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Predictive Capabilities of a Finite Difference Model of Copper Leaching in Low Grade Industrial Sulfide Waste Dumps[1]

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A finite difference model describing industrial leaching of low grade sulfide waste and efforts to test the model are reviewed. The model includes air convection, heat balance, temperature dependent mixed oxidation kinetics, and bacterial catalysis. The model is shown to have general validity, but detailed predictions of how a given waste will leach in a given dump are not possible. The model is useful at this point mainly as a guide or framework within which questions can be formulated and judgements made. KEY WORDS: dump leaching, copper leaching, finite difference model, bacterial catalysis, weathering, acid mine drainage, secondary enrichment.

INTRODUCTION

In the mining of low grade (< 1 wt.%) porphyry copper ore it is common industrial practice to pile the "waste" material, that is the material which does not contain enough copper to justify crushing, floating, and smelting, in such a way that it can be leached. Where space permits these piles are constructed in a deliberate geometry. Where space does not permit, the waste simply fills canyons or gullies (see Fig. 1). Water is distributed on the waste piles and copper, liberated by essentially an accellerated weathering process, is flushed out. The copper is then stripped from the solutions which are recirculated. The amount of copper recovered by this process is significant. About 20% or $100 million worth of Kennecott's copper production comes from this source.

Because the leaching process is significant economically, substantial research to optimize the process is justified. We have reported previously (Cathles and Apps, 1975; Cathles, Reese and Murr, 1977) some of the research we have done to understand and thereby improve the leaching process. This

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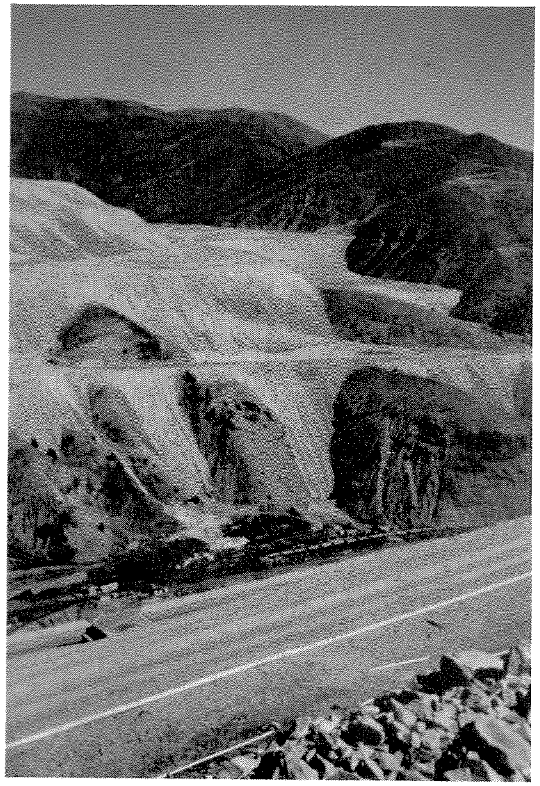

Figure 1. View of typical waste dump at Kennecott's Bingham Canyon mine. In foreground pipe distributing leach solution to dump surface can be seen. Just below the foreground dump surface is a haulage road (note truck). Railroad in valley gives scale of dumps in background.

paper is not intended to report new results but rather to review the kinds of modeling that have been done and critically to examine its successes and failures from a somewhat philosophical point of view. Industrial dump leaching is interesting because it is carried out under fairly controlled or discoverable conditions but is of large enough scale that, as in many geological problems, factors become significant which cannot easily be measured or duplicated in the laboratory. Thus some kind of a model is necessary. Our overall interest in this paper is to discuss the extent to which the model we have constructed can be said to have predictive capabilities. Briefly we have found that although many unknown features predicted by the model have been found to exist or be true, it is not presently possible to accurately predict how a given waste type will leach in a given dump. Whether this is due to relatively

easily remedied incomplete knowledge or more fundamental practical barriers is unclear.

In what follows the model and the manner in which it was calibrated against actual dumps will be described. Finally we review the predictions of the model and the ways in which we have attempted to test it.

THE MODEL

The model has been described in Cathles and Apps (1975) and updated and summarized in Cathles, Reese, and Murr (1977). The reader is referred to these papers for details. We start with the chemistry of leaching, then include kinetics and finally satisfy physical constraints such as heat balance in the dump, the convection of air through the dump, and overall chemical mass balance. The result is a model which, given definitions of initial conditions, boundary conditions, and physical chemical and kinetic parameters, predicts the history of leaching as well as the thermal and convective history of any dump.

Chemically, copper sulfide minerals can be leached only after they are oxidized. As copper sulfide (chalcopyrite) is leached, the generally more abundant iron sulfide (pyrite) is also leached. Assuming FPY moles of pyrite are oxidized for every mole of chalcopyrite, the chemistry of leach reactions (plus minor modifications required by mass balance in the recycled leach solutions) dictate that for every gram of copper oxidized the following amount of oxygen be consumed and heat generated:

$$\text{grams of } O_2 \text{ consumed/grams copper oxidized} = 1.75 + 1.91 \text{ FPY} \quad (1)$$

$$\text{killocalories produced/grams copper oxidized} = 2.89 + 5.41 \text{ FPY} \quad (2)$$

Since a liter of air contains 0.28 g O_2 and leach solutions exiting from leach dumps typically contain about this much copper (i.e., 0.28 g copper/liter), (1) also indicates

$$\frac{\text{liters of air}}{\text{liters of leach solution}} \approx 1.75 + 1.91 \text{ FPY} \quad (3)$$

In actual dumps of our experience FPY is generally greater than 20. Therefore much more air must circulate through a dump (and have its oxygen consumed) than water. In fact it is quickly apparent from the *amount* of oxidant required by the leaching process that only air convection through the dump can provide the oxidant required by the leach reactions. The leach solution cannot carry enough oxidant in dissolved form. That air does convect through the dumps is evident in many cases from the "blast" of hot wet air exiting from holes drilled into the dump.

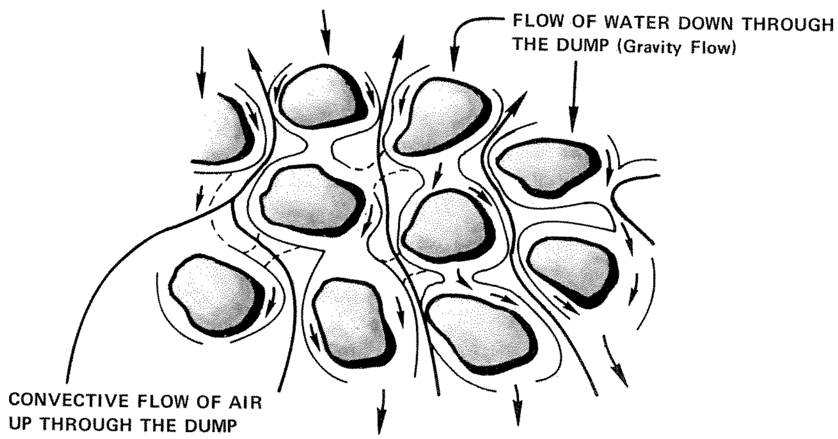

Figure 2. Schematic drawing of flow of air and water through dump. Such flow can be simultaneous but water flow is usually only episodic (occurring only during periods of time when solutions are applied to the dump surface).

The kinetics of leaching can be conveniently described by a "shrinking core" model commonly used in chemical engineering and metallurgy (e.g., Levenspiel, 1967, p. 344). We envision a flow of water around individual waste particles as shown in Figure 2. Each individual waste particle is idealized to spherical form as shown in Figure 3. If x is the fraction of copper remaining in a given waste particle or in a specified volume of the dump:

$$\frac{\partial x}{\partial t}=\frac{-3x^{2/3}\,B(T)}{6\,\tau_D\,x^{1/3}\,(1-x^{1/3})+\tau_C} \tag{4}$$

Parameter values are defined in Table 1. τ_C and τ_D can be equated to expressions containing physical and chemical rock parameters and their values estimated from inspection of the waste material (see Cathles and Apps, 1975). The factor $B(T)$ is discussed shortly.

If we distinguish sulfide from nonsulfide copper minerals by adding an S or NS subscript to τ_C, τ_D, and so forth, the temperature dependence of leaching can be introduced. For example

$$\tau_{CS}(T)=\tau_{CS}(T_0)\,\exp\,(E^*_{CS}/RT_0-E^*_{CS}/RT) \tag{5}$$

$B(T)$ in equation (4) was found necessary to adequately reflect bacterial catalysis of the leaching process. As shown in Figure 3, bacteria within the dump catalize at least the oxidation of Fe^{2+} to Fe^{3+} (consuming dissolved oxygen). Because of its high solubility under leach conditions (pH <2.5), Fe^{3+} can diffuse much more rapidly into the waste particle interior than can dissolved oxygen and is responsible for the sulfide oxidation. The bacteria

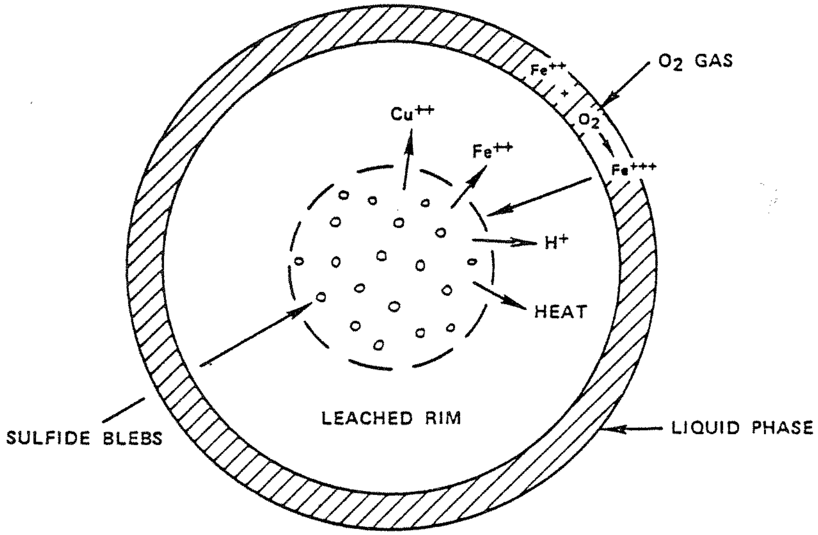

Figure 3. Cross section of waste particle showing critical steps in leaching process. Bacteria catalize the oxidation of Fe^{2+} to Fe^{3+}.

become sick at about 50°C and finally die or become inactive at about 55°C. A crucial step in the oxidation chain is interrupted, and this is reflected in the model kinetics through the factor $B(T)$:

$$\begin{aligned} &B(T)=1.0 && T\leqslant T_{sick}\\ &B(T)=T_{kill}-T/T_{kill}-T_{sick} && T_{sick}<T\leqslant T_{kill}\\ &B(T)=0.0 && T_{kill}\leqslant T \end{aligned} \tag{6}$$

The rate of production of copper, $\mathscr{R}_{Cu}$, the rate of production (actually always consumption) of oxygen, $\mathscr{R}_{O_2}$, and the rate of generation of heat, $\mathscr{R}_A$, (all in grams or calories per cubic centimeter of dump per second) are now easily described by combining equations (1), (2), and (4).

$$\begin{aligned} \mathscr{R}_{Cu}&=\rho_T G_S H([O_2]^g)\,\frac{\partial x_S}{\partial t}+\rho_T\,G_{NS}\,\frac{\partial x_{NS}}{\partial t}\\ \mathscr{R}_{O_2}&=-\rho_T G_S H([O_2]^g)\,(1.75+1.91\text{ FPY})\,\frac{\partial x_S}{\partial t}\\ \mathscr{R}_A&=\rho_T G_S H([O_2]^g)\,(2.89+5.41\text{ FPY})\,\frac{\partial x_S}{\partial t} \end{aligned} \tag{7}$$

$H([O_2]^g)$ is the heavyside step function and has a value of unity if $[O_2]^g>0$ and is zero if $[O_2]^g=0$, reflecting the fact that sulfide minerals in the dump will be

Table I. Model Parameters Both Measured and Determined Through Modeling for the Utah Copper Division Midas Test Dump, Chino Mines Division Test Dumps #1 and #2, and for the New Mexico Tank Experiment[a]

Parameter	Meaning	Value for Midas Test Dump*	Value for Chino Test Dump #1, 2 (Chino Type I waste)	Value for New Mexico Tank (Chino) Type I waste
Quantities assumed known				
R	Gas constant (cal/°C mole)		2	
ρ_T	Density of dump as a whole (g/cm³)		2.04	
ρ_l	Density of water phase in dump (g/cm³)		1.0	
ρ_g	Density of air in dump		see Cathles and Apps (1975)	
C_l	Heat capacity of water phase (cal/g °C)		1.0	
C_g	Heat capacity of water saturated air (cal/g °C; T in °C)		0.126 + 0.0283T	
Measured quantities				
G_S	Sulfide Cu grade (wt.%)	0.12%	0.24–0.29%	0.20%
G_{NS}	Nonsulfide Cu grade (wt.%)	0.03%	0.12–0.07%	0.15%
FPY	Moles pyrite oxidized per mole of sulfide copper oxidized	47	12	15.4
T_{AVE}	Average ambient temperature	5°C	13	14.5
T_{AMPL}	Amplitude of seasonal temperature variation	12.5°C	10	11
Model determined quantities				
τ_{CS}	Time in months to leach typical sulfide waste fragment at 25°C if diffusion is fast	200 months	250–300	850
τ_{DS}	Time in months to leach typical waste fragment if chemical reactions are fast	1000 months	150	150
E^*_{CS}	Activation energy for sulfide leaching	13,000 cal/mole	15,000	25,000
E^*_{DS}	Activation energy for Fe^{3+} diffusion in water	5,000 cal/mole	5,000	5,000
τ_{CNS}	Same as above but for nonsulfide copper	200 months	250–300	6
τ_{DNS}	Same as above but for nonsulfide copper	500 months	150	6
E^*_{CNS}	Activation energy for nonsulfide leaching	13,000	13,000	13,000
E^*_{DNS}	Diffusional activation energy for nonsulfide leaching	5,000	5,000	5,000
T_{sick}	Temperature at which bacteria became sick	55°C	55	50
T_{kill}	Temperature at which bacteria became inactive	65°C	65	55
k	Permeability of the waste (darcys) (1 darcy = 10^{-8} cm²)	1000	1000	~0.27 (see Murr et al., 1977)

[a] After Cathles, Reese, and Murr (1977).

oxidized only if oxygen is present in the gas-filled pores of the dump. Nonsulfide copper, which is leached by acid produced by leach reactions elsewhere, is not under this restriction.

The physical aspects of the model are defined by conservation of energy, momentum, and mass:

$$\rho_T C_T \frac{\partial T}{\partial t} = (\rho_l C_l V_l - \rho_g C_g V_g)\, \partial T/\partial t + \mathscr{R}_A + K_T\, \partial^2 T/\partial t^2$$

$$V_g = k_{AVE}/\mu_g\, \Delta P/H; \qquad \Delta P = F(O_2, T, \text{water vapor})$$

$$[O_2]^g = [O_2]^g_{STP} - \int_{path} \mathscr{R}_{O_2}\, dz/V_g \geq 0 \tag{8}$$

The energy equation accounts for heat advection by both water and air (gas). V_l and V_g are the Darcy velocity of liquid and gas through the dump in cubic centimeters per square centimeter per second. The surface of the dump is assumed to be at average ambient temperature, and therefore varies according to the yearly temperature cycle. The dump is on a 20-ft thick impermeable rock pad the base of which is fixed at the average ambient temperature. Water is assumed to be applied to the dump at ambient temperature.

The momentum equation is just Darcy's law of flow through porous media. ΔP is calculated over the entire thickness of the dump and reflects the buoyant effects of depleted oxygen, increased temperature, or added water vapor content (a light component of air). The air flow is assumed to be vertical only, a good approximation for small dumps.

The mass balance equation simply tracks an air pocket along as it moves through the dump and keeps track of how much oxygen has been removed. Oxygen concentration in the air is of course always equal to or greater than zero.

The equations in (8) were solved using the alternating direction implicit finite difference technique. These equations, in a sense, represent a predictive model of the dump leaching process. Given an appropriate choice of initial conditions, boundary conditions, and parameter values, the model will predict the leach history of any dump in any environment.

CALIBRATION OF THE MODEL

The model described in the previous section was calibrated against the leaching data from five well-studied Kennecott test dumps. One particularly good example, the Midas Test Dump (built and operated by Kennecott's Utah Copper Division), is shown in Figure 4. Test holes probed the interior of the dump for both oxygen concentration and temperature. The figure shows the dump 5 months after the start of leaching. The center of the dump has heated

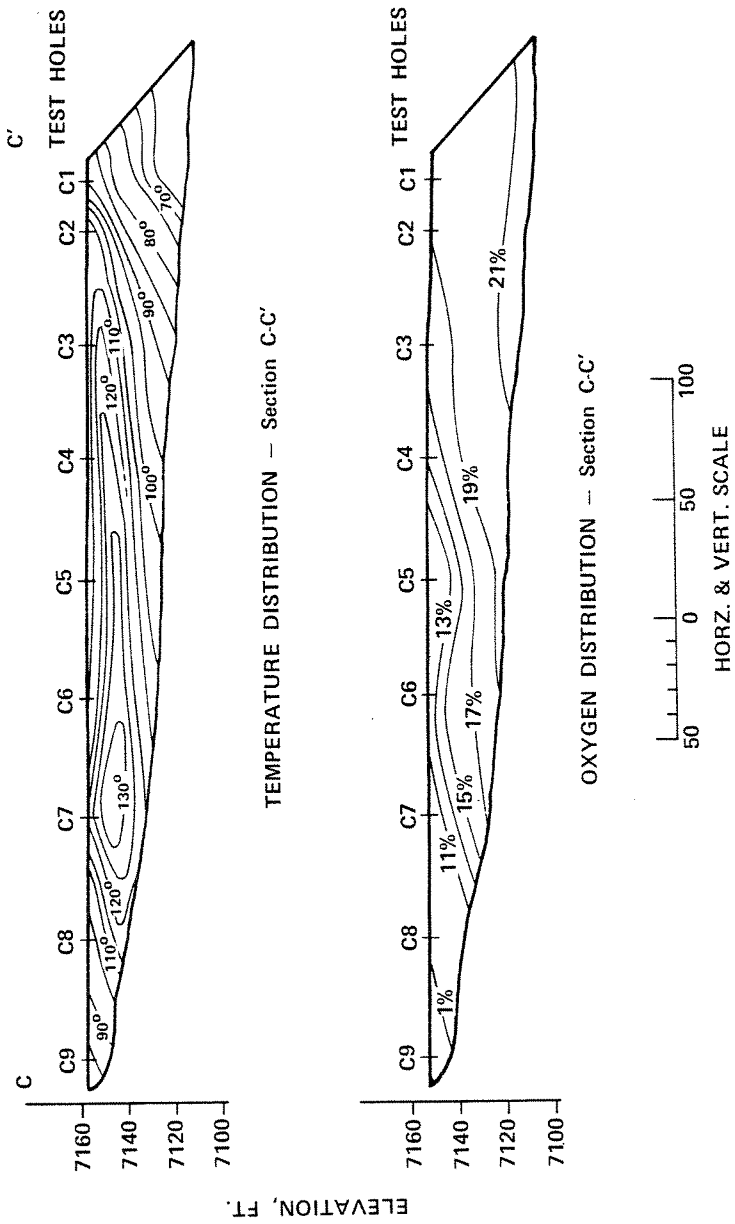

Figure 4. Cross section through Midas Test Dump, run by Kennecott's Utah Copper Division. Temperature (°F) and oxygen profiles were measured through concentrically nested casing pipe in holes (C1–C9) drilled into dump. The oxygen profiles are horizontal with maximum oxygen concentration at the base suggesting that flow is primarily vertical up through the dump from a high permeability base.

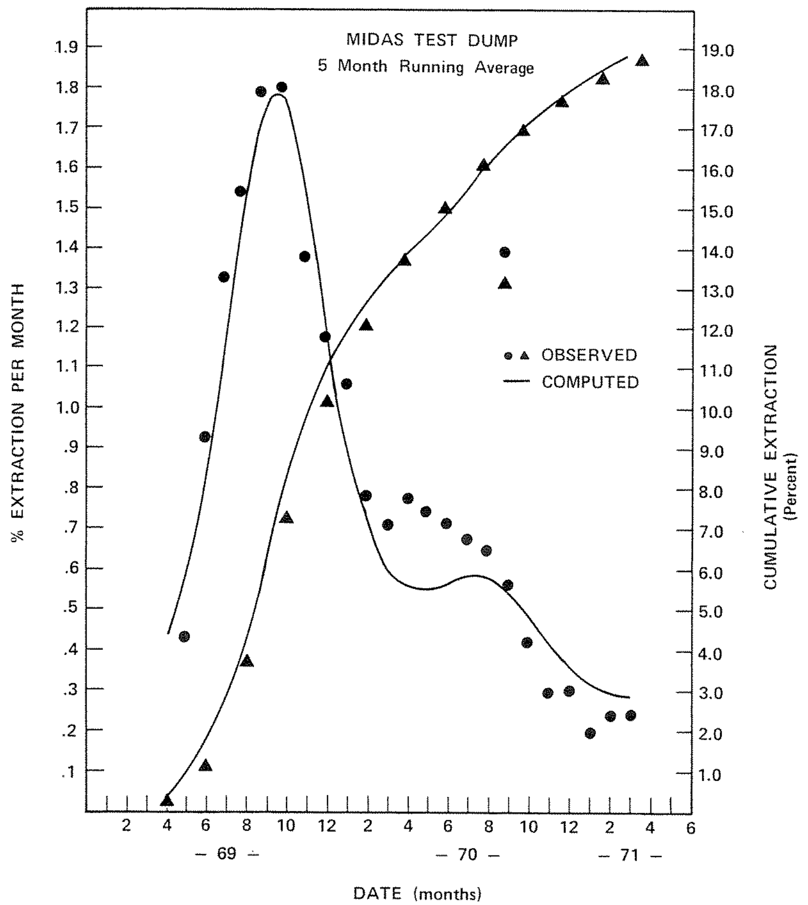

Figure 5. Comparison of computed and observed rate of leaching (circles) and cumulative copper leached (triangles) for Midas Test Dump of Figure 4.

up dramatically (130°F); the oxygen profiles show that air is convecting in the high permeability base of the dump and is being depleted by sulfide reactions as it horsetails up through the dump. The horizontal character of the oxygen profiles indicates the appropriatives of the one-dimensional (vertical only) air flow model for at least this case. More details are given in Cathles and Apps (1975).

Figure 5 compares the leach history observed to the leach history of the model using parameter values given in Table 1 (Midas Test Dump Column). The leach rate (both model and observed) increased strongly at first as the dump heated up. The subsequent drop resulted from the depletion of easily

accessible copper and the assertion of diffusion controlled shrinking core leach kinetics. The effect of the yearly temperature cycle is seen in both observed and model data in the drop off "tails" of the leach rate curves.

MODEL PREDICTIONS

The calibrated model made several predictions regarding the nature of dumps and the leaching processes that were useful in themselves or because they were susceptible to test.

First of all, the model ranked variables according to this degree of impact on the efficiency of the leaching process (see Cathles and Apps, 1975). Variables susceptible to deliberate change with a large impact on leach efficiency or rate could be identified and field tests initiated. Several tests of this type are now being carried out by operating divisions of Kennecott. Also, factors that would be changed by proposed process changes could be evaluated. For example, the model indicated that a great deal more acid was generated and neutralized inside the dump than was commonly added to the leach solution stream. Thus, other than the effects of added acid on salt precipitation near the dump surface, the model suggested that the elimination of acid additions should have little impact on the leaching process. Similarly, the model indicated that a great deal more iron is solubilized and precipitated within the dump than is added to the solutions by the stripping out of copper in the iron cementation process. Thus replacing the cementation process with a process (such as solvent extraction) which adds no iron to the solutions should not affect leaching efficiency.

For dumps such as the Midas Test Dump to leach as observed, model permeabilities of ~ 1000 darcys are required. The rate of warming of the dump is a stringent control since this depends almost solely on the amount of oxygen consumed and this oxygen must be supplied by some minimum amount of air convection. Such high permeabilities are extremely vulnerable to test.

The model supports the existence of a critical bacterially catalized step in the leaching process. There is no evident inorganic reason for the leach rate to show strong temperature dependence to ~ 50°C and then stop. Without the $B(T)$ factor dump temperatures would in many cases continue to climb until the water in the dumps boiled. Yet low grade sulfide waste dumps are only very rarely (if ever) observed to have internal temperatures greater than 65°C.

Finally the shrinking core kinetic model predicts that easily observable rims leached of copper (and iron) sulfides should be found around non-decrepitated waste particles in dumps under leach for substantial periods of time (decades). No such leached rims had been observed, but neither had they ever been looked for.

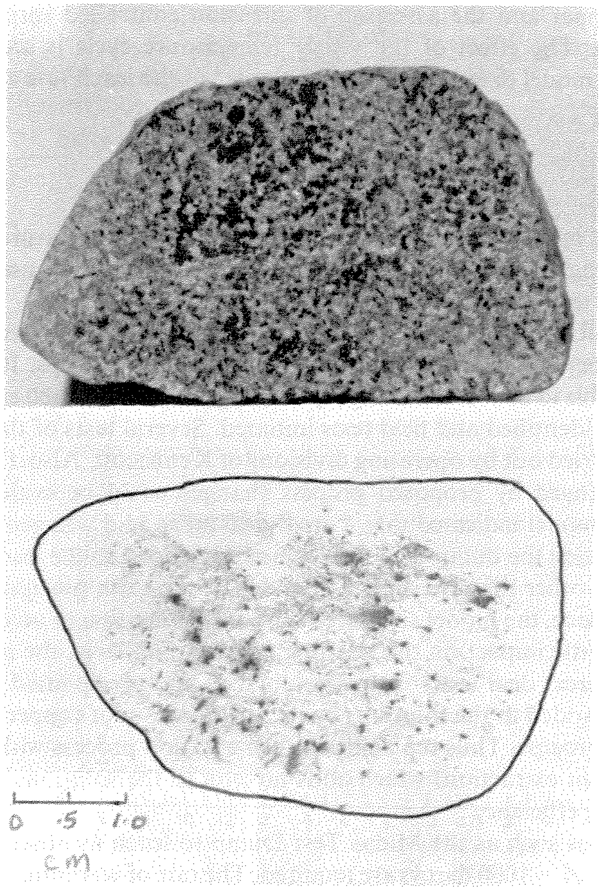

Figure 6. Typical waste particle cut in half. A copper print of the waste particle (bottom figure) clearly shows the presence of a leached rim. The absence of chalcopyrite in rims such as this one can also be verified by point counting sulfide blebs under a microscope.

VERIFICATION OF MODEL PREDICTIONS

The first test was to search in a determined way for the predicted leached rims. About half a ton samples was collected by a collegue, Frank Dudás, from Kennecott's waste dumps, and analyzed. Three hundred of the samples were cut and copper prints made. The copper printing technique proved a quick way to screen for the copper sulfide distribution in the bisected samples. The method followed was essentially that described by Gutzeit (1943). Copper leached rims, like the one shown in Figure 6, proved ubiquitous. The leached

rims were not apparent in hand specimens or in thin sections under the microscope. Point counts of sulfide grain abundance confirmed the rims, however. Other interesting features were noted such as secondary enrichment of copper sulfides in the interior of the fragments inside the leached rim (produced by the inward diffusion of leached copper), precipitation of Ca as basanite ($CaSO_4 \cdot \frac{1}{2}H_2O$), precipitation of jarosite, bleached rims caused by acid neutralization in the fragments, and so forth. We hope to describe these

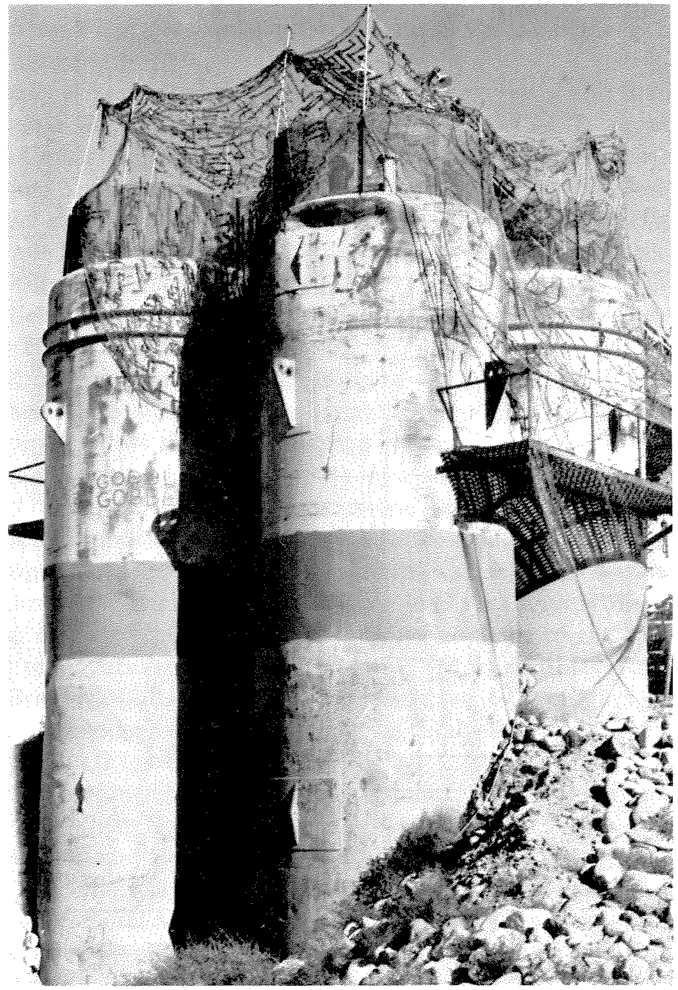

Figure 7. New Mexico Institute thermally insulated stainless steel tanks used in dump leach simulation test. Tanks are 40 ft high (about 1/3 buried) and 10 ft in diameter. Camouflage netting is to shield tops from sun. Catwalks provide access to sampling ports.

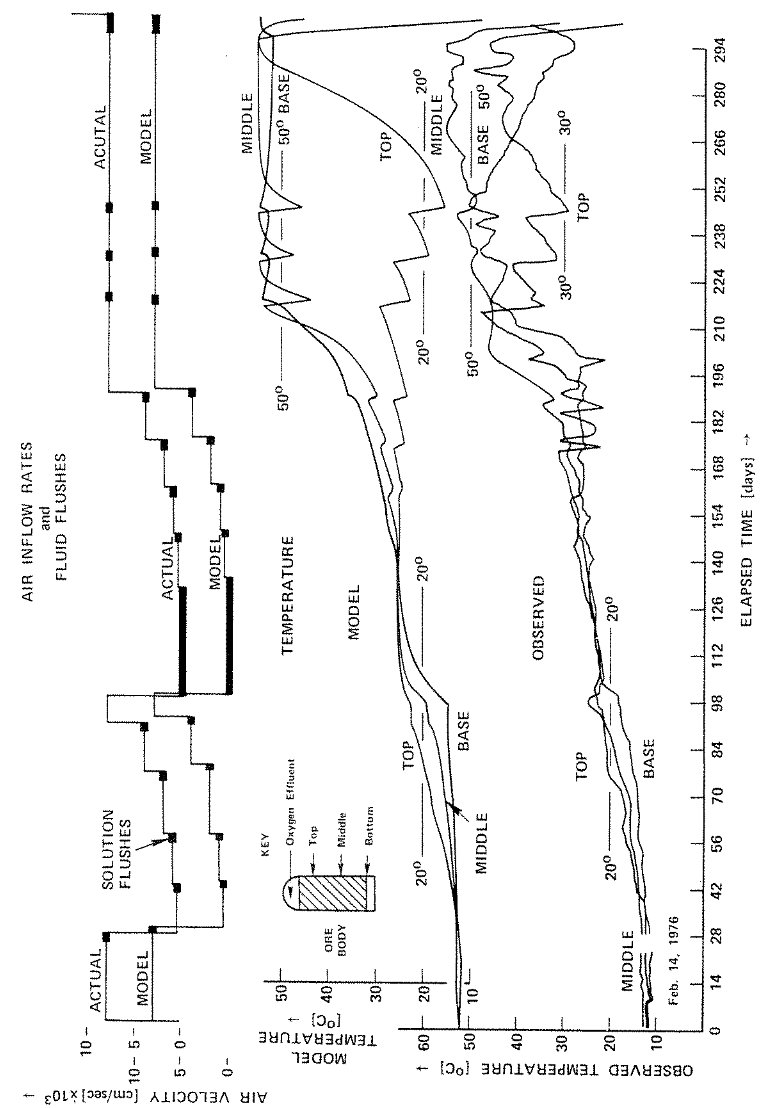

Figure 8. Comparison of temperature response of column predicted by model to that observed (parameter values as in Table 1). History of air injection and solution flushes is also shown (both as it actually was and as it was assumed to be by the model for case of program construction).

features in a subsequent publication. The important thing here is that the prediction that leached rims should be easily observable was confirmed.

Predicted dump permeability is more problematic. During leach fluid application the top surface permeability of a dump can be reduced to a few darcys or less (as indicated by ponded percolation rates). However air injection tests show gas permeabilities in the dump interior to be so high as to be unmeasurable. Even at injection rates of 500 SCFM, the small observed pressure drop is entirely attributable to that expected to occur in the pipe and tubing string. In the dump interior at least, the model permeability predictions seem confirmed.

Finally a major test of the model was designed in a 10-ft diameter 40-ft high double walled thermally insulated tank (see Fig. 7) at the John D. Sullivan Center for In Situ Mining Research at the New Mexico Institute of Mining and Technology in Socorro, New Mexico. The test was designed using the model described above and results of the test predicted. The test was carried out by New Mexico Institute personnel under the direction of Dr. Larry Murr, chairman of the Metallurgy Department and is described in greater detail in Cathles, Reese and Murr (1977) and Murr, Cathles, Reese, Hiskey, Popp, Brierley, Bloss, Berry, Schlitt, and Hsu (1977). The most dramatic and easily testable prediction of the model was that the column should heat up to ~55°C (but no hotter) in 5 to 8 months.

Figure 8 shows that the prediction was confirmed by the test. The best fitting model to the first year of test data shown in Figure 8 matches the observed data quite well. Note, for example, that the middle and top of both observed and model columns cool when leach solutions are applied, but the base temperatures are increased by solutions warmed in their transit through the column. Bacterial activity was high in the column from the start of leaching; the bacterial activity decreased in portions of the column which reached temperatures greater than ~50°C (Murr, Cathles, Reese, Hiskey, Popp, Brierley, Bloss, Berry, Schlitt, and Hsu 1977, Figure 7a, d). This supports the model hypothesis of bacterial catalysis as a necessary link in the leaching chain (Figure 3).

Model parameters were constrained quite closely by the column data and there was very little trade off possible between different variables. That is, one variable could not be adjusted to cancel the effects of changing the value of another. The analysis of the column data in terms of the model is discussed in Cathles, Reese, and Murr (1977). The results of that analysis are summarized in Table 1, which compares the values parameters were anticipated to have before the test on the basis of analysis of test dumps, to the values determined in the column test.

It is clear from Table 1 that although the model can be made to match observations quite closely parameter values are quite different from those anticipated. The principal differences are a significantly larger than expected value of the chemical sulfide leach time, τ_{CS}, a much larger than expected chemical sulfide activation energy, E^*_{CS}, and a much faster than expected leaching of nonsulfide copper (reflected in low values of τ_{CNS} and τ_{DNS}).

The larger value of τ_{CS} is actually in better agreement with initial estimates from rock characteristics of 903 months. (Cathles and Apps, 1975; Cathles, Reese, and Murr, 1977). The large value of E^*_{CS} is explicable in terms of the increase in Fe^{3+} concentration with temperature observed in the column. Assumption of constant Fe^{3+} was a known weakness in the model (Cathles, Reese, and Murr, 1977); a high value of E^*_{CS} is a convenient method of correcting this deficiency.

From the point of view of predicting waste leaching the biggest surprise was the very fast flushing of nonsulfide copper. This was recognized as a possibility but was not indicated by analysis of the test dump data and was therefore not expected in the column test. Excuses could be hypothesized. For example, the column waste sat uncovered and exposed to the air for a substantial time before it was loaded into the column. Some preleaching might have occurred at this time. Some of these questions will be answered when the column is examined mineralogically after the test. Nevertheless we were very surprised by the rapid rate of nonsulfide leaching.

We concluded from the column test and its analysis: (1) The general validity of the model described in the first part of this paper was confirmed. (2) The model should be useful for exploring changes from base case situations. But (3) we are still a long way from being able to reliably predict how a particular dump constructed of a particular waste type will leach (Cathles, Reese, and Murr, 1977).

CONCLUSIONS AND DISCUSSIONS

We have constructed a useful and successful model of the dump leaching process. It has provided insights and guidance to improvement of an economically significant industrial process. The model has made many predictions (permeability, bacterial catalysis, the existence of leached rims) that have been confirmed. The model was successfully used to predict the general features of a large scale column test. However the model cannot yet be used to accurately predict how a given dump or known waste type will leach. We were badly off in detailed predictions of the New Mexico tank experiment.

Prediction of the leach behavior of a given waste prior to leaching is clearly a critical area where further work is needed. It may be that small column tests in conjunction with modeling of the sort presented here will tighten our predictive capability. It may be that accurate prediction of the leach of a new dump will, as a practical matter, always be beyond our ability.

Fortunately models need not depend entirely on a full predictive capability for their utility or justification. The conceptual insights provided by such a model are useful in themselves, even industrially. Careful testing of the model gives added confidence in those insights and increases their usefullness.

ACKNOWLEDGMENTS

The work reported here would not have been possible without the help and support of many people. The initial model was conceptualized with the help of John Apps, then at Kennecott's Metal Mining Division—Research Center in Salt Lake City (now at the Lawrence Berkeley Laboratory in Berkeley, California). The author participated on a Metal Mining Division Task Force on Dump Leaching under the direction of Dave Reese. Interaction with leaching personnel on this task force made possible the initial calibration of the model. Frank Dudás, in collaboration with the author, collected and analyzed waster material to document the leached rims. Collaboration with Larry Murr at the New Mexico Institute of Mining and Technology made possible the most stringent test of the model. Jonathan Jackson of Kennecott's Metal Mining Division Research Center ran the air injection tests that allowed inference of interior dump permeability and kindly allowed us to cite his results. The author would like to thank Kennecott Copper Corporation for support of the research reported in part in this paper and for permission to publish the results.

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