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Recovery of Metal Values from Low Grade Copper Sulfide Ores

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ABSTRACT

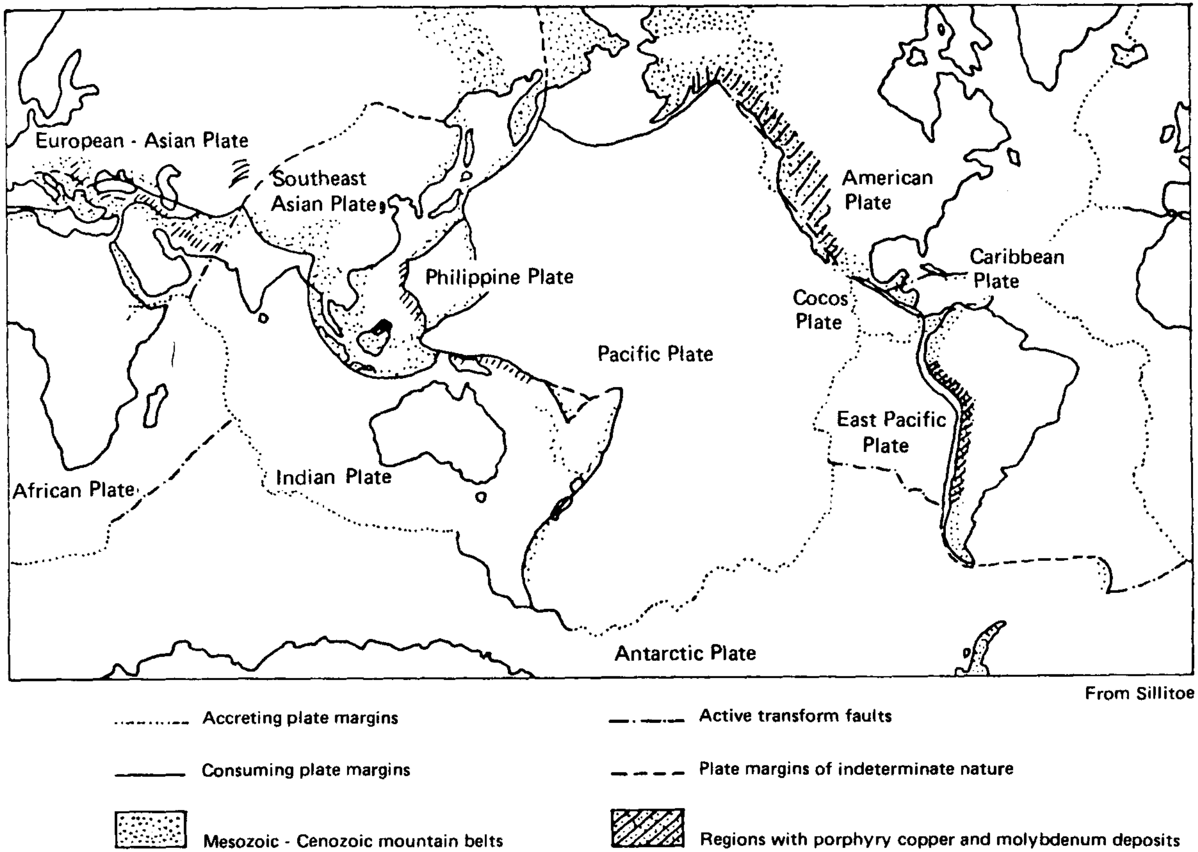
In the United States approximately 12 percent of the new copper produced comes from dump leaching of low grade waste rock from open pit mining. While this amount of copper is significant it is unusual, even for massive dumps, for steady-state recovery rates to exceed 20 percent. Basic physical and chemical 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.

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 crystallization of the magma. Dissolved mineral in water causes movement and deposition of primary minerals in cracks and fissures. 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 sulfides. Typically a copper deposit will have an upper zone of oxidized minerals with a zone of secondary enrichment below and primary mineral-ization 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



From Sillitoe

FIGURE 1. Sillitoe's Plate Tectonic Model for the Origin of Porphyry Copper Deposits.

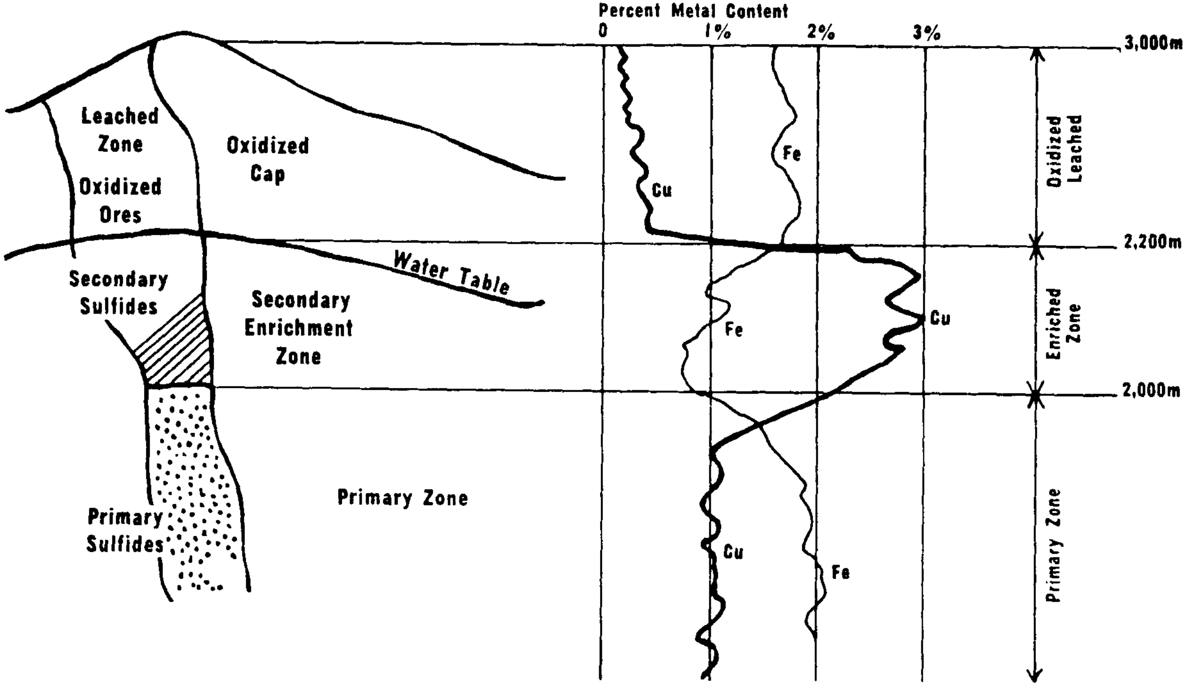
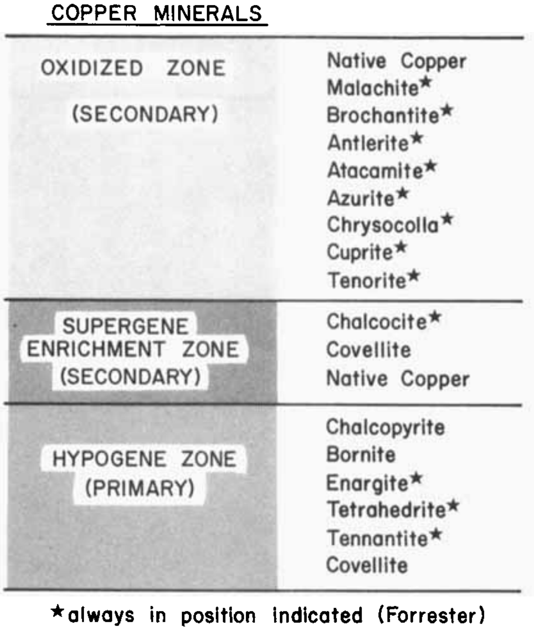


FIGURE 2. A schematic cross section of a typical copper porphyry.



COPPER MINERALS

OXIDIZED ZONE (SECONDARY)	Native Copper Malachite★ Brochantite★ Antlerite★ Atacamite★ Azurite★ Chrysocolla★ Cuprite★ Tenorite★
SUPERGENE ENRICHMENT ZONE (SECONDARY)	Chalcocite★ Covellite Native Copper
HYPOGENE ZONE (PRIMARY)	Chalcopyrite Bornite Enargite★ Tetrahedrite★ Tennantite★ Covellite

★always in position indicated (Forrester)

FIGURE 3. Minerals typically formed in oxidation, supergene enrichment, and hypogene zones. (5)

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-

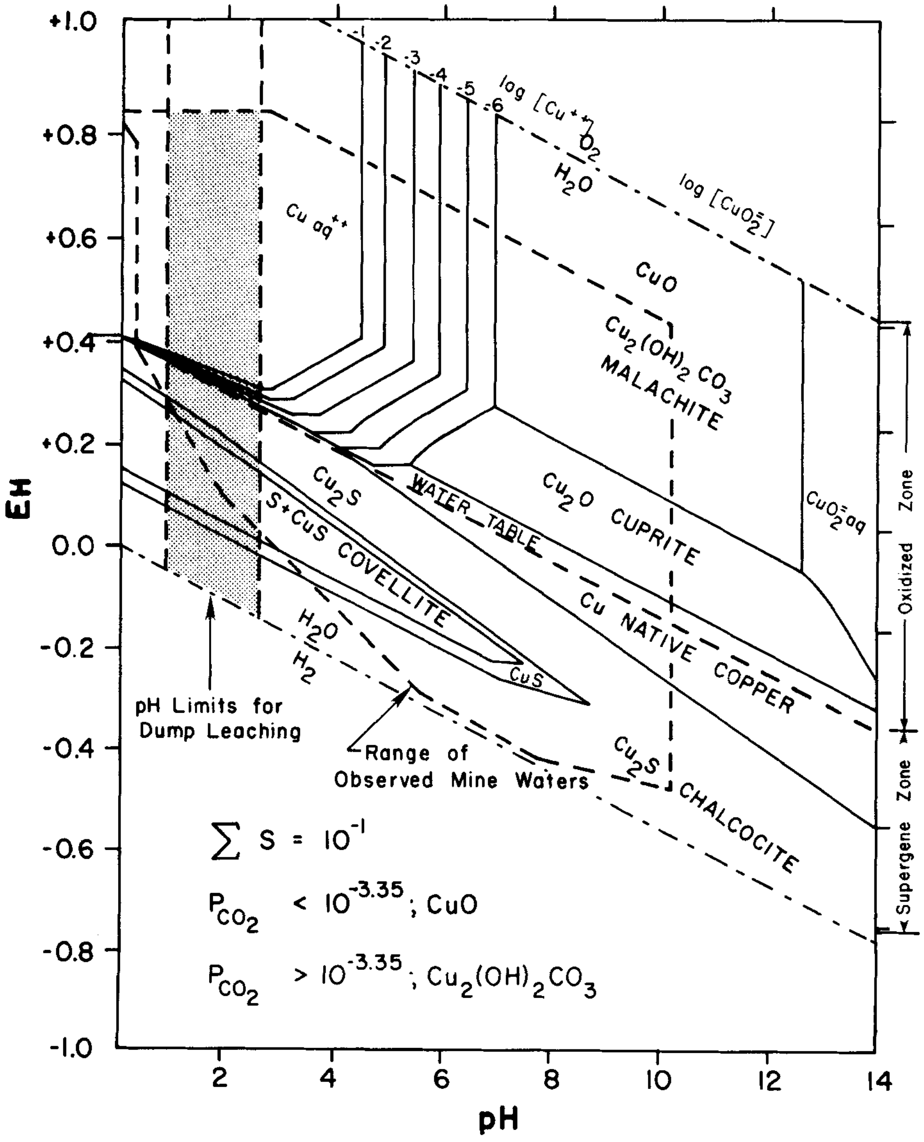


FIGURE 4. Pourbaix diagram for the Cu-S-H_2O-CO_2 system showing the region observed for natural mine waters and the region expected for dump leaching of copper oxide and sulfide ores.

TABLE 1. 1978 Copper Production (Schlitt (6)). Statistics for Western Copper Operations with Significant Leach Output

	Copper Production, Tons		
Company	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 Consol.	20,700	18,000	46.5
	991,180	217,380	18.0

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 equal quantities 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. 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. 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. (Darcy refers to hydraulic conductivity or permeability. Permeability in cm/sec is converted to Darcy's by multiplying by 1045.) 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 or the dump than the fine material, causing stratification. Without appropriate ripping stratification may affect the flow pattern within the dump.
4. Sorption: Solutions bearing dissolved metals may pass through regions containing non-gravitational water at lower concentrations. Trapping of metal

values will occur by inward diffusion into the pore structure of the rocks and into stagnant aqueous regions.

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 extend 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

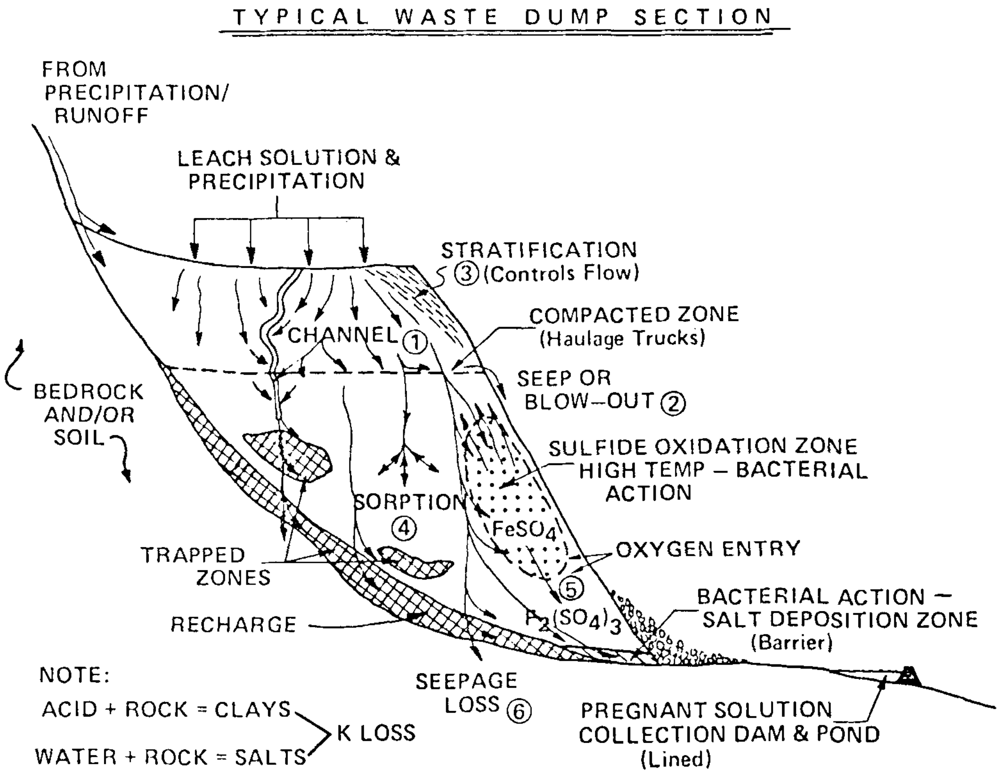


FIGURE 5. Cross section of dump illustrating hydrodynamic features according to Whiting. (8)

13 years old, the operating data are important since they established actual operating 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

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)

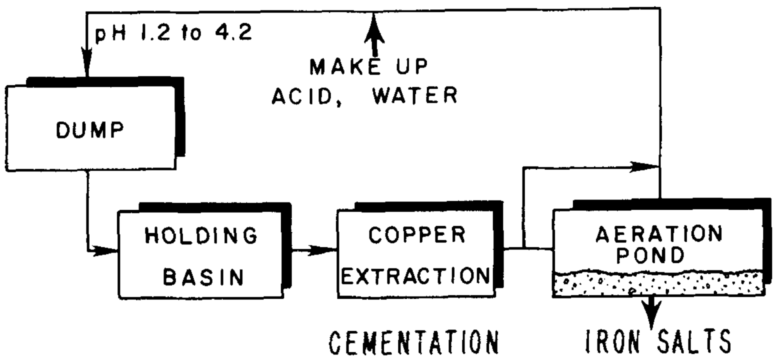
				DUMP EFFLUENT				COPPER CEMENTATION EFFLUENT		
Company	Principle Copper Minerals	Estimated tonnage 1000's tons (1968)	Solution Flow Rate (gpm)	Copper	(Fe)(total)	Fe^{III}/Fe^{II}	pH	(Fe)(total)	Δ(Fe)total	$\Delta(Fe)_T/Cu$
AS & R, Silver Bell, Arizona	Chalcopyrite and chrysocolla	30,000	1,000	1.09	0.58	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.

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, its pH, and the ferrous to ferric ion ratio. This latter ratio is an indication of the effectiveness of the bacteria within the dump. The ferric to ferrous ratio is a good relative measure of the bacterial activity. Ratios above 1.0 indicate significant 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 emerge from the dump, good bacterial activity occurs. Dump solutions emerging from dumps in which adequate bacterial activity occurs have temperatures in the range of 30^0 to 35^0C. 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



CEMENTATION

$Cu^{+2} + Fe = Cu + Fe^{+2}$

SOLVENT EXTRACTION

$2\,RH + Cu^{+2} = R_2Cu + 2\,H^+$

IRON REMOVAL:

$2\,Fe^{+2} + O_2 + 2\,H^+ = 2\,Fe^{+3} + H_2O$ *(Slow)*

$6\,Fe^{+3} + 4\,SO_4^{-2} + 14\,H_2O = 3\,Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O\downarrow + 10\,H^+$

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 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 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 paractice.

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, since the latter includes the rest portion of the total rest cycle(10). The application rate is the leach solution flow rate per unit area of surface to which it is being applied, typically 1/4 to 1/5 of the total area available for application. On the average application rates observed to give best results vary from less than 20 ℓm^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. 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°C the solubility of oxygen in pure water is 2.3 x 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 chemoautotroph 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 chemoautotroph deriving its energy from the oxidation of elemental sulfur, thiosulfate, or sulfide as contained in heavy metal sulfides. Sulfur oxidation produces sulfuric acid in place, an essential feature in maintaining open porosity in dump leaching. Pyrite is a strong acid producer supplying ferrous iron which is subsequently oxidized to the ferric state in the presence of T. ferrooxidans. 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. Thermodynam-ically, 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

$$(Fe)_3(SO_4)_2(OH)_5\cdot 2H_2O + 5H^+ = 3Fe^{+3} + 2SO_4^= + 7H_2O \quad (2)$$

for which log K is -2.7. The iron sulfate complex equilibria are

$$Fe^{+3} + SO_4^= = FeSO_4^+ \quad (3)$$

and

$$Fe^{+3} + 2SO_4^= = Fe(SO_4)_2^- \quad (4)$$

with log K values of 4.15 and 5.4 respectively. Accordingly, at pH=2.3 the ferric ion activity would be approximately 8.6×10^{-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. his 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 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)

$$CuCO_3 \cdot Cu(OH)_2 + 4H^+ = 2Cu^{+2} + CO_2 + 3H_2O \qquad (5)$$

(azurite)

$$2CuCO_3 \cdot Cu(OH)_2 + 6H^+ = 3Cu^{+2} + 2CO_2 + 4H_2O \qquad (6)$$

(chrysocolla)

$$CuO \cdot SiO_2 \cdot 2H_2O + 2H^+ = Cu^{+2} + SiO_2 + 3H_2O \qquad (7)$$

(calcite)

$$CaCO_3 + 2H^+ + SO_4^{-2} + H_2O = CaSO_4 \cdot 2H_2O + CO_2 \qquad (8)$$

(chlorites)

$$H_4Mg_3Si_2O_9 \cdot y\, H_4\, Mg_2\, Al_2\, Si_2\, O_9 = (6+6y)H^+ + (2+2y)\, SiO_2 + (3+2y)Mg^{+2} + 2y\, Al^{+3} + (5+5y)H_2O \qquad (9)$$

(biotite)

$$H_2K(Mg)_{3x}(Fe)_{6-3x}\,Al(SiO_4)_3 + 10\,H^+ = K^+ + 3xMg^{+2} + (6-3x)Fe^{+2} + Al^{+3} + 3SiO_2 + 6H_2O \quad (10)$$

(K-feldspar alteration to K-mica)

$$3KAlSi_3O_8 + 2H^+ + 12H_2O = KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6H_4SiO_4 \quad (11)$$

(K-mica alteration to Kaolinite)

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ = 3Al_2Si_2O_5(OH)_4 + 2K^+ \quad (12)$$

(Kaolinite)

$$Al_2Si_2O_5(OH) + 6H^+ = 3Al^{+3} + H_2O + 2H_4SiO_4 \quad (13)$$

Acid-generating reactions:

(Chalcopyrite oxidation)

$$CuFeS_2 + 16Fe^{+3} + 8H_2O = Cu^{+2} + 17Fe^{+2} + 2SO_4{}^{-2} + 16H^+ \quad (14)$$

(covellite oxidation)

$$CuS + 4H_2O + 8Fe^{+3} = Cu^{+2} + SO_4^{-2} + 8Fe^{+2} + 8H^+ \quad (15)$$

(pyrite oxidation)

$$FeS_2 + 8H_2O + 14Fe^{+3} = 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \quad (16)$$

(iron hydrolysis to hydrated hematite)

$$2Fe^{+3} + (3+x)H_2O = 6H^+ + Fe_2O_3\cdot xH_2O \quad (17)$$

(iron hydrolysis to hydrogen jarosite)

$$Fe^{+3} + \frac{7}{3}H_2O + \frac{2}{3}SO_4^{-2} = \frac{5}{3}H^+ + \frac{1}{3}Fe_3(SO_4)_2(OH)_5.2H_2O \quad (18)$$

(iron hydrolysis to jarosite salts)

$$Fe^{+3} + \frac{1}{3}M^+ + 2H_2O + \frac{2}{3}SO_4^{=} = \frac{1}{3}MFe_3(SO_4)_2(OH)_6 + 2H^+ \quad (19)$$

(chalcopyrite alteration to chalcocite)

$$5CuFeS_2 + 11CuSO_4 + 8H_2O = 8Cu_2S + 5FeSO_4 + 8H_2SO_4 \quad (20)$$

Neutral reactions:

(chalcopyrite alteration to covellite)

$$CuFeS_2 + CuSO_4 = 2CuS + FeSO_4 \tag{21}$$

(chalcocite)

$$Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4 \tag{22}$$

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 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

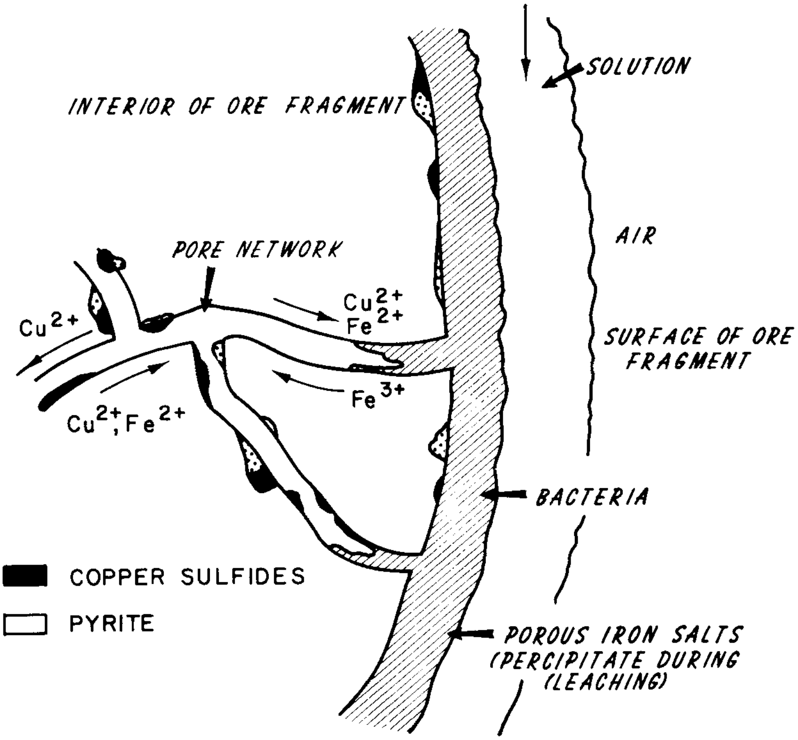


FIGURE 7. Ore fragment showing pore network and diffusion of ions.

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 operation.

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 showing the pore structure and diffusion of ions. 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 distinct partile within the ore fragment. 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 transfer 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. The Fe III produced diffuses through the pore structure reaction 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. 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

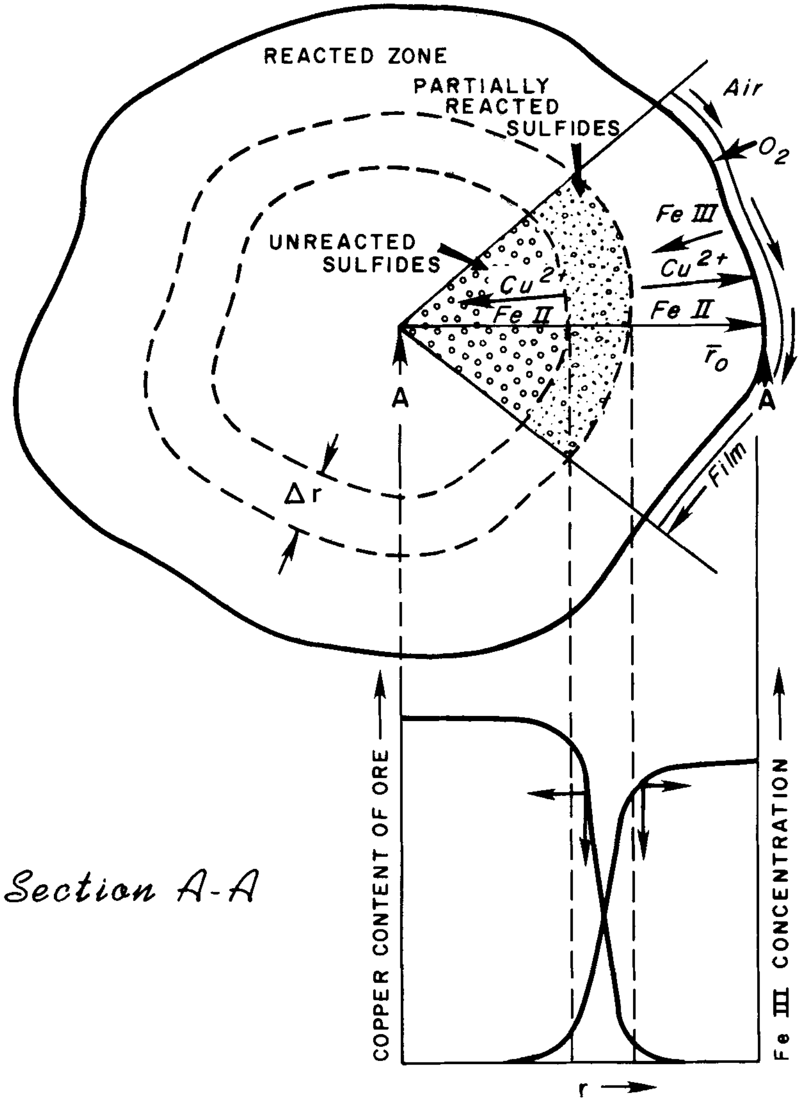


FIGURE 8. Ore fragment showing reacted and unreacted regions and diffusing ions.

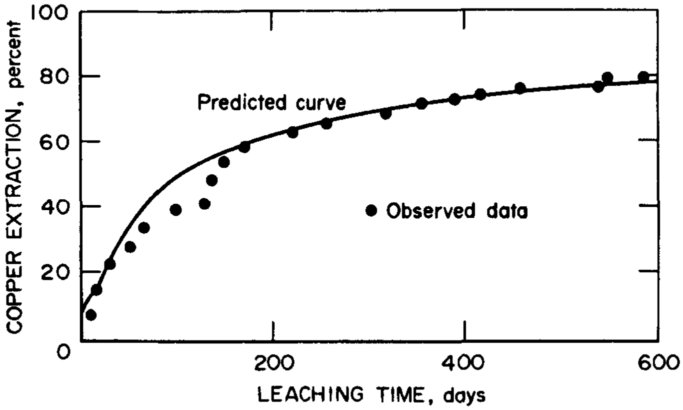


FIGURE 9. Predicted copper extraction for monzonite ore.

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 seconday 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 section 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

$$1 - 2/3\alpha - (1-\alpha)^{2/3} + \frac{\beta}{r_o}[1-(1-\alpha)^{1/3}] = \frac{\gamma}{r_o^2} t \qquad (23)$$

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 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 diffusivities 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

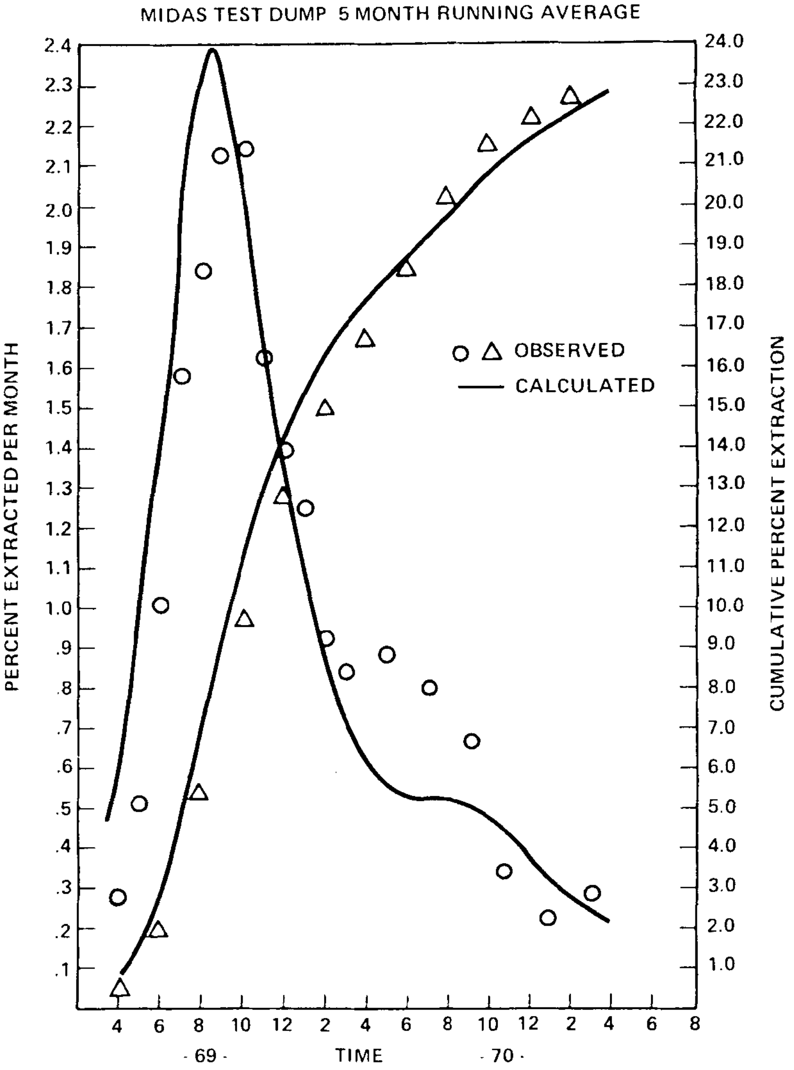


FIGURE 10. Comparison of observed and calculated dump behavior.

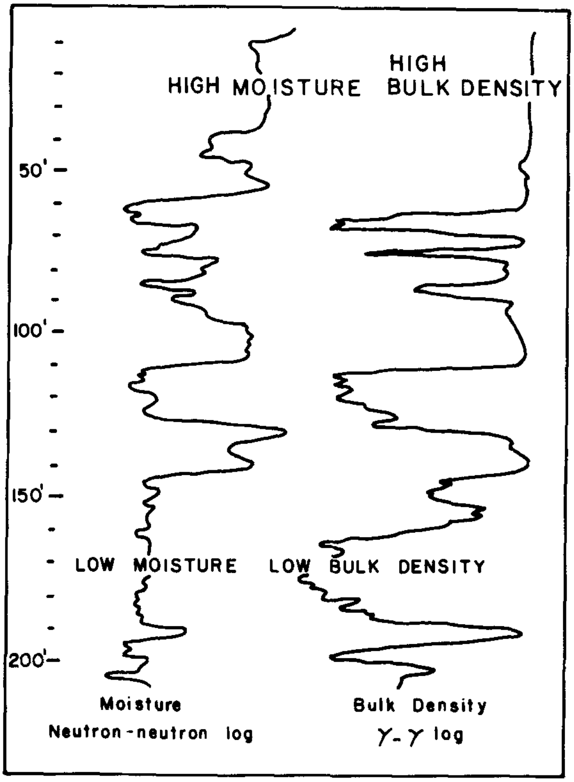
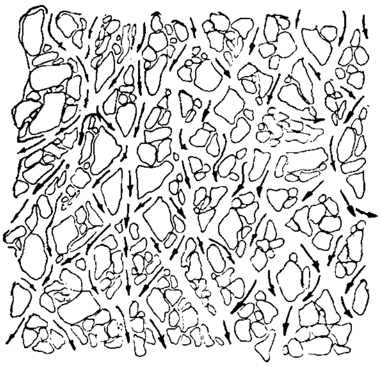


FIGURE 11. Well log-data from Kennecott's Chino dump, showing variations in moisture and density.

within a dump.(23) Solution by-pass zones or particles clusters may behave like individual ore fragments; i.e., 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

Low bulk density



High bulk density

FIGURE 12. Illustration showing effect of compaction on fluid flow within a dump, according to Roman. (23)

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 ($\sim$ 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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