ACID MINE DRAINAGES AT MAMUT COPPER MINE, SABAH, MALAYSIA

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ABSTRACT. Malaysia’s only copper mine is located in Sabah, East Malaysia. The mine was started in 1975 and ceased operation in 1999. As expected acid mine drainage (AMD) pollution is gradually becoming evident at the abandoned mine area. This type of environmental problem, however, is relatively new in Malaysia. Nevertheless, Universiti Malaysia Sabah (UMS) is at the forefront of basic and applied AMD research in the country. This paper provides an overview on some of the research findings, in particular with references to the characteristics of the local AMDs and the potentials of using calcareous materials for its treatment. In general, seepages water at the mine pit area have low pH (2.90 – 3.75), high and variable total acidity (176 – 1697 mg CaCO₃/L), high TDS (302 – 2673 mg/L), high sulphate (292 – 2808 mg/L) and elevated concentrations of dissolved metals (Al, Mn, Fe, Cu and Zn). By contrast, the seepages at the tailing dam is alkaline (pH > 7.0) and according to Acid Base Accounting (ABA) test the tailings have negligible AMD potential. Meanwhile, calcareous sandstone and calcareous mudstone have significant acid neutralization and heavy metal removal ability when tested on the AMD samples. The overall efficiency, however, is dependent on a number of factors, including the strength (i.e total acidity) of the AMD.

KEYWORDS. Acid mine drainages; calcareous materials; heavy metals; tailings.

INTRODUCTION

Mamut Copper Mine (MCM), located in Sabah, East Malaysia, was the only copper mine in Malaysia. It was operational from 1975 to 1999, and during this period the open-cast mine generated about 250 Mt of overburden and waste rocks and over 100 Mt of tailings. The overburdens and waste rocks were dumped at various sites near the mine pit while the tailings were deposited in a tailing dam known as Lohan Tailing Dam (LTD) located in a valley about 1000 m below the mine. Various environmental issues associated with the mine have been reported, in particular during its operational phase. These include water quality degradation and siltation (Rahman et al., 1984; Jopony & Murtedza, 1994). The most apparent and widespread problem associated with base metal mines is acid mine drainage (AMD) and this is particularly significant in abandoned mines (Banks et al., 1997). With references to experiences and examples in ex-mining areas elsewhere (Filipek et al., 1987; Kim & Chon, 2001; Espana et al., 2005) AMD can potentially be an environmental problem at MCM. Moreover, currently no remedial measure is in place at the ex-copper mine site. Inputs of AMD into the surrounding areas inevitably can cause adverse impacts to the water quality and aquatic life of the receiving rivers. In fact, AMD pollution is gradually becoming evident at MCM.
Scientific information on the AMD at the former copper mine (MCM) is crucial towards understanding the environmental problem as well as the development of preventative measures to alleviate the local AMD problem. This paper provides an overview on some of the findings of AMD research in Universiti Malaysia Sabah, in particular with references to the characteristics of the AMDs at MCM and the potentials of using locally available calcareous materials for its treatment.

**MATERIALS AND METHODS**

AMD samples were collected from various sites in the mine area, including the mine pit (Stella, 2008; Cyril, 2005; Chuen, 2005). The samples were analysed for selected water quality parameters according to the standard methods (APHA, 1999). Batch neutralization experiments were carried on selected AMD samples using 0.01 M NaOH as well as calcareous materials, namely calcareous sandstone, CSS, and calcareous mudstone, CMS (Cyril, 2005; Chuen, 2005). The final pH as well as the concentrations of dissolved metals were determined. The experimental procedures were according to Polat et al. (2002). Batch leaching tests were also carried out to investigate the effect of repeated exposure to AMD (i.e AMD loading) on the pH neutralization efficiency of CSS and CMS (Cyril, 2005). Meanwhile, ABA test was performed on samples of mine tailings from the tailing dam (Tong, 2005) in accordance to the methods described by Skousen et al. (2002), O’Shay et al. (1990) and Sobek et al. (1978). Analysis of seepage water samples at the bottom of the tailing embankments were also carried out (Tong, 2005).

**RESULTS & DISCUSSION**

**Physicochemical Characteristics of Acid Mine Drainages at MCM**

The AMDs at MCM have variable physicochemical properties (Table 1). Similar to AMDs elsewhere, the AMDs at MCM have low pH (i.e acidic), high TDS, high acidity, high sulphate and elevated concentrations of dissolved heavy metals (in particular Fe, Al, Mn, Cu and Zn). The acidic pH of the AMDs suggests that the waste rocks dumps at MCM are net acid generator (Ferguson & Erickson, 1988). The acid production can be attributed to oxidation of metal sulphides present in the mine wastes.

The total acidity value varies distinctively among the AMD samples. In fact, based on its total acidity value the AMDs at MCM can be grouped into high strength (> 1000 mg CaCO₃/L), medium strength (400 – 1000 mg CaCO₃/L) and low strength (< 400 mg CaCO₃/L) AMD (Stella, 2008). Determination and comparison of the free and mineral acidity of the AMD samples showed significant contribution (i.e 67-93 %) of mineral acidity towards the total acidity (Figure 1). This is in agreement with the results reported by Chon & Hwang (2000) and Espana et al. (2005) for AMD samples in Korea and Spain, respectively. The total acidity (in particular mineral acidity) is attributed to dissolved metals, and the dominant metals in the AMDs at MCM are Fe, Al, Mn, Cu and Zn (Table 1). A good correlation was obtained between total acidity and dissolved Al, and dissolved Al, Fe and Mn (Stella, 2008). These metal ions can readily undergo hydrolysis reactions at specific pH condition and liberate H⁻ into solution.
### Table 1. Some physicochemical characteristics of AMD at MCM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
<th>S8</th>
<th>S9</th>
<th>S10</th>
<th>S11</th>
<th>S12</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ph</strong></td>
<td>2.90</td>
<td>2.92</td>
<td>2.91</td>
<td>3.12</td>
<td>2.95</td>
<td>3.10</td>
<td>3.04</td>
<td>2.92</td>
<td>3.42</td>
<td>3.75</td>
<td>3.44</td>
<td>3.35</td>
</tr>
<tr>
<td><strong>TDS</strong></td>
<td>1235</td>
<td>1240</td>
<td>1217</td>
<td>1009</td>
<td>746</td>
<td>1028</td>
<td>1540</td>
<td>2673</td>
<td>450</td>
<td>302</td>
<td>1673</td>
<td>492</td>
</tr>
<tr>
<td><strong>Acidity</strong></td>
<td>382</td>
<td>394</td>
<td>382</td>
<td>809</td>
<td>706</td>
<td>905</td>
<td>1333</td>
<td>1697</td>
<td>282</td>
<td>192</td>
<td>499</td>
<td>176</td>
</tr>
<tr>
<td><strong>Sulphate</strong></td>
<td>1692</td>
<td>1730</td>
<td>1714</td>
<td>1620</td>
<td>1118</td>
<td>1705</td>
<td>2181</td>
<td>2808</td>
<td>598</td>
<td>292</td>
<td>2236</td>
<td>466</td>
</tr>
<tr>
<td><strong>Fe</strong></td>
<td>5.4</td>
<td>4.4</td>
<td>3.9</td>
<td>0.7</td>
<td>2.6</td>
<td>4.4</td>
<td>1.2</td>
<td>7.1</td>
<td>0.9</td>
<td>0.1</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Al</strong></td>
<td>28.5</td>
<td>29.4</td>
<td>28.1</td>
<td>78.3</td>
<td>63.3</td>
<td>92.5</td>
<td>115.1 92.1</td>
<td>19.2</td>
<td>50.1</td>
<td>12.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mn</strong></td>
<td>24.2</td>
<td>21.1</td>
<td>18.9</td>
<td>13.3</td>
<td>11.5</td>
<td>30.6</td>
<td>32.3</td>
<td>79.8</td>
<td>9.9</td>
<td>2.7</td>
<td>34.5</td>
<td>3.8</td>
</tr>
<tr>
<td><strong>Cu</strong></td>
<td>7.2</td>
<td>7.1</td>
<td>7.1</td>
<td>22.2</td>
<td>10.4</td>
<td>16.3</td>
<td>22.2</td>
<td>47.0</td>
<td>6.1</td>
<td>2.0</td>
<td>18.8</td>
<td>4.7</td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td>3.9</td>
<td>3.8</td>
<td>3.9</td>
<td>5.4</td>
<td>5.6</td>
<td>7.7</td>
<td>9.6</td>
<td>25.4</td>
<td>3.0</td>
<td>0.4</td>
<td>7.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

TDS, sulphate and metals are in mg/L; Total acidity in mg CaCO3/L. Source: Stella (2008).

![Figure 1. Proportion of free acidity and mineral acidity of the total acidity in AMD samples at MCM](image)

Titration with 0.01 M NaOH showed that the AMD samples have varying buffering characteristics (Stella, 2008). The volume of base required to increase the pH to 7.0 or higher depends on the strength (i.e. total acidity) of the AMD (Figure 2). Samples with high total acidity show strong pH buffering at pH range 3.5 to 4.5. The higher is the acidity the more significant is the buffering (or the longer is the lag time in the neutralization process) and the greater is the amount of base required. This can be attributed to hydrolysis of Fe and Al, which is significant at pH 3.5-4.0 and 4.0-4.5, respectively (Totsche et al., 2006). The reactions release H+ ions into solution, which subsequently react with OH- ions added via NaOH. This result in initial no significant change in pH in the region of pH 3.5-4.5. After all the Fe and Al ions in solution have undergone hydrolysis, subsequent addition of base will produce a significant increase in pH.
Neutralization of AMD Using Calcareous Materials

The pH of the AMD samples increased with contact time upon mixing with CSS and CMS (Figure 3 & Figure 4). The increase, however, was relatively slow and an optimum pH was only attained after 6h. The pH value at a particular time was dependent on the type of calcareous material as well as the type of AMD (Cyril, 2005). CMS produced a higher pH compared to CSS, while for a specific calcareous material the pH attained for AMD1 > AMD2 > AMD3. Comparatively, the total acidity of AMD3 > AMD2 > AMD1. By contrast, the interaction of an aqueous acid solution (H₂SO₄; pH ~ 3.0) with CSS and CMS produced a pH value of 7.0 within 1h contact time. (Note: AMD1, AMD2 and AMD3 refer to three of the AMD samples listed in Table 1).
The carbonate content of CSS and CMS is approx. 51% and 46%, respectively, and the dominant carbonate mineral present is calcite (Cyril, 2005). The ability of CSS or CMS to increase the pH can be associated with the calcite (CaCO\(_3\)) present. This mineral undergoes dissolution to generate alkalinity (i.e. HCO\(_3^-\) & OH\(^-\)) which subsequently reacts with proton (H\(^+\)) present (Stumm & Morgan, 1996). Due to its low solubility and slow dissolution rate, the calcite mineral requires adequate time to release equivalent amount of alkalinity to neutralize the acidity present (Cox, 1998; Sherlock et al., 1995). Its solubility, however, is higher at low pH thus the increase in pH was more apparent during the first hour of contact time. The slow increase in pH as well as the low increase in pH (in particular for AMD3) can be attributed to pH buffering by dissolved metal ions, as described earlier for neutralization with NaOH.

The neutralization efficiency of CSS and CMS increased with increase in solid-solution ratio or dosage of material: 1:2 > 1:5 > 1:10 > 1:25 > 1:50 (Figure 5). A higher dosage would generate higher amount of alkalinity into solution, thus resulting in higher neutralization. Therefore, the lower efficiency of CSS can be compensated by using larger dosage (and longer contact time).
The neutralization efficiency of CSS increased with decrease in particle size of the material (Figure 6). This was more apparent at low dosage or solid-solution ratio (i.e 1:50) and short contact time (i.e 1h). Nevertheless, the final pH attained remains AMD1 > AMD2 > AMD3. A similar trend, though less obvious, was observed for CMS. Thus, both CSS and CMS are equally effective in neutralizing the AMD samples when used as fine (< 0.5 mm) particles, and in particular when the solid solution ratio is high (i.e 1:2). This dependency of neutralization efficiency on the particle size of the material can be attributed to the increase in total surface area available for reaction with proton (Menendez et al., 2000).

The neutralization efficiency of the materials (in particular CSS) is sensitive to total acidity loading (Figure 7). It can only sustain its neutralization efficiency up to a certain cumulative acidity loading beyond which the efficiency will decline. It can be effective for a specific volume of AMD1 but ineffective for the same volume of AMD3 since the total acidity that need to be neutralized is much higher in the case of AMD3. Continuous or long-term exposure of the calcareous materials to AMD resulted in Fe oxide and/or Al oxide coating on the surfaces of the particles. The existence of Fe oxide coating give reddish brown colouration to the particles, and is more apparent during interaction with AMD3. This is commonly known as armouring effect, and it will renders the calcite in the materials inactive or relatively insoluble and thereby retards its acid neutralization efficiency (Simon et al., 2005; Zimkiewick et al., 1997).

Heavy Metal Removal During Neutralization

The increase in pH of the AMD during neutralization with NaOH solution resulted in the removal of Fe, Al, Cu, Zn and Mn from solution (Figure 8). The effective pH (i.e 100 % removal), however, is dependent on the type of metal: Fe (pH ~ 4.0), Al (pH ~ 5.0), Cu (pH ~ 7.0), Zn (pH ~ 8.0) and Mn (pH ~ 10.0). This trend in metal removal is in good agreement with those reported by Lee et al. (2002) and Munk et al. (2002). The principal process contributing towards the metal removal is the sequential precipitation of respective metal hydroxide. For example, Fe and Cu are precipitated as Fe(OH)₃ and Cu(OH)₂ at pH ~4.0 and pH ~ 7.0, respectively. The cumulative amount of precipitate formed increases with pH, as well as the strength of the AMD (Stella, 2008; Chuen, 2005).
Comparatively, metal removal during interaction with calcareous materials (CSS and CMS) is characterized by a rapid initial phase followed by a relatively slower phase (Figure 9). The rate of removal, however, is lower compared with CaCO₃ powder. The pattern of metal removal closely resembles the variation in pH (Chuen, 2005). The efficiency of metal removal also depends on the type of metal, whereby Fe > Cu > Zn > Mn (Figure 10). Other factors affecting metal removal include type of AMD, solid-solution ratio and particle size, while the removal is attributed to chemisorption and metal precipitation (Chuen, 2005).
Characteristics of Mine Tailings and it’s Seapages Water
The measured Neutralization Potential (NP) and Acid Potential (AP) values of the tailing samples ranged 27.7 to 49.8 kg CaCO₃ per tonne (ave = 36.9) and 4.1 to 13.8 kg CaCO₃ per tonne (ave = 7.9), respectively (Figure 11). These characteristics can be associated with the presence of acid neutralizing minerals (e.g calcite and silicates) and acid producing minerals (e.g pyrite) in the tailings (Tong, 2005). The calculated Net Neutralization Potential (NNP) and NP/AP ratio of the tailings ranged 21.7 to 37.0 kg CaCO₃ per tonne (ave = 28.9) and 3.1 to 7.1 (ave = 5.0), respectively (Figure 12 & Figure 13). The variability in the AP and NP values, and hence NNP and NP/AP, is likely due to variable content of the acid producing and acid neutralizing minerals in the tailings, as well as on the limitations of the test method (Paktunc, 1999; Skousen et al., 1997).

Mine wastes with NNP > 20 kg CaCO₃ per tonne are classified as net acid neutralizer while those with NP/AP ratios greater than 3.0 are classified as non-acid producing (Brodie et al., 1991). Therefore, based on the data for limited samples the tailings can be classified as net acid neutralizer or non-acid producing. The ability of the tailing materials per unit weight to neutralize acid is significantly higher compared to its ability to generate acid.
Figure 11. Estimated NP and AP of mine tailings samples

Figure 12. Calculated NNP of mine tailings samples

Figure 13. Calculated NP/AP of mine tailings samples
The tailings seepage water samples (n=5) have the following characteristics: pH (7.16 – 7.30), conductivity (3.44 – 4.30 mS/cm), TDS (1753 – 2223 mg/L), sulphate (406 – 603 mg/L), Fe (0.05 – 0.31 mg/L), Mn (0.81 – 2.30 mg/L), Cu (0.18 – 0.75 mg/L) and Zn (0.28 – 0.42 mg/L). The alkaline pH is in agreement with the non-acid producing characteristic of the tailings.

Comparatively, the pH, conductivity and sulphate of the surface water sample at the spillway is 7.57, 0.26 mS/cm and 45 mg/L, respectively. The seepage water and the surface water is only similar in term of pH. Despite the alkaline pH, the high sulphate and conductivity or TDS of the seepages water is typical for AMD. This feature is a strong indication of active acid production, through in-situ pyrite oxidation, in the LTD tailing body but the proton, \( H^+ \), generated seemed to be effectively neutralized by the acid neutralizing minerals present (Banwart & Malmstrom, 2001). Certainly, the prevailing high solid-solution ratio and long contact time (i.e slow infiltration rate) conditions within the tailing body contributed partly to this effect. By contrast, the sulphate ions generated during the oxidation process undergo limited interaction (Carlsson et al., 2003). Consequently, the seepage water is enriched with sulphate. Meanwhile, dissolved iron is precipitated as iron hydroxides at the seepage outlets due to the alkaline pH.

CONCLUSION

The AMDs at MCM have variable physicochemical properties, in particular with respect to total acidity and dissolved metals. It is important to take into consideration the variation in total acidity during treatment of the AMDs with alkaline materials. Locally available materials, namely CSS and CMS, can potentially be used for treatment of the AMDs. This treatment can increase the pH of the AMD besides reducing the concentration of dissolved metals. Nevertheless, a number of factors need to be considered when implementing AMD treatment using these materials. For example, it need to be designed with references to the type of material used and the characteristics (incl. total acidity) of the AMD. Meanwhile, according to the ABA test the copper mine tailings are non-acid producing (i.e NNP > 20 kg CaCO$_3$ per tonne and NP/AP > 3.0) and therefore the occurrence of acidic leachates (AMD) from the tailings deposit seemed to be very unlikely.

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