THE RECLAMATION OF HEAPS USED FOR

ACID LEACHING

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ABSTRACT

    Chemistry and physics of bacterially enhanced, acid leaching of
waste dumps are reviewed from the prospective of subsequent
reclamation practices. Methods for treating acid mine waters and
preventing their continuance are considered. Since many questions and
uncertainties still persist, research needs are emphasized.

INTRODUCTION

Several mines in British Columbia are examining the technical and economic potentials of acid-leaching their existing or yet-to-be-built waste dumps for additional copper recovery. The Gibraltar Mines dump leach project has just recently become operational. While substantial information has already been published on the establishment of bacterially enhanced leaching operations, information on how to terminate this leaching and reclaim these dumps is relatively sparse. This paper represents a class assignment by students in a course on "Treatment of Mineral Industry Effluents" in the Department of Mining and Mineral Process Engineering at the University of British Columbia. The object was to review relevant mine dump construction practices, dump chemistry and bio-chemistry with a view to establishing important links to subsequent reclamation procedures.

While revegetation of leached dumps can be troublesome and costly the main concern is with the quality of ground waters or runoff waters from a previously leached dump. Low pH and the oft-resulting elevated heavy metals concentrations can produce significant off-site impacts over the long term.

In this paper, the chemistry and rate controlling reactions of acid mine water generation are first reviewed briefly, together with some operating constraints of dump construction and operation. Methods for predicting the changing balance of acid generating minerals with acid consuming minerals as the dump leaches are described. Finally short and long term methods of reducing the rate of acid production are discussed.

We hope that this review might lead to the collection and dissemination of existing operating data on dump leaching relevant to development of reasonable reclamation methods.

Underlining the need for additional research to fill gaps in published information on acid-dump-leaching is a secondary objective.

Chemistry and Physics of Acid-Dump Leaching

Additional economic metal recovery can sometimes be achieved by leaching waste dumps containing sub-milling grades of metal values. Copper is the most common metal recovered by this technology (1). In-place dump leaching can be applied either to preexisting waste dumps not designed to be leached or to planned dumps placed on bases or layers constructed to be impermeable to the leach solutions. Acidic leach solutions are distributed over the surface of the dump, previously levelled and loosened (often by "ripping") to allow ready ingress of the acidic leach solutions. Metal-laden solutions emanating from the toe of the dump are collected and treated by solvent extraction, ion exchange or cementation plants to recover the valuable metals. Over a period of several months or even years, metal recovery might typically reach 60-70%.

In general, for acid leaching to be economic, copper sulphide containing dumps must either be natural producers of acidic-mine-water or be very close to that condition. To generate acidic mine water naturally, waste dumps must in general: (1) contain acid-producing minerals (such as pyrite and pyrrhotite) in excess of acid-consuming minerals (such as carbonate rocks); (2) be sufficiently porous to allow oxygen infiltration; (3) contain an abundant and active population of microbes - i.e., "Thiobacillus ferroxidans" which use atmospheric carbon-dioxide as a carbon source for cell growth and, which oxidize ferrous iron and sulphides for growth energy. The resulting high ferric ion concentration normally becomes the dominant and powerful oxidizing agent which together with the sulphuric acid also produced results in rapid leaching of the sulphide minerals. Figure 1 presents a highly simplified explanation of such a bacterially enhanced leaching reaction. While pyrite is shown to be the mineral attacked, copper sulphide minerals, although usually present in lesser amounts, are similarly solubilized.
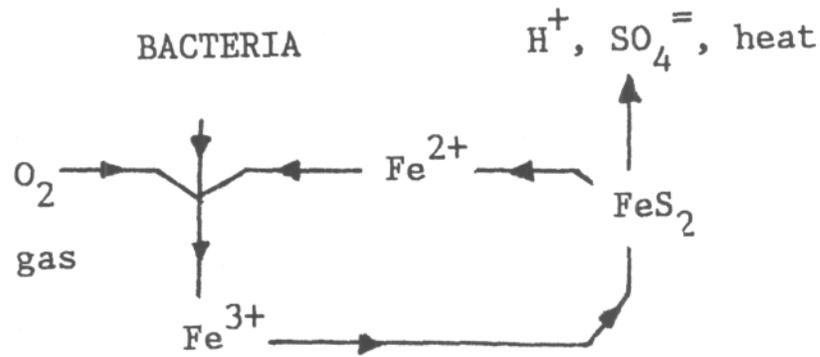
Figure 1 Simplified cyclic nature of bacterially
enhanced acid mine water generation

Although <u>Thiobacillus ferroxidan</u> bacteria are normally indigenous to sulphide dumps, to grow and multiply rapidly, they may require additional nutrients, such as nitrogen, phosphate, and the temperature and acidity must all be optimum. High (> 50°C) and low (< 5°C) temperatures and pH's > ~ 4 will curtail their activity. Certain chemicals called his biocides can also kill or render dormant these bacteria.

The chemistry of the acid leaching reaction is relatively simple, and proceeds in stages. Pyrite or pyrrhotite are almost always involved in the generation of acid mine waters. As an approximation, one mole of pyrite can be oxidized by 3 1/2 moles of oxygen dissolved in water to produce one mole of dissolved ferrous sulphate plus one mole of sulphuric acid. As early oxidation reactions progress and as the pH in the dump reduces to around 3 or 4 bacterial action picks up and produces rapidly escalating concentrations of ferric ion (Fe which then supercedes dissolved oxygen as the predominant oxidizing agent. The rate of acid generation (and the rate of leaching of copper) then depends not so much on the chemistry of the reactions as the physics. In other words, the rate of supply of oxidant (Fe the sulphide surfaces via diffusion mechanisms then controls the rate of leaching.

Although chemically, one expects sulphide minerals such as chalcocite (Cu_2S), covellite (CuS), bornite (Cu_5FeS_4) and pyrite to leach more readily than chalcopyrite this effect is seldom observed in practice. Since the surface electrochemical reactions involved in the oxidation of all these sulphides are fast compared to the rate of supply of oxidant, all these minerals leach in practice at approximately the same rate once the initial "incubation period" is exceeded (2). By "incubation period" we mean the time required for initial acidity to develop and for bacteria to fluorish.

Figure 2 which is based on data taken from Table 1 attempts to illustrate how the rate of supply of oxidant controls pyrite (or chalcopyrite) leach rate (2). This figure shows that oxidant reaches the sulphide surfaces via air convection, air diffusion or water diffusion. Rates of diffusion were calculated using the constants given in Table 1. Figure 2 indicates that with oxygen as oxidant, pyrite (and/or chalcopyrite) would be expected to leach at a rate of about 0.04% per month (line A - lower left corner).
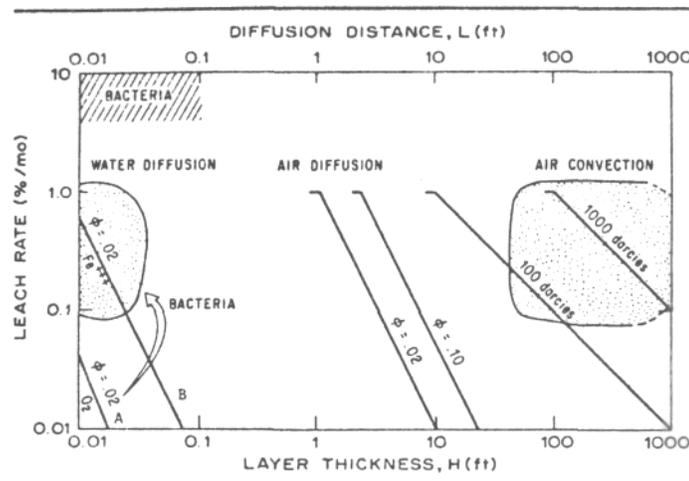

Figure 2 The rate at which pyrite blebs can be leached out of rock or coal fragments is controlled by the rate at which oxidant (O_2 or ferric iron) can reach the blebs. Oxidant transport into the spoil pile is by air convection or by diffusion through air-filled voids. Oxidant transport into coal or rock fragments is by aqueous diffusion. Dotted areas indicate the leach rate and transport mechanisms operative in industrial copper waste dumps. Bacteria could provide ferric iron and allow pyrite leaching at the rate indicated by the cross-hatched area at the upper left if the pyrite were directly exposed to the leach solutions. In realistic cases, where oxidant must diffuse into the spoil fragments, bacterial generation of ferric iron increases the leach rate as shown by the open arrow at the lower left.

(Ref. 2)

Figure 2

Symbol	Definition	Air	Water
D' (cm^2/sec)	Diffusion constant	0.178	2×10^{-5}
ϕ	Formation or rock porosity	0.02 - 0.2	0.02 - 0.1
D (cm^2/sec)	Effective diffusion constant $\simeq D'\phi/5$	$7\text{-}71 \times 10^{-4}$	$8\text{-}40 \times 10^{-8}$
C (g/cm^3)	Oxygen concentration	2.8×10^{-4}	8.6×10^{-6}
ρ	Density	1.3×10^{-3}	1.0

Table 1. Parameter values used in calculations in Figure 1 and in the text are listed here. D, the effective diffusion constant for either individual spoil fragments or the spoil pile, is estimated from D' by multiplying by the formation porosity value and dividing by a tortuosity, assumed to have a value of 5, of the channels in which diffusion takes place. (Ref. 2)

TABLE 1

Bacterial action typically generates Fe concentrations of the order of 1000 ppm or higher which escalates the predicted leach rates into the order of 0.1-1.0% per month (Line B, Fig. 2). These are typical of leach rates often achieved in acid leaching of copper waste dumps. Figure 2 also indicates that oxygen can diffuse through air-filled spaces into a dump much faster than through water-filled pores. Table 1 shows that the much higher diffusion constant of oxygen in air and the nearly 3OX higher concentration of oxygen in air than in air-saturated water jointly account for this effect. Figure 2 also indicates that to support leach rates approaching 1% per month at dump thicknesses in excess of approximately 10 ft, air convection becomes critically important. The exothermic nature of the sulphide oxidation reactions creates heating within the zones of rapid oxidation and a chimney effect in the dump. This effect sometimes results in higher leach rates in cold weather than in hot weather due to increased convection currents generated by the larger temperature differences.

While an understanding of Figure 2 could be crucial in conducting a successful dump leaching operation, the same principles might obviously be important in attempting to halt generation of acid mine waters. This will be discussed further in later sections.

MINE RECLAMATION GUIDELINES AND REGULATIONS

B.C. reclamation guidelines provide operators with a series of general requirements applicable to the reclamation of leached-waste dumps. Grading dump faces to < 27° is recommended unless operators can show validity of doing otherwise. Steps should also be taken to "ensure long-term water quality is preserved" and to ensure "all potential acid generating material shall be disposed of in a manner which prevents acid mine drainage" can also be found. The government also requires monitoring procedures to ensure that potentially toxic materials are disposed of in a manner which prevents adverse effects.

While general statements in guidelines and acts abound it is very clear that in large part onus is on the mining industry operators to develop reclamation technology to ensure high standards at reasonable costs.

B.C. and Federal regulators have set effluent guidelines or standards to preserve water quality (15,16). Table II shows examples of existing standards in comparison to ranges of contaminants typically present in acidic mine waters.

TABLE II

CONTAMINANT CONCENTRATIONS

	B.C. Ministry of Environ. dissolved, ppm (lowest levels)	Federal, total, ppm	Typical A.M. Water dissolved, ppm
As	0.10	1.0	1.0
Cu	0.05	0.6	20
Pb	0.05	0.4	5
Zn	0.20	1.0	3
pH	6.5	-	1.5 - 3.5

MONITORING OF WASTE DUMPS

Chemical analyses of runoff waters or waters seeping from a waste dump provides an indirect measure of leaching reactions occurring perhaps deep within a dump. Figure 3 shows how heavy metal concentrations and pH changed during one six hour period following a heavy rain on an acid-producing dump (3). While heavy metal and dissolved $SO_4^=$ concentrations peaked towards the end of this six hour drainage event, total contaminant releases were actually highest near the peak flow rate. This figure serves well to indicate that monitoring both flow rates and contaminant concentrations is crucial to understanding the severity of an acid mine water problem.
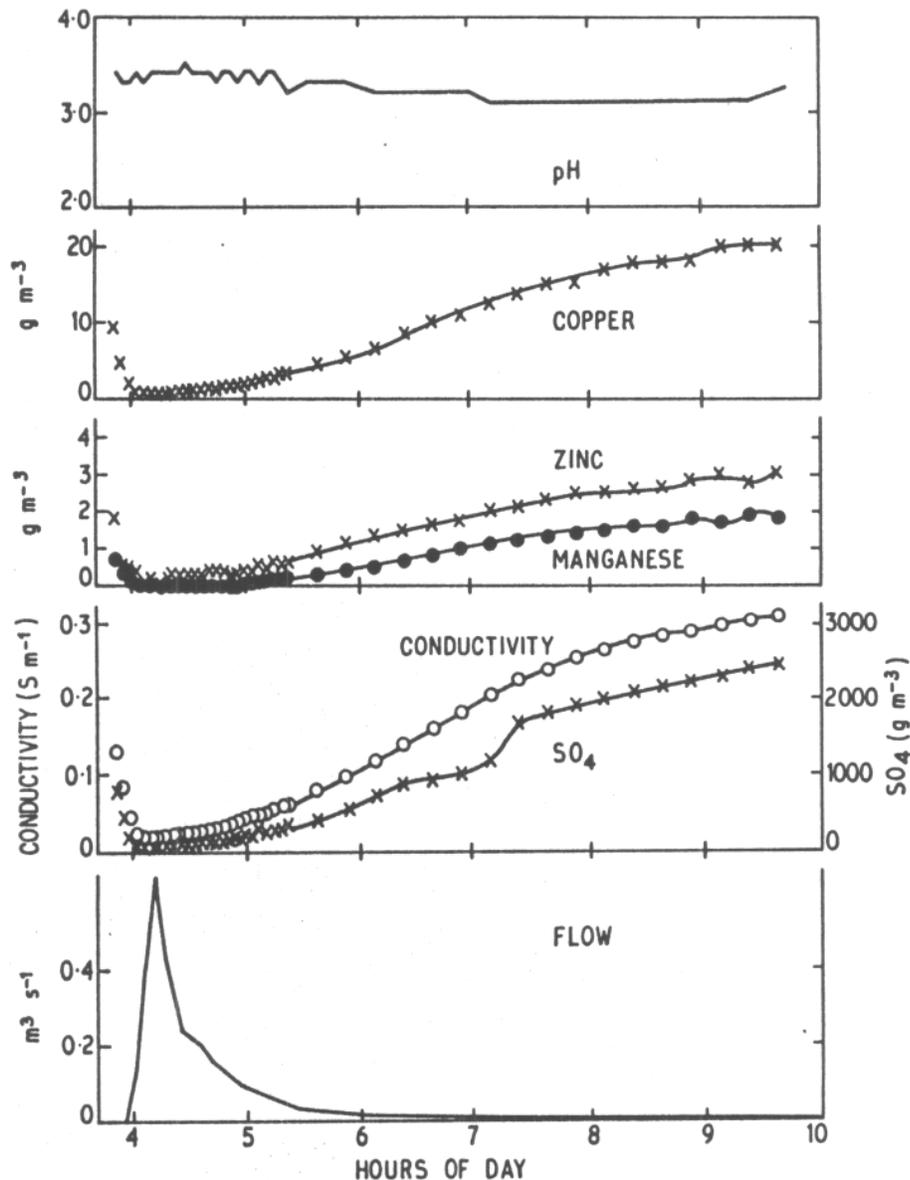

Fig. 3   Quality of runoff water during an event commencing 4 a.m. 4th March, 1977. (Ref. 3)

Basic questions about the progress of acid-base rock accounting as the dump leaches seem as yet unanswered. Does dump leaching consume acid-producing components faster than acid-consuming rocks? If so the dump would be left in a state less able to generate acidic-mine waters naturally than prior to the leaching. If the opposite is true, the acidic mine water problem might be worsened at least until the acid producing minerals are consummed. Periodic sampling (drilling) and acid-base accounting should answer the above questions and indicate the potential problems that might continue after dump leaching is terminated.

Acid-base accounting laboratory-test procedures differ in detail (4), (5), (6). The potential of waste rock to produce acid or alkaline runoff or seepage waters can be indicated by making two determinations :

(A)   maximum potential acidity is usually equated chemically to determining total sulphur content of a small but representative sample and considering that all of this sulphur might be converted to sulphuric acid. The acid production potential can be variously expressed as kg sulphuric acid per tonne of sample or as calcium carbonate equivalent to neutralize (1% sulphur = 31.25 kg calcium carbonate per tonne of sample). Should significant sulphur, in the original waste rock sample exist in non-acid producing forms (such as inorganic sulfates or organic sulphur) this first determination will markedly overestimate acid-producing potential.

(B)   Measure of the neutralizers present in the waste rock is called either acid consuming potential (5) or neutralization potential (4). In the B.C. Research procedure a 10 g ground-sample of the material is titrated with cold H_2SO_4 until a constant pH of 3.5 is attained (5). This test can take many hours or perhaps days. In the Sturm Environment Services procedure, a sample is treated with an excess of HCl and heated to speed up reactions. Excess HCl is back-titrated with a standard base to pH=7 (4). This

test takes only a few hours. Results can again be expressed as
acid consuming potential in kg H_2SO_4 per tonne or as $CaCO_3$
equivalents per tonne. Subtracting potential acidity from
neutralization potential then indicates potential acidity. In
the sturm procedure, a negative value exceeding 5 tonnes
$CaCO_3$/1000 tonnes of rock is said to indicate a potential acid
producer.

When using the B.C. Research procedure, if the acid producing
potential exceeds the acid-consuming potential then the waste rock
might naturally go acid. In the B.C. Research procedure, confirmation
tests could then be conducted where an acidified sample is inoculated
with <u>Thiobacillus ferrooxidans</u> to run a more realistic kinetic-type
test (5). If the pH attained is less than 3.5 a net acid production
hazard is said to be confirmed.

Arguments can be made for and against each of the above two
methods of acid-base accounting. The speed of the hot-acid titration
procedure makes it much more attractive if samples are numerous.
Ferguson (6) has recently evaluated the above procedures and found
that the chemically-determined "static-type" tests were often accurate
in predicting drainage quality. Kinetic test methods are not commonly
used due to their longer duration and higher cost.

MITIGATION TECHNIQUES

After shutting down a waste dump leach project, operators can
expect to have to treat continuing acid mine drainage in the short
term. Longer term methods to terminate acid production are much more
desirable since otherwise treatment might be expected to continue for
dozens or even hundreds of years.

<u>Treatment</u> most often involves collection and addition of alkaline
reagents, such as lime, to neutralize acidity and to precipitate
dissolved heavy metals. Sometimes neutralization should be preceeded
by an oxidation stage to make several metals more readily precipitate

as hydroxides. Local B.C. treatment plants have been well reported in our technical literature (7,8). Figure 4 shows highly simplified schematic flowsheets of such treatment plants. Capital and operating costs can both be high and low-density precipitate sludge disposal problems can be difficult.
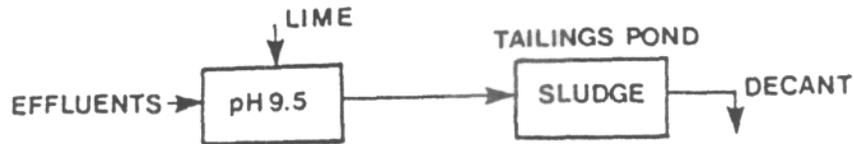

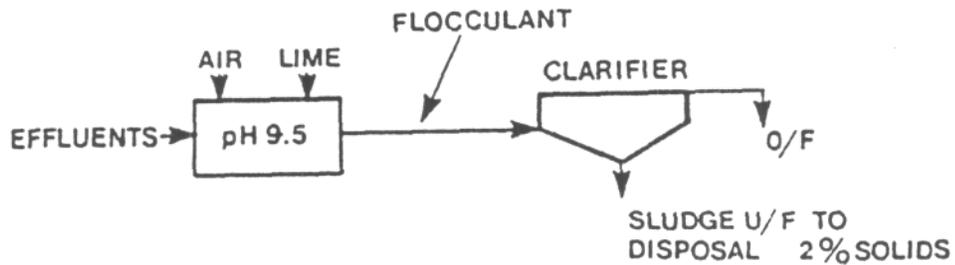Figure 4a Simple neutralization flow sheet
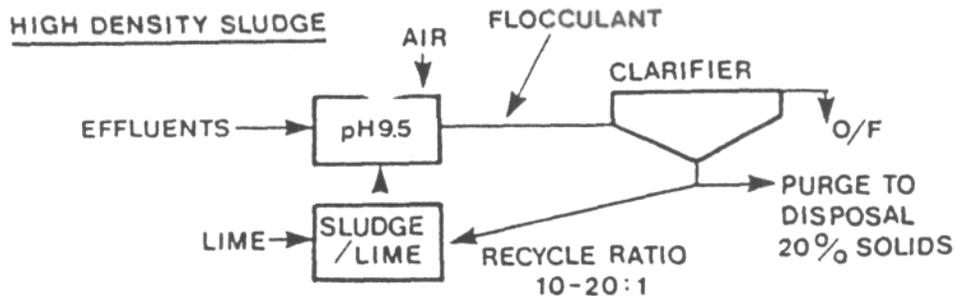

Figure 4b Neutralization plus flocculation

Figure 4c High density sludge flowsheet

Figure 4 Alternatives in treating AMD with lime (Ref. 17)

Passive water treatment systems sometime offer the prospect of continuous low cost treatment of AMD. These systems attempt to utilize natural geochemical processes such as: dilution, oxidation, neutralization, absorption and precipitation for heavy metal removal and acid neutralization. Basic components of a passive treatment system include an ion exchange medium, a neutralization medium and an aeration device.

Several studies have been made of the use of "WETLANDS" to treat AMD (9). A peat bog filled with sphagrum moss seems to offer an effective organic ion exchange medium. This moss has high tolerance of strongly acidic conditions and can remove four or five times as many cations as clays for example. In addition sulphate-reducing bacteria thrive in the anerobic bottom of bog. These bacterial appear capable of precipitating metal sulphides by microbiological processes (10). Following bog-removal of most heavy metal ions, excess acidity can be removed by passing the effluent through or over limestone barriers or trenches. Several artificially constructed wetland treatment sites are under evaluation in Pennsylvania and West Virginia (11). One major practical problem is the large area requirement for a bog to handle high flow rates.

Termination and Prevention of Acid Mine Drainage generally requires minimizing access of reactants such as air and water to areas undergoing biologically enhanced oxidation. Sealing techniques might also be preceded by the injection of biocides and neutralizers to attempt to "turn off" the acid-producing reactions quickly.

Bacteriacides that have been tested with significant success are mainly anionic surfactants such as sodium lauryl sulphate (SLS). These reagents act at concentrations from 2-5 mg/l and are themselves biodegradable. At low concentrations the surfactant is said to decrease the activity of pH sensitive enzymes within the bacterium. At high concentrations SLS can kill the bacteria by disagrregation of their cell walls (12).

Field trials of SLS have been conducted at coal refuse sites in West Virginia (12) and at Equity Silver Mine in B.C. (13). In West Virginia, application of SLS (as a 30% solution-diluted 175:1) amounted to -150 lbs SLS/acre. Over a one to three month period, water quality improved dramatically as shown in Figure 5. After four months, contaminant concentrations slowly rose to near previous levels. Similar testwork at Equity Silver Mines produced negligible improvement in contaminant levels (13). This failure was believed due to the rapid hydrolysis of SLS in the highly acidic Equity waste dump. Prior effective alkaline injection might have enabled the SLS to become biocidal before it degraded in the dump.
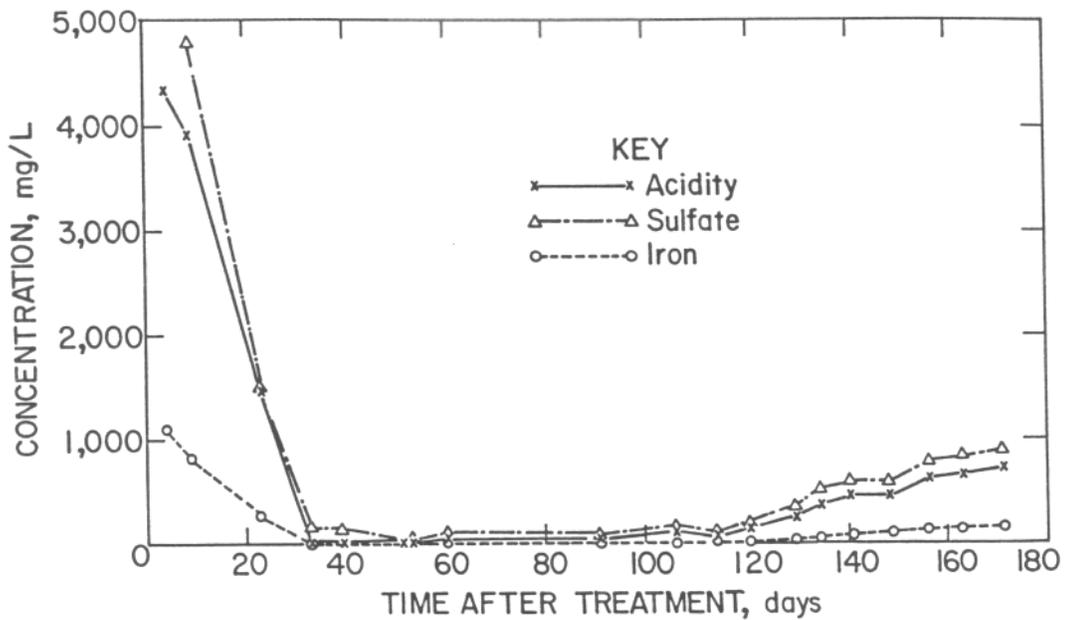

Fig. 5 Improvement in drainage quality following
surfactant solution application (Ref. 11).

Alkaline Injection tests both in Pennsylvania and at Equity
Silver have been largely unsuccessful. In Pennsylvania a 4% lime
slurry was injected using 15 wells 90 meters up-gradient from an AMD
seepage area. In one test nearly 120 tons of lime were injected over
an eight month period (12). Minimal impact was observed due
apparently to the deposition of the lime suspension in the immediate
vicinity of each injection well. Solubility of $Ca(OH)_2$ was deemed too
low for it to act effectively throughout the spoil pile. Sodium
carbonate was recommended for subsequent testing. At Equity injection
of an alkaline sludge into a waste rock dump caused an initial
significant decrease in dissolved copper and zinc levels as shown in
Figure 6. After around 90 days however, re-dissolution of metal
hydroxides in the injected sludge increased concentrations of these
two heavy metals above those emanating previously. These results did
however show promise and probably deserve further testwork -
particularly if alkaline injection can be combined with later sealing
techniques.

Minimizing access of air to a waste dump is generally regarded as
the most effective long term measure for reducing AMD. Sometimes
water-flooding can achieve this goal (4). More often, methods to seal
the surface of the dump with impervious "coverings" must be sought.
Membrane liners are usually too expensive and possibly ineffective in
the long term.

Testwork by Harries and Ritchie at the Rum Jungle mine site are
particularly interesting (14). These authors have conducted testwork
on two test dumps over the last 10 years. They examined attempts to
limit the influx of air and water by recontouring and top covering the
dump with graded clay and sands. The top of one dump was resloped at
a maximum 5° and covered with 22 cm of compacted clay plus 25 cm of
sand and then another 15 cm of gravelly sand. The sides were resloped
at 1:3 horizontal and given a somewhat similar sealing-cover. The
tops were also revegetated to provide erosion control. Holes were
drilled to provide temperature probes and gas compositions within the
dump. Figure 7 shows the steady reduction in oxygen concentration at
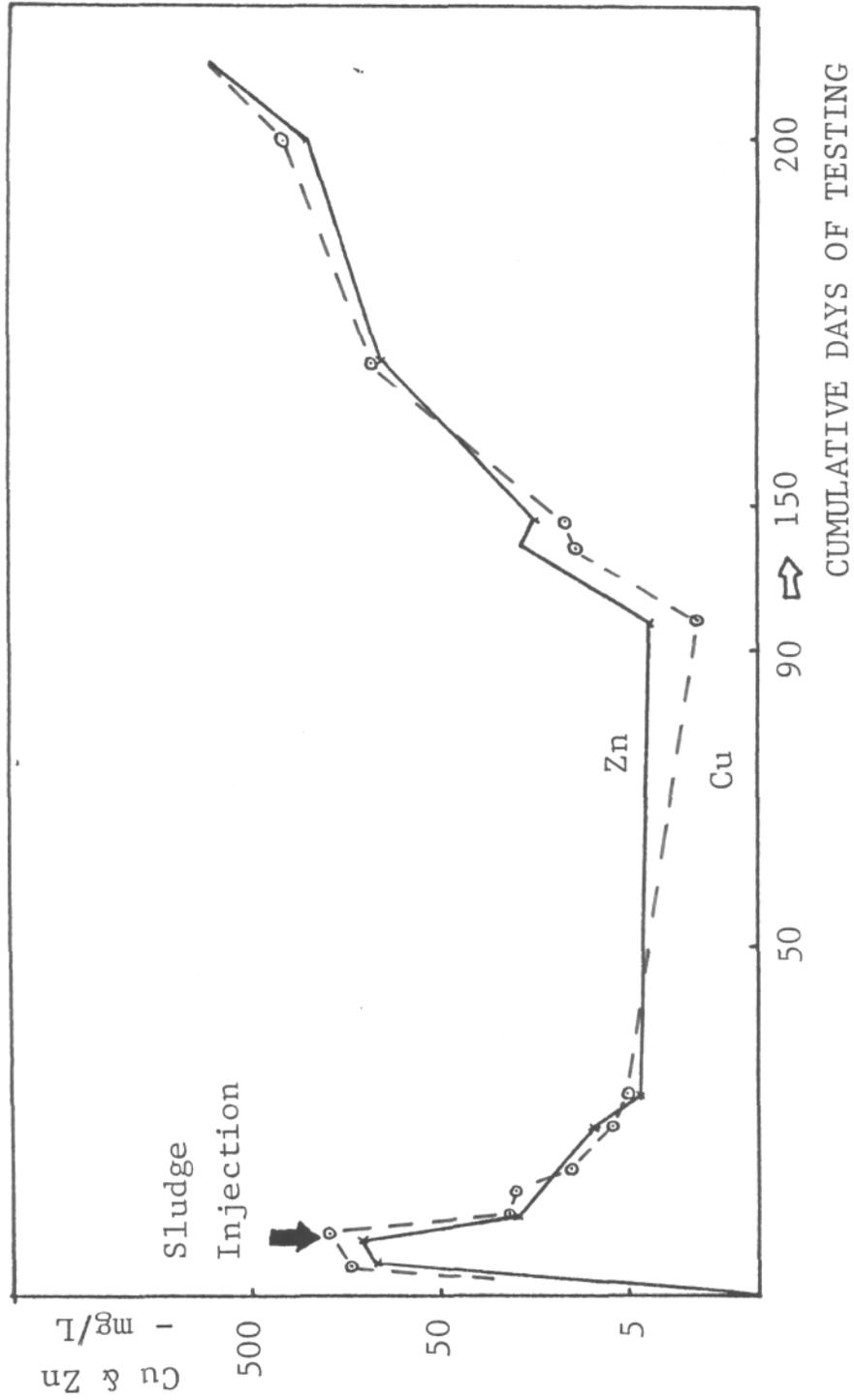a 15 cm depth in one of the probe holes. Figure 8 illustrates how

Fig. 6 Effect of injection of A.M.D. sludge in waste dump
(Ref. 7)

temperatures also declined in response to this sealing technique.
Harries and Ritchie conclude that their clay/soil cover was reasonably
effective in reducing the oxidation rate within the dump over an
extended period. In more recent times they have found that air again
has started to penetrate the cover and they expect that oxidation might
again increase. They have not communicated the cause of this
deterioration in the clay/soil cover seal. Their results do however
lend considerable hope that surface sealing covers might prevent or at
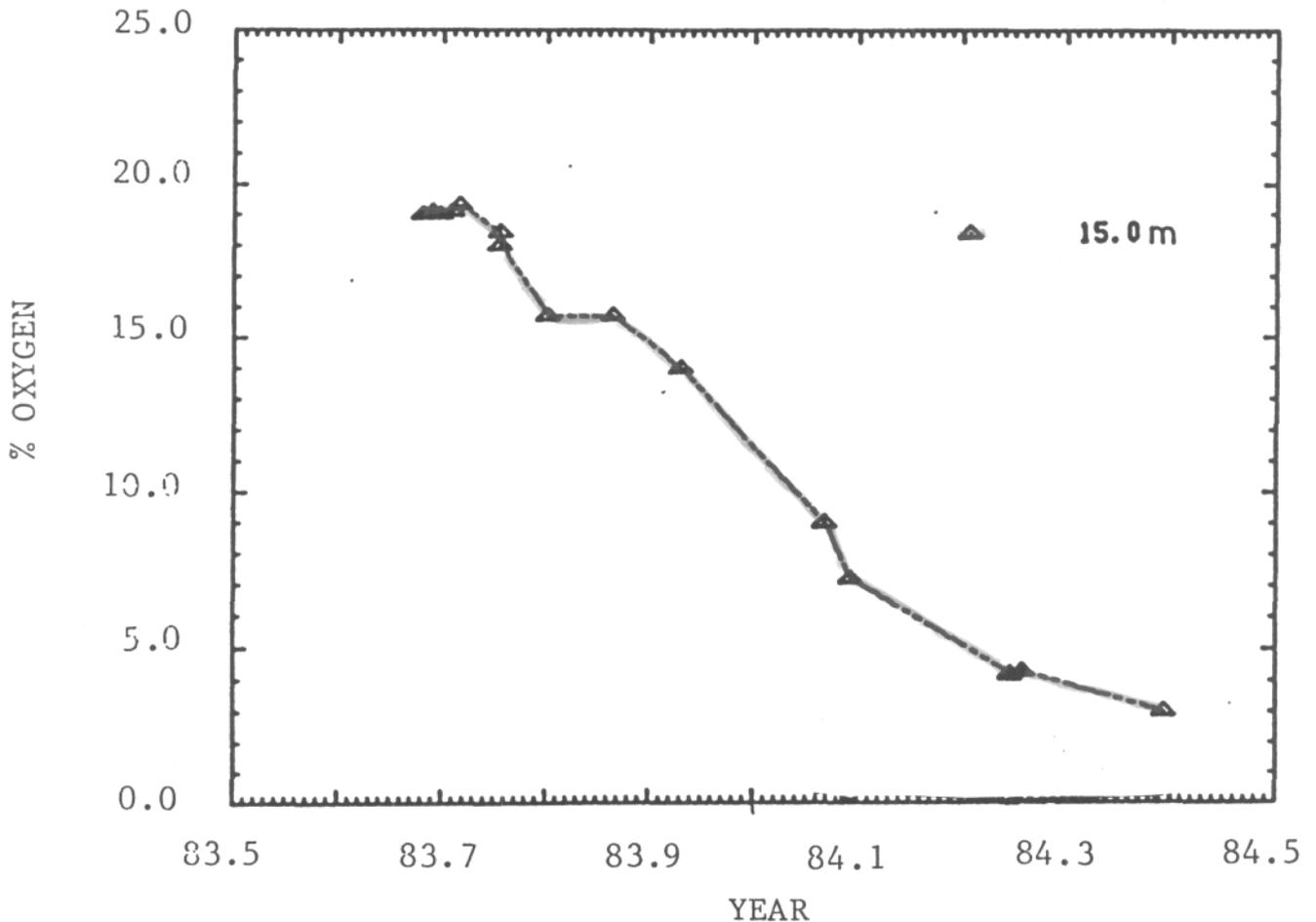least control AMD from rehabilitated leached dumps!14).

Fig. 7 Drop in oxygen concentration as a function of time.
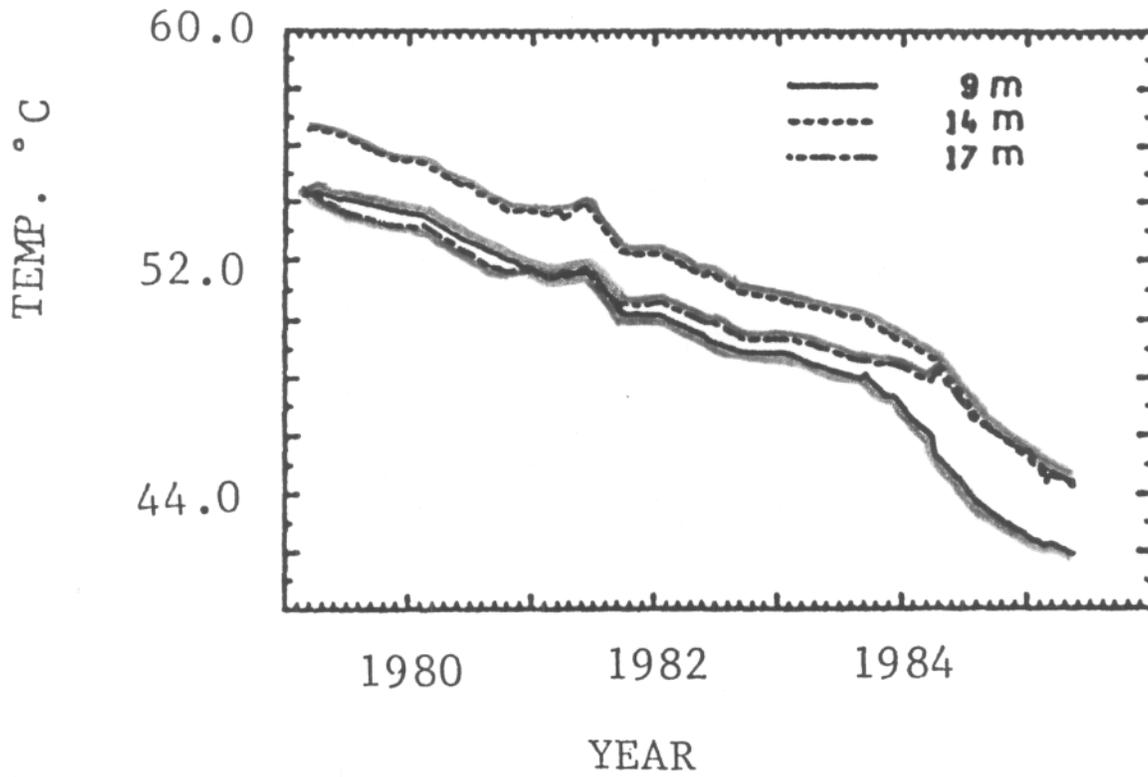(from Harries & Ritchie 1985) (Ref. 14)

Fig. 8 Temperature reduction as a function of time.
(Harries & Ritchie 1985) (Ref. 14)

CONCLUSIONS AND RECOMMENDATIONS

Careful blending of waste dump materials to ensure acid mine
water will not form naturally will generally be the most advisable
operating procedure. If this is impossible or if dumps are designed
to be acid-leached then reasonable reclamation technology should be
designed in to the mine plan. As shown in this review, no inexpensive
and completely effective remedial measures are yet available once acid
mine waters have formed. Research into new methods is needed
particularly in the western regions where the impact of waste rock
dumps probably far exceeds the impacts of mill tailings. Surface
sealing techniques appear at present to have most merit for
preventing restart of acid generation.

ACKNOWLEDGEMENT

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