# RELEASE OF HEAVY METALS FROM AMD TREATMENT SLUDGES – IMPLICATIONS FOR MANAGING SLUDGE IN PERPETUITY

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## ABSTRACT

*Neutralisation of AMD using an alkaline reagent precipitates sludges dominated by poorly crystalline ferric hydroxide, often with high levels of adsorbed heavy metals (e.g. copper and zinc). Neutralisation sludges produced at mine sites are frequently disposed of into pit lakes or old workings, where they will encounter low pH water.*

*Experimental studies showed that when AMD treatment sludges are exposed to acidic water, they will release metals into solution. Iron, aluminium, copper and zinc begin to be leached at pH 2.5-3, ~4.5, ~5.5 and 6-6.5 respectively. The initial release of Cu and Zn is very rapid; 20-30% and 30-40% respectively are removed within the first 5 minutes at a pH of 4. The rate of release slows, apparently exponentially, after 1 hour. If the sludge is subjected to low pH (<2.5) conditions for long enough, the heavy metal component will almost completely dissolve. The experiments also showed that sludges precipitated by standard neutralisation procedures and reagents all have a similar susceptibility to metal release. Sludges with a high neutralising potential (e.g. a greater content of unreacted neutralising agent) are more resistant to acid attack, but only in that they neutralise more acid before the pH reduces to levels where heavy metal leaching occurs. The long-term chemical instability of AMD treatment sludges under acid conditions has significant implications. Sludge dissolution does not increase the acidity of the water to which it is exposed, but substantially increases the metal loading. If sludge precipitated by neutralisation of acidic open pit water is disposed back into the pit, it will at least partially dissolve. Simple modelling assumes that if the system is open to the addition of more AMD to the pit, the pH remains constant and dissolution of the AMD treatment sludge substantially increases metal concentrations. For typical AMD, this process will double copper and zinc levels in 10-15 years. If the lake is a closed system, with no addition of AMD, it can be modelled using a High Density Sludge (HDS) treatment system, where treatment sludge is recycled and mixed with untreated AMD. In this case the pH rises as more sludge is recycled; dissolved copper and zinc concentrations initially increase as these species are dissolved from the added sludge, but then decrease as the increased pH lowers the metal solubility. For typical treatment of AMD from a pit lake, the change from increase to decrease in copper and zinc concentrations does not occur until almost all the AMD has been treated.*

*In both open and closed system scenarios the higher metal loads contributed to the AMD by sludge dissolution will increase the volume of sludge precipitated per unit volume of acid water treated. As a result, AMD treatment sludges should not be allowed to come into contact with acid waters, even for short periods of time. Thus mine disposal is not generally a wise option.*

## 1. INTRODUCTION

Neutralisation of Acid Mine Drainage (AMD) by adding an alkaline reagent, usually hydrated lime, produces sludges generally dominated by poorly crystalline/amorphous ferric hydroxide (ferrihydrite), often with high levels of adsorbed heavy metals, and frequently also containing gypsum. The long-term chemical stability of these AMD treatment sludges is a significant problem, because they have the potential to release metals back into the environment if they are exposed to low pH water. As a result, AMD treatment sludges may be classified as hazardous waste, limiting disposal options; disposal can often represent a significant proportion of overall AMD treatment costs.

The physical properties of AMD treatment sludges can be substantially improved by the High Density Sludge (HDS) process (Tremblay and Hogan, 2000), which produces a sludge with 15-70 wt% solids, compared to <5 wt% for standard hydrated lime neutralisation sludges (Brown et al. 2002; CEMI 2004; Tremblay and Hogan 2000; Zinck et al. 1997). This process is also claimed to enhance the chemical stability of neutralisation sludges (Brown et al. 2002; CEMI 2004). In addition, two proprietary products (KB-1 and Bauxsol) claim to precipitate sludges with superior chemical stability. KB-1 (manufactured by KEECO, USA) is designed to encapsulate the metals precipitated from AMD in low reactivity silica (Anderson and Roma 2003; Mitchell and Wheaton 1999). Bauxsol (Virotec Pty Ltd, Australia) is manufactured from a seawater-neutralised bauxite refinery residue, with additives such as MgO or $Ca(OH)_2$. Bauxsol removes metals from AMD by a combination of direct precipitation and adsorption (McConchie et al. 2000, 2002).

Two leach tests have been commonly employed to quantify the chemical stability of AMD treatment sludges. The most widely used, the Toxicity Characteristic Leaching Procedure (TCLP, US EPA method 1311), was designed to simulate co-disposal with municipal (putrescible) waste (US EPA 1998), so the leachate is an organic acid (acetic acid). The alternative Synthetic Precipitation Leaching Procedure (SPLP, US EPA method 1312) uses a mixture of inorganic acids (nitric and sulphuric) as the leachate (US EPA, 1998); because it simulates an acid rain scenario, the leachate is only moderately acidic (pH 4.2).

Neither of these procedures was specifically designed for evaluating AMD treatment sludge leachability, and as a result they do not model common mine site disposal environments, i.e. mixed with tailings or waste rock, backfill within the mine, or collection ponds (Zinck et al. 1997). Sludges in these environments are likely to encounter a virtually unlimited supply of waters acidified by sulfide oxidation (pH <3), and neither of the standard procedures (TCLP or SPLP) test for sludge chemical stability under these conditions, due to the type and small volume of acid used in these tests**.**

McDonald et al. (2006b) developed a new leach test (Strong Acid Leach Test, SALT) that more closely reflects mine disposal environments where sludges could come in contact with a virtually unlimited supply of acid, lowering the pH of the sludge pore water. SALT involves a series of leach tests with increasing strengths of $H_2SO_4$ extractant solution added to each test, so that the most acid leachate solution has a pH of <2.5 after 18 hours of end-over-end mixing. The proportion of metals leached was plotted against pH to derive a leaching curve for the sludge being tested.

McDonald et al. (2006a) also developed a kinetic leach test, in order to better understand how and why heavy metals are leached from AMD treatment sludges. For this test, the pH was maintained at 4 and samples taken periodically for 18 hours; this enabled the rate of metal release to be investigated. The kinetic test simulates disposal of AMD treatment sludge in a moderately acidic environment, such as a pit lake or AMD collection pond, and can by itself provide a good indication of the chemical stability of the sludge, although SALT results are required to fully characterise sludge leachability.

This paper reviews the results from the SALT and kinetic testing, and uses them as the basis for modelling pit lake water chemistry in a system where AMD treatment sludge is disposed into a pit lake.

## 2. METHODS

The methods used for AMD neutralization and SALT are described in detail in McDonald et al. (2006b) and for the kinetic test in McDonald et al. (2006a). A brief summary is provided below. Synthetic AMD was prepared as 150 L batches of dark brown liquid containing 1200 mg $L^{-1}$ ferric Fe, 110 mg $L^{-1}$ Al, 100 mg $L^{-1}$ Cu and 100 mg $L^{-1}$ Zn (all ± 10 mg $L^{-1}$), made up with tap water. The pH was lowered to 2.3 with sulphuric acid, giving a total sulphate concentration of ~4000 mg $L^{-1}$.

### 2.1 Batch Reactor

Batches of 150 L of AMD were neutralised in a mixed 170 L polyethylene tank. The neutralisation reagents hydrated lime, limestone and KB-1 (Table 1) were added as 15 wt% slurries; Bauxsol powder was added directly to ensure that Virotec's recommended dosing rate of 0.3g $L^{-1}$ per 4 hours was not exceeded. The pH, EC, Oxidation Reduction Potential (ORP) and temperature of the AMD were monitored by standard meters installed with appropriate probes. Once neutralisation was complete, mixing and aeration (if used, Table 1) continued for 18-20 hours to ensure thorough oxidation of the treated water and sludge, as would naturally occur over time during sludge storage/disposal. The sludge was allowed to settle for 24 hours and then collected for analysis.

### 2.2 High Density Sludge (HDS) Reactor

The laboratory scale High Density Sludge (HDS) plant consisted of three 1.1 L reactors and a 1 L separation funnel for solid/liquid separation. A total of 250 L of synthetic AMD (pH 2.3) was pumped into reactor 1 at a rate of 25 mL $min^{-1}$; AMD retention time was approximately 20 minutes in each reactor. All three reactors were constantly sparged with air. The overflow from the separator (treated water) flowed into a collection container, and the underflow (sludge) was pumped into reactor 1 at a recycle rate of 18-22 after an initial start-up period (i.e. 18-22 g dry wt of solids were pumped into reactor 1 for each gram of solids precipitated from the AMD neutralisation). The recycled sludge raised the pH in reactor 1 to between 6.7 and 7.2. A 10 wt% hydrated lime slurry was pumped into reactor 2 to increase the pH to 9 to complete the treatment.

### 2.3 SALT Leach Testing

Each sludge slurry was mixed to ensure homogeneity, and then a subsample equivalent to 50 g dry solids (calculated from the wt% solids of the slurry) was added to a plastic leach vessel along with 1L of the appropriate leachate (see below), mixed end-over-end at 30 rpm for 18 hours, and allowed to settle for 1–2 hours. The extractant fluid was carefully poured off the top and filtered (0.45 µm). The period of end-over-end mixing, as used in TCLP, SPLP and other sludge studies (e.g. Aube et al. 2005), is a more aggressive procedure than the sludge will undergo at a mine site, but effectively simulates the extended leaching time of the disposal environment, and allows the leaching to proceed to completion. Each sludge sample was leached by a series of solutions composed of sulphuric acid diluted to 1L; the pH of the extractant solution decreased by ~1pH unit with each test, such that the pH at the end of the first extraction was ~6 and that at the end of the last test was ~2. The volume of sulphuric acid for each extraction was chosen to achieve the required pH.

**Table 1. Details of neutralisation procedures**

| Run name | Neutralisation equipment | AMD composition | Neutralisation reagent | Final treatment pH | pH of supernatant water after settling (24h) | Reagent use | Reaction time (minutes)[1] | Air sparging |
|---|---|---|---|---|---|---|---|---|
| Run 1 | 170 L reactor | ferric | 15 wt% hydrated lime slurry | 10.04 | 9.19 | 4.06 g/L | 189 | Started 95 minutes after neutralisation started |
| Run 2 | 170 L reactor | ferric | 15 wt% hydrated lime slurry | 9.57 | 8.85 | 3.64 g/L | 64 | Continuous |
| Run 3 | 170 L reactor | ferric | 15 wt% limestone slurry | 5.17 | | 5.85 g/L | 53 | Continuous |
| | | | 15 wt% hydrated lime slurry | 9.55 | 9.09 | 4.99 g/L | 92 | |
| Run 4 | 170 L reactor | ferric | 15 wt% limestone slurry | 5.17 | 7.71 (after 4 days sparging) | 5.88 g/L | 77 | Continuous, including for four days between adding $CaCO_3$ and $Ca(OH)_2$ |
| | | | 15 wt% hydrated lime slurry | 9.11 | 8.85 | 0.26 g/L | 5 | |
| Run 5 | 170 L reactor | ferric | 15 wt% KB-1 slurry | 9.41 | 9.18 | 5.07 g/L | 152 | Continuous |
| Run 6 | 170 L reactor | ferric | Bauxsol powder, added directly to AMD at the Virotech recommended rate of 0.3g/L/4 hours. | 8.22 | 8.33 | 11.71 g/L | 21 days | No sparging as neutralisation was conducted over 21 days. |
| Run 7 | HDS Plant. 250L of AMD was treated to allow time for density to build up. | ferric | 10 wt% hydrated lime slurry. Lower concentration slurry used to reduce chance of HDS plant blockage. | Reagent added as required to keep reactor 2 at a pH of 9. | 8.37 | 3.46 g/L | 133 min (water) / 26.7 hr (sludge)[2] | Continuous into all 3 reactors |

[1]Reaction time for Runs 1–6 is the time taken to add reagent. Further reagent dissolution or Fe oxidation may occur after this.
[2]Average residence time of water/sludge in HDS plant after initial start-up period. Total treatment time for Run 7 was 8 days.

### 2.4 Kinetic Leach Testing

In this method, 25.0 g of oven-dried (40°C) AMD treatment sludge was added to a 600 ml beaker along with 500 ml of deionised water, and fully dispersed using sonication for 10 minutes with occasional stirring. The pH was allowed to stabilise for 5 minutes before a slug of concentrated sulphuric acid was added; the volume of sulphuric acid was not set, but calculated to reduce the solution pH to 4-5. To maintain the pH at 4.0, sufficient 1.4 M sulphuric acid was added to the stirred sludge using a peristaltic pump to balance the increase in pH due to dissolution of the sludge. 50 ml samples of the stirred sludge and the extractant fluid (leachate) were taken at 5, 15, 30, 45, 60, 90, 120, 180 minutes and 18 hours after the initial dose of sulphuric acid was added. Each sludge sample was immediately vacuum filtered to 0.45 µm, acidified and stored for analysis in an airtight container.

## 3. RESULTS AND DISCUSSION

### 3.1 Sludge Composition

The sludges from Runs 1–7 consisted predominantly of amorphous ferric oxy-hydroxide and crystalline gypsum (McDonald et al. 2006b), other than the Bauxsol sludge (Run 6) which lacked gypsum. In addition many sludges contained a minor calcite phase. The sludges from Runs 1, 3 and 4 (lime and limestone neutralisations) and Run 7 (HDS) have very low values of the magnetic hysteresis parameters indicating that there is very little, if any crystallinity of the iron hydroxide component within these sludges, so they are composed of amorphous ferrihydrite (see McDonald et al. 2006b for explanation). The sludge from Runs 2 and 5 has higher magnetic hysteresis parameters indicating the presence of a small component of very fine-grained (~3nm) goethite crystallites. The hysteresis response of sludges from Run 6 (Bauxsol) was very similar to the reagent, indicating that the crystallinity of these sludges is dominated by components inherited from the reagents; this is also evident in the sludge mineralogy.

### 3.2 SALT Results

To obtain a clear idea of the chemical stability of a sludge, it should be leached under a variety of pH conditions, including low pH values, and SALT was developed for this purpose. In TCLP and SPLP the initial pH of the leachate is fixed (so the final pH of the leachate is determined by the neutralising potential of the sludge), whereas in SALT the final pH of the leachate is important. Sufficient acid is added to overcome the sludge's neutralising potential, and hence much greater amounts of metals are liberated into the extracting fluid. Thus SALT measures how tightly metals are bound to the sludge, rather than how much alkalinity the sludge contains.

Several conclusions are evident from the SALT tests (Figures 1–4). Firstly, as expected, the lower the pH of the leaching solution, the more metals were leached from all sludges. Secondly, all the reagents used in this study generated sludge with similar chemical stability, except for the Bauxsol and KB-1 sludges, which released more aluminium because both reagents contain this element (McDonald et al. 2006b). The HDS hydrated lime sludge (Run 7) has a higher density than normal hydrated lime sludge (Run 2), due to its lower water content and coarser gypsum crystals (Brown et al. 2002), but has the same leachability. Thirdly, different metals leach at very different rates and begin to be liberated at substantially different pH values (Figures 1-4).

Iron begins to dissolve at pH 3; the amount mobilised increases greatly (probably exponentially) at lower pH values, so that ~40% of the iron in the sludge has been liberated at a pH of 2-2.5. These results (Figure 1) reflect the solubility of poorly crystalline ferric oxyhydroxides (ferrihydrite); under very oxidising Eh conditions, the stability boundary between ferrihydrite and soluble iron (as $Fe^{3+}$) lies at a pH of 2.5-3 (Drever 1997).

Aluminium starts to be released into the leachate at a higher pH (~4.5), and is leached more slowly as the pH drops, such that 60-70% is in solution at pH 2-2.5. This probably reflects the solubility of poorly crystalline aluminium hydroxide.

Copper begins to leach at around pH 5.5 and virtually all of it is in solution at pH 2-2.5. Zinc starts to be mobilised at a pH value of 6.5 and ~100% is soluble by pH 2.5. Copper and zinc are present in AMD treatment sludges as various species adsorbed onto the surface of the poorly crystalline ferric oxyhydroxide (Kinniburg et al. 1976; Webster et al. 1998). The copper and zinc desorption curves from the present experiments (Figures 3, 4) are not mirror images of typical adsorption curves for these metals on ferric oxides/hydroxides (Kinniburg et al. 1976; Webster et al. 1998; Dzombak & Morel, 1990), in that desorption is complete at pH values well below those at which adsorption typically commences (2-2.5 compared to 3.5-5).

Trendlines fitted to the data (Figures 1–4) allow prediction of the proportion of metals that will be leached from a sludge at a specific pH. Although there is some spread in the data, the trendlines for Cu and Zn (elements with the most scatter) both have high $R^2$ values (0.94, 0.75 respectively). The aluminium data from Runs 5 and 6 were not included when calculating the aluminium trendline, as the reagents KB-1 and Bauxsol contain this element. The SALT leach results for the KB-1 sludge contain two points (pH 2.34, 3.21) that fall below the trend for that sludge, probably due to sludge inhomogeneity.

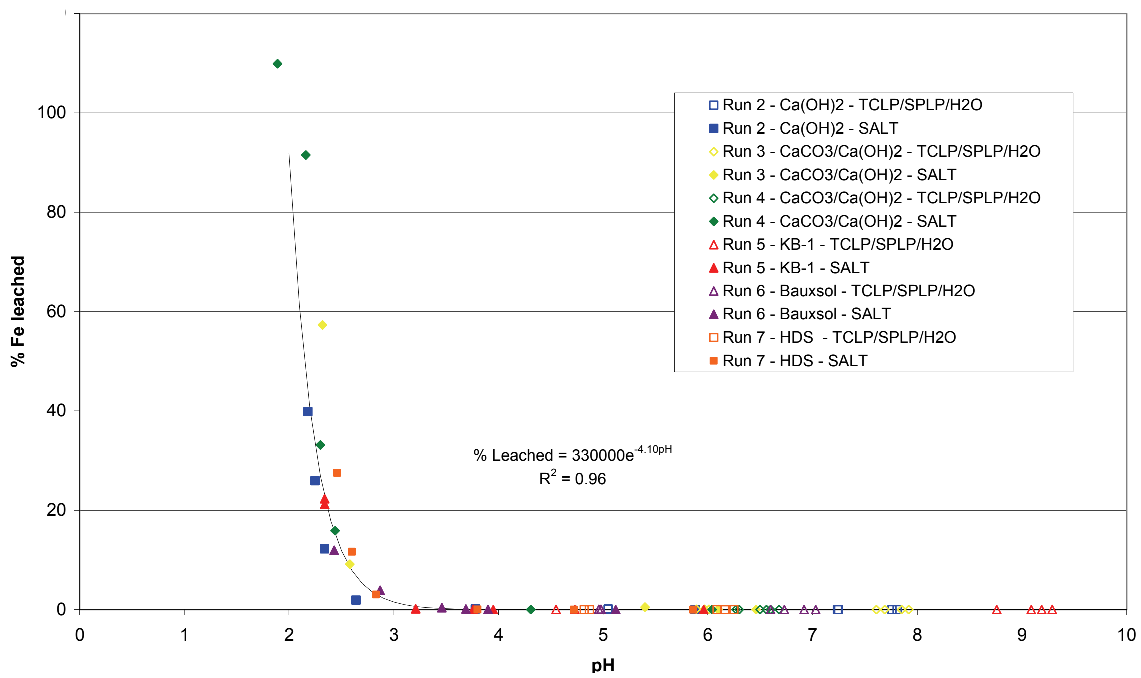


**Fig. 1.** **Percentage of iron leached from sludge versus pH of extractant solution**

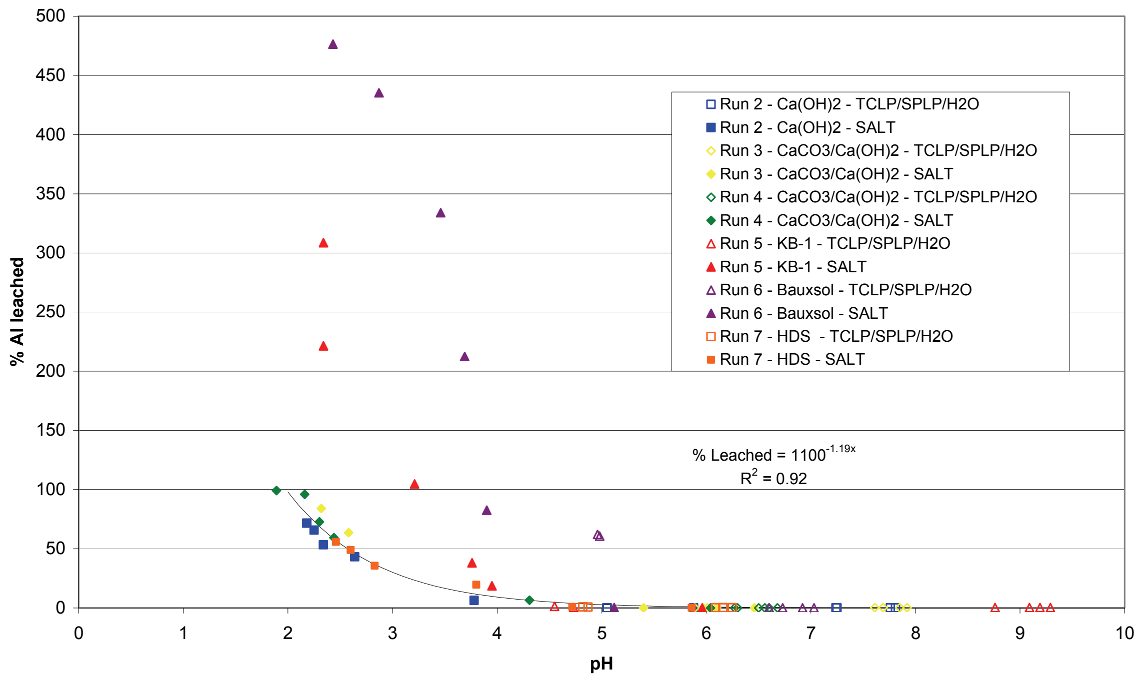


**Fig. 2. Percentage of aluminium leached from sludge versus pH of extractant solution**

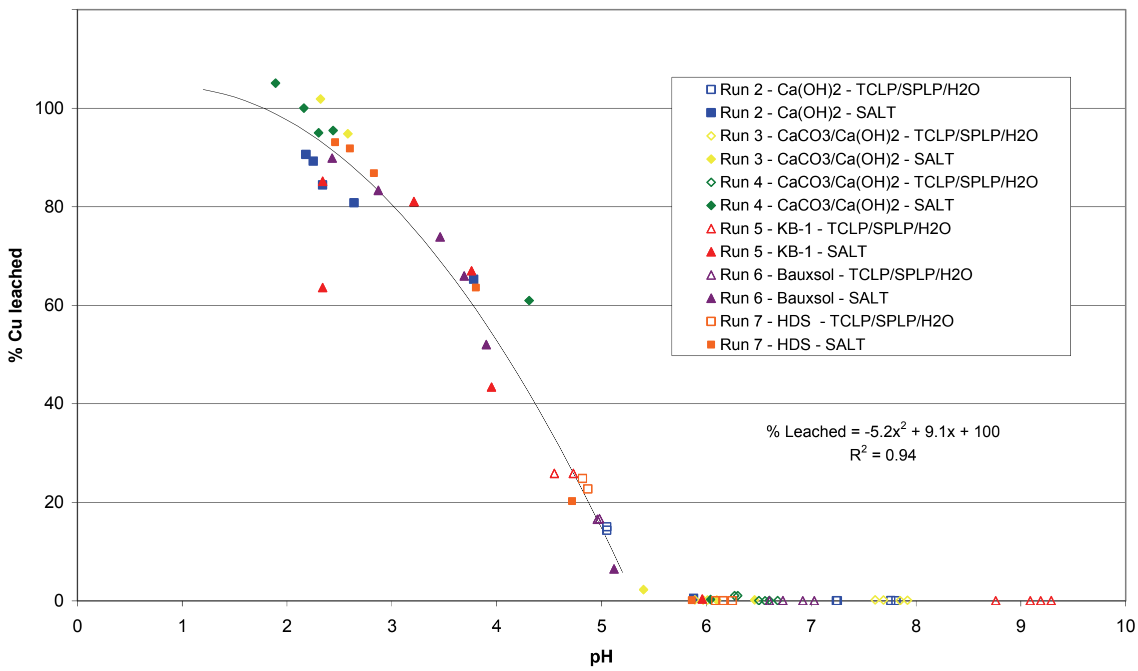


**Fig. 3. Percentage of copper leached from sludge versus pH of extractant solution**

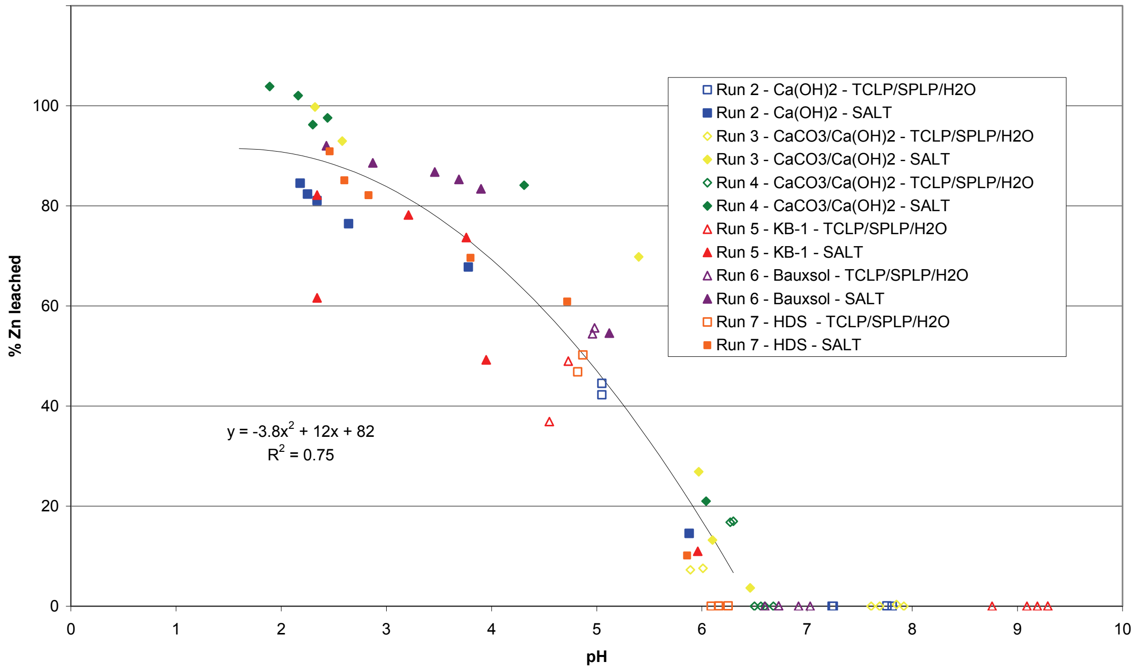


**Fig. 4. Percentage of zinc leached from sludge versus pH of extractant solution**

Similar results have been encountered in other studies. Watzlaf and Casson (1990) found that iron and manganese release from sludges increased with pH decrease in a stirred beaker, and in column leach experiments simulating co-disposal with tailings, Clarke (2000) noted that leachate aluminium concentrations rose sharply after the neutralisation capacity of the tailings/sludge mixtures had been exhausted and the pH of the leachate within the column dropped.

### 3.3 Kinetic Test Results

Kinetic testing showed that the leaching of Cu and Zn from the Run 1–7 sludges is initially very rapid and reduces over time, apparently exponentially (Figures 5 and 6). Approximately 20-30% and 30-40%, respectively of the copper and zinc was leached within the first 5 minutes, representing ~50% of the total amount of these metals leached during the kinetic tests. The rate of release slowed dramatically after 1 hour.

All the sludges, except that generated from Run 6 (Bauxsol), have similar copper release curves (Figure 5), and hence exhibit a similar chemical stability with respect to copper. For Run 6 the amount of copper leached after 18 hours of mixing was similar to the other runs (Figure 5) but the rate of release was slower; however, the mineral grains within the Bauxsol reagent were too coarse to be suspended by the overhead stirrer used, and thus the slower rate of copper release may be due to incomplete mixing rather than slower reaction kinetics. Kinetic tests were repeated for Runs 1 and 6 (not shown) to assess reproducibility, and variation between repeats was excellent with differences of only 2-4% after 18 hours of mixing. The small variations in the proportion of copper leached from different sludges before 90 minutes are probably not significant.

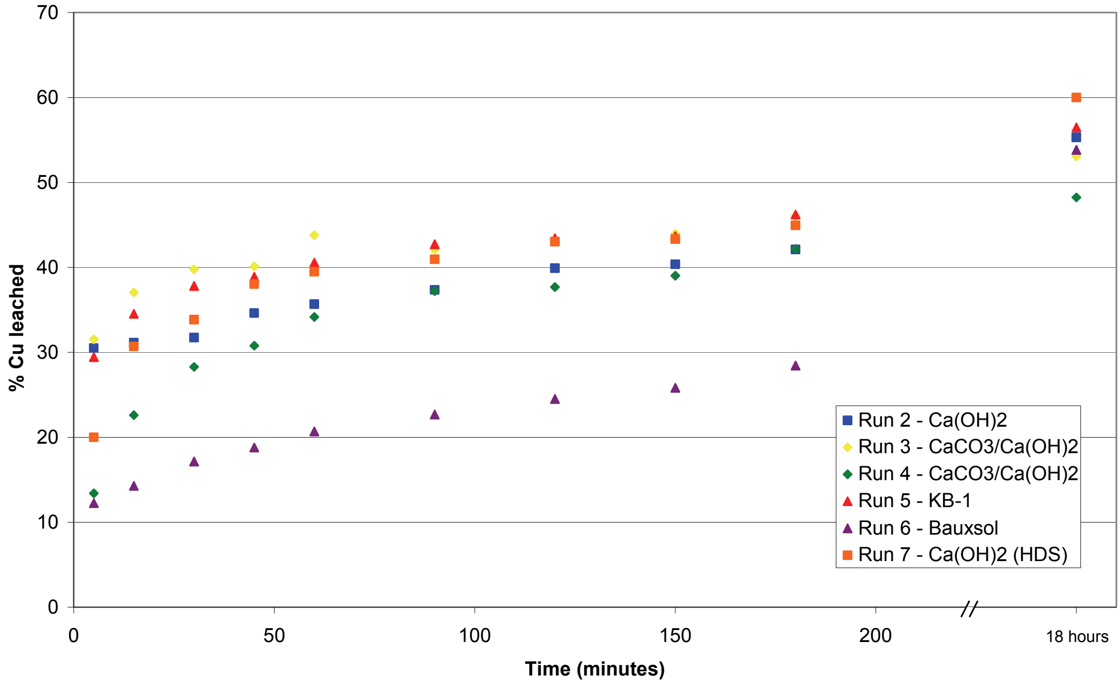


**Fig. 5.** **Rate of copper release from sludges precipitated from oxidised AMD**

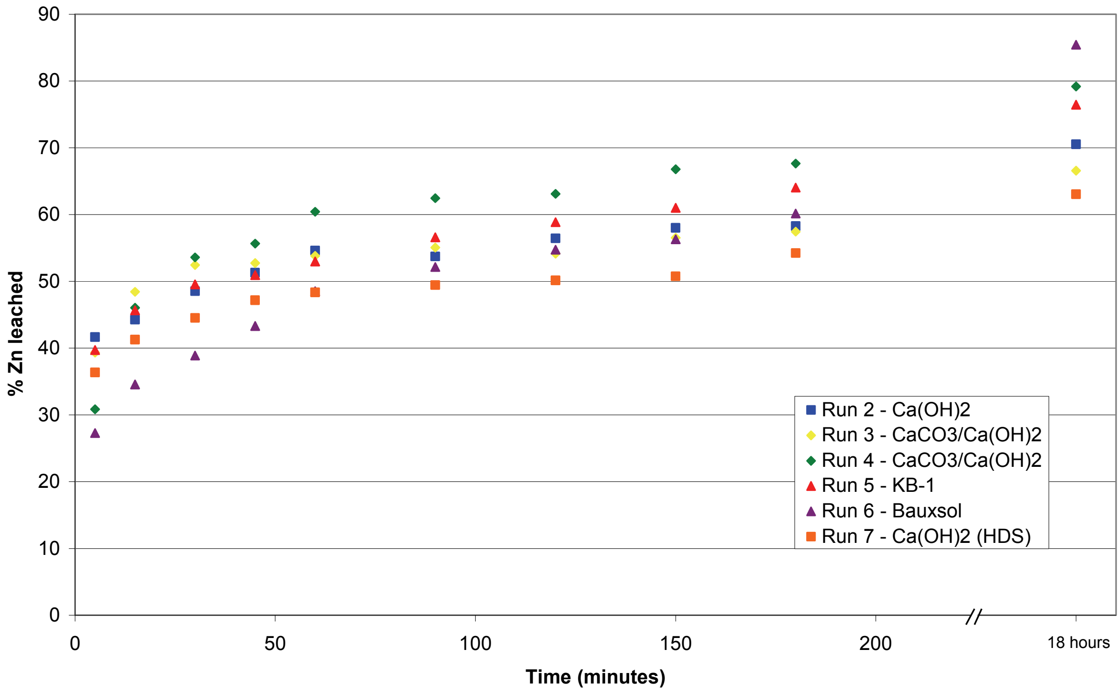


**Fig. 6.** **Rate of zinc release from sludges precipitated from oxidised AMD**

The zinc leach curves (Figure 6) exhibit 10-20% spread in results, consistent with the variations evident in the previous SALT results (McDonald et al. 2006b). Repeat kinetic testing of sludges generated in Runs 1, 2 and 6 (not shown) showed variations of only 3-7%

in the amount of zinc leached after 18 hours, indicating that the spread in the proportion of Zn leached over the different runs may be related to slight variations in the neutralisation and leaching procedures rather than the reagent used, because sludges from the two separate limestone neutralisations show ~15% difference in leachability of zinc at the end of the kinetic tests.

After 18 hours all sludges had leached 50-60% of their copper content and 65-85% of their zinc content, and these results compare well with Strong Acid Leach Test (SALT) results from the same sludges (see above). Given the variability within the results, there is no difference in chemical stability between sludges formed by standard lime neutralisation and those precipitated by other reagents or processes (KB-1, Run 5; Bauxsol, Run 6; HDS, Run 7). Differences in chemical stability between repeat neutralisations are greater than differences between reagents. These results confirm the previous SALT results, which showed that Fe, Cu and Zn release from AMD treatment sludges was not dependent on which neutralising reagent/process was used, but on pH. Hence a sludge's chemical stability is governed by its neutralising potential, because sludges with a higher neutralisation potential can neutralise a larger volume of acid before the pH drops to levels where the metals in the sludge are mobilised.

The initial rapid release of large amounts of Cu and Zn from all sludges, over a period of minutes, shows that AMD neutralisation sludges will quickly leach adsorbed metals into acid water. This is potentially of great concern, as it indicates that if the sludges are placed in an acid environment, even for a short time, they will rapidly liberate substantial amounts of heavy metals into the surrounding ground or surface waters.

Copper and Zn are probably present in AMD treatment sludges as hydroxide species adsorbed onto the surface of the poorly crystalline ferric oxyhydroxide (Kinniburgh et al. 1976, Webster et al. 1998). The initial very rapid release of Cu and Zn during the kinetic tests followed by the exponentially decreasing rate of metal release with time (Figures 5 and 6) is probably indicative of surface desorption reactions tending towards equilibrium.

## 4. MODELLING

To test the impact of sludge dissolution in a mine water disposal situation, a scenario was developed loosely based on the Mt Morgan site (Jones et al. 2003), where AMD is collected in a pit lake, treated in a lime HDS plant, and the treatment sludge deposited back into the pit lake. Input water chemistries used in the model are those of the synthetic AMD in this paper and the measured pit lake water at Mt Morgan (Jones et al. 2003).

**Table 2. Measured water chemistry**

| Parameter | Mt Morgan (Jones et al. 2003) | Synthetic AMD |
|---|---|---|
| pH | 2.8 | 2.3 |
| Conductivity | 11000 | |
| Fe (total) | 248 | 1200 |
| Fe (II) | 3 | |
| Al | 720 | 110 |
| Cu | 36 | 100 |
| Zn | 25.3 | 100 |

| Table 2 (cont'd) Parameter | Mt Morgan (Jones et al. 2003) | Synthetic AMD |
|---|---|---|
| Cd | 0.15 | |
| Mn | 81 | |
| Ca | 520 | |
| Mg | 1240 | |
| $SO_4$ | 12100 | 4000 |

All values in mg $L^{-1}$ except for pH and conductivity ($\mu S\ cm^{-1}$).

The pit lake at Mt Morgan contains approximately 9000 ML of water; 630 ML would need to be treated every year to reduce the risk of an uncontrolled spill to less than 1% (Jones et al. 2003). Thus the modelling assumes that the treatment plant is operated at 630 ML $year^{-1}$ for the simulation period.

The laboratory experiments presented above show that the leachability of AMD treatment sludge is mainly dependent on solution pH, and that leaching occurs very rapidly: in a stirred solution at pH 4, 20-30% of copper and 30-40% of Zn was leached in 5 minutes, and 30-40% of copper and 40-50% of Zn was leached in 30 minutes.

When the AMD treatment sludge at Mt Morgan is disposed to the pit late, a proportion of this sludge will re-dissolve and increase the metals concentration within the pit lake according to the general equation:

$$M^{n+}(OH)_n\ (s) + nH^+ = M^{n+} + nH_2O \qquad [1]$$

This reaction will consume $H^+$ and release metal ions, and thus increase the pH. As the metal hydroxide sludge dissolves, the pH will increase and the metal solubility will decrease (because metal solubility is determined by pH), until equilibrium is reached. However, a large amount of AMD treatment sludge would need to be dissolved to increase the pH significantly. It should be noted that metal dissolution according to equation 1 will not change the acidity of the water. However, if the treatment sludge contains alkalinity (from unreacted neutralisation reagent), then dissolution of the treatment sludge will decrease the acidity of the pit water and increase the pH.

Modelling of pit lake disposal of AMD treatment sludge at Mt Morgan can be considered in terms of either a “closed” or an “open” system. In a closed system, there is no addition of AMD to the lake, so if AMD is removed from the lake, treated and the sludge returned to the lake metal concentrations in solution will initially increase as the sludge dissolves. However, if the pH increases due to dissolution of metal hydroxides and neutralisation by unreacted reagent retained in the sludge, the metal’s solubility and hence concentration will decrease. In contrast, in an open system, additional AMD flows into the lake over time. This is likely (depending on the inflow rate compared to rate of treatment sludge addition) to maintain a constant pH, even when AMD treatment sludge is being added to the pit lake. Metal concentrations will therefore increase due to sludge dissolution, although the increases may be marginally diluted if the input of additional AMD is greater than the amount of AMD being withdrawn for treatment.

### 4.1 Sludge Disposal into an Open System

If the treatment plant at Mt Morgan was operated at the calculated capacity to maintain the risk of uncontrolled discharge at less than 1% (630 ML $year^{-1}$), then 7% of the lake volume will be treated every year and the resulting treatment sludge returned to the lake. As stated above, it is assumed that for an open system any increase in pH from treatment sludge dissolution will be minor and AMD inflows will maintain the original pH: 2.8 in the case of Mt Morgan and 2.3 in the case of the synthetic AMD. The proportion of precipitated metals re-dissolved from the AMD treatment sludge, as determined by SALT results, is presented in Table 3.

**Table 3. Proportion of metals re-dissolved from AMD treatment sludge**

| Metal | Percentage dissolved from sludge at pH 2.8 | Percentage dissolved from sludge at pH 2.3 |
|---|---|---|
| Fe | 5 | 50 |
| Al | 40 | 70 |
| Cu | 85 | 90 |
| Zn | 85 | 90 |

Although SALT is a leach test that uses end-over-end mixing for only 18 hours, it is still believed to adequately represent pit lake disposal as:

- Kinetic testing shows that metals are rapidly dissolved.
- Some mixing will occur as disposed sludge settles through the water column.
- A much greater time period (at least years to decades) is involved for the pit lake disposal scenario.
- If the lake is receiving recharge from acid groundwater, this may percolate through the sludge.

Thus, a model was constructed where 630 ML (7%) of AMD was treated so that the metals completely precipitated to form a metal hydroxide sludge, this sludge was disposed to an acid pit lake, and a proportion of the treatment sludge dissolved according to Table 3. The model assumes a net zero water balance, i.e. AMD removed and treated is replaced by fresh AMD of the same water chemistry. Results of the modelling are presented in Table 4.

The concentration of copper and zinc was found to double in 13 years for both water chemistries. The proportion of iron and aluminium dissolved is greater in the synthetic AMD because of its lower pH, so the rate of increase of the concentrations of these metals is greater for the synthetic AMD than for the Mt Morgan AMD. The concentrations of aluminium in both synthetic and Mt Morgan AMD, and the concentration of iron in synthetic AMD, doubled in less than 30 years.

Dissolution of metal hydroxides will not alter the overall acidity of the system, as the increase in pH is balanced by the increase in metal acidity (equation 1). However sludge dissolution has implications for ongoing AMD neutralisation, due to the higher metal load it contributes to the AMD still requiring treatment. This will progressively increase the volume of sludge precipitated per unit volume of acid water treated. In addition, if uncontrolled discharge of untreated AMD was to occur, environmental damage may be greater or occur over a greater area due to the increased metal concentrations.

**Table 4. Modelling results**

| | Initial conc. | Conc. after 1 year | % increase (1 year) | Conc. after 10 years | % increase (10 years) | Years to double conc. |
|---|---|---|---|---|---|---|
| **Mt Morgan Chemistry** | | | | | | |
| Fe | 248 | 248.9 | 0.35 | 256.8 | 3.2 | 200 |
| Al | 720 | 740.2 | 2.8 | 949.0 | 28.2 | 27 |
| Cu | 36 | 38.1 | 6.0 | 64.2 | 68.2 | 13 |
| Zn | 25.3 | 26.8 | 5.9 | 45.1 | 68.2 | 13 |
| **Synthetic AMD Chemistry** | | | | | | |
| Fe | 1200 | 1,242.0 | 3.5 | 1692.7 | 36.3 | 22 |
| Al | 110 | 115.4 | 4.9 | 177.5 | 53.8 | 16 |
| Cu | 100 | 106.3 | 6.3 | 184.2 | 73.3 | 13 |
| Zn | 100 | 106.3 | 6.3 | 184.2 | 73.3 | 13 |

### 4.2 Sludge Disposal into a Closed System

In a closed system, AMD removed from the lake for treatment is not replaced by fresh AMD, and hence over time dissolution of the sludge has the potential to raise the pH to such a level that metals become less soluble; eventually equilibrium will be reached.

A HDS treatment system is analogous to pit lake disposal of sludge in a closed system, in that a large proportion of treatment sludge obtained by neutralising the AMD is recycled and mixed with untreated AMD. High recycle ratios[1] are often used in order to obtain a high density sludge and at the same time partially neutralise the influent AMD, as a result both of metal dissolution and the presence of unreacted neutralisation agent in the sludge. In reality, a HDS treatment plant is actually an open system, as fresh AMD is constantly being introduced. However, for the purposes of this model, a HDS treatment plant resembles a closed system, as the rate of sludge recycle is high when compared to the volume of AMD added.

The HDS experiment described above (Run 7) showed that the pH rises as the recycle ratio increases (Table 5), and an indication of the concentrations of metals in solution can be interpolated from the SALT results (Figures 3-4). However the sludge:eluent ratio in the SALT tests was significantly different from that in the HDS experiment, so the results should be used as a guide only. Nevertheless the experiments show that for a recycle ratio of 20 (i.e. 20 g of sludge was added during neutralisation for every 1 g of sludge precipitated), the

[1] Recycle Ratio is the dry weight of neutralisation sludge that is mixed with the influent AMD for each unit mass (dry weight) of sludge precipitated from the neutralization of the AMD. For example, if neutralisation of a volume of AMD yields 5 g (dry weight) of sludge, then a recycle ratio of 5 means that 25 g of sludge is added during the AMD neutralisation.

pH rose to circum-neutral (there was a significant contribution to the neutralisation from unreacted neutralisation agent in the sludge), and as a result the concentrations of the dissolved metals fell to very low levels.

**Table 5. pH of HDS reactor for different sludge recycle ratios**

| Recycle Ratio | pH | Percentage of species added to system (AMD and sludge) that is in solution[1] | |
|---|---|---|---|
| | | Copper | Zinc |
| 0 (Raw AMD) | 2.3 | 100 | 100 |
| 2 | 3[2] | 80 | 85 |
| 3.3 | 3.5[2] | 65 | 75 |
| 5 | 4 | 50 | 65 |
| 8 | 5 | 15 | 45 |
| 13 | 6 | 0 | 20 |
| 17 | 6.5 | 0 | 0 |

[1]From Figures 3–4
[2]Value interpolated from other data

Recycling treatment sludge to the AMD during neutralisation adds copper and zinc to the system, so dissolved copper and zinc concentrations will initially increase as these species are dissolved from the added sludge, but will then decrease as the increased pH lowers the metal solubility. As a guide to the relative influences of these two processes, a simplified calculation was performed, multiplying the percentage of copper and zinc that will be released into solution (Table 5) by the total concentration of copper or zinc in the system (i.e. from recycled sludge and AMD; Figure 7).At recycle ratios of approximately 5 and 8 (for copper and zinc respectively), the concentrations of metals in solution will begin to decrease. In the case where AMD treatment sludge is disposed to a pit lake, lower “recycle rates” would be expected and therefore levels of metals in solution will rise. Although mixing would not be as extensive as in the above experiments, copper and zinc dissolution will still occur, as the kinetic testing showed that significant proportions of these metals dissolved within 5 minutes at a pH of 4. Lower pH values (AMD often pH <3) would increase the rate and extent of metal dissolution.

These results are relevant to treatment of Mt Morgan AMD, but they can be applied only approximately, as the Mt Morgan AMD has a different composition to the synthetic AMD used in the experiments, and as a result it is not known exactly what pH will be achieved at any given recycle ratio. Furthermore, in the experiments the treatment sludge and AMD completely mix, however in a pit lake mixing would become less complete over time as sludge volumes build up on the pit lake floor, slightly reducing the dissolution of metals from the sludge However, general trends at Mt Morgan are expected to be similar to the experiments, in that dissolved metal concentrations will increase significantly at lower recycle ratios, and high recycle ratios (>5-10) are required before copper and zinc concentrations begin to decrease.

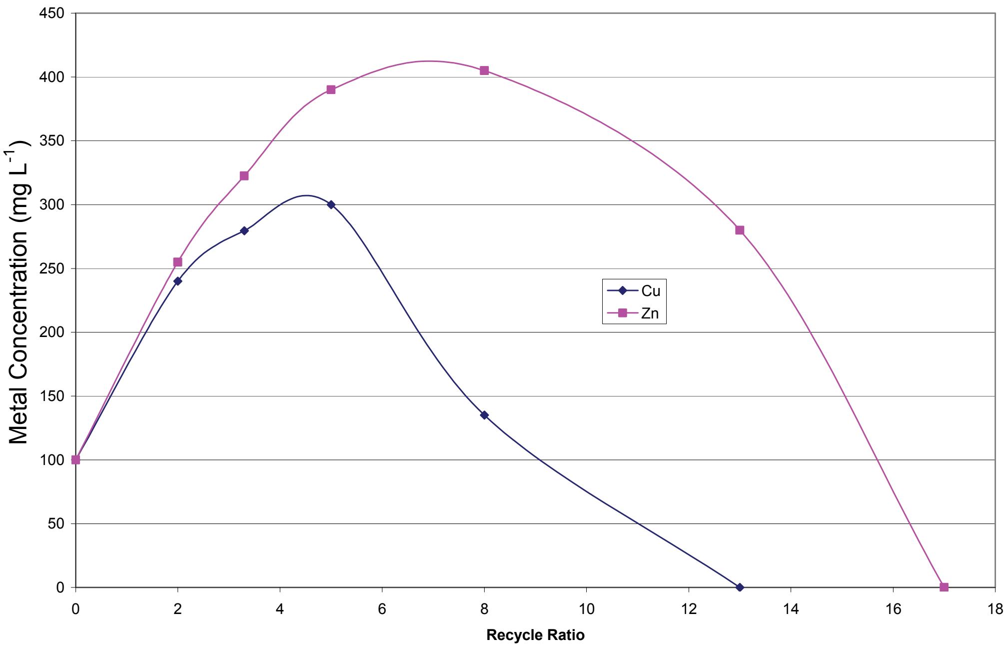


**Fig. 7. Predicted copper and zinc concentrations in a closed system**

If AMD from Mt Morgan is treated at 630 ML year$^{-1}$ (7% of the lake volume), then 7% of the sludge that would be precipitated by neutralising the entire lake is added back to the lake, i.e. the recycle ratio is 0.07. Furthermore, if this is considered as a closed system (no additional AMD entering the pit lake), then over time the AMD volume will reduce and the sludge volume increase, so that the recycle ratio increases (Table 6), but only rises above three after 12 years, for the final two years of treatment. At these moderately low recycle ratios, copper and zinc concentrations increase markedly (Figure 7). If the synthetic AMD was treated at the rate proposed for Mt Morgan, copper concentrations would increase by ~2.5 times and zinc concentrations by ~3 times after 14 years of treatment, and the change from increase to decrease in copper and zinc concentrations would not occur until ~15 years, when almost all the AMD had been treated..

**Table 6. Recycle ratio assuming Mt Morgan pit lake acts as a closed system**

| Year | Pit lake volume (ML) | Recycle ratio |
|---|---|---|
| 1 | 9000 | 0.07 |
| 2 | 8370 | 0.15 |
| 3 | 7740 | 0.23 |
| 4 | 7110 | 0.32 |
| 5 | 6480 | 0.41 |
| 6 | 5850 | 0.52 |
| 7 | 5220 | 0.64 |
| 8 | 4590 | 0.78 |
| 9 | 3960 | 0.94 |

| Table 6 (cont'd) | | |
|---|---|---|
| **Year** | **Pit lake volume (ML)** | **Recycle ratio** |
| 10 | 3330 | 1.13 |
| 11 | 2700 | 1.36 |
| 12 | 2070 | 1.66 |
| 13 | 1440 | 2.10 |
| 14 | 810 | 2.88 |
| 15 | 180 | 6.38 |

## 5. CONCLUSIONS AND RECOMMENDATIONS

The results of strong acid leaching show that once the neutralisation potential of an AMD treatment sludge is exhausted, the sludge becomes chemically unstable and begins to leach Fe, Al, Cu and Zn at pH values of 2.5-3, ~4.5, ~5.5 and ~6.5 respectively. Zinc is of particular concern, as it begins to leach at a near neutral pH. The kinetic tests have shown that in sludges formed by standard AMD neutralisation procedures and reagents (lime, limestone, Bauxsol, KB-1 and HDS lime), heavy metals like Cu and Zn are adsorbed onto the surface of the amorphous ferrihydrite, and are very rapidly released if the sludge is exposed to acid conditions. The sludges formed by the different reagents and procedures all exhibit similar chemical stability. Therefore, it is important to ensure that AMD treatment sludges do not come into contact with acid waters, even for short periods of time. Sludges with a high neutralising potential are more resistant to acid leaching only in the sense that they can neutralise more acid in pore waters before the pH reduces to levels where heavy metal leaching occurs.

Simple modelling shows that if sludge precipitated by neutralisation of acidic open pit water is disposed of back into the pit, it will at least partially dissolve. In an open system, where additional AMD flows into the lake to maintain a constant pH, dissolution of the AMD treatment sludge being added to the pit lake will substantially increase metal concentrations. For typical AMD, this process will double copper and zinc levels in 10-15 years, and double aluminium and iron concentrations in <30 years.

In a closed system, there is no addition of AMD to the lake, and the system can be modelled using a HDS treatment system, where a large proportion of treatment sludge obtained by neutralising the AMD is recycled and mixed with untreated AMD. HDS experiments showed that the pH rises as more sludge is recycled. Dissolved copper and zinc concentrations initially increase as these species are dissolved from the added sludge, but then decrease as the increased pH lowers the metal solubility. If typical AMD from a pit lake is treated at 7% of the lake volume per year, the change from increase to decrease in copper and zinc concentrations does not occur until ~15 years, when almost all the AMD has been treated. In both closed and open systems, dissolution of metal hydroxides will not alter the overall acidity of the system, as the increase in pH is balanced by the increase in metal acidity. However the higher metal loads contributed to the AMD still requiring treatment will increase the volume of sludge precipitated per unit volume of acid water treated.

Therefore AMD treatment sludges should not be allowed to come into contact with acid waters, even for short periods of time. Thus mine disposal is not generally a wise option. If site characteristics favour disposal of treatment sludges within an acidic pit lake, site-specific test work should be conducted to determine the likely long-term impacts on the sludge volume and composition, and the cost implications, and to enable suitable management measures to be put in place.

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