CHEMISTRY OF IRON (Fe) IN ACID MINE DRAINAGE (AMD) AND AMD-CONTAMINATED SURFACE WATER

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CLARIFICATION

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ABSTRACT

The concentrations of Total Fe (Fe_T) and distribution of Fe^{2+} and Fe^{3+} in selected AMD and AMD-contaminated river water samples from Ranau, Sabah were determined according to the standard method for the examination of water and wastewater. The pH and E_h values of these samples were also analyzed. The results obtained showed that Fe_T in all AMD samples were relatively high in the range of 0.29-11.90 mg/L and comprising of 64.5% Fe(III) and 35.5% Fe(II). Fe_T and Fe(III) were generally high at low pH (i.e. $pH<4$) and oxidizing ($E_h>545mV$) condition whereas Fe(II) was significant at lower E_h (i.e $<545mV$). The river water samples were less acidic (i.e. $pH>4$), and therefore, comparatively low in Fe_T at 0.16 mg/L-0.25 mg/L with only Fe(III) present as the dominant species. These results indicate that the distribution of Fe(III) and Fe(II) species and subsequently the concentration of Fe_T in the AMD and AMD-contaminated river water samples was strongly influenced by the prevailing pH and E_h.

ABSTRAK

Jumlah kepekatan logam ferum terlarut (Fe_T) dan juga taburan spesis Fe^{2+} dan Fe^{3+} dalam saliran asid lombong (AMD) dan air sungai yang tercemar dengan AMD telah ditentukan berdasarkan kaedah piawai untuk analisis air dan air tercemar. Selain itu, nilai pH and E_h setiap sampel juga diukur. Hasil yang diperolehi menunjukkan bahawa Fe_T sampel AMD secara relatifnya adalah tinggi iaitu dalam julat bacaan 0.29-11.9 mg/L dan ianya terdiri daripada 64.5% Fe(III) dan 35.5% Fe(II). Kandungan Fe_T dan Fe(III) adalah tinggi terutamanya pada keadaan pH yang rendah (iaitu $pH<4.0$) dalam keadaan pengoksidaan yang tinggi ($E_h>545mV$). Kandungan Fe(II) sebaliknya didapati signifikan pada nilai E_h yang lebih rendah ($E_h<545mV$). Sampel air sungai yang dikaji adalah kurang asidik (iaitu $pH>4$) dan dengan itu, Fe_T adalah rendah iaitu pada kepekatan 0.16-0.25 mg/L, dan spesis Fe yang dominan ialah Fe(III). Pada keseluruhannya, taburan Fe(II) dan Fe(III) dan selanjutnya kepekatan Fe_T dalam AMD dan air sungai yang tercemar dengan AMD sangat bergantung kepada nilai pH dan E_h semasa.

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LIST OF SYMBOLS AND ABBREVIATIONS

Fe	iron
Fe^{2+}	ferrous ion
Fe(II)	ferrous ion
Fe^{3+}	ferric ion
Fe(III)	ferric ion
g/cm^3	gram per centimeters cubic
e^-	electron
pE	redox potential
E_h	electrochemical potential
mV	millivolts
mg	milligram
L	liter
m	mili
M	molarity
V	volume
nm	nanometer
µm	micrometer
>	greater than
<	lesser than
%	percentage

CHAPTER 1

INTRODUCTION

1.1 Context and Relevance of Study

Pyrite, FeS_2, is a common sulfide mineral that contains iron (Fe) as its major element. It can be found in most magmatic and igneous rocks, sedimentary deposits as well as hydrothermal deposits. As such, pyrite is often exposed to the environment by mining and metallurgical activities. The oxidation of exposed pyrite through weathering process often brought about the formation of acid mine drainage, an environmental problem of serious concern today in mining industry (Evangelou, 1995).

The mechanism of acid mine drainage formation is a combination of two reactions involving the interchanging oxidation states of iron. The oxidation of pyrite can be initiated by ferric (Fe^{3+}) ions or oxygen followed by a further oxidation of ferrous (Fe^{2+}) ions in the presence of oxygen (Evangelou, 1995; Singer & Stumm, 1970). This reaction resembles a cyclic reaction mechanisms resulting in products such as sulfuric acid (H_2SO_4), sulfate ions, ferrous ions and ferric ions.

Fe^{2+} produced can substantially oxidize to Fe^{3+}, which in turn may contribute towards the oxidation of the parent mineral (Sengupta, 1993). At $pH > 3.5$, Fe^{3+} may also undergo hydrolysis to release additional acidity (Singer & Stumm, 1970). The highly acidic environment formed during this oxidation process further promotes the dissolution of the mineral matrix and cause the mobilization of trace metals into solution (Sengupta, 1993). As a consequence, seepages or leachates from mine waste dumps often display low pH values (i.e. $pH < 3.5$) and an elevated levels of dissolved ions, which therefore commonly termed as acid mine drainage, AMD (Evangelou, 1995; Sengupta, 1993; Stumm & Morgan, 1996).

Direct inputs of AMD into receiving water can lead to a decrease in pH and subsequent increase in the concentration of dissolved metals (including Fe) (Sengupta, 1993). The total dissolved Fe, in this case, is contributed by Fe^{2+} and/or Fe^{3+}. Upon released into receiving streams, AMD tends to be diluted fairly rapidly due to mixing and dilution (Baker, 1994). This phenomenon coupled with competing chemical processes decisively affect the distribution of iron ($Fe^{2+}$and Fe^{3+}) (Allen *et al.*, 1995; Baker, 1994; McKnight *et al.*, 2001).

As the occurrence of redox process is profound in aqueous system, iron may exist as free Fe^{2+} or Fe^{3+} ions or as organic ferrous and ferric complexes (Allen *et al.*, 1995; Clarkson *et al.*, 1999; Luther, 1995). As such, the proportion or activity of Fe^{2+} and Fe^{3+} (i.e. Fe^{3+}/Fe^{2+}ratio) will alter as iron participates in redox reactions (O'Sullivan *et al.*, 1997).

According to McKnight *et al.* (2001), the redox chemistry of iron often links to chemical reactions such as photoreduction of Fe^{3+}, dissolution-precipitation of ferric hydroxides as well as microbial oxidation of Fe^{2+}. Other chemical reaction includes complexation reaction with organic ligands (Allen *et al.*, 1995).

Besides redox potential, the chemical stability of iron species also depend on other factors. Among these factors include pH, dissolved oxygen and temperature of the aqueous system (Bachman *et al.*, 2001; Baker, 1994; Luther, 1995; O'Neill, 1993; O'Sullivan, 1997). In AMD, the oxidation of Fe^{2+} to Fe^{3+} is a pH dependent reaction (Sengupta, 1993). In fact, it is very slow below pH 6 (Stumm & Morgan, 1996; Evangelou, 1995). However, when pH approaches neutrality where aerobic condition (high E_h) is distinct, Fe^{3+} is by far the predominant species and it is prone to undergo hydrolysis to form the insoluble ferric hydroxides polymers with hydroxyl ions (Clarkson *et al.*, 1991; O' Neill, 1993; Silver, 1993). Under suitable condition (i.e. negative E_h), Fe^{3+} can be reduced back to the soluble Fe^{2+} (O'Neill, 1993).

As described above, the speciation of Fe (as Fe^{2+} & Fe^{3+}) in AMD and AMD-contaminated water is dependent on several factors, the dominant being redox potential (E_h) and pH. The chemical speciation can have a profound effect on the total concentration of dissolved Fe, as well as the overall water chemistry. Information on iron chemistry in AMD and AMD-contaminated water is, however, lacking. Therefore, studies on the aqueous geochemistry of iron are important towards the understanding the behavior of Fe in AMD as well as in AMD-contaminated water.

In Sabah, AMD is prevalent at a former copper mine in Ranau and several rivers in the area are known to be affected by AMD inputs causing a considerable damage to the river ecosystem (Jopony & Murtedza, 1994).

1.2 Objectives

The objectives of this study are:

a. To determine the total concentration of Fe (Fe_T) in AMD and AMD-contaminated river water samples

b. To determine the concentration and distribution of ferrous ion, Fe^{2+} and ferric ion, Fe^{3+} in AMD and AMD-contaminated river water samples

c. To investigate the relationship between ferrous ion, Fe^{2+} and ferric ion, Fe^{3+}, pH and redox potential (E_h)

1.3 Scope of study

In this study, the concentrations and distribution of Fe(II) and Fe(III) in water samples collected from several AMD sources and AMD-contaminated rivers at Mamut Copper Mine and its vicinity will be determined. Other water quality parameters, in particular redox potential (E_h) and pH, will be also be recorded.

CHAPTER 2

LITERATURE REVIEW

2.1 Occurrence of Iron in Nature

Iron has been considered the sixth most abundant element in the universe judging from the fact that the core of the earth's crust is mainly composed of liquid iron while the mantle contains high proportion of ferromagnesian (Clarkson *et al.*, 1991; O'Neill, 1993). It is the most versatile of all elements and known to exhibit some unique properties (Clarkson *et al.*, 1991; Silver, 1993). Generally, iron can be found in many crustal rocks such as hematite (Fe_2O_3), magnetite, chalcopyrite ($CuFeS_2$), arsenopyrite ($AsFeS_2$), limonite, bornite and pyrite (FeS_2) (Clarkson *et al.*, 1991; O'Neill, 1993; Silver, 1993).

Pure iron (Fe, atomic number 26, atomic mass = 55.8, density of 7.9 g/cm^3) is a silvery-white, shiny and malleable metal that can rust rapidly in moist air. Having the electronic configuration of $4d^2 3d^6$ in its elemental form, the unpaired electron often give rise to the magnetic properties of iron and therefore, are of great importance in understanding its redox chemistry (Silver, 1993). Depending upon the oxidation state and the nature of ligands, iron oxidation number can vary from 0 to 5 (Silver, 1993).

In biological environment, it can change from 0 to +2 in ferromagnesium minerals and eventually to +3 (Clarkson *et al.*, 1991).

In the aquatic ecosystem, iron may exist as colloids, suspensions, dissolved as well as complex-iron forms in the presence of other mineral and organic matter (Holzbecher, 2001; Luther, 1995). The concentration of dissolved iron in water is generally low. However, the concentration of iron in AMD and immediately downstream AMD-impacted rivers often display an unusually high value (Bachman *et al.*, 2001; McKnight *et al.*, 2001).

2.2 Chemistry of Iron

2.2.1 Ferrous Ion

Ferrous ion or commonly denoted as Fe(II), is one of the most common oxidation state of iron. In the absence of air and in non-oxidizing acids, the stable form of Fe(II) species usually exist as free ions. Capable to mobilize freely in aquatic medium, Fe(II) can form several complexes with large number of ligands with most of these are either octahedral or distorted octahedral (Silver, 1993). Pure aqueous solution of Fe(II) without the presence of any complexing agents however, is in the form of visible pale turquoise hexaquo ferrous ion, $[Fe(H_2O)_6]^{2+}$. This complex can easily convert to ferric form in the presence of molecular oxygen in acid solution (Manahan, 1999; Silver, 1993).

Fe(II) is also very easily oxidized under alkaline conditions. In the presence of hydroxides, $[Fe(H_2O)_6]^{2+}$ will be neutralized through the exchanged of hydrogen ions based on the following equation.

$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O \qquad (2.1)$$

Oxygen in the air oxidizes the Fe(II)hydroxide precipitate to Fe(III)hydroxide. Thus, most hydroxides of Fe(II) will precipitate out from aqueous solutions (Silver, 1993).

The oxidation mechanism of Fe(II) to Fe(III) basically involves FeO_2^+ ion. Kinetics studies on this reaction showed that the attack of Fe^{2+} on FeO_2^+ will form a binuclear species known as the transient intermediate according to the following equation (Silver, 1993).

$$FeO_2^+ + Fe(H_2O)^{2+} \longrightarrow Fe(OOH)^{2+} + Fe(OH)^{2+} \qquad (2.2)$$

This reaction then proceeds to a rapid decomposition of hydroperoxo ion to form Fe(III) and HO_2^-, which can be further oxidized to form more Fe(III) or decompose to generate oxygen molecules, O_2 (Foole *et al.*, 1995; McKnight *et al.*, 2001; Silver, 1993).

In biological environment, the oxidation of Fe(II) to Fe(III) can be microbial catalyzed by the colony of phototrophic bacteria *Thiobacillus ferooxidans* that thrives ideally in a very low pH environment as such in an AMD (Evangelou, 1995; Manahan, 1999; Sengupta, 1993). Clearly, in an anaerobic condition, Fe(II) will be a hydrogen donor in promoting the bacteria activity. *Thiobacillus ferroxidans* has known long for its role in accelerating the rate of oxidation Fe(II) to Fe(III) (Manahan, 1999).

2.2.2 Ferric Ion

Another species of iron in nature is ferric ion or commonly denoted as Fe(III). With a stable valence state of +3, Fe(III) acquired 5 electrons in its d-orbital. As such, it easily forms salts with all common anions except with those that have more reducing abilities i.e. iodide. In a low pH solution, Fe(III) can be crystallized into the pale-violet hydrated form. In its complex form of $[Fe(H_2O)_6]^{3+}$, Fe(III) here is surrounded by water ligands. As the pH of this solution is gradually raised to approximately above 2-3, condensation occurs thereafter forming a yellow colored solution.

$$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O \tag{2.3}$$

Fe(III) readily undergo hydrolysis to free acids according to the equation below.

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \tag{2.4}$$

This reaction then proceeds to form colloidal gels, which eventually precipitates at near neutral pH as visible reddish brown precipitate (Silver, 1993). This sequence can be described by following expression;

$$Fe^{3+} \xrightarrow{pH\sim1} Fe(OH)^{2+} \xrightarrow{pH\sim3} Fe_2(OH)_2^{4+} \xrightarrow{3<pH<10} Fe(OH)_3 \tag{2.5}$$

This brown precipitate is thought to be responsible for the low solubility of Fe(III) at pH 7 (Silver, 1993). In aqueous system, it has a profound impact towards the geochemical cycle of other trace metals as it can co-precipitate with other particles (Holzbecher, 2001).

2.3 Chemistry of Acid Mine Drainage Formation

AMD formation is a chemical process involving a complex series of inter-related weathering reactions cycle (Stumm & Morgan, 1996). Metal sulfides in general are relatively unstable under anaerobic environment. However, upon exposure to persistent oxidizing condition and the presence of water, these minerals will oxidize. The oxidation of pyrite has been extensively studied and has been reviewed by Evangelou (1995). The following equations show the general accepted sequence of pyrite reactions:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4 + 4H^+ \quad (2.6)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2.7)$$

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 + 12H^+ \quad (2.8)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.9)$$

In the initial step, pyrite is oxidized by oxygen to produce sulfuric acid and ferrous ion (Equation 2.6 and Equation 2.7). The second step involves the conversion of ferrous ion to ferric ion. Under very acid condition (i.e. pH <3.5), the solid mineral of Fe(III) does not form and most Fe(III) will remain in solution (Equation 2.7).

The third step involves hydrolysis of ferric ion in water to form solid ferric hydroxide and the additional acidity. Clearly, following the increase of acid production when pH drops, oxidation of pyrite by ferric ion (Equation 2.9) now becomes the primary mechanism for acid production. This cyclic propagation of acid

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