EVALUATION OF ACID PRODUCTION POTENTIAL OF MINING WASTE MATERIALS: LABORATORY AND PILOT PLANT PROCEDURES

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Introduction

The oxidation of reduced sulphur compounds and ferrous iron by the leaching bacterium Thiobacillus ferrooxidans, resulting in acid generation and metals solubilization, has long been recognized as a naturally occuring process that can be exploited in mining operations (I, 2). Indeed, methods of promotion and acceleration of biological activity have been so successful that bioleaching of copper sulphide concentrates is now considered technically feasible (3, 4, 5) and less polluting then smelting methods.

However, acidic effluents emanating from many coal and sulphide mines, often attributed to biological activity, is recognized as an environmental hazard. Inhibiting these naturally occurring organisms on a practical scale is much more difficult than accelerating their activity.

This paper details the chemistry of biologically assisted acid production and describes methods developed to determine whether or not a mining waste material has the capability to become acid producing when left exposed to the atmosphere. If initial tests show a material to be a potential acid producer, then scale-up testing, in the form of column leach tests on -5 cm core or -20 cm material, will elucidate the characteristics of effluents emanating from such materials and what effect climatic conditions have upon these characteristics. Such information is essential for the physical design of waste piles so that acid production can be minimized, and for the conceptual design of effluent treatment facilities.

Background and Theory

The production of acid mine waters arises from the oxidation of metallic sulphide minerals, particularly those containing iron.

In theory, this oxidation can occur either chemically or biologically, but in practice the bacterium T. ferrooxidans is always present in acid mine waters, suggesting that the organism plays a major role in the formation of acid mine waters.

T. ferrooxidans is a unique bacterium; its energy for growth is obtained from the oxidation of sulphur compounds (e.g. sulphides) and ferrous iron. The bacterium requires an aquatic environment, but air is the source of the oxygen and carbon dioxide required. The bacterium also requires a source of ammonia nitrogen as well as small amounts of phosphate, calcium and magnesium, which are usually present in natural waters.

Numerous evidence exists which suggests that T. ferrooxidans can attack sulphide minerals by direct oxidation of the sulphide moiety (6-10). An enzyme containing a sulphydryl group is postulated to attack the sulphide ion, and a polysulphide chain is built up (II). The sulphur atoms on this chain are ultimately oxidized through to the sulphate ion form which is released into solution. Ferrous iron, if present, is oxidized simultaneously to the ferric form by a different enzyme system.

Microbiological acid production from sulphide minerals can be illustrated using pyrite as an example.

(I)

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \longrightarrow$$

$$4\,Fe(OH)_3 + 8\,H_2SO_4$$
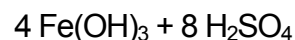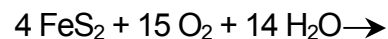
This equation represents the complete hydrolysis of all the ferric iron and the production of two moles of sulphuric acid per

mole of pyrite. In practice, we find that in an acidic environment, the iron does not precipitate as ferric hydroxide, but rather as a basic ferric sulphate or jarosite type mineral, represented by the formula:

$A Fe_3(SO_4)(OH)_6$ where A can be

H_3O^+, NH_4, K^+, Na^+, etc.
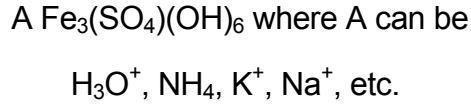
Assuming all iron precipitates as hydronium-jarosite, the following equation represents the oxidation of pyrite.

(2)

$$12\,FeS_2 + 45\,O_2 + 34\,H_2O \longrightarrow$$
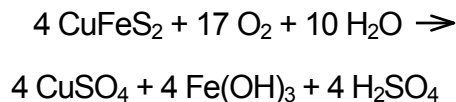
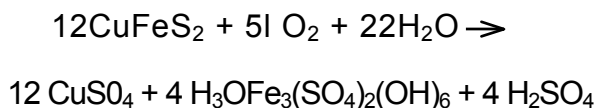$$4\,H_3OFe_3(SO_4)_2(OH)_6 + 16\,H_2SO_4$$
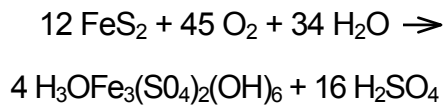
In this case, 1.33 moles of sulphuric acid are produced per mole of pyrite. In practice, neither equation (1) nor equation (2) applies completely, and the actual amount of sulphuric acid produced in a natural situation will be dependent upon a combination of reaction (1) and (2) and will vary between 0.67 and 1 mole of acid per mole of sulphide present. At high pH values, reaction (1) predominates, while at acid pH values (<3.5), more jarosite is formed.

If the mineralization contains a copper sulphide such as calcopyrite, acid can be produced according to either reactions (3) or (4), thus producing 0.5 miles or 0.17 moles of acid per mole of sulphide respectively.
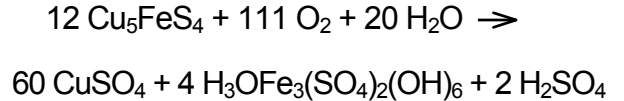
(3)

$$4\,CuFeS_2 + 17\,O_2 + 10\,H_2O \longrightarrow$$

$$4\,CuSO_4 + 4\,Fe(OH)_3 + 4\,H_2SO_4$$

(4)

$$12\,CuFeS_2 + 51\,O_2 + 22\,H_2O \longrightarrow$$

$$12\,CuSO_4 + 4\,H_3OFe_3(SO_4)_2(OH)_6 + 4\,H_2SO_4$$

However, some sulphides, such as bornite (Cu_5FeS_4) will be net acid consumers when oxidized, as shown by the following reaction.

(5)

$$12\,Cu_5FeS_4 + 111\,O_2 + 20\,H_2O \longrightarrow$$

$$60\,CuSO_4 + 4\,H_3OFe_3(SO_4)_2(OH)_6 + 2\,H_2SO_4$$

Other non-ferrous sulphides such as millerite (NiS) and sphalerite (ZnS) also undergo direct biochemical oxidation, which can be represented as follows:

(6)

$$MS + 2O_2 \longrightarrow MSO_4$$
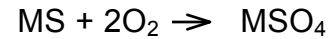
where M = Zn, Ni, Pb, Co, etc.

Acid is neither consumed nor produced in this solubilization reaction. However, these sulphate salts do have an acidic pH which mobilizes the metals they contain.

From the foregoing discussion, it is evident that iron sulphides such as pyrite are the major contributors to acid production, and that the maximum possible amount of acid generation is one mole per mole of sulphide present. In practice, the amount of free acid produced is usually considerably less due to incomplete sulphur oxidation, since not all the sulphide will be accessible to the bacteria, to oxygen and to water.

T. ferrooxidans is also capable of producing acid by the oxidation of dissolved components in water emanating from mining and milling operations. In this paper we will concern ourselves only with the formation of strong acid, that is, sulphuric, and not with the formation of weak organic acids resulting from heterotrophic growth on available organic matter.

Two possible sources of strong acid arise from soluble components; the oxidation of ferrous iron and the oxidation of reduced sulphur compounds such as thiosulphate or polythionates. If ferrous iron is present, it will oxidize slowly as follows:
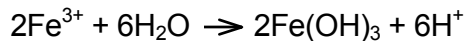
(7)

$$2\,Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow$$

$$2Fe^{3+} + H_2O$$
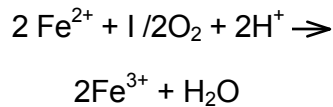
However, if <u>T. ferrooxidans</u> is present, the rate of this reaction can be increased by up to 500,000 times (12).

Although reaction (7) consumes acid, the ferric iron produced is less soluble than the ferrous iron, and it tends to hydrolize, releasing its acid content:
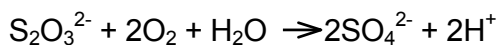
(8)
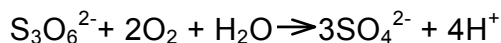
$$2Fe^{3+} + 6H_2O \rightarrow 2Fe(OH)_3 + 6H^+$$

Thus, a net gain of 2 moles of hydrogen ions per mole of ferrous iron is obtained if the hydroxide product is formed.

With reduced sulphur compounds, either chemical or biological oxidation can take place, depending on conditions. The amount of acid released would depend on the ionic species present, the nature of the associated cations and the mode of oxidation. Three possible situations are given by equations (9), (10), and (11).
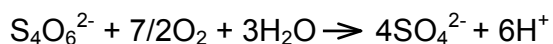
(9)

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$$

(10)

$$S_3O_6^{2-} + 2O_2 + H_2O \rightarrow 3SO_4^{2-} + 4H^+$$

(11)

$$S_4O_6^{2-} + 7/2O_2 + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+$$

These three equations assume complete oxidation of all the reduced sulphur compounds, a result normally occuring only in the presence of sulphur oxidizing bacteria. Chemical oxidation in the acidic environment is usually incomplete.

Principle of Acid Production Potential Test Procedure

A small-scale test procedure has been developed to determine whether a waste material has the potential to produce acidic effluents (13). For the purpose of this paper, we will briefly discuss the principle of the method.

To determine whether a waste material has the potential to become acid producing, the acid consuming capability of the material, expressed as kg H_2SO_4/tonne waste, is determined by chemical titration of a finely ballmilled sample (-400 mesh). This number is compared with the maximum theoretical amount of sulphuric acid which could be produced, calculated stoichiometrically from the sample's total sulphur content. If the alkaline content of the sample consumes significantly more acid than could theoretically be produced, there is no danger that the waste, in run-of-mine size, will become a source of acidic effluents. The sample is classified as a non-acid producer.

However, if the opposite is true, that is, the waste material could theoretically produce more acid than it can consume, a biological leach test must be performed to determine how much of the contained sulphur can be converted into sulphuric acid. This biological test consists of mixing into a 250 mL baffle bottom Erlenmeyer flask, 15-30 grams of -400 mesh sample with 70 mL of a nutrient medium (14). The test pH is stabilized at 2.2-2.5 over a period of a few days, followed by inoculation with an active culture of <u>T. ferrooxidans.</u> The flask is loosely stoppered and put onto a gyratory shaker in an incubation room, which has a CO_2 - enriched atmosphere and is temperature controlled at 35°C. This procedure ensures conditions ideal for bacteria! growth. An active bacterial population will be indicated by steadily decreasing sample pH as biochemical sulphide oxidation occurs. At this point, the flask receives further incremental additions of sample, and the effect on pH is closely monitored. If the test pH rises and approaches the sample's natural pH, then the waste material is confirmed to be a non-acid

producer, because any acid produced bio-logically is consumed by alkaline components in the material. However, if the test pH remains low, indicative of a steady net acid production, then the waste material is con-firmed to be a potential acid producer.

Acid-base accounting provides a prac-tical method to assess the acid producing-acid consuming characteristics of all waste materials within a mining operation. By com-positing sections of core of appropriate length from drilling operations and subjecting numerous such composites to an assessment of their alkalinity and sulphur content, both expressed in equivalent kg H_2SO_4 per tonne, a depth profile for each drill hole can be readily established (Figure I). Examination of the depth profiles of a series of drill holes will readily show consistent layers of acid producing and acid consuming materials. It must be understood, however, that any such accounting is based on the worst possible acid production conditions, since it is assumed in the purely chemical tests applied, that all the sulphur present in the sample will be converted into sulphuric acid. In practice, this is not necessarily the case, since not all the sulphur may be present in a form avail-able or accessible to biological conversion. For example, organic bound sulphur, often found in coal mining operations cannot be oxidized by the leaching bacterium.

Scale-Up Testing Principle and Procedure

Since the acid production tests are per-formed on a small scale, on finely ground material and under conditions ideal for bio-logical growth, scale-up effects must be con-sidered in order to realistically evaluate a waste material. Obviously, the degree of sul-phide oxidation that can take place depends on the distribution of the sulphide mineral in the waste. If finely disseminated, little at-tack may occur, while if the sulphides are present on fracture planes, extensive oxi-dation may occur. Similar limitations apply to the distribution of the acid consuming ingredients of the waste.

Factors that will affect the biological conversion of sulphides in a run-of-mine

waste are numerous and extremely difficult to assess. Major factors are:

- Ratio of exposed sulphide material to alkaline gangue
- Distribution of the sulphide minerals in the waste
- Depth of oxygen penetration into the waste pile
- Amount and depth of moisture pene-tration into the waste pile and effect-ive mineral surface wetting
- Length of dry periods
- Presence of inhibiting soluble metals
- Temperature

Preventing water and/or air from entering the waste pile will eliminate the danger of acid production. However, on a practical scale, such preventative measures may not be feasible. Thus, provisions must be made to minimize acid production and to provide treatment facilities for the acidic effluents produced. A scale-up test procedure has been developed, which is performed on either core material or run-of-mine waste, that will assess the acid-producing character of run-of-mine waste and characterize the effluents produced from such wastes as a result of natural leaching processes.

Appropriately sized sample material is placed in 2 to 6 meter high columns and leached with re-circulating neutral pH distill-ed water to which an active culture of T. ferrooxidans has been added. Such recircl-lotion keeps any free acid produced in the leach circuit and thus enhances the rapid establishment of an environment amenable to microbiological sulphide oxidation processes. Samples of the recirculating solutions are assayed at appropriate intervals to determine the rate of increase of selected metals and chemical of environmental concern. A list of the typical water quality parameters of con-cern to British Columbia coal and metal mine operators (Tables I and 2, respectively) is quite comprehensive, and shows that analyt-ical costs associated with frequent solution assays can be a signifcant financial factor in a major testing program.

As would be expected, the pH of the effluents produced from waste materials

Figure I

Typical Acid-Base Account
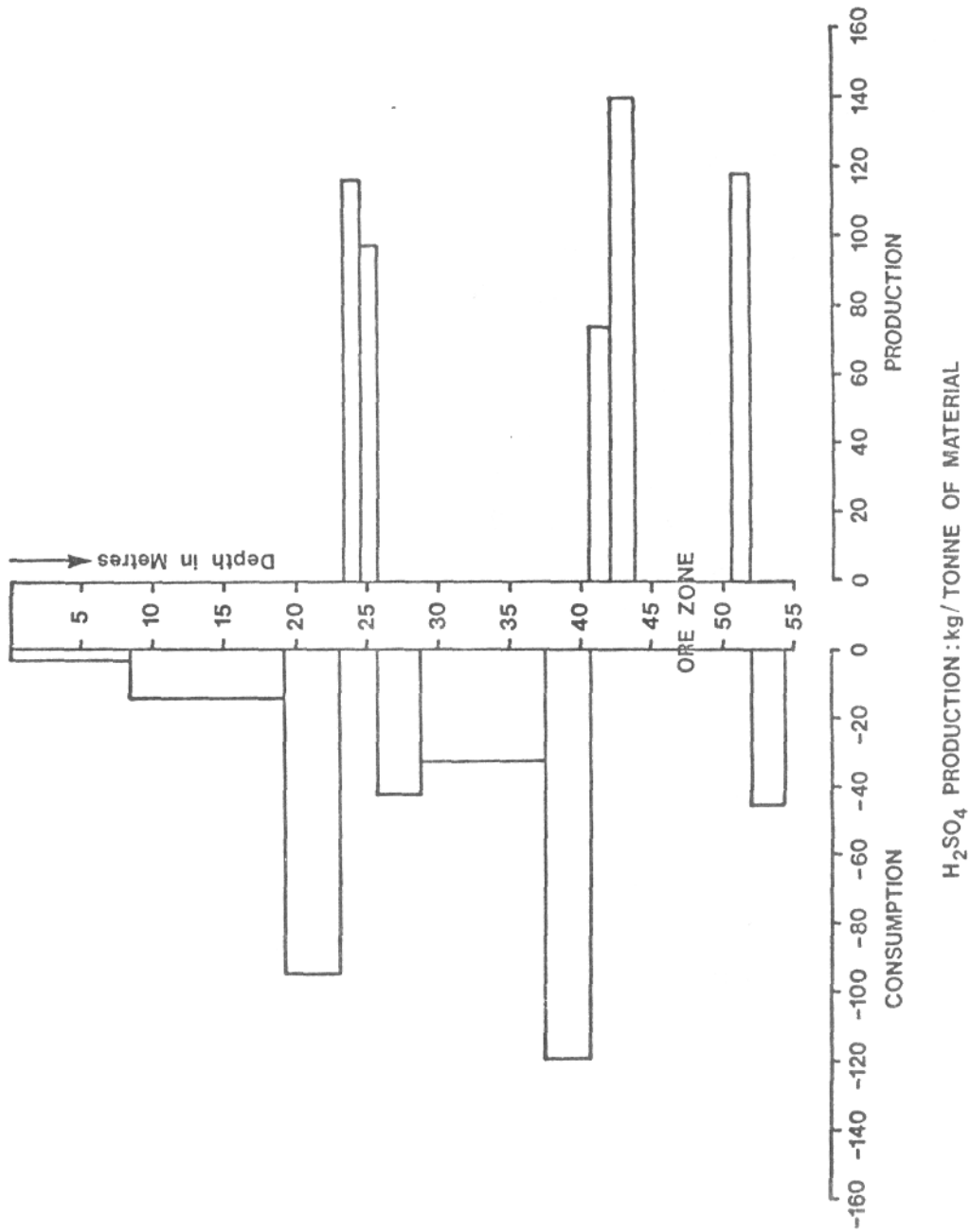
Table I

Water Quality Parameters

Coal Mine Development

Temperature

PH

Dissolved Oxygen

Dissolved Solids

Suspended Solids

Volatile Suspended Solids

Turbidity

Alkalinity

Specific Conductance

Total Organic Carbon

Hardness (calculated)

Sulphate

Total Phosphate

Nitrate and Nitrite

Ammonia

Fluoride

Total Calcium

Total Magnesium

Total Mercury

Dissolved Zinc

Dissolved Copper

Dissolved Iron

Dissolved Mercury

Dissolved silver

Dissolved Lead

Dissolved Arsenic

Dissolved Cadmium

Table 2

Water Quality Parameters

Metal Mine Development

Temperature

PH

Dissolved Oxygen

Dissolved Solids

Suspended Solids

Volatile Suspended Solids

Turbidity (NTU)

Alkalinity

Dissolved Magnesium, Calcium

Specific Conductance

Sulphate

Ammonia

Total Carbon

Total Organic Carbon

Phenol

Total Mercury

Total Phosphorus

Ortho Phosphate

Ortho Phosphate

Dissolved Phosphorus

Nitrite

Nitrate

Dissolved Arsenic

Dissolved Iron

Dissolved Copper

Dissolved Manganese

Dissolved Zinc

Dissolved Lead

plays an important role in solution quality. Not only does the pH control the solubility of various metals, but, in the case of the sulphide wastes, a low pH encourages biological breakdown of metal sulphides, thus increasing the rate of solubilization of corresponding metal sulphides as well as production of ferric sulphate lixiviant. The onset of rapid biological sulphide oxidation commences when the pH of the solution in contact with the waste, through natural causes, has reached a value between 4.5 and 4.0 (Figure 2). Rapid increases in copper and iron concentrations coincide with the establishment of a high oxidation potential, normally above 600 mV (relative to calomel).

If the pH does not decrease below 5 (Figure 3), rapid biological activity does not occur, the oxidation potential remains below 600 mV, and dissolved metal concentrations remain low. In some tests carried out in our laboratories, copper and iron concentrations remained below 0.2 mg/L and O.I mg/L, respectively, when 100 kg of waste was leached with 20 litres of water.

If a material proves to become acid producing under the continuous recirculating leaching method employed, it is important to determine if such material will remain acid producing when submitted to single pass leaching with simulated rain water, since such leaching will remove acid rather than accumulate it. During a long dry spell, the leaching bacteria will continue to oxidize sulphides, produce acid, and cause high concentrations of metal values and salts in the interstitial waters. During a rain period, the percolating rain will wash the waste materials and remove a portion of the dissolved species, thus producing their relatively high concentration in the effluent emanating from the waste. It is of great importance to determine if, after washing by rain, the remaining interstitial water will again become acidic. This is very much a function of the acid-producing characteristics of the wastes and the amount of oxygen that can penetrate into the waste. Unless the waste is moderately acid producing, the neutralizing effect of the rain water may remove sufficient acidity

from the interstitial waters to prevent subsequent biological activity. In cases where the waste material remains acidic, the characteristics of effluents to be produced from a commercial-sized dump of such waste can be determined reasonably accurately, providing information of great assistance to the designer of the effluent treatment facilities.

We prefer to make such determinations in 6-meter high columns on -20 cm material. By subjecting the waste material to rest cycles with a duration similar to the length of dry spells at mine site, followed by washing with quantities of neutral pH water at a rate equivalent to, for example, a 10 year — 4 hour maximum rainfall, a reasonably accurate assessment can be made of the maximum amount of the various metals and salts that can be extracted per thousand tonnes of waste. Only when the information obtained from such an assessment is available can a practical assessment be made of the need to minimize effluent production by making the waste dump impermeable. If treatment facilities are unavoidable, advantage can sometimes be taken of the biological acid production by recovering some of the metal values of economic importance from the effluents.

In many cases when a composite sample of waste material proves to be non-acid producing, it should be recognized that small portions of such a composite may produce acid. It is therefore important to obtain an exact understanding of the location, in the wastes to be mined, of any sulphide materials present, however small their relative proportion. During the mining of such wastes, special attention can then be given to such sulphides, and methods can be designed to ensure that localized acid production, within a dump of waste materials, will not occur.

An obvious method to prevent the production of acid effluents from waste dumps is to place potentially acid producing waste deep inside a dump, preferably totally surrounded by alkaline materials. Such alkaline materials do have a dual role; they will neutralize any acid draining from pockets of acid producing mterial, but, probably more

Figure 2

**Effect of pH Upon Metal Concentration in Effluents
From Acid-Producing Waste Material**
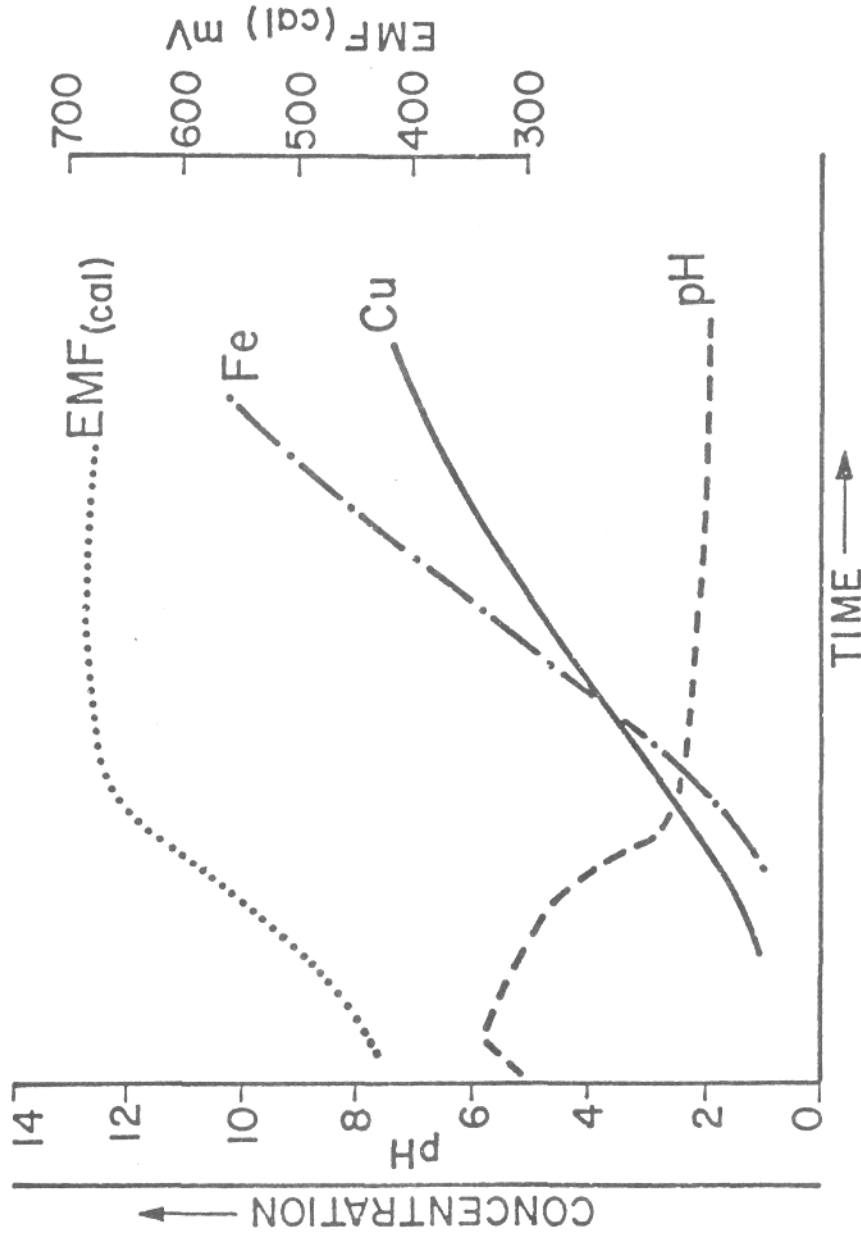
Figure 3

**Effect of pH Upon Metal Concentration in Effluents
From Non-Acid-Producing Waste Material**
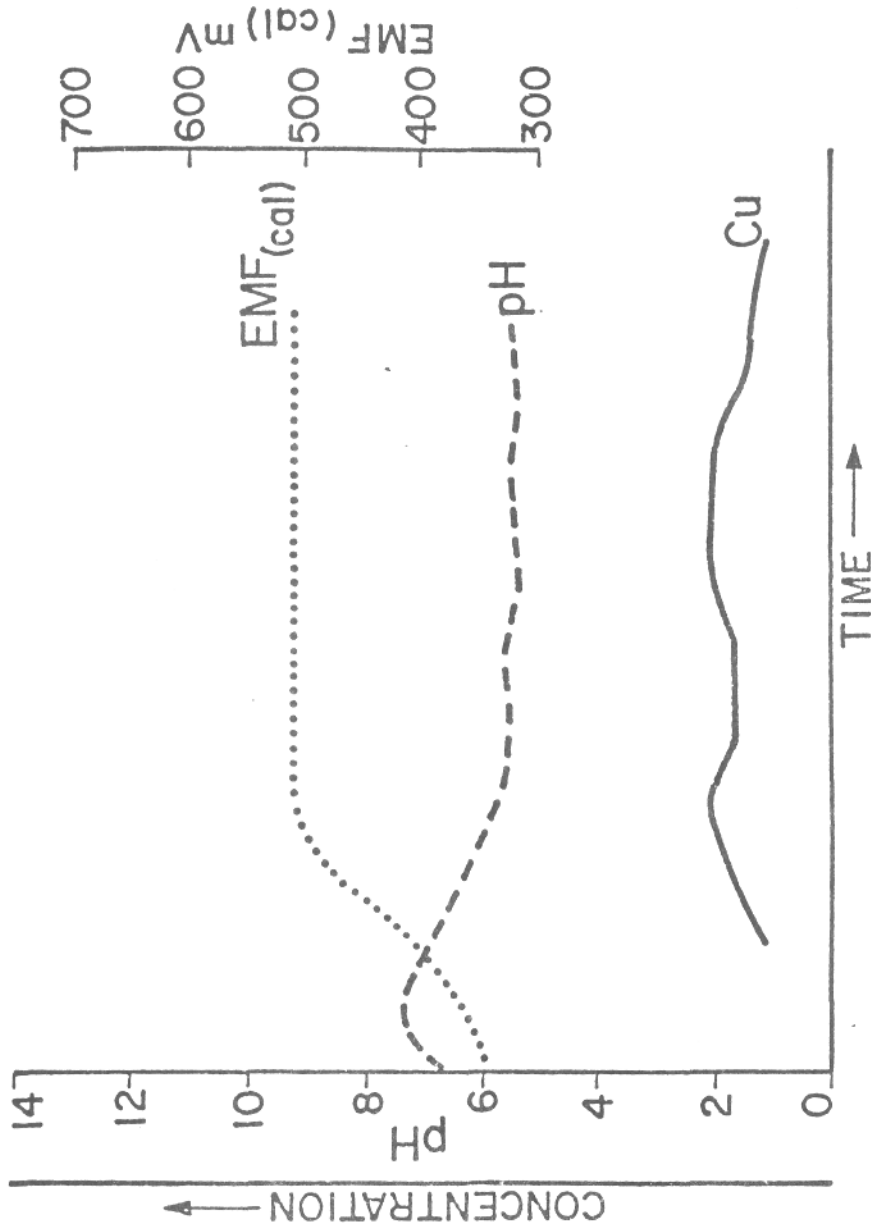
importantly, the small quantities of, for example, $CaCO_3$ that will dissolve in rain-water percolating through the alkaline waste, will react at the mineral surfaces with any sulphuric acid produced, thus coating the mineral surfaces with a layer of calcium sulphate which will help prevent subsequent bacterial sulphide oxidation by interfering with water flow and oxygen diffusion to the mineral surfaces. A series of tests are currently in progress at B.C. Research to verify the above concept.

Another disposal method to be evaluated is that of storage below the ground-water level so that the waste is at all time flooded. Although water is a necessary ingredient for the bacterial oxidation process, equally important is the availability of oxygen at the mineral surface to convert the sulphide into sulphate. Since water does not normally hold more than 10 mg/L dissolved oxygen, the rate at which acid can be produced in a submerged system is directly proportional to the flow of water through the waste and the oxygen content of the water. Most importantly, however, the concentration of sulphate that can be produced is limited by the amount of oxygen dissolved in the water since oxygen diffusion from the air into the water and then through the water to the mineral surfaces is an extremely slow process. Therefore, if the groundwater contains 10 mg/L oxygen, no more than 96/64 x 1 0 = 1 5 mg/L sulphate can be produced.

$$S^= + 2O_2 \quad SO_4^=$$
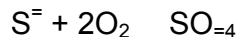
$$M_{O2} = 32$$

$$M_{SO4} = 96$$

Conclusions

From the foregoing description of waste material testing, it is apparent that any testing program should be carefully designed to incorporate variations in waste characteristics and climatic conditions, as well as waste dump configuration and dump construction methods. The results of a properly executed test program can be used to prevent or minimize the quantity of acid effluent produced and can have a significant effect on the cost of the necessary effluent treatment facilities by preventing over-design.

References

1. Malouf, E.E. and Prater, J.D. "Role of Bacteria in the Alteration of Sulfide Minerals," J. Metals, 13, May, 1969, 353-356.

2. Malouf, E.E. "The Role of Micro-Organisms in Chemical Mining," Mining Engng., Nov. 1977, 43-46.

3. Chen, C.S., Huddleston, R.L. and Johnson, M.A. "Bioleaching of Chalcopyrite Concentrate." 4th Joint A.I.Ch.E. — C.S.Ch.E. Chem. Eng. Conf. Vancouver, September 9-12, 1973.

4. Torma, A.E., Ashman, P.R., Olsen, T.M. and Bosecker, K. "Microbiological Leaching of Chalcopyrite Concentrate and Recovery of Copper by Solvent Extraction and Electrowinning," Metall., 33, May, 1979, 479-484.

5. McElroy, R.O. and Bruynesteyn, A. "Continuous Biological Leaching of Chalcopyrite Concentrates: Demon stration and Economic Analysis" in Murr, L.E., Torma, and J.A. Brierley (eds.), Metallurgical Applications of Bacterial Leaching and Related Micro biological Phenomena. New York: Aca demic Press Publishers, 1978, 526 pp.

6. Duncan, D.W., Landesman, J. and Walden, C.C. "Role of Thiobacillus ferrooxidans in the Oxidation of Sulfide Minerals," Can. J. Microbiol., 13, 1967, 397-403.

7. Beck, J.V. and Brown, D.G. "Direct

Sulfide Oxidation in the Stabilization of Sulfide Ores by Thiobacillus ferro-oxidans," J. Bacteriol., 96 (4), Oct. 1968, 1433-1434.

8. Duncan, D.W. and Walden, C. C. "Micro biological Leaching in the Presence of Ferric Iron," Developments in Industrial Microbiology. Vol. 13, 1972, 66-74.

9. Sakaguchi, H., Tor ma, A.E. and Silver, M. "Microbiological Oxidation of Syn thetic Chalcocite and Covellite by Thi-obaci llys ferrooxidans," Appl. Environ. Microbiol., 31 (I), Jan. 1967, 7-10.

10. Torma, A.E. "Microbiological Oxidation of Synthetic Cobalt, Nickel and Zinc Sulfides by Thiobacillus ferrooxidans," Revue Canadienne de Biologie, 3D, 1971, 209-216.

11. Silver, M. "Metabolic Mechanisms of Iron-Oxidizing Thiobacilli," in Murr, L.E., Torma, A.E. and J.A. Brierley (eds.), Metallurgical Applications of Bacterial Leaching and Related Micro-biological Phenomena. New York; Aca-demic Press Publishers, 1978, 526 pp.

12 Lacey, D.T. and Lawson, F. "Kinetics of the Liquid-Phase Oxidation of Acid Ferrous Sulphate by the Bacterium Thi obacillus ferrooxidans," Biotech. Bioeng., 12 (I), Jan. 1970, 29-50.

13 Bruynesteyn, A. and Duncan, D.W. "Determination of Acid Production Po-tential of Waste Materials." Paper pre-sented at AIME Annual Meeting (A-79-29), New Orleans, Feb. 19-21, 1979.

14 Silverman, M.P. and Lundgren, D.G. "Studies on the Chemoautotrophic Iron Bacterium Ferrobacillus ferrooxidans," J. Bacteriol., 77 (5), May 1959, 647-652.