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Chapter 10

Attempts To Model the Industrial-Scale Leaching of Copper-Bearing Mine Waste

L. M. Cathles

Department of Geological Sciences, Cornell University, Ithaca, NY 14853

The problem of how to match models and reality is fundamental to the safe disposal of hazardous waste and other chemical problems in the natural environment. Research on industrial processes carried out in natural or near-natural settings can provide particularly valuable insights for two reasons: (1) the scale of industrial processes, being intermediate between laboratory and nature, is small enough to allow careful monitoring and post-mortem investigation, and (2) the commercial value of these enterprises, in many cases, already has encouraged and funded extensive model development and testing. Examples include copper leaching in low-grade industrial sulfide-waste dumps, *in situ* leaching of copper from unmined formations, and tertiary oil recovery by steam flooding. Here we describe some studies carried out on copper-heap and *in situ* leaching in the 1970's. The modeling and testing clearly revealed the fundamentals of the heap-leaching process, suggested some new approaches for improving the leach efficiency of the dumps, and provided a basis for optimizing the design of new dumps including completely new kinds of dumps. The work also led to some novel field tests. The accurate, *a priori* prediction of the behavior of a new dump remains elusive, however, despite excellent models and extensive testing.

For the last 50 years or so it has been common practice to leach copper from material that must be mined to access ore but which contains too little copper itself to be processed by crushing, froth flotation, and smelting. This leaching is accomplished by deliberately applying water to the top surface of heaps of waste material. The water exits the dump acidified and copper-laden. The copper is typically removed by passing the solutions through vats containing scrap iron. The copper replaces the iron and the iron-rich solutions are recirculated through the dumps. The resulting copper

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"precipitate" is removed and sold. In some cases the waste heaps can be very large, filling entire canyons near the mine. Where more land is available, the heaps are generally about 75 ft thick and 300 ft across and are shaped like long fingers, and are called finger dumps.

The dumps are significant economically. In the 1970's Kennecott Copper Corporation obtained about 20% of its copper production (or $100 million of copper per year) from leaching waste dumps. By the 1970's some of Kennecott's dumps had been leached for over 30 years. The initial recovery of copper from the dumps had been spectacular, causing them to be named "Bluewater I", "Bluewater II", etc., after the bright-blue copper-sulfate color of the water. With time, however, the copper concentration in the leach solutions steadily declined. Significantly, this decline was proportional to the inverse of the square root of the time.

These dumps have taught us much about the modeling of natural (or near-natural) processes. Some of what was learned and some pertinent references are given below.

Leaching Copper-Bearing Mine Waste

Quantitative investigation of the leaching process (1) quickly suggested two important controls: The first derives from the fact that sulfide material must be oxidized to be solubilized. The oxidant is supplied by the oxygen in air convecting into the waste dumps. The stoichiometry is such that 20 to 40 times more air than water must circulate through the dump and have its oxygen removed to solubilize the copper observed in the waters exiting from typical dumps. The air convection is driven in large part by the heat generated by the exothermic sulfide-oxidation reactions. The dumps heat to between 55 and 65°C. Convection is assisted (and started) by the fact that oxygen-deficient air is lighter than air with normal oxygen content, and air saturated with water vapor is less dense than drier air.

That air convection is an important factor in dump leaching was confirmed in retrospect by a well-instrumented test dump (1). The Midas Test Dump, operated at Kenecott's Bingham Canyon Mine, had nests of 4 concentric pipes installed and instrumented with thermocouples during construction so that air samples could be drawn from 4 different depths in the 40-ft-thick dump. The dump heated to ~55°C six months after the start of leaching. Oxygen content was near normal at the base of the dump and 50 to 100% depleted at the top, indicating that air was convecting into the high permeability base of the dump and then upward. The base of a dump is more permeable because large boulders roll to the base during construction and are subsequently overlain by finer material as the dump is built outward. Oxygen concentration decreased as the air moved upward. The pattern of oxygen concentration was exactly the opposite of that expected if oxygen was diffusing into the dump; in which case the oxygen content should have been greatest at the top and least at the base.

Air convection is also evident in larger dumps where air visibly (e.g. smoke from a match) moves into some holes drilled into the dump, and out of others. The outward flow of warm, moist air from such holes is sufficient to easily steam a stamp off an envelope. Where a grid of holes has been drilled, a coherent pattern of air convection is observed.

The second factor controlling the rate of leaching that was evident early in our studies was the control of leach rate by the progressive development of "leached rims" on waste fragments in the dumps (1,2). The existence of such leached rims, or rims from which all copper sulfides have been leached, was suggested by the inverse-square-root-of-time decline of copper concentration in dump effluent, and also by kinetic calculations. No one had previously observed such rims. In fact they are not apparent even in sectioned waste fragments. However if the copper-sulfide distribution is imaged by exposing the cut fragment to nitric acid fumes and pressing it on chemically prepared blotter paper, or if the sulfide distribution is point-counted under a microscope, the presence of leached rims is immediately evident. In fact, investigation also showed another interesting phenomenon. Leached copper diffuses into the waste fragment as well as out through the leached rim. This inward diffusion leads to the secondary enrichment of chalcopyrite ($CuFeS_2$) in the interior of the fragments to covellite (CuS) and chalcocite (CuS_2). In dumps permeable enough to support good air convection, the rate of leaching is controlled by the rate of diffusion of oxidant (Fe^{3+}) through the growing leached rim.

These controls provided a basis for the construction of a model (1) of the dump-leaching process that included both kinetic control by diffusion through growing leached rims, and the supply of oxidant by air convection. This model was tested and calibrated against all available Kennecott test-dump data, especially that from the Midas Test Dump. The heating and leaching of the Midas Test Dump could be simulated by the model very well as shown in Figure 1. The modeling of larger dumps, however, suggested that the presence of another control had been missed: the bacterial catalysis of the oxidation of Fe^{2+} to Fe^{3+}. In the absence of this control the model indicated dumps should heat to temperatures close to boiling and not stop at 55 to 65°C as is observed. *Thiobacillus ferrooxidans* bacteria are known to go dormant at about 55°C, with some high-temperature strains remaining active to 65°C. The model was refined to include bacterial catalysis and the model dumps then operated in the temperature range observed in real dumps (2). The model was also extended to two spatial dimensions (3).

The final test of the model was provided by column tests at the New Mexico Institute of Mining and Technology (4,5). The columns used were surplus liquid oxygen (rocket propellant) storage tanks. Each was double walled, 40 ft high, 10 ft diameter, stainless steel, with 1 ft of perlite insulation between the walls. One of these columns was instrumented to our design, and filled with 160 metric tonnes of mine waste form Kennecott's Chino Mines Division at Santa Rita, New Mexico. A schedule of solution flushes and detailed predictions of column temperature and copper recovery were made from the parameters determined from the modeling analysis of four test dumps at Santa Rita. The most unequivocal of the model predictions was that the 160 tonnes of waste would heat up to 55 to 65°C in about 6 months, and then cycle in temperature according to the ambient temperature and solution flush schedule.

The column was leached for two full years, first under contract from Kennecott, and later with funding from the National Science Foundation - Research According to National Needs (NSF-RANN) program. The operation of the column confirmed major aspects of the model predictions, in particular the heating up to 55-65°C. In fact the

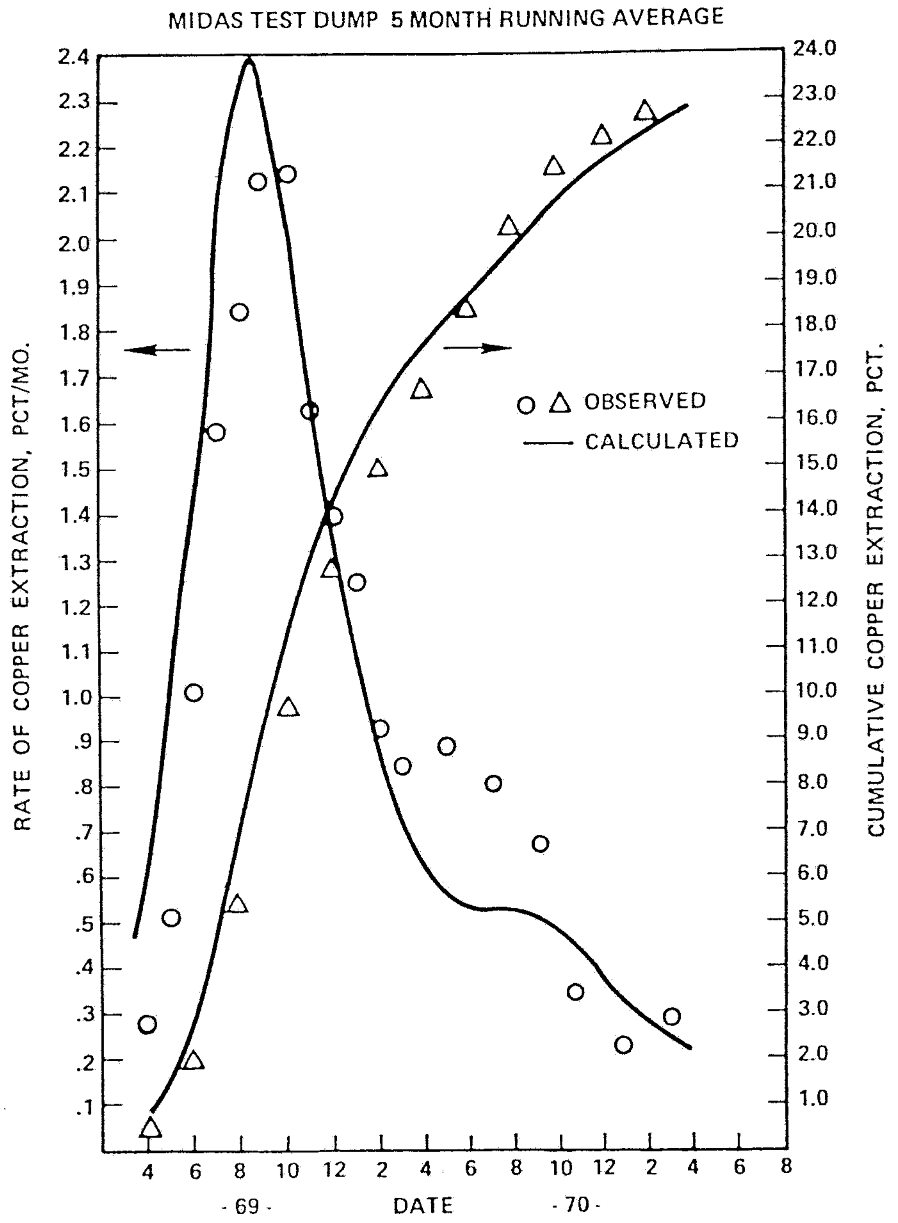

Figure 1. Model predictions of the cumulative extraction and rate of extraction of copper from the 40 ft high Midas Test Dump agree well with the observed rates. Reproduced with permission from ref. 1, copyright 1975 Metallurgical Transactions.

gradual development of the higher temperature strain of bacteria could be seen in the temperature response of the column. Details of the amount and rate of copper leaching were missed by the model, although with recalibration, the model was able to describe all aspects of the leaching very well. In fact the modeling was accurate enough to require inclusion of a finite thermal conductivity of the insulated column walls to simulate the test results accurately.

The column operation provided other insights. At the end of the experiment rodamine-B dye was added to the leach solution, and a careful record kept of the red-stained percentage of the waste as it was unloaded and assayed. Fifty-seven percent of the copper originally in the waste was removed in the two years of leaching whereas only 50% of the waste was stained red. The clear implication of this observation is that the flow pattern shifted with time during leaching. I suspect that this is a general phenomenon. It is required, for example, to explain the very uniform oxygen isotopic alteration of the ocean crust. Shifting of flow patterns so as, on average, to provide uniform rock access, has important implications for the long-term rates of migration of contaminant fronts.

Discussion and Conclusions

The experience of modeling waste dumps is unusual in the intensity and thoroughness with which models were tested. This was allowed by the tractable scale of test dumps, the availability (at the right time) of large columns and the willingness of New Mexico Institute personnel to work on the project, and by the economic importance of the process to industry. Some conclusions of broader interest can be extracted from this work.

First it was possible to develop good models with good predictive capability. The models provided and continue to provide a very useful framework for designing optimum dumps and identifying ways to improve the operation of old dumps (such as air injection) and in assessing the magnitude of expected benefits. Model-guided observation is very useful. For example models directed attention to leached rims and instigated a deliberate search for them. Models led to clarification of the role of bacterial catalysis.

Second the experience indicates the importance of combining modeling and observation and constantly testing and refining the models developed in terms of the objectives of the project. Kennecott formed a task group consisting of engineers, line managers, research scientists, and dump operators for this purpose. This task group met frequently over a four-year period. The interaction was at times sobering. I remember in particular on one occasion explaining to a dump operator that directing water specifically to hot spots on the dump, which was their deliberate practice, was the wrong thing to do. The hot areas should be encouraged because heat promotes faster leaching. Further modeling, in fact the discovery of the importance of bacterial catalysis, proved me quite wrong and the operator quite right. Hot areas cease to leach if the temperature gets too hot. Models with bacterial catalysis included showing that the application of water to overly hot areas will dramatically speed leaching, just as the operator suggested. Sometimes the exchange went the other way. For example as the work progressed it became clear that great amounts of effort had, in retrospect, been wasted trying to fertilize dump bacteria and dissolve iron sulfate and unclog the dumps by applying ammonia bisulfite to the leach solutions. The bacteria have sufficient nutrients in the waste water. Permeability reduction by iron sulfate precipitation is a problem mainly very near the dump surface and is best remedied by plowing or adding acid to the leach solutions. If dumps are oxygen starved, air injection may make economic sense, a possibility that could not have been appreciated in the absence of modeling.

Model development provided a basis for deliberately designing optimum dumps and dump operation. It also suggested the laboratory measurements and procedures that could best lay the groundwork for predicting how new kinds of dumps might operate. These procedures were later applied to investigating whether pyrite could be economically removed from coal by heap leaching (6), or whether copper-waste dumps could be effectively operated in the Andes at over 15,000 ft elevation where temperatures drop below freezing every day of the year. The analysis results (7) are shown Figure 2.

The models of the copper-waste leaching process were not able to predict in detail how a waste of given type would leach, as was evident from the failure of the New Mexico column to match predicted leaching details. Whether better predictions could have been made had the procedures used in predicting coal depyritization by heap leaching (6) been applied to the Santa Rita waste is at present unclear. The New Mexico column waste was not analyzed in this fashion, and the coal leaching predictions were never subjected to the ultimate test of heap construction and operation. My own experience suggests that although models are useful, and often the *only* way to understand and predict a natural process, model predictions of natural processes should not be expected to be capable of fully accurate *a priori* predictions. If, however, an experiment or process can be monitored for a time, good models can be calibrated, and much better predictions made.

Industrial processes of other kinds may also be relevant as natural analogues of hazardous-waste disposal. I have limited myself here to the discussion of just one example. Other examples might be briefly mentioned because of their chemical relevance and the obscurity of the literature in which they are published. One is a tracer experiment performed to assess the accessibility to diffusional leaching of the matrix blocks that lie between the fractures in a porphyry copper deposit. The hope was to leach the matrix with a lixiviant introduced through the fractures. The difference in arrival time between a diffusing (NaCl) tracer and a non-diffusing tracer (in this case 0.5 micron silica beads) provided a direct measure of diffusional accessibility. A field test appeared to confirm this theory (8). Matrix diffusion is important because it is one of the principal factors determining how fast a contaminant front will migrate. Another example of chemical interest is the application of heap leaching models to acid mine drainage. As shown in Figure 3, bacterially catalyzed Fe^{3+} oxidation of pyrite, facilitated by air convection through a coal waste pile before the pile is buried, can proceed at rates similar to those observed in copper waste dumps (~1% per month). This rapid oxidation can produce enough acid (stored as jarosite salts) in one year to acidify 20 inches per year of infiltrating rainfall to pH 2 for 108 years after the waste is

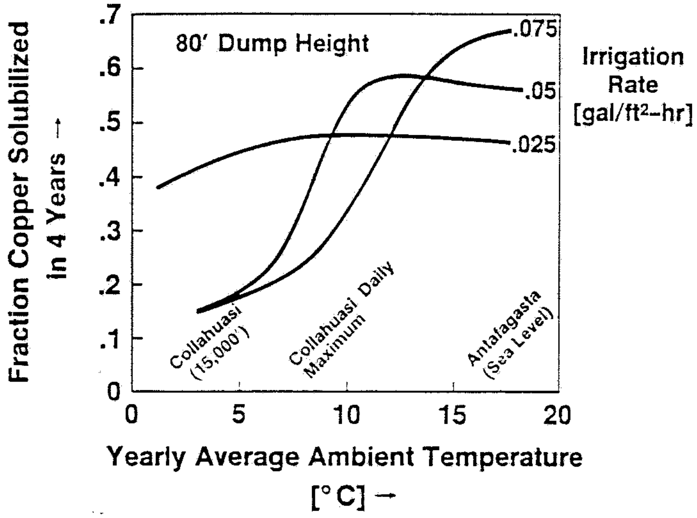

Figure 2. Model calculations show that the copper waste dumps should operate effectively in cold climates provided the average rate at which flush waters are applied to their top surface (the irrigation rate) is reduced to about a third of the optimum rate in warmer climates. Reproduced with permission from ref. 7, Chevron Oil Field Research Company Technical Report.

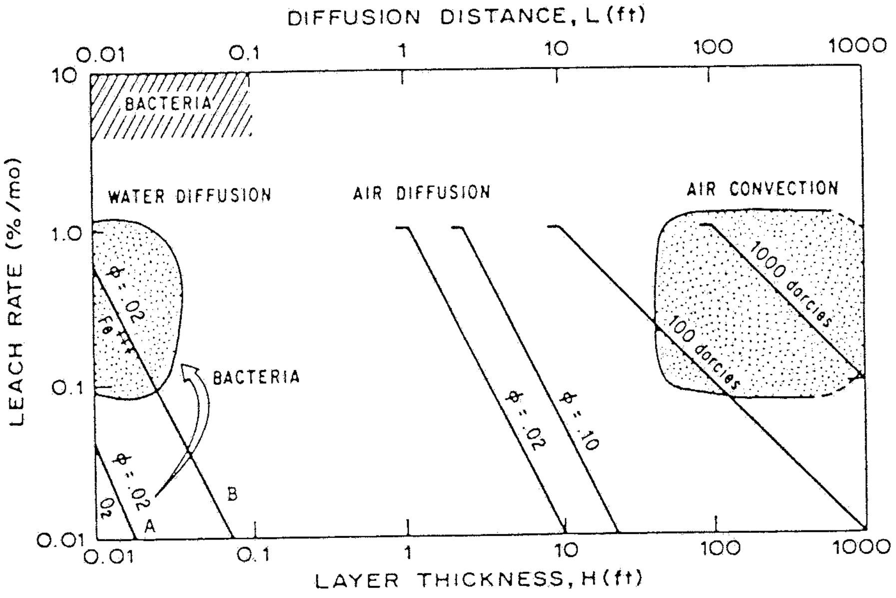

Figure 3. Leaching of copper waste at commercial rates of ~1% per month from >70 ft high dumps is made possible by air convection and bacterial catalysis (two stippled regions). Air convection is necessary to supply oxidant to the interior of the dump at the required rates. Bacterial catalysis is necessary to oxidize Fe^{2+} to Fe^{3+} by O_2. The high concentrations of Fe^{3+} in the dump waters speeds the diffusion of oxidant into the rock fragments in the dump by a factor of ~17 (open arrow, left side of diagram). Reproduced with permission from ref. 9, copyright 1982 The Pennsylvania State University.

buried (9). This is an unconventional view of the origin of acid mine drainage and suggests remedial procedures very different from those in current use.

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