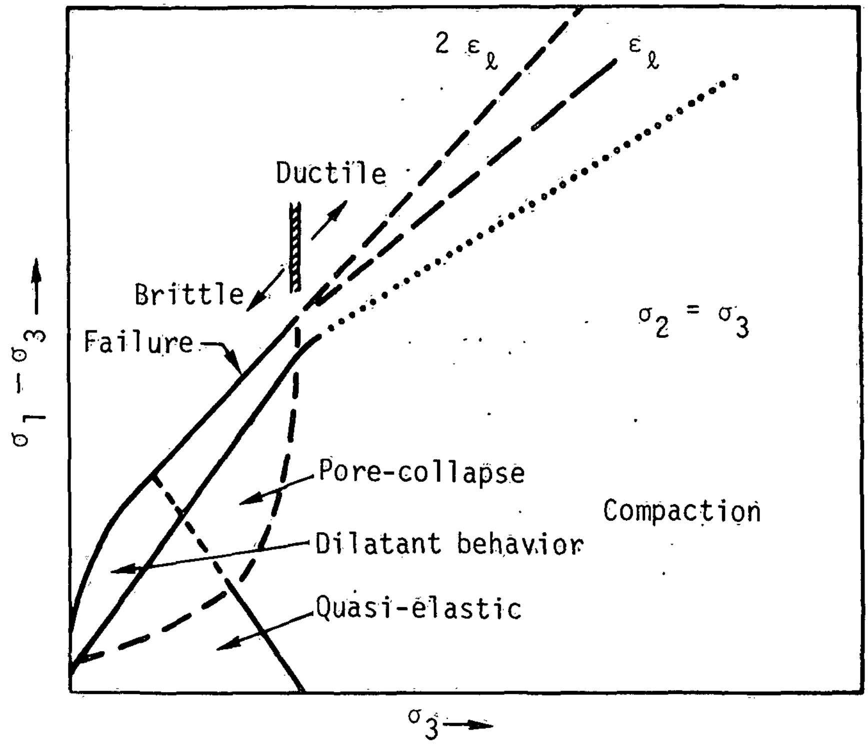

Fig. 4. Schematic representation of boundaries in shear-stress/confining-pressure space for noncyclically loaded rock. Axial strains shown for ductile failure are values of permanent strain. After Schock *et al.* (1973).

collapse and ductile failure envelopes, are all defined in terms of the system variables. In Fig. 4, all of these boundaries are shown in a general, not a rigorous sense. That is, they are movable in both coordinates and may not even exist for a given rock type (e.g., compaction in low-porosity rock). Within a given region, a third system variable may be used to define a constitutive relation, such as has been shown for dilatant and compacting material.

Some qualifications not shown in Fig. 4 must be considered. The influence of water has been mentioned, but it has not been quantified to allow treatment in this sense. More studies are needed. The effect of strain rate likewise is not shown. Cyclical loading affects strength (Peng *et al.*, 1974), dilatant behavior (Scholz and Kranz, 1974), as well as compaction (Schock *et al.*, 1976). The effect of the intermediate principal stress may also be important (Handin *et al.*, 1967; Mogi, 1972); the symmetry of the cratering process at early times notwithstanding. More studies to define and describe this effect are called for. Finally, sample size can be a serious problem, in terms of critical phenomena excluded by the limited size of laboratory samples. Pratt *et al.* (1976) show that failure shear stress can be a strong function of sample size.

Despite these limitations, the observations represented schematically in Fig. 4 provide insight into the processes taking place, and they suggest ways in which these processes may be modeled. Through a study of the mathematical form of the model, we may achieve a better understanding of the physical processes that control the behavior.

Acknowledgment—This work was performed under the auspices of the U.S. Energy Research and Development Administration under Contract No. W-7405-Eng-48.

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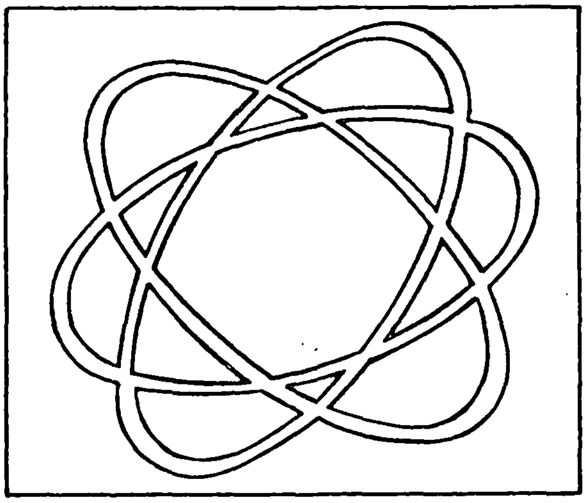
MINERAL INDUSTRIES BULLETIN

Volume 22 January 1979 Number 1



Recovery of uranium by in situ solution mining

Christopher H. Cox
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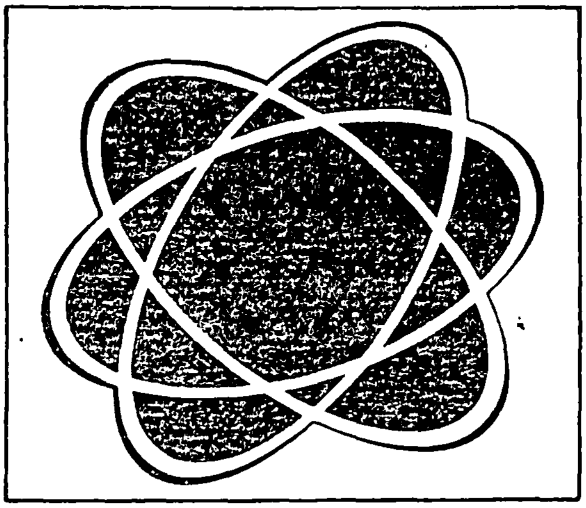

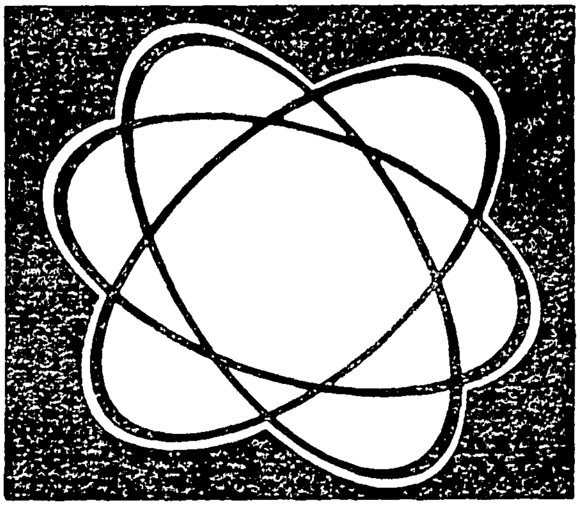

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Colorado School of Mines Mineral Industries Bulletin, v. 22, no. 1, January 1979. Published bi-monthly by the Colorado School of Mines, Golden, Colorado 80401. Second-class postage paid at Golden, Colorado. Copyright 1979 by Colorado School of Mines. Subscription $8.00 per current year. Single copy or back issue $2.50. ISSN 0010-1745

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Recovery of uranium by in situ solution mining

Christopher H. Cox
William J. Roushey

INTRODUCTION

In situ mining has been defined as a selective mining technique whereby the ore mineral that has not been moved from its geologic setting is preferentially leached from the host rock through the use of specific lixiviants (chemical leaching solutions) and the mineral value subsequently recovered. The technology employed can be applied for the recovery of copper as well as uranium, however, this discussion will be limited to the processing of uranium-bearing deposits.

This method of mining, also referred to as "solution mining," usually consists of a pattern of wells which are suitable for injection of a lixiviant and recovery of the uranium-bearing liquor. Uranium is recovered by drilling into the ore body, circulating a lixiviant to dissolve the mineral, extracting the values from the pregnant liquor, and regenerating the lixiviant for continued use underground (Lewis and others 1976).

For 1977, the Department of Energy estimated that 15,900 short tons of U_3O_8 will be contained in 10.3 million short tons of ore mined by U.S. producers (Li and Wiebmer 1978). In addition, 800 short tons of U_3O_8 will be recovered from heap leaching, mine waters, in situ methods, and low-grade stockpiles. Of these methods, in situ recovery has contributed less than 1 percent of United States U_3O_8 supplies for 1977. William C. Larson of the U.S. Bureau of Mines predicts that this 1 percent level will be exceeded in 1978.

Today, in situ mining warrants evaluation in comparison to conventional mining and surface milling before a decision is made as to the optimum method to be used *to bring many new ore bodies into production.* Feasibility studies should include an economic comparison of conventional surface and underground techniques versus in situ solution mining.

Increasing interest in this technique is understandable since solution mining offers several advantages compared to conventional mine-mill complexes. The advantages include:

(1) Minimal surface disturbance;
(2) Personnel exposure to radiation is eliminated;
(3) Lower grade ore can be treated and thus the recoverable reserves of uranium increase;
(4) Lower capital costs, improved cash flow, and generally, greater return of investment;
(5) Less waste generation on land restoration;
(6) Shorter lead time to production.

The obvious disadvantages are potential groundwater contamination and a lower level of uranium extraction.

The intent of this report is to familiarize the reader with the pertinent aspects of solution mining. In an attempt to achieve this goal, the following subjects will be discussed in the pages that follow:

- History of solution mining
- Site feasibility
- The solution mining process
- Environmental considerations and regulations

HISTORY OF SOLUTION MINING

The application of in situ leaching methods to

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0010-1745/79/2201-0001 $03.00/0

recover inorganic mineral values dates back as early as the 1890s (Sievert and others 1970). Copper values were the focus of initial in situ attempts. For example, Austin in 1910 described a process for the leaching of copper from porous rock by percolating solutions through an ore body and collecting the dissolved copper values in various underground passages.

Virtually all of the in situ methods up until the mid-1950s involved solution collection that required the use of underground shafts or drifts. Livingston in 1957 however proposed a method for in-place solution mining that involved no previous underground systems or slurry handling. His approach, which was the first that applied some of the fundamentals of fluid flow commonly used in the petroleum industry to the recovery of mineral values, involved the injection of a leaching solution into the ore through wells or bore holes. To recover solubilized mineral values, Livingston recognized the need for controlling the flow of the underground leaching solution. Fluid was to be controlled by drilling multiple wells for both injecting and producing fluids and to interchange periodically the roles of the various wells.

The problems of formation plugging were first considered by Fitch and Hurd. In their patent for subterranean leaching, they proposed to generate the leach solution in situ. To minimize the problem of plugging, water was to be injected into the formation followed by the addition of an acidifying gas. Fitch and Hurd realized also that fluid control and containment could be troublesome in a permeable deposit that was initially dry. To achieve fluid control, they proposed flooding the ore body and sections of the surrounding formation with an inert fluid. Thus during the leaching phase, vertical and horizontal fluid management could be obtained by controlling the relative injection rates of the inert fluid and leaching solution.

Instead of injected water, Gardner and Ritchie suggested that fluid control could be obtained by using the natural groundwater. For vertical control their method called for selecting an ore body below the natural water table. Horizontal control was achieved by encompassing a producing well with several injection wells. To determine fluid migration and to maintain pressure control in the area surrounding the injection pattern, monitor wells were placed beyond the injection wells. The method also involved flooding of the deposits with leach solution after which withdrawal and injection rates were equalized.

Commercial production of yellow cake from liquors generated from in situ mining of an intact uranium ore body was first achieved by Ritchie in 1963 at Utah International's Wyoming properties. The next company to employ in situ techniques commercially was Atlantic Richfield in 1975 at their "George" Clay West property in Texas. The design production rate of the Clay West operation was 250,000 lb of U_3O_8 per year. The status of other solution mining ventures is summarized in table 1.

SITE FEASIBILITY

The potential amenability of an ore body to exploitation by in situ mining techniques is influenced by both mineralogical and geological factors. With respect to mineralogy, the uranium must be in a form and at a certain grade that will allow recovery of the U_3O_8 values. Integrated with the mineralogical configuration of the uranium are the specific geological (Hancock 1977) conditions that must prevail to allow recovery of uranium. These criteria are as follows:

- For containment of solution, the ore body should be a relatively horizontal bed underlain by impermeable strata.
- To achieve solution flow, the ore body must be below the static water table.
- For development of a well field, the permeability, porosity, and hydrology of the deposit must be favorable.

Assuming these conditions are satisfied, then development of the property is similar to development of a conventional mine. Exploration drilling is followed by development drilling to determine the grade, size, depth, and shape of the deposit. The cores are logged and analyzed to identify the physical and chemical properties of the ore, including the permeability and porosity of the rock. Pumping tests are performed to determine the natural direction and rate of flow of water in the aquifer. This information is used in controlling the flow of injected lixiviant between wells.

Table 1. – *Summary of solution mining ventures*

Company	Location	Status
U.S. Steel Corporation	Clay West, Texas	Mining and expanding
	Burns, Texas	Mining
U.S. Steel and Niagara-Mohawk	Clay West, Texas	Mining and expanding
Cleveland Cliffs	Pumpkin Buttes, Wyo.	Proposed pilot
International Energy Corporation	Zamzo, Texas	Mining
	Pawnee, Texas	Mined out
	Three Rivers, Texas	Mining
Mobil	O'Hern site Bruni, Texas	Mining
	Holiday el Mesquit, Texas	Under construction
Rocky Mountain Energy	Casper, Wyoming	Operating pilot proposed commercial
Union Carbide	Palangona Dome Site, Duval County, Texas	Mining and under-expansion
Wyoming Minerals	Bruni, Texas	Mining
	Lamprecht, Texas	Mining
	Weld County, Colo.	Operating pilot
	Irigaray Site, Wyo.	Operating pilot proposed commercial

Core samples are subjected to laboratory investigations to determine the amenability of the ore to leaching. Acids such as sulfuric and alkaline carbonates are the two principal lixiviants used to leach uranium. Sulfuric acid systems generally achieve high yield and efficient recoveries, especially when the uranium values are present as conglomerates encased by other minerals. The problem with sulfuric acid is that it also solubilizes large amounts of impurities that must be removed at the surface recovery plant to permit recirculation of the solution. The acid system is further complicated by the interaction of sulfuric acid with clays, calcite, silica, etc. to form gypsum and silica gels that reduce the permeability of the rock and eventually may plug the formation.

Although the carbonate system cannot treat a conglomerate mineralization of uranium to the high degree that the acid system is capable of, the method is an excellent choice for in situ leaching of sandstone type ores when the uranium is exposed as a precipitate on the surface of the sand grains.

Carbonate lixiviants, by contrast to acids, are selective and will generally dissolve only the uranium values, thus precluding contamination of leach solution, plugging, and loss of porosity in the formation.

For these reasons, carbonate lixiviants are generally preferred. One notable exception is Rocky Mountain Energy's pilot operation near Casper, Wyoming. The "clean" nature of the sandstone treated at this operation and the lower level of troublesome impurities, such as calcium, has allowed for the application of sulfuric acid. Of the carbonate lixiviants, solutions of ammonium carbonate-ammonium bicarbonate are usually employed even though sodium carbonate is far less expensive. The sodium ion can react and swell certain clays that may be present and reduce the permeability of the deposit.

Once the amenability of the ore to leaching has been established, field tests are performed to confirm the chemistry and develop additional hydrological data. The field studies may initially be as simple as a pulse test while at a later date, a pilot plant may be operated to simulate the production facility. Since in situ leaching is relatively new and novel to the minerals industry, most companies have chosen the pilot plant route. Additional laboratory studies are performed in conjunction with the field tests to develop definitive plant design data. Environmental and legal constraints are evaluated and the ability of the in situ process to meet these requirements is determined. The environmental considerations are discussed in a separate section of this *Bulletin*. The decision to initiate full-scale mining depends on the results of the development work and project feasibility studies.

Although the development program may seem complicated, development of an ore body for solution mining can be completed in 2 to 3 years in contrast to 7 to 10 years for conventional mining. The steps required to develop a property for in situ leaching are compared in table 2 to the stages necessary to bring a conventional mine-mill complex on line (Hunkin 1975):

Table 2. — *In situ leaching development compared to conventional mine-mill complex*

Open Pit Mines	Underground Mines	Solution Mining
Development drilling	Development drilling	Development drilling
*Stripping	*Shaft sinking	–
*Mine waste	Development drifting	–
*Waste dump	*Waste dump	-
Develop ore faces	Develop stopes	Drill wells
*Drill, blast	Drill, blast	Leach uranium
Load	*Muck out*	-
Haul	Haul	–
–	Hoist	–
–	Haul to mill	Pump solution to mill
*Crush		
*Grind		
Leach uranium		
Liquid-solid separation		
IX or SX concentration		
Precipitate, dry, package		
*Tailings dam operations		Recirculate leach solutions
Stages to produce salable product		
16	17	8

*Stages generally producing significant changes in land surface, water quality, personnel safety and radiation exposure.

SOLUTION MINING OPERATION

If the results of the feasibility study indicate that the uranium deposit can be economically and environmentally exploited using in situ solution mining techniques, the property can be commercialized. The solution mining operation can be subdivided into two general categories.

- Well field design and operation
- Surface recovery plant

These two areas will be discussed as follows.

WELL FIELD DESIGN AND OPERATION

Most of the leachable uranium deposits are in the form of a sandstone roll front. According to Hunkin (1975), it is possible that 30 to 50 percent of these deposits are amenable to processing using in situ leaching technology. A cross section of a typical well field for solution mining of a sandstone roll front is shown in figure 1 (Wyoming Minerals Corp.).

In plain view of a field, several different types of well patterns have been investigated, but the five-spot pattern is probably the most common. A typical five-spot pattern, as used at the U.S. Steel-Dalco Clay West property is shown in figure 2.

Well development is perhaps the single most important aspect of solution mining. Injection wells are typically 4 inches in diameter and cased with polyvinyl chloride (PVC) pipe cemented to the surface. Production wells are usually 4 to 6 inches in diameter, cased with

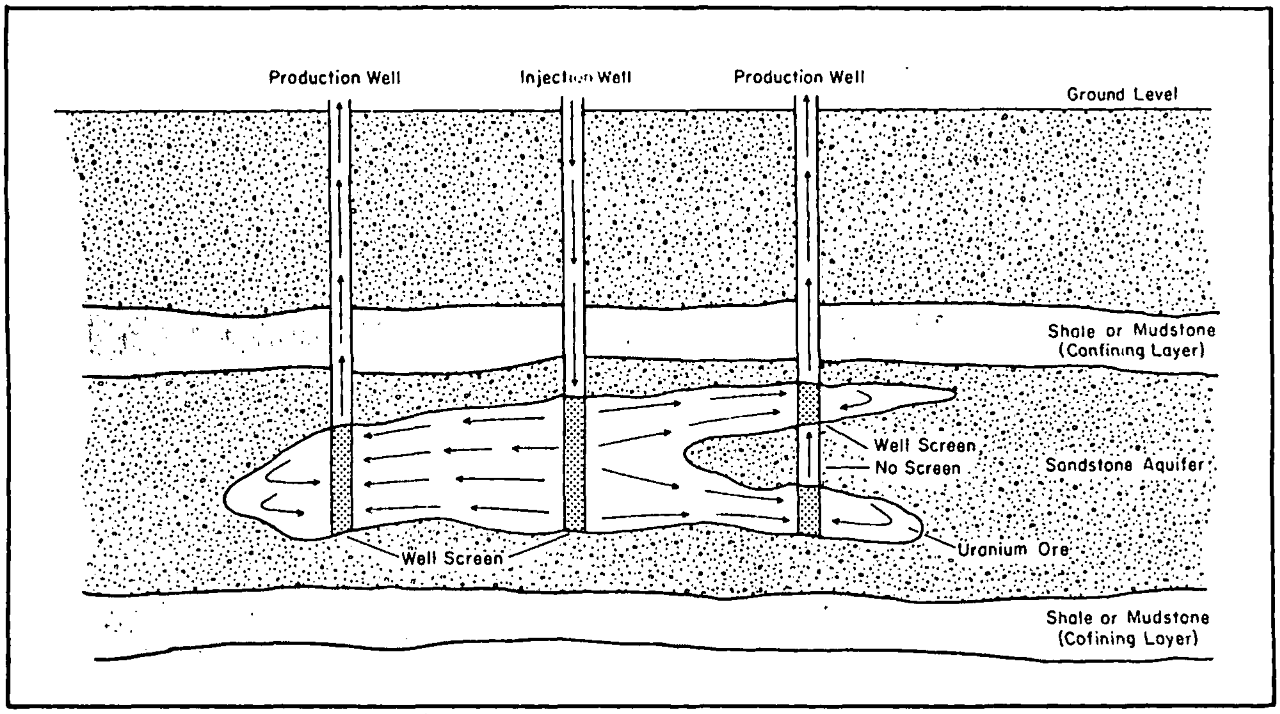

Figure 1. – Vertical cross section of typical well field.

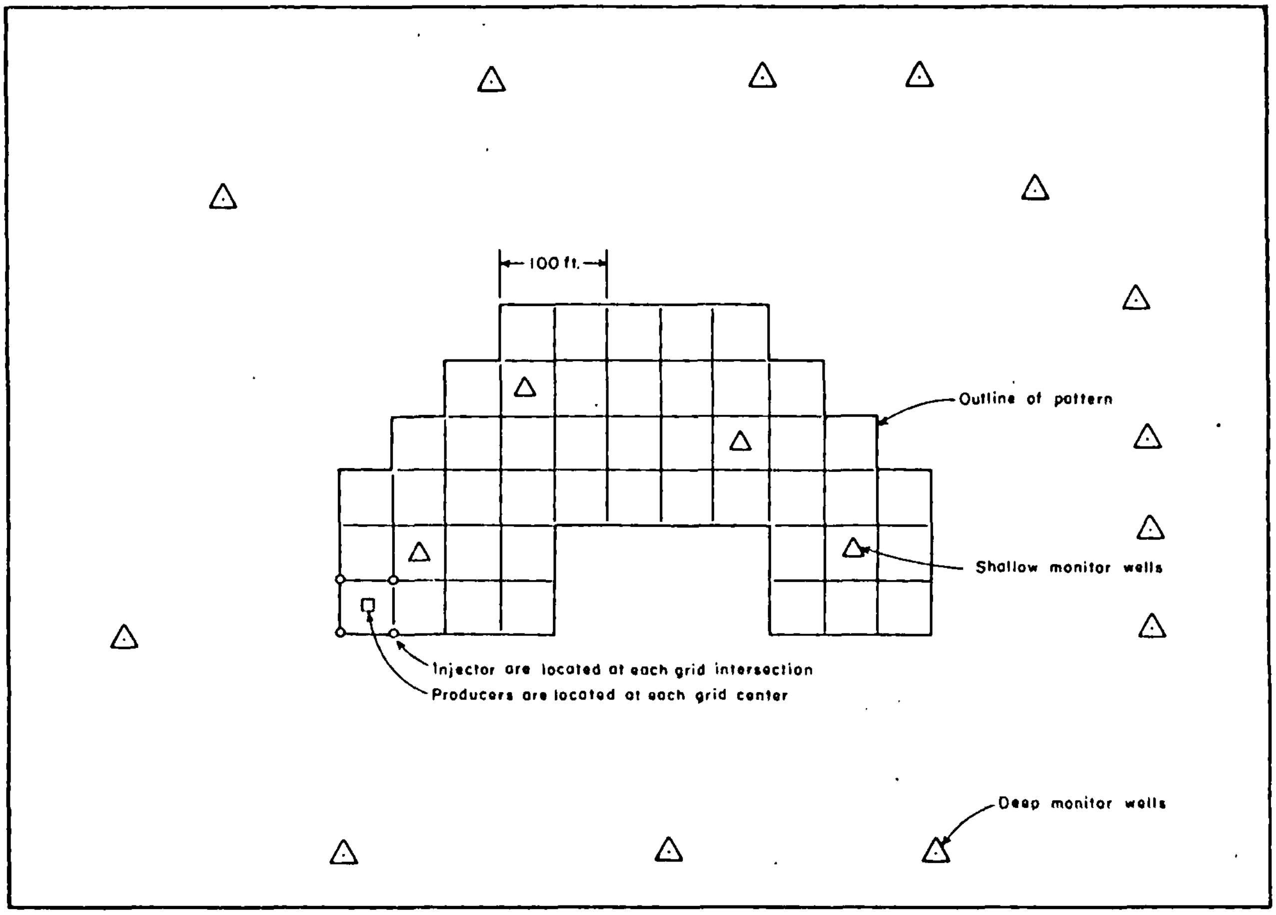

Figure 2. – Clay West well field pattern.

PVC, and also cemented to the surface. The continuous casing is interrupted where the well intersects the mineralized zones to allow introduction of lixiviant. An example of well construction is shown in figure 3 (Wyoming Minerals Corp.).

Certain operators have installed tail pipes at the end of the casing to allow suspended solids to settle inside the pipes but below the level of the screens. In so doing, screen plugging is minimized. Also, production wells are often gravel-packed in low permeability areas to increase capacity.

Proper selection of a drilling mud and drilling water is also critical to well development. Certain drilling muds can plug the aquifer near the well, but this problem can be avoided by using organic muds since these muds decompose to CO_2 and water within days after use. One popular organic mud is a guar gum based material known commercially as Revert. If possible, the natural groundwater should be used in the drilling operation. The groundwater is in ionic equilibrium with the deposit whereas foreign water may upset this equilibrium and promote clay swelling (Hancock 1977).

Solutions introduced into the formation via injection wells must pass through the ore zone, solubilized uranium values, and be pumped out via production wells prior to being further processed above ground. The injection of lixiviant forms hydraulic gradients within the aquifer. This gradient, together with the withdrawal rate at the production well, determines the direction and velocity of the solution flow. Solution flow is toward the production well since the hydraulic head at that point is less than developed at the point of injection. Thus, the pumping rates and pressures can be used to confine the lixiviant to the desired area. Normally, more liquor is withdrawn than injected to prevent solution migration and contamination of the groundwater.

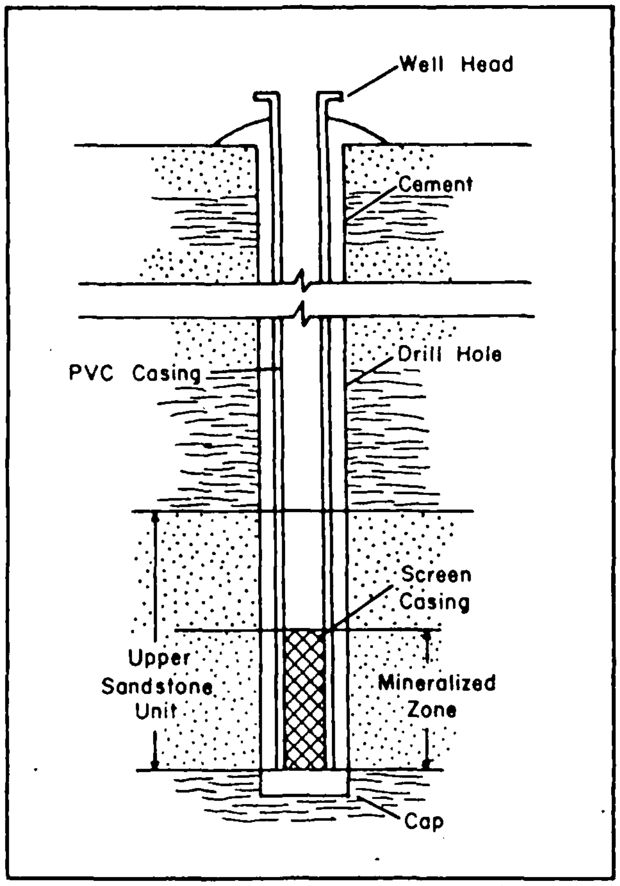

Figure 3. – Well construction.

Monitor wells are placed in the uraniferous aquifer as well as outside the ore zone to detect escaping solution. If solution migration is noted, then the hydraulic gradient can be adjusted to force the liquor back into the well field.

SURFACE RECOVERY PLANT

Uranium-bearing "pregnant" liquor is collected from the recovery wells and pumped to the plant area. The liquor is usually clarified and then treated in ion exchange columns to remove the uranium. The ion exchange columns are similar to water softeners and contain a resin that adsorbs the dissolved uranium preferentially to other dissolved salts. The "barren" liquor from the ion exchange (IX) columns is reconstituted with reagents and returned to the injection wells. The uranium is removed from the loaded resin with another solution and yellow cake is precipitated from this concentrated product liquor. The uranium recovery flow sheet for the Clay West plant is shown in figure 4 (Engineering and Mining Jour. 1975) while pertinent characteristics of selected commercial and pilot plant operations are summarized in table 3. A more detailed description of plant, chemistry, and operations follows.

As evidenced by the data presented in table 3, all of the plants listed use a solution of ammonia carbonate or ammonium bicarbonate for leaching. Although the reaction between the lixiviant and the uranium minerals is complex, the reaction can be simplified as follows:

$$UO_3 + (NH_4)_2CO_3 + 2NH_4HCO_3 \rightarrow (NH_4)_4UO_2(CO_3)_3 + H_2O$$

An oxidant is also added to the lixiviants to promote the oxidation of uranium from the plus 4 valence state (UO_2) to the plus 6 state (UO_3). The most frequently used oxidant is hydrogen peroxide (H_2O_2) and the concentration of H_2O_2 in the leach liquor is usually maintained at less than 1 gpl. An excess of $(NH_4)_2CO_3$ and NH_4HCO_3 is maintained in the leaching solution to ensure that the gangue minerals do not consume all of the reagent, thereby leaving none for dissolution of the uranium. Most operators have used very dilute lixiviants (5 gpl total carbonate-bicarbonate or less) supposedly to minimize reagent costs in the event that solution is lost to the formation. However, recent investigations have demonstrated definite advantages to using higher strength lixiviants. These advantages include:

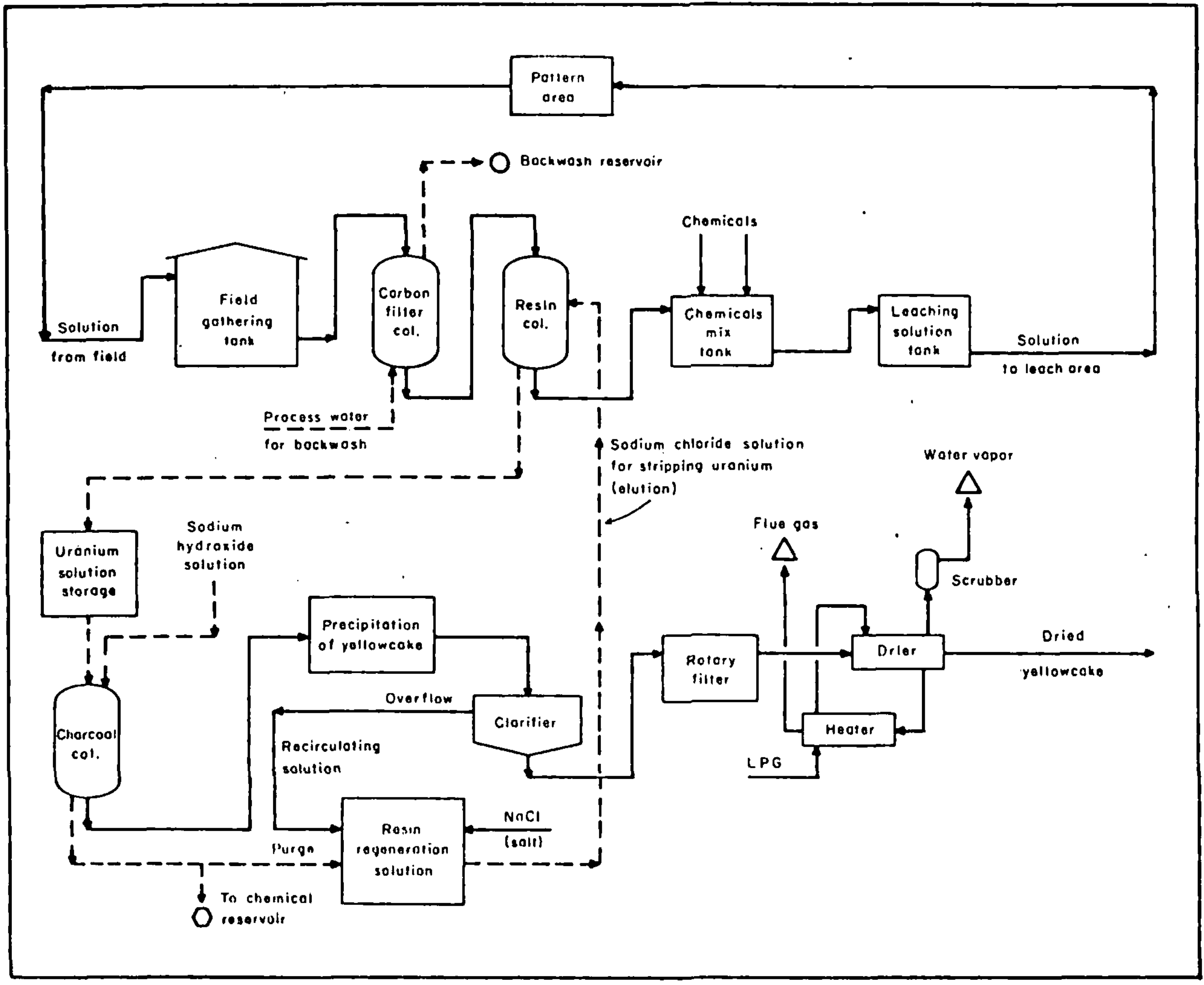

Figure 4. – Uranium extraction flow sheet, Clay West, Texas.

(1) The rate at which uranium is extracted from the ore increases significantly as the lixiviant concentration increases.

(2) The amount of calcium extracted decreases as the lixiviant strength increases.

Although use of higher strength lixiviants are advantageous in some respects, the capacity of the resin for uranium tends to decrease as the lixiviant concentration increases. A compromise must therefore be attained which results in a rapid rate of U_3O_8 extraction, minimum calcium dissolution, and efficient resin loading.

Calcium control is extremely important to a solution mining operation and therefore any methods that minimize calcium dissolution deserve consideration. Dissolved calcium often precipitates on the resin which can lead to plugging the IX column. Also, residual calcium that may be present in the recycled lixiviant can precipitate underground and reduce the permeability of the formation. Furthermore, the radium content of the recirculating liquors tends to follow the calcium concentration, that is, the concentration of radium increases as the calcium concentration increases. A few operators have attempted to remove calcium from the plant feed liquor by adjusting the pH and precipitating calcium carbonate. However, the small amount of calcium that remains in solution after precipitation eventually coats the resin beads and the calcium carbonate precipitate usually contains a sufficient quantity of uranium to warrant reprocessing. Even though the higher strength lixiviants minimize calcium dissolution, an acid wash cycle should be incorporated in design of the IX units to allow for periodic removal of the calcium.

Examination of the flow sheet shown in figure 4 reveals a carbon column installed ahead of the ion exchange unit. The purpose of this device is to remove suspended solids from the pregnant liquor which, in turn, prevents the resin bed from becoming plugged with particulate matter. Other devices, such as settling units and sand filters, can be used to clarify the liquor, but the use of a carbon column here is presumably to remove dissolved organic contaminants.

Depending on the solids content of the incoming

Table 3. — *Plant characteristics Texas — Carbonate Process — 1975*

	Westinghouse	Mobil	ARCO	DALCO
Leach system	Carbonate multiple recirculation	Carbonate multiple recirculation	Carbonate multiple recirculation	Carbonate multiple recirculation
Filtration	Metal screen	Sand filter	Carbon column	Carbon column
Concentration	Resin bead IX	Resin bead IX	Resin bead IX	Resin bead IX
IX system adsorption	USBM Expanded bed	Fixed bed	Fixed bed	Fixed bed
Elution	Counter current Column NH_4Cl	Fixed bed $(NH_4)_2CO_3$	Fixed bed NaCl	Fixed bed NaCl
Leach reagents	NH_3 CO_2 H_2O_2	NH_3 CO_2 Oxidant	NH_4HCO_3 O_2	NH_4HCO_3 O_2
Precipitation	$HCl + NH_3$	NH_3, CO_2 Recovery steam	NaOH	NaOH
Product	Slurry	Slurry	Solid	Slurry

Source: Hunkin 1976.

liquor and the type of ion exchange column in use, clarification may not be necessary. Fixed bed ion exchange columns require clear liquor while some moving bed systems are claimed to be able to tolerate solids concentrations as high as 3 percent. Probably a solids load this high will require decreased solution flow with a subsequent loss in plant capacity.

All solution mining operations use resin ion exchange to recover the dissolved uranium in contrast to the majority of conventional mills that use solvent extraction to concentrate the values. The uranium content of pregnant liquors generated by in situ leaching is usually low (0.150 gpl or less) in comparison to the grade of liquor produced in a conventional milling circuit. At this low concentration, resin is preferred over solvent for extracting the uranium. This stems from the fact that organic losses make the use of solvent extraction economically unsuitable at the large solution volume and low concentrations typically generated during in situ processing. Also, the use of solvent extraction is unknown for alkaline leaching systems. The uranium content of the barren liquor from the ion exchange columns can be maintained at 1 to 2 ppm U_3O_8.

Several different types of resins and ion exchange columns can be used to recover the uranium. Various types of resins are manufactured for a wide variety of applications, but for uranium recovery, the base anionic type is used. These resins are semirigid gels prepared as spherical beads and are rather specific for the tetravalent uranyl tricarbonate anion $(UO_2(CO_3)_3)^{-4}$. This uranium ion is adsorbed on the resin by displacing a mobile anion constituent of the bead. A partial listing of suitable resins is outlined below:

Resin	Manufacturer
Amberlite IRA 430	Rohm and Haas Co.
Dowex 21K	Dow Chemical Co.
Duolite A-101D	Diamond Alkali Co.
Ionac A-580	Ionac Chemical Co.
Permutit S-700	Permutit Research and Development Center

The theoretical capacity of all of these resins for uranium is approximately the same. However, in actual practice, the loading capacity will vary from 1 to 5 lb of U_3O_8 per cubic foot of resin. This wide variation in loading capacity is the result of variations of lixiviant concentration, grade of pregnant liquor, pH, and purity of the feed solution. Other anions in solution will compete with the uranium for sites on the resin and reduce the loading capacity of the material.

Uranium is removed from the loaded resin by displacing the uranium ion with another anion. The data presented in table 3 indicates that 3 of the 4 plants use a chloride-based salt to regenerate (elute) the loaded resin. Although cloride is an extremely effective eluent, a small amount of the chloride will be transferred to the barren liquor which is regenerated and recycled to the injection wells. Since the leaching-recovery cycle is essentially a closed circuit, the chloride anion in the returning pregnant liquor can increase to a level that eventually may impair the loading capacity of the resin. For this reason, contemporary operators are considering other eluents such as ammonium carbonate-ammonium bicarbonate. This eluent is not as effective as chloride and some other anions, but it does have the added advantage of chemical uniformity for the entire system, that is, extraneous ions, such as chloride, are not introduced to the aquifer. Therefore, well restoration is less complicated. Obviously, eluent selection will affect downstream processing, in particular, precipitation. This aspect is to be covered in paragraphs to follow.

Most resins cost approximately \$100 per ft^3 but since they are continually reused, the operating cost attributed to resin replacement is low. A very small percentage of the initial resin charge must be replaced as the beads gradually disintegrate by attrition.

Ion exchange is not new to the mining and chemical industry but there are several new developments in ion exchange hardware. Three of the four plants described in table 3 use fixed bed ion exchange columns, but interest in expanded or moving bed systems is growing. Four of the seven plants on the drawing boards in 1975 incorporated expanded bed IX columns. As indicated by its name, the resin in a fixed bed unit is stationary. Solution flow is usually downward through the resin bed. In contrast, the resin in a moving bed system is physically moved counter-current to the flow of solution. Fixed bed systems are batch operated but extra columns are installed so the flow of solution is not interrupted while a loaded column is washed and eluted. Moving bed systems are semi-continuous or truly continuous.

The Higgins Loop (Brooke 1976), the NIM column (National Institute for Metallurgy), the Himsley column (Himsley 1976), and the Porter column are among the moving bed systems receiving widespread attention today. The reader is referred to references at the end of this paper which deal with this equipment in detail.

Most moving bed systems offer several advantages compared to fixed bed units. These advantages include:

- Reduced capital cost
- Reduced resin inventory
- Reduced space requirements
- Ability to handle unclarified liquor

On the other hand, moving bed columns require rather sophisticated instrumentation and are therefore more complicated than fixed bed units.

Yellow cake can be precipitated from the concentrated ion exchange product liquor by several techniques. Conventional resin elution with NaCl solutions is followed by a caustic precipitation of the yellow cake. Another circuit employs NH_4Cl for elution with the resultant pregnant liquor acidified with HCl prior to precipitation with NH_3. The most intriguing method, however, is the use of live steam to drive the ammonia and carbon dioxide from the product liquor. The gases can be recovered and used to reconstitute the ammonium carbonate lixiviant. Furthermore, this precipitation technique does not introduce any unwanted, extraneous ions into the closed circuit. The resulting product can be sold as a slurry or dried and shipped as a solid.

ENVIRONMENTAL CONSIDERATIONS AND REGULATIONS

Compared to conventional mining and milling, the solution mining process impacts the environment very little. The in situ method has a negligible effect on such factor as surface disturbance, interference with natural groundwater quality, and distribution and aerial discharge of radio nuclides (Hancock 1977). It has been estimated that in situ leaching generates 1 to 2 lbs of solid waste per pound of U_3O_8 recovered compared to the half ton of waste produced from conventional systems (Hunkin 1975). These solid wastes are comprised of degenerated resin, suspended solids removed from the process solutions, and various precipitates — such as calcium carbonate. By comparison, a conventional uranium mill processing 0.10 percent ore will generate approximately 1000 lb of solid waste per lb of U_3O_8. Exposure to radiation in a solution mining operation is minimal and air pollution is virtually nonexistent.

Nevertheless, in situ leaching has its own special environmental problems. As previously mentioned, a greater quantity of solution is recovered from the aquifer than is injected. The excess solution, together with other liquid wastes from the plant, must be dealt with. At the Clay West operation, these solutions are stored in PVC lined reservoirs. These reservoirs were designed so that the net annual evaporation rate exceeded the amount of waste solutions generated each year. Excess freeboard was installed to facilitate periods of heavy rainfall (Narayan 1976). However, plants in regions where the evaporation rate is minimal may find mechanical evaporators a necessity or may be forced to build reservoirs capable of storing all waste solutions generated throughout the life of the operation.

Although the groundwater in most uraniferous formations is unusable due to naturally high levels of radium, the operator cannot abandon the well field after the leaching cycle is complete. The formation must be flushed until the groundwater is restored to near its original chemical composition. The state of Texas requires that the water be restored to within 10 percent of baseline-conditions that existed before in situ leaching was initiated (Hunkin 1975). This stipulation poses a serious threat to the future of solution mining. The carbonate and residual uranium can be flushed from the formation quite readily. A significant quantity of the ammonia, however, is absorbed by clays that do not release the NH_4^+ ion easily. Thus, ammonia gradually "bleeds" into the aquifer water. Although the resulting concentrations of ammonia are probably not considered toxic, the ammonia can decompose and form nitrates, which are considered harmful if consumed in certain amounts. Groundwater restoration will become a controversial issue, especially since the natural water is usually contaminated to begin with.

However, assuming the water in the formation can be restored to the baseline, the operator is faced with disposing of large quantities of the solution withdrawn from the aquifer during restoration operations. Clay West personnel have proposed disposing of this solution and other plant waste streams in deep (4,500 ft) wells. Reportedly, their plans have been accepted by the state.

Once a particular field is exhausted and the groundwater restored, the wells are filled with sealant to within a few feet of the surface. The well casings are severed 4 to 6 ft below ground level and the surface is restored.

Federal and state environmental regulations are in a constant state of flux. The Nuclear Regulatory Commission (NRC) has the responsibility of issuing "source material licenses" to operators but the NRC has relinquished its authority to states that agree to enforce the federal regulations. On the other hand, the Environmental Protection Agency (EPA) has the authority to completely prohibit the discharge of toxic pollutants but the exact scope of EPA authority is unclear. For those reasons, it is not possible to prepare a general list of the various permits required for a solution mining operation or define legislation that regulates the actual operation — in each case, federal and state authorities must be consulted.

However, in situ operations are definitely covered by the Safe Drinking Water Act (SDWA) of 1974. This act was intended to protect underground drinking water sources, and as a result established maximum impurity levels. To enforce this act, underground injections that endanger drinking water sources were prohibited after December 17, 1977 unless a permit has been obtained from EPA.

The Federal Water Pollution Control Act (FWPCA) may also affect in situ leaching operations. This act prohibits the discharge of pollutants into navigable waters from a point source without a National Pollution Discharge Elimination System (NPDES) permit. Although groundwater cannot be considered navigable, the FWPCA allows for local administration of NPDES and most states have included restrictions on underground water (Root).

The majority of solution mining operations is currently located in Texas and state regulations governing in situ leaching have been defined. Since Texas is an "agreement" state, the Texas Department of Health has authority to issue the source materials license. The license requires a description of the process (including waste disposal plans), a discussion of the extent of personnel exposure to radiation, and an environmental statement. The second step involves applying for an operating waste control permit from the Texas Water Quality Board (TWQB). A public hearing must be held in the county of the proposed operation and a notice must be published 30 days prior to the date of the hearing. The report from the hearing commission is presented to the TWQB for approval. Restrictions of the permit are:

(1) Upon termination of operations, the groundwater must be restored to within 10 percent of baseline;

(2) Water quality must be monitored in strategically placed wells surrounding the operating area.

However, neither operators nor companies in the developmental stage of a property consider these requirements to be oppressive (Hunkin 1975).

ECONOMIC CONSIDERATIONS

In comparison to conventional uranium processing, for example open-pit mining coupled with a typical milling operation, in situ solution mining is economically attractive. In situ generally requires much lower initial capital investment, less time to bring a property into commercial operation and eliminates the need of a conventional mill.

Little economic data is available for in situ operation because solution mining groups are generally reluctant to publish cost information. However, one recent publication presented by the Rocky Mountain Energy Company at the 1977 Uranium Mining Technology Conference (Phillips 1977) does present some realistic economics. Phillips compared capital and operating costs of conventional processing to those of solution mining.

Comparisons were based on mining and milling 1,000 tpd of ore grading 0.10 percent U_3O_8. Conventional mining by open pit was used at a reasonable stripping ratio. Milling costs were referenced to a conventional acid leaching, solvent extraction and precipitation. Acid consumption was assumed at 60 lb/ton of ore and overall recovery was estimated at 90 percent.

Solution mining figures were base wells drilled into a 0.10 percent U_3O_8 ore body with the number of production and injection wells equal. Each well, either injection or production, was assumed to be 5 in. diameter, case well PVC, and cemented to the surface. Wells are spaced at 50-ft intervals and the injection rate was assumed at 10 gpm per well. The cost of a 500-ft well was estimated at $12/ft. Uranium-bearing liquor was estimated to contain 50 ppm U_3O_8 and processed in ion exchange columns followed by solvent extraction. Overall recovery was estimated at 60 percent of the solution mining operation.

The capital and operating costs of the two cases are compared in table 4. Wherever possible, the in situ costs were made consistent with the open-pit model. For example, general and administrative and infrastructure were calculated in proportion to the staffing of the two operations — approximately 220 employees for the 1,000 tpd open-pit operation versus about 80 people for solution mining. The term "mining" as applied to in situ leaching refers to well field costs including well construc-

Table 4. — *Open pit — in situ comparison for treating a 0.1% U_3O_8 ore body*

	Open Pit	In Situ
Operating costs \$ /lb U_3O_8		
Mining	13.22	5.90
Milling	3.89	6.76
General and administrative	1.67	1.40
Reclamation	0.44	0.12
Royalty and taxes	2.00	2.00
	21.22	16.18
Investment \$ millions		
Mine mobile and shops	11.5	1.2
Mill and tailings	15.0	6.5
Roads, site preparation	1.0	1.0
Total capital	27.5	8.7
Working capital	3.0	0.9
Initial well field	—	3.0
Pre-stripping	7.0	—
Infrastructure	4.0	1.3
Total initial investment	41.5	13.9
Rate of return (%)	15	41
Payout (yr)	5.6	2.0

tion, pumps, power, and surface well field work. This comparison demonstrates how significant "mining" costs are to both types of operation.

The cost comparison demonstrates that in situ leaching would provide much lower costs if applied to a 0.1 percent U_3O_8 deposit. However, conservation of resources and a more predictable recovery rate are two reasons why solution mining should not be applied to shallow higher grade ore bodies at this time.

The short payout periods associated with solution mining would allow application of this technique to very small ore bodies. Further data developed around deposits containing as low as 0.05 percent U_3O_8 indicated high solution mining cost, yet application would be potentially economical. Conventional mining and milling could probably not be supported by such a low grade.

A more general comparison was presented by Borkert and Gerity (1978) in a paper presented at the 1978 South Texas Uranium In Situ Seminar. Their comparison evaluated a group of hypothetical uranium deposits using the three more sensitive depositional characteristics of grade, size, and depth.

After establishing an equitable means of cost distribution for open pit and in situ mining, a cost analysis determined that the economic health of a mining venture is most sensitive to the ratio of depth versus grade thickness. To illustrate this sensitivity, graphs were plotted with their parameters against various economic results (figures 5, 6, and 7).

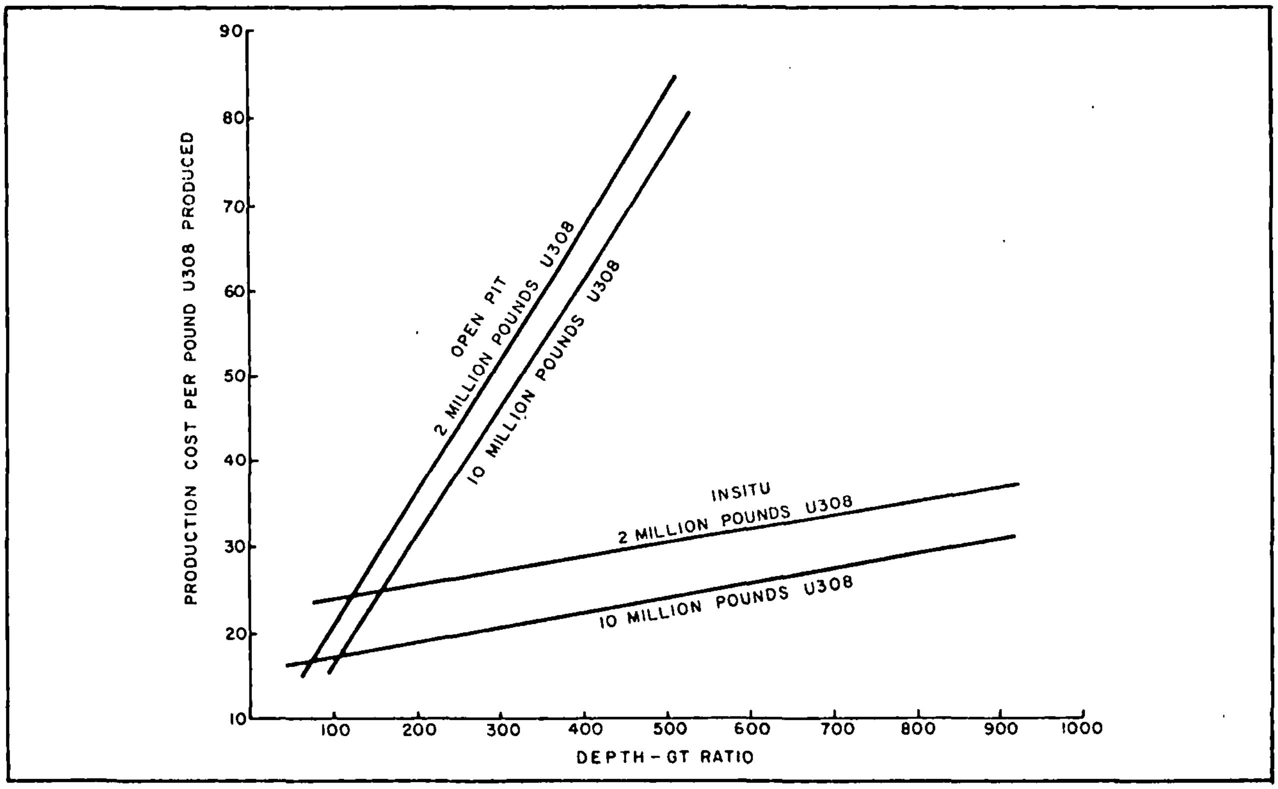

Figure 5. — Total capital plus operating cost of open pit and in situ mining at various depth to grade-thickness ratios.

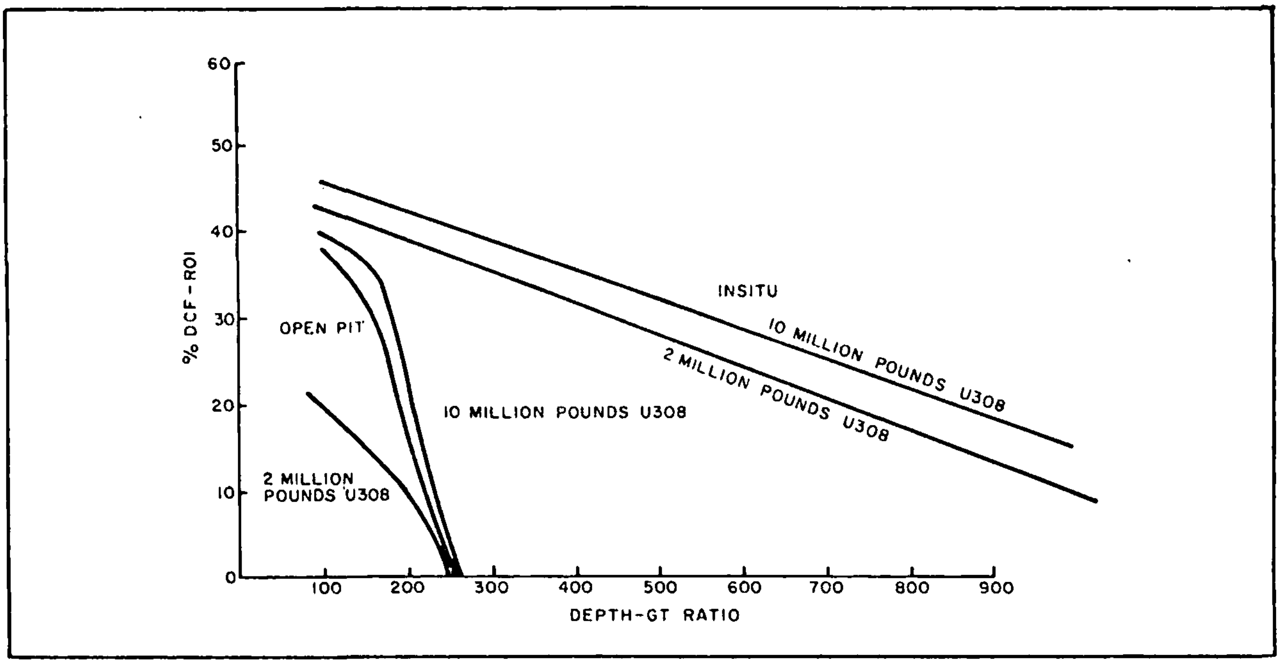

Figure 6. — Percent discounted-cash-flow/return-on-investment of open pit and in situ mining at various depth to grade-thickness ratios.

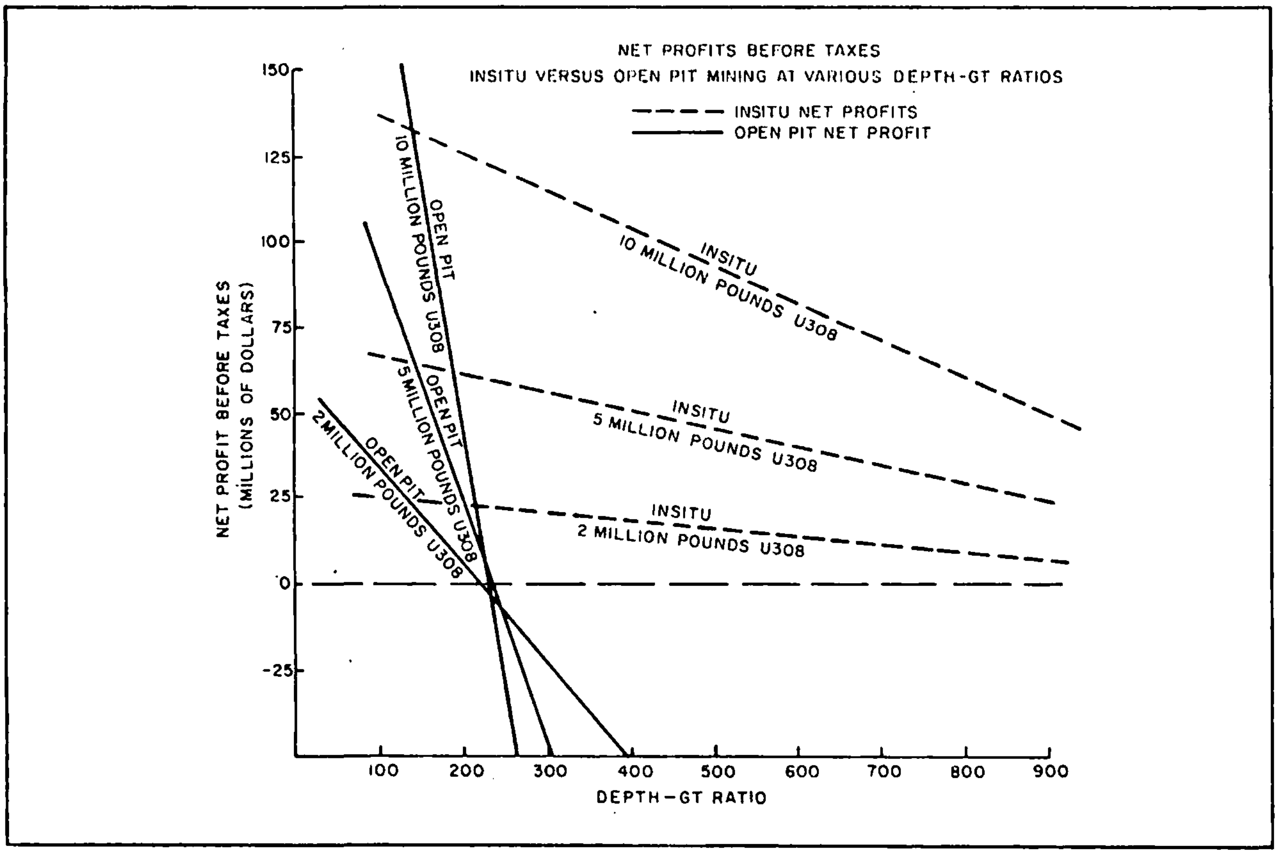

Figure 7. — In situ versus open-pit mining at various depth to grade-thickness ratios.

The cost analysis suggests that at uranium values of $40/pound, open-pit mining becomes unprofitable at strip ratios that are greater than 30:1, a grade thickness of 0.5 or less, or a depth to grade ratio of greater than 200. The in situ operations yield a better profit at higher grade thicknesses, and, depending on ore body characteristics, increased profits can be realized by increasing the spacing of pattern holes. Thus these economics, together with the process advantages of in situ solution mining, show this method to be a competitive approach to the exploitation of uranium sedimentary deposits.

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ROLE OF POLYSULFIDE-IONS DURING ELECTROLYSIS OF SULFIDE-ALKALI SOLUTIONS OF ANTIMONY

UDC 669.753.7

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It is considered that the harmful effect of polysulfide-ions on electrolysis results is manifested by their oxidation of trivalent antimony to pentavalent and in dissolution of the cathode deposit [1-3]:

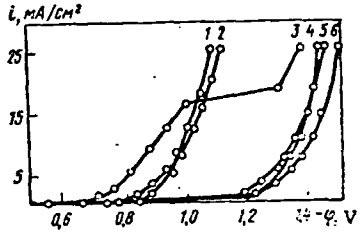

Fig. 1. Polarization of antimony electrode at 25°C in solutions (in g/l):
1 - 30 Sb^{3+}, 80 Na_2S;
2 - 30 Sb^{5+}, 80 Na_2S;
3 - 30 Na_2S_2; 4 - 30 Na_2SO_3; 5 - 30 Na_2SO_4;
6 - 30 $Na_2S_2O_3$

$$Sb + S_x^{-2} \rightarrow SbS_3^{-3} + S_x^{-2} \rightarrow SbS_4^{-3}$$

We note that the rate of metallic antimony dissolution in Na_2S_2 is rather high [4]. However, the magnitude of the standard potentials for the following reactions [5, p. 750]

$$S_2^{-2} + 2e \rightarrow 2S^{-2} \quad \varphi_o = 0.524V$$

$$2S^{-2} + 2e \rightarrow 3S_2^{-2} \varphi_o = 0.506V$$

also indicates the possibility of direct polysulfide-ion reduction at the cathode.

We attempted to study the possibility of S_x^{-2} -ion participation in the concurrent reactions of cathode reduction during electrolysis of sulfide-alkali solutions of antimony. Stationary polarization curves were plotted by conventional means [6] with use of the P-307 potentiometer. Saturated calomel half-cells served as comparison electrodes. The cathode was made from grade Su000 antimony. The cathode space was separated from the anode space (anode - platinum) by a porous diaphragm; the cell was thermostatted. Solutions of sodium polysulfides were obtained by dissolution of stoichiometric amounts of elemental sulfur in an Na_2S solution.

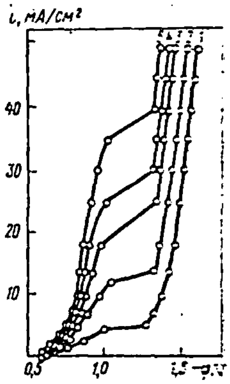

Fig. 2. Relationship of antimony-electrode polarization, at 25°C, to Na_2S_3 concentration, g/l:
1 - 5; 2 - 20; 3 - 30; 4 - 40; 5 - 50.

As follows from the experimental data, the cathodic polarization curves in solutions of $Na_2S_2O_3$, Na_2SO_3, and Na_2SO_4 (Fig. 1) have an identical character and can be found within the area of negative potentials sufficient to separate hydrogen at the antimony [7]. Reduction of tri- and pentavalent antimony occurs at much greater positive potentials, while the uniform nature of the polarization curves for SbS_3^{-3} and SbS_4^{-3}-ions is noteworthy. The latter is in agreement with the data presented by Sevryukov and Murti [8].

With still more positive potentials (by 50-170 mV) only the polysulfide-ions are reduced. Comparing the potentials for the discharge of S_x^{-2}-ions and sulfide-anions of antimony -- at identical current density values -- shows that with the joint presence in the electrolyte of these ions one should find that polysulfide-ions would be reduced first. However, their reduction is accompanied by the appearance on the curves of threshold-current areas with a subsequent sharp shift in the potential to values corresponding to the hydrogen-separation process.

The emergence of a threshold current area was noted at potentials of about -1.0V, at the same time that the potential for the cathode in the industrial electrolytic cell is close to -0.92V [9]. The maximum current density increases with increases in the concentration of sodium polysulfide (Fig. 2), as well as with increased temperatures (Fig. 3). In order to clarify the nature of the threshold current, Sb polarization curves were plotted in an Na_2S solution in their relationship to the solution mixing rate.

As follows from experimental data (Fig. 3), an increase in the number of mixer revolutions will lead to an increase in the threshold current. Hence, once can conclude that the threshold current has a diffusion nature; this is because with an increase in the solution mixing rate there is a reduction in the diffusion-layer thickness and the delivery of reducible ions to the electrode is facilitated.

In the electrolysis of sulfide-alkali solutions under conditions approximating industrial (20 g/l Sb, 100 g/l Na_2S, 20 g/l NaOH, t = 60°C, i_c = 250 A/m²) it was found (Fig. 4) that an increase in the concentration of polysulfide-ions leads to an extremely sharp drop in the antimony current efficiency. Moreover, following

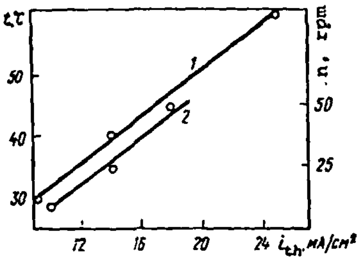

Fig. 3. Relationship of threshold current to the temperature (1) and the number of mixer revolutions (2) at $[Na_2S_2]$ = 20 g/l.

the addition of > 10 g/l elemental sulfur to the solution at the cathode not only does no cathode form, but there is even some drop in the weight of the iron cathode. Evidently, the primary process at the cathode is precisely the reduction of S_x^{-2}-ions.

In analyzing the experimental data, one notes that the likely probability of S_x^{-2} and SbS_3^{-3}ions discharge should depend on the relationships of their concentration and on the current density at the cathode. An increase of the antimony concentration in a solution leads to a shift in the polarization curves for SbS_3^{-3}-ions in a positive direction. An increase in the current density with a simultaneous drop in the polysulfide-ions concentration leads to a discharge of the latter in the threshold-current system. To sum up. all of these measures should contribute to an increase in the antimony current efficiency.

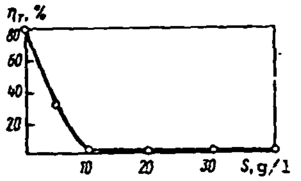

Fig. 4. Relationship of antimony current efficiency to the the concentration of S_x^{-2}ions in the solution.

If one keeps in mind that under industrial electrolysis conditions there is a constant formation of S_x^{-2}-ions at the anode [1], as well as in the solution itself due to oxidation with oxygen [10], then the need becomes clear for a maximum reduction of their concentration in the circulation electrolyte. Accumulation of polysulfide-ions in the electrolyte is one of the main reasons for the up to 48-50% drop in antimony current efficiency under industrial conditions.

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