ACID BUFFERING CHARACTERISTICS OF ACID MINE DRAINAGE

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ABSTRACT

Acid mine drainage (AMD) samples, AMD S1 and AMD S2, from Mamut Copper Mine (MCM), Ranau, Sabah were investigated for its acid buffering characteristics by potentiometric titration with NaOH. The AMD has the following characteristics: pH~2.56, total acid= 343-365 mg $CaCO_3$/L, dissolved Fe= 2.4-2.5 mg/L, Mn= 11.3-11.9 mg/L, Cu= 4.4-4.5 mg/L, Zn= 2.6-2.7 mg/L, Al= 3.1 mg/L. For comparison, acidified distilled water as well as Fe(III) and Al(III) solutions were also tested. The results showed that acidified distilled water exhibited a gradual increase in pH with increasing amount of base added. Comparatively, Fe(III) and Al(III) solutions required higher amount of base to attain pH 7.0, and this increased with the concentration of Fe(III) and Al(III). In the case of AMD, a much higher amount of base was required to raise its pH to 7.0. This can be attributed to the strong buffering at pH 3.5-5.0, which was more apparent than those exhibited by the Fe(III) and Al(III) solutions.

ABSTRAK

Sampel saliran asid lombong (AMD), AMD S1 dan AMD S2 dari Lombong Tembaga Mamut (LTM), Ranau, Sabah telah dikaji ciri-ciri penimbalan asid secara titratan potensiometrik dengan NaOH. AMD mempunyai ciri-ciri berikut: pH~2.56, keasidan jumlah= 343-365 mg $CaCO_3$/L, kepekatan logam Fe= 2.4-2.5 mg/L, Mn= 11.3-11.9mg/L, Cu= 4.4-4.5 mg/L, Zn= 2.6-2.7 mg/L, Al= 3.1 mg/L. Air suling berasid, serta larutan Fe(III) dan Al(III) juga dikaji untuk tujuan perbandingan. Hasil kajian menunjukkan bahawa air suling berasid menunjukkan peningkatan pH yang berperingkatan dengan amaun bes yang ditambahkan. Larutan Fe(III) dan Al(III) pula memerlukan amaun bes yang lebih tinggi untuk mencapai pH 7.0 dan ini meningkat dengan kepekatan Fe(III) dan Al(III). Untuk kes AMD, amaun bes yang diperlukan untuk mencapai pH 7.0 adalah jauh lebih tinggi dan ini dapat dikaitkan dengan penimbalan pH di pH 3.5-5.0, magnitud peningkatan pH ini lebih ketara berbanding larutan Fe(III) dan Al(III).

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ABBREVIATIONS AND SYMBOLS

~	nearly to/ about
<	less than
>	more than
AAS	Atomic absorption spectrophotometer
Al	Aluminium
AMD	Acid mine drainage
Cu	Copper
Eq	Equation
Fe	Iron
MCM	Mamut Copper Mine
Mn	Manganese
TDS	Total dissolved solids
Zn	Zinc
E_c	Electrical conductivity
mg/L	Milligram per liter
ppm	Part per million
mg/ml	Milligram per mililiter
mg $CaCO_3$/L	Milligram calcium carbonate per liter
µS/cm	Microsiemens per centimeter
µg/L	Microgram per liter
K_{sp}	Solubility product
%	Percent
mmol L^{-1}	Milimole per liter
µm	micrometer
µm/ml	micrometer per mililiter
nm	nanometer
mL	mililiter
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
$CaCO_3$	Calcium carbonate
OH^-	Hydroxide
H^+	proton
H_2CO_3	Carbonic acid
Fe(III)	Iron(III)
Al(III)	Aluminium(III)

CHAPTER 1

INTRODUCTION

1.1 Mining and the Environment

Mining is a process where valuable minerals or other geological materials from the earth are extracted, usually from ore bodies or veins. The industry provides the impetus to open up new lands, creating towns, providing numerous jobs to the local population and improvements of basic infrastructures (Sengupta, 1993). Locally, mining has an important place in the annals of Malaysia's development and presently it is one of the important income earners for the country (Wu, 1999).

Mining, like other industrial activities, however have negative impacts to the surrounding environment. The deleterious effects include deposition of huge amounts of solid wastes including mine tailings (Dudka and Adriano, 1997), contamination of soils by heavy metals (Ciccu *et al.*, 2003), turning land into a useless wasteland, and destruction of aquatic life (Swift, 1982). In fact, many present-day problems are associated with abandoned historical mines (Banks *et al.*, 1997).

One of the most common and significant post-mining environmental problems is acid mine drainage, AMD (Gray, 1997). Typically, AMD is characterized by low pH, high acidity, high TDS, high conductivity, high sulfate and elevated concentration of heavy metals (Singh 1987; Gray 1998; Nordstrom *et al.*, 2000; Bell *et al.*, 2001).

Inputs of AMD can have adverse effects on the receiving water quality. Typically, AMD-impacted rivers have acidic pH, low alkalinity, high TDS, sulphate and dissolved metals (Filipek *et al.*, 1987; Sengupta, 1993; Nordstrom *et al.*, 2000; Shaver *et al.*, 2006). This has lead to various environmental problems. Therefore, AMD need to be treated prior to discharge.

One of the treatment methods for AMD is neutralization using alkaline or calcareous materials (i.e. to increase the pH to near 7). This neutralization process, however, is not as simple and easy as it may seem. It can be hindered by the low solubility of the alkaline or calcareous materials as well as the significant presence of dissolved metals in the AMD (Younger *et al.*, 2002; Hammarstrom *et al.*, 2003; Hedin, 2006). The dissolved metals, in particular Fe and Al, will contribute towards mineral acidity, which in turn enables the AMD to resist the changes in pH during neutralization. Consequently, the efficiency of a neutralization process can be dependent on the characteristics of the AMD.

1.2 Acid Mine Drainage in Sabah

Figure 1.1 Mamut Copper Mine in Ranau, Sabah.

The Mamut Copper Mine in Ranau, Sabah (Figure 1.1) ceased operation in 1999. During its operational phase, various environmental issues have been reported (Murtedza *et al.*, 1985; Jopony & Murtedza, 1994). Like other abandoned mines elsewhere, this mine left behind a legacy of AMD problem. Presently, AMD at this mine area are left untreated. As a result, several rivers in the area are showing signs of AMD pollution.

1.3 Objectives of Study

The objectives of the study are:

(i) To determine the changes in pH of the local acid mine drainage (AMD) during neutralization process.

(ii) To determine the effect of dissolved heavy metals (Fe and Al) in solution on neutralization process.

1.4 Scope of Study

This study focused on the changes in pH of AMD samples collected from Mamut Copper Mine, in Ranau Sabah during neutralization process. The significance of dissolved metals (Fe and Al) in the neutralization process is further investigated using acidic aqueous solutions containing varying concentrations of Fe and Al.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Mine Drainage Formation and Characteristics

AMD is a widespread environmental issue resulting from the oxidation of sulfide minerals on to exposure to both oxygen and water. There are various types of sulfide minerals but pyrite, marcasite and pyrrhotite are perhaps the most common sources of AMD production. The oxidation process result in the production of iron- and aluminium- rich sulphuric acid solutions with high levels of trace metals (Singer and Stumm 1970; Drever 1997).

2.1.1 Oxidation of Pyrite

The oxidation of pyrite, FeS_2, can involve the following reactions (Eq. 2.1-2.4) (Singer & Stumm, 1970; Sengupta, 1993; Evangelou, 1995):

Oxidation of pyrite by O_2 :

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{2.1}$$

Oxidation of Fe^{2+} by O_2 :

$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O \quad (2.2)$$

Precipitation Of Fe^{3+} :

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \quad (2.3)$$

Oxidation of pyrite by Fe^{3+} :

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.4)$$

The first important reaction is the oxidation of the sulfide mineral in the presence of oxygen. The mineral is oxidized into dissolved ferrous iron (Fe^{2+}), sulfate and hydrogen (Eq. 2.1). The dissolved ferrous iron (Fe^{2+}) as well as the sulfate (SO_4^{2-}), and the two moles of hydrogen ions represent an increase in the total dissolved solids and total acidity of water. If the environment is sufficiently oxidizing, which is dependent on O_2 concentration, pH and bacteria activity, much of the liberated ferrous iron (Fe^{2+}) will be oxidized to ferric iron (Fe^{3+}) according to the Equation 2.2 with the consumption of acidity. Equation 2.2 is the rate-determining step in pyrite oxidation as the conversion of ferrous iron to ferric iron is slow at pH below 5 under abiotic conditions.

The ferric iron (Fe^{3+}) formed (Eq. 2.2) will remain in solution if the pH maintain below 3.5. It however, undergoes hydrolysis and precipitation as the pH > 3.5. The precipitation as into ferric hydroxide ($Fe(OH)_3$) simultaneously lowering the pH (Eq. 2.3) by producing three moles oh hydrogen ions.

Any Fe^{3+} which does not undergo precipitation from solution can oxidize additional pyrite (Eq. 2.4), generating much greater amounts of ferrous iron, sulphate, and acidity.

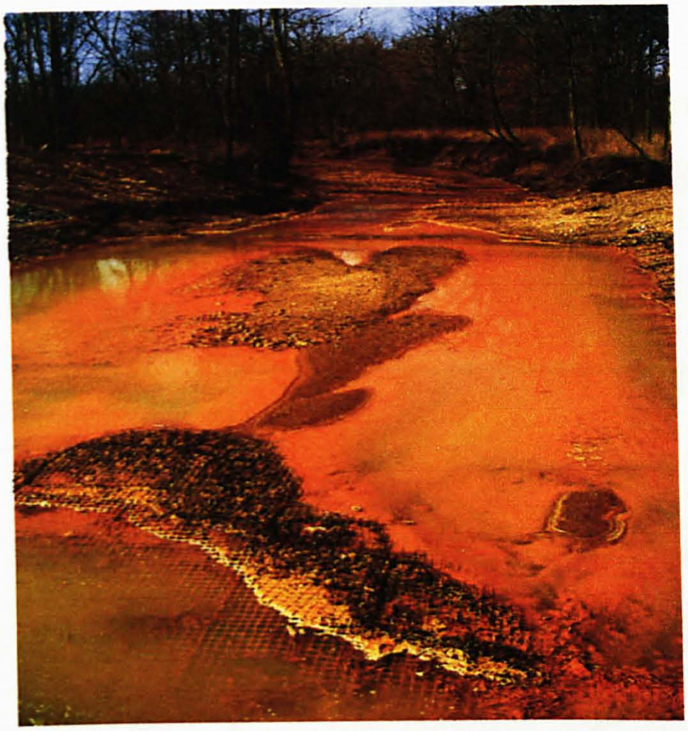

Figure 2.2: Yellow boy in a stream receiving acid drainage from surface coal mining.
Source: Hardesty (2005)

2.1.2 Factors Affecting Acid Generation During Pyrite Oxidation

The primary factors determining the rate of acid generation during pyrite oxidation include oxygen concentration and solution pH (Smith and Shumate, 1970), the presence of *Thiobacillus* bacteria (USEPA, 1971), particle size (McKibben & Barnes, 1986), presence of carbonate minerals, and type of sulphide mineral.

a. Effects of pH

The kinetics of oxidation of ferrous iron which can occur either abiotically or biotically, is dependent on pH. According to Stumm and Morgan (1996), the kinetic of the oxidation can be represented as follows:

$$\frac{-\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = k[\mathrm{Fe}^{2+}][\mathrm{OH}^-]p_{O_2} \qquad (2.6)$$

The oxidation rate is independent of pH at low pH. On the contrary, at higher pH (>5) the second order dependence on [OH⁻] is apparent (Figure 2.3).

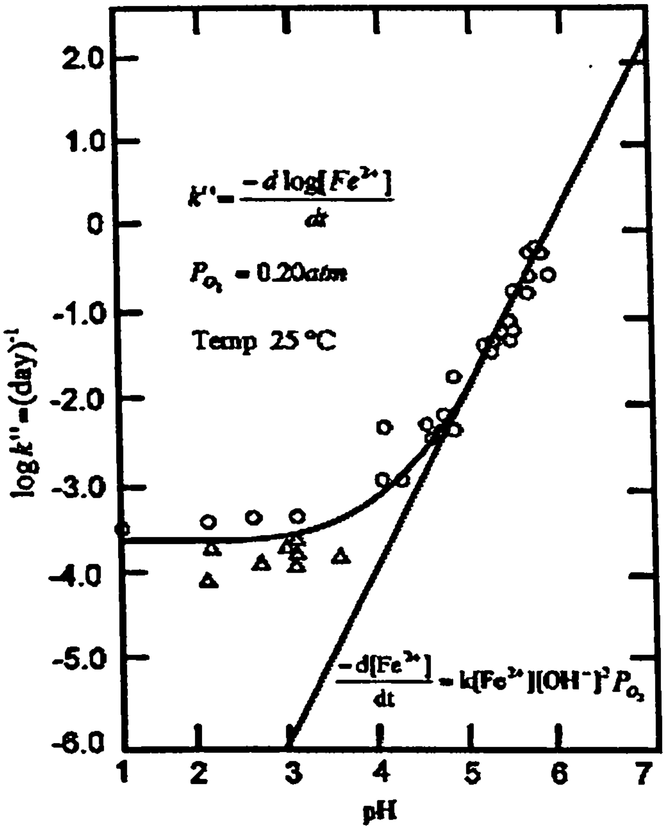

Figure 2.3: Oxidation rate of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) as a function pH (p_{O2} = 0.20 bar).

Also, the hydrolysis reaction of iron depends on total Fe^{3+} and pH as well. Under equilibrium conditions, only a negligible concentration of dissolved ferric iron exist at pH 3 (Figure 2.4).

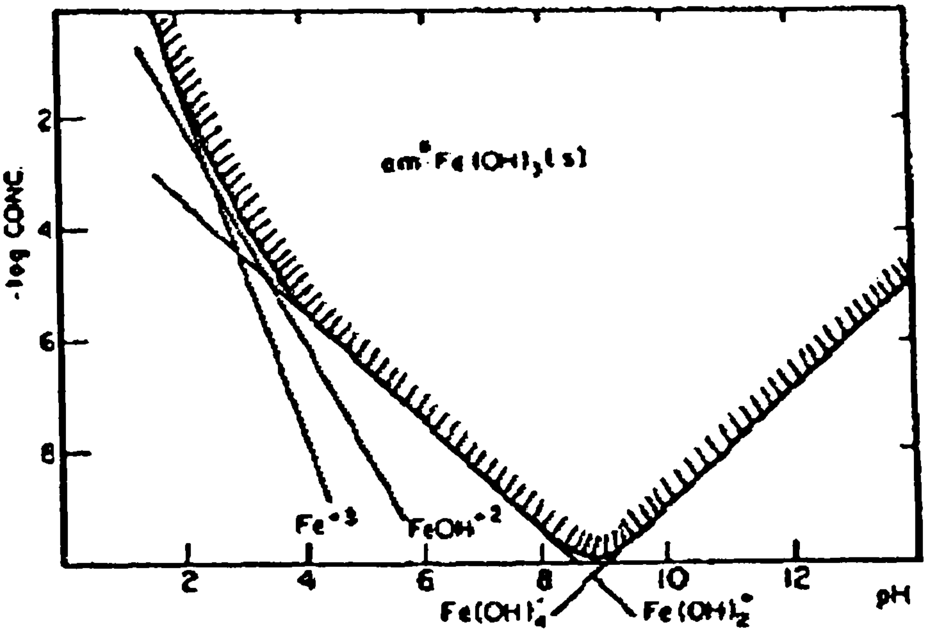

Figure 2.4: Solubility diagram of Fe(OH)$_3$ which is dependent on pH.
Source: Stumm & Morgan (1981)

b. Effect of oxygen concentration

Oxidation of pyrite only occurs in the presence of both water and oxygen. Oxygen plays the role as the terminal electron acceptor by oxidation of ferrous iron (Fe^{2+}) to ferric ion (Fe^{3+}) (Evangelou & Seta, 1999). The rate of pyrite oxidation will rise when the concentration of oxygen increase. This leads to more generation of acid. Hence, it can be concluded that the overall rate of pyrite oxidation is dependent on the oxygen concentration.

c. Effects of bacteria

Bacteria play a major role in accelerating the rate of acid generation. The sulfide-oxidation process is accelerated by about 100 times in the presence of *Thiobacillus* bacteria compared with an abiotic control (Mielke *et al.*, 2003).