# Sulphide Oxidation in Pyritic Overburden A Controlled Leach Column Study

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## ABSTRACT

There have been few long-term studies of sulphide oxidation under controlled conditions. The object of this study was to investigate the oxidation and leaching characteristics of pyritic mine material under conditions that were commensurate with field conditions but which could be controlled and monitored on a long term basis. The test material - overburden from Woodlawn Mines Pty Ltd - was packed into a 300 cm high column and leached with water at an infiltration rate of 256 mm $y^{-1}$ for 5 years. Chemical conditions within the column were continuously monitored by sensors embedded in the overburden and leachate from the base of the column was analysed weekly. The study examined the relationships between heavy metal release and gas, moisture, and chemical conditions in the column.

## INTRODUCTION

There is increasing concern about the problems of acid drainage at mines working pyritic ores. In recent years there have been several well publicized instances of acid drainage polluting surface waters (e.g. Captains Flat [1] and Rum Jungle [2]), and this has created a greater awareness of the need to manage mine wastes in ways that minimize the risks to the environment, but which are still practical and economical. Better waste management can be achieved more readily if the processes involved in acid formation are clearly understood. This paper describes a long-term study of the oxidation and leaching characteristics of sulphidic mine spoil under conditions typically encountered in the field. The long-term requirement was in recognition of the fact that pyritic mine spoils often generate acid drainage for many years following exposure to natural leaching agents. The leaching study was conducted in a large column set up with automated controls and computer data logging facilities to minimized operator input.

## COLUMN CONSTRUCTION AND INSTRUMENTATION

The column was constructed from Vinidex PVC pipe and assorted Vinidex PVC fittings (Figure 1). The pipe was 300 cm in length and had an internal diameter of 30 cm. Overburden within the column was supported above the sealed base by a perforated Perspex plate, allowing leachate to freely drain from the overburden and into tubing connected to a collection flask. The top of the column was also covered by a Perspex plate which prevented dust entering the column and also minimized evaporative loss of water from the overburden. Air in the cavity above the overburden was replaced by a diaphragm pump operating for 30 minutes on a six-hourly cycle. This maintained the air space at near atmospheric composition. Leach water was added to the overburden surface as a once-daily batch addition through a clock operated peristaltic pump.

Sample ports were located through the pipe sidewall at five depths equi-spaced by about 40 cm. At each depth there was a suite of eight ports (three 25 mm i.d., one 15 mm i.d., and four 12 mm i.d.), evenly spaced around the circumference of the column and designed to accommodate a range of probe types. The 25 mm ports were used for solids or liquid sampling, inspection, and accommodating the water suction and humidity probes. The 15 mm ports were used to house oxygen probes, and the 12 mm ports were used for gas sampling and for housing temperature and redox potential probes.

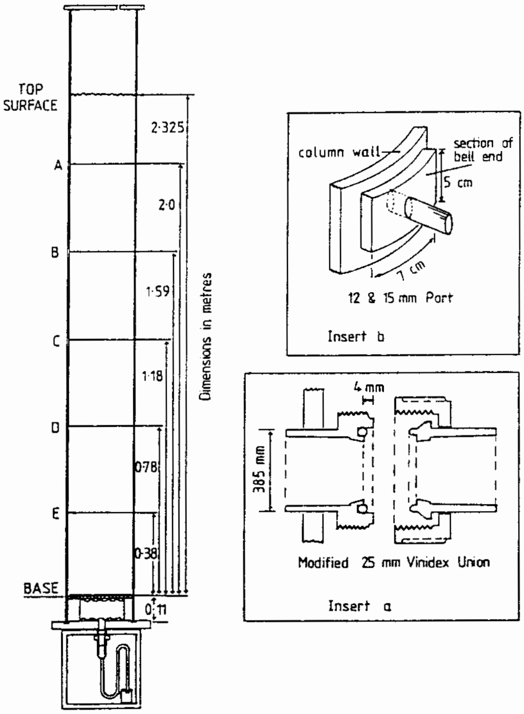

**Figure 1.**

**Scale drawing of column showing positions of ports; insert a, the 25 mm port; insert b, the 15 mm and 12 mm port.**

Temperatures were detected with chromel-alumel thermocouples. The redox probes were made from rectangular sheets of 0.1 mm thick platinum welded to platinum wire leads, and redox potentials were measured with reference to a calomel electrode located outside the column and level with the base plate (i.e. at the saturation point). Humidity was measured with a Phys-Chemical Research Corporation Humeter Model B humidity meter equipped with a five-position switch box and a set of five PCRC-11 HPB probes. The instrument response was 0 to 100 per cent relative humidity in the temperature range -5 to 75 $^{o}$C. Water matric potentials were measured with porous cup tensiometers (pressure range of 0 to 100 kPa absolute) coupled with Bell and Howell BHL-4400 pressure transducers. The ceramic cups were packed in a layer of fine material to ensure good contact with the overburden. The temperature, redox and matric potential probes were interfaced with an Apple IIc personal computer [3], which provided automatic data logging and facilitated data analysis.

## EXPERIMENTAL PROCEDURES

The sulphidic overburden was supplied by Woodlawn Mines Pty Ltd, NSW. It consisted mainly of gravel with some fines and a few large boulders. Gross material was removed with a 25 mm sieve and the remaining material was used in the as-received condition. A subsample of overburden was further sieved into 4 size fractions and these fractions were subsequently milled to < 0.2 mm and analysed for total sulphur, sulphate sulphur, and acid-extractable (boiling conc. HCl) heavy metals (Table 1).

A total of 296 kg of overburden was packed into the column giving a total depth of 233 cm, a bulk density of 1.83 g $cm^{-3}$ and a total porosity of 0.27. The overburden was initially wetted-up by batch addition of deionised water at rates up to 500 mL $d^{-1}$ until drainage appeared from the base of the column (i.e. 118 days after commissioning). The batch addition of water was then immediately cut back to 50 mL $d^{-1}$. This rate, equivalent to an annual rainfall of 256 mm with total infiltration and zero evaporation, was considered to be commensurate with field leach rates, taking normal evaporation and infiltration effects into account.

**Table 1. Composition of Woodlawn Overburden**

| Assay | | Particle Size (mm) | | | | |
|---|---|---|---|---|---|---|
| | | <0.2 | 0.2 - 0.5 | 0.5 - 2 | 2 - 25 | Bulk |
| Size Distr. | (%) | 8.9 | 7.4 | 19.4 | 64.3 | 100 |
| Total S | (%) | 1.39 | 2.57 | 2.37 | 2.18 | 2.18 |
| $SO_4$ - S | (%) | 0.71 | 0.66 | 0.48 | 0.25 | 0.37 |
| Acid Sol. Fe | (%) | 5.96 | 5.63 | 5.35 | 4.27 | 4.73 |
| Acid Sol. Cd | (mg $kg^{-1}$) | 8.5 | 9.2 | 9.6 | 6.8 | 7.6 |
| Acid Sol. Cu | (mg $kg^{-1}$) | 2070 | 3390 | 3500 | 2600 | 2790 |
| Acid Sol. Ni | (mg $kg^{-1}$) | 24 | 22 | 20 | 18 | 19 |
| Acid Sol. Pb | (mg $kg^{-1}$) | 940 | 930 | 990 | 500 | 670 |
| Acid Sol. Zn | (mg $kg^{-1}$) | 2840 | 3130 | 3070 | 2120 | 2440 |
| pH (1:2, $H_2O$) | | 3.9 | 5.1 | 4.3 | 4.2 | 4.2 |

A total of 125 litres of deionised water was added to the overburden surface in 5 years of column operation. About 70 percent of this volume was subsequently recovered as leachate. Another 20 per cent remained in the column as pore water, and the remaining 10 percent was probably lost from the surface of the column by evaporation (i.e. in the air displaced from the air-cavity above the overburden). The rate of leaching was roughly equal to one pore water volume per year, that is, it took 1 year for water to travel the length of the column.

Leachate from the base of the column was collected on a weekly basis and analysed for pH and for the heavy metals cadmium, copper, iron, lead, nickel, and zinc. In the fourth and fifth years of leaching the pore space in the column was analysed twice weekly by withdrawing a gas sample with a hypodermic syringe inserted through a septum on a 12 mm port. The sample was immediately analysed for oxygen and carbon dioxide by gas chromatography.

## RESULTS

The principal metals in the Woodlawn overburden were iron, copper, zinc, and lead (Table 1). These metals were thought to be associated mainly with sulphidic mineralization. An X-ray diffraction (XRD) scan of the overburden material indicated the presence of pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena

(PbS). The total and sulphate sulphur contents of the overburden were 2.18% and 0.37% respectively. Non-sulphate sulphur was presumably present as sulphide. The presence of some sulphate in the overburden may indicate that the overburden had weathered slightly prior to being leached in the column, but it was also noted that when leaching began there was no initial flush of soluble ions from the overburden, a pattern often encountered with materials containing readily soluble salts.

After the initial wetting up period, the humidity in the column was high (i.e. between 99 and 100 per cent), the matric suction of the overburden was low (i.e. typically between 5 and 10 kPa), and the temperature in the column varied in unison with the ambient temperature maintained by the air-conditioning unit within the laboratory (i.e. 20 to 23 °C). The redox potential during the first 200 days was independent of depth and varied between 0.62 and 0.68 V (SCE). By the fifth year redox potential was slightly lower at around 0.5 to 0.6 V. These mixed potentials were the sum of dominant oxidizing and reducing reactions taking place in the interstitial waters of the column. The measured values indicate that redox conditions were conducive to pyrite oxidation.

The results of leachate composition are given in Table 2, averaged over yearly intervals. During the first year of leachate discharge, the pH of leachate decreased from an initial high of 3.6 to around 2.2. This decrease was independent of changes in flow rate or matric potential but concurred with a marked increase in leachate iron. Decreasing pH and increasing iron are indicators of increasing sulphide oxidation. The steady increase in sulphide oxidation rate during the first year can probably be attributed to population growth of bacteria with the capacity to catalysis the oxidation process.

**Table 2. Leaching of heavy metals from overburden**

| Time (y) | Accum. Vol (L) | pH | Cd | Cu | Fe | Ni | Zn |
|---|---|---|---|---|---|---|---|
| | | | Average concentration (mg $L^{-1}$) | | | | |
| 0 - 1 | 17.343 | 3.05 | 88 | 7550 | 190 | 120 | 22000 |
| 1 - 2 | 31.982 | 2.20 | 91 | 8300 | 2590 | 130 | 22500 |
| 2 - 3 | 54.559 | 2.20 | 57 | 5700 | 4310 | 120 | 14000 |
| 3 - 4 | 71.323 | 2.27 | 28 | 3200 | 4160 | 110 | 6400 |
| 4 - 5 | 83.052 | 2.90 | 18 | 2500 | 2150 | 130 | 4400 |
| | | | Metal released (mg $kg^{-1}$ overburden) | | | | |
| 0 - 5 | 83.052 | – | 16 | 1560 | 786 | 34 | 3980 |

After twelve months of leaching, the rate of sulphide oxidation steadied then remained relatively constant throughout the second, third, and fourth years. Leachate pH fluctuated between 2.1 and 2.3 until the fifth year when it progressively increased again, reaching 3.0 to 3.3 in the latter half of that year. Since the matric potential of the overburden remained essentially unchanged, it would seem that the slowing in sulphide oxidation was caused by a depletion in reactive sulphide minerals.

The pattern of heavy metal release from the overburden varied for different metals. The concentrations of cadmium, copper, and zinc in leachate varied in unison, remaining fairly constant during the first two years then decreasing in an exponential fashion during the last three years. Nickel, on the other hand, was leached at a constant concentration during the whole five years, whereas lead did not leach at all. It is interesting to compare the amounts of metals leached per kilogram of overburden during the five year period (Table 2) with the amounts extracted by boiling conc. HCl acid (Table 1). For copper and lead, the amounts released by acid were much greater than the amounts leached from the column. This may indicate that the oxidation of copper and lead bearing sulphide minerals was still not complete after five years, or alternatively, that formation of secondary minerals in the overburden limited the leaching of these two metals. The latter is almost certainly the case for lead. For zinc, cadmium, and nickel the acid extractable results were of similar order of magnitude to, but consistently less than, the amounts leached from the column. As such, a more suitable test may be required to test the potential leachability of these metals

Typical pore gas concentrations within the column during the last year of leaching are given in Table 3. The concentration of oxygen decreased in an almost linear fashion from atmospheric levels at the surface (i.e. 21 %) to almost zero at a depth of 150 cm. This indicates a major sink for oxygen at a reaction front located just above the base of the column. Also, the linear nature of the profile above the reaction front indicates that the reaction was rate limited by oxygen diffusion [4]. The rate of oxygen diffusion was assessed by temporarily sealing the top of the column and measuring the rate of decrease in oxygen concentration in the air cavity above the overburden. In a 48-hour period the rate of oxygen loss was linear and corresponded to an oxygen flux at the overburden surface of $4\times10^{-10}$ mole oxygen $cm^{-2}$ $sec^{-1}$. The corresponding apparent diffusion coefficient for oxygen in the top 150 cm of overburden was 0.00786 $cm^2$ $sec^{-1}$ which is more than an order of magnitude less than the diffusion coefficient for oxygen in air (i.e. 0.203 $cm^2$ $sec^{-1}$). This comparatively low apparent diffusion coefficient can be attributed directly to the low air-filled porosity of the overburden, which typically was less than 0.09.

**Table 3. Oxygen and carbon dioxide in overburden pore space**

| | | Depth (cm) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 33 | 74 | 115 | 145 | 195 | 233 |
| $O_2$ | (%) | 20.9 | 17.3 | 10.7 | 6.4 | 2.1 | <1.0 | <1.0 |
| $CO_2$ | (ppm) | 330 | 320 | 400 | 900 | 2280 | 4830 | 6920 |

The profile for carbon dioxide was virtually the inverse of the oxygen profile. In the upper half of the column the carbon dioxide concentrations were close to atmospheric but concentrations were markedly higher in the lower half. The carbon dioxide found at depth was presumably formed by the reaction of acid with gangue minerals. The absence of any concentration gradient within the top half of the column means that carbon dioxide formed near the base of the column must have been removed again as it diffused upward. Some carbon dioxide would have reacted with the influent water and formed carbonic acid. The remainder may have been incorporated into secondary minerals or alternatively may have been utilized by microbes as an energy source.

## DISCUSSION

The mechanisms for chemical and biological oxidation of pyrite have been studied in some detail [5,6,7] and there is now general agreement regarding key reactions. The oxidation of pyrite is initiated by oxygen in the presence of water according to the reaction:

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \qquad (1)$$

The ferrous ions are then oxidized either chemically or biologically (via *Thiobacillus ferrooxidans*) to ferric ions,

$$4\,FeSO_4 + 2\,H_2SO_4 + O_2 \rightarrow 2\,Fe_2(SO_4)_3 + 2\,H_2O \qquad (2)$$

which may then act to oxidize more pyrite,

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4{}^{2-} + 4\ H^+ \qquad (3)$$

or, if insufficient acid is present, may hydrolyse and precipitate from solution as either ferric hydroxide or a jarosite type mineral. The reactions describing these precipitation reactions are, respectively,

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad (4)$$

$$3\ Fe^{3+} + A^+ + 2\ SO_4{}^{2-} + 6\ H_2O \rightarrow AFe_3(SO_4)_2(OH)_6 + 6\ H^+ \qquad (5)$$

where $A^+$ can be $H^+$, $K^+$ or $Na^+$. On the basis of the above reactions, the acid production potential of pyrite lies between 1.5 and 2 mol $H^+$ per mol sulphide depending on whether jarosite or ferric hydroxide, or a combination of both, precipitates form. The overburden material used in this study contained about 1.8%, sulphide which converts to maximum acid production potential per kilogram of overburden of 1.1 mol $H^+$ (or 1100 meq). Of course, not all of this acid potential would be expected to appear in leachate as $H^+$. In fact $H^+$ accounts for only a small part of the acidity of leachate. Most of the acidity was present as metal ions released into solution by oxidation of sulphide minerals (e.g. $Fe^{3+}$, $Fe^{2+}$, $Cu^{2+}$, and $Zn^{2+}$) or by dissolution of gangue minerals such as alumino-silicates (e.g. $Al^{3+}$). Also, the presence of significant amounts of $Mg^{2+}$ and $Ca^{2+}$ in leachate signifies some acid neutralization by gangue minerals.

In the five years of leaching, the total release of cations from the overburden was about 400 meq $kg^{-1}$ of overburden, or roughly one-third of the maximum acid production potential. This indicates that considerable reserves of sulphide remained in the overburden after five years. Furthermore, the marked decrease in sulphide oxidation rate during the fifth year would seem to indicate that much of the remaining sulphide was not in a readily oxidizable state. Although the original distribution of sulphide minerals in the overburden was fairly even throughout the particle size range (Table 1), it would have been the finer fractions with their high reactive surface area that had greatest exposure to chemical and biological leaching agents. In contrast, sulphide minerals embedded in very coarse material would have received little exposure to leaching agents. At least 80% of the surface area of Woodlawn overburden was due to material of less than 2 mm, yet this material contributed only 37% to total weight. It may be significant that the sulphide in the finer fractions contributed approximately 350 meq $kg^{-1}$ to the acid production potential of the overburden, which is close to the 400 meq $kg^{-1}$ value for cation release.

An indication of the aqueous and solid-phase speciation of iron within the column can be obtained by examination of the pH and redox potential of the system as well as the respective activities of ions that interact with Fe (i.e. $SO_4$, OH and K). A convenient method of illustrating the interrelationships between these variables is a pe-pH diagram such as the one presented in Figure 3 (after Dubrovsky et al. [8]). This diagram shows the dominant aqueous and solid phases for iron in a system with K, $SO_4$ and Fe activities typical of those found in leachate from pyritic mine wastes. The shaded area that indicates the field of measured pH and pe values for leachate in Woodlawn overburden lies very close to the $Fe^{2+}$/jarosite boundary line. It is possible, therefore, that iron release from the column was limited by jarosite formation.

This hypothesis can be tested further by comparing the ion activity product (IAP) for jarosite in overburden leachate with the published solubility product ($K_{so}$) for jarosite. The MINEQL speciation model [9] was used to calculate the ion activities in a solution with a composition similar to that of column leachate during the third year of the study (i.e. pH=2.2, pe=6.9, Fe=0.078 M, K=0.01 M, Mg=0.17 M, Cu=0.089 M, Zn=0.215 M, and $SO_4$=0.55 M). The log IAP value for jarosite calculated from the computed activities was -98.5, which falls within the range of $pK_{so}$ values reported for jarosite (i.e. -94.6 to -98.8) and, as such, indicates a likely equilibrium of leachate Fe with jarosite.

An important consequence of jarosite formation is that even when all pyrite is consumed, the system remains buffered against pH rise. For example, any shift toward higher pH results in alteration of jarosite to ferric hydroxide, a change that involves release of $H^+$:

$$KFe_3(SO_4)_2(OH)_6 + 3\,H_2O \rightarrow 3\,Fe(OH)_3 + K^+ + 2\,SO_4^{2-} + 3\,H^+ \qquad (5)$$

It has been concluded by Miller [10] that even in the absence of pyrite oxidation, that spoil containing jarosite and ferric hydroxide would remain acidic with a pH of approximately 3.2 until the jarosite was entirely removed by leaching. It is worth noting that during the latter half of the fifth year of leaching of Woodlawn overburden the pH varied within the range 3 to 3.3.

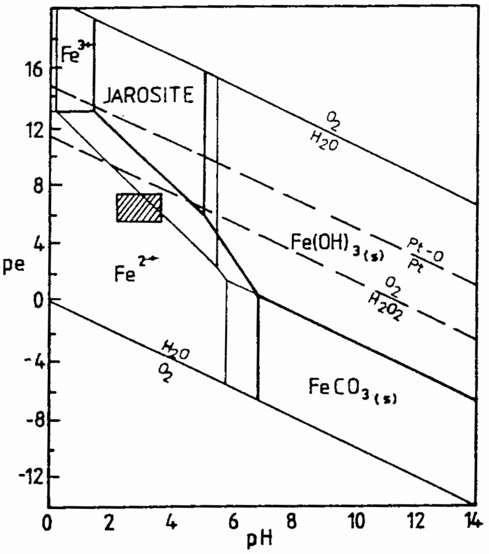

**Figure 3.**

**Plot of pe-pH for Fe species and solid phases. Heavy line defines field drawn for log Fe=-4.05, log K=-3, log SO4 =-2; thin line is for log Fe =-1.79, log k=-2.5, log SO4 =-1.8. After Dubrovsky et al. [8]. Hatched area encloses column values.**

The processes involved in the release of other metals from the overburden may have been similar to those described above for iron. The oxidation of metal sulphide minerals may be due to either direct microbial attack in the presence of oxygen or from leaching by ferric ions derived from pyrite. The two oxidation reactions are respectively described by

$$MS + 2\,O_2 \rightarrow M^{2+} + SO_4^{2-} \qquad (6)$$

$$MS + 8\,Fe^{3+} + 4\,H_2O \rightarrow M^{2+} + SO_4^{2-} + 8\,H^+ + 8\,Fe^{2+} \qquad (7)$$

where M represents a metal cation such as Cu, Zn, or Pb. Once the cation is free it may remain in solution or it may reprecipitate as a secondary mineral. An example of the latter is the formation of insoluble lead sulphate. This precipitation reaction would explain the absence of lead in leachate but the solubilities of copper sulphate and zinc sulphate are much too high to account for the concentrations of copper and zinc in leachate. Even the less soluble hydroxy-type minerals do not account for measured leachate concentrations. We might therefore conclude that the release of these two metals was directly related to their respective sulphide oxidation rates. This conclusion is supported by the fact that there was significantly less copper and zinc in leachate during the third and fourth years even though pH remained virtually unchanged (i.e. solubility showed no pH-dependence). A final point that should be mentioned, however, is that metals that normally would not form insoluble precipitates under strong acid conditions may be taken out of solution by co-precipitation. An example of this is the inclusion of copper in jarosite residues formed on the surface of chalcopyrite [7]. The existence of co-precipitation in this study has yet to be established, but XRD scans of the weathered overburden may be helpful in this regard.

## CONCLUSIONS

There are several important conclusions arising from this study with regard to the leaching of sulphidic mine spoils in leach columns. First, the leaching characteristics of pyritic mine spoils cannot properly be assessed by short-term, benchtop leach tests, since such tests are not sensitive to factors that regulate weathering in field situations. Second, the capacity for oxygen to diffuse into the material is probably the major factor limiting the oxidation of sulphide. Diffusion rate, in turn, is affected by the moisture status of the material so it is essential that the leaching conditions imposed on a column of material are consistent with conditions that would normally be encountered in the field. Third, there is a wide variation in the exposure of sulphide minerals within spoil to leaching agents, so the distribution of particle sizes in the study material should at least roughly correspond with that in mine heaps. Finally, the rates of ion release from leached material may not necessarily relate to sulphide oxidation rate, since secondary mineral formation may occur in material below the oxidation zone. However, if the physical and chemical environment within reacting material are quantified by use of selected sensors and probes, then thermodynamic principles can be utilized to predict long-term ion leaching patterns.

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