ALUMINUM SPECIATION RESULTING FROM CHEMICAL PRECIPITATION OF Al-BEARING ACID ROCK DISCHARGE

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Acid rock discharge (ARD) or acid mine drainage (AMD) formed through the oxidation of sulfide minerals (usually pyrite) is a major source of water contamination and impairment in both coal and hard rock mining regions throughout the worldwide. Aluminum, as an environmentally toxic contaminant, is found in some acid rock discharge (ARD) and acid mine drainage (AMD) locations. The composition of ARD/AMD is complex leading to variable effluent Al concentrations that are site specific.

The purpose of this research is to understand the interactions of suspended and soluble aluminum with sulfate and silicates during the active treatment of acid mine drainage (AMD) or acid rock drainage (ARD). Active treatment consists of a multi-basin system with NaOH neutralization followed by settling of formed precipitates before discharge to surface waters. Measured supernatant compositions were compared with calculated values from MINEQL+ computerized equilibrium model.

NaOH neutralization of aqueous aluminum with minimal levels of sulfates and silicates resulted in amorphous $Al(OH)_3$, and not crystalline gibbsite (crystalline $Al(OH)_3$). Results showed that sulfates from AMD/ARD reduce the soluble supernatant aluminum, with the concomitant formation of new colloidal sized particles which were mainly basaluminite with some amorphous $Al(OH)_3$.Total aluminum levels (soluble + particulate) in the supernatant can exceed numerical discharge standards for aluminum if there is insufficient settling time in the settling basins, as may occur during wet weather events. Similar observations were made with the presence of silicates. Silicates can also reduce soluble Al concentration immediately after pH adjustment due to the formation of Al-silicate precipitates with the concomitant increase in small aluminum-silicate bound particles. This can also increase the total level of aluminum discharged from an active treatment system for AMD/ARD.

Particle size analysis revealed that sulfate and/or silicates reduced the mean suspended particle size from that which would have existed from the sole formation of amorphous $Al(OH)_3$. Suspended aluminum levels will lead to an increase in the total Al that would be in a settling tank discharge.

Temperature affects the equilibrium constant for all formed species of aluminum precipitates. Calculations with the MINEQL+ model show the significant increase of soluble aluminum that will exist during warm summer temperatures at all pH values. Minimum effluent total aluminum levels on the order of 0.5 mg/L can exist at discharge pH values in pH range of 6.0 to 7.0, however these aluminum levels are exceeded during warm summer months at pH values greater than 7 when the soluble Al contribution to the total aluminum discharge will increase. This suggests that for field operations, close control of pH is necessary especially during warm weather and during wet weather events if elevated discharge levels of aluminum are to be avoided.

Key words: acid mine drainage (AMD); acid rock drainage (ARD); aluminum; basaluminite; sulfate; silicate; active treatment; particle size distributions; temperature

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1.0 INTRODUCTION

Acid Rock discharge (ARD) and/or Acid mine drainage (AMD) is a major source of water contamination in both coal and hard rock mining regions throughout the worldwide (Sasowsky *et al*., 2000; Bunce *et al*., 2001). ARD and/or AMD result from the oxidation of substances that contain an abundance of sulfide minerals (often pyrite, which is iron-sulfide). ARD/AMD can have net acidity ranging from zero to several thousand mg/L (as $CaCO_3$) and can be strongly acidic with a pH ranging from 2 to 6 or more (Rose and Cravotta, 1998, Cravotta *et al*., 1999; Nordstrom and Alpers, 1999). ARD/AMD usually contains high concentrations of dissolved sulfate (SO_4^{2-}), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3}) (Cravotta *et al*., 1999; Nordstrom and Alpers, 1999).

Aluminum can enter surface or ground waters by the dissolution of alumino-silicates (Essington, 2004) or by ion-exchange processes (Vazquez *et al*. 2010a and 2010b; Tan, 2000) if the pH of the water becomes low enough (acidic). ARD/AMD often contains high levels of aluminum if the surface soils contain a high level of alumino-silicate materials (smectite and kaolinite clays). A number of papers have reported that the high concentrations of aluminum have occurred in the ARD or AMD. For example, Cravotta (2008) reported that over 50% of 140 abandoned coal mines in Pennsylvania had an aluminum concentration in its discharge ranging from 1 mg/L to 100 mg/L with pH between 2.5 to 7.3.

Aluminum is recognized as being highly cytotoxic to plant and animal life (Chadwick and Whelan, 1992; Birchall *et al*., 1989; Golub and Domingo, 1996). Starting in 1980s the toxicity of aluminum was realized to be a major factor influencing the aquatic organisms and communities in acidic habitats (Cronan and Schofield, 1979; Drablos and Tollan, 1980; Muniz and Leivstad, 1980). Research on the biological effects of acidification have supported the conclusion that Al is a major factor responsible for the demise of biotic communities (Dillon *et al*., 1984; Campbell and Stokes, 1985; Schindler *et al*., 1985; Charles, 1991; Scheuhammer, 1987 and 1991; Chadwick and Whelan, 1992; Birchall *et al*., 1989; Golub and Domingo, 1996). Aluminum is considered to be toxic for algae when its concentration is higher than 0.46 mg/L (Peterson *et al*., 1974; Gostomski, 1990; Marsh, 1999). Aluminum is also harmful to adult fish, causing iono-regulatory, respiratory failures, or a mixture of both (Muniz and Leivstad, 1980; Howells *et al*., 1983; Poston, 1991; Handy, 1993; Rosseland and Staurnes, 1994; Exley *et al*., 1991). It is considered that 0.46mg/L Al would be toxic for aquatic fish (Spry and Wiener, 1991; Rosseland *et al*., 1990 and 1992; Rosseland and Staurnes, 1994). Some researchers reported that Al in water could lead to Al accumulation in fish organs like kidneys, the skeleton and gills (Rodushkin *et al*., 1995) and would accumulate in the brain and heart of the rainbow trout due at chronic exposure levels (Exley, 1996).

1.1 ARD/AMD TREATMENT

ARD/AMD treatment encompasses two broad categories, active and passive treatment. Active treatment involves the addition of the neutralizing chemicals to the source of the ARD/AMD, to a treatment system for ARD/AMD, or directly to the stream that has been influenced. Passive treatment encompasses a variety of techniques to raise the pH and reduce metal ions concentration through a constructed treatment or containment project without active chemical injection. In general, the primary passive technologies include aerobic and anaerobic wetlands, anoxic limestone drains (ALD), vertical flow ponds, alkalinity producing systems (APS), limestone ponds, and open limestone channels (OLC).

In all ARD/AMD treatments, two goals should be achieved: the neutralization of acidity and the removal of metal ions. Metal ions in ARD can be removed by gravity separation of metal precipitates produced in the acid neutralization processes (Skousen *et al*., 1998 and 2000; Maree and Plessis, 1994). Thus, the efficiency of the metal removal depends on the pH control and the sedimentation of the precipitates in the ARD neutralization system. Actual settling rates of the precipitates depend on the chemistry of ARD/AMD, as well as the size and density of the primary particles, solution pH and ionic strength, and the surface chemistry of solids.

For Al-bearing ARD/AMD, it is considered that during neutralization, most aluminum ions can be removed by precipitation due to the formation of insoluble hydroxide compounds or other precipitates, such as Al-sulfate or Al-silicate precipitates. pH neutralization for ARD/AMD is the useful way to remove aluminum from an aqueous discharge. In general, it is considered that the aluminum concentration in water is controlled by the solubility of aluminum hydroxide. However, the reactions of aluminum precipitation from ARD/AMD in actual conditions are more complex and predictions of total discharged aluminum are difficult. ARD/AMD often contains high concentration of sulfate and sometimes silicate, which influence both the character of precipitates and the species of Al-complexes and aluminum precipitates. The possible aluminum precipitates formed during pH increasing of ARD/AMD are not only aluminum hydroxides, but also aluminum hydroxysulfate and aluminum-silicate, since aluminum has a demonstrated affinity for both sulfate and silicate (Taylor *et al*., 1997; Bigham and Nordstrom, 2000). Bigham and Nordstrom (2000) observed the basaluminite and alunite in field. Also, according to pure solution solubility constants, the solubility of some aluminum sulfate compounds (such as basaluminite ($Al_4(OH)_{10}SO_4$)) is less than aluminum hydroxide.

1.2 PROJECT BACKGROUND AND PROBLEM STATEMENT

Al-bearing ARD has been an environmental problem since 1960s at Jonathan Run, an aluminum-containing acid rock discharge site located in Centre County, Pennsylvania (Hedin Environmental, 2003). Water quality changes in Jonathan Run initially occurred in the 1960's during the construction of Interstate 80 near Snow Shoe, Pa. Previous research determined that the primary source of contamination originated from an acidic sandstone fill that was used to construct the embankment of I-80. The stream flows through a culvert under this embankment and visible Al precipitates were found downstream of this culvert (Neufeld *et al*., 2007).

In May, 2003, two pilot-scale flush box treatment pilot systems that contained rock limestone were installed by Hedin Environmental in north of I-80 near Jonathan Run to experimentally treat the Al-bearing acidic discharge. In 2003 and 2006, Hedin Environmental (2008) monitored the operation of flush boxes in Jonathan Run. In 2003, soluble Al concentration in the effluent from flush boxes ranged from 0.4 to 18.1 mg/L in pH range of 4.5 to 5.9 for Box 1, and 0.2 to 0.7 mg/L in pH range of 4.7 to 6.2 for Box 3 (Weaver *et al*., 2004). The soluble Al concentrations in effluent from flush boxes in Jonathan Run were less than the theoretical solubility of amorphous $Al(OH)_3$ (as modeled with Mineql+), and higher than the theoretical solubility of gibbsite (Figure 1.1). Analysis of the aged sludge collected from the field showed that gibbsite was not formed in flush boxes (Pu *et al*., 2010). These results indicated that some reactions of Al-sulfate compounds might be occurring in flush boxes to form the Al-precipitates other than $Al(OH)_3$, which also caused the reduction of soluble Al concentrations in that discharge.

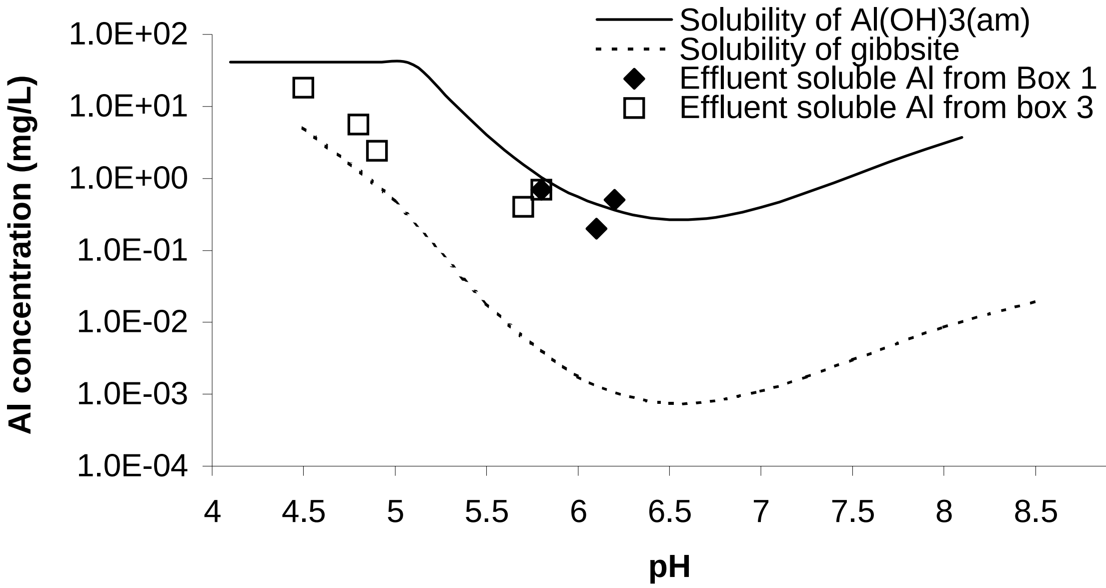


Figure 1.1 Effluent soluble Al concentrations from flush boxes located in Jonathan Run. (Theoretical curves of solubility of Al compounds (amorphous $Al(OH)_3$ and gibbsite) was calculated by using Mineql+ model; □ and ■: effluent soluble Al concentrations from flush boxes located in Jonathan Run (Weaver et al. 2004)).

Other researchers (Adams and Rawajfih, 1977; Nordstrom *et al*., 1984; Herrmann and Baumgartner, 1992; and Kim and Kim, 2003a and 2003b) also reported that the actual aluminum precipitates found in the acid mine drainage were aluminum hydroxysulfate if the sulfate concentration was relative high and the aluminum solubility was higher than the theoretical concentration. Therefore, it is reasonable to suppose that the presence of other ions, such as sulfate and silicate, could influence the mechanism of aluminum removal, since the species of aluminum precipitates may not be gibbsite (crystalline aluminum hydroxide), thus the suitable pH for aluminum removal should be different from the theoretical value that is based on the reported solubility of gibbsite. In other words, in actual conditions, the minimum soluble level of aluminum may occur at a different pH that for gibbsite, and the actual soluble aluminum concentration may be higher than the theoretical concentration predicted from considering only gibbsite. This is current basis for aluminum regulation from AMD and ARD discharges in many locals. Furthermore, there is not enough information about the aluminum concentration as influenced by sulfate, silicate and temperature (winter and summer conditions) at various pH values. Therefore, this dissertation explores and defines the combined influence of pH for aluminum removal in ARD treatment when the other ions (such as sulfate and silicate) are present during winter and summer conditions, and makes suggestions as to what reasonably can be done in the field.

This fundamental information may be useful to regulatory agencies, and to the Pennsylvania Department of Transportation (PennDOT) who is responsible for remediating an acid rock discharge along I-80 in Centre County, Pennsylvania. This research may have a practical application in the support of applied research and associated design activities being done by others in the remediation of Jonathan Run.

Numerous reports have focused on the soluble product of aluminum compounds in dilute and equilibrium conditions (Shah Singh and Brydon, 1969; May *et al*., 1979; Xiao *et al*., 1998). However, the actual chemistry of ARD is complex and the water is likely in a non-equilibrium condition. Many researchers have reported that the amorphous $Al(OH)_3$ was the primary species of Al-precipitates (Nordstrom *et al*., 1984; Nordstrom and Ball, 1986; Lee *et al*., 2002; Pu *et al*., 2010), although the theoretical long-term equilibrium species of Al-precipitates is crystalline $Al(OH)_3$ (gibbsite) and/or one or more forms of Al-sulfate and hydroxyaluminosilicate. Other researchers have reported that Al-sulfate precipitates were detected in the field (Taylor *et al*., 1997; Bigham and Nordstrom, 2000; Kim and Kim, 2003a and 2003b; Pu *et al*., 2010). The effluent from an active NaOH treatment system includes both suspended and soluble Al phases. It is important to have an understanding of the total effluent aluminum concentration that is likely to be achieved. While there are many reports of aluminum containing precipitates, few report the nature and speciation of the associated aqueous dissolved aluminum. Therefore, the goal was achieved by accomplishing the following objectives:

1. Determine the effects of sulfate and silicate on aluminum concentration during the active neutralization/treatment and subsequent settling of Al-bearing ARD with NaOH;

2. Investigate aluminum precipitation behavior in the active treatment and subsequent settling of Al-bearing ARD/AMD with NaOH;

3. Evaluate the interactions between sulfate and silicate on suspended Al solids in active treatment and subsequent settling of Al-bearing ARD/AMD with NaOH.

4. Evaluate the possible effluent Al concentration from active treatment of Al-bearing ARD in Jonathan Run with NaOH and the effect of water temperature (winter and summer conditions) on effluent Al concentration.

In order to achieve these goals, two groups of experiments were conducted with calibrated sulfate and silicate concentrations. The experiments without silicate examined the influence of sulfate and pH only on the soluble and suspended Al concentration, as well as the species of Al-precipitates formed in neutralization of Al-bearing ARD/AMD with NaOH. The experiments containing silicate focused on the effect of silicate and pH only on aluminum concentration. The suspended aluminum concentration with settling time was measured and suspended particulate size distribution were determined to investigate the influence of sulfate and silicate separately and together on the settling of "fine" particulate aluminum solids at different pH values and water chemistries. The sludge (particles) formed in experiments was also measured with different methods to determine the possible species of Al-precipitates formed in the neutralization process.

1.3 SCOPE AND ORGANIZATION OF DISSERTATION

Following Chapter 1 with overall introduction of the dissertation, Chapter 2 is the literature review. Chapter 3 introduces the experimental materials and methods, which include the experimental procedures and the methods of water samples and sludge analysis; Chapter 4 provides the results of the effect of sulfate on Al concentration, which include the effect of sulfate on both total and soluble Al concentration at different pH values after different settling time, as well as the effect of sulfate on the suspended particles size distribution in the supernatant. Furthermore, the sludge analysis provides the information of the chemical characteristics of Al-precipitates with settling time at different pH. Chapter 5 provides results regarding the effect of silicate on Al concentration and suspended particles size distribution at different pH. The interaction of sulfate and silicate on the suspended particle distribution will also be discussed in this chapter. Chapter 6 provides the results of laboratory experiments with field ARD collected from Jonathan Run in Centre County, PA. These analyses are compared to experimental results with calculations provided by the Mineql+ computerized equilibrium model. Furthermore, the effect of temperature on effluent Al concentrations is discussed in this chapter. This dissertation in concluded with Chapter 7 that contains conclusions and chapter 8 that is recommendations for future research.

2.0 LITERATURE REVIEW

2.1 Al-BEARING ARD/AMD

ARD and/or AMD are formed by the oxidation of sulfide minerals (often pyrite, which is iron-sulfide). The mechanisms of pyrite oxidation have been investigated since 1970s (Singer and Stumm, 1970; Moses *et al*., 1987; Nicholson *et al*., 1989a and 1989b; Brown and Jurinak, 1989; Moses and Herman, 1991). The oxidation of pyrite by atmospheric O_2 produces H^+, SO_4^{2-} and Fe^{2+} (Singer and Stumm, 1970):

$$FeS_2(s) + 7/2\ O_2(g) + H_2O \rightarrow Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 2H^+(aq) \quad (2.1)$$

Fe^{2+} (ferrous) can be oxidized by O_2 into Fe^{3+} (ferric), which in turn hydrolyzes and releases additional amounts of acid (Nordstrom, 1982a):

$$2Fe^{2+} + \tfrac{1}{2}\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O \quad (2.2)$$

Therefore, ARD/AMD usually contains high concentrations of dissolved sulfate (SO_4^{2-}), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}) and can be strongly acidic (Rose and Cravotta, 1998; Cravotta *et al*., 1999; Nordstrom and Alpers, 1999).

If the oxidation of pyrite occurs in a location that contains a high presence of alumino-silicate materials (smectite and kaolinite clays) and the pH of the water becomes low enough (acidic), the aluminum could enter surface or ground waters by the dissolution of alumino-silicates (Essington, 2004) or by ion-exchange processes (Vazquez *et al*., 2010a and 2010b; Tan, 2000). For example, kaolinite ($Al_2Si_2O_5(OH)_4$) can dissolve in acid water by the following reaction (Krauskopf and Bird, 1995) (where K is the equilibrium constant and log K= -7.43):

$$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2SiO_2(aq) + 5H_2O \qquad (2.3)$$

In addition, aluminum ions, Al^{3+}, attracted to the negative charged surfaces of clay minerals can be released by exchange with other positive ions (Tan, 2000):

$$3M^+ + Al\text{-clay} \leftrightarrow M_3\text{-clay} + Al^{3+} \qquad (2.4)$$

In equation 2.4 M^+ represents the metal ions. For example, Fe^{3+}, Fe^{2+}, or Mg^{2+} can wholly or partly replace the Al^{3+} ions in the octahedral layers of clay minerals. These processes could increase the concentration of Al^{3+} in surface water. The elevated aluminum levels in natural surface waters and aquifers caused by ARD/AMD have been a worldwide contamination (Gray, 1998). A number of papers have reported that the high concentration of aluminum occurred in ARD/AMD. Dubikova *et al*. (2001) reported the aluminum concentration of an AMD discharge from a mine site was up to 1100 mg/L of aluminum at Sobove, Slovakia. Cravotta (2008) reported that over 50% of 140 abandoned coal mines in Pennsylvania showed that the aluminum concentration of the discharge was from 1 mg/L to 100 mg/L at pH between 2.5 to 7.3. Cravotta considered that aluminosilicate in shale associated with coal deposits could be sources of dissolved Al in the low-pH coal mine discharge samples (Cravotta, 1994; Cravotta *et al*., 1994). Rose and Ghazi (1998) reported that aluminum was the most mobile metals at low pH and the aluminum concentration could be as high as about 1000 mg/L. They assumed that the release of sulfate (200-500 mg/L) resulted in the formation of aqueous aluminum-sulfate complexes that serve to further soluble aluminum.

2.2 AQUATIC ALUMINUM SPECIES

2.2.1 Background

Aluminum is relatively insoluble at neutral pH values (6~6.5), but its solubility increases under more acidic and more alkaline conditions. The amount of Al in solution from normal weathering on the earth is a small proportion of the total Al in the environment, but perturbations of normal weathering can substantially increase Al mobility (Hendershot *et al*., 1996). Aqueous aluminum species are complex. First, aqueous Al is comprised of inorganic Al-hydroxyl species (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$), and the proportion of which varies with pH. Because of the high positive charge of the trivalent aluminum ion, the aluminum ions can form a tight bond with water molecules to form a hydration shell (Nordstrom and May, 1996). The Al^{3+} hydrolyzes readily in aqueous conditions and forms a series of hydrolysis species as summarized in Table 2.1. The concentration of Al-OH complex is pH dependent. At low pH values, aqueous Al is almost entirely present as Al^{3+}. As pH increase, Al undergoes hydrolysis, resulting in a series of OH^- complexes ($Al(OH)^{2+}$ and $Al(OH)_2^+$) and decrease in solubility (Nordstrom and May, 1996).

Second, aqueous Al also forms inorganic complexes with either F^- (Bi, 2001; Bi *et al*., 2001) or SO_4^{2-} (Akit *et al*., 1985; Driscoll and Postek, 1996; Nordstrom and May, 1996) depending on pH (the formation of which also varies with pH), the concentration of the inorganic ligands, ionic strength, and water temperature.

Third, aluminum forms both weak and strong complexes with organic materials such as humic and fulvic acids that tend to keep Al in solution and make it less toxic to organisms. It has been well established that Al forms strong complexes with OH^-, and SO_4^{2-} (Roberson and Hem, 1967). There are some reports of aluminum-silicate complexes too (Browne and Driscoll, 1992; Luciuk and Huang, 1975).

Finally, there is an exchangeable fraction of Al with soils, sediments, and precipitated organic material (Driscoll and Postek, 1996). In assessments of the environmental chemistry of aluminum, it is useful to distinguish among species of aqueous aluminum hydroxyl complexes.

Table 2.1 Aluminum complexation reactions and equilibrium data

Complexes	Log K	Ref.
Al-hydroxyl complexes		
$AlOH^{2+} + H^{+} \leftrightarrow Al^{3+} + H_2O$	5.0	May *et al*., 1979
$Al(OH)^{2+} + 2H^{+} \leftrightarrow Al^{3+} + 2H_2O$	10.1	May *et al*., 1979
$Al(OH)_3^{0} + 3H^{+} \leftrightarrow Al^{3+} + 3H_2O$	16.8	May *et al*., 1979
$Al(OH)_4^{-} + 4H^{+} \leftrightarrow Al^{3+} + 4H_2O$	22.7	Nordstrom and May, 1996
$Al_2(OH)_2^{4+} + 2H^{+} \leftrightarrow 2Al^{3+} + 2H_2O$	7.69	Lindsay, 1979
Al-sulfate complexes		
$Al^{3+} + SO_4^{2-} \leftrightarrow AlSO_4^{+}$	3.5	Nordstrom and May, 1996
$Al^{3+} + 2SO_4^{2-} \leftrightarrow Al(SO_4)^{2}$	5.0	Nordstrom and May, 1996
Al-phosphate complexes		
$Al^{3+} + H_2PO_4^{-} \leftrightarrow AlH_2PO_4^{2+}$	3.1	Nordstrom and May, 1996
$Al^{3+} + HPO_4^{2-} \leftrightarrow AlHPO_4^{+}$	7.4	Nordstrom and May, 1996

As mentioned above, aluminum in ARD may come from the dissolution and/or ion exchange of clay minerals. It is reasonable to suppose that there is high fraction of Al-silicate soluble complexes or fine clay colloids in the "soluble fraction". Thus it is valuable to study the effect of silicate on the total dissolved aluminum in ARD during a treatment processes. Even though aluminosilicate is a typical component of many inorganic minerals, the extent of dissolved aluminosilicate formation in surface waters is only recently being investigated. Perhaps because the chemical structure and thermodynamic properties of such aluminosilicate complexes were at one time virtually unknown (Driscoll and Schecher, 1990), their extent and importance in nature were largely a matter of conjecture. However, both laboratory (Chappell and Birchall, 1988; Exley and Birchall, 1993) and field studies (Browne and Driscoll, 1992) described the formation of dissolved aluminosilicate in acidic waters. Chappell and Birchall (1988) suggested that aluminosilicate could be amorphous protoimogolite (*hydroxyl-aluminum silicate*) precursors with variable stoichiometry (Si:Al ratio from 0.3 to 0.6) that form preferentially at pH from 5.5 to 6.0. Exley and Birchall (1993) further described the formation mechanisms of this complex whereby aluminum hydroxide nucleation is inhibited. In contrast, Browne and Driscoll (1992) proposed the existence of several discrete aluminosilicate complexes for which they derived thermodynamic properties and specific stoichiometry (Al:Si = 1:1, 2:1, and 2:2). It should be noted that Browne and Driscoll (1992)'s observations have been difficult to repeat at the relatively low Si (< 1mg/L) concentrations found in most surface waters (LaZerte *et al*., 1997).

The existence of dissolved aluminosilicate, if confirmed in nature, would be very important not only to the accurate interpretation of dissolved Al and Si chemical speciation, but also to the interpretation of effects on organisms in the presence of aluminosilicate (especially algae). Many studies (Chappell and Birchall, 1988; Browne and Driscoll, 1992; Exley and

Birchall, 1993) suggest that aluminosilicate formation may only be significant in waters containing relatively high concentrations of dissolved Si. Aluminosilicate formation in these studies was restricted to Si concentrations above 2800 to 14000 mg/L, although some evidence suggests aluminosilicate may form at concentrations as low as 1000 mg/L (Birchall *et al*., 1989). Therefore, this complex may only be significant in waters with relatively high dissolved Si concentrations (e.g., streams or waters with low pH), and be of less importance in acidic lakes, which tend to be relatively low in Si (Driscoll and Newton, 1985; Findlay and Kasian, 1986). In their review, Cooke *et al*. (1993) also mentioned that silicates, if concentrated enough ($Si:Al \geq 4$ $Al=0.2mg/L$), may help control residual Al toxicity from alum treatments. However, little empirical evidence exists to support this hypothesis.

2.2.2 Polynuclear aluminum species

For systems of low Al concentration and low pH, mononuclear Al species (Al^{3+}, $AlOH^{2+}$, etc.) seem adequate to explain Al hydrolysis. However, in studies for which base, such as NaOH, is added to the system or at high Al concentrations, evidence suggests the existence of polynuclear Al species. Polynuclear Al species include $Al_2(OH)_2{}^{4+}$, $Al_3(OH)_8{}^{+}$, $Al_6(OH)_{12}(H2O)_{16}{}^{2+}$, the tridecameric Al_{13} polynuclear species and $Al_{13}O_4(OH)_{24}(H_2O)_{17}{}^{2+}$ (Bertsch and Parker, 1996). It is easy to envision the formation of crystalline gibbsite from the combination of these species and through aging of many hexameric rings of polynuclear $Al_6(OH)_{12}(H_2O)_{16}{}^{2+}$. There is little direct experimental evidence for many of these polynuclear structures, but 27NMR spectroscopy has yielded good evidence for the existence of the tridecameric $Al_{13}O_4(OH)_{24}(H_2O))_{17}{}^{2+}$ species (Bertsch and Parker, 1996). In contrast, Jardine and Zelanzny (1996) believe that polynuclear species are transient intermediates in the formation of crystalline $Al(OH)_3$, and a solution will consist only of mononuclear Al and the stable solid phase at true equilibrium.

2.3 ALUMINUM PRECIPITATION FROM ARD

2.3.1 Species of Al-precipitates formed in neutralization of ARD/AMD

Aluminum has only one oxidation state in aqueous systems, Al^{+3}. In general, the primary reaction of aluminum removal in ARD/AMD treatment processes is considered as the formation of aluminum hydroxide (Hem, 1985; Nordstrom and Ball, 1986):

$$Al^{+3} + OH^{-} \leftrightarrow Al(OH)_3\downarrow \tag{2.5}$$

At pH between 6.0 and 7.0, the theoretical solubility of $Al(OH)_3$ in distilled water at 25ºC is less than 0.01 mg/L, with the minimum solubility occurring at pH ~ 6.5. Aluminum hydroxide is amphoteric and the solubility of aluminum hydroxide increases with increasing or decreasing pH from that pH.

There are two kinds of aluminum hydroxide: gibbsite and amorphous aluminum hydroxide. Gibbsite, which is the crystal construction aluminum hydroxide, shows a lower aqueous solubility than amorphous $Al(OH)_3$. Therefore, the theoretical precipitates of aluminum hydroxide formed in ARD/AMD treatment should be gibbsite if the solution is in an equilibrium condition. Some researchers reported that the precipitation from ARD neutralization included gibbsite (Guesek and Wildeman, 2002), whereas others report that the formed aluminum hydroxides are amorphous (Nordstrom *et al.,* 1984; Nordstrom and Ball, 1986; Lee *et al*., 2002). For example, Lee *et al*. (2002) have studied aluminum precipitation from acid mine drainage by titration with NaOH and found the precipitates were amorphous by X-ray analysis. The similar results also had been reported by other investigators (Nordstrom *et al*., 1984; Nordstrom and Ball, 1986). Since the solubility of gibbsite is about 100 times less than amorphous aluminum hydroxide, the predicted effluent Al concentration from a treatment system of ARD/AMD is much different when different species of aluminum hydroxide appear as aluminum precipitates and colloidal particles.

Precipitation of aluminum from ARD/AMD in actual field conditions is more complex. ARD/AMD often contains high concentration of sulfate and depending on location silicate, both influence the character of precipitates. The possible aluminum precipitates formed during the neutralization of acidic ARD/AMD are not only aluminum hydroxides, but also aluminum hydroxysulfate and aluminum-silicate, especially since aluminum has a demonstrated affinity for both sulfate and silicate (Taylor *et al*., 1997; Bigham and Nordstrom, 2000). Some researchers (Nordstrom *et al*., 1984, Herrmann and Baumgartner, 1992; Kim and Kim, 2003a and 2003b) have reported that other species of aluminum precipitates formed in the presence of other anions.

Al-sulfate precipitates are often observed in field at AMD/ARD discharge sites. For example, Kim and Kim (2003b) reported that Al-sulfate precipitates, which were like basaluminite, were observed down-stream of a coal mine field in Taebaeg, Korea. Sanchez Espana (2005, 2006, and 2008) also observed that amorphous to poorly crystalline Al-oxyhydroxysulfate formed in Odiel river watershed when they investigated 64 AMD discharges from 25 different mines in Huelva, SW Spain. These results agree with the published work of Adams and Rawajfih (1977), who identified basaluminite and alunite precipitating in acid soils, as well as with the published works by Chapman *et al*. (1983) and Berger *et al*. (2000), who interpreted the natural Al precipitates formed in AMD from Australia, New Mexico, as amorphous to poorly crystalline basaluminite and/or hydrobasaluminite, respectively. Totsche *et al*. (2003), who studied the Al precipitates formed by neutralization of acidic waters from pit lakes in Lusatia, Germany, also obtained a mixture of several Al hydroxysulfate with variable stoichiometry. In addition, Nordstrom and Alpers (1999) and Bigham and Nordstrom (2000) concluded that a poorly ordered hydrobasaluminite is the most probable forms of Al precipitates from acid sulfate solutions.

Soluble silicate influences the precipitation of aluminum in water. "Soluble silicate" is defined as silicate that is monomeric, containing only one silicon atom and formulated as $Si(OH)_4$. The reported solubility of silicate varies from report to report. The concentration of silicate (as SiO_2) in surface waters reported by investigators is typically in the range of 1-150mg/L (Alexander *et al*., 1954; Stoeber, 1967; Brace and Matijevic, 1977; and Clesceri *et al*., 1989). Some researchers (Exley and Birchall, 1992; Farmer and Lumsdon, 1994) have reported the formation of hydroxyaluminosilicate (HAS) species or co-precipitates in the conditions of diluted solutions with silicate. Exley and Birchall (1992) have studied the interaction between silicate acid and aluminum at low aluminum concentrations. They found that HAS can be formed in such solutions, depending on silicate acid concentration and pH values. At higher aluminum concentrations (10^{-4} M), Birchall (1990) found that the interaction between aluminum and silicate acid gives higher aluminum solubility at around neutral pH value. However, other researcher's results (Reiber *et al*., 1995) are not entirely consistent with these conclusions. Research reports (Sullivan and Cosby, 1998, Gustafsson *et al*., 1998, Neal and Williams, 1988) are not conclusive and suggest that when silicate is present, the predominant mineral phases acting on Al solubility control could be aluminum in equilibrium with (1) gibbsite (crystalline $Al(OH)_3$) (Sullivan and Cosby, 1998); (2) a mixed phase of amorphous $Al(OH)_3$ and aluminosilicate (Gustafsson *et al*., 1998); (3) a metastable aluminosilicate phase (Neal and Williams, 1988).

2.3.2 The possible Al concentration from a NaOH active ARD/AMD treatment system

In general, the likely soluble Al concentration in an effluent from an ARD/AMD treatment system used in calculation and design is the solubility of aluminum hydroxide (gibbsite or amorphous aluminum hydroxide). However, those assumptions are not true and, as mentioned above, the possible species of Al-precipitates formed in an ARD/AMD treatment system, which control the soluble Al concentration, are not only aluminum hydroxide, but also Al-sulfate and Al-silicate. In prediction of soluble Al concentrations, the solubility constants of the possible Al-precipitates are used to determine the final soluble Al concentrations. Since the solubility constant is measured in pure diluted waters, and at equilibrium conditions, the actual soluble Al concentrations in an ARD/AMD treatment system might deviate from the theoretical Al solubility due to the non-equilibrium conditions existing in effluent.

Cravotta (2008) investigated the Al concentrations of 140 coal mine drainages in Pennsylvania with a data summary shown in Figure 2.1. In Figure 2.1, it is shown that the total dissolved aluminum concentration varied to a large extent (more than two orders) for the same pH value. This phenomenon implied that pH is not the only factor that controls the dissolved aluminum. As mentioned above, aluminum ions can form complexes with the other anions, such as silicate, sulfate etc. Therefore, it is reasonable to conclude that the aluminum concentration in the ARD sites as sampled is influenced by some other ions that can form complexes with Al. Cravotta (2008) also reported that the actual dissolved Al^{3+} concentration could be controlled by jurbanite ($AlSO_4(OH)\cdot 5H_2O$) at pH<5 and amorphous $Al(OH)_3$ at pH>5. As mentioned above, amorphous Al hydroxysulfate precipitates have been reported for a variety of AMD sites (Nordstrom and Ball, 1986; Alpers *et al*., 1994; Robbins *et al*., 1996 and 1999; Williams and Smith, 2000; Williams *et al*., 2002; Thomas and Romanek, 2002). Some researchers have reported that Al solubility was controlled by jurbanite in AMD settings (Filipek *et al*., 1987; Cravotta, 1994; Perry, 2001). Nevertheless, Nordstrom *et al.* (2006) argue against solubility control of Al at pH < 4.5 by jurbanite or any other mineral. Bigham and Nordstrom (2000) explained that if jurbanite or another phase with similar stoichiometry limited the concentration of dissolved Al in AMD, an inverse correlation between Al and SO_4 would be expected for low-pH samples instead of the observed positive correlation.

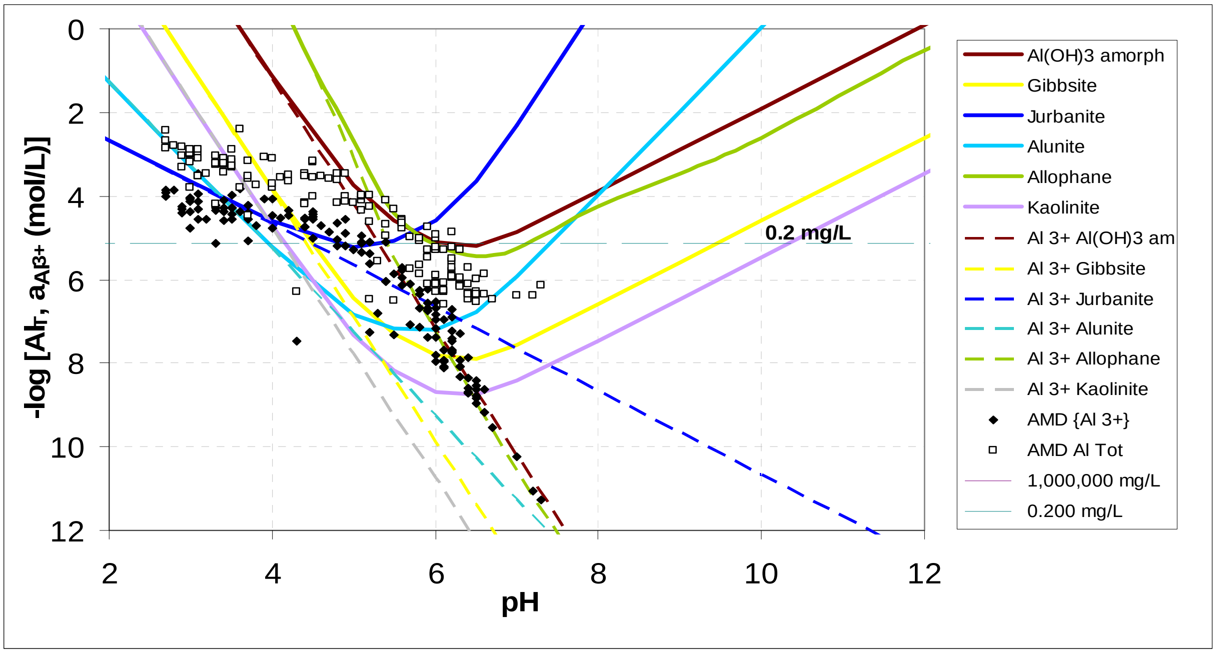


Figure 2.1 Total dissolved Al of 140 AMD samples in Pennsylvania and the theoretical Al hydroxide/hydroxysulfate solubility (After Cravotta, C.A., 2008)

The data in Figure 2.1 show actual values of both soluble and total aluminum in AMD for the actual 140 sites in Pennsylvania (Cravotta, 2008). In Figure 2.1, it can be seen that the suspended Al solids were about 1-2 fold higher than soluble Al concentration, which indicated that the suspended Al concentration control is an important factor in total effluent Al concentration from an ARD/AMD treatment system. Therefore, the settling characteristic of Al-precipitates species is different, and influences the final effluent aluminum concentration after the treatment processes. Unfortunately, there is not enough information about the settling characteristics of the Al-sulfate and Al-silicate precipitates.

2.3.3 Settling of suspended Al particles

The ability of particulate and colloidal aluminum to settle influences the total effluent-discharged aluminum concentration. This is an important issue for regulatory purposes. Since aluminum precipitates can be present in the form of small diameter suspended solids, complexes or colloids, the formation and settling of precipitates will cause the total aluminum in the discharge to be higher than that calculated from equilibrium information and influence the actual removal efficiency of the treatment system (Luciuk and Huang, 1974). Researchers reported that the amorphous aluminum precipitates might be formed when the pH of ARD increased (Nordstrom *et al*., 1984; Nordstrom and Ball, 1986; Bigham and Nordstrom, 2000; Lee *et al*., 2002). The study of the formation and fate of aluminum-bound particulates is important for purposes of this dissertation.

2.4 STUDY OBJECTIVES

The main objective of this study was to determine the total and dissolved aluminum concentrations originating from ground and surface waters in the effluent after the active treatment of Al-bearing ARD/AMD with NaOH. Based on the simulation with the Mineql+ equilibrium model and the preliminary experiments, the most significant factors on dissolved and total aluminum are the presence of silicate, sulfate, water temperature, and pH at different settling times. The following are the specific objectives of this research:

1 To determine the effect of sulfate and silicate on aluminum concentration during Al-bearing ARD treatment with NaOH. In this task, there are several subtask included:

  1.1 To evaluate the effect of sulfate on soluble and total Al concentration in NaOH treatment processes under different pH conditions. These experiments included a series of synthetic ARD water experiments and comparing the experimental results with the MINEQL+ model.

  1.2 To evaluate the effect of silicate on soluble and total Al concentration in Al-bearing ARD treatment with NaOH. These experiments included a series of synthetic ARD water experiment with different silicate and sulfate concentrations. These experimental results were compared with Mineql+ model to discuss the equilibrium state of solution.

2 To discuss the sedimentation characteristics of aluminum precipitates produced in the treatment processes. The subtasks in this research include:

  2.1 To evaluate the sedimentation characteristics (the particle size distribution during the sedimentation) associated with aluminum removal in the NaOH neutralization/treatment processes.

  2.2 To evaluate the effect sulfate and silicate on suspended particle size distribution.

3 To simulate the Al-bearing ARD treatment with NaOH in laboratory with temperature to illustrate the influence of cold and warm water temperatures (simulating winter and summer conditions) on the sensitivity of pH to discharged aluminum.

3.0 METHODS AND MATERIALS

3.1 INTRODUCTION

This chapter describes the methods and materials used in this research. It is divided into four sections: materials, the batch experiments, common analytical techniques, and the introduction of Mineql+ model, which is the software used to simulate the aqueous state. The materials section includes the synthetic ARD and reagents used in the study. The batch experiments describe experimental procedures of ARD neutralization with NaOH to determine the effects of sulfate and silicate on the aluminum removal during the ARD treatment processes. Analytical techniques include water chemistry analysis and sludge analysis. These techniques of sludge analysis include scanning electron microscope (SEM), energy-dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD), and thermogravimetry analysis (TGA). The Mineql+ computerized chemical equilibrium model is used to help in the understanding of aqueous states.

3.2 MATERIALS

3.2.1 Synthetic ARD

Synthetic ARD was used to obtain the fundamental information of the aluminum species and concentration resulting from NaOH neutralization of Al-bearing ARD/AMD. In this research, the components of synthetic ARD were prepared based on the measured constituents of the acidic discharge in Jonathan Run located at Snow Shoe, PA. The main components of the synthetic ARD are presented in Table 3.1. The initial aluminum concentration of synthetic ARD was about 50 mg/L. The initial sulfate concentration of synthetic ARD was selected as an independent variable, and was 0, 190, and 889 mg/L, which made the molar ratios of Al:SO_4 equal to 1:0, 1:1, and 1:5, respectively. NaCl was added to the synthetic ARD at levels of ~860 and 1080 mg/L when the molar ratios of Al:SO_4 are 1:1 and 1:0 respectively to keep the ionic strength of solution constant. The water acidity (hot acidity (APHA, 2005)) was around 100 mg/L. The hot acidity was selected for analysis of acidity due to the samples containing high hydrolysable ions such as aluminum, iron, and manganese.

Each reagent was prepared as stock solution. Different volumes of stock solutions were mixed and diluted to a working volume of 15 L in the experiments according to the designed concentrations.

Table 3.1 The constituents of synthetic ARD water in the experiments of the effect of sulfate on the aluminum removal (mg/L)

pH	Al	Mn	Ca	Mg	SO_4
3.5	50	7.4	10	12	0-~889

The main components of the synthetic ARD used in the experiments for the effect of silicate on aluminum removal are presented in Table 3.2. The initial Al concentration of synthetic ARD used in the experiments for the effect of silicate on Al removal was about 25 mg/L. The initial sulfate concentration of synthetic ARD was changed between 0 and 450 mg/L and the initial silicate concentration (as Si) for the synthetic ARD was 25 and 65 mg/L (as silicon) to make the molar ratio of Al:Si=1:1 and 1:2.5, respectively. Three different molar ratios of Al:Si:SO_4 of synthetic ARD were used as 1:1:0, 1:1:5 and 1:2.5:5.

Table 3.2 The constituents of synthetic ARD water in the simulation experiments of the effect of silicate on the aluminum removal (mg/L)

pH	Al	Mn	Ca	Mg	Silicate	SO_4
3.5	25	7.4	10	12	25~65	0~450

3.2.2 Reagents

Chemicals used in this study were: sodium hydroxide (USP, Fisher), sodium chloride (trace 99.7%, Fisher), calcium chloride (99.7%, Fisher), sodium sulfate (USP, Fisher), aluminum chloride (ACS 99.7%, Fisher), manganese chloride (USP, Fisher), magnesium chloride (USP. Fisher), ferric chloride (USP. Fisher), and nitric acid (ACS. 99.7%, Fisher).

All stock solutions were prepared with DI water. The stock solutions and/or reagent grade salts were used to prepare solutions along with a predetermined dose of 1M HNO_3 or 1M NaOH to obtain the targeted pH for reactions. The pH was maintained within ± 0.1 units of the designated value through the further addition of HNO_3 and/or NaOH. Aqueous silicate solutions were prepared with the method after Davis *et al*. (2001). All lab glass ware was cleaned according to the following protocol: (1) soaking 2 hours in 2 % laboratory detergent, (2) rinsing with 10% nitric acid, (3) washing and rinsing at least three times with DI water; and drying before use.

3.3 BATCH EXPERIMENTAL METHODS

3.3.1 Experimental procedure

The batch neutralization and settling experiments were done in a 20 liter glass jar with a diameter of ~30cm. In these experiments, 5 % NaOH (wt%) solution was added into 15 liters of synthetic ARD and stirred for 5 minutes to let the solution mixed completely, then stirring was stopped and the precipitates were allowed to settle. During the experiments, the position of the sludge–supernatant interface was recorded with time and the water samples were collected at the point that is 10cm under water surface at times of 30 min, 60 min, 120 min, 240 min, 480 min, 1 day, and 2 days. After the water samples (~150-200 ml each time) were collected, half of samples were immediately filtered with a 0.45μm Millipore filter. Both filtered and unfiltered samples immediately received 1 drop of HNO_3 (1+1) and were stored at 4ºC for later analysis. The filtered samples were used to measure the soluble concentration, whereas the unfiltered samples were used to measure the total concentration. The solution headspace was open to the atmosphere during these experiments as would occur in the field. The pH value of solution was measured by a Fisher Accumet 25 benchtop pH electrode meter with Fisher Scientific Accumet pH electrode. All experiments were conducted at room temperature (20°C ± 2°C). The sketch of experimental procedure was shown in Figure 3.1.

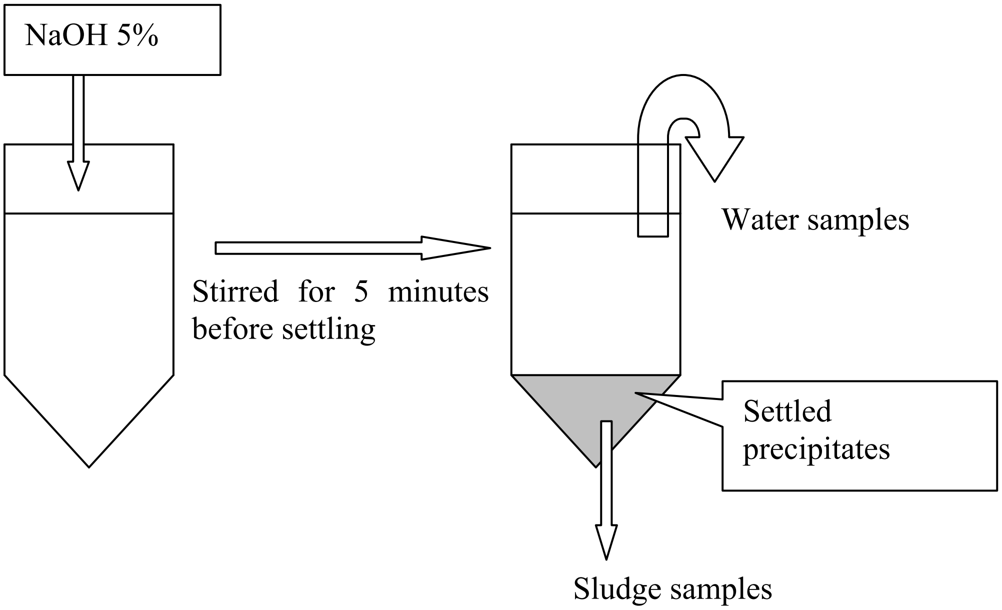


Figure 3.1 Schematic of the batch experimental procedure

During the experiments, the sludge was collected after 30 minutes and 48 hours of settling and separated from water by centrifuging at 8500G for 15 minutes in a Fisher Scientific AccuSpin Model 400 benchtop centrifuge and washed by DI water three times. The separated precipitates were dried at room temperature. The dried precipitates were used for XRD, TGA, and SEM analysis. The samples for SEM analysis were dried in oven at 80-90°C for two hours to remove the sorbed H_2O (Shah Singh and Brydon, 1969).

3.3.2 Experiments to determine the influence of sulfate

A set of experiments were conducted at room temperature 20 ± 2 °C to evaluate the effects of sulfate (molar ratio of Al:SO_4 =1:0, 1:1, and 1:5 respectively) and pH (~5.5 to 8.5) on aluminum removal, and to study the reactions that control the soluble aluminum concentration and the characteristics of Al-precipitates formed in the experiments. Al concentration was fixed at about 50 mg/L, which is an average Al concentration of Al-bearing ARD in Jonathan Run (Neufeld *et al*., 2007). The experiments were done based on the procedure as described above.

Both filtered and unfiltered samples were immediately acidified and stored at 37ºF until analysis. Samples were analyzed for the total and soluble metal ions (Ca, Mn, Mg, and Al) and the anion (SO_4^{2-}). Precipitates were collected at 30 minutes and 48hrs of settling. Precipitates were separated with centrifuge and dried at room temperature as described above. The reactor was open to atmosphere and pH values of the solutions were measured at the end of experiment, which was used as the pH value of the experiment, although the pH value have slightly decreased from the beginning to the end.

3.3.3 Experiments to determine the influence of silicate

A set of experiments were conducted to evaluate the effects of silicate (molar ratios of Al: silicate: sulfate =1:1:0, 1:1:5, and 1:2.5:5) on aluminum removal and to study the controlling reaction of soluble aluminum concentration in the process and the characteristics of aluminum precipitates formed in the experiments. The experiments were conducted with a 25mg/L initial aluminum concentration and with a range of pH values (5.5-8.5) using the same reactors that were used in sulfate experiments. Aqueous silicate solutions were prepared was following the methods described by Davis *et al*. (2001). During the experiments, the silicate stock solution was added into synthetic ARD at the same time with NaOH solution. The experimental procedure was also the same as that one previously described.

3.4 ANALYTICAL METHODS

3.4.1 Chemical analysis

All analysis was performed in accordance with Standard Methods for the Examination of Water and Wastewater (APHA, 2005), EPA methods (USEPA, 2005) or Hach methods (Hach, 2003). All unfiltered and filtered water samples were first digested with microwave digestion before the total and dissolved concentrations of metal ions were measured. Dissolved concentrations of metal were measured after filtering the samples through 0.45 μm Millipore filter, then digesting the filtrate. The particle size distribution was measured with a Microtrac S3500 particle size analyzer.

3.4.1.1 Analysis of metal ions

Metal ions, including Ca, Mg, and Mn were measured using an atomic absorption spectrometer (AA) (Perkin Elmer Model 1100B, Norwalk, CT) in accord with Standard Method #3111 (APHA, 2005). Al concentration was also measured by AA, however aluminum concentrations were lower than 2.0mg/L, the colorimetric HACH method was used (as described below). Before the analysis, all samples were microwave digested in accord with USEPA method 3015 (USEPA, 1994) as described above.

3.4.1.2 Al Analysis

The concentration of aluminum was measured using the Aluminon method (HACH method 8012) (Hach, 2003). The samples were digested before analysis. In this analysis procedure, the aluminum color indicator can combine with aluminum in aqueous samples to form a red-orange color and the intensity of color is proportional to the aluminum concentration. For the analysis, the standard samples were made each time to produce the standard curve that was used to determine the concentration of samples and ascorbic acid was added to remove iron interference. The working range of concentration for this method is between 0.008 to 0.8 mg/L. When the Al concentration in the samples was more than 0.8 mg/L but less than 2 mg/L, samples were diluted to suitable Al concentrations within the above range, and analyzed with the Aluminon technique. The samples were measured by using flame atomic absorption spectrometry (AAS) (Perkin Elmer Model 1100B, Norwalk, CT) when Al concentration was higher than 2 mg/L. During the aluminum analysis, the standard samples were used each time for quality control.

3.4.1.3 Sulfate analysis

The concentration of sulfate was measured by turbidimetric method (APHA, 2005). In this analysis procedure, barium chloride crystal was added into a 10ml sample and stirred for one minute, and then the mixture is allowed to react for 5 minutes. Sulfate ions in the sample will react with barium ions and form the precipitates of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The turbidity of solution was measured with Spectronic 20 at 420 nm. The original sample matrix was used as the blank. The standard curves were obtained with the series of standard solution from 2 mg/L to 70 mg/L. If the samples contained a high sulfate concentration, they were diluted with DI water to provide a concentration in the working measurement range analysis, and the diluted samples were used as blank in these cases.

3.4.1.4 Silicate analysis

Silicate was measured by the Silicomolybdate method (HACH, 2003). In this analysis, one pillow of Molybdate reagent powder (HACH) was added into 10 ml sample. After the powder dissolved completely, one pillow of Acid Reagent Powder (HACH) was added. After 10 minutes, one pillow of Citric Acid Powder (HACH) was added and the mixture reacted for two minutes. The silicate in the sample reacted with Molybdate reagent powder and citric acid powder to form a yellow silicomolybdic acid complexes and the intensity of silicomolybdic acid complexes was determined with Spectronic 20 at 452 nm. The original sample is used as the blank. The standard curves were obtained with a series of standard samples from 1.0 to100 mg/L.

3.4.1.5 pH analysis

The pH value of the solution was measured by a Fisher Accumet 25 benchtop pH electrode meter, equipped with Fisher Scientific Accumet pH electrode. The pH meter was standardized with 4.0, 7.0, and 10.0 buffers purchased from Fisher Scientific prior to each batch test.

3.4.2 Particle size analysis

The particle size was analyzed with a Microtrac S3500, which use tri-laser technology to measure the particle size distribution. The Microtrac S3500 tri-laser system allows light scattering measurements to be made from the forward low angle region to almost the entire angular spectrum (approximately zero to 160 degrees). The measurement capability of Microtrac S3500 is from 0.024 to 2800 micrometers, which is suitable for experiments conducted in this research.

3.4.3 Precipitate analysis

3.4.3.1 Scanning electron microscope (SEM)

In this study, the morphological features of the precipitates were measured using a Philips XL30 scanning electron microscope (SEM). The energy-dispersive x-ray microanalysis system, Oxford Instruments INCA, was used to perform energy dispersive spectroscopy (EDS) analysis. The topography and chemical compositions of the sludge formed in the experiments were studied. The chemical compostions of the sludge were measured with energy-dispersive spectrometer (EDS).

3.4.3.2 X-ray diffraction (XRD)

The primary tool used for determining crystallization of the precipitates was X-ray diffraction (XRD). The diffractometer was used in this study is a Rigaku instrument (Rigaku, Japan). The Rigaku diffractometer uses Cu radiation ($K\alpha_1$ and $K\alpha_2$), and is operated at 35 kV and 25 mA. The beam profile is maintained by a 1° divergence slit, a 1° scatter slit, and two 0.3° receiving slits. All the XRD samples were step-scanned in step interval of 0.1° and 2 s counting time.

3.4.3.3 Thermogravimetry analysis (TGA)

Thermogravimetric Analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative thermogravimetry (DTG) curve, which is a plot of the rate of change of mass with respect to temperature against temperature, was used to tell the point at which weight loss was most apparent.

A Perkin Elmer TGA 7 Thermogravimetric Analyzer was used for the thermogravimetric analysis (TGA). TGA of precipitates were run with heating rate of 10 °C/min. Weight loss was determined for 6-10 mg samples in alumina crucibles at temperatures ranging from 25 °C to 1000 °C.

3.5 MINEQL+ MODEL

Mineql+ chemical equilibrium modeling software is a chemical equilibrium model that is used for calculating aqueous speciation, solid phase saturation states, and precipitation-dissolution at low temperatures (0-50ºC) in aqueous systems with low to moderate ionic strength. Dissolved ions in solution interact with each other to form complexes, and possibly form solid phases (precipitates). In a typical natural aqueous system there may be 10 to 20 major chemical components dissolved in solution. These components have the potential to form hundreds of dissolved chemical complexes, and solids phase precipitates. In Mineql+ chemical equilibrium model, it is assumed that all reactions have completed and are in equilibrium with one another in the system, which means that the output results are based on the equilibrium conditions. Therefore, with the chemical equilibrium database, this model provides a thermodynamic snapshot of the system: the pH, ionic strength, the distribution of dissolved chemical species, the amount of solid phase formed, etc. However, this model does not consider the effect of time on some reactions that have kinetic restrictions which require long time to arrive equilibrium (Schecher and McAvoy, 1998). In simulation experiments, Mineql+ chemical equilibrium model has been used to study the possible reactions that occur in the processes.

In this study, the saturation index (SI) values of different possible species of Al-precipitates after different settling time were calculated by Mineql+ model. These SI values of compounds are used to evaluate the equilibrium states of solution in experiments. Input data for these calculations were measured components of the supernatant measured after predetermined times of settling. A negative SI value indicates that solution is unsaturated with the indicated compounds, whereas the positive SI value indicates that the solution is supersaturated with this compound. If the SI value is zero, it indicates that the solution is in an equilibrium condition.

The solubility of each possible Al-precipitate was also calculated by Mineql+ model. The input data for these solubility calculations was the initial Al concentration of the synthetic ARD with the final pH value of 5.0 to 8.5. The temperature was selected at 20°C and the effects of ionic strength were considered.

4.0 EFFECT OF SULFATE ON ALUMINUM SPECIATION AND CONCENTRATION DURING ACTIVE TREATMENT OF ARD

4.1 INTRODUCTION

In general, there are two categories of ARD/AMD treatment systems, passive and active treatment systems. Passive treatment systems, which are limestone-based, low in cost and little maintenance, are effective on treating acidic discharge with relatively low flow and low metal concentrations (Skousen *et al*., 2000). Active treatment systems, which require continuous addition of alkalinity (such as from NaOH, Na_2CO_3, $Ca(OH)_2$, and NH_3) into the drainage, are usually used for high metal concentration and/or high flow rate. The active treatment system is expected to be installed and in operation quicker than passive treatment system and requires less land space.

Generally, the formation of $Al(OH)_3$ is considered as the primary reaction of Al removal during ARD treatment processes:

$$Al^{+3} + 3H_2O \leftrightarrow Al(OH)_3\downarrow + 3H^+ \qquad (4.1)$$

However, the precipitation of aluminum from natural ARD/AMD is complex. ARD/AMD often contains high concentrations of sulfate, and silicate that could influence the composition of precipitates. The possible aluminum precipitates formed as a consequence of pH adjustment of ARD (or ARD) are not only aluminum hydroxides, but also Al-hydroxyl-sulfate.

The strong affinity that aluminum has for sulfate in the form of basaluminite and alunite has been observed by Taylor *et al*. (1997) and Bigham and Nordstrom, (2000). They reported that although the solubility of aluminum appeared to corresponding to aluminum hydroxides, analysis of the composition of formed precipitates suggested that amorphous basaluminite and aluminum hydroxysulfate were in solution, the proportions of which were pH dependent. Several previous studies (Karathanasis *et al*, 1988; Sullivan *et al*, 1988; Neal *et al*, 1987; Van Breeman, 1973) have reported that a jurbanite-like precipitates, having a molar stoichiometry of Al:OH:SO_4=1:1:1, might control the activity of Al^{3+} in acidic, SO_4-rich waters. Adams and Rawajfih (1977) found that amorphous basaluminite ($Al_4(SO_4)(OH)_{10}.5H_2O$) was precipitated during titration of aluminum sulfate with Na-, K- and Ca-hydroxides, and Nordstrom *et al* (1984) have also suggested that the most common phase in mine-drainage systems seems to be an amorphous Al hydroxysulfate with basaluminite stoichiometry. Herrmann and Baumgartner (1992) and Kim and Kim (2003a and 2003b) have also reported that other compositions of aluminum precipitates can also be formed in the presence of other anions. Nordstrom *et al.* (2000) found in both field and laboratory experiments that the precipitates of basaluminite ($Al_4(OH)_{10}SO_4$)/hydrobasaluminite($Al_4(OH)_{10}SO_4 \cdot 12\text{-}36(H_2O)$) significantly delayed the formation and equilibration of stable minerals.

Many researchers have investigated the solubility product of aluminum compounds in dilute and equilibrium conditions (Shah Singh and Brydon, 1969; May *et al*, 1979; Xiao *et al*, 1998). However, the actual chemistry of ARD is complex and the water could be in nonequilibrium conditions. Some researchers have reported that the amorphous $Al(OH)_3$ was the primary species of Al-precipitates (Nordstrom *et al.*, 1984; Nordstrom and ball, 1986; Lee *et al*., 2002; Pu *et al*., 2010), although the theoretical equilibrium species of Al-precipitates should be gibbsite and/or Al-sulfate. Meanwhile, some other researchers have reported Al-sulfate precipitates were detected in field (Taylor *et al*., 1997; Bigham and Nordstrom, 2000; Kim and Kim, 2003a and 2003b).

In treatment systems, it is important to know the effluent aluminum concentration that could be achieved. However, most of reports focused on the species of precipitates, but few of them involved the aqueous aluminum phase and aluminum concentrations. In this chapter, the effect of sulfate on Al concentration and the species of Al-precipitates formed at different pH and settling times have been studied. Three experimental series at different sulfate concentrations have been done to simulate the neutralization processes of Al-bearing ARD/AMD. The three different sulfate concentrations were in the molar ratio of $Al:SO_4$ equal to 1:0, 1:1, and 1:5, respectively. For each series experiments, the pH values were controlled in the range of about 5.5 to 8.5.

This chapter presents the results of experiments and discusses the possible species of Al-precipitates, which might control the Al concentration, formed in experiments or in the settling tank. First, section 4.2 presents the total and soluble aluminum concentrations at different pH at short (30 minutes) and long (48 hours) settling times in the experiments, following with the results of XRD, TGA, and SEM analysis to show the characteristics of precipitates formed at the different conditions (section 4.3). Section 4.4 shows the change of Al and sulfate concentrations with settling time. Section 4.5 presents the simulation results of Mineql+ model to discuss the possible species of Al-precipitates that might control the soluble Al concentration. Section 4.6 presents the suspended particle size distribution under different conditions in experiments. Section 4.7 is the discussion of the effect of sulfate on suspended particle size distribution. Section 4.8 presents conclusions of the effect of sulfate on Al-bearing ARD/AMD treatment.

4.2 ALUMINUM CONCENTRATIONS WITH SULFATE AT DIFFERENT pH VALUES

As mentioned above, in this study, synthetic ARD with three different initial sulfate concentrations have been used. The initial sulfate concentration was 0, ~180, and ~890 mg/L, and the molar ratio of Al:SO_4 was 1:0, 1:1, and 1:5, respectively. The initial Al concentration of synthetic ARD was controlled as 50 mg/L, which was the actual Al concentration of ARD in Jonathan Run. In each series of experiments, the final pH was controlled in the range of 5.5 to 8.5. Water samples were collected after addition of NaOH solution at different settling time. The filtered water samples (passed through 0.45 µm) represented the soluble Al concentration, whereas the unfiltered samples represented the total Al concentration. The difference between total and soluble Al concentration represented the suspended Al concentration in the experiments.

4.2.1 Soluble Al concentration at different pH and sulfate concentrations

Figure 4.1-4.3 show soluble Al concentration in experiments with different sulfate concentrations at different pH values after short (30 minutes) and long (48hours) settling time. In experiments without sulfate (Al:SO_4 molar ratio = 1:0), soluble Al concentrations at different pH after 30 minutes and 48 hours of settling are shown in Table 4.1. In Table 4.1, it can be seen that the minimum soluble Al concentration occurred at pH~6.5 (0.32 mg/L at 30 minutes and 0.27 mg/L at 48 hours of settling), and the soluble Al concentration increased with both increasing and decreasing of pH from that pH (Figure 4.1). In Figure 4.1, it could be seen that soluble Al concentration did not change much from 30 minutes to 48 hours of settling at all pH. At pH equal to 6.5, the soluble Al concentration was 0.27 mg/L after 48 hours of settling, which was only about 0.05 mg/L lower than that at 30 minutes of settling. The Mineql+ model calculated the theoretical solubility of aluminum for amorphous $Al(OH)_3$ as 0.33 mg/L and 0.001mg/L for gibbsite (crystalline $Al(OH)_3$).

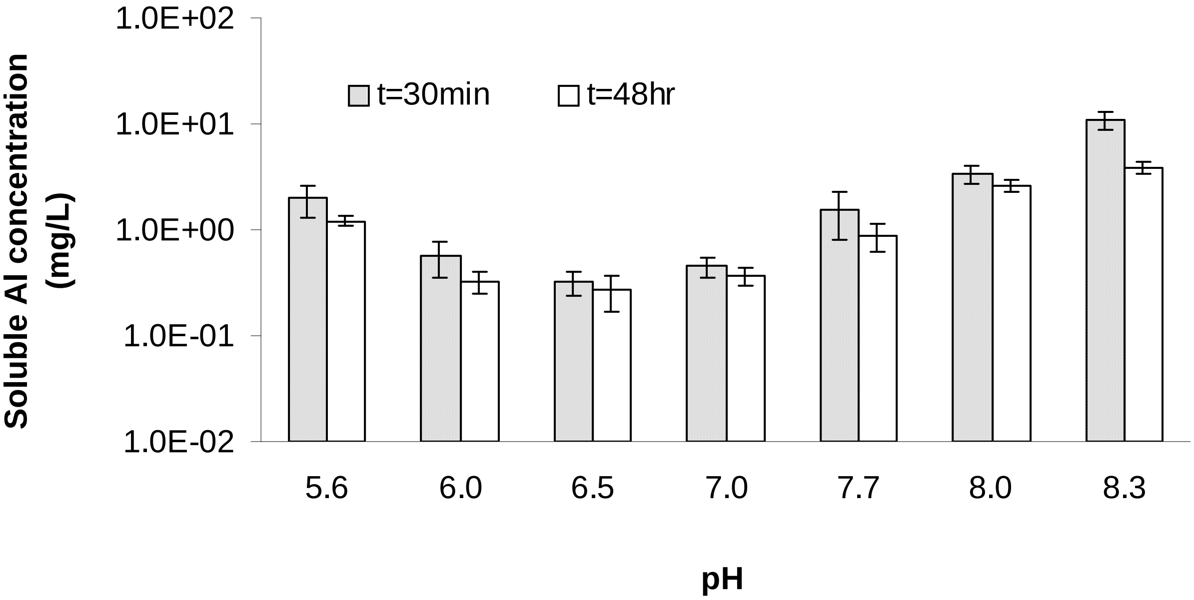


Figure 4.1 Soluble Al concentrations in the experiments with no sulfate ($Al:SO_4=1:0$) at different pH values (5.5-8.5) after 30 minutes and 48 hours of settling

Table 4.1 Soluble Al concentrations after different settling time at different pH values (mg/L) (initial Al concentration ~50 mg/L)

Al:SO_4=1:0 (M/M)			Al:SO_4=1:1 (M/M)			Al:SO_4=1:5 (M/M)		
pH	Detention time		pH	Detention time		pH	Detention time	
	30 min	48 hours		30 min	48 hours		30 min	48 hrs
5.6	1.97	1.21	5.6	1.86	0.31	5.5	1.21	0.21
6.0	0.56	0.33	6.0	0.39	0.14	6.0	0.43	0.03
6.5	0.32	0.27	6.6	0.24	0.09	6.6	0.25	0.02
7.0	0.45	0.37	7.2	0.48	0.13	7.1	0.39	0.04
7.7	1.55	0.89	7.5	0.92	0.36	7.5	1.18	0.16
8.0	3.31	2.62	8.0	3.6	1.8	8.0	3.20	1.32
8.3	4.97	3.91	8.3	8.05	2.92	8.4	5.52	2.81

The soluble Al concentrations in experiments with low sulfate (Al:SO_4 equal 1:1) are shown in Figure 4.2 and listed in Table 4.1. The minimum soluble Al concentration was 0.24 mg/L and 0.09 mg/L after 30 minutes and 48 hours of settling, respectively. The minimum soluble Al concentration also occurred at neutral pH (= 6.6) and the change of soluble Al with pH showed a similar tendency as in experiments when sulfate was absent. The change of soluble Al concentration with pH value in these two experiments shows that pH could strongly influence the soluble Al during neutralization of Al-bearing ARD in either presence or absence of sulfate.

Comparing the soluble Al concentrations after 48 hours of settling, it can be found that soluble Al concentrations in experiments that contained sulfate were less than those in the experiments without sulfate, although the soluble Al concentrations at 30 minutes of settling had no significant difference. Al concentrations were reduced somewhat as the time of settling increased indicating the possible formation of small colloidal sized particles with sulfates that needed more time to settle. This observation was supported in the following section regarding to particle size analysis.

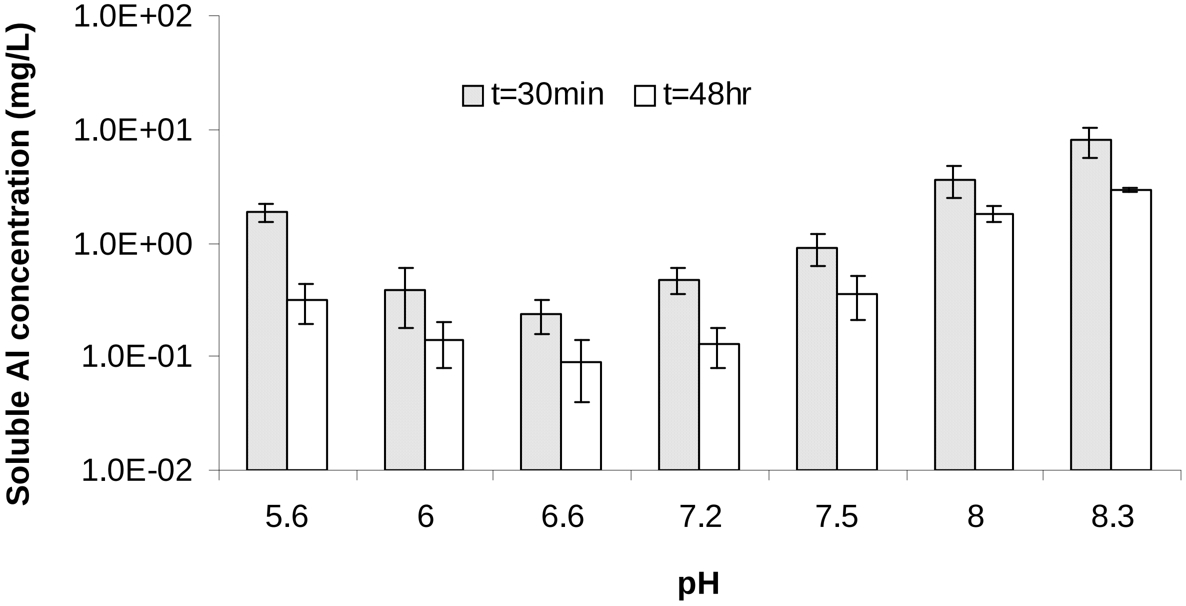


Figure 4.2 Soluble aluminum concentrations in the experiments that the molar ratio of Al:SO_4 equal to 1:1 at different pH values (5.6-8.3) after 30 minutes and 48 hours of settling

The soluble Al concentrations in experiments with higher sulfate (Al:SO_4=1:5) are shown in Figure 4.3 and data listed in Table 4.1. At pH=6.6, the soluble Al concentration was 0.25 mg/L and 0.02 mg/L after 30 minutes and 48 hours of settling, respectively. These values were also the minimum soluble Al concentration in this series experiments. Comparing the soluble Al concentration in these three experiments, it can be found that the value in experiments without sulfate after short settling time (30 minutes) did not change very much for a given pH. For example, the soluble Al concentration was 0.56mg/L, 0.39 mg/L, and 0.43 mg/L at pH=6.0 and 3.31 mg/L, 3.60 mg/L, and 3.20 mg/L at pH=8.0 in experiments with no sulfate (Al:SO_4=1:0), low sulfate ($Al:SO_4=1:1$), and high sulfate ($Al:SO_4=1:5$), respectively. However, with the increasing of settling time, at the higher sulfate concentrations, the soluble Al concentration became lower at prolonged settling times (48 hours). At 48 hours of settling, soluble Al concentration in the experiments with $Al:SO_4=1:5$ was from 0.02 to 1.32 mg/L at pH from 5.5 to 8.0, whereas soluble Al concentration was from 0.27 to 2.62 mg/L and 0.09 to 1.80 mg/L in experiments without sulfate and with lower sulfate concentrations, respectively. These results support the observation that sulfates could decrease the soluble Al concentration in the neutralization of Al-bearing ARD/AMD under certain conditions.

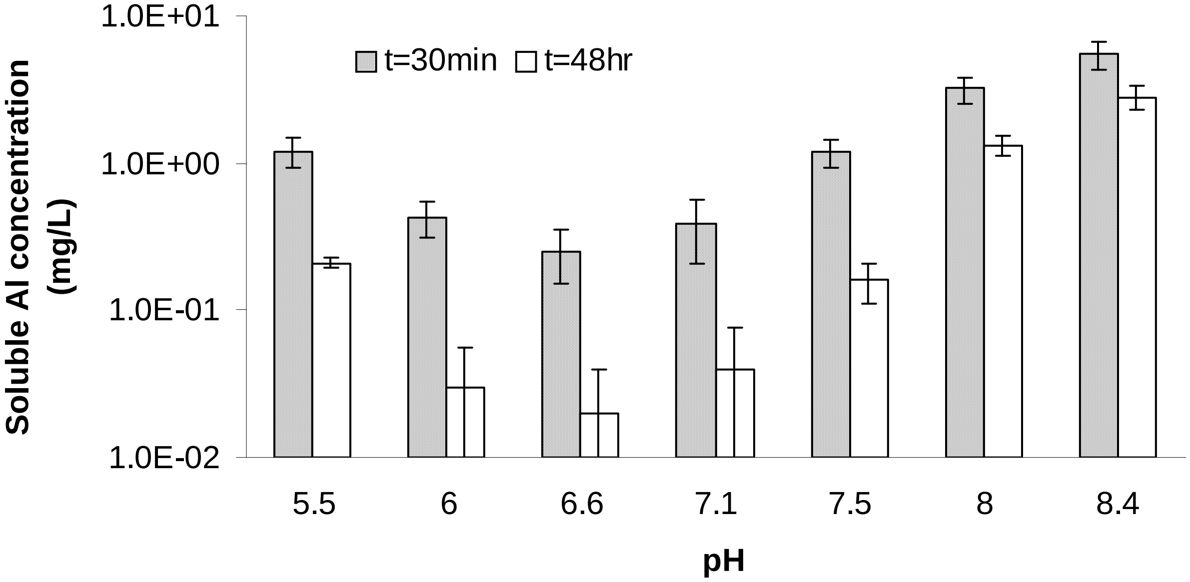


Figure 4.3 Soluble aluminum concentrations in the experiments that the molar ratio of $Al:SO_4$ equal to 1:5 at different pH values (5.5-8.4) after 30 minutes and 48hours of settling

In the three experimental series, the soluble Al concentration showed the minimum soluble Al concentration occurred at pH around 6.5, following with increase of soluble Al concentration as pH decreased or increased from neutral.

Figure 4.4 presents soluble Al concentrations when the supernatant pH was maintained at pH=6.0 and 8.0 with three Al:SO_4 molar ratios, and after 30 minutes and 48 hours of settling. Results are as follows: after 30 minutes of settling, soluble Al concentration was in the range of 0.39 mg/L to 0.56 mg/L at pH=6.0 and 3.20 mg/L to 3.60 mg/L at pH = 8.0.

After 48 hours of settling, soluble Al concentration was in the range of 0.02 to 0.33 mg/L at pH=6.0 and 1.32 to 2.62 mg/L at pH=8.0. The soluble Al concentration at pH= 6.0 was lower than that at pH=8.0 after both the short (30 minutes) and long (48 hours) of settling. The data suggested that pH is a critical parameter when operating the treatment system of Al-bearing ARD/AMD and (excursions resulting in) elevation of pH will result in increases in soluble Al concentrations even after extended times in the settling tank.

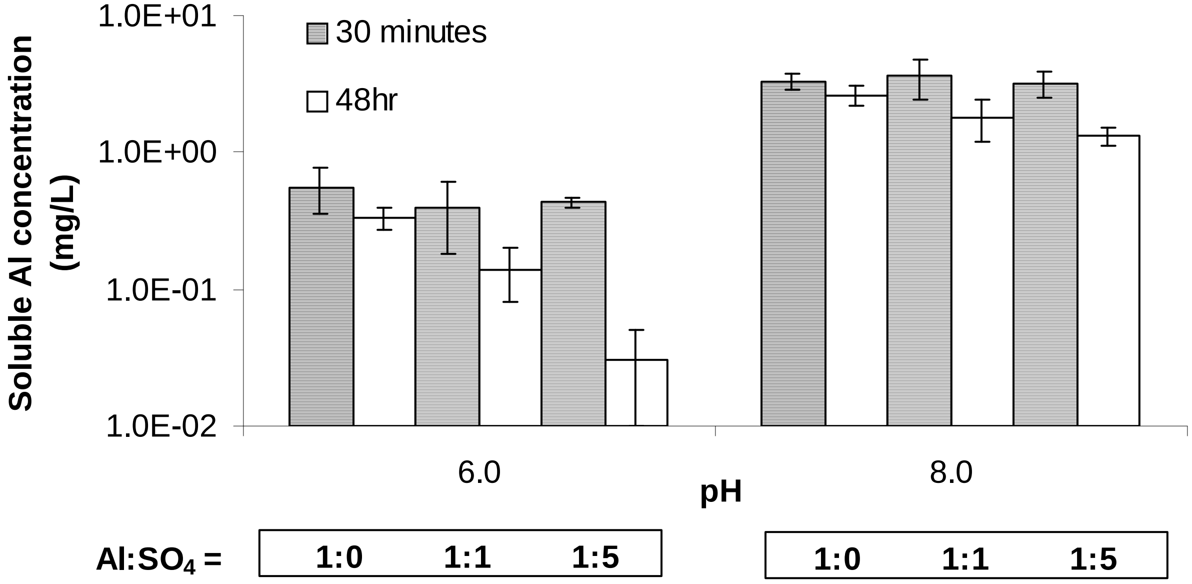


Figure 4.4 Soluble Al concentration at different settling time at pH=6.0 and 8.0

In Figure 4.4, it can be also found that the sulfate concentration can influence soluble Al concentration as well. . After 30 minutes of settling at pH = 6, the soluble Al concentration was 0.56 mg/L, 0.39 mg/L, and 0.43 mg/L at pH=6.0 with Al:SO_4 molar ratios = 1:0, 1:1, and 1:5, respectively. The soluble Al concentration at pH =8.0 was 3.31 mg/L, 3.60 mg/L, and 3.20 mg/L with Al:SO_4 molar ratios = 1:0, 1:1, and 1:5, respectively. The data showed that soluble Al concentrations in different sulfate concentration experiments were close after short settling time (30 minutes). After 48 hours of settling, soluble Al concentration became 0.33 mg/L, 0.14 mg/L, and 0.03mg/L at pH=6.0 and 2.62 mg/L, 1.80 mg/L, and 1.32 mg/L at pH=8.0, respectively. The change of soluble Al concentration in experiments with different sulfate concentrations showed that sulfate could be expected to decrease soluble Al concentrations in Al-bearing ARD neutralization after long settling times. Note that this observation is for soluble Al only. The influence of sulfate on particle size and supernatant total aluminum after settling is outlined below. As mentioned above, soluble Al concentration in experiments with different sulfate concentrations showed that the presence of sulfate decreased soluble Al concentration after long settling time (Figure 4.4). In experiments without sulfate, soluble Al concentration changed little from short (30 minutes) to long settling time (48 hours), whereas soluble Al concentrations in experiments that contained sulfate decreased from 30 minutes to 48 hours of settling. Furthermore, the higher the initial sulfate concentration in experiments, the lower the soluble Al concentration after long settling time (48 hours). In experiments without sulfate, soluble Al did not change much from short to long settling time. For example, the soluble Al concentration was 0.32 mg/L and 0.27 mg/L after 30 minutes and 48 hours of settling at pH=6.5. This phenomenon indicated that Al precipitation in experiments without sulfate achieved in equilibrium condition immediately after pH change. Since the mechanism of Al removal in experiments without sulfate is the formation of aluminum hydroxide, it is reasonable to suppose that the solution was in equilibrium with aluminum hydroxide in the neutralization of Al-bearing ARD after short settling time. In the experiments that contained sulfate, soluble Al concentration decreased with increasing of settling time. Therefore, it is assumed that the slower formation of Al-sulfate precipitates caused the decreasing of soluble Al concentration. The equilibrium states of solution in experiments will be discussed in Section 4.5.

4.2.2 Total Al concentration at different pH and sulfate concentrations

Figure 4.5-4.7 show total Al concentrations (soluble Al plus suspended Al) in experiments with different sulfate concentrations after short and long settling time at different pH with the associated data listed in Table 4.2. In experiments with molar ratio of Al:SO_4=1:0 (no sulfate) at pH range of 5.5 to 8.5, total Al concentration was from 1.48 to 7.30 mg/L (Figure 4.5) after 30 minutes of settling, whereas it was from 1.54 to 10.10 mg/L and 1.73 to 11.31 mg/L in experiments with low sulfate concentrations (Al:SO_4=1:1) (Figure 4.6) and with high sulfate concentrations (Al:SO_4=1:5) (Figure 4.7), respectively. Comparing total Al concentration in different experiments, it can be found that this value in experiments without sulfate was lower than that in experiments with high sulfate (Al:SO_4=1:5) at short settling time (30 minutes).

With increasing of settling time (up to 48 hours), total Al concentration varied from 0.33 to 5.61 mg/L in experiments with no sulfate (Al:SO_4=1:0), while total Al concentration was from 0.31 to 3.28 mg/L and 0.30 to 3.45. mg/L in experiments with Al:SO_4=1:1 and Al:SO_4=1:5, respectively. The total Al concentration at pH above 8.0 showed that final total Al concentration in experiments with high sulfate concentration was lower than that in experiments without sulfate.

Table 4.2 Total Al concentrations at settling times of 30 minutes and 48 hours at different pH (mg/L) and molar aluminum to sulfate ratios (Initial Al concentration ~50 mg/L)

Al:SO_4=1:0 (M/M)			Al:SO_4=1:1 (M/M)			Al:SO_4=1:5 (M/M)		
	Detention time			Detention time			Detention time	
pH	30 min	48 hours	pH	30 min	48 hours	pH	30 min	48 hrs
5.6	3.25	1.54	5.6	3.25	0.61	5.5	2.45	0.59
6.0	2.25	0.44	6.0	1.54	0.46	6.0	2.02	0.31
6.5	1.57	0.33	6.6	1.54	0.31	6.6	1.73	0.30
7.0	1.48	0.48	7.2	1.89	0.57	7.1	2.14	0.34
7.7	3.02	1.31	7.5	2.29	0.68	7.5	4.24	0.75
8.0	4.41	2.87	8.0	4.61	2.15	8.0	4.56	1.81
8.3	7.30	5.60	8.3	10.1	3.28	8.4	11.31	3.45

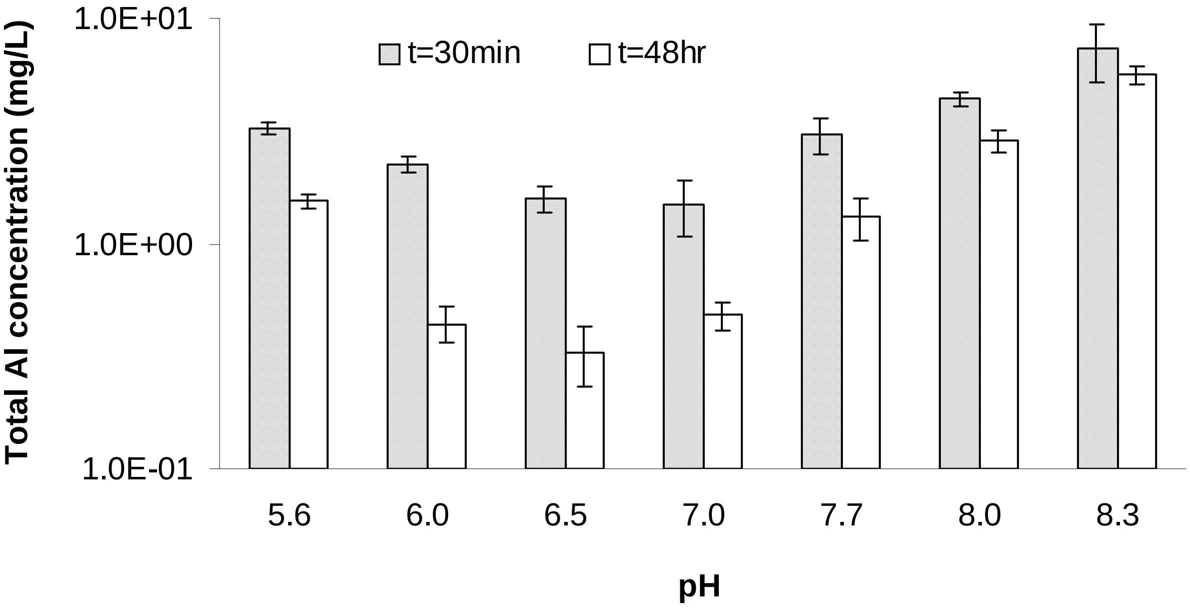


Figure 4.5 Total Al concentrations at different pH after 30 min and 48 hr of settling in experiments without sulfate

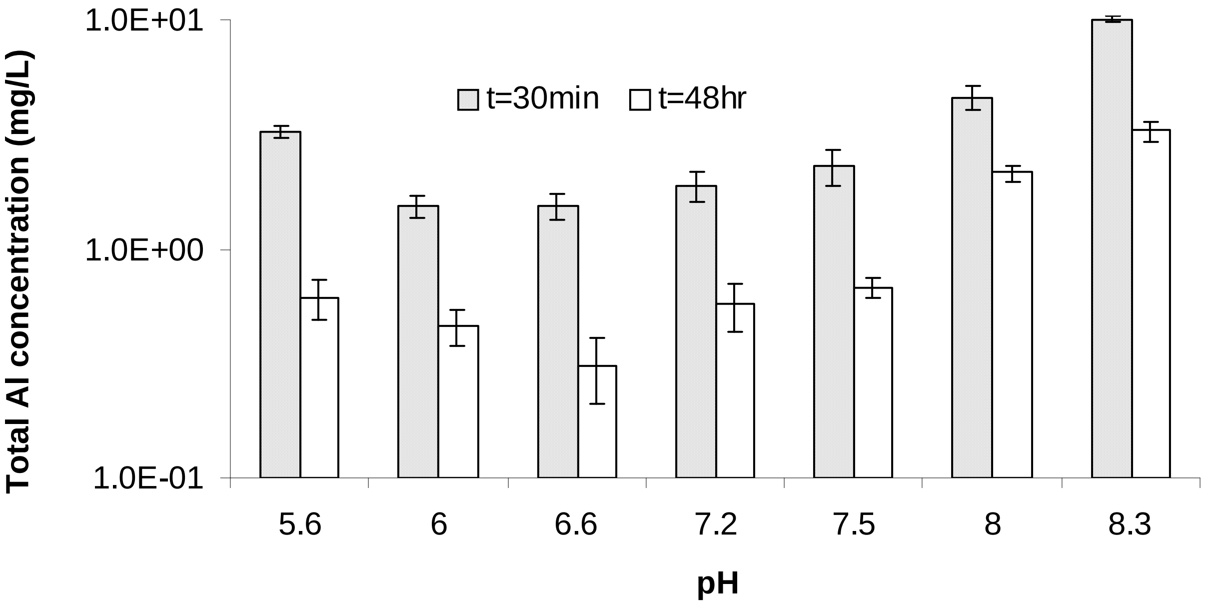


Figure 4.6 Total Al concentrations at different pH after 30 min and 48 hr of settling in experiments with low sulfate concentration (Al:SO_4=1:1)

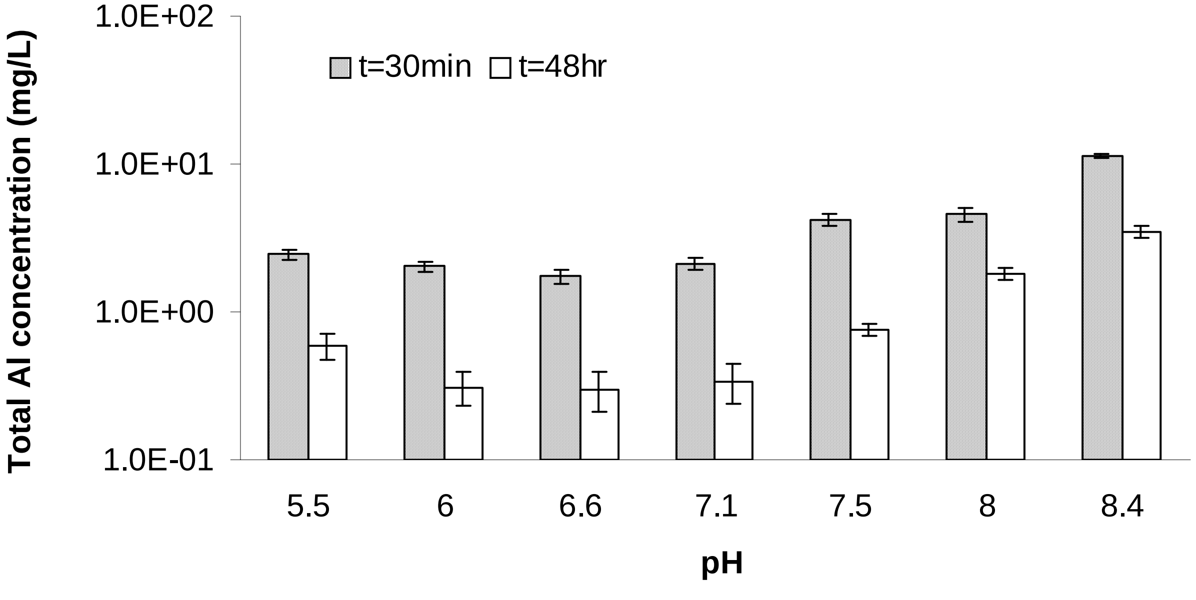


Figure 4.7 Total Al concentrations at different pH after 30 minutes and 48 hours of settling in experiments with high sulfate concentration (Al:SO_4=1:5)

Figure 4.8 presents total Al concentration after short and long settling time at pH =6.0 and 8.0 in experiments with different initial sulfate concentrations. After 30 minutes of settling, the total Al concentration was 2.25 mg/L, 1.54 mg/L, and 2.02 mg/L at pH=6.0, and 4.41 mg/L, 4.61 mg/L, and 4.54 mg/L at pH=8.0 when molar ratio of Al:SO_4 equal to 1:0, 1:1, and 1:5, respectively. After 48 hours of settling, the total Al concentration reduced to 0.44, 0.46, and 0.31 mg/L at pH=6.0, and 2.87, 2.15, and 1.81 mg/L at pH=8.0 when molar ratio of Al:SO_4 equal to 1:0, 1:1, and 1:5, respectively. The data showed that total Al concentration was lowered by allowing for longer settling time, and total Al concentration increased as the pH excursion went from 6 to 8, which indicated that pH is also critical parameter for controlling total Al concentration in ARD/AMD treatment processes. Furthermore, total Al concentration at long settling time was lower when solution contained high sulfate concentration. Since the total Al concentration includes soluble Al ions and suspended Al solids, it is important to valuate the change of suspended Al solids with sulfate concentration to better understand the possible total aluminum concentration and species of precipitates likely to be formed in the effluent from an ARD/AMD NaOH active treatment system.

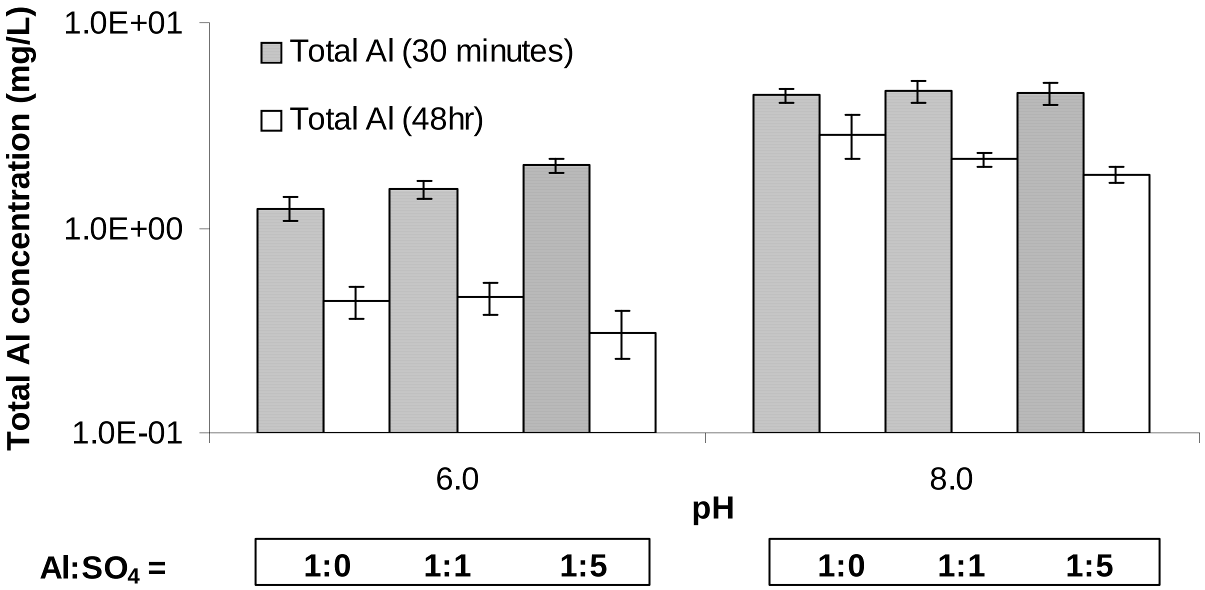


Figure 4.8 Total Al concentrations at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling

4.2.3 Suspended Al concentration at different pH and sulfate concentrations

As indicated above, supernatant samples were collected after 30 minutes and 48 hours of settling. These samples were filtered with a 0.45μm membrane filter to separate soluble aluminum from aluminum-containing suspended solids. Figure 4.9-4.11 present data of Al associated with suspended particulates in experiments with different initial aluminum to sulfate ratios after 30 minutes and 48 hours of settling. At pH range of 5.5 to 8.0 and after 30 minutes of settling, suspended Al concentration was in the range of 1.03 to 1.79 mg/L (pH=5.6~8.0) (Figure 4.9) when sulfate was absent, whereas it was in the range of 1.01 to 1.41 mg/L and 1.24 to 3.06 mg/L in experiments with low sulfate (Al:SO_4=1:1) (Figure 4.10) and high sulfate (Al:SO_4=1:5) (Figure 4.11), respectively. Comparing suspended Al concentration in different experiments, there was not a significant difference after short settling time. When settling time became longer

(48 hours), suspended Al concentration reduced from 0.06 to 0.42 mg/L in experiments without sulfate (Al:SO_4=1:0), while it was from 0.22 to 0.44mg/L and 0.28 to 0.64 mg/L in experiments with low and high sulfate concentrations, respectively.

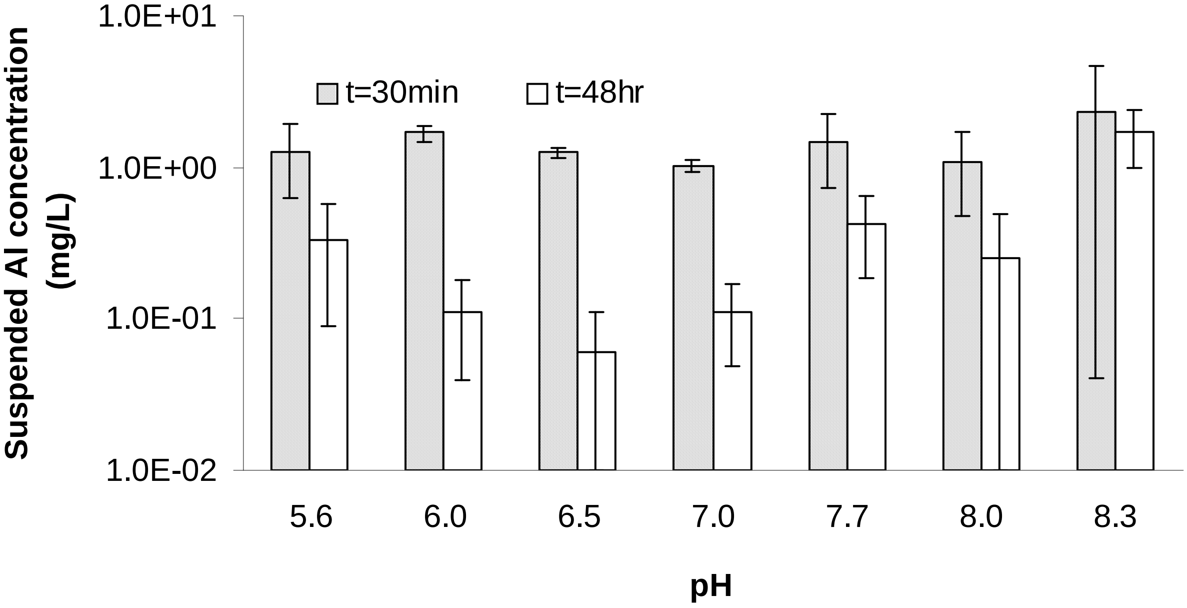


Figure 4.9 Suspended Al concentrations at different pH after 30 minutes and 48 hours of settling in experiments without sulfate (Al:SO_4=1:0)

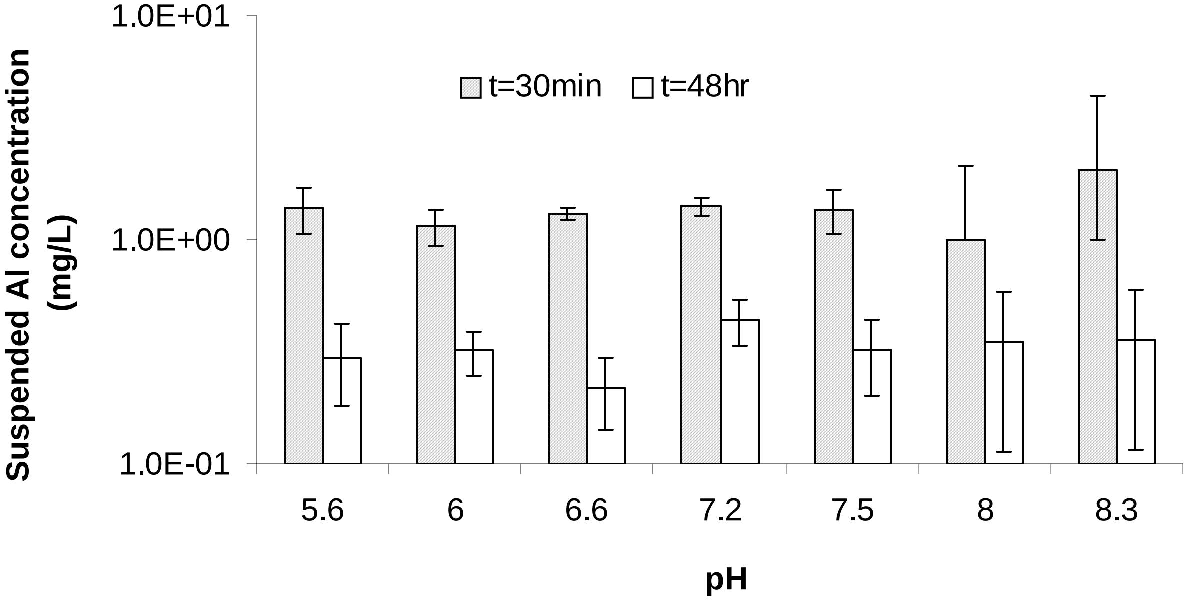


Figure 4.10 Suspended Al concentrations at different pH after 30 minutes and 48 hours of settling in experiments with low sulfate concentration (Al:SO_4=1:1)

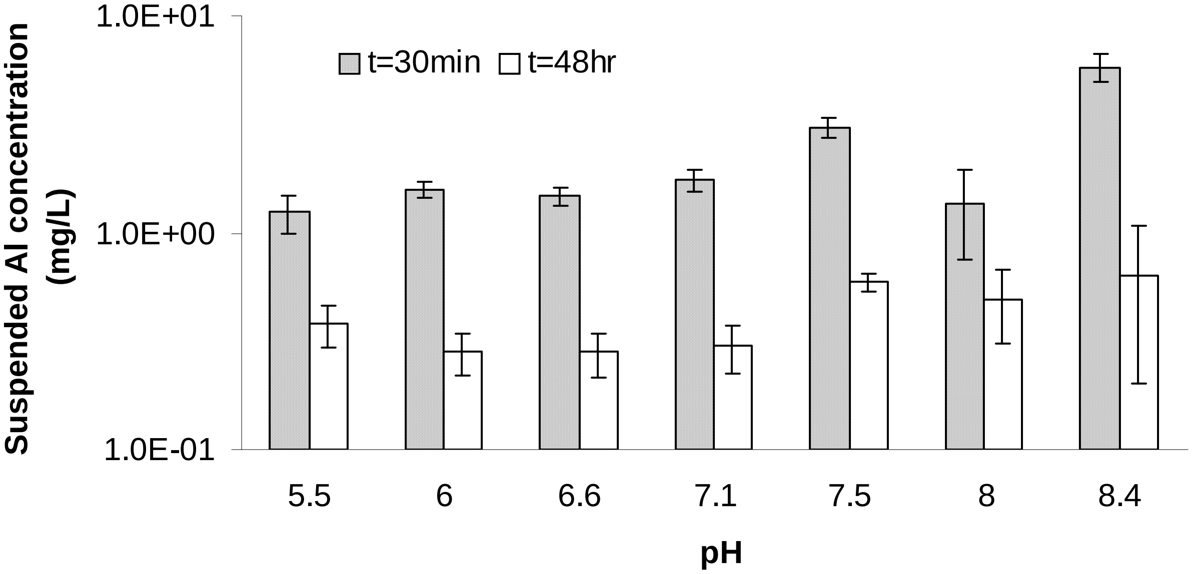


Figure 4.11 Suspended Al concentrations at different pH after 30 minutes and 48 hours of settling in experiments with high sulfate concentration (Al:SO_4=1:5)

Figure 4.12 shows the suspended Al concentration after short and long settling times at pH=6.0 and 8.0 in experiments with different sulfate concentrations. The data showed that elevated sulfate levels increased suspended-aluminum containing solids in the supernatant, thus increasing the suspended aluminum to be expected in Al-bearing ARD/AMD treatment system. As it was expected, the longer settling times allowed for lower residual suspended solids. In addition, higher sulfate levels caused more suspended aluminum to remain in the supernatant. As shown in Figure 4.4 and 4.8, the presence of sulfate in solution reduced both soluble and total Al concentrations. Therefore, the reduction of total Al concentration was only due to the reduction of soluble Al concentration when sulfate was present in solution. The saturation index values (in Section 4.5.1) indicated that the reduction of soluble Al concentration was due to the formation of Al-sulfate precipitates. The high suspended Al concentration in the supernatant was due to the change of species of suspended Al solids. The detailed discussion is present in Section 4.7.

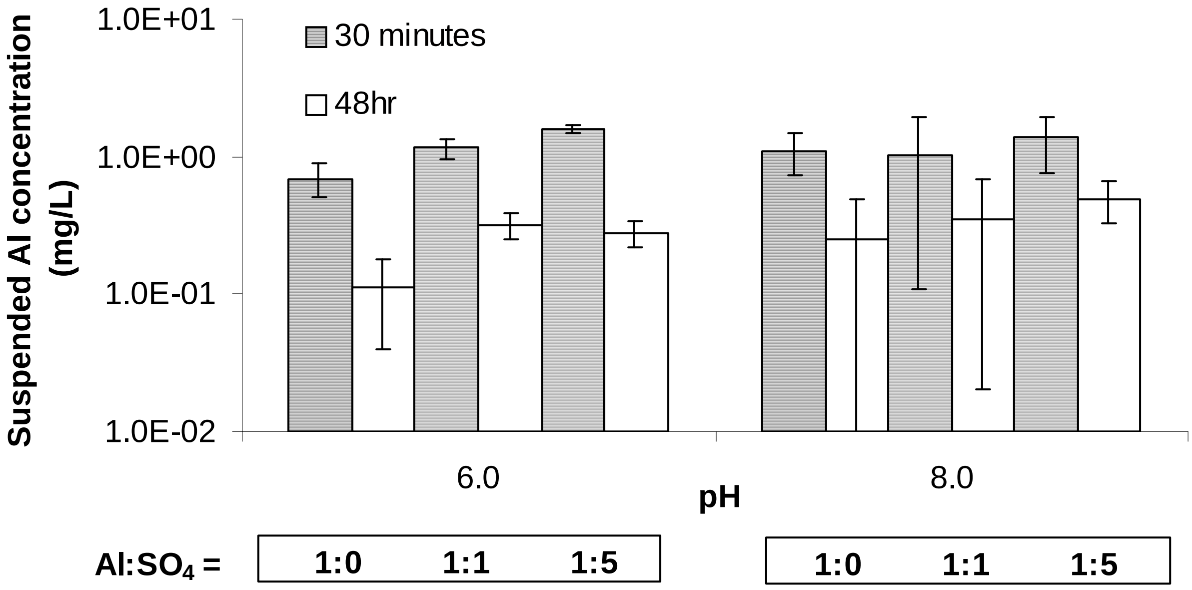


Figure 4.12 Suspended Al concentrations at 30 minutes and 48 hours of settling at pH=6.0 and 8.0

4.3 PRECIPITATE (SLUDGE) COMPOSITION ANALYSIS

In above discussion, it was assumed that the species of aluminum in precipitates formed was Al-sulfate in experiments that contained sulfate, resulting in the decrease of soluble Al concentration with settling time. To test this hypothesis, sludge formed in experiments was collected at 30 minutes and 48 hours. After collection, the sludge was separated from water by centrifuge and washed by DI water for three times. The separated precipitates were dried at room temperature for TGA and XRS analysis. The samples were dried two hours at 85°C to remove the adsorbed H_2O (Brydon and Shah Singh, 1969) for SEM analysis. In this section, the results of sludge analysis will be presents as following parts: XRD, TGA, and SEM.

4.3.1 XRD analysis

X-ray diffraction (XRD) yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. XRD is a powerful technique used to characterize the crystallographic structure. In this study, sludge samples were dried at room temperature and ground into powder in a ceramic crucible. Figure 4.13-4.15 present the XRD results of sludge formed in experiments without sulfate. Figure 4.13 shows that the pattern of sludge formed at pH = 5.6 was lack of peaks indicating that no crystalline precipitates were formed. Since the solution did not contain sulfate, the likely species of Al-precipitates was aluminum hydroxides. In general, there are two different structures of aluminum hydroxides: crystalline and amorphous $Al(OH)_3$. The crystalline $Al(OH)_3$ is gibbsite whose solubility is much lower than that of amorphous $Al(OH)_3$. Therefore, gibbsite (crystalline $Al(OH)_3$) is theoretically formed if the solution is in an equilibrium condition. However, the

XRD patterns show that crystalline phases were not detected in the precipitates formed after both 30 minutes and 48 hours of settling at pH =5.6.

Similar to sludge formed at pH=5.6, the XRD patterns of sludge formed at pH = 6.5 (Figure 4.14) and 8.0 (Figure 4.15) were also lack of sharp peaks. Since the major gibbsite diffraction peaks appear at *d*-spacings of 4.8 and 4.3 Å (Leonard, 1973; Huang *et al*., 2002), the absence of the peaks at these angles indicated that gibbsite was not produced. XRD patterns of precipitates show that only amorphous phase with low intensity, broad peaks were formed in the experiments. The XRD patterns of sludge formed at other pH values (shown in Appendix A) were similar to the patterns of Figure 4.13-4.15. Therefore, it is reasonable to conclude that gibbsite was not formed in neutralization of Al-bearing ARD/AMD in the range of pH=5.6 to 8.3 during 48 hours of detention time.

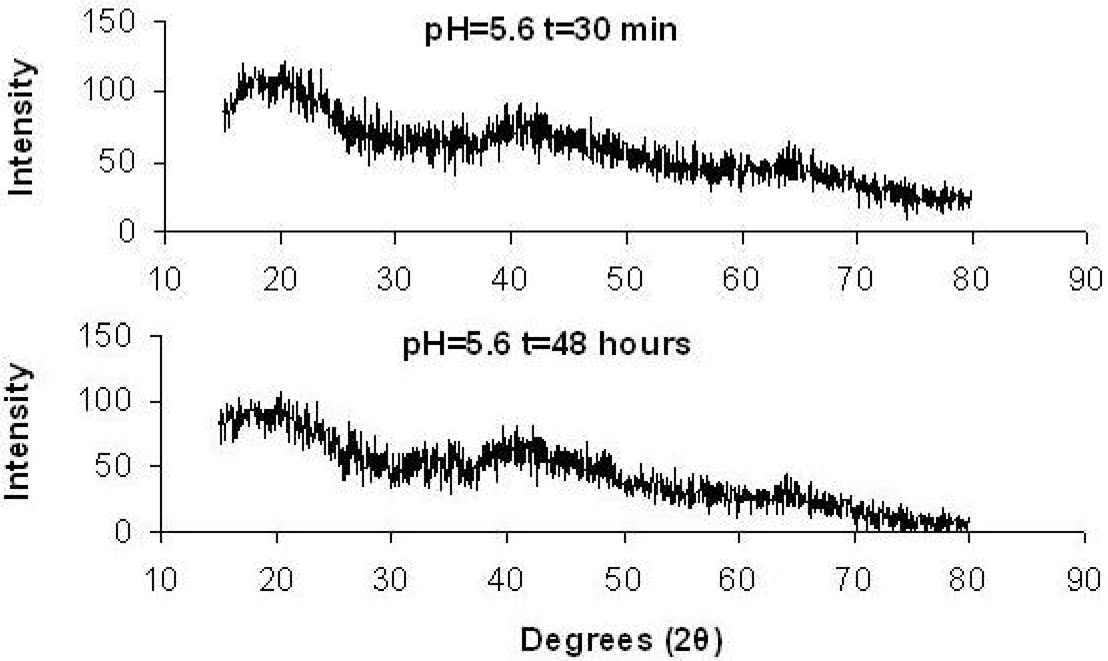


Figure 4.13 XRD pattern of sludge formed in experiments without sulfate at pH=5.6 after 30 minutes and 48 hours of settling

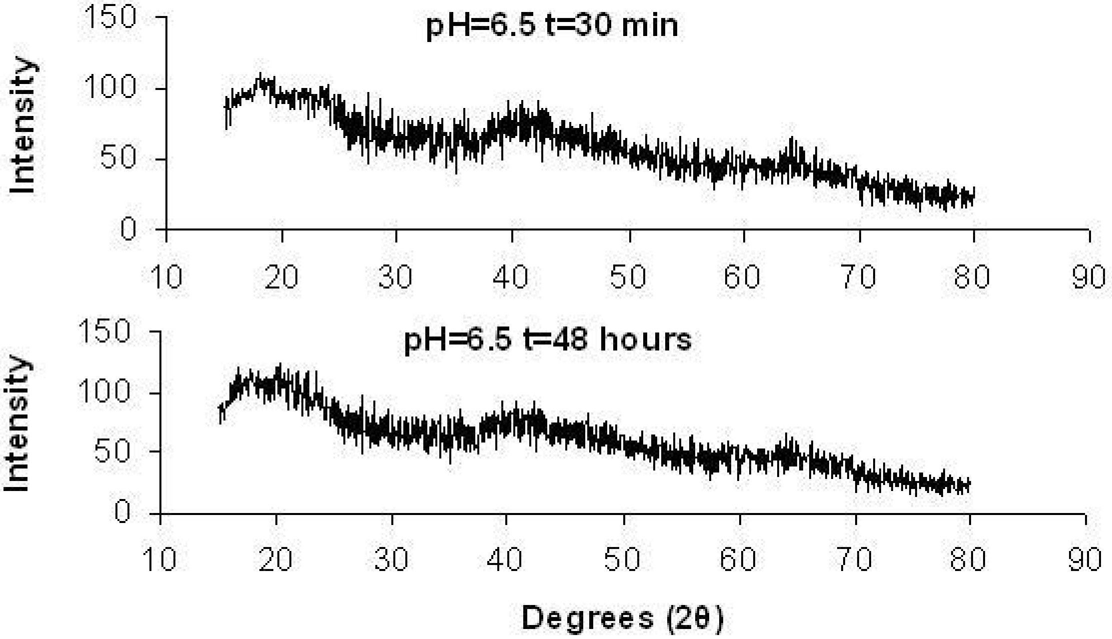


Figure 4.14 XRD pattern of sludge formed in experiment without sulfate at pH=6.5 after 30 minutes and 48 hours of settling

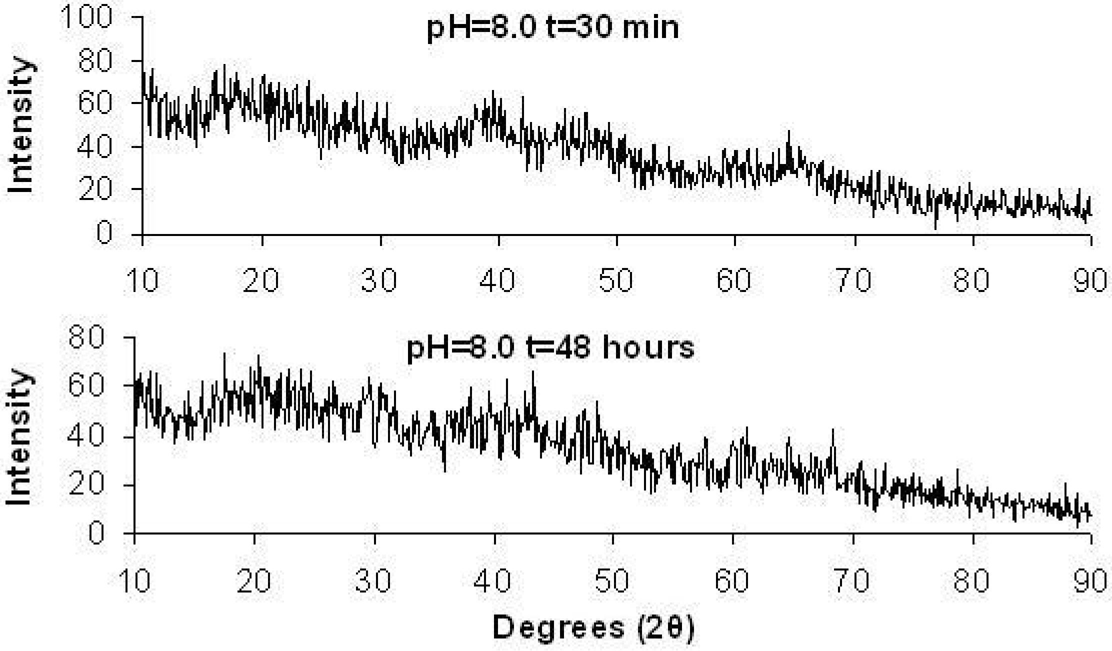


Figure 4.15 XRD pattern of sludge formed in experiment without sulfate at pH=8.0 after 30 minutes and 48 hours of settling

In Figure 4.16, XRD pattern of precipitates formed in experiments with low sulfate contents (Al:SO_4=1:1) at pH = 6.6 also lacked sharp peaks. Other XRD patterns of precipitates formed at other pH values were similar to the patterns of Figure 4.16 (in Appendix A). Similar to the experiments without sulfate, the XRD patterns showed that crystalline $Al(OH)_3$ (gibbsite) was not formed in the experiments with sulfate. Compared with soluble aluminum concentration at 48 hours in experiments without and with sulfate contents (Table 4.1 and Figure 4.4), it can be found that the soluble Al concentration in experiments without sulfate was higher than that in experiments with sulfate. The conclusion drawn from this phenomenon suggested that the sulfate can affect the Al solubility during the neutralization of Al-bearing ARD and the soluble Al concentration decreased by the formation of Al-sulfate precipitates when sulfate is present in solution.

Similar to the precipitates formed in experiments with lower sulfate contents, the XRD pattern shows that no apparent crystalline peaks were detected for precipitates formed in experiments of high sulfate concentrations (Al:SO_4=1:5) at pH=6.6 after both short (30 minutes) and long time (48 hours) of settling (Figure 4.17). The XRD patterns of precipitates formed at other pH values were similar to the pattern of sludge at pH = 6.6 (shown in Appendix A). The high signal-to noise ratio indicated that highly amorphous nature of the precipitates.

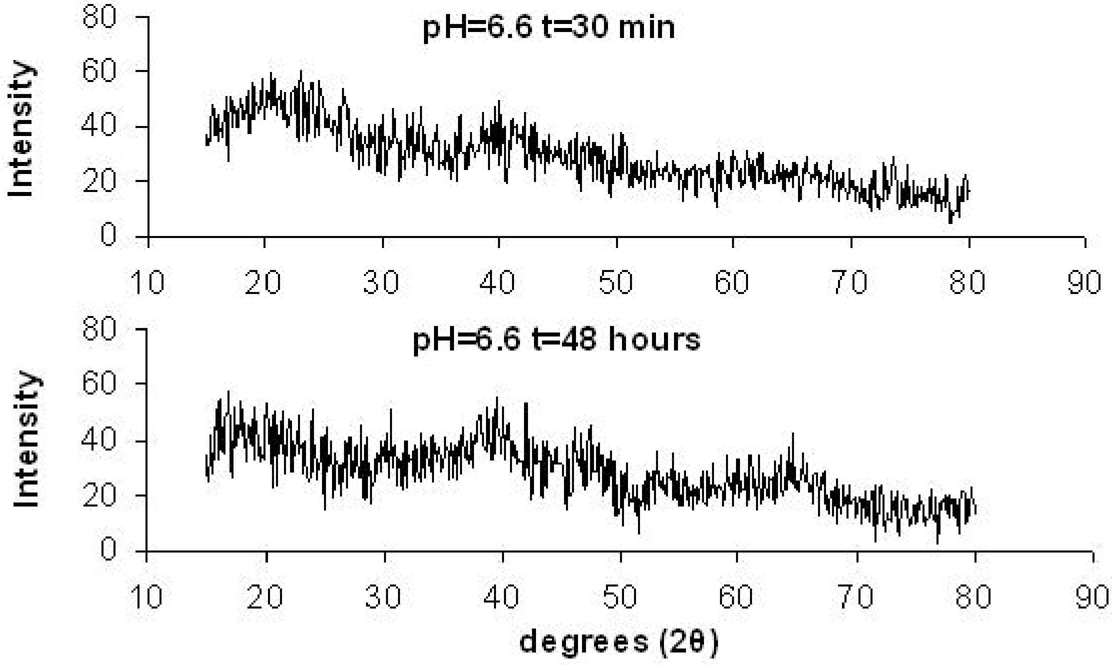


Figure 4.16 XRD for sludge formed in experiment of low sulfate (Al:SO_4=1:1) at pH=6.5

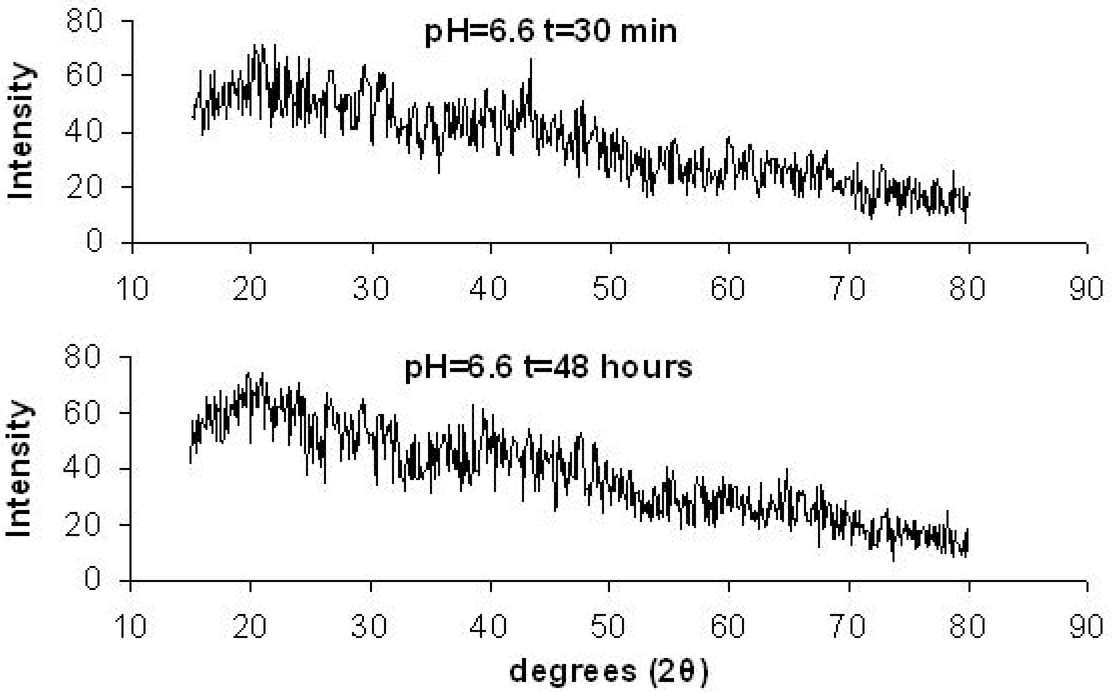


Figure 4.17 XRD for sludge formed in experiment of low sulfate (Al:SO_4=1:5) at pH=6.6

4.3.2 TGA analysis

Since XRD cannot provide a quantitative estimate of the amount of aluminum hydroxide or other mineral phases in a sample, TGA was utilized to further characterize and quantify the precipitates formed in the experiments. TGA is used to determine weight change with temperature change. The weight change can show the hydroxyl and SO_3 proportion in the precipitates, thus TGA is well-suited for this application since $Al(OH)_3$ and Al-hydroxyl-sulfate have a dehydration reaction with an associated weight loss (Karathanasis and Harris, 1994) and Al-hydroxyl-sulfate has a de-sulfate reaction with a weight loss between 800-1000ºC (Brydon and Shah Singh, 1969). A derivative thermogravimetry (DTG) curve, which is a plot of the rate of change of mass with respect to temperature against temperature, was used in this thesis to show the point at which weight loss was most apparent.

The weight loss below 100ºC was primarily due to the vaporization of absorbed water (Brydon and Shah Singh, 1969). The weight proportion of hydroxyl in precipitates was the part of weight loss between 100-400ºC. The weight loss proportion of precipitates over that temperature is shown in Table 4.3. As shown in Table 4.3, the fraction of weight loss of dehydration was from 32.1% to 33.0% for sludge formed at 30 minutes of settling, and the weight loss of hydration was from 32.0% to 32.7% for sludge formed after 48 hours of settling. The data showed that there was no significant difference for the fraction of dehydration between sludge formed at 30 minutes and 48 hours. In other words, the chemical composition of sludge did not change with settling time in experiments without sulfate. The DTG curves of the precipitates in the experiments without sulfate showed that the weight loss primarily occurred between 70-300ºC (Figure 4.18), which is lower than the reported dehydration temperature for crystalline $Al(OH)_3$ (gibbsite: ~350ºC) (Karathanasis and Harris, 1994). There was no significant weight loss after 400ºC, which indicated that only aluminum hydroxides were formed and the species of aluminum hydroxides was in the form of amorphous which was supported by the XRD results. This result indicates that the crystalline $Al(OH)_3$ (gibbsite) was not formed during the treatment process (48 hours), although the gibbsite might be formed in aged sludge (Berkowitz *et al.*, 2005). In Table 4.3, it can be seen that the proportion of Al_2O_3 in sludge was from 58.4 to 60.7 % (The proportion of metal oxide was determined by SEM analysis). According to the proportion of Al_2O_3 and fraction of dehydration from 100-400° C, the molar ratio of O/Al was calculated as shown in Table 4.3. Here, the ratio of O/Al equals the ratio of OH/Al. In Table 4.3, it can be seen that the O/Al (or OH/Al) was from 3.00 to 3.08, which was close to the theoretical ratio of $Al(OH)_3$.

Table 4.3 Fractional weights lost of precipitates (TGA analysis)

Experimental conditions			Thermogravimetric analysis								SEM analysis[5] (molar ratio)	
			Composition of precipitates (%)						TGA cal[4] (molar ratio)			
pH	$Al:SO_4$	Time	Absorbed H_2O	Dehydration	Other weight loss[1]	SO_3	Residues[2] (after 1000ºC)					
			<100ºC	100-400ºC	400-800ºC	800-1000ºC	Al_2O_3	MO[3]	O/Al	Al:S	O/Al	Al:S
5.6	1:0	30 min	5.6	33.0	1.4	0.2	59.3	0.3	3.08	--	3.03	--
		48 hr	5.2	32.6	1.3	0.1	59.7	0.6	3.05	--	3.05	--
6.5	1:0	30 min	4.6	32.2	1.2	0.1	60.7	0.6	3.00	--	3.04	--
		48 hr	5.3	32.7	0.9	0.1	60.4	0.3	3.04	--	2.99	--
8.5	1:0	30 min	6.4	32.1	1.9	0.1	58.4	0.5	3.06	--	2.98	--
		48 hr	6.2	32.0	1.2	0.2	59.3	0.6	3.03	--	3.08	--
5.6	1:1	30 min	5.4	30.8	2.1	2.7	58.8	0.4	2.96	34.67	2.93	32.83
		48 hr	5.4	30.2	2.0	3.7	58.6	ND[6]	2.92	24.84	2.90	24.55
6.6	1:1	30 min	5.0	31.1	2.0	2.5	58.3	1.1	3.01	37.26	2.92	34.18
		48 hr	4.6	30.7	1.6	3.5	58.8	0.7	2.96	26.45	2.89	25.73
8.4	1:1	30 min	5.0	31.2	1.7	2.2	59.6	0.3	2.97	43.53	2.92	43.50
		48 hr	5.1	29.0	1.4	7.4	56.8	0.5	2.88	12.22	2.83	10.73
5.5	1:5	30 min	4.6	30.9	1.2	3.5	59.7	0.2	2.93	27.15	2.94	27.42
		48 hr	5.3	29.4	1.4	5.8	58.0	ND	2.87	15.65	2.80	15.75
6.6	1:5	30 min	4.8	30.8	1.8	3.1	57.8	1.7	3.02	29.71	2.91	28.79
		48 hr	5.3	29.2	2.0	5.8	57.2	0.4	2.89	15.54	2.82	15.95
8.3	1:5	30 min	5.1	30.5	2.1	3.3	58.1	0.9	2.98	28.31	2.86	28.18
		48 hr	5.0	27.8	1.6	9.2	55.4	0.9	2.84	9.55	2.74	9.39

[1]: The other weight loss between 400-800ºC could be due to the decomposition of carbonate (Frost et al. 2009). The carbonate came from the dissolution of CO_2 during the experiments;

[2]: The residue of TAG included the aluminum oxides and other metal oxides (such as Mn, Ca, and Mg). The proportion of Al_2O_3 and other metal oxides was decided by SEM analysis;

[3]: MO represents the total proportion of metal oxides in residues;

[4]: TGA cal: calculation with the weight loss of precipitates. During the calculation, the oxygen of O/Al was the part of oxygen combine with Al as OH.

[5]: The samples for SEM analysis had been dried at 85ºC to remove the absorbed water;

[6]: ND: not detected.

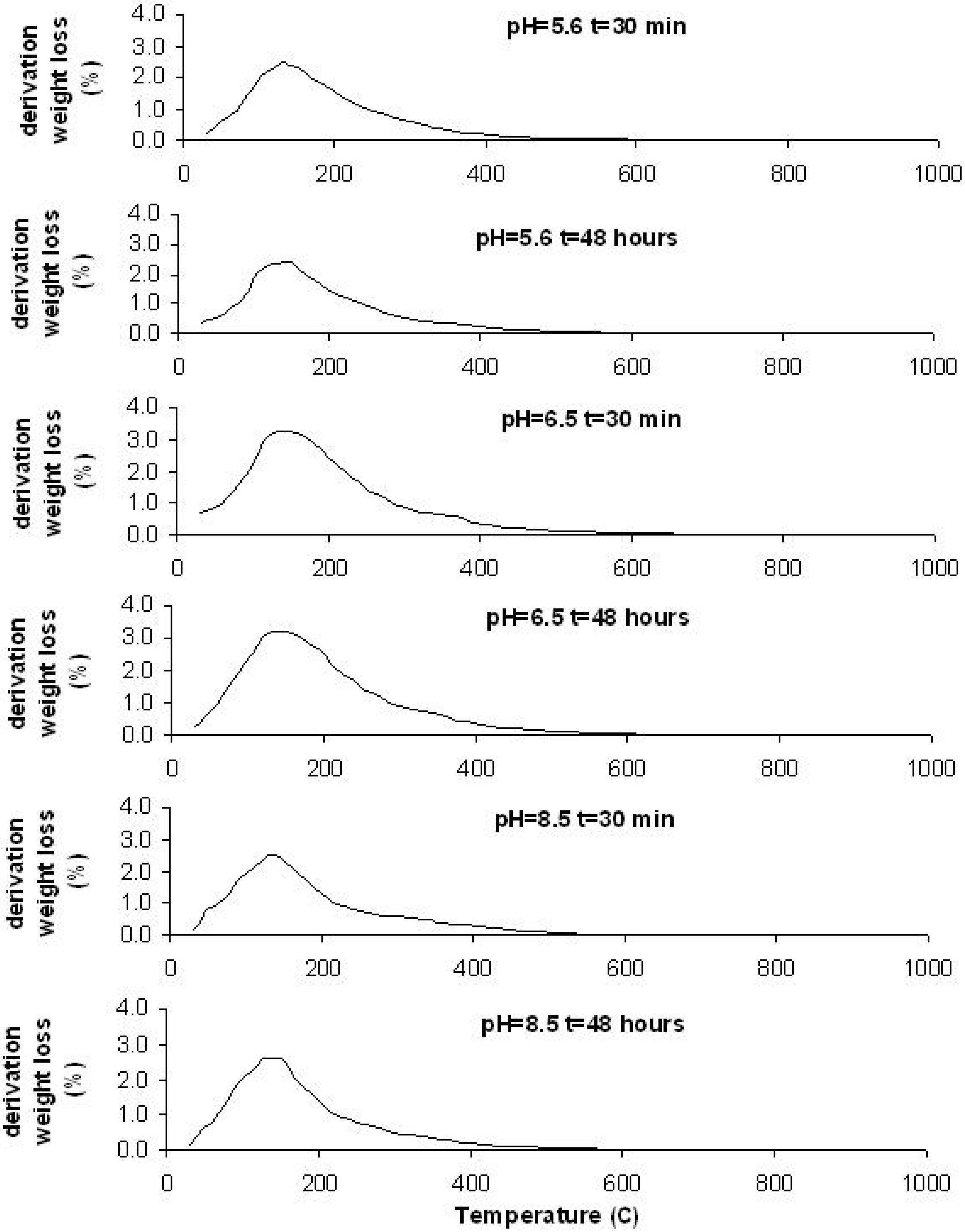


Figure 4.18 DTG curves for sludge formed in experiments that did not contained sulfate after 30 minutes and 48 hours of settling.

The weight loss proportion of sludge formed at 30 minutes and 48 hours of settling in experiments that contained sulfate is shown in Figure 4.19 and 4.20 (data present in Table 4.3). The fractional weight loss (as % of original weight) showed that SO_3 fraction (fraction of weight loss from 800-1000ºC) in precipitates increased with settling time.

For the precipitates formed in experiments with low sulfate ($Al:SO_4=1:1$) (Figure 4.19), the weight loss before 90ºC represented the vaporization of absorbed water from precipitates. The second weight loss occurred between 100-400ºC, which was due to the dehydration of precipitates.

The third weight loss occurred in the range of 800-1000ºC, which represents the evaporation of SO_3. The residues are metal hydroxides, most of which are Al_2O_3. In Table 4.3, it can be seen that the weight loss of dehydration was from 30.8% to 31.2% for sludge formed after 30 minutes of settling, and 29.0% to 30.7% for sludge formed after 48 hours of settling. The weight loss after 800ºC was caused by SO_3 evaporation. The weight fraction of SO_3 was from 2.2% to 2.7% for sludge formed at 30 minutes, and 3.5% to 7.4% for sludge formed at 48 hours. The TGA data showed that the amount of hydroxyl decreased from 30 minutes of settling to 48 hours of settling, while the sulfur content increased. Since the fraction of hydroxyl of $Al(OH)_3$ was larger than that in Al-sulfate compounds (such as basaluminite), the TGA data implied that the proportion of Al-sulfate in precipitates increased with increased retention time in the settling basin when sulfate was in solution.

The weight loss of precipitates in experiments with higher sulfate levels shows a similarity to the precipitates formed in the experiments with low sulfate concentration (Figure 4.20). The weight loss of dehydration was from 30.5% to 30.8% for 30 minutes, and 27.8% to

29.4% for 48 hours. The weight loss of SO_3 evaporation (800-1000°C) was from 3.1% to 3.5% for 30 minutes, and 5.8% to 9.2% for 48 hours.

Compared with the weight loss of precipitates formed in experiments with low sulfate concentrations, it can be found that the sulfur fraction in precipitates increased with the increase of sulfate concentration and settling time. The increase of sulfur fraction indicated that sulfate ions combined with Al ions (reaction) and suspended Al-solids(sorption) to form precipitates that settled later. In Table 4.1, it can be seen that soluble Al concentration decreased over time and the SI values (in Section 4.5) showed that the solutions became unsaturated with amorphous $Al(OH)_3$. This was due to the decrease of soluble Al concentration caused by the reaction of sulfate with soluble Al.

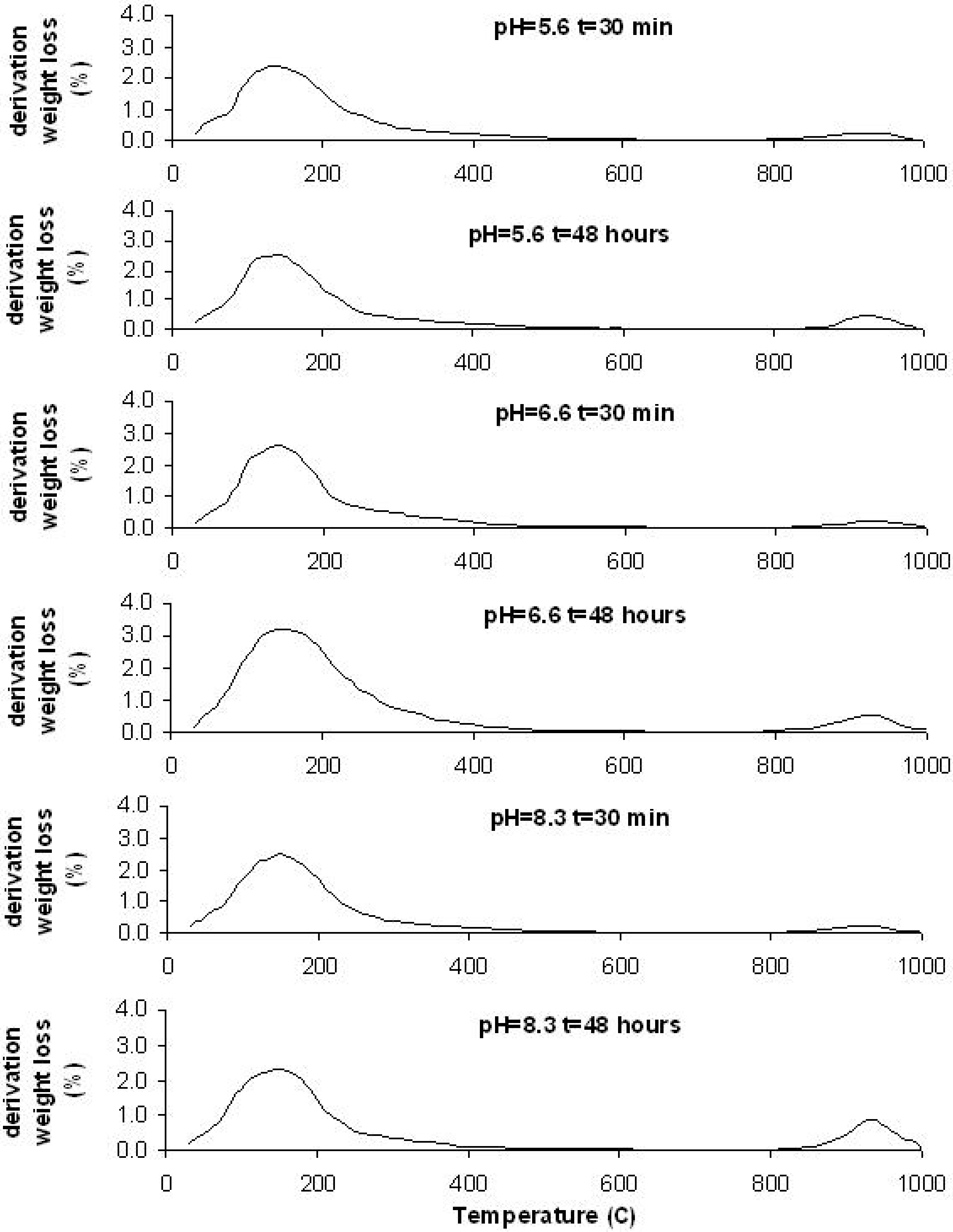


Figure 4.19 DTG curves for sludge formed in experiments with low sulfate concentrations (Al:SO_4=1:1) after 30 minutes and 48 hours of settling.

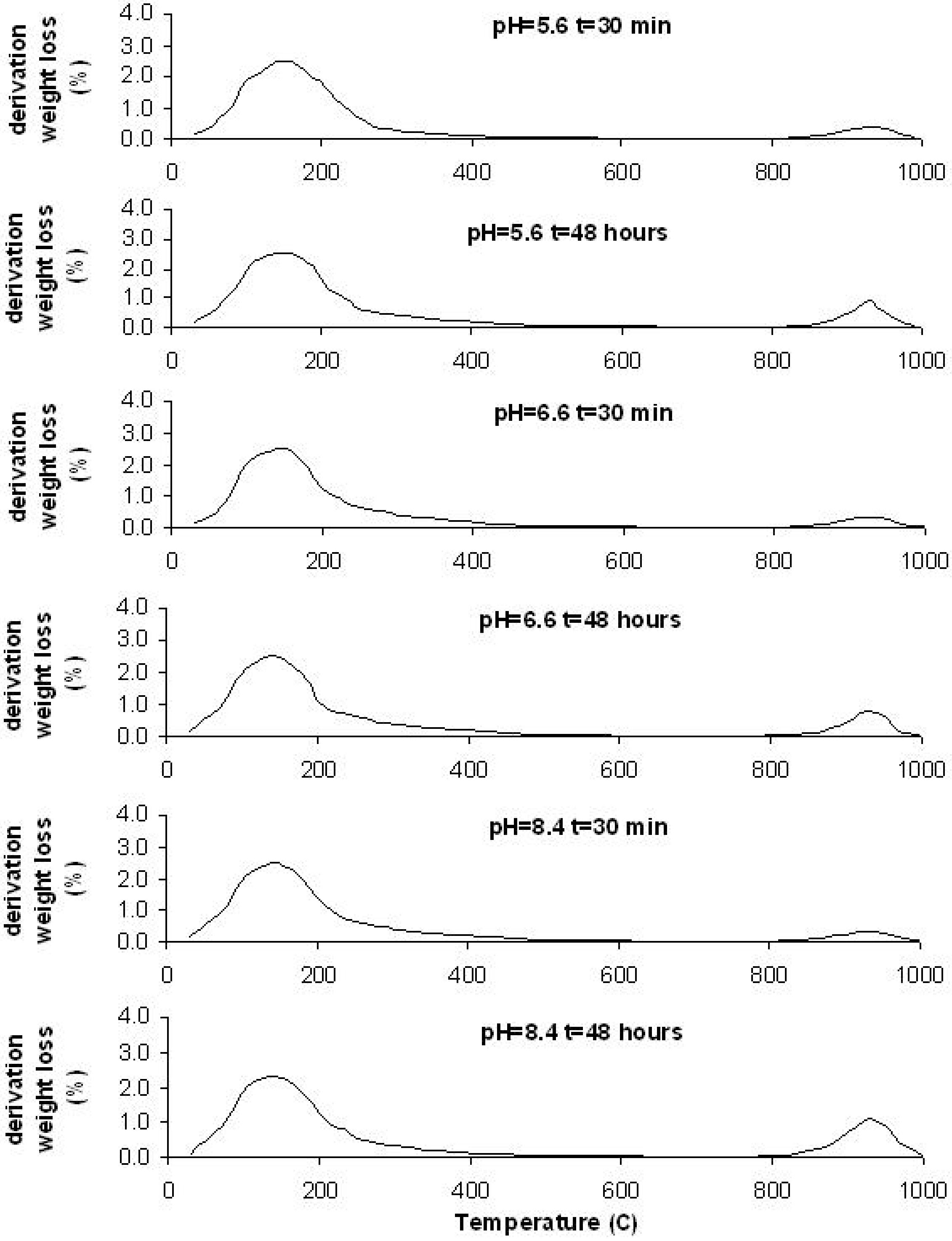


Figure 4.20 DTG curves for sludge formed in experiments with high sulfate concentrations (Al:SO_4=1:5) after short and long settling time

4.3.3 SEM analysis

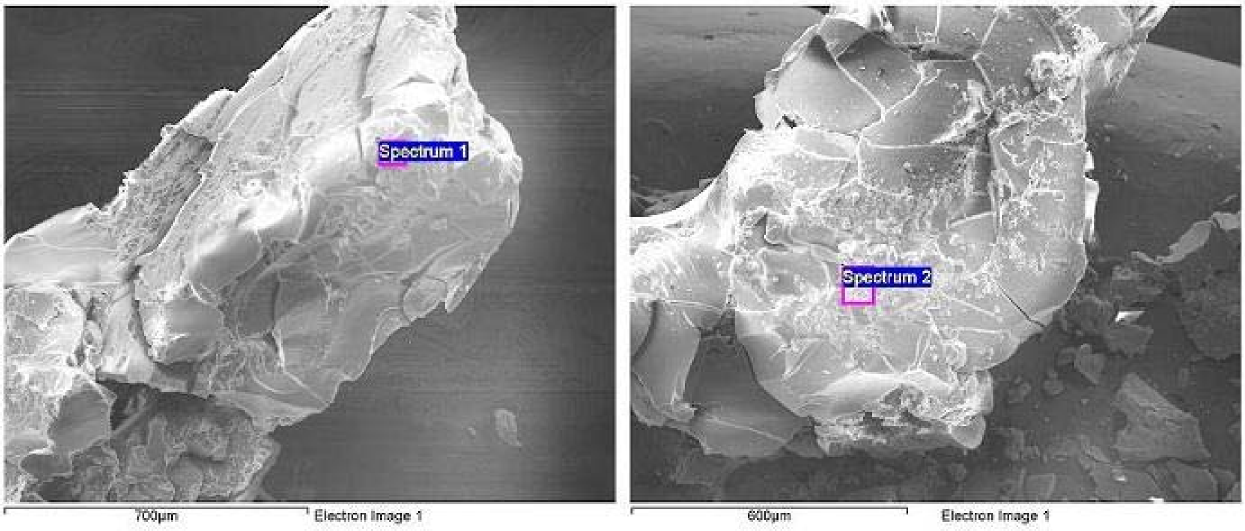
TGA analysis provided the overall proportion of hydroxyl and SO_3 in sludge. However, the sludge might be composed of particulates of different chemical species. In order to identify the chemical compositions of the sludge particulates that were in differently morphologic, SEM analysis was used to analyze the micro-particulates of sludge.

SEM analysis was performed on the precipitates formed in experiments of different sulfate concentrations, along with EDS analysis. Figure 4.21 and 4.22 are the SEM images of sludge collected after 30 minutes and 48 hours of settling in experiments with low sulfate concentration ($Al:SO_4=1:1$) at pH =6.6 and 8.3, respectively. The precipitates formed at pH=6.6 had been analyzed by TEM. In TEM analysis, the selected area diffraction pattern (SAD) was taken for the particles. In this SAD pattern, the amorphous ring was observed instead of diffraction spots, so these particles were not crystalline (Appendix B). These results are consistent with the XRD analysis results.

Figure 4.23 and 4.24 are the SEM images of sludge collected after 30 minutes and 48 hours of settling in experiments with high sulfate concentration ($Al:SO_4=1:5$) at pH =6.6 and 8.4, respectively. Similar to experiment with low sulfate concentration, the sludge particulates formed in high sulfate concentration was also in forms of amorphous. The morphological features in Figure 4.21– 4.24 showed that sludge formed in all experiments was composed of amorphous particulates. The SEM images of other samples are shown in Appendix B.

The chemical components of sludge collected after different settling time at different pH values are presented in Table 4.4 (measured with EDS). The chemical composition was measured for several locations in sludge samples and the average value of all the points was calculated. In Table 4.4, it can be found that precipitates contained different elements, including

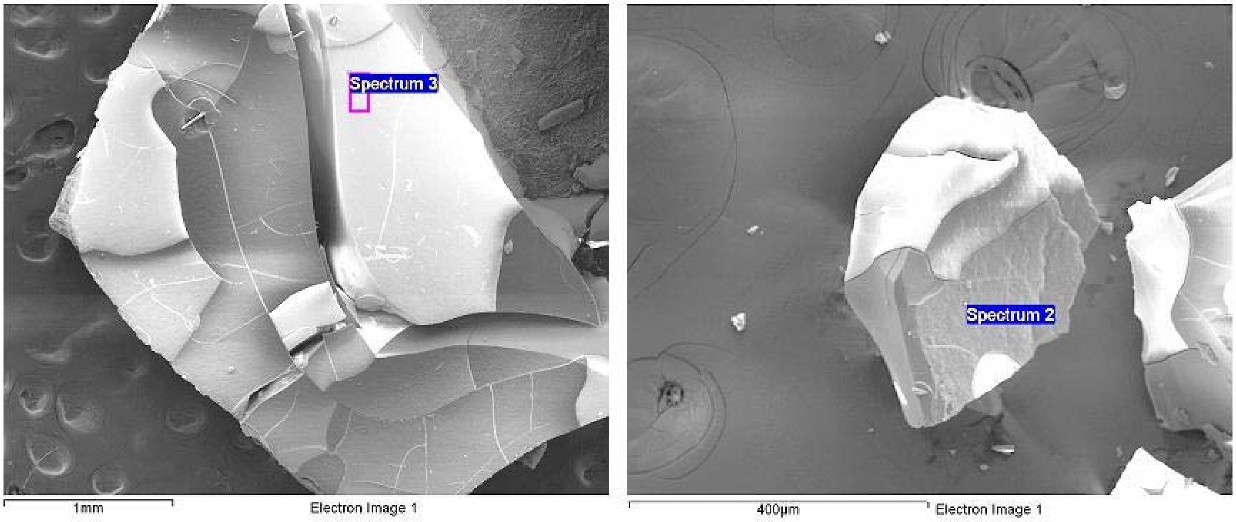
Al, Mg, Ca, Mn, O, and S, and the contents varies with pH values and initial sulfate concentrations.



sludge at 30 minutes

sludge at 48 hours

Figure 4.21 SEM image of sludge formed in experiment of low sulfate concentration (Al:SO_4=1:1) at pH=6.6



Sludge at 30 minutes

Sludge at 48 hours

Figure 4.22 SEM image of sludge formed in experiment with low sulfate concentration (Al:SO_4=1:1) at pH=8.3

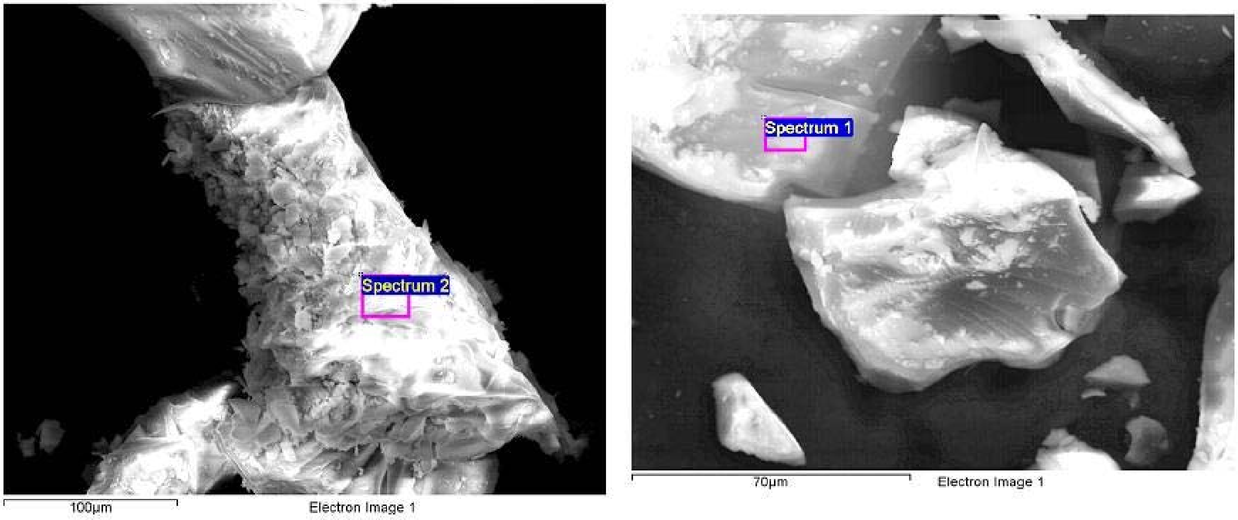
Table 4.4 Compositions of precipitates formed in the experiments (EDS analysis)

Al:SO_4=1:1																				
	pH=5.6				pH=6.0				pH=6.6				pH=7.5				pH=8.3			
	30min		48 hr		30min		48 hr		30min		48 hr		30min		48 hr		30min		48 hr	
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
C	3.4	2.3	5	1.1	3.8	2.8	6.8	2.1	4.8	2.8	6.8	2.1	5.5	1.1	4.2	0.6	6.6	1.5	4.4	0.6
O	73.9	3.7	73.5	2.4	73.6	2.6	72.8	3.5	73.5	2.6	72.8	3.5	73.4	1.5	73.4	3.2	73.0	1.3	73.2	3.2
Mg	ND[3]	ND	ND	ND	0.2	0.2	0.6	0.7	0.2	0.1	0.6	0.4	ND	ND	0.2	0.2	ND	ND	0.2	0.2
Al	21.9	1.9	20.7	1.7	21.6	2.1	19.2	1.7	20.6	2.1	19.1	1.7	20.4	0.5	20.1	1.2	19.7	1.1	20.1	1.2
S	0.7	0.3	0.8	0.3	0.5	0.1	0.6	0.2	0.6	0.1	0.7	0.2	0.6	0.2	1.9	0.4	0.5	0.2	1.9	0.4
Ca	ND	ND	ND	ND	0.2	0.1	ND	ND	0.2	0.1	ND	ND	ND	ND	0.2	0.2	ND	ND	0.2	0.2
Mn	0.1	0.1	ND	ND	0.1	0.1	ND	ND	0.1	0.2	ND	ND	0.1	0.1	ND	ND	0.2	0.1	ND	ND
Al/O[1]	2.94		2.91		2.96		2.96		2.99		2.95		2.94		2.86		2.93		2.83	
Al:S[2]	31.29		25.88		43.20		32.00		34.33		27.29		34.00		10.58		39.40		10.58	
Al:SO_4=1:5																				
	pH=5.5				pH=6.0				pH=6.6				pH=7.5				pH=8.4			
	30min		48 hr		30min		48 hr		30min		48 hr		30min		48 hr		30min		48 hr	
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
C	4.3	1.6	1.2	2.3	3.9	1.0	3.7	1.4	4.0	1.0	4.3	1.4	6.8	1.3	5.2	2.3	7.7	1.3	6.2	2.0
O	73.8	2.6	73.9	3.6	73.7	2.5	73.8	3.5	73.5	2.5	73.3	3.5	73.1	3.2	72.6	1.9	72.9	3.2	72.6	1.9
Mg	ND	ND	ND	ND	0.3	0.1	0.2	0.2	0.3	0.1	0.2	0.2	ND	ND	0.5	0.4	ND	ND	0.4	0.3
Al	21.1	1.0	23.5	1.8	21.0	0.8	21.2	1.6	21.1	0.8	20.9	1.6	19.3	1.1	19.8	2.1	18.6	1.1	18.6	2.1
S	0.8	0.1	1.4	0.4	0.6	0.4	1.0	0.3	0.6	0.4	1.2	0.3	0.6	0.2	1.6	0.6	0.7	0.2	2.0	0.6
Ca	ND	ND	ND	ND	0.2	0.1	0.1	0.1	0.3	0.1	0.1	0.1	ND	ND	0.3	0.2	ND	ND	0.3	0.2
Mn	0.04	0.02	ND	ND	0.3	0.2	ND	ND	0.2	0.2	ND	ND	0.2	0.1	ND	ND	0.2	0.1	ND	ND
Al/O	2.94		2.80		3.02		2.94		2.99		2.87		2.96		2.82		2.94		2.81	
Al:S	26.4		16.8		35.0		21.2		35.2		17.4		32.2		12.4		31.0		9.3	

[1] Al:O: the corrected atomic ratio of Al:O. In this atomic ratio, the O atomic % was subtracted the oxygen that was combined with C (as CO_2), Si (as SiO_2), and S (as SO_4^{2-});

[2] Al:S: the atomic ratio of Al:S;

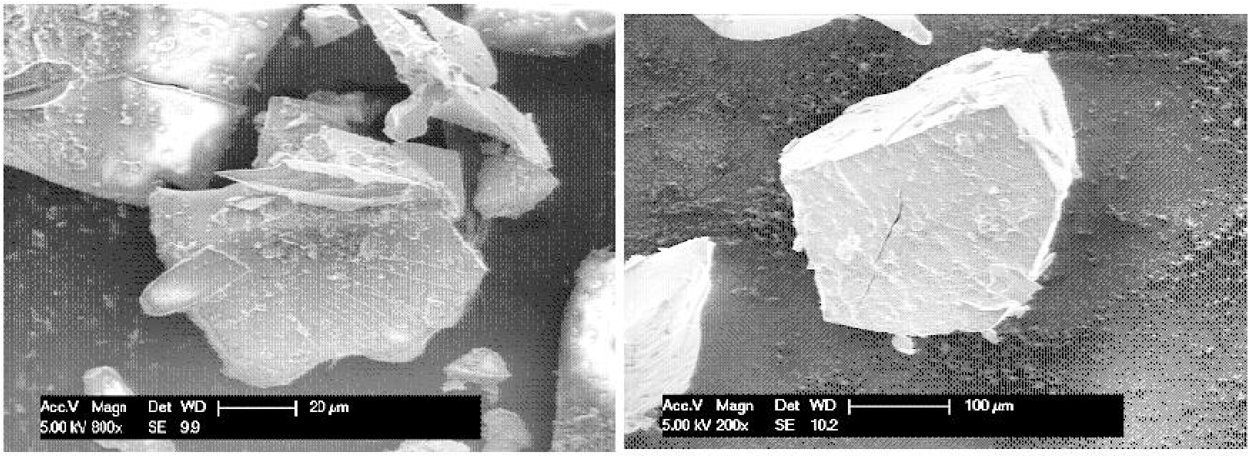
[3] ND: not detected



Sludge at 30 minutes

Sludge at 48 hours

Figure 4.23 SEM image of sludge formed in experiment with high sulfate concentration (Al:SO_4=1:5) at pH=6.6



Sludge at 30 minutes

Sludge at 48 hours

Figure 4.24 SEM image of sludge formed in experiment with high sulfate concentration (Al:SO_4=1:5) at pH=8.4

The oxygen element in sludge could be combined with H (as OH^-), C (as CO_2), and S (as SO_4^{2-}). The amount of OH^- can be calculated by subtracting the oxygen that was combined with C (as CO_2), and S (as SO_4^{2-}). Therefore, the molar ratio of Al/OH^- in sludge can be calculated too. Table 4.4 presents the molar ratio of Al/OH in sludge formed in different sulfate concentration and pH values after 30 minutes and 48 hours of settling. The molar ratio of $Al:OH^-$ of sludge formed after 30 minutes of settling was 1:2.94, 1:2.96, 1:2.99, 1:2.97, and 1:2.92 at pH = 5.6, 6.0, 6.6, 7.5, and 8.3 in experiments with low sulfate ($Al:SO_4$=1:1), respectively, whereas the molar ratio of $Al:OH^-$ of sludge formed in experiments with high sulfate ($Al:SO_4$=1:5) was 1:2.94, 1:3.02, 1:2.99, 1:2.96, and 1:2.94 at pH=5.5, 6.0, 6.6, 7.5,and 8.4, respectively. In the experiments with low sulfate concentration, after 30 minutes of settling, the precipitates contained approximately 0.5 % to 0.7% S (average molar percentage) in pH range of 5.6 to 8.3. In high sulfate conditions ($Al:SO_4$=1:5), the precipitates contained 0.6% to 0.8% S (average molar percentage) in pH range of 5.5 to 8.4. The data show that sulfur content in sludge did not change much with pH value and sulfate concentration after short settling time (30minutes).

When settling time became longer (48 hours), the Al:OH ratio of precipitates became 1:2.91, 1:2.96, 1:2.95, 1:2.86, and 1:2.83 at pH=5.6, 6.0, 6.6, 7.6, and 8.3 in experiments with lower sulfate concentration, respectively. In experiments with high sulfate concentration, Al:OH ratio was1:2.80, 1:2.94, 1:2.87, 1:2.82, and 1:2.81 at pH =5.5, 6.0, 6.6, 7.5, and 8.4, respectively.

The Al:S ratio in sludge was 31.3, 43.2, 34.3, 34.0, and 39 at pH= 5.6, 6.0, 6.6, 7.0, 7.5, and 8.4 in experiments with lower sulfate after 30 minutes of settling, respectively, whereas the Al:S ratio was 26.4, 35.0, 35.2, 32.2, and 31.0 at pH= 5.5, 6.0, 6.6, 7.0, 7.5, and 8.3 in experiments with high sulfate concentration, respectively. The Al:S ratio in sludge indicated that the sulfur content was not significantly different amongst the sludge formed at different pH values at the 30 minute settling time. However, after the longer settling time of 48 hours, the Al:S ratio of sludge formed in low sulfate experiments was from 10.6 to 32.0, which was higher than that exhibited by the sludge formed in the higher sulfate experiments (9.3 to 21.2). The Al:S ratio after short and long settling time indicated that the proportion of sulfate-precipitates increased after long settling time (48 hours).

The high Al:S ratio occurred at pH=6.0 (32.0 and 21.2 when $Al:SO_4$=1:1 and 1:5, respectively) and pH=6.6 (27.3 and 17.4 $Al:SO_4$=1:1 and 1:5, respectively) after long settling time (4 8hours). The lowest $Al:SO_4$ ratio occurred at high pH values (~8.3). The lowest Al:S ratio was 10.6, and 9.8 in sludge formed in experiments of low sulfate, and high sulfate, respectively. The data of Al:S ratio in sludge formed at different pH values revealed that more Al-sulfate formed at high pH conditions (~8.3) than at lower pH values. Kim and Kim (2003b) observed similar results that basaluminite precipitates were formed in the downstream of acid mine drainage where the pH was from 7~8.3.

The Al:OH ratio of sludge formed in low sulfate experiments was in the range of 1:2.83 to 1:2.96 after 48 hours of settling, whereas the Al:OH ratio was in the range of 1:2.80 to 1:2.94 in high sulfate experiments (Table 4.4). The theoretical molar ratio of Al:OH of $Al(OH)_3$, jurbanite, and basaluminite is 1:3, 1:1, and 1:2.5, respectively. The fact that the Al:OH ratio was close to the theoretical ratio of $Al(OH)_3$ indicated that most of sludge was in forms of amorphous $Al(OH)_3$.

4.3.4 Summary results of sludge analysis

The lack of peaks in XRD patterns of sludge suggested that no crystalline precipitates formed in both experiments with and without sulfate. The precipitates formed in experiments were in forms of amorphous (both $Al(OH)_3$ and Al-sulfate) Both TGA and SEM analysis showed that sulfur content was not a significant difference among different pH after 30 minutes of settling. After 48 hours of settling, the sulfur content in sludge increased and the high level sulfate increased the sulfur contents in sludge. Furthermore, the EDS results showed that Al:S ratio in sludge formed at neutral pH was the highest, which indicated that the formed Al-sulfate precipitates at neutral pH was the least.

4.4 INFLUENCE OF SETTLING TIME ON SUPERNATANT ALUMINUM AND SULFATE CONCENTRATIONS

The composition of ARD in the field is complex and the effluent after NaOH neutralization of Al containing ARD includes both soluble and suspended Al solids. In actual conditions, the reactions of Al-precipitation that influence the Al removal efficiency in Al-bearing ARD treatment systems might show different reaction rates. At outdoor temperatures, some reactions will be completed within the a short time frame, whereas others *(such as crystallization reactions)* will occur slowly, even though the later reactions of Al-precipitation are thermodynamically favored and generate a lower solubility of Al-precipitates. In active ARD/AMD treatment systems in the field, the detention time in the settling basin is flow dependent and will vary with advent of wet weather conditions. Therefore, time of settling after NaOH neutralization is a critical independent variable for this thesis, which can lead to a better understanding of the likely discharge of aluminum species and total aluminum concentrations. This section will discuss the change of Al concentration in both suspended and soluble forms with settling time. The results presented above showed that the presence of sulfate can affect soluble Al concentration in experiments. Therefore, the change of sulfate concentration in experiments will be examined as well.

4.4.1 The change of soluble and suspended Al concentrations with settling time

4.4.1.1 The change of soluble Al concentration with settling time

Figure 4.25 shows the change of soluble Al concentration with settling time from 30 minutes to 48 hours at pH = 6.0, and 8.0 when solution contained different sulfate concentration (the change of soluble Al concentration at other pH values are shown in Appendix C). The soluble Al concentration was measured after 30 minutes, 60 minutes, 2 hours, 4 hours, 24 hours, and 48 hours of settling. From Figure 4.25, it can be found that sulfate in solution reduced the soluble Al concentration and pH was the critical parameter for final soluble Al concentration. In most experiments, after 4 hours of settling, the reduction rate of Al concentration became slow.

To study the Al removal rate in experiments with settling time, the rate of soluble Al reduction (dC/dt) at different pH was calculated. Figure 4.26 shows the Al concentration reduction rate with settling time at pH =6.0 and 8.0 in experiments with different sulfate concentrations. In this figure, it can be found that the rate of soluble Al removal became very slow after 4 hours of settling in all cases. In experiments without sulfate, the Al removal rate became zero after 24 hour of settling (soluble Al concentration did not decrease from 24 hours to 48 hours of settling). The slow removal rate indicated that the Al concentration changed slowly after 4 hours of settling. These data indicated that Al concentration could be considered in an approximately steady in solution, although it still reduced in a very slow rate in experiments with sulfate. The Al removal rate is compared with the removal rate of sulfate in the following section.

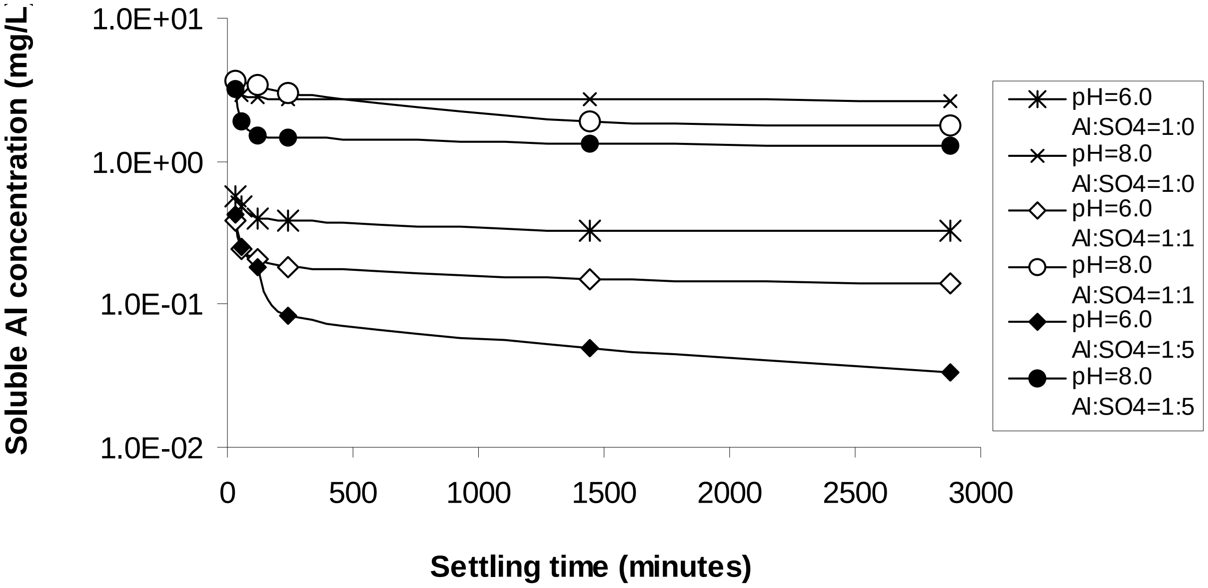


Figure 4.25 Soluble Al concentration change with settling time at pH=5.6

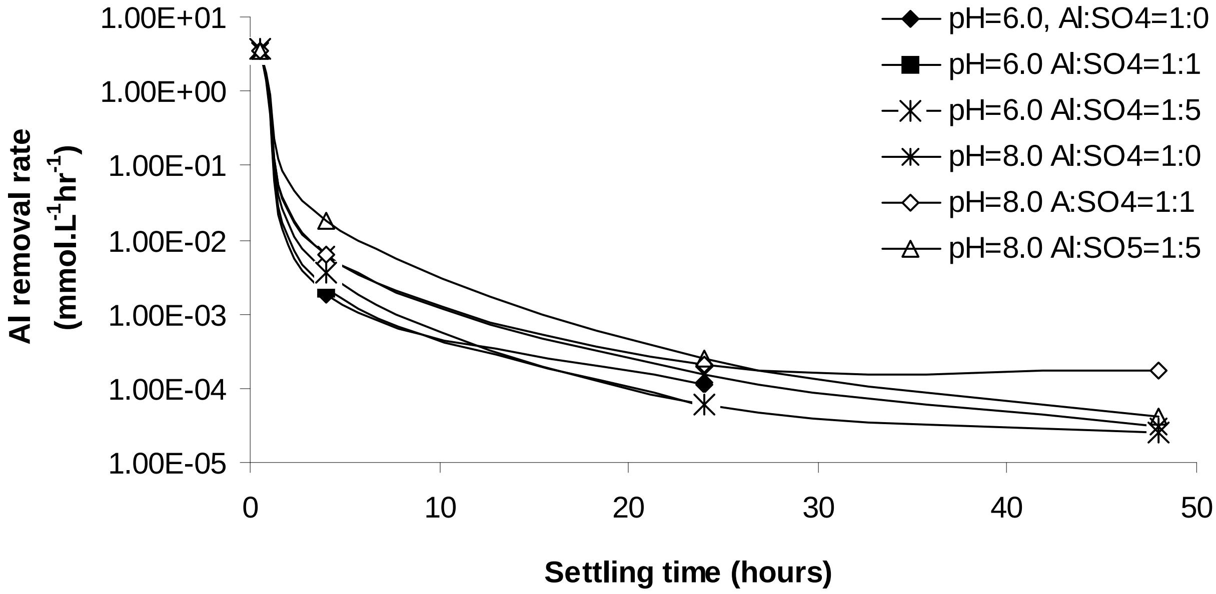


Figure 4.26 Al removal rate with settling time at pH=6.0 and 8.0 in experiment with different sulfate concentration.

4.4.1.2 The change of suspended Al concentration with settling time

In the ARD/AMD treatment systems with settling tanks, the total discharge or effluent aluminum consists of the sum of both soluble Al and particulates containing Al. Small particles containing aluminum are formed after chemical neutralization, followed by chemical reformation and possible crystallization taking place in the settling tank. The overall settling characteristics of Al-precipitates are important to assess the likely total aluminum discharge from a NaOH chemical neutralization system for AMD and ARD. Figure 4.27 presents the suspended Al concentration with settling time at pH =6.0, and 8.0 when different sulfate concentration was in solution (Appendix C present the total and soluble Al concentration over settling at other pH)

From Figure 4.27, it can be seen that the suspended Al concentration was lower in experiments without sulfate. The high sulfate concentration in solution increased suspended Al concentration. The tendency of suspended Al concentration with sulfate was different from that of soluble Al concentration, which reduced with high sulfate concentration.

As indicated above, in presence of sulfate, the suspended Al concentration after 48 hours of settling was higher than that in the experiments without sulfate in pH range from 6.0 to 8.0, while the soluble concentration was lower (shown on Figure 4.25). There are two reasons that can cause this phenomenon. The first is that the “new” produced particles had small size and remained in solution. The other is that the absorption of sulfate by Al-precipitates can reduce the settleable ability of suspended Al particles. Therefore, to evaluate the change of sulfate concentration could help to understand the reason that caused the different tendency.

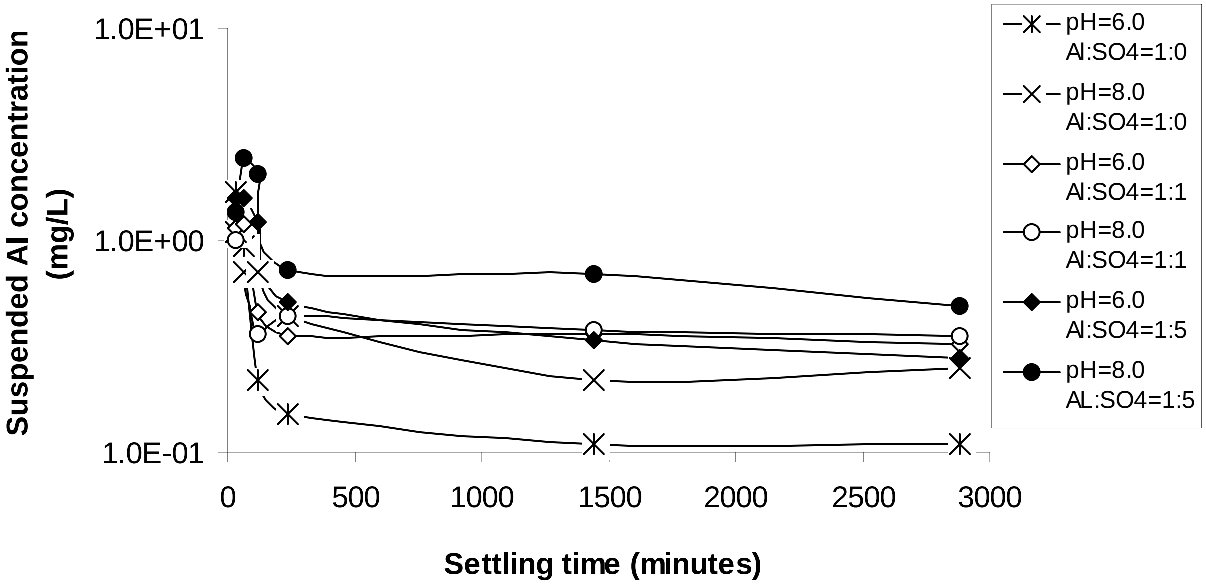


Figure 4.27 Suspended Al concentration with settling time at pH=6.0 and 8.0 when solution contained different sulfate concentrations

4.4.2 The change of total and soluble sulfate concentration with settling time

4.4.2.1 The change of soluble sulfate concentration with settling time

Figure 4.28 and 4.29 present the soluble sulfate concentration with settling time at different pH in experiments with low and high sulfate concentration, respectively. From Figure 4.28, it can be seen that the sulfate concentration continuously decreased with settling time in the whole experiments. The continuous reduction of soluble sulfate concentration showed that sulfate was not in steady state in all experiments. Furthermore, it appears that the soluble sulfate reduction was associated with settling time, which made sense given that insoluble aluminum sulfate was formed with settling time. The soluble Al concentration remained stable after 24 hour of settling, whereas the soluble sulfate concentration showed continuous reduction throughout the experiments.

The continuous reduction of sulfate concentration indicated the formation of sulfate-precipitates throughout the experiments. The sludge analysis with SEM (EDS) showed that the sulfur content increased with settling time and the other metal contents were almost constant from 30 minutes to 48 hours of settling. Thus it is reasonable to conclude that these sulfate-precipitates were Al-sulfate precipitates.

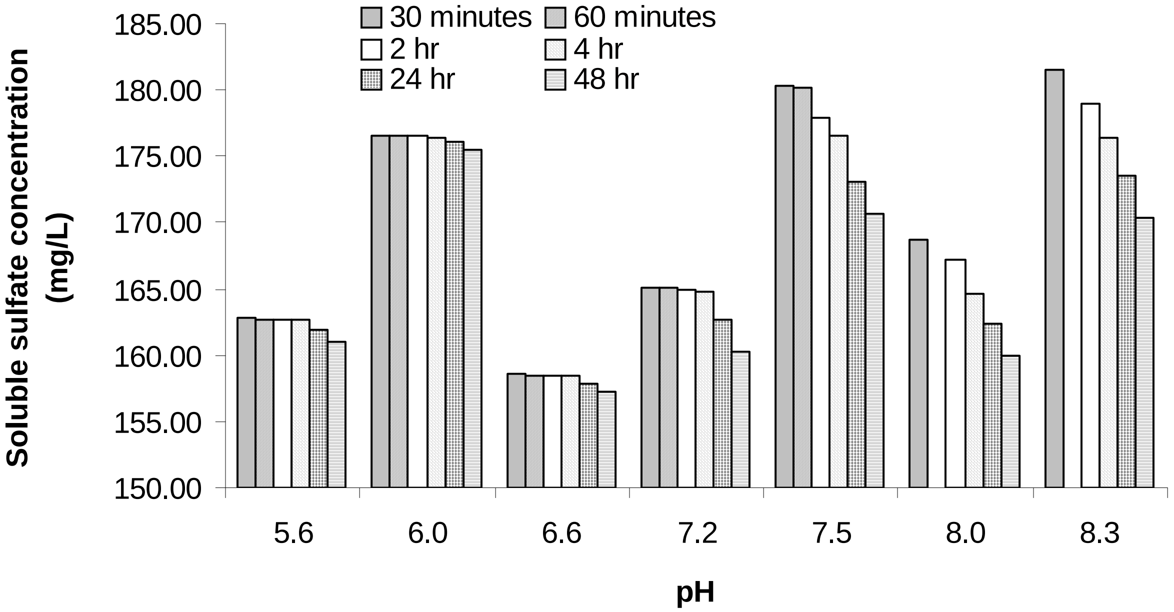


Figure 4.28 Soluble sulfate concentration with settling time at different pH in experiments of low sulfate ($Al:SO_4 = 1:1$)

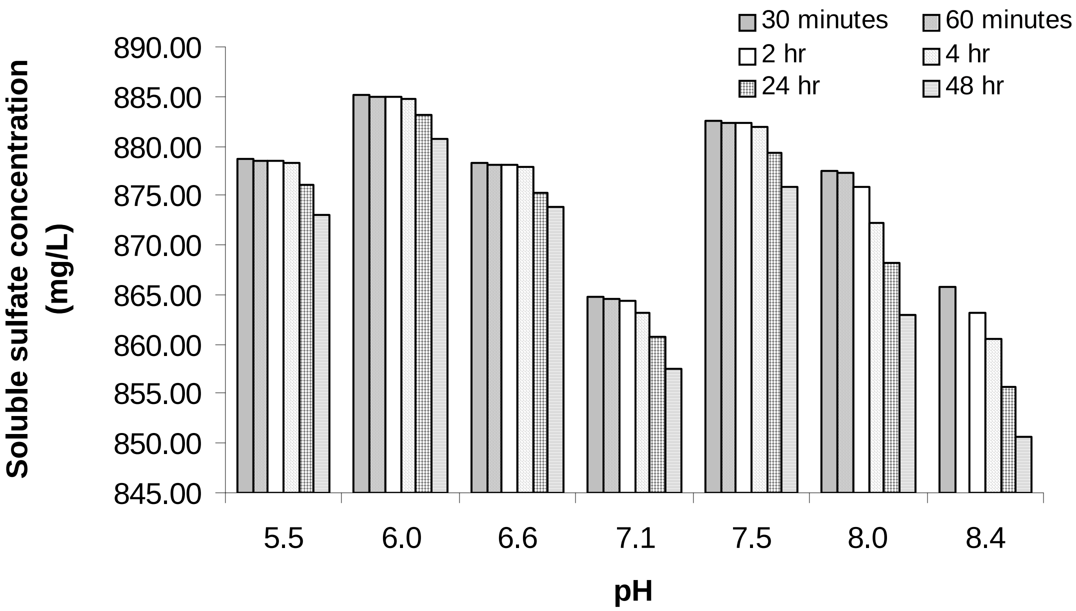


Figure 4.29 Soluble sulfate concentration with settling time at different pH in experiments of high sulfate ($Al:SO_4 = 1:5$)

Figure 4.30 and 4.31 show the removal rate of sulfate with settling time at different pH in experiments with low and high sulfate concentrations. From Figure 4.30, it can be found that the sulfate removal rate was higher at high pH values and the lowest rate occurred at pH=6.0. The removal rate of sulfate was the maximum within the first 30 minutes of settling, and decreased with settling time. After 4 hours of settling, the sulfate removal rate became constant. Figure 4.30 shows the removal rate of sulfate over settling in experiments with low sulfate concentration (1:1). From Figure 4.31, it can be seen that the tendency of removal rate of sulfate in experiments with high sulfate concentration was similar to the experiments with low sulfate concentration. When high sulfate concentration was in solution, the removal rate of sulfate did not show a significant difference among pH values after 4 hours of settling. Comparing with the removal rate of Al in Figure 4.26, it can be found that the removal rate of sulfate was higher than the removal rate of Al. The removal rate of sulfate and Al was not synchronized indicated that some Al-precipitates were re-dissolved in solution, because the soluble Al concentration was less than the solubility of amorphous $Al(OH)_3$.

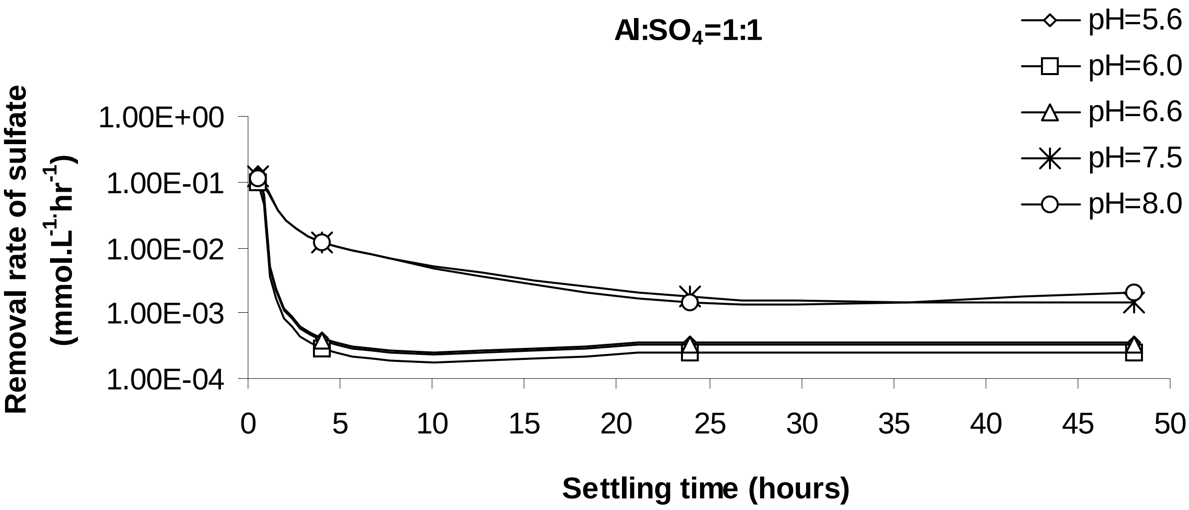


Figure 4.30 Removal rate of sulfate with settling time at different pH in experiments with low sulfate concentration ($Al:SO_4$=1:1)

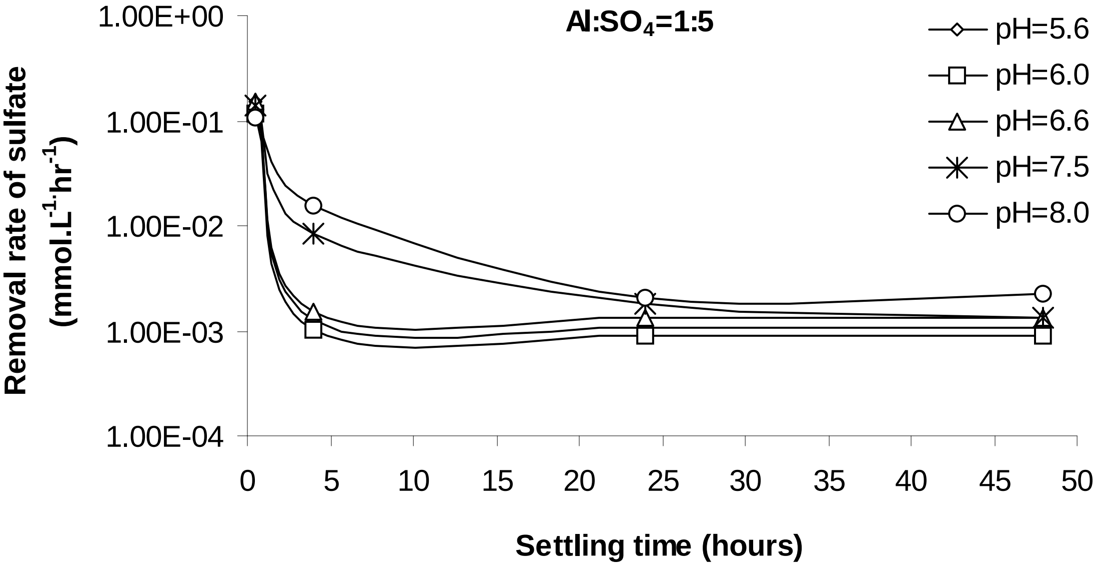


Figure 4.31 Removal rate of sulfate with settling time at different pH in experiments with high sulfate concentration ($Al:SO_4$=1:5)

Table 4.5 presents the ratio of removal amount of Al:SO_4 in solution within different settling time interval. In this table, it can be found that the overall removal amount of Al was much more than the removal amount of sulfate, which indicated that most of aluminum was removed by formation of aluminum hydroxide. Within the first 30 minutes of settling after pH adjustment, the ratio of removal amount of Al to sulfate was the maximum. Since the soluble Al concentration reduced for more than 90% within the first 30 minutes of settling, the high ratio of removal Al to sulfate indicated that only little of aluminum was combined with sulfate to form precipitates within the first 30 minutes after pH adjustment. In other words, the main precipitates formed within the first 30 minutes after pH adjustment were aluminum hydroxide.

When settling time was long, the ratio of removal amount of Al to sulfate reduced and became less than 1 after 4 hours of settling, which indicated the primary reaction became Al-sulfate precipitation. In other words, the Al-sulfate precipitates became the main reaction to influence soluble Al concentration after long settling in settling tank in an active treatment system of Al-bearing ARD/AMD. In Table 4.5, the ratio of removal amount of Al:SO_4 showed that the value was smaller at high pH, which indicated that more Al-sulfate precipitates formed at high pH conditions.

According to the sludge analysis results, the chemical compositions showed that the contents of other metal elements (other than Al) did not change from 30 minutes to 48 hours of settling, which indicated that the reduction of sulfate in solution was only due to the formation of Al-sulfate precipitates. Since the possible species of Al-sulfate precipitates in these experiments were jurbanite and basaluminite, the molar ratio of Al:SO_4 in these compounds are 1:1 and 4:1, respectively. If all sulfate removal was due to the formation of Al-sulfate precipitates, the lower ratio of removal amount of A;:SO4 (<1) indicated that some sludge re-dissolved to keep the soluble Al concentration stable.

Table 4.5 The ratio of removed amount of Al: SO_4 with settling time at different pH (mol/L:mol/L)

Al:SO_4= 1:1	pH					
	Time	**5.6**	**6.0**	**6.6**	**7.1**	**7.5**	**8.0**
	0-48hr	22.89	27.97	24.26	21.01	10.72	10.34
	0-30 min	28.62	34.78	29.60	34.44	30.16	31.26
	30-4hr	28.58	7.86	4.01	1.07	0.42	1.43
	4-24hr	0.15	0.22	0.03	0.03	0.08	0.13
	24hr-48hr	0.085	0.062	0.000	0.000	0.022	0.083
Al:SO_4= 1:5	pH					
	Time	**5.6**	**6.0**	**6.6**	**7.2**	**7.5**	**8.0**
	0-48hr	13.73	17.38	14.28	14.08	10.18	8.71
	0-30 min	23.69	31.74	23.72	36.12	22.31	32.03
	30-4hr	8.67	3.59	1.07	0.47	0.78	1.19
	4-24hr	0.08	0.07	0.09	0.20	0.37	0.12
	24hr-48hr	0.035	0.029	0.010	0.007	0.044	0.004

4.4.2.2 The change of total sulfate concentration with settling time

Figure 4.32 and 4.33 present the change of total sulfate concentration with settling time in experiments with low and high sulfate concentration, respectively. In Figure 4.32 and 4.33, the total sulfate concentration reduced from 30 minutes to 48 hours in the experiments, which was similar to the tendency of soluble sulfate concentration with settling time.

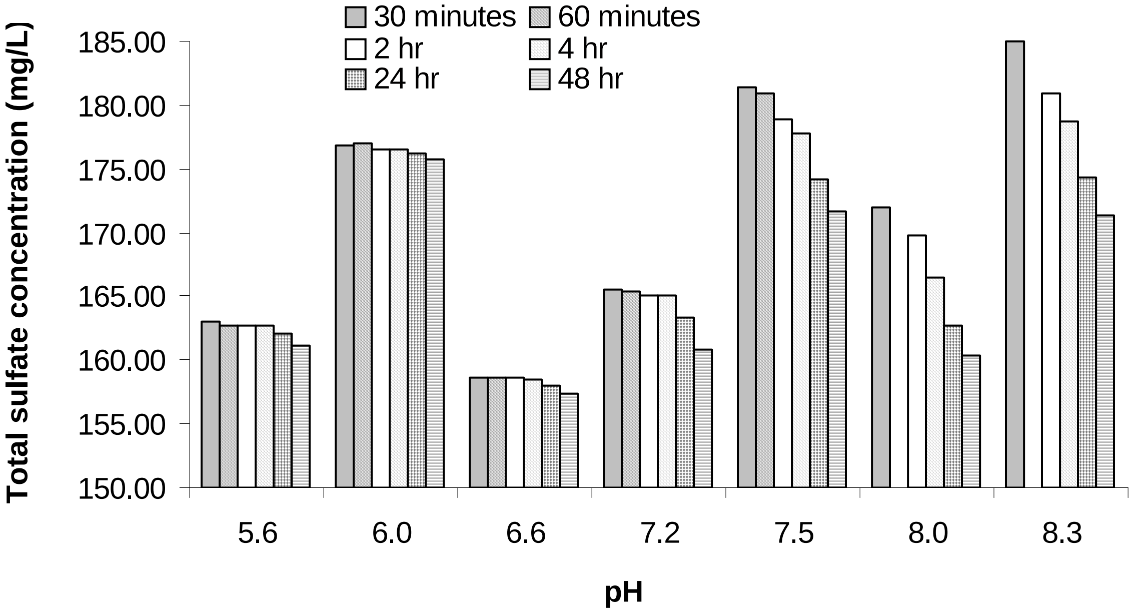


Figure 4.32 Total sulfate concentration with settling time at different pH in experiment of low sulfate ($Al:SO_4$ =1:1)

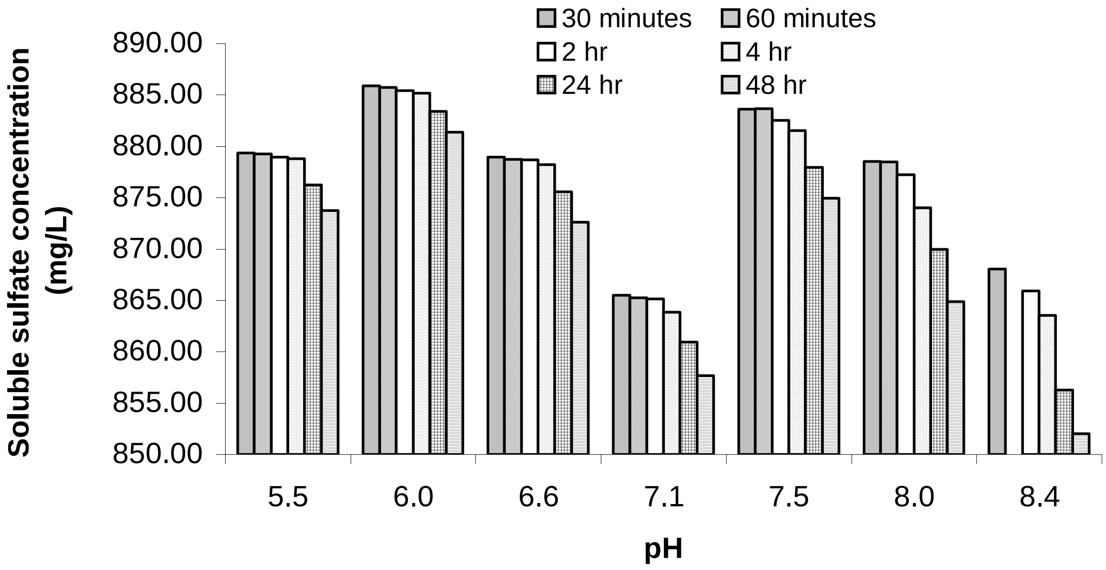


Figure 4.33 Total sulfate concentration with settling time at different pH in experiment of high sulfate ($Al:SO_4$ =1:5)

Figure 4.34 and 4.35 present the change of suspended sulfate concentration over time in experiments with low and high sulfate concentration, respectively. In Figure 4.34 and 4.35, it can be seen that the suspended sulfate concentration was higher at high pH values, which indicated that more sulfate-precipitates remained in the supernatant at high pH. Furthermore, the suspended sulfate concentration became constant after 4 hours of settling. Therefore, it is reasonable to conclude that the reduction of total sulfate concentration was due to the reduction of soluble sulfate concentration after long settling time (>4 hours), which caused by reactions of aluminum with sulfate to form insoluble precipitates.

As indicated above, the presence of sulfate increased the suspended Al solids. The reason was the formation of Al-sulfate precipitates which was in small size and remained in the supernatant. Comparing the suspended Al concentration and sulfate concentration, it can be found that the molar ratio of $Al:SO_4$ in suspended solids was close to 4:1, which indicated that the species of Al-sulfate precipitates were basaluminite ($Al_4(OH)_{10}SO_4$). The detail of the discussion about suspended solids is shown in Section 4.6.

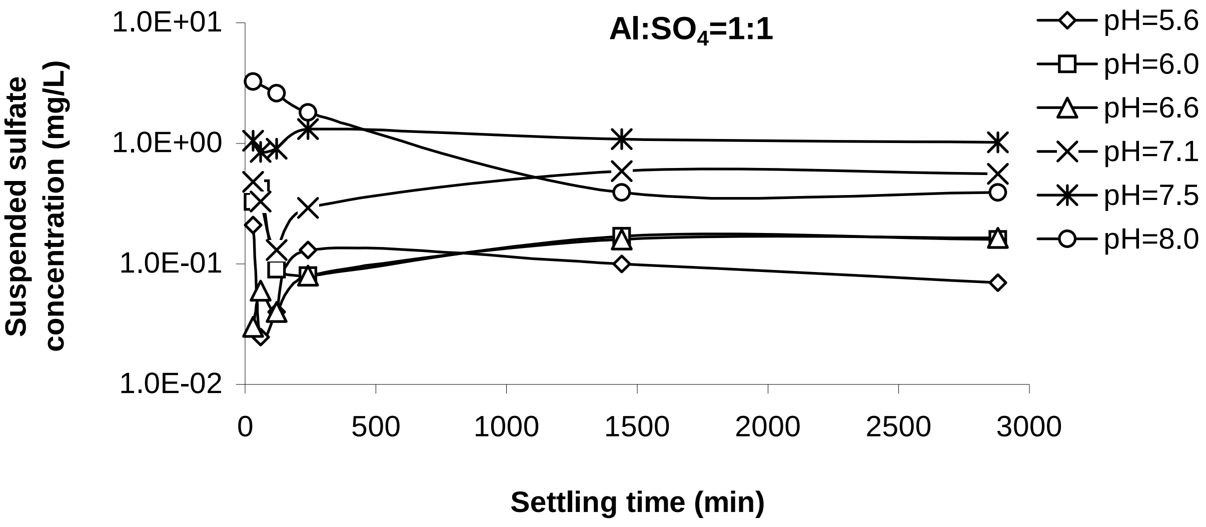


Figure 4.34 Suspended sulfate concentration with settling time in experiments with low sulfate (Al:SO_4=1:1)

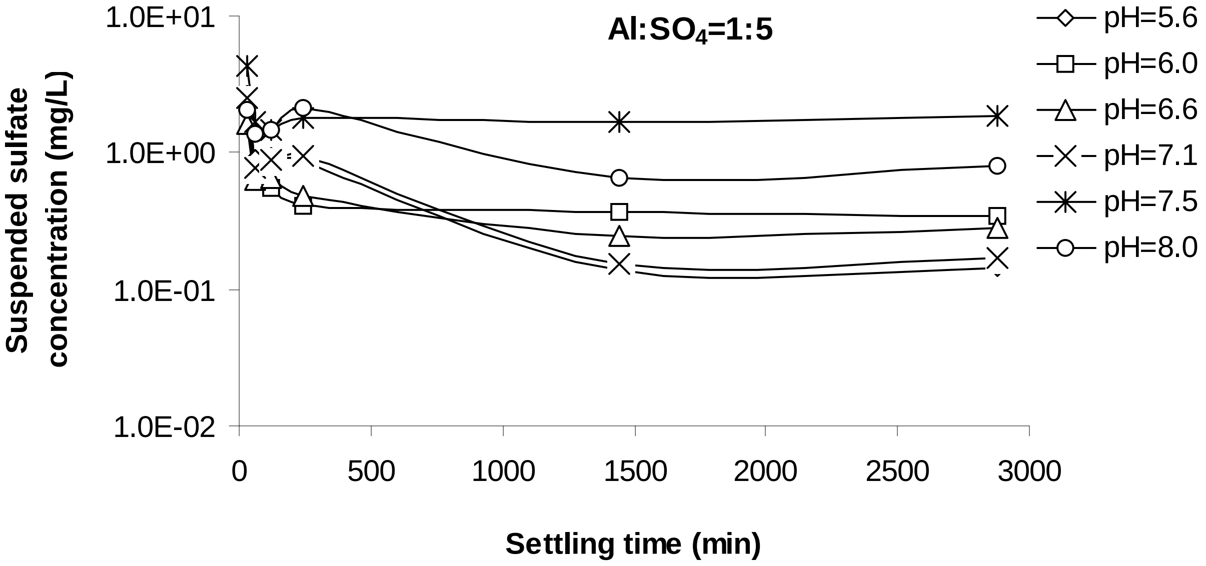


Figure 4.35 Suspended sulfate concentration with settling time in experiments with high sulfate (Al:SO_4=1:5)

4.5 SIMULATION WITH MINEQL+ MODEL

Mineql+ chemical equilibrium modeling software was used to simulate the neutralization process of Al-bearing ARD and predict the final formed precipitated compounds with the lowest solubility. In Mineql+ chemical equilibrium model, the system assumes that all reactions are in equilibrium. With the chemical equilibrium database, this model provides a thermodynamic snapshot of the system: the pH, ionic strength, the distribution of dissolved chemical species, and the amount of solid phase formed, etc. However, this model does not consider the effect of time on some reactions that have kinetic restrictions (Schecher and McAvoy, 1998). In order to calculate the solubility and saturation index (SI) value of a possible kind of aluminum precipitates, this kind of aluminum precipitates was selected as the only possible aluminum precipitate. Therefore the total soluble aluminum concentration calculated by Mineql+ model represented the solubility of this aluminum precipitates at the calculated pH values.

4.5.1 The saturation index values of Al-compounds in the experiments

Saturation index (SI) is a calculated number used to predict the compound stability of water. It indicates whether the water will precipitate, dissolve, or be in equilibrium with this compound. The saturation index (SI) is defined as SI=log(IAP/K_{sp}), where IAP is the ion activity product of the dissolved precipitate constituents, and K_{sp} is the solubility product of the precipitates (such as amorphous $Al(OH)_3$ or basaluminite ($Al_4(OH)_{10}SO_4$), etc.). If the SI value is less than zero, it indicates that solution is non-saturated state for this compound and precipitation of this compound will not happen. If SI>0, it indicates that the solution is supersaturated with this compound and then this compound may be precipitated. The saturation index (SI) of different aluminum compounds (amorphous aluminum hydroxide, gibbsite, and basaluminite) in this study was calculated with Mineql+ model. In the calculation of SI of each compound, the input data was the actual concentration measured in the experiments.

4.5.1.1 The saturation index of Al-compounds in the experiments without sulfate ($Al:SO_4=1:0$)

Since the possible aluminum precipitates formed in experiments without sulfate were only amorphous and/or crystalline $Al(OH)_3$, they were selected as the possible aluminum precipitates in SI calculation. All thermodynamic constants have been taken from the databases of this software. The input data was the measured components of solution at 30 minutes and 48 hours of settling. The calculated SI values of different Al-compounds at different pH after 30 minutes and 48 hours of settling time were shown in Appendix D. The SI values of the two compounds were plotted as a function of pH (Figure 4.36).

At 30 minutes of settling, SI value of amorphous $Al(OH)_3$ was from –0.03 to 0.23, which was close to zero (Figure 4.36). Therefore, it is concluded that soluble Al was in theoretical equilibrium with amorphous $Al(OH)_3$ immediately after NaOH addition during Al-bearing ARD treatment. When settling time became longer (48hr), SI value of amorphous $Al(OH)_3$ slightly decreased, which was from –0.17 to 0.08. The SI value of amorphous $Al(OH)_3$ at different pH values was still close to zero, which indicated that the solution was still in equilibrium with amorphous $Al(OH)_3$.

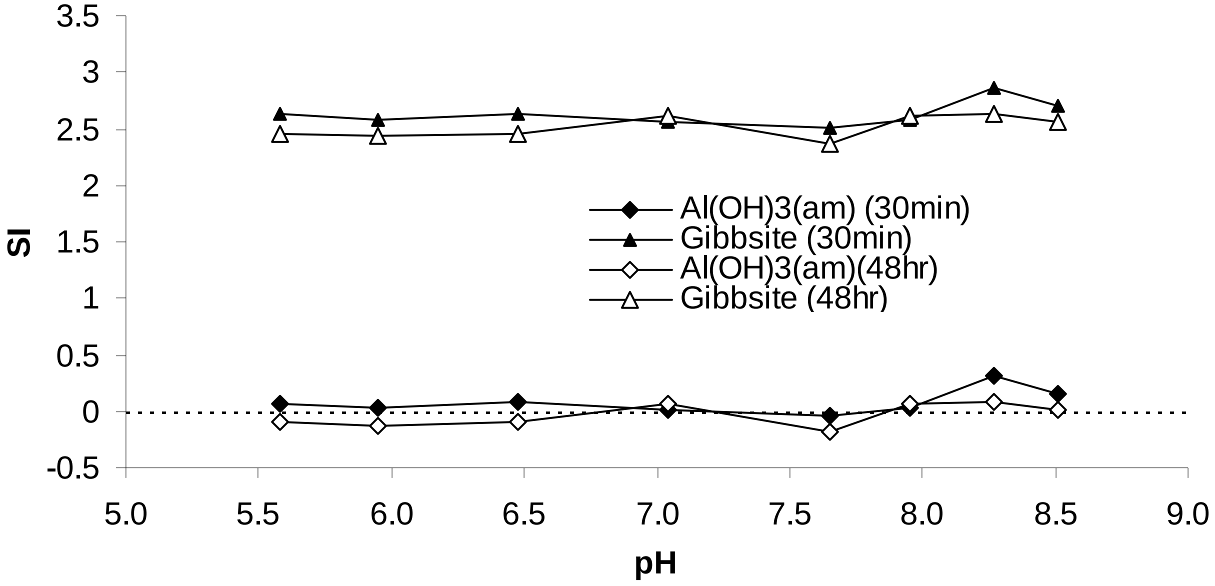


Figure 4.36 SI values of amorphous and crystalline $Al(OH)_3$ in experiments without sulfate after 30 minutes and 48 hours of settling

After 30 minutes of settling, SI value of gibbsite was from 2.5 to 2.9 (Figure 4.36), which was always much larger than zero. The high SI values indicated that the solution would have been supersaturated with gibbsite. After 48 hours of settling, the SI value of gibbsite slightly reduced and was in the range of 2.4 to 2.6, which was higher than 2 and indicated that the solution was also supersaturated with gibbsite after 48 hours of settling. However, sludge analysis (XRD analysis in Figure 4.13-4.15) revealed that crystalline aluminum hydroxide, gibbsite (crystalline $Al(OH)_3$, was not detected in sludge formed after both short and long settling time. Therefore, it is reasonable to conclude that the experiments without sulfate were in equilibrium with amorphous $Al(OH)_3$ immediately after NaOH addition. In other words, formation of amorphous $Al(OH)_3$ occurred immediately and became in equilibrium during 30 minutes after pH changed and gibbsite, crystalline $Al(OH)_3$, was not formed even after 48 hours of settling.

4.5.1.2 The saturation index of Al-compounds in the experiments with low sulfate ($Al:SO_4=1:1$)

In the experiments that contained sulfate, the possible species of Al-precipitates include Al-sulfate compounds, such as jurbanite and basaluminite. In Mineql+ model database, according to the components of solution in this study, the possible Al-precipitates formed are jurbanite ($Al(OH)SO_4$), amorphous $Al(OH)_3$, gibbsite (crystalline $Al(OH)_3$), and basaluminite ($Al_4(OH)_{10}SO_4$). The previous simulation showed that jurbanite cannot be formed if pH of solution is higher than 5.5. Therefore, jurbanite was not considered as a possible species of Al-precipitates. In SI calculation for the experiments with sulfate, only three kinds of Al-compounds, amorphous $Al(OH)_3$, gibbsite (crystalline $Al(OH)_3$), and basaluminite ($Al_4(OH)_{10}SO_4$), were selected as the possible species of aluminum precipitates. The SI value of amorphous $Al(OH)_3$ was from -0.14 to 0.40 at 30 minutes of settling (Figure 4.37and Appendix D). These SI values indicated that the solution was approximately in equilibrium with amorphous $Al(OH)_3$, which was similar to experiments without sulfate. The SI values of gibbsite and basaluminite were from 2.4 to 2.8 and 1.8 to 5.4, respectively. The data indicated that the solution was supersaturated with both gibbsite and basaluminite after 30 minutes of settling. When settling time became longer (48hr), all SI values of amorphous $Al(OH)_3$ declined and became less than zero (from –0.12 to –0.74). The negative values of SI indicated that the solution was unsaturated with amorphous $Al(OH)_3$. The SI value of amorphous $Al(OH)_3$ suggested that some reactions, which decreased the soluble Al concentration, occurred between 30 minutes to 48 hours of settling. Although the SI values of gibbsite and basaluminite also decreased, they were still higher than 1 (SI values were in the range of 1.2 to 4.5 for basaluminite, and 1.4 to 1.8

for gibbsite). Therefore, the solutions were still supersaturated with gibbsite and basaluminite after 48 hours of settling in experiments with low sulfate concentration.

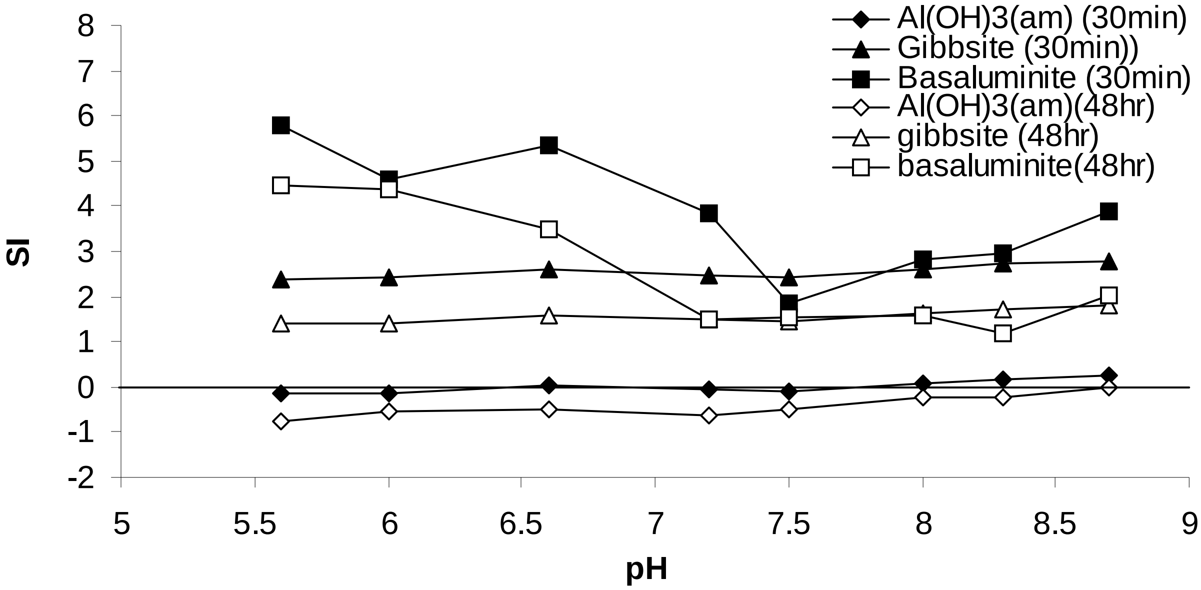


Figure 4.37 SI values of possible Al-precipitates (amorphous $Al(OH)_3$, gibbsite, and basaluminite) in experiments of low sulfate ($Al:SO_4$=1:1) after 30 minutes and 48 hours of settling

4.5.1.3 The saturation index of Al-compounds in the experiments with high sulfate ($Al:SO_4$=1:5)

In experiments with high initial sulfate concentration ($Al:SO_4$=1:5), SI value of amorphous $Al(OH)_3$ was also close to zero (from -0.18 to 0.02) after short settling time (30minutes), whereas the SI values of gibbsite and basaluminite were from 2.4 to 2.6 and 2.5 to 6.7, respectively (Figure 4.38). The high SI values of gibbsite and basaluminite indicated the solution was strongly supersaturated with gibbsite and basaluminite after 30 minutes of settling. When settling time became longer (48 hours), all SI values declined. The change of SI values was due to the reduction of Al concentrations. The SI value for amorphous $Al(OH)_3$ decreased going from equilibrium (SI = -0.18 to 0.02) to unsaturated (SI =-0.32 to -1.6). The negative SI value of amorphous $Al(OH)_3$ was due to the decrease of Al concentration, which indicated that other precipitates could be formed (such as Al-sulfate precipitates). The negative SI value of amorphous $Al(OH)_3$ in these experiments was similar to that in experiment with low sulfate ($Al:SO_4=1:1$). The SI values of gibbsite and basaluminite in experiments with high sulfate ($Al:SO_4=1:5$) were less than that in experiments without and with low sulfate ($Al:SO_4=1:1$), but most of them were still higher than 2. These results indicated that the solution was not in equilibrium conditions.

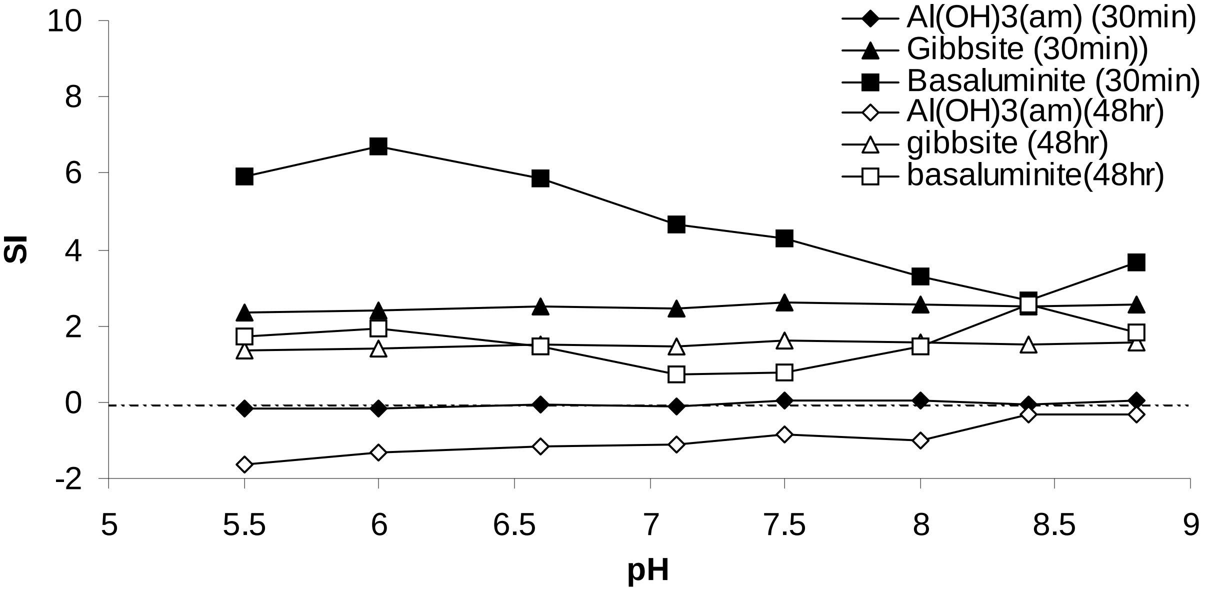


Figure 4.38 SI values of possible Al-precipitates (amorphous $Al(OH)_3$, gibbsite, and basaluminite) in experiments of high sulfate ($Al:SO_4=1:5$) after 30 minutes and 48 hours of settling

4.5.2 Comparison of soluble Al concentrations in experiments with theoretical solubility of possible Al-precipitates

In the processes of Al-bearing ARD treatment with NaOH, the actual sludge might be the mixture of different Al-precipitates. In order to discuss the effect of sulfate on soluble Al concentration, theoretical solubility of each possible Al-precipitate was calculated and compared with the soluble Al concentration after 30 minutes, 120 minutes, and 48 hours of settling. The change of soluble Al concentration might help to understand the possible reactions occurred that controlled soluble Al concentration. In the calculation of solubility of Al-precipitates in experiments, the components of synthetic ARD were used as the initial composition of solution. Mineql+ model is used to calculate the solubility of Al at each pH point for each possible Al-precipitate.

Figure 4.39 shows the theoretical solubility of amorphous $Al(OH)_3$ and gibbsite at each pH point in experiments without sulfate. In Figure 4.39, it can be found that the soluble Al concentrations after short and long settling time were close to the theoretical solubility of amorphous $Al(OH)_3$. The data indicated that amorphous $Al(OH)_3$ was the compound that controlled the soluble Al concentration if sulfate was absent in experiments.

Figure 4.40 shows the theoretical solubility of amorphous $Al(OH)_3$, gibbsite, jurbanite, and basaluminite in experiments with low sulfate concentration (1:1). In Figure 4.40, it can be seen that soluble Al concentration decreased with settling time. After 30 minutes of settling, soluble Al concentration in experiments with low sulfate concentration was close to the solubility of amorphous $Al(OH)_3$. Since the solubility of jurbanite was higher than actual Al concentration, it implied that jurbanite was not the Al-compound that controlled the Al concentration in experiments. When settling time became longer, the soluble Al concentration decreased and became lower than the solubility of amorphous $Al(OH)_3$. The reduction of soluble Al concentration was due to the formation of Al-precipitates with solubility less than amorphous $Al(OH)_3$. This phenomenon indicated that the final soluble Al concentration was not controlled by amorphous $Al(OH)_3$.

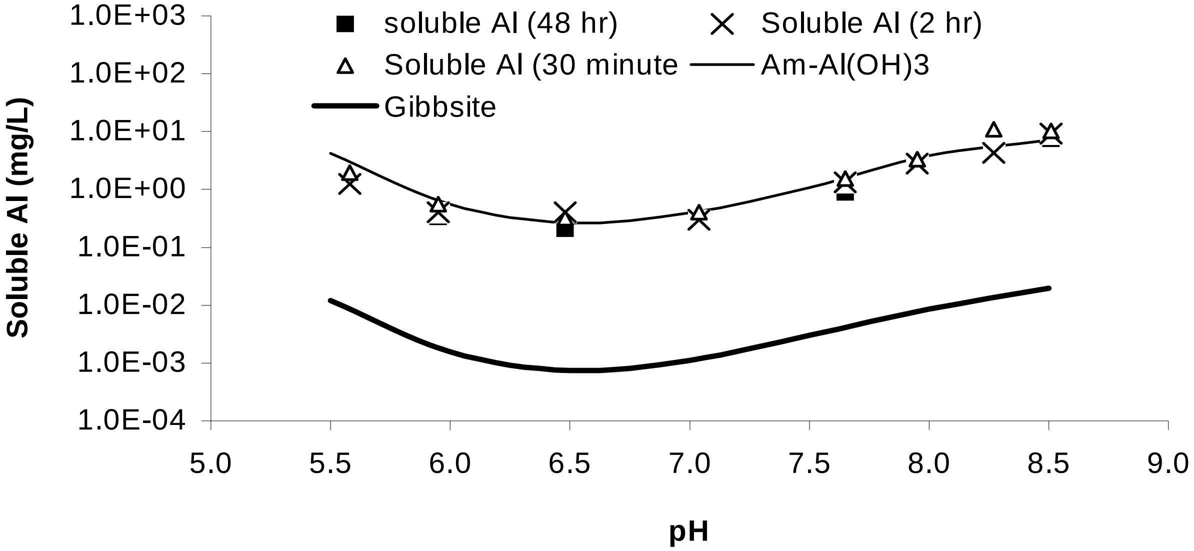


Figure 4.39 Theoretical solubility of gibbsite and amorphous $Al(OH)_3$ and actual soluble Al concentration at different pH in experiments without sulfate ($Al:SO_4=1:0$) after 30 minutes, 2 hours, and 48 hours of settling.

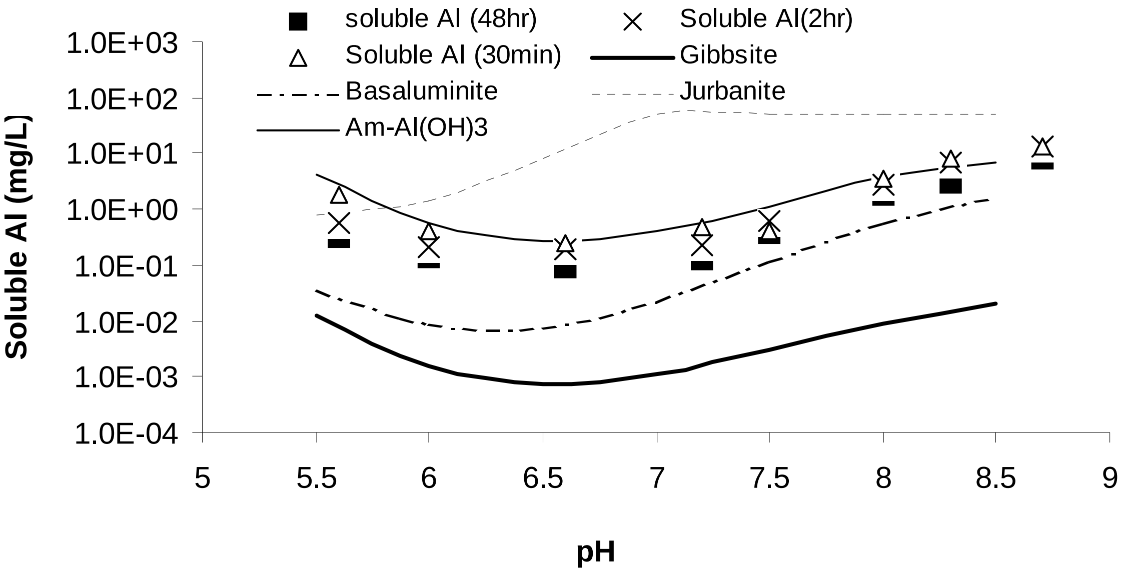


Figure 4.40 Theoretical solubility of possible Al-precipitates and actual soluble Al concentration at different pH in experiments with low sulfate (Al:SO_4=1:1) after 30 minutes, 2 hours, and 48 hours of settling.

Figure 4.41 presents the theoretical solubility of amorphous $Al(OH)_3$, gibbsite, jurbanite, and basaluminite in experiments with high sulfate concentration (Al:SO_4=1:5). Similar to the experiments with low sulfate concentration, it can be found that the solubility of jurbanite was higher than soluble Al concentration at any pH point in experiments with high sulfate concentration. Therefore, it can be concluded that jurbanite was not the compound that controlled soluble Al concentration during Al-bearing ARD neutralization. Also, the soluble Al concentration after 30 minutes of settling was close to the solubility of amorphous $Al(OH)_3$. These results indicated that the main reaction of amorphous $Al(OH)_3$ controlled soluble Al concentration in the short period after pH elevated by NaOH addition. With increasing of settling time, soluble Al concentration became lower than the solubility of amorphous $Al(OH)_3$ and tended to be close to the solubility of basaluminite and gibbsite. The decrease of soluble Al concentration in experiments that contained sulfate indicated that the effluent soluble Al concentration from an actual treatment system might be lower than that from amorphous Al(OH)3 since the ARD/AMD contains relative high sulfate. (However, as shown above, there is an increase in total aluminum due to increases in small aluminum-bound particles.)

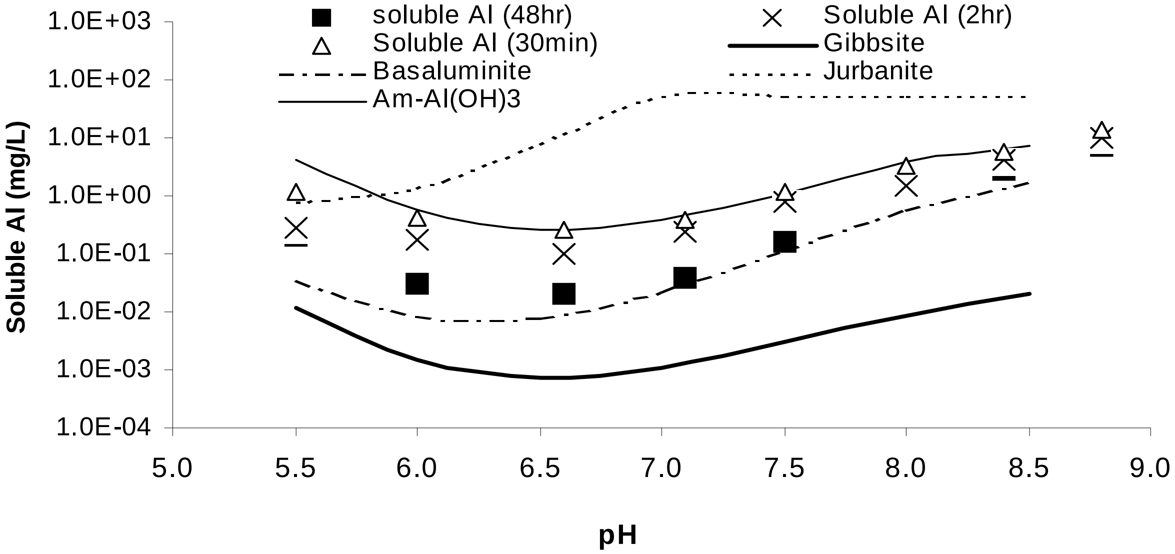


Figure 4.41 Theoretical solubility of possible Al-precipitates and actual soluble Al concentration at different pH in experiments with high sulfate (Al:SO_4=1:5) after 30 minutes, 2 hours, and 48 hours of settling.

4.6 POSSIBLE REACTIONS CONTROLLING SOLUBLE Al CONCENTRATIONS

As mentioned above, the sludge composition and the change of soluble Al concentration with settling time implied that the reduction of soluble Al concentration was due to the formation of Al-sulfate precipitates, and the most likely species of Al-sulfate precipitate was basaluminite. In this section, a method based on mass balance will be built to discuss the possible reactions that would be the key reactions controlling the soluble Al concentration.

4.6.1 The amount of aluminum in solution and in solids

In experiments, any solute is in two phases, solid or soluble. The solid phase includes sediment and colloidal or suspended particles. The total solute concentration is the sum of all soluble and colloidal/suspended particles. It is assumed that the reduction of solute concentration was due to the formation of solid phases or precipitates. Then amount of solute in each phase could be calculated.

All initial solutes in experiments were in soluble state. Based on the principle of mass balance, the amount of sludge at time *t* can be calculated using following equation (Al units in molar concentration mol/L):

$$W^t = [C]_{total}^{initial} - [C]_{total}^{t} \tag{4.2}$$

Where: W^t is the amount of sludge produced after time *t* of settling.

$[C]_{total}^{initial}$ and $[C]_{total}^{t}$ represent the initial solute concentration and total solute concentration at time *t*, respectively.

The total amount of precipitates (including both settling down and suspended solids) produced from t_1 to t_2 can be calculated by using the soluble concentration with equation:

$$P^{t1-t2} = [C]_{so\,\mathrm{lub}\,le}^{t1} - [C]_{so\,\mathrm{lub}\,le}^{t2} \tag{4.3}$$

Where: P_{Al}^{t1-t2} is the amount of "new" precipitates produced from time t_1 to t_2. These precipitates might be formed as settled sludge or as suspended particles in solution,;

$[C]_{soluble}^{t1}$ and $[C]_{soluble}^{t2}$ represent the soluble concentration at t_1 and t_2, respectively, molar/L;

The removal rate of a solute is:

$$r = \frac{[C]_{soluble}^{t1} - [C]_{soluble}^{t2}}{t2 - t1} \tag{4.4}$$

At time *t*, the amount of suspended solids is:

$$S^t = [C]_{total}^{t} - [C]_{soluble}^{t} \tag{4.5}$$

Therefore, in the experiment, the amount of Al-precipitates can be calculated with the equations:

$$P_{Al}^{t1-t2} = [Al]_{soluble}^{t1} - [Al]_{soluble}^{t2} \tag{4.6}$$

$$P_{Al}^{48hr_2} = [Al]_{initial} - [Al]_{soluble}^{48hr} \tag{4.7}$$

$$W_{Al}^{t} = [Al]_{total}^{initial} - [Al]_{total}^{t} \tag{4.8}$$

$$W_{Al}^{48hr} = [Al]_{total}^{initial} - [Al]_{total}^{48hr} \tag{4.9}$$

$$W_{Al}^{t1-t2} = [Al]_{total}^{t1} - [Al]_{total}^{t2} \tag{4.10}$$

$$S_{Al}^{t} = [Al]_{total}^{t} - [Al]_{soluble}^{t} \tag{4.11}$$

Where: P_{Al}^{48hr} represents the overall Al-precipitates produced after 48 hours of settling. These Al-precipitates could be in the form of sludge and suspended particles;

P_{Al}^{t1-t2} is the amount of Al-precipitates produced between time t1 and t2;

W_{Al}^{t} and W_{Al}^{48hr} is the total amount of Al-precipitates that have settled down after time *t* and 48 hours, respectively. These Al-precipitates could be in form of Al-hydroxide and/or Al-sulfate if sulfate is present in experiments. They represent the Al-precipitates that had been settled down, which does not include the Al-precipitates suspended in solution;

W_{Al}^{t1-t2} is the amount of Al-sludge produced from time *t1* to time *t2* of settling;

S_{Al}^{t} represents the amount of suspended Al solids at time *t* of settling;

$[Al]_{total}^{initial}$ is the initial Al concentration in the experiments;

$[Al]_{total}^{t}$ and $[Al]_{total}^{48hr}$ are the total Al concentrations after time *t* and 48 hours of settling, respectively;

$[Al]_{so\,\mathrm{lub}\,le}^{t}$ and $[Al]_{so\,\mathrm{lub}\,le}^{48hr}$ are the soluble Al concentrations after time *t* and 48 hours of settling, respectively.

The amount of Sulfate-precipitates in the experiments is:

$$P_{SO_4}^{t} = [SO4]_{so\,\mathrm{lub}\,le}^{initial} - [SO4]_{so\,\mathrm{lub}\,le}^{t} \tag{4.12}$$

$$P_{SO_4}^{48hr} = [SO4]_{initial} - [SO4]_{so\,\mathrm{lub}\,le}^{48hr} \tag{4.13}$$

$$P_{SO_4}^{t1-t2} = [SO4]_{so\,\mathrm{lub}\,le}^{t1} - [SO4]_{so\,\mathrm{lub}\,le}^{t2} \tag{4.14}$$

$$W_{SO_4}^{t} = [SO_4^{2-}]_{total}^{initial} - [SO_4^{2-}]_{total}^{t} \tag{4.15}$$

$$W_{SO_4}^{48hr} = [SO_4^{2-}]_{total}^{initial} - [SO_4^{2-}]_{total}^{48hr} \tag{4.16}$$

$$W_{SO_4}^{t1-t2} = [SO_4^{2-}]_{total}^{t1} - [SO_4^{2-}]_{total}^{t2} \tag{4.17}$$

$$S_{SO_4} = [SO_4^{2-}]_{total}^{t} - [SO_4^{2-}]_{so\,\mathrm{lub}\,le}^{t} \tag{4.18}$$

Where: $P_{SO_4}^{t}$ and $P_{SO_4}^{48hr}$ represent the total sulfate-precipitates produced after time t and 48 hours of settling, respectively. These sulfate-precipitates could be in the form of sludge and suspended particles;

$P_{SO_4}^{t1-t2}$ is the amount of sulfate-precipitates produced between time t_1 and t_2;

$W_{SO_4}^{t}$ and $W_{SO_4}^{48hr}$ are the total amount of sulfate sludge that had been settled down after time *t* and 48hr of settling.

$W_{SO_4}^{t1-t2}$ is the amount of sulfate-sludge produce from 30 minutes to 48 hours of settling;

$S_{SO_4}^{t}$ is the amount of suspended sulfate solids in solution after time *t* of settling, respectively;

$[\mathrm{SO}_4^{2-}]_{total}^{initial}$ is the initial total sulfate concentration in the experiments;

$[SO4]_{total}^{t}$ and $[SO_4]_{total}^{48hr}$ are the total sulfate concentrations after time *t* and 48 hours of settling, respectively;

$[SO4]_{so\,\mathrm{lub}\,le}^{t}$ and $[SO_4]_{so\,\mathrm{lub}\,le}^{48hr}$ are the soluble sulfate concentrations after time *t* and 48 hours of settling, respectively.

Therefore, the molar ratio of Al:S in sludge collected after time *t* and 48 hours of settling in experiments can be calculated by using the change of Al and sulfate concentrations in solution.

$$\left(Al\big/S\right)_{sludge}^{30\,\mathrm{min}} = \left(Al\big/SO_4\right)_{sludge}^{30\,\mathrm{min}} = \frac{W_{Al}^{30\,\mathrm{min}}}{W_{SO_4}^{30\,\mathrm{min}}} = \frac{[Al]_{total}^{initial} - [Al]_{total}^{30\,\mathrm{min}}}{[SO_4^{2-}]_{total}^{initial} - [SO_4^{2-}]_{total}^{30\,\mathrm{min}}} \tag{4.19}$$

$$\left(Al/S\right)_{sludge}^{48hr} = \left(Al/SO_4\right)_{sludge}^{48hr} = \frac{W_{Al}^{48hr}}{W_{SO_4}^{48hr}} = \frac{[Al]_{total}^{initial} - [Al]_{total}^{48hr}}{[SO_4^{2-}]_{total}^{initial} - [SO_4^{2-}]_{total}^{48hr}} \tag{4.20}$$

The molar ratio of Al:S of suspended solids at time *t* and 48 hours can be calculated as:

$$\left(Al/SO_4\right)_{suspended}^{t} = \frac{S_{Al}^{t}}{S_{SO_4}^{t}} = \frac{[Al]_{total}^{t} - [Al]_{soluble}^{t}}{[SO_4^{2-}]_{total}^{t} - [SO_4^{2-}]_{soluble}^{t}} \tag{4.21}$$

$$\left(Al/SO_4\right)_{suspended}^{48hr} = \frac{S_{Al}^{48hr}}{S_{SO_4}^{48hr}} = \frac{[Al]_{total}^{48hr} - [Al]_{soluble}^{48hr}}{[SO_4^{2-}]_{total}^{48hr} - [SO_4^{2-}]_{soluble}^{48hr}} \tag{4.22}$$

Therefore, according to the above equations, the molar ratio of Al:S in any phase could be calculated. Based on the change of Al:S molar ratio in sludge, suspended solids and the produced precipitates, the possible reactions that might control the species of Al-precipitates and Al concentrations will be discussed in next section

4.6.2 Calculation the proportion of sulfate precipitates in sludge and suspended Al-solids

In experiments, initial Al and sulfate concentrations had been measured before NaOH addition. According to equation 4.19 and 4.20, the molar ratios of Al:S in sludge after 30 minutes and 48 hours of settling were calculated. The calculated values are listed in Table 4.6. From Table 4.6, it can be found that although the calculated values are slightly less than the measured values, the difference between measured from calculated results at same pH was less than 10%, which confirming the SEM analysis results were accurate. In experiments, some sulfate ions might be absorbed by sediment, and resulted in reduction of sulfate concentration in aqueous phase. These absorbed sulfate ions could be removed from the precipitates during the sludge sample preparation for SEM analysis. This might be the reason that SEM analysis showed a slightly higher Al:S molar ratio (lower sulfate content). Unfortunately, our experiments cannot isolate the effect of absorption and reaction of sulfate. The future research could be focused on this question.

Table 4.6 Molar ratios of Al:S in sludge after 30 minutes and 48 hours of settling

	SEM analysis		Calculation[*]	
Settling time	30 min	48 hour	30 min	48 hour
pH	**$Al:SO_4$=1:1**			
5.6	31.3	25.9	28.6	23.3
6.0	43.2	32.0	34.8	28.8
6.6	34.3	27.3	29.6	24.7
7.5	34.0	11.9	30.3	11.4
8.3	39.4	10.6	37.0	11.1
	$Al:SO_4$=1:5			
5.5	26.4	16.8	23.7	13.8
6.0	35.0	21.2	31.6	17.9
6.6	35.3	17.4	30.9	14.6
7.5	32.2	12.4	22.3	11.5
8.4	31.0	9.8	29.9	8.2

[*]: Molar ratio of Al:S in sludge was calculated by using equation 4.21 and 4.22

The formation of Al-precipitates reduced soluble Al concentration. According to the composition of synthetic ARD, the theoretical possible species of Al-precipitates include $Al(OH)_3$ and Al-sulfate precipitates (jurbanite and basaluminite). The simulation results of Mineql+ model indicated that the formation of $Al(OH)_3$ was not the only mechanism to reduce the Al concentration in experiments when sulfate was present. Considering the soluble Al concentration was less than the solubility of amorphous Al(OH)$_3$ after 48 hours, the formation of Al-sulfate caused the soluble Al concentration decreasing (less than the solubility of amorphous Al(OH)). In Figure 4.37-4.39, SI values of Al-compounds indicated that the reduction of soluble Al concentration was due to the formation of Al-sulfate precipitates after long settling time. The formation of Al-sulfate precipitates reduced both Al and sulfate concentration. Therefore, a calculation of the molar ratio of Al to sulfate (sulfur) in sludge and suspended particles at different times will help to understand the processes of Al removal during and after the NaOH neutralization of Al-bearing ARD.

If it is assumed that the reduction of concentration was due to the formation of precipitates, the amount of Al- and sulfate-precipitates can be calculated by equation 4.6- 4.7 and 4.12-4.14, respectively. For example, after 30 minutes of settling, the amount of Al-precipitates produced (in forms of both sludge and suspended particles) is:

$$P_{Al}^{30\,\min} = [Al]_{initial} - [Al]_{soluble}^{30\,\min}$$

Where the amount of produced sulfate-precipitates is:

$$P_{SO_4}^{30\,\min} = [SO_4]_{initial} - [SO_4]_{soluble}^{30\,\min}$$

The molar ratio of Al to sulfate in precipitates (total of sludge and suspended particles) is:

$$Al/S = \frac{P_{Al}^{30\,\min}}{P_{SO_4}^{30\,\min}} = \frac{[Al]_{initial} - [Al]_{soluble}^{30\,\min}}{[SO_4]_{initial} - [SO_4]_{soluble}^{30\,\min}} \qquad (4.23)$$

After addition of NaOH in experiments, Al precipitation occurred and most Al-precipitates were settleable. However, some Al-solids remained in aqueous phase. These suspended particles could grow and settle due to floc formation over time, or remain in colloidal in the supernatant for long time. These suspended particles can actually increase the effluent Al concentration from the ARD treatment system. To evaluate the characteristics of these particles is important to improve the treatment efficiency and possibly to understand an approach to meet future discharge aluminum standards from AMD and ARD sites.

Previous data indicated that the reactions of Al-sulfate precipitation occurred in experiments. Therefore, the suspended Al-precipitates can be in two forms: $Al(OH)_3$ and/or Al-sulfate. According to the change of Al and sulfate concentration, the molar ratio of Al:S in suspended solids can be calculated with equation 4.21and 4.22.

Table 4.7 presents the molar ratio of Al:S in suspended solids at different settling time . In Table 4.8, it can be seen that the molar ratio of $Al:SO_4$ of suspended particulates were high within two hours of settling, which indicated that most suspended particles in the supernatant was in the form of $Al(OH)_3$ when settling time was less than two hours. When settling time became longer, the molar ratio of $Al:SO_4$ in suspended solids decreased. The reduction of molar ratio indicated that the proportion of suspended Al-sulfate particles increased. Furthermore, the molar ratio of $Al:SO_4$ in suspended particles became almost constant after 24 hours of settling, which indicated that the compositions of suspended particles in the supernatant was the same after 24 hours of settling. From Figure 4.28 and 4.29, the soluble sulfate concentration continuously reduced throughout experiments, which implied that sulfate precipitates were produced continuously. However, from Figure 4.27, 4.36, and 4.37, it can be found that the suspended Al and sulfate concentration were almost constant after 24 hour of settling. Therefore, after 24 hours of settling, the species of “new” formed precipitates should be the same species as the suspended particles in the supernatant. In Table 4.7, it can be seen that the value of molar ratio of $Al:SO_4$ in suspended particles was around 4.0, which is the theoretical molar ratio of

Al:SO_4 in basaluminite. This result indicated that basaluminite was the primary species of Al-sulfate precipitates formed in the experiments.

Table 4.7 Molar ratio of Al:S in suspended solids after different settling time

pH	**5.6**	**6.0**	**6.6**	**7.0**	**7.5**	**8.0**	**8.3**
Time	**Al:SO_4 = 1:1**						
30 min	9.9	24.0	115.6	20.4	16.4	13.8	10.3
2 hr	9.2	13.3	23.0	21.3	16.2	10.1	9.6
4 hr	4.1	10.0	9.8	10.2	8.2	6.7	6.1
24 hr	4.1	5.0	5.0	5.1	4.7	5.4	4.9
48 hr	3.4	4.9	4.7	5.1	4.9	3.9	4.4
	Al:SO_4 = 1:5						
30 min	5.5	7.1	8.1	6.4	5.2	7.6	5.2
2 hr	8.2	14.3	13.3	12.5	14.3	12.4	9.2
4 hr	6.1	6.6	6.2	7.0	9.1	6.3	6.2
24 hr	4.0	4.2	4.1	4.4	4.2	4.7	4.0
48 hr	4.5	3.8	4.0	4.2	3.7	3.6	3.1

4.6.3 The possible reactions in neutralization of low sulfate Al-bearing ARD/AMD

The soluble Al concentration in experiments without sulfate showed that the formation of Al$(OH)_3$ occurred and was completed immediately after pH was adjusted. After 30 minutes of neutralization, the soluble Al concentration of experiments without sulfate remained stable. The sludge analysis also showed the Al:OH molar ratio of sludge was close to the theoretical molar ratio of Al$(OH)_3$. These results suggested that the formation of Al$(OH)_3$ was a fast reaction and the main reaction for Al removal during Al-bearing ARD/AMD treatment. The calculation of Mineql+ chemical equilibrium computer model also showed that the SI values of amorphous $Al(OH)_3$ was close to zero in the whole experiments when sulfate was absent, which indicated the solution in equilibrium with amorphous $Al(OH)_3$ after 30 minutes of settling. In other words, most of aluminum was removed by $Al(OH)_3(am)$ precipitation.

On the other hand, in experiments with sulfate, the soluble Al concentration became lower and less than the theoretical solubility of amorphous $Al(OH)_3$ after long settling time. The calculation with the Mineql+ model shows that solution became unsaturated with amorphous $Al(OH)_3$ in the experiments when sulfate was present. The sludge analysis showed that no crystalline precipitates formed and this indicated that the reduction of Al concentration was not due to the formation of gibbsite, which is the crystalline $Al(OH)_3$ and can be transformed from amorphous $Al(OH)_3$. TGA and SEM analysis showed that sulfur content in sludge increased with sulfate concentration and settling time, which indicated that sulfate influences Al concentration neutralization of ARD by the formation of Al-sulfate. The removal rate of aluminum and sulfate in experiments showed that the primary reaction was the formation of Al-sulfate precipitates after 4 hours of neutralization and this reaction controlled the soluble Al concentration in the processes of Al-bearing ARD neutralization.

The molar ratio of Al:S in suspended particles revealed the sulfate content in suspended particles increased with settling time and it was close to the theoretical molar ratio of basaluminite. Therefore, it is reasonable to assume that the formation of basaluminite in the treatment of Al-bearing ARD is the key reaction to reduce the soluble Al concentration.

4.7 PARTICLE SIZE DISTRIBUTION

Suspended particulate Al solids are the primary Al source in effluents from active treatment systems. In order to understand the influence of suspended particulate Al solids on effluent Al concentration in Al-bearing ARD/AMD treatment, the particle sizes in the supernatants have been measured. The particle size distribution was obtained with a Microtrac S3500, which uses the tri-laser technology to measure the particle sizes. The measurement range of Microtrac S3500 is from 0.75 to 2800 micrometers.

4.7.1 The suspended particle size distribution in different experiments

Figure 4.42 shows the suspended particles size distribution in experiments without sulfate ($Al:SO_4=1:0$) after 30 minutes and 48 hours of settling at pH=6.0 and 8.0. The median diameter of suspended particles was ~ 40 and 22 μm at pH =6.0 and 8.0 after 30 minutes of settling, respectively. After 48 hours of settling, the median diameter of particles became 25 and 40 μm at pH=6.0 and 8.0, respectively. The data of particle diameter show that the median diameter of particles a pH =8 became larger, while the median diameter of particles at pH = 7 became smaller with time of settling. Most of suspended particles were still larger than 10 μm at both pH values even after 48 hours of settling. These data indicate that most suspended particles were larger size and could settle when the settling time is long enough (>48 hours).

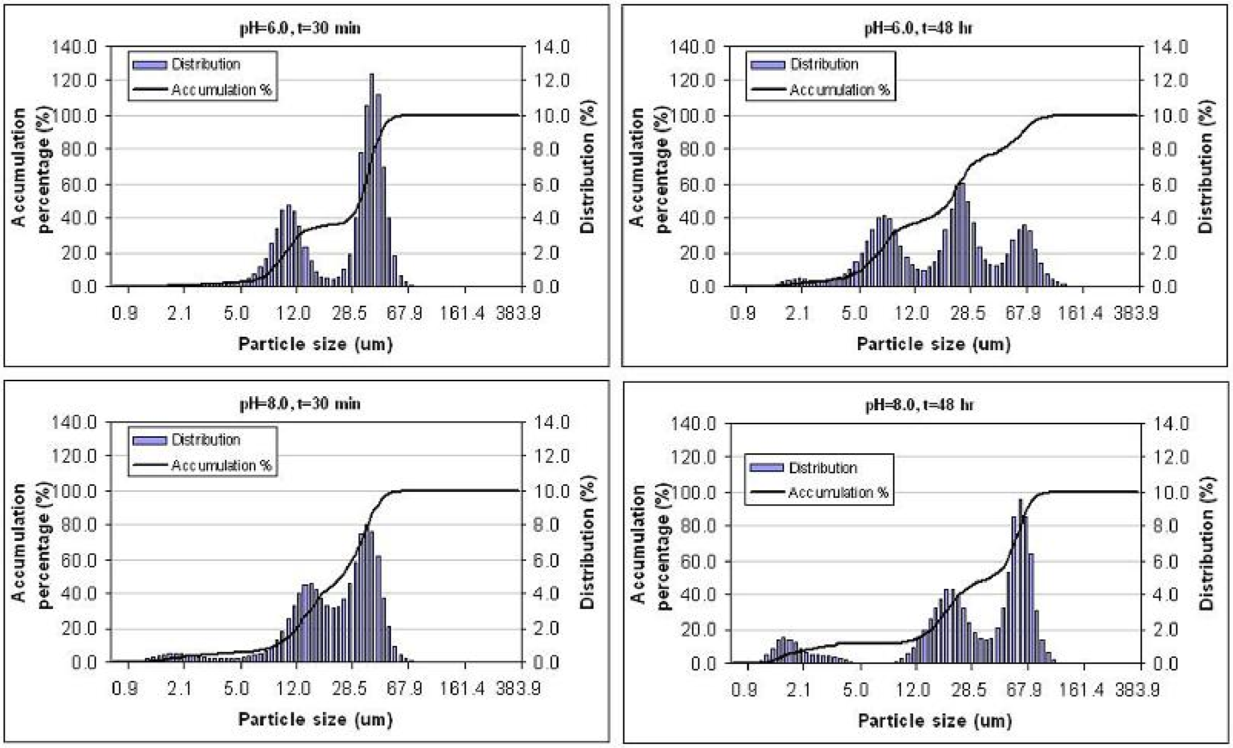


Figure 4.42 Particle size distribution in the supernatant in experiments without sulfate (Al:SO_4=1:0) at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling

Figure 4.43 shows the particle size distribution at pH =6.0 and 8.0 after 30 minutes and 48 hours of settling when molar ratio of Al:SO_4 equals 1:1. After 30 minutes of settling, 55% of particle size distribution was in the range of 30-60 μm. The median diameter of suspended particles was around 45 μm at pH=6.0 and 43.5 μm at pH=8.0. After 48 hours of settling, the median diameter of suspended particles decreased to about 2μm at both pH=6.0 and 8.0. At pH=6.0, about 77% of suspended particles were larger than 28 μm at 30 minutes, whereas about 74% of suspended particles were less than 5 μm at 48 hours. At pH=8.0, about 81% of suspended particles were larger than 28 μm at 30 minutes, whereas about 64% of particles were smaller than 5 μm at 48 hours. The data show the fraction of small sized particles in suspended particles increased with settling time in experiment of low sulfate concentration (Al:SO_4 ratio=1:1).

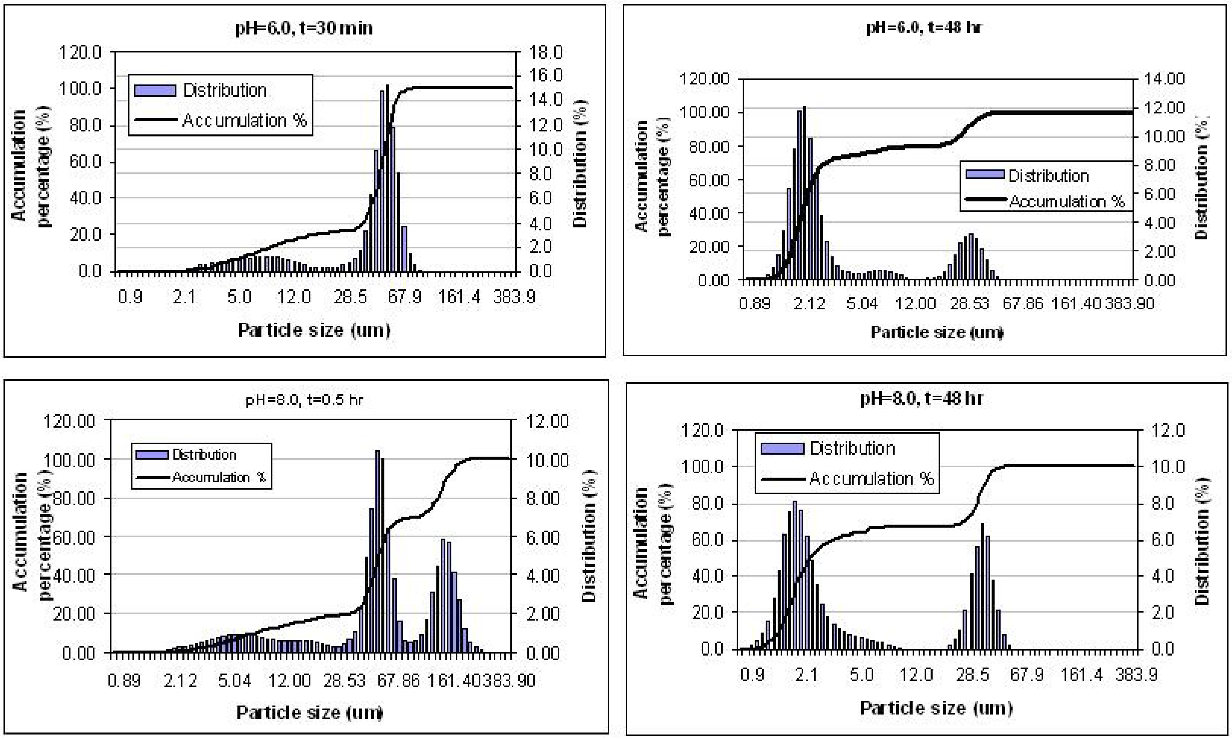


Figure 4.43 Particle size distribution in experiments with low sulfate concentration (Al:SO$_4$=1:1) at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling

Figure 4.44 presents the particle size distribution in experiments with high sulfate concentration (Al:SO$_4$=1:5) at pH=6.0 and 8.0. After 30 minutes of settling, the median diameter of suspended particles was about 24 and 35 μm at pH=6.0 and 8.0, respectively. At pH=6.0, over 50% of particles were in the range of 20 to 65 μm, whereas about 50% of the particles were in a somewhat narrower range of 20 to 50 μm at pH=8.0. After 48 hours of settling, the median diameter of suspended particles were 2 μm and 5 μm at pH=6.0 and 8.0, respectively. At pH =6.0, over 60% of the suspended particles were in the range of 1.0 to 3.0 μm, whereas about 65 % of suspended particles was in the range of 3.5 to 7.0 μm at pH=8.0. At 48 hours of settling, only about 30% and 1% suspended particles were larger than 12 µm at pH=6.0 and 8.0, respectively. In experiments without sulfate, about 65% and 85% suspended particles were larger than 12 µm at pH=6.0 and 8.0 after 48 hours of settling. Therefore, these data indicate that the suspended particle size would decrease after a long settling time when solution contained sulfate.

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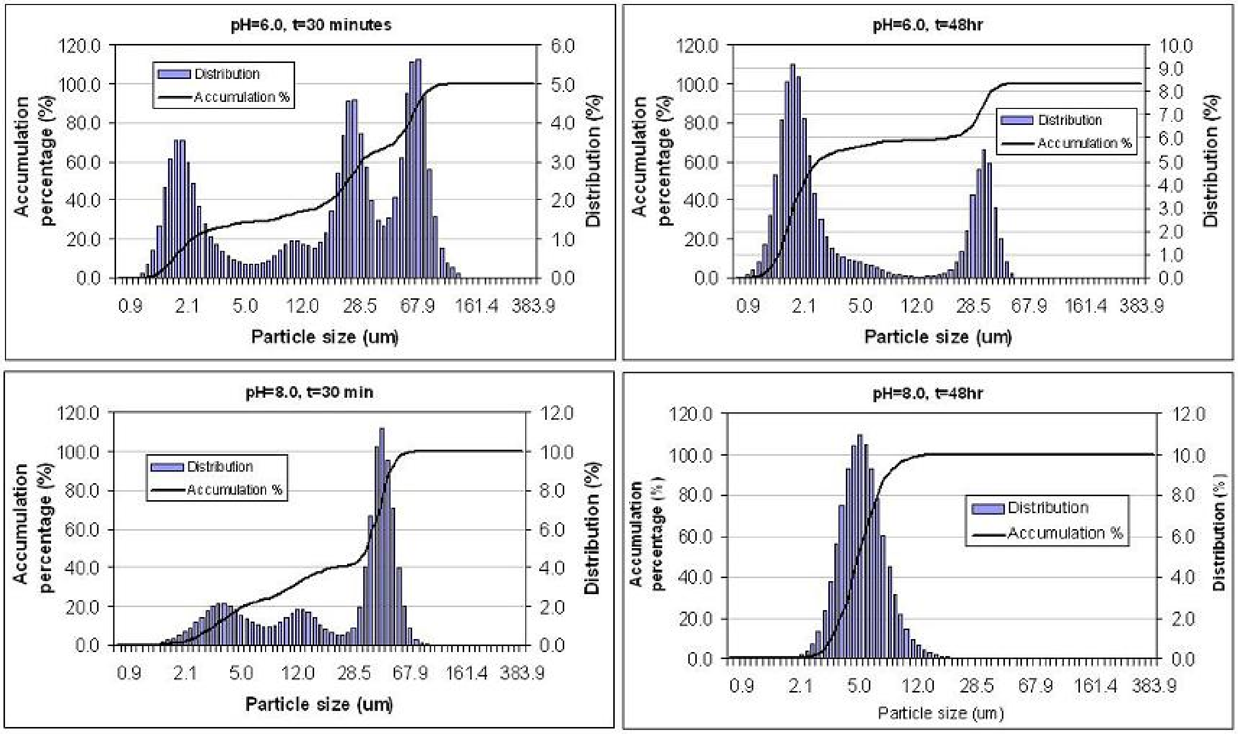


Figure 4.44 Particle size distribution in the supernatant at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling when Al:SO_4=1:5

4.7.2 Effect of suspended particle size on Al concentration

As discussed in Section 4.2.3, the suspended Al concentration was reduced when solution contained sulfate. Figure 4.45 shows the relationship of the suspended Al concentration to the suspended particle size. Form Figure 4.45, it can be seen that the low suspended Al concentration occurred in experiments without sulfate, corresponding with larger suspended particles in the supernatant. As described in last section, when solution did not contain sulfate, about 65% and 85% of suspended particles were larger than 12 μm at pH =6.0 and 8.0 after 48 hours of settling, respectively. The large particle size indicates the better settling characteristics.

At pH=6.0, the suspended Al concentration was 0.30 and 0.28 mg/L when solution contained low and high sulfate concentration, respectively, whereas the suspended Al concentration was 0.39 and 0.45 mg/L at pH=8.0. The suspended Al concentration did not show a significant difference between the experiments with low and high sulfate concentration. The similar phenomenon could be found in the suspended particle size distribution. At pH=6.0, only about 20% and 30% of suspended particles were larger than 12 μm after 48 hours of settling in experiments with low and high sulfate concentration, respectively. At pH=8.0, only about 30% and 1% of suspended particles were larger than 12 μm.

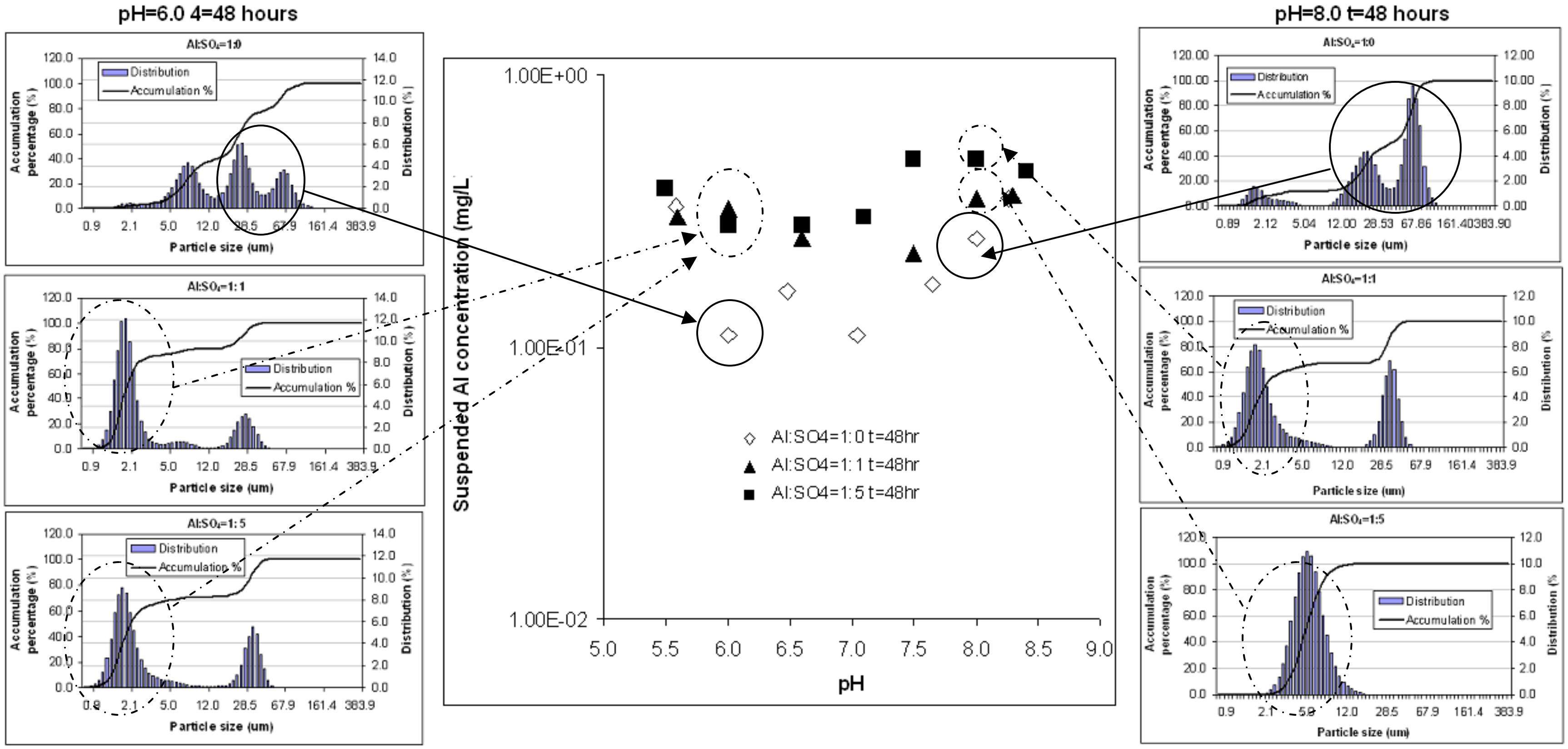


Figure 4.45 Effect of suspended particles size on suspended Al concentration in experiments

Assuming the density of smaller suspended particles was the same as the larger suspended particles, the contribution of suspended particles to suspended Al concentration was calculated. At pH =6.0, after 30 minutes of settling, about 0.16 and 0.18 mg/L of suspended Al concentration was contributed by the suspended particles that were less than 5 μm in experiments with low and high sulfate concentration, respectively, which was only ~14 % and 12% of the <u>suspended</u> Al concentration. After 48 hours of settling, about 0.24 and 0.19 mg/L of suspended Al concentration was contributed by the small suspended particles (<5 μm) in experiments with low and high sulfate concentration, respectively, which was 75.5% and 68% of total suspended Al concentration. Furthermore, compared with the concentration at 30 minutes, it can be found that the amount of smaller suspended particles at 48 hours was more than at 30 minutes when solution contained sulfate, which indicates the number of smaller suspended particles (<5 μm) increased with settling time at pH=6.0. When solution did not contain sulfate, the suspended Al concentration was 0.04 mg/l and 0.01 mg/L was contributed by small suspended particles (<5 μm) after 30 minutes and 48 hours of settling, respectively, which indicates that the amount of small suspended particles decreased with settling time when solution did not contain sulfate at pH=6.0

At pH=8.0, 0.07 and 0.22 mg/L of suspended Al concentration was contributed by the small suspended particles after 30 minutes of settling in experiments with low and high sulfate concentration, respectively. After 48 hours of settling, the smaller suspended particles (<5 μm) contributed about 0.23 and 0.26 mg/L of suspended Al concentration in experiments with low and high sulfate concentration, respectively. in experiments without sulfate, small particles contributed about 0.06 and 0.03 mg/L suspended Al concentration after 30 minutes and 48 hours of settling, respectively. These data indicate that amount of smaller suspended particles also increased with settling time at pH=8.0. Therefore, it is reasonable to conclude that the increase of suspended Al concentration with elevated sulfate levels was due to the increase of small suspended Al solids, which can remaining in solution. According to the analysis in Section 4.6.2, the main species of suspended particles changed to basaluminite when settling time was longer than 24 hours. Therefore, it was concluded that the formation of basaluminite after 24 hours to form small Al-sulfate particles, which remained in solution to cause the increase of, suspended Al solids.

4.7.3 The relationship of reaction rate to suspended particle size

Figure 4.46 shows the change of Al concentration with settling time in experiments with low and high sulfate concentration at pH=6.0 and 8.0. From the semi-log plots of Al concentration vs. settling, it is observed that two phenomena occurred in experiments: one was for the first 2 hours of setting, and the other was from 4 hour to 48 hours of settling. In the first 2 hours, Al concentration reduced quickly, which indicates the faster reaction rate occurred. From 4 to 48 hours, the Al concentration changed slowly, which indicates a slower settling rate occurred.

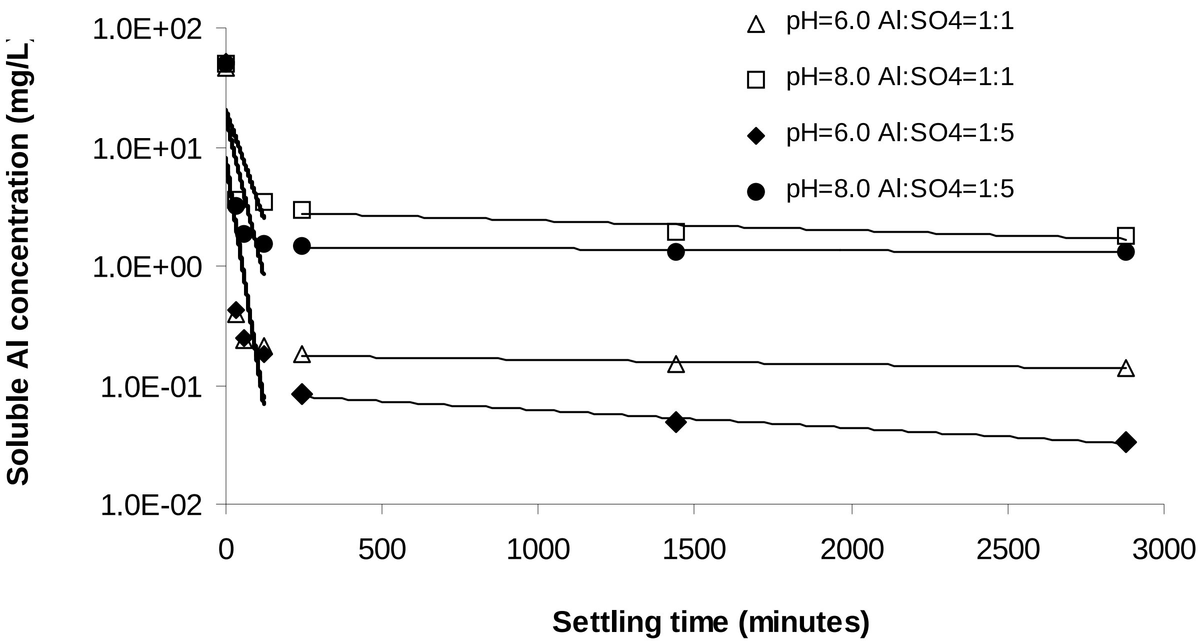


Figure 4.46 Change of Al concentration with settling time in the experiments with low and high sulfate concentration (Al:SO4=1:1 and 1:5， respectively)

In experiments with low sulfate, the particle size analysis showed that at 30 minutes, about 75% and 80% suspended particles was larger than 28 μm at pH=6.0 and 8.0, respectively, whereas only about 14% and 7% suspended particles was less than 5 μm at pH=6.0 and 8.0, respectively. After 48 hours, about 7.5% and 26% suspended particles was larger than 28 μm at pH=6.0 and 8.0, respectively, but about 75.5% and 65% of suspended particles was less than 5 μm. These suspended particle size distribution showed that most suspended particles was larger at 30 minutes, whereas most suspended particles was small at 48 hours.

In experiments with higher sulfate concentration (Al:SO_4=1:5), after 30 minutes of settling, about 45% and 60% suspended particles was larger than 28 μm, whereas only about 12% and 15% suspended particles was smaller than 5 μm at pH=6.0 and 8.0, respectively. After 48 hours of settling, only 20% and 0% suspended particles was large than 28 μm, whereas about

70% and 55% suspended was smaller than 5 μm at pH=6.0 and 8.0. These suspended particle sizes also indicate that the suspended particle size reduced with settling time.

Combined with the information of reaction rate, it can be found that the faster reaction rate corresponded with the larger suspended particles, which indicate the quicker settling rate. This phenomenon occurred at the first 2 hours after pH adjustment. The slow reaction rate occurred at the time from 4 hours to 48 hours of settling corresponding with the small suspended particles, which indicate the slow settling rate. In Section 4.4.2, it was concluded that the main reaction was the formation of amorphous Al(OH)3 within the first 2 hours of settling, and after 4 hours, the primary reaction was the formation of Al-sulfate precipitates (basaluminite). Therefore, it is concluded that the formation of $Al(OH)_3$ occurred faster and the precipitates could be combined to form large particles, which was easy to settle down. The formation of Al-sulfate precipitates was slow accompanying the formation of small Al-sulfate precipitates, which were difficult to settle.

4.7.4 Factors that influence suspended particle sizes

Table 4.8 presents the data of median diameter of suspended particles and main range of suspended particles size after 30 minutes and 48 hours. At pH=6.0, the median diameter of suspended particles was 40, 45, and 24 μm after 30 minutes of settling in experiments with the ratio of $Al:SO_4$ equal to 1:0, 1:1, and 1:5, respectively. The median particle diameter did not show a significant change in experiments with or without sulfate after short settling time, although the median diameter of particles in experiments with high sulfate concentration ($Al:SO_4$=1:5) was slightly smaller than others. After 48 hours of settling, the median diameter of suspended particles in experiments without sulfate reduced to 25 μm, whereas the median diameter of suspended particles reduced to 2.0 and 2.0 μm in experiment with Al:SO$_4$ ratio equal to 1:1 and 1:5, respectively. In the experiments when sulfate was present, most of suspended particles (>60%) were in the range of 1.0 to 3.0 μm, whereas most of particles (80%) were larger than 10 μm in experiments without sulfate.

Table 4.8 The median diameter and main fractional scale of suspended particles size distribution at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling (diameter: μm)

Al:SO$_4$	**pH=6.0**				**pH=8.0**			
	Median size		Main range of particle size (proportion percentage %)		Median size		Main range of particle size (proportion percentage %)	
	30 min	48hr	30 min	48hr	30 min	48hr	30 min	48hr
1:0	40	25	30-50 (55%)	10-40 (~80%)	22	40	5-10 (20%), and 15-50 (40%)	15-30 (35%), and 45-80 (35%)
1:1	45	2.0	30-60 (50%)	1.3-3.0 (60%)	45	2.0	40-55 (50%)	1.0 – 5.0 (65%)
1:5	24	2.0	20-65 (50%)	1.0-3.0 (60%)	35	5.0	20-50 (50%)	3.5-7.5 (65%)

At pH=8.0, the median diameter of suspended particles was 22, 45, and 35 μm after 30 minutes of settling in experiments with the ratio of Al:SO$_4$ equal to 1:0, 1:1, and 1:5, respectively. The median diameter of suspended particles in experiments without sulfate was relative small at pH=8.0 after 30 minutes of settling. After 48 hours of settling, the median diameter of suspended particles became 40, 2.2, and 5.0 μm in experiments of Al:SO$_4$= 1:0, 1:1, and 1:5, respectively. The median diameter of particles in experiments with sulfate became smaller than that in experiments without sulfate. Meanwhile, most of suspended particles were in the range of 1.0 to 5.0 µm and 3.5 to 7.0 µm when the ratio of Al:SO_4 equal to 1:1 and 1:5, respectively, whereas 90% of suspended particles were larger than 10 µm in experiments without sulfate. The median diameter of suspended particles and particle size distribution at pH=6.0 and 8.0 shows that suspended particle size decreased after a long settling time (48 hours) when solution contained sulfate. The probable reason was that the formation of basaluminite, which was in small size and became the main species of suspended particles.

Table 4.9 shows the suspended Al and sulfate concentration after 30 minutes and 48 hours of settling. After 30 minutes of settling, suspended Al concentration was 1.69, 1.15, 1.59 at pH=6.0 and 1.10, 1.01, and 1.36 at pH=8.0 in experiments with ratio of Al:SO_4 equal to 1:0, 1:1, and 1:5, respectively. When settling time was 48 hours, the suspended Al concentration was 0.11, 0.32, and 0.28 mg/L at pH=6.0 and 0.25, 0.35, and 0.49 mg/L at pH=8.0 corresponding to the ratio of Al:SO_4 equal to 1:0, 1:1, and 1:5, respectively. The suspended Al concentration was higher when sulfate was present, although the suspended particle size was smaller. In other words, the presence of sulfate reduced the size of suspended particulate Al solids and remained them in the supernatant, following with a relative high-suspended Al concentration. According to the discussion in Section 4.6, the molar ratio of Al:SO_4 of suspended particles over settling indicated that the primary reaction was the formation of basaluminite and the main species of suspended particles was basaluminite after 24 hours of settling when sulfate was present in solution. Therefore, it can be concluded that the suspended basaluminite particles in the supernatant were small and can remain in the supernatant for long time after neutralization of Al-bearing ARD/AMD.

Table 4.9 Suspended Al and sulfate concentration at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling

		pH=6.0			**pH=8.0**		
Al:SO_4	Setting time	Al (mg/L)	SO_4 (mg/L)	Al:SO_4 (molar ratio)	Al (mg/L)	SO_4 (mg/L)	Al:SO_4 (molar ratio)
1:0	30 min	1.69			1.10		
	48 hr	0.11			0.25		
1:1	30 min	1.15	0.17	24.0	1.01	0.26	13.8
	48 hr	0.32	0.231	4.9	0.35	0.32	3.9
1:5	30 min	1.59	0.31	7.1	1.36	0.64	7.6
	48 hr	0.28	0.28	3.8	0.49	0.49	3.6

4.8 SUMMARY AND CONCLUSIONS

This chapter has evaluated the effects of sulfates on Al removal during Al-bearing ARD/AMD treatment. Laboratory experiments were conducted to evaluate the effects of sulfates on both suspended and soluble Al concentrations in a laboratory synthesized Al-bearing acidic rock discharge with different Al:SO_4 molar ratios (1:0, 1:1, and 1:5) at different pH values. The results suggested that pH is a critical parameter during Al-bearing ARD treatment and increasing pH (from neutral value) would result in increase of soluble aluminum concentrations even after extended (48 hour) settling times.

The influences of sulfates alone on soluble and suspended aluminum appeared to be of secondary importance as compared to the overall influence of pH. The presence of sulfates in solution reduced the soluble Al concentration, with concomitant formation of small sized Al-sulfate particles, which mainly basaluminite. The reduction of soluble Al concentration by the formation of basaluminite appeared after a long settling time (>4 hours). When the sulfate was absent in solution, the soluble Al concentration was almost constant after 30 minutes of settling. However, elevated sulfates concentrations increased the formation of small suspended particulate Al solids, which could remain in the supernatant for long time and thus increase the suspended Al concentration, even if the total concentration might reduce after long settling time.

Saturation index (SI) values calculated by using MINEQL+ computerized equilibrium model showed that solution could be in equilibrium with amorphous $Al(OH)_3$ within the first 30 minutes, following in unsaturated with amorphous $AL(OH)_3$ if sulfates was present in solution.

Sludge analysis with XRD revealed that no crystalline precipitates were produced in experiments. This result indicated that the reduction of soluble Al concentration was not due to the formation of gibbsite (crystalline $Al(OH)_3$). Furthermore, TGA and SEM analysis showed that sulfate content in sludge increased with settling time and the initial sulfate concentration. The sulfate content in sludge indicated that Al-sulfate precipitation occurred in experiments and resulted in soluble Al concentration reduction to be less than the theoretical solubility of amorphous $Al(OH)_3$.

Reduction rate of aqueous aluminum and sulfate with settling time revealed that the formation of $Al(OH)_3$ was the main precipitate product occurring within the first 30 minutes of neutralization. When sulfates was present, the primary reaction after 4 hours of settling became the formation of Al-sulfate precipitates, which mainly basaluminite. The formation of basaluminite caused the reduction of soluble Al concentration after a long settling time (48 hours).

The molar ratio of Al:SO_4 of suspended particles showed composition of suspended particles became unchanged after 24 hours of settling. The value of molar ratio of Al:SO_4 of suspended particles in the supernatant was close value of Al:SO_4 in basaluminite. Based on these results, it is concluded that the formation of basaluminite is the key reaction to reduce the soluble Al concentration and the main species of suspended Al solids in the supernatant was basaluminite after 24 hours of setttling.

Suspended particle size distributions revealed that the presence of sulfate reduced the suspended particle sizes in the supernatant yielding a relative higher suspended Al concentration. By comparing the particles size after 30 minutes and 48 hours of settling, it was found that pH alone did not influence the suspended particle size in the supernatant. The reduction of suspended particle sizes were companied with the increase of sulfate ratio in the suspended particles. It is concluded that the Al-sulfate precipitates (basaluminite) tended to remain in the supernatant as small sized particles and thus increase the total effluent Al concentration from active ARD treatment system.

5.0 EFFECT OF SILICATE ON ALUMINUM SPECIATION AND CONCENTRATION DURING ACTIVE TREATMENT OF ARD

5.1 INTRODUCTION

As mentioned above, the precipitation of aluminum from natural ARD and/or AMD is complex. The possible aluminum precipitates formed as a consequence of pH adjustment of ARD/AMD are not only aluminum hydroxides, but also Al-hydroxyl-sulfate (Herrmann and Baumgartner, 1992; Taylor *et al*. 1997; Bigham and Nordstrom, 2000; Kim and Kim, 2003a) and hydroxyaluminosilicate (Sullivan and Drever, 2001). In Chapter 4, effects of sulfate on Al concentration and species of precipitates have been investigated. Besides sulfate, soluble silicate can also influence the precipitation of aluminum in water. Interactions between silicic acid and aluminum can occur over wide concentration ranges (Exley and Birchall, 1992; Farmer and Lumsdon, 1994; and Brace and Matijevic, 1977) and may lead to the formation of hydroxyaluminosilicate (HAS) precipitates or co-precipitates with other precipitates (Duan and Gregory, 1996 and 1998).

In natural waters, the concentration of silicate (as SiO_2) reported by investigators is typically in the range 1-150mg/L (Siever, 1953; Alexander *et al*., 1954; Stoeber, 1967; Brace and Matijevic, 1977; Clesceri *et al*., 1989). Therefore, it is important to understand the effects of silicate and the interactions between silicate and sulfate on Al concentration and removal efficiency during Al-bearing ARD/AMD treatment processes.

In Chapter 4, experimental results indicated that the presence of sulfate reduced the soluble Al concentration by formation of Al-sulfate precipitates, basaluminite. However, when both silicate and sulfate are present in solution, the possible species of Al-precipitates include $Al(OH)_3$, Al-sulfate, and Al-silicate. Since ARD/AMD contains high sulfate concentration, it is also important to understand the interactions between sulfate and silicate. In this study, results from three series of laboratory experiments are presented. The molar ratio of $Al:Si:SO_4$ equal to 1:1:0, 1:1:5, and 1:2.5:5 were selected to evaluate the effects of sulfate and silicate on Al concentration during Al-bearing ARD neutralization. Final pH values were in the range of 5.5 to 8.5. The sludge was collected at short (30minutes) and long (~48 hours) times of settling. These sludge samples were analyzed with a scanning electron microscope (SEM), equipped with an energy-dispersive X-ray spectrometer (EDS).

This chapter presents the results for experiments of the effect of silicate on Al concentration and discusses the interactions of sulfate and silicate on Al concentration during ARD/AMD neutralization. First, total and soluble aluminum concentrations at different pH after different settling time in the experiments are presented, following the results of sludge analysis to show the characteristics of sludge formed on different conditions. The effect of silicate on particle size of suspended Al-solids is also evaluated.

5.2 THE CHANGE OF SOLUBLE ALUMINUM CONCENTRATION WITH SILICATE AT DIFFERENT pH VALUES

5.2.1 Soluble Al concentration at different pH and silicate concentrations

Three different sets of batch experiments had been conducted to evaluate the influence of silicate on soluble and total Al concentrations that could exist in Al-bearing ARD/AMD treatment system with NaOH. The molar ratios of Al:Si:SO_4 were 1:1:0, 1:1:5, and 1:2.5:5, respectively. The initial Al concentration was controlled to be 25mg/L. As mentioned above, water and precipitate samples were collected after 30 minutes and 48 hours. This section presents the soluble and total Al concentrations at different pH values after 30 minutes and 48 hours of settling under different molar ratios.

5.2.1.1 Soluble Al concentration in experiments of the molar ratio of Al:Si:SO_4=1:1:0

Figure 5.1 presents the soluble Al concentrations after 30 minutes and 48 hours of settling at different pH values when sulfate was absent and silicate concentration was low (Al:Si:SO_4=1:1:0). The data are present in Table 5.1. Soluble Al concentrations in these experiments varied with pH. After 30 minutes of settling, at pH from 6.0 to 7.2, soluble Al concentration was in the range of 0.16 to 0.34 mg/L. The minimum soluble Al concentration was 0.16 mg/L occurred at pH=6.4. At pH ≥ 8.0, the soluble Al concentrations increased to more than 2 mg/L. This is different from the case where the pH = 6.0 to 7.2, which the soluble Al concentration was 0.34 mg/L and 0.68 mg/L, respectively. The soluble Al concentration increased sharply as the pH increased beyond 7.6.

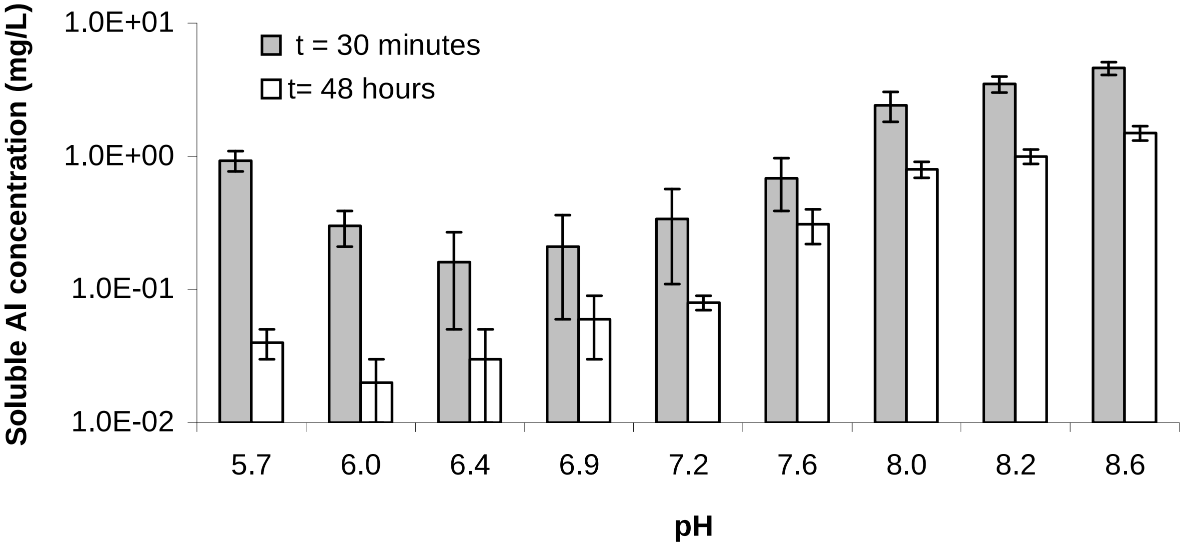


Figure 5.1 Soluble Al concentration in experiment with Al:Si:SO_4=1:1:0 after 30 minutes and 48 hours of settling

Soluble Al concentration decreased after 48 hours of settling. Soluble Al concentration became very low in the range of pH = 5.7 to 7.2. At pH from 5.7 to 7.2, all the soluble Al concentrations were less than 0.1 mg/L and in the range of 0.02 to 0.08 mg/L. Compared with concentration at low pH (≤ 7.2), soluble Al concentration was relative high when pH ≥ 8.0. In Table 5.1, it can be seen that soluble Al concentration was 0.8 to 1.5 mg/L at pH =8.0 to 8.6. This indicates that pH control is critical to meet low aluminum discharge levels from the settling tank, and wet weather conditions (simulated by the 30 minutes settling time) would result in relative high effluent soluble Al concentration.

The soluble Al concentration decreased from 30 minutes to 48 hours of settling indicating that the solution was not in equilibrium condition after only 30 minutes of settling. Since the information shown above suggests that gibbsite is not a possible precipitate in experiments, the possible Al-precipitates in this experiment are amorphous Al$(OH)_3$ and Al-silicate precipitates. The soluble Al concentration after 30 minutes of settling indicated the formation of Al-silicate precipitates causing the reduction of soluble Al concentration to be less than the theoretical solubility of amorphous Al$(OH)_3$.

Table 5.1 Total and soluble Al concentration after 30 minutes and 48 hours of settling at different pH (mg/L)

Al:Si:SO_4=1:1:0					**Al:Si:SO_4=1:1:5**					**Al:Si:SO_4=1:2.5:5**				
Settling time	30 minutes		48 hours			30 minutes		48 hours			30 minutes		48 hours	
pH	Total	Soluble	Total	Soluble	**PH**	Total	Soluble	Total	Soluble	**pH**	Total	Soluble	Total	Soluble
5.7	1.44	0.93	0.21	0.04	5.6	2.03	1.26	0.44	0.04	5.6	3.03	1.16	1.35	0.14
6.0	1.40	0.30	0.21	0.02	6.0	1.58	0.45	0.24	0.02	6.0	1.86	0.41	1.22	0.01
6.4	1.12	0.16	0.21	0.03	6.4	1.18	0.31	0.24	0.02	6.7	2.04	0.29	1.15	0.01
6.9	1.23	0.21	0.22	0.06	6.9	1.21	0.27	0.27	0.03	7.1	1.97	0.25	1.18	0.02
7.2	1.09	0.34	0.22	0.08	7.3	1.73	0.57	0.33	0.13	7.6	3.24	1.3	1.32	0.12
7.6	1.49	0.68	0.48	0.31	7.8	2.48	1.78	0.53	0.24	8.0	4.27	2.14	1.49	0.21
8.0	3.51	2.42	1.07	0.80	8.0	3.81	2.40	0.64	0.31	8.6	7.68	4.47	2.65	0.40
8.2	4.42	3.51	1.36	1.00	8.4	5.37	4.32	0.64	0.33					
8.6	5.41	4.62	1.89	1.50										

5.2.1.2 Soluble Al concentration in experiments of the molar ratio of Al:Si:SO_4=1:1:5

Figure 5.2 shows soluble Al concentration at different pH and settling time in experiments with low silicate and high sulfate concentration (Al:Si:SO_4=1:1:5). The data are present in Table 5.1. After 30 minutes of settling, soluble Al concentration changed from 0.27 to 0.57 mg/L in pH range of 6.0 to 7.3. These soluble Al concentrations were slightly higher than the soluble Al level in experiments without sulfate. Similar to the experiments of sulfate absent, soluble Al concentration appeared a relative higher level when pH was higher (≥8.0). At pH from 7.8 to 8.4, soluble Al concentrations were from 1.78 to 4.32 mg/L after 30 minutes of settling.

After 48 hours of settling, all the soluble Al concentrations decreased sharply and became very low at pH in the range of 5.6 to 7.3, which was similar to the soluble Al concentrations in experiments without sulfate after long settling time. These data implied that the presence of sulfate did not significantly influence the soluble Al concentration when silicate was present at low pH levels. At high pH level, soluble Al concentrations were 0.31 and 0.33 mg/L at pH=8.2 and 8.4, respectively. These Al concentrations were much lower than those in experiments without sulfate (1.07 mg/L at pH=8.0 and 1.36 at pH=8.2), which indicated that the presence of sulfate could decrease the soluble Al concentration at pH ≥ 8.

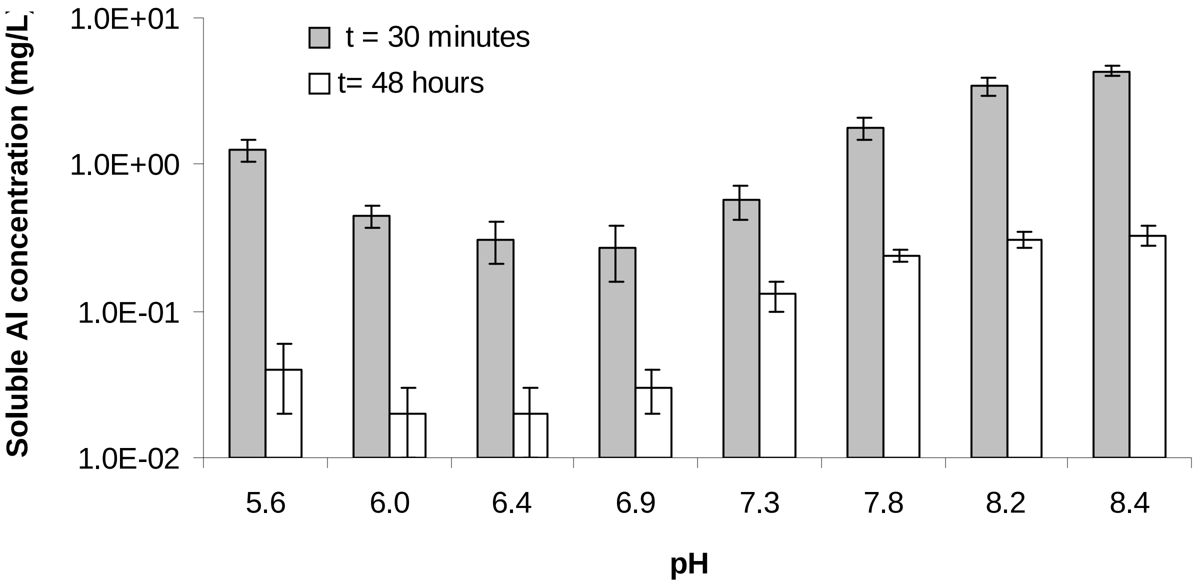


Figure 5.2 Soluble Al concentration in experiment of Al:Si:SO_4=1:1:5 after 30 minutes and 48 hours of settling

5.2.1.3 Soluble Al concentration in experiments of the molar ratio of Al:Si:SO_4=1:2.5:5

Figure 5.3 presents soluble Al concentration at different pH values after 30 minutes and 48 hours of settling in experiments with high silicate and sulfate concentrations (Al:Si:SO_4=1:2.5:5) and data were shown in Table 5.1. At pH=6.0 to 7.1, soluble Al concentrations were in the range of 0.25 to 0.41 mg/L after 30 minutes of settling, which was in the same level as in experiments with low silicate concentration (with and without sulfate). The soluble Al concentration was 1.16 mg/L at pH = 5.6, and increased from 1.3 to 4.47 mg/L when pH > 7.5.

After 48 hours of settling, soluble Al concentration decreased to no more than 0.02 mg/L at pH=6.0 to 7.1, whereas soluble Al concentration was 0.12, 0.21, and 0.40 mg/L at pH=7.6, 8.0, and 8.6, respectively. In Figure 5.3, it can be seen that the soluble Al concentration was in a low level at high pH range (>7.5) after 48 hours of settling.

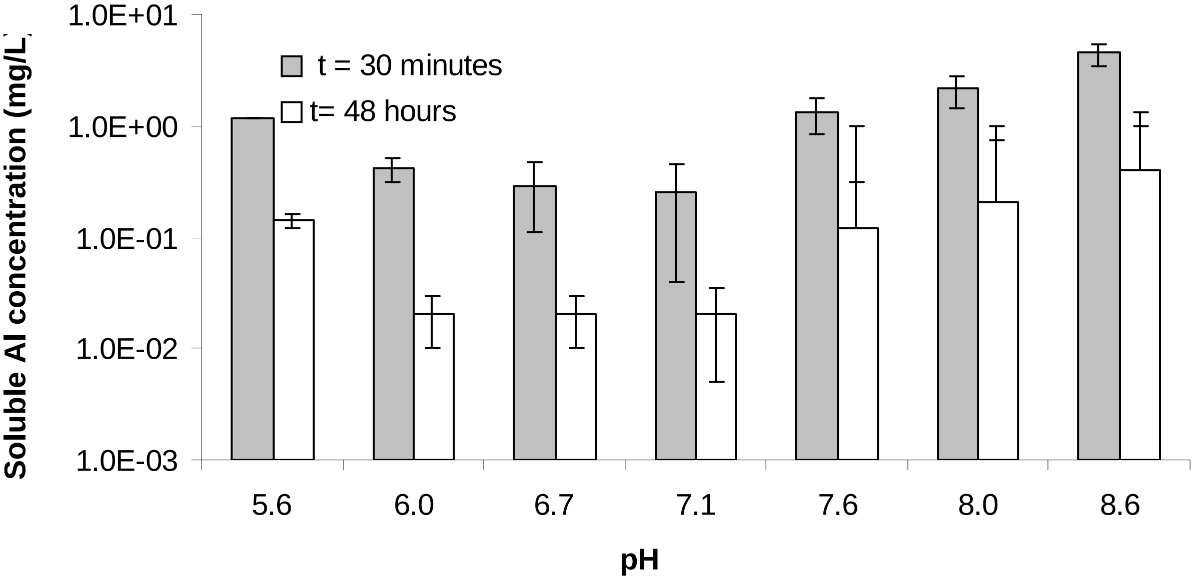


Figure 5.3 Soluble Al concentration in experiment of Al:Si:SO_4=1:2.5:5 after 30 minutes and 48 hours of settling

5.2.1.4 The interactive effect of silicate and sulfate on soluble Al concentration

Figure 5.4 shows the soluble Al concentration at pH =6.0 and 8.0 after 30 minutes and 48 hours of settling in experiments with molar ratio of Al:Si:SO_4 equal to 1:0:0, 1:0:5, 1:1:0, and 1:1:5. From Figure 5.4, it can be seen that compared with experiments without both sulfate and silicate, soluble Al concentration decreased after 48 hours of settling when sulfate and/or silicate was present. Furthermore, soluble Al concentration was lower when silicate was present. At high pH (=8.0), the soluble Al concentration was lowest when both sulfate and silicate were present in solution. The results indicated the silicate reduced the effluent soluble Al concentration during neutralization of Al-bearing ARD/AMD.

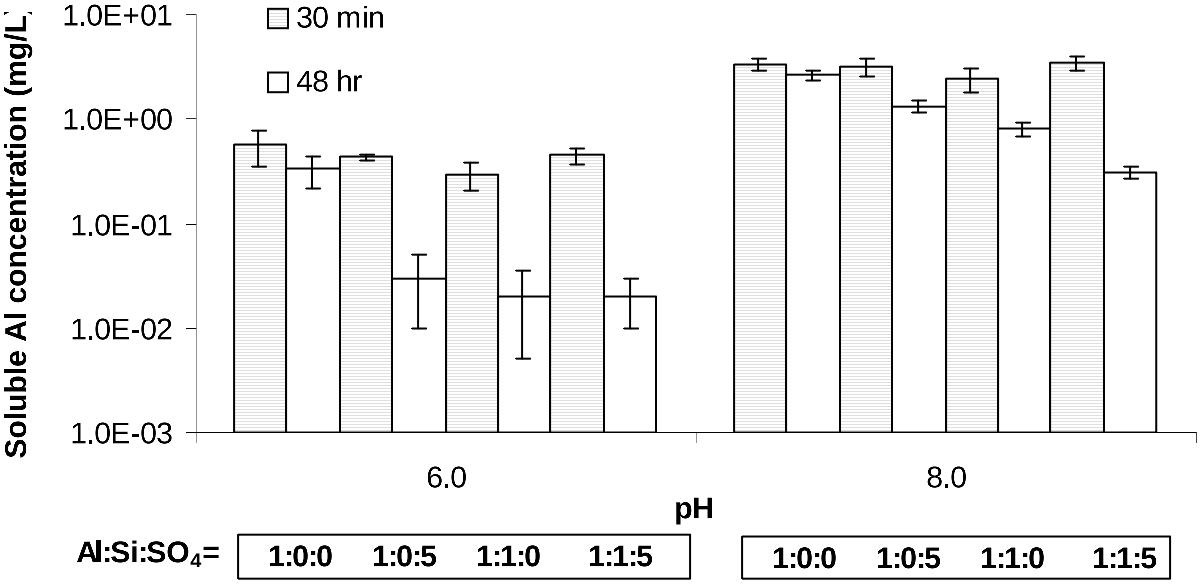


Figure 5.4 Soluble Al as influenced by silicate and sulfate at pH = 6.0 and 8.0, at settling times of 30 minutes and 48 hours at designated molar ratios of Al:Si:SO_4

Figure 5.5 presents soluble Al concentration in experiments with different silicate concentrations (Al:Si:SO_4 equal to 1:1:0, 1:1:5, and 1:2.5:5) at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling. After 30minutes of settling, soluble Al concentration was in the range of 0.30 to 0.45 mg/L at pH=6.0, and 2.14 to 3.41 mg/L at pH=8.0. After 48 hours of settling, soluble Al concentration reduced to 0.01~0.02 mg/L at pH=6.0, and 0.21~0.80 mg/L at pH=8.0. These experimental results showed that soluble Al concentration at pH=6.0 was much lower than those at pH=8.0 after both 30 minutes and 48 hours of settling. These data suggest that the pH is the most important parameter for controlling final soluble Al concentration during Al-bearing ARD/AMD treatment.

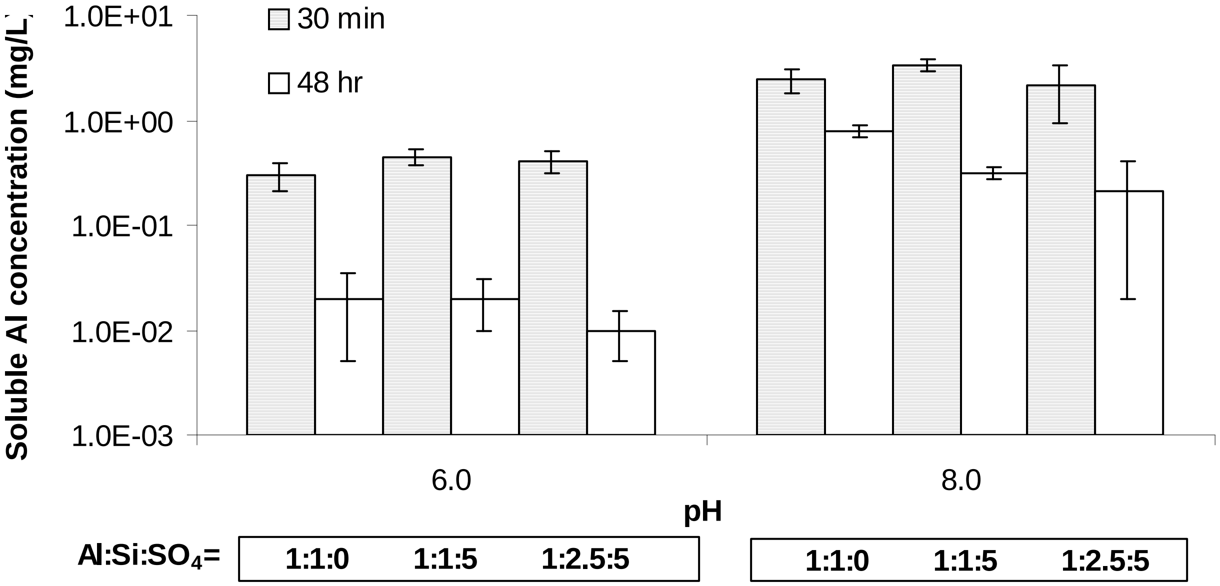


Figure 5.5 Soluble Al concentration at pH=6.0 and 8.0 after different settling time under different silicate concentrations

At pH=6.0, when solution contained low silicate concentration (Al:Si=1:1), soluble Al concentration had no significant difference when sulfate was present or absent after 48 hours of settling. However, when silicate concentration was high (Al:Si=1:2.5), soluble Al concentration was lower compared with that in experiments with low silicate concentration. At pH=8.0, when silicate concentration was low, the presence of sulfate reduced soluble Al concentration too. In experiments with the same sulfate concentration, high silicate level reduced the soluble Al concentration. These results indicated that both sulfate and silicate and combination of them reduced the soluble Al concentration in neutralization of Al-bearing ARD/AMD.

Saturation Index

The SI values of amorphous $Al(OH)_3$ in experiments were -0.19, -0.15, and -0.14 at pH=6.0, and -0.11, -0.04, and -0.16 at pH=8.0 when $Al:Si:SO_4$ ratios equal to 1:1:0, 1:1:5, and

1:2.5:5 after 30 minutes of settling, respectively. Different from SI values in experiments without silicate, all the SI values were negative when silicate was present in solution, although the values were not much lower than zero. The SI values indicated that the solutions were unsaturated with amorphous $Al(OH)_3$ within the first 30 minutes after pH adjustment when silicate was present. In other words, the reduction of soluble Al concentration was not only due to the formation of amorphous $Al(OH)_3$, but also the formation of Al-silicate precipitates. After 48 hours of settling, the SI values of amorphous $Al(OH)_3$ reduced to -1.37, -1.45, and -0.60 at pH=6.0, and -0.59, -1.00, and -0.89 at pH=8.0 when $Al:Si:SO_4$ ratios equal to 1:1:0, 1:1:5, and 1:2.5:5, respectively. The reduction of SI values of amorphous $Al(OH)_3$ was due to the reduction of soluble Al concentration. Since the solutions were unsaturated with amorphous $Al(OH)_3$ within the first 30 minutes after pH adjustment, the reduction of soluble Al concentration from 30 minutes to 48 hours of settling was attribute to the formation of Al-silicate and/or Al-sulfate precipitates.

5.2.2 Total Al concentration at different pH values and silicate concentrations

5.2.2.1 Total Al concentration in experiments of the molar ratio of $Al:Si:SO_4$=1:1:0

Figure 5.6 shows the change of total Al concentration (soluble + suspended) with pH and settling time in experiments without sulfate ($Al:Si:SO_4$=1:1:0) and data is listed in Table 5.1. In Figure 5.6, it can be seen that total Al concentration appeared little change, which was in the range of 1.09 to 1.49 mg/L at pH=5.7 to 7.6 after 30 minutes of settling. At pH ≥ 8.0, total Al concentration increased with pH value increasing and was 3.51, 4.42, 5.41 mg/L at pH=8.0, 8.2, and 8.6, respectively. Increasing of settling time (after 48 hours), total Al concentration decreased to ~0.22 mg/L at pH = 5.7 to 7.2. At this pH range, total Al concentrations were almost a constant. At high pH level, total Al concentration was 1.07, 1.36, and 1.89 mg/L at pH=8.0, 8.2, and 8.6, respectively.

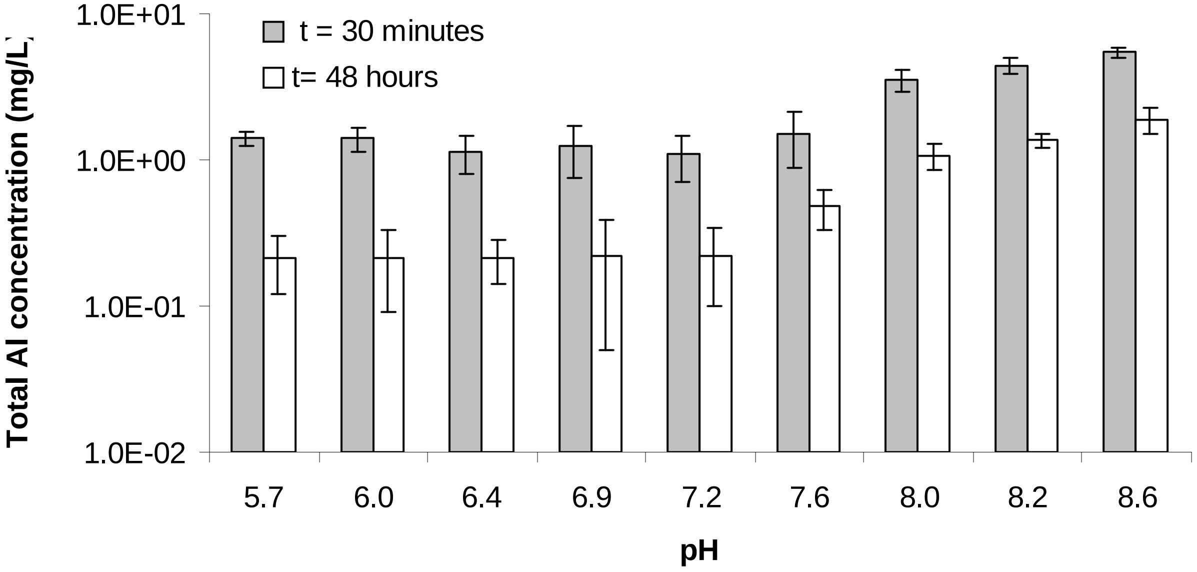


Figure 5.6 Total Al concentration in experiments of Al:Si:SO_4 = 1:1:0 after 30 minutes and 48 hours of settling

5.2.2.2 Total Al concentration in experiments of the molar ratio of Al:Si:SO_4=1:1:5

Figure 5.7 shows total Al concentration in experiments with molar ratio of Al:Si:SO_4=1:1:5 after 30 minutes and 48 hours of settling. After 30 minutes of settling, total Al concentration was in the range of 1.18 to 2.03 mg/L at pH=5.6 to 7.3, whereas total Al concentration was 2.48, 3.81, and 5.37 mg/L at pH=7.8, 8.2, and 8.4, respectively. After 48 hours of settling, total Al concentration was in the range of 0.24 to 0.33 mg/L at pH = 5.6 to 7.3, whereas total Al concentration was in the range of 0.53 to 0.64 mg/L at pH=7.8 to 8.4. Total Al concentration at high pH levels ($\geq$8.0) in these experiments showed a relative lower concentration than those in experiments without sulfate. In pH range of 8.0 to 8.6, total Al concentration was in the range of 1.07 to 1.89 mg/L in experiments without sulfate, which was higher than 1.0 mg/L (Figure 5.6). The reduction of total Al concentration was primarily due to the reduction of soluble Al concentration when sulfate was present in experiments when pH $\geq$8.0.

5.2.2.3 Total Al concentration in experiments of the molar ratio of Al:Si:SO_4=1:2.5:5

Figure 5.8 shows total Al concentration after different settling time at different pH in experiments with high silicate concentration (Al:Si:SO_4=1:2.5:5). After 30 minutes of settling, total Al concentration was in the range of 1.86 to 7.68 at pH=5.6 to 8.6. These total Al concentrations were higher than those in experiments of low silicate concentration. After 48 hours of settling, total Al concentration was still higher than 1.0 mg/L, where total Al concentration was less than 0.5 mg/L at pH <7.5 in experiments with low silicate levels. In these experiments with high silicate concentration, the total Al concentration remained in high level, although the soluble Al concentration was in low levels, which indicates that high silicate level in solution increased total Al concentration due to the increase of suspended Al solids.

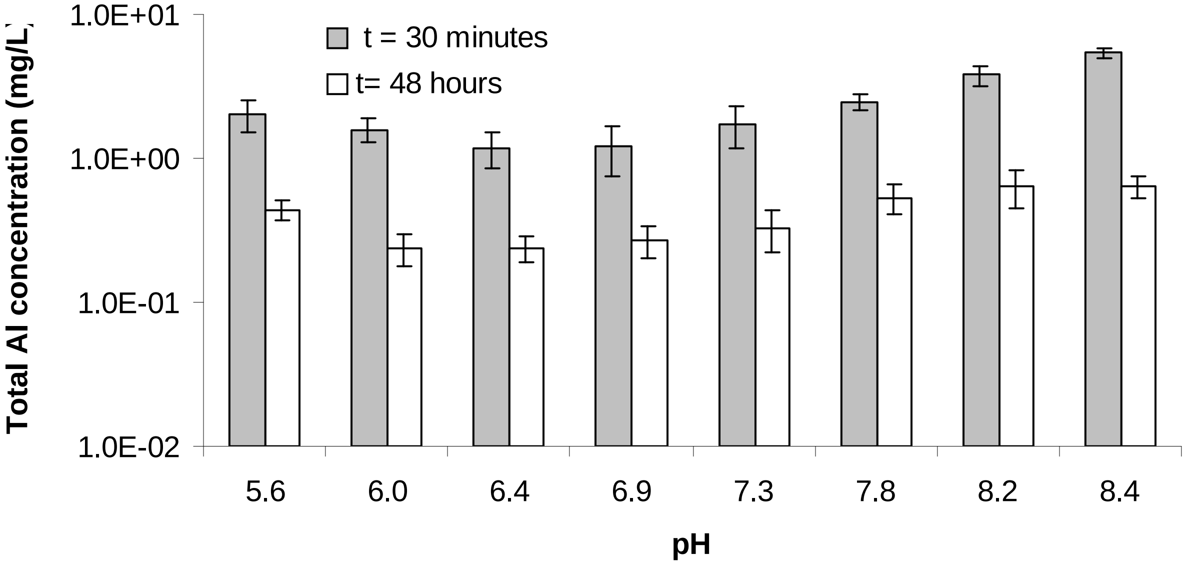


Figure 5.7 Total Al concentration in experiments of Al:Si:SO_4=1:1:5 after 30 minutes and 48 hours of settling

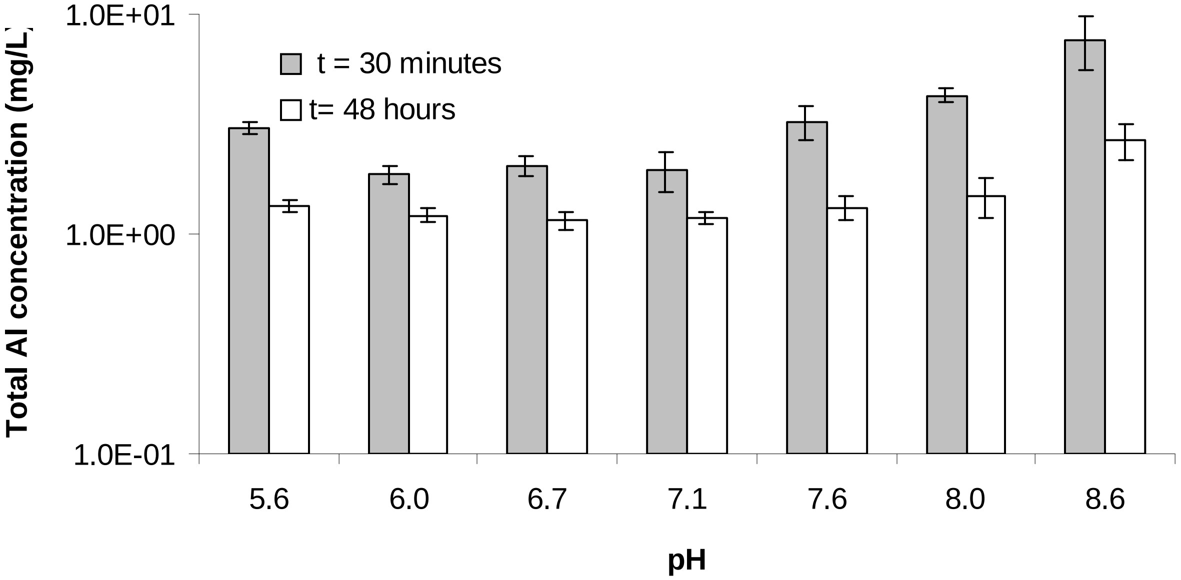


Figure 5.8 Total Al concentration in experiment of Al:Si:SO_4=1:2.5:5 after 30 minutes and 48 hours of settling

To evaluate the effect of pH on total Al concentration at different silicate concentrations, total Al concentration at pH=6.0 and 8.0 was used as index. Figure 5.9 shows total Al concentration in experiments with different silicate concentrations at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling (corresponding data listed in Table 5.1). After 30 minutes of settling, total Al concentration was in the range of 1.40 to 1.86 mg/L at p H=6.0, and 3.51 to 4.27 mg/L at pH=8.0. After 48 hours of settling, total Al concentration was 0.21, 0.24, and 1.22 mg/L at pH=6.0, and 1.07, 0.64, and 1.32 mg/L at pH=8.0 when molar ratio of Al:Si:SO_4 equal to 1:1:0, 1:1:5, and 1:2.5:5, respectively. Comparing total Al concentration after 30 minutes and 48 hours of settling, it can be found that it was in relative high level when silicate concentration was high, although the soluble Al concentration was not a significant difference (Figure 5.4). This result indicated that the high level of silicate reduced the settleable proportion of particulate Al solids and caused the high level of suspended Al concentration.

In Figure 5.10, the suspended Al concentration (the difference between total and soluble Al concentration) where silicate and sulfate were absent is compared to that where silicate and/or sulfate were present at pH=6.0 and 8.0. From Figure 5.10, it can be seen that the suspended Al concentration was the lowest when both silicate and sulfate were absent in solution. The result indicated that the presence of either silicate or sulfate and both increased the suspended Al solids in the supernatant. Figure 5.11 shows suspended Al concentrations at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling when solution contained low and high silicate concentration, respectively. From Figure 5.11, it can be seen that the suspended Al concentration was the highest when silicate concentration was the highest (Al:Si:SO_4=1:2.5:5). The data indicated that high silicate concentration could increase the suspended Al particles in effluent. Therefore, high silicate shows a negative influence on total effluent Al concentration.

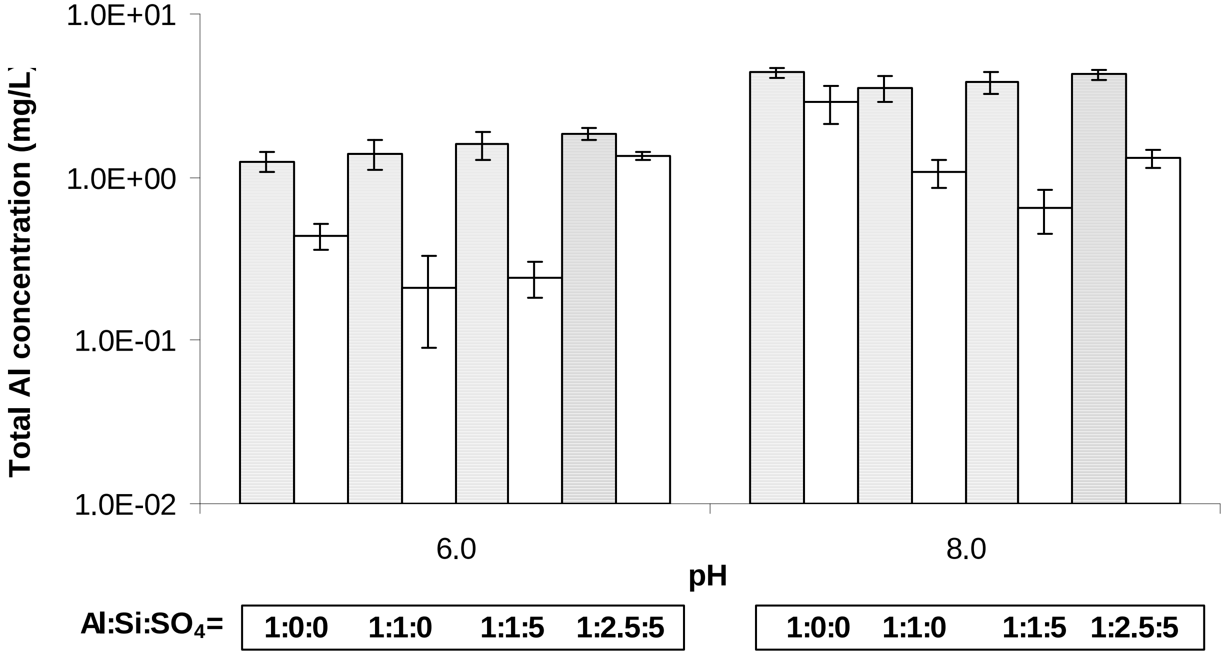


Figure 5.9 Total Al concentration after different settling time at pH=6.0 and 8.0 under different silicate levels

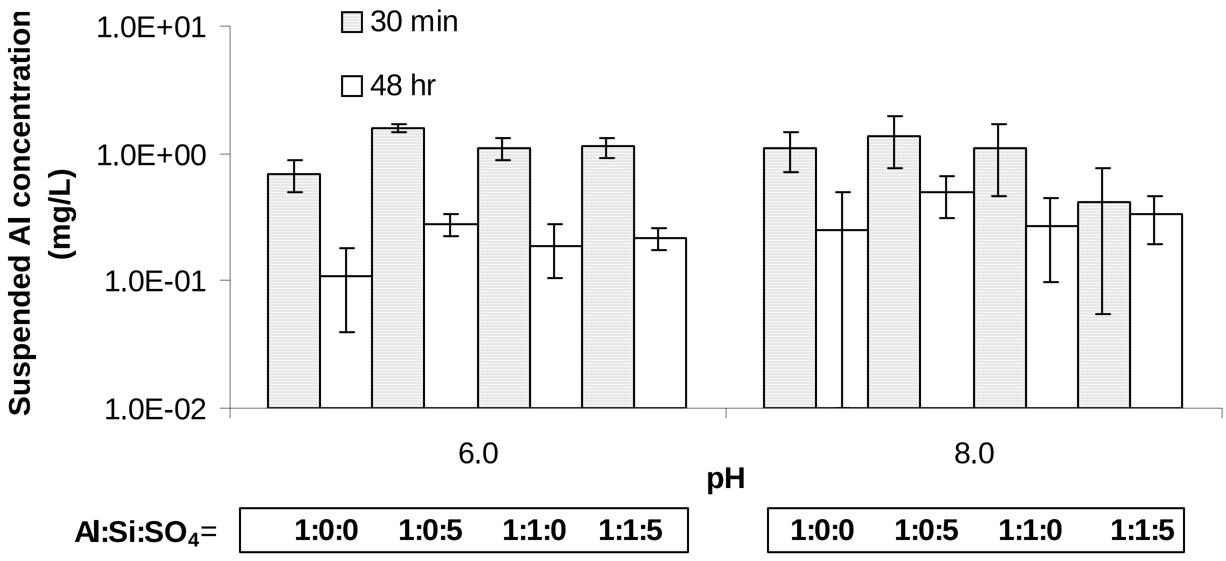


Figure 5.10 Suspended Al concentration in designated experiments that contained different silicate and sulfate concentrations at pH=6.0 and 8.0 after different settling time.

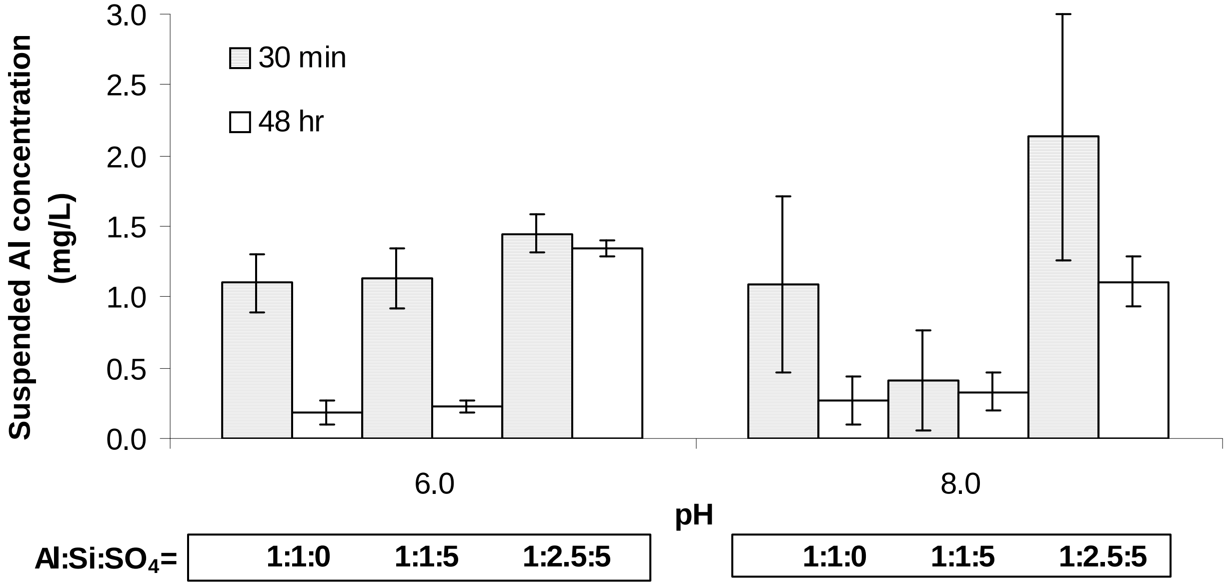


Figure 5.11 Suspended Al concentration under different silicate concentrations at pH=6.0 and 8.0 after different settling time

5.3 SLUDGE ANALYSIS

This section presents the information of the characteristics of sludge. Sludge samples were collected after 30 minutes and 48 hour of settling. The sludge samples were analyzed by XRD and SEM/EDS to determine the characteristics and chemical compositions of sludge.

5.3.1 Results of XRD analysis

In Section 5.2, soluble Al concentrations at different pH values after 30 minutes and 48 hours of settling have been present. The low level of soluble Al concentration revealed that amorphous

$Al(OH)_3$ was not the species of Al-precipitates to control soluble Al concentration in experiments, which indicated other species of Al-precipitates formed. To determine the species of Al-precipitates is important in understand the change of Al concentration when silicate is present in treatment systems. It is well known that some compounds have same chemical formula, but with a different structure, following with the different solubility. For example, as mentioned above, gibbsite, which is crystal with much lower solubility than amorphous $Al(OH)_3$, has the same chemical formula as amorphous $Al(OH)_3$. In experiments, the reduction of soluble concentration could be attributed to the formation of gibbsite or some other species of Al-precipitates, such as Al-silicate precipitates. If the Al-precipitates were in the form of crystal, XRD pattern could determine their species.

Figure 5.12 is the XRD scan pattern of sludge collected in experiment with molar ratio of $Al:Si:SO_4=1:1:0$ after 48 hours of settling at pH=6.0. In Figure 5.12, it can be seen that there is no peaks indicating that no crystalline precipitates formed. Since the solution contained silicate, the possible Al-precipitates include $Al(OH)_3$ and Al-silicate precipitates. $Al(OH)_3$ could be in two forms: crystalline and amorphous. Crystalline $Al(OH)_3$, gibbsite, has low product solubility and is the theoretically formed species in this experiment compared with amorphous $Al(OH)_3$. However, XRD indicated that crystalline precipitates were not detected. Therefore, the reduction of soluble Al concentration to be lower than the solubility of amorphous $Al(OH)_3$ was due to the formation of Al-silicate precipitates. In Figure 5.12, the peaks for identifying Al-silicate crystalline were also missing. The XRD result indicated that only amorphous precipitates with low intensity and broad peaks were formed in this experiment and the Al-silicate precipitates were also in the form of amorphous.

The XRD analysis confirmed that the sludge collected after 48 hours of settling did not contain crystalline materials. In generally, crystalline does not transform into amorphous structure, but the reverse process can happen. Therefore, it is reasonable to believe that no crystalline precipitates had been produced in the experiment of molar ratio of Al:Si:SO_4=1:1:0 within 48 hours of settling.

Figure 5.13 is the XRD pattern of sludge formed in experiment with molar ratio of Al:Si:SO_4=1:1:0 after 48 hours at pH =8.0. Similar to the XRD pattern of sludge collected at pH=6.0 after 48 hours of settling, this pattern shows no obvious peaks for crystalline materials. The XRD analysis of sludge formed at pH=6.0 and 8.0 shows that no crystalline was formed in the experiments with molar ratio of Al:Si:SO_4=1:1:0.

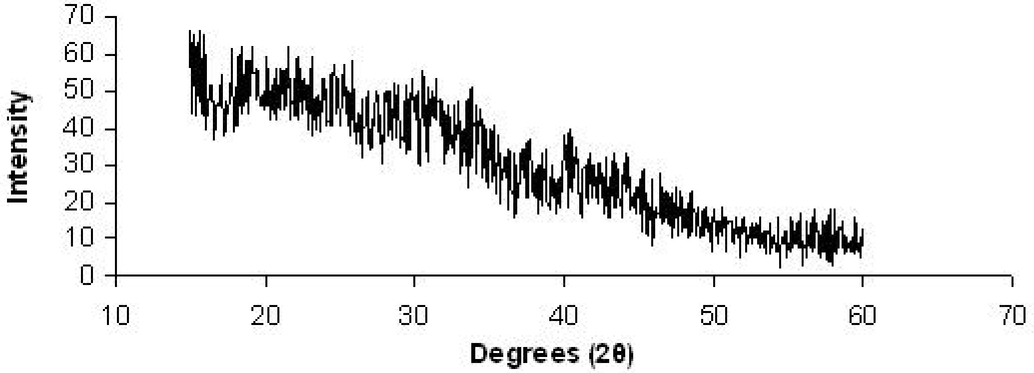


Figure 5.12 XRD pattern of sludge collected in experiment with molar ratio of Al:Si:SO_4=1:1:0 after 48 hours of settling at pH =6.0

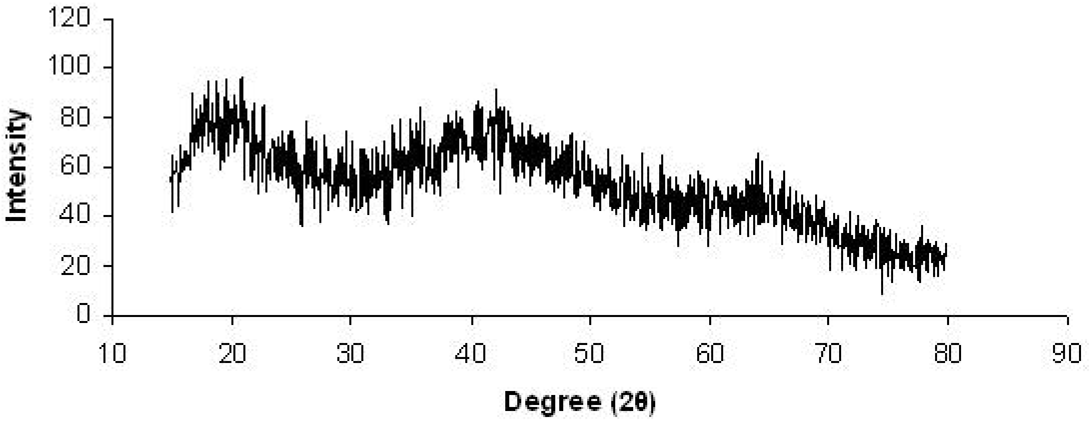


Figure 5.13 XRD pattern of sludge collected in experiment with molar ratio of Al:Si:SO_4=1:1:0 after 48 hours of settling at pH=8.0

Figure 5.14 shows XRD pattern of sludge formed in experiments with molar ratio of Al:Si:SO_4=1:1:5 at pH=6.0 and 8.0 after 48 hours. Figure 5.15 shows the XRD pattern of sludge formed in experiments with molar ratio of Al:Si:SO_4=1:2.5:5 at pH=6.0 and 8.0 after 48 hours of settling. From Figure 5.14 and 5.15, it can be observed that the XRD patterns of the sludge formed in these experiments were also lack of peaks to identify the crystal precipitates when both silicate and sulfate were present. The data also indicated that no crystalline was formed in the experiments with the presence of sulfate.

In Chapter 4, the analysis showed that the sludge formed in experiments without silicate contained Al-sulfate precipitates and XRD patterns indicated that the Al-sulfate precipitates were in the form of amorphous. Figure 5.14 and 5.15 indicated that the Al-sulfate precipitates, if they had been produced in the experiments where silicate was present in solution, were also in the form of amorphous.

According to all the XRD patterns of the sludge in this study, the precipitates formed in Al-bearing ARD/AMD treatment with NaOH, whether they are aluminum hydroxide, aluminosulfate, or aluminosilicate, are in forms of amorphous rather than crystalline. Therefore, in the design process of ARD/AMD treatment, amorphous compounds constants should be prevailed in prediction of effluent soluble Al concentration, not the crystalline constants.

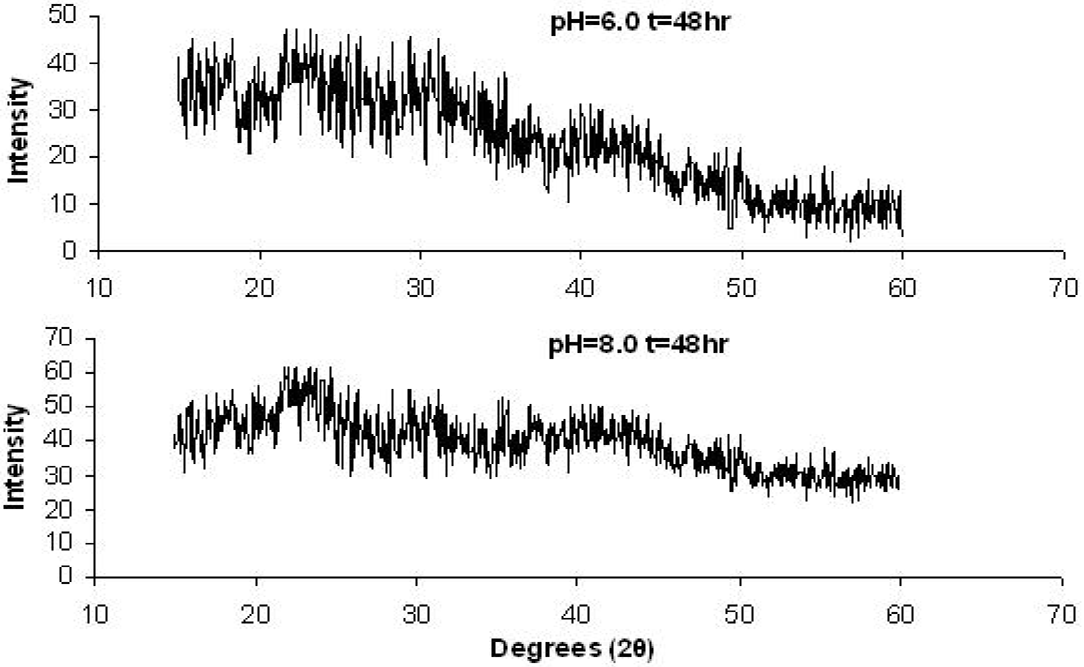


Figure 5.14 XRD patterns of sludge collected in experiments with molar ratio of Al:Si:SO_4=1:1:5 after 48 hours of settling at pH=6.0 and 8.0

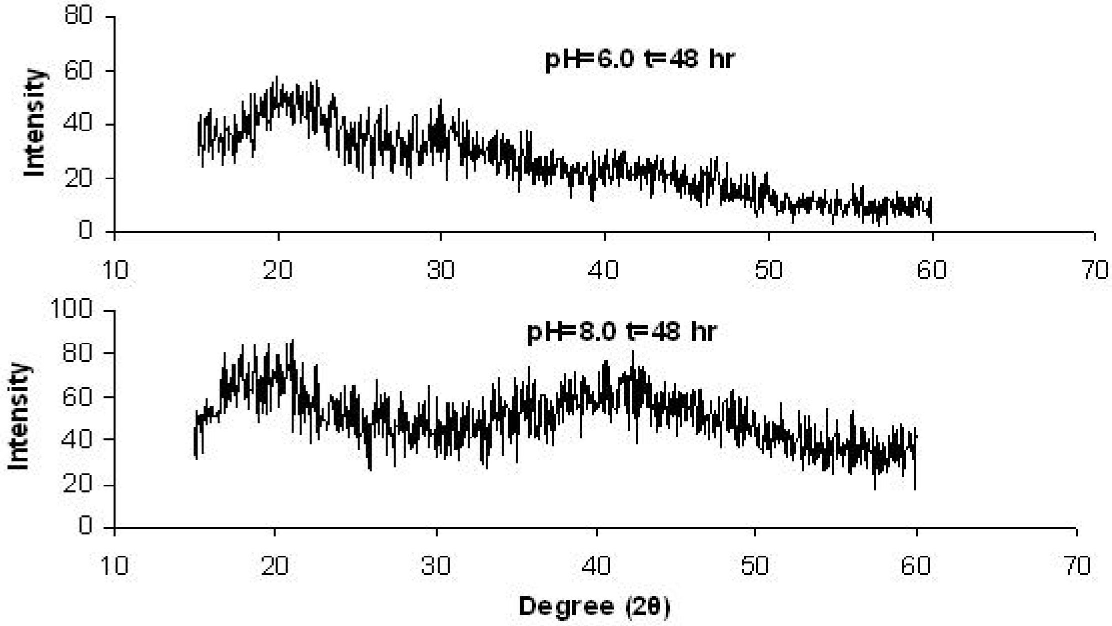


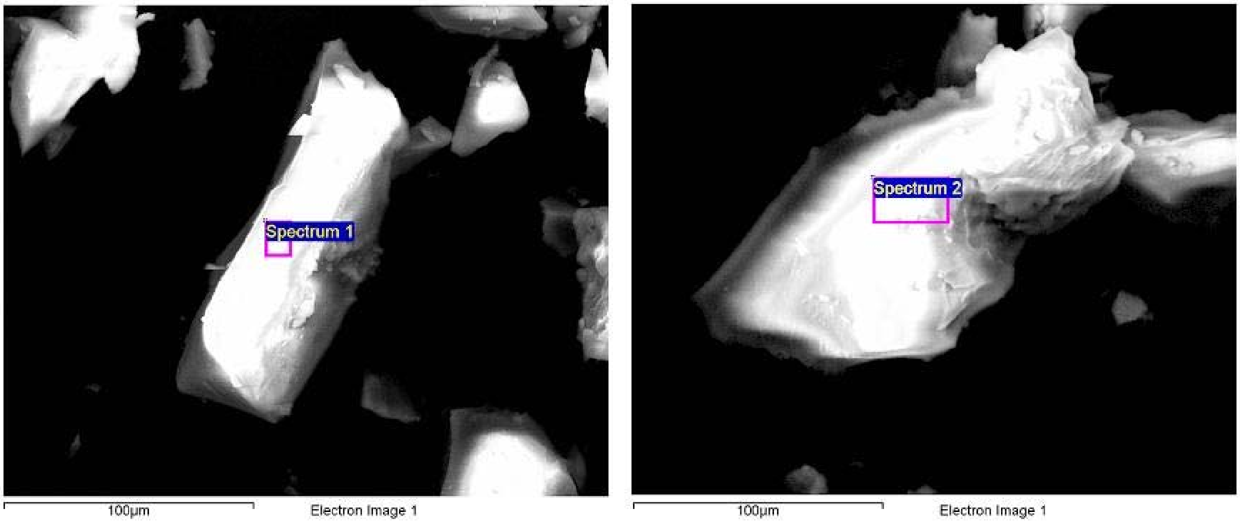
Figure 5.15 XRD patterns of sludge collected in experiments with molar ratio of Al:Si:SO_4=1:2.5:5 after 48 hours of settling at pH=6.0 and 8.0

5.3.2 Chemical compositions of sludge

5.3.2.1 Composition of sludge formed in experiments after 30 minutes of settling

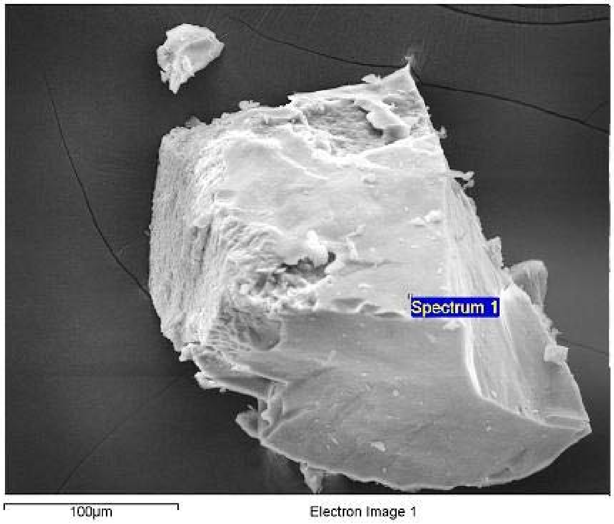
Figure 5.16 is a set of SEM images of precipitates formed in experiments with different silicate and sulfate concentrations at pH=6.0 after 30 minutes of settling. The chemical compositions were measured in different locations of precipitate samples and the average of all points was listed in Table 5.2. In SEM analysis, it was not found any different morphological characteristics among the sludge particles. Figure 5.16 shows the typical morphological image of the sludge samples. In Table 5.2, it can be seen that the precipitates contained multiple elements, including Al, C, O, Si, S, Mn, Na, and Cl, and the contents changed with silicate and sulfate concentrations.

The silicon content (molar percentage) was 3.0%, 5.1%, and 5.9% in sludge formed in experiments with molar ratio of Al:Si:SO_4=1:1:0, 1:1:5, and 1:2.5:5, respectively. The observation that the silicon content increased in sludge formed where sulfate was in solution shows that the presence of sulfate increased silicate precipitation. The molar ratio of Al:Si of kaolinite, which is a possible Al-silicate precipitate formed in these experiments, is 1:1, however the measured molar ratio of Al:Si was 5.16, 3.01, and 2.07 in sludge, respectively. The higher molar ratios of Al:Si indicated that other species of Al-precipitates were formed as well. In the experiments where sulfate was present, the molar ratios of Al:S were 82.1 and 73.5 in sludge formed in the experiments with low and high silicate concentration, respectively *(high aluminum and low sulfur)*. Based on these observations, it was concluded that sludge contained very little amount of Al-sulfate precipitates. Therefore, $Al(OH)_3$ was the most likely product of Al-precipitates formed in the experiments under these conditions, and XRD pattern of the sludge confirmed that $Al(OH)_3$ formed in these experiments was amorphous. In order to estimate the amount of $Al(OH)_3$ in sludge, the molar ratio of O/Al was calculated. In the calculation, the corrected atomic oxygen percentage was obtained by subtracting the oxygen combined with C (as CO_2), S (as SO_4) and Si (as SiO_2). The calculated molar ratio of O/Al was 3.26, 3.43, and 3.70 in experiments with molar ratio of Al:Si:SO_4=1:1:0, 1:1:5, and 1:2.5:5 after 30 minutes of settling, respectively. These O/Al ratios were higher than the theoretical molar ratio of $Al(OH)_3$. The possible reason is that silicate might have been precipitated in the form of $Si(OH)_4$ in sludge. Therefore, the sludge contained Al- precipitates in the form of $Al(OH)_3$ and/or Al-silicate, or as kaolinite ($Al_2Si_2O_5(OH)_4$). Furthermore, the silicate precipitates were also in two forms: $Si(OH)_4$ and Al-silicate precipitates. The amount of Al-sulfate precipitates was neglected, since no significant amount of sulfate was present in sludge.



Al:Si:SO4=1:1:0 pH=6.0
30 minute

Al:Si:SO4=1:1:5 pH=6.0
30 minute



Al:Si:SO4=1:2.5:5 pH=6.0
30 minutes

Figure 5.16 SEM images of sludge formed in experiments with different silicate and sulfate concentrations at pH=6.0 after 30 minutes of settling

Table 5.2 Chemistry compositions of sludge formed at pH=6.0 after 30 minutes of settling

	$Al:Si:SO_4$=1:1:0		**$Al:Si:SO_4$=1:1:5**		**$Al:Si:SO_4$=1:2.5:5**	
Element	Weight %	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	5.6	8.3	2.7	4.2	4.7	7.2
O	65.4	72.6	63.2	72.4	62.0	72.2
Na	0.5	1.8	2.2	1.8	1.4	1.8
Al	23.4	15.4	22.8	15.5	17.7	12.2
Si	4.7	3.0	7.9	5.1	8.9	5.9
S	ND[4]	ND	0.3	0.18	0.3	0.17
Cl	ND	ND	0.5	0.27	ND	ND
Mn	0.4	0.13	0.3	0.10	0.3	0.10
Total	100.0	100	100.0	100	100.0	100
O/Al[1]		3.26		3.43		3.70
$[O/Al]s_{i(OH)4}$[2]		2.86		2.77		2.74
$[O/Al]_{kao}$[3]		3.44		3.89		4.82
Al/Si		5.16		3.01		2.07
Al/S				86.1		73.5

[1]: Corrected O/Al molar ration: subtracted the oxygen combined with C (asCO_2), S (as SO_4), and Si (asSiO_2).

[2]: $[O/Al]_{si(OH)4}$[2] assuming all Si in sludge was in the form of $Si(OH)_4$. Calculation equation in Appendix E;

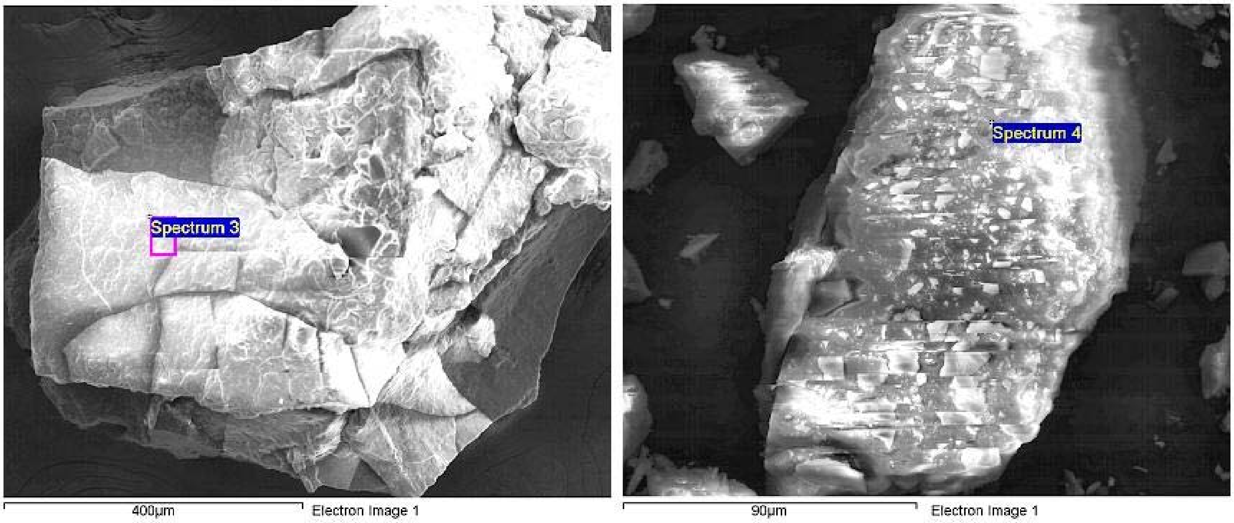
[3]: $[O/Al]_{kao}$ assuming all Si in sludge was in the form of kaolinite ($Al_2Si_2O_5(OH)_4$). Calculation equation in Appendix E;

[4]: ND: not detected.

The calculation method is present in Appendix E. In Table 5.2, it can be seen that all the ratios of $[O/Al]_{si(OH)}$ were less than 3, which indicated that all sludge formed in these three experiments contained Al-silicate precipitates. This result can explain the low soluble Al concentration after 30 minutes of settling. Furthermore, the values of $[O/Al]_{kao}$ also deviated from 3 indicating that some silicate in sludge was not in the form of Al-precipitates.

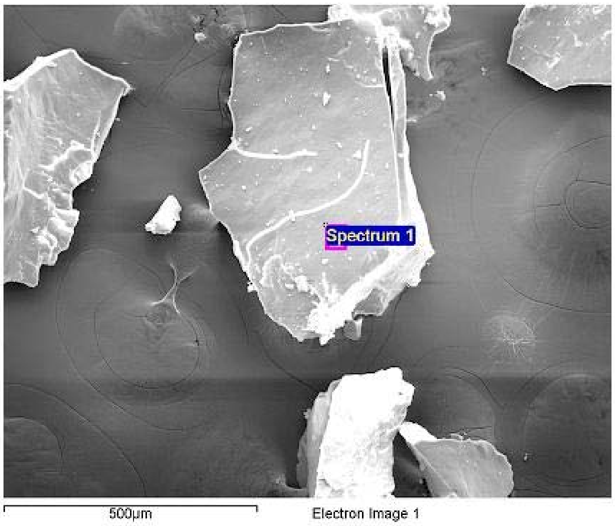
Figure 5.17 is a set of SEM images of precipitates formed in experiments of different silicate and sulfate concentrations at pH=8.0 after 30 minutes of settling. Similar to the sludge formed at pH=6.0, the sludge formed at pH=8.0 was also no significantly morphological difference. Chemical composition is listed in Table 5.3. In sludge formed in the experiment without sulfate, the silicon content was 3.1% (atomic percentage) close to the value in sludge formed at pH=6.0 after 30 minutes of settling. The silicon content was 9.7% and 11.0 % in sludge formed in experiments with molar ratio of $Al:Si:SO_4=1:1:5$ and 1:2.5:5, respectively. These silicon contents were not only higher than those in sludge formed in experiments without sulfate, but also higher than those in sludge formed at pH=6.0. Therefore, the presence of sulfate can enhance the precipitation of silicate and the high pH of solution also increased the silicate sediment. Similar to sludge formed at pH=6.0, sludge contained some silicate in the form of $Si(OH)_{4(s)}$ at pH=8.0. The value of $[O/Al]_{kao}$ was far away from 3 in sludge formed in the experiments with sulfate, which implied that most of silicon was in the form of $Si(OH)_{4(s)}$. These data also support the conclusion that sulfate can enhance silicate sedimentation in the form of $Si(OH)_{4(S)}$. The values of $[O/Al]_{si(OH)}$ indicated that there were some Al-silicate precipitates in sludge.

From Table 5.3, it can be found that sulfur content in sludge formed at pH = 8.0 was higher than that at pH=6.0, although the concentration was still low. The sulfur content was 0.29% and 0.25 % in sludge formed in low and high silicate experiments, respectively.



Al:Si:SO4=1:1:0 pH=8.0
t=30 minutes

Al:Si:SO4=1:1:5 pH=8.2
t=30 minutes



Al:Si:SO4=1:2.5:5 ph=8.0
t=30 minutes

Figure 5.17 SEM images of sludge formed in experiments with different silicate and sulfate concentrations at pH=8.0 after 30 minutes of settling

Table 5.3 Chemistry compositions of sludge formed at pH=8.0 after 30 minutes of settling

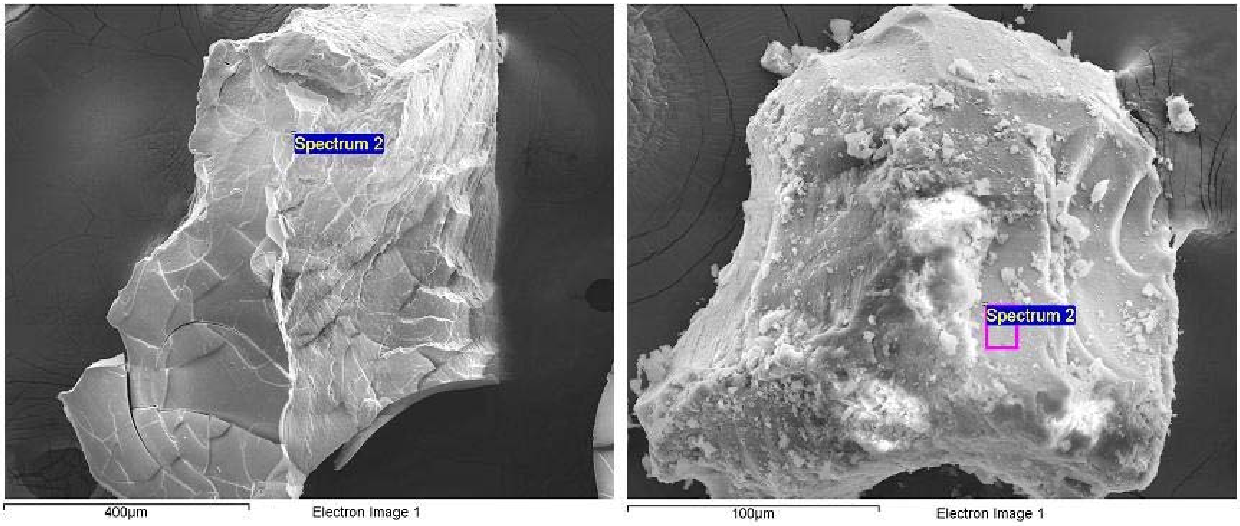
	Al:Si:SO$_4$=1:1:0		**Al:Si:SO$_4$=1:1:5**		**Al:Si:SO$_4$=1:2.5:5**	
Element	Weight %	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	4.8	7.8	1.1	1.7	1.3	2.0
O	58.4	70.9	62.3	72.8	61.2	71.5
Na	0.5	1.8	0.6	1.8	2.8	1.8
Al	22.2	16.0	18.9	13.1	16.7	11.6
Si	4.5	3.1	14.5	9.7	16.5	11.0
S	ND	ND	0.5	0.29	0.4	0.25
Cl	0.4	0.22	0.3	0.16	0.4	0.23
Mn	1.4	0.49	1.8	0.61	0.6	0.22
Total	100	100	100.0	100	100.0	100
O/Al		3.08		3.72		3.84
$[O/Al]_{si(OH)}$		2.68		2.24		1.93
$[O/Al]_{kao}$		3.22		7.20		30.33
Al/Si		5.12		1.35		1.05
Al/S				44.8		46.5

Figure 5.18 is a set of SEM images of sludge formed at pH=6.0 after 48 hours of settling. The chemical components are listed in Table 5.4. After long settling time, the sulfur content in sludge had increased a little. After 48 hours of settling, the sulfur content was 0.6% and 0.3% in sludge formed in experiments with molar ratio of Al:Si:SO$_4$=1:1:5 and 1:2.5:5, respectively, which was a little higher than that in sludge formed after 30 minutes of settling. The molar ratio of Al/S was 23.2 and 41.7, whereas it was 86.1 and 73.5 at 30 minutes of settling. The increase of sulfur content in sludge indicated that Al-sulfate might be formed after long settling time. It

was observed that soluble Al concentration at pH=6.0 in the experiment with sulfate was lower than that in the experiment without sulfate after long settling time (48 hours), whereas there was no significant difference after 30 minutes of settling. This phenomenon implied that sulfate could also influence the soluble Al concentration by the formation of sulfate-precipitates in the experiments with presence of silicate after long settling time.

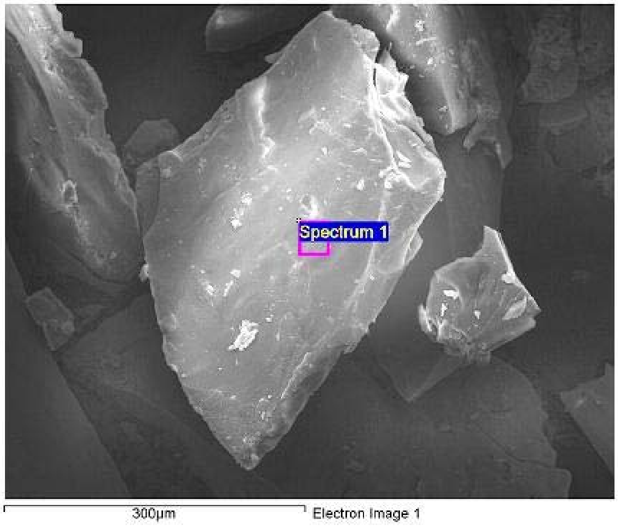
Table 5.4 Chemistry compositions of sludge formed at pH=6.0 after 48 hours of settling

	Al:Si:SO_4=1:1:0		**Al:Si:SO_4=1:1:5**		**Al:Si:SO_4=1:2.5:5**	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	5.4	8.1	3.8	5.7	4.6	6.8
O	63.4	71.1	64.1	72.6	63.7	71.8
Na	1.7	1.8	1.0	1.8	0.8	1.8
Al	23.5	15.6	19.9	13.4	18.6	12.4
Si	4.6	3.0	9.7	6.3	10.4	6.7
S	ND	ND	1.0	0.58	0.5	0.30
Cl	1.1	0.56	0.5	0.26	0.4	0.22
Mn	0.3	0.11	0.0	0.00	1.0	0.31
total	100.0	100	100.0	100	100.0	100
O/Al		3.13		3.47		3.50
$[O/Al]_{si(OH)}$		2.75		2.53		2.43
$[O/Al]_{kao}$		3.28		4.32		4.67
Al/Si		5.26		2.14		1.86
Al/S				23.2		41.7



Al:Si:SO4=1:1:0 pH=6.0
t=48 hours

Al:Si:SO4=1:1:5 pH=6.0
t=48 hours



Al:Si:SO4=1:2.5:5 pH=6.0
t=48hours

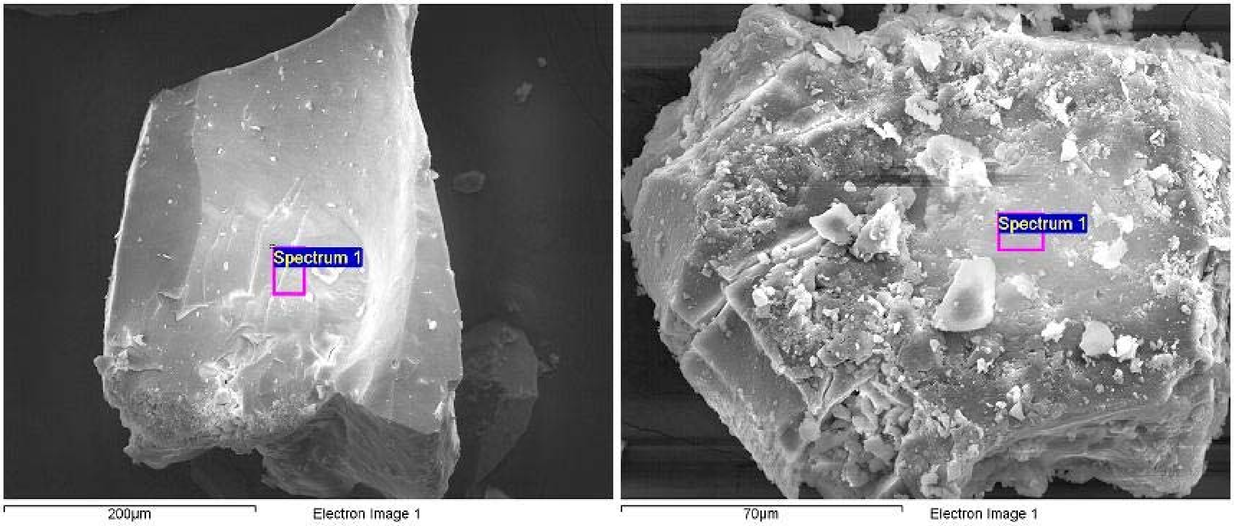
Figure 5.18 SEM images of sludge formed in experiments with different silicate and sulfate concentrations at pH=6.0 after 48 hours of settling.

From Table 5.4, the silicon content did not show a significant change with settling time. The silicon content in sludge was 3.1%, 6.3%, and 6.8% in experiments with molar ratio of Al:Si:SO_4=1:1:0, 1:1:5, and 1:2.5:5 after 48 hours, respectively, whereas it was 3.0%, 5.1%, and 5.9% after 30 minutes of settling, respectively. The molar ratio of Al/Si was 5.26, 2.14, and 1.86

after 48 hours of settling, whereas it was 5.16, 3.01, and 2.07 after 30 minutes of settling. These data indicated that the settling time did not show a significant effect on silicate sediment at pH=6.0. The values of $[O/Al]_{si(OH)}$ and $[O/Al]_{kao}$ indicated that the composition of sludge was complex, and both Al-silicate precipitates and solid $Si(OH)_4$ were in sludge.

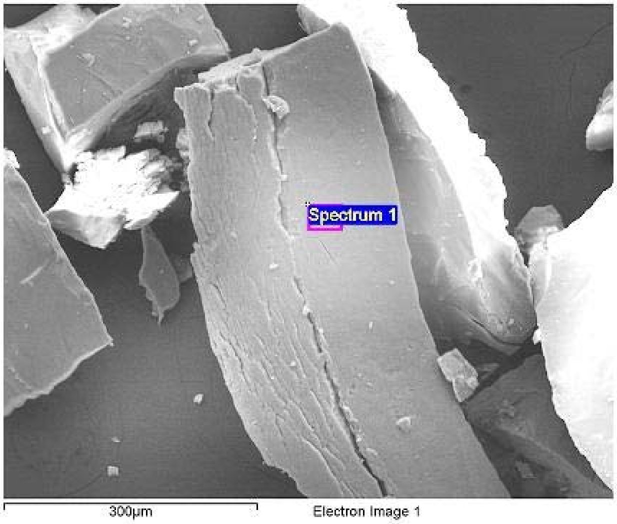
Figure 5.19 is the set of SEM images of sludge formed at pH=8.0 after 48 hours of settling. The chemical components data are listed in Table 5.5. In Table 5.5, silicon content was 5.7%, 6.3%, and 8.2% in sludge formed in experiments with molar ratio of $Al:Si:SO_4$=1:1:0, 1:1:5, and 1:2.5:5, respectively. Compared with sludge formed at pH=6.0 without sulfate, the silicon content increased at pH=8.0 after 48 hours of settling. In experiments with sulfate, silicon content did not show a significant change even though it was a slightly higher at pH=8.0 after 48 hours of settling. The Al/S ratio in sludge was 37.2 and 29.2 and these values were similar to those in sludge formed at pH=6.0. The soluble Al concentration at pH= 8.0 in experiments without sulfate was also higher than that in experiments with sulfate after 48 hours of settling. This phenomenon also appeared at pH=6.0. Therefore, it was concluded that sulfate reduced the soluble Al concentration after long settling time in presence of silicate in solution, although it did not influence the soluble Al concentration after short settling time (30 minutes).

The values of $[O/Al]_{si(OH)}$ and $[O/Al]_{kao}$ are also listed in Table 5.5. $[O/Al]_{si(OH)}$ values were from 2.32 to 2.37, which indicated that the some silicon in sludge was in the form of Al-silicate precipitates. $[O/Al]_{kao}$ values were from 3.37 to 4.01, which indicated that $Si(OH)_{4(s)}$ was also formed in sludge.



Al:SI:SO4=1:1:0
t=48 hours

Al:Si:SO4=1:1:5
t=48 hours



Al:Si:SO4=1:2.5:5
t=48 hours

Figure 5.19 SEM images of sludge formed in experiments with different silicate and sulfate concentrations at pH=8.0 after 48 hours of settling

Table 5.5 Chemistry components of sludge formed at pH=8.0 after 48 hours of settling

	Al:Si:SO_4=1:1:0		**Al:Si:SO_4=1:1:5**		**Al:Si:SO_4=1:1:5**	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	7.1	10.4	6.6	9.8	5.3	7.9
O	64.4	70.9	63.9	70.9	65.4	72.6
Na	0.4	1.8	0.7	1.8	0.4	1.8
Al	17.6	11.5	16.5	10.8	14.9	9.8
Si	9.1	5.7	9.9	6.3	12.9	8.2
S	0.0	0.00	0.5	0.29	0.6	0.33
Cl	0.6	0.32	0.5	0.26	0.4	0.20
Mn	0.7	0.24	1.4	0.44	0.2	0.06
total	100.0	100	100.0	100	100.0	100
O/Al		3.37		3.48		4.01
$[O/Al]_{si(OH)}$		2.37		2.32		2.34
$[O/Al]_{kao}$		4.22		4.81		11.57
Al/Si		2.01		1.73		1.20
Al/S				37.2		29.2

5.4 MEASURED AND THEORETICAL SOLUBLE ALUMINIUM CONCENTRATIONS WITH SETTLING TIME

Sludge analysis shows that silicate reduced the soluble Al concentration after a short settling time (30 minutes), since no crystalline material in sludge formed in experiments without sulfate was detected by XRD. The sludge components showed that silicate could be settled as both Al-silicate and $Si(OH)_{4(s)}$. This section presents simulation of experiments using the Mineql+ computerized equilibrium model. In the simulation, the silicate was input as $Si(OH)_4$.

5.4.1 The change of soluble Al concentration with settling time in the experiment of molar ratio of Al:Si:SO_4=1:1:0

In the experiments of molar ratio of Al:Si:SO_4 = 1:1:0, the initial aluminum concentration was about 24-26 mg/L.. Figure 5.20 presents soluble Al concentration at initial, after 30 minutes, and 48 hours of settling after pH adjustment. Two theoretical solubility curves are also presented in Figure 5.20. One is the theoretical solubility of amorphous $Al(OH)_3$. The other is the theoretical solubility of kaolinite. Solubility was calculated by Mineql+ model. In the calculation, gibbsite was not considered as the possible species of Al-precipitates since XRD analysis revealed no crystalline produced in experiments.

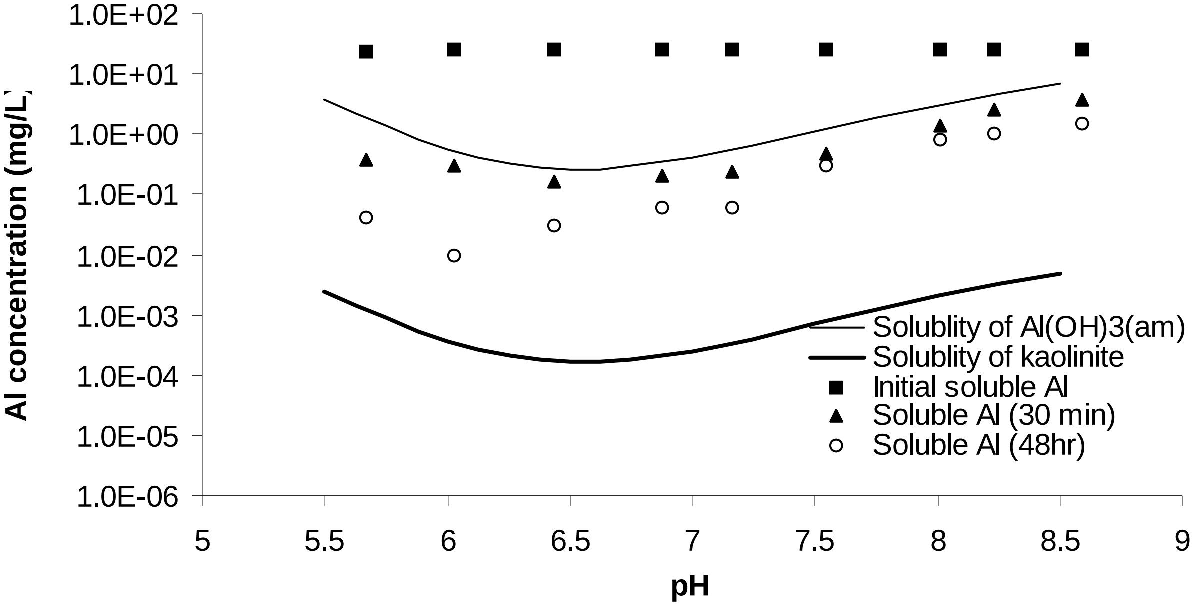


Figure 5.20 Soluble aluminum concentrations after 30 minutes and 48 hours of settling at different pH in experiment with the molar ratio of $Al:Si:SO_4$=1:1:0 and theoretical solubility of $Al(OH)_3$(am) and kaolinite

Comparing soluble aluminum concentration measured in experiments with the theoretical solubility of Al-compounds, it could be found that soluble aluminum concentration after 30 minutes of settling was lower than the solubility of amorphous $Al(OH)_3$. This result indicated that the solution was unsaturated with amorphous $Al(OH)_3$ within the first 30 minutes after pH adjustment. However, the soluble Al concentration at short settling time (30 minutes) was higher than the solubility of kaolinite, which meant the solution was supersaturated with kaolinite after short settling time. Considering soluble Al concentration in experiments was lower than the solubility of amorphous $Al(OH)_3$ and the sludge formed at 30 minutes of settling contained Al-silicate precipitates, it was reasonable to conclude that not only amorphous $Al(OH)_3$, but also Al-silicate precipitates (such as kaolinite) had been formed within the first 30 minutes after pH adjustment, and the formation of Al-silicate reduced soluble Al concentration to be lower than solubility of amorphous $Al(OH)_3$.

When settling time became longer (~48 hours), soluble Al concentration decreased. The reduction of soluble Al concentration indicated that some soluble aluminum ions had reacted with silicate to form Al-silicate precipitates. However, soluble Al concentration was still higher than the solubility of kaolinite. This phenomenon indicated that the solution was still non-equilibrium and supersaturated with kaolinite after 48 hours of settling.

5.4.2 The change of soluble Al concentration with settling time in the experiment of molar ratio of Al:Si:SO_4=1:1:5

Figure 5.21 presents soluble aluminum concentrations at different setting time and different pH when the molar ratio of Al:Si:SO_4 was 1:1:5. Similar to Figure 5.20, the solubility was calculated by Mineql+ model. Gibbsite was not considered as possible Al-precipitates that can control soluble Al concentration in experiments. Similar to the experiment without sulfate, calculation result showed that the theoretical species of aluminum precipitates in equilibrium condition was only kaolinite.

In Figure 5.21, soluble Al concentrations were a little less than the solubility of amorphous $Al(OH)_3$ at short detention time (~30 minutes), but much higher than the solubility of kaolinite. The result indicated that most of precipitates should be in the form of amorphous $Al(OH)_3$. Since the theoretical solubility (solubility of kaolinite) was lower than the soluble Al concentration in the experiments, the solution was not in equilibrium. When settling time became longer (~ 48 hour), soluble Al concentration decreased, but it was still much higher than the theoretical solubility (kaolinite solubility). The soluble Al concentration in these experiments indicated that the solution was also non-equilibrium when sulfate was present. Similar to the experiments without sulfate, the solution was unsaturated with amorphous $Al(OH)_3$ and supersaturated with kaolinite.

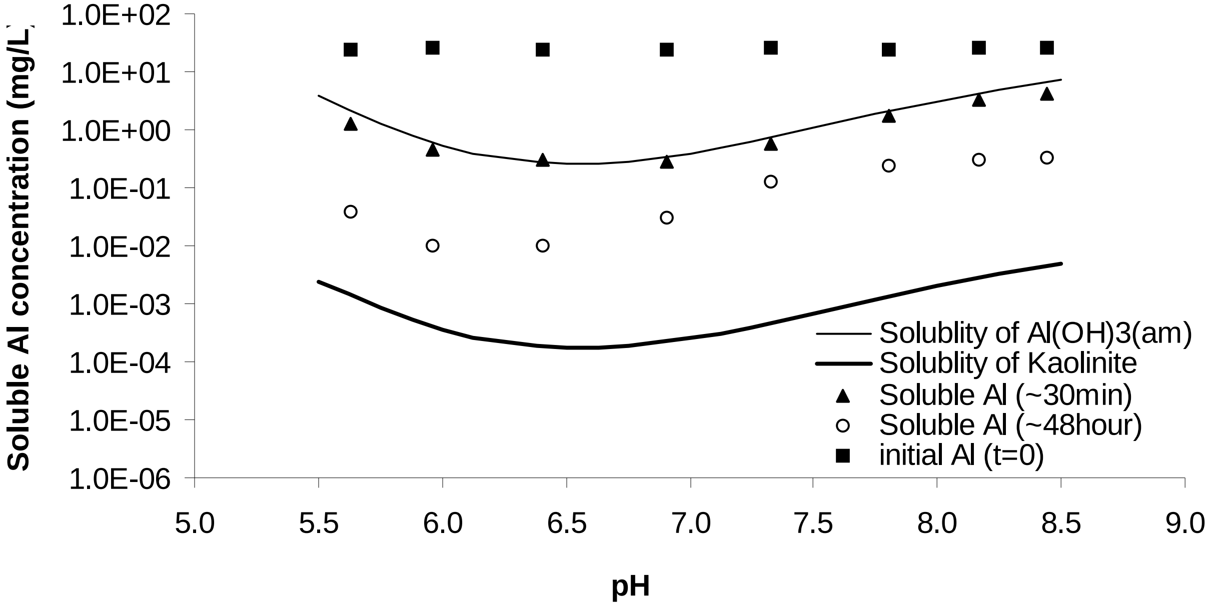


Figure 5.21 Soluble Al concentrations after 30minutes and 48 hours of settling at different pH in experiment with molar ratio of $Al:Si:SO_4$=1:1:5 and theoretical solubility of $Al(OH)_3$(am) and kaolinite.

5.4.3 Soluble Al concentration with settling time in the experiment of molar ratio of $Al:Si:SO_4$=1:2.5:5

In this series experiments, the molar ratio of $Al:Si:SO_4$ was 1:2.5:5. The final pH value was in the range of 5.6 to 8.6. Figure 5.22 shows soluble aluminum concentration decreased as settling time increase from initial to 30 minutes and 48 hours at different pH. In Figure 5.22, similar to the above figures, the solubility of amorphous $Al(OH)_3$ and kaolinite was calculated by Mineql+

model. Gibbsite was not considered as possible Al-precipitates during calculation. As in the other two experiments, the calculation results showed that the theoretical species of Al-precipitates in equilibrium condition was only kaolinite. From Figure 5.22, it could also be found that similar to the experiments with lower silicate concentration, the soluble Al concentration was a little less than the solubility of amorphous $Al(OH)_3$ and much higher than the solubility of kaolinite after short settling time (~30 minutes). When settling time became longer (~48 hours), although the soluble aluminum concentration decreased, it was still much higher than the solubility of kaolinite (theoretical solubility). These results indicated that most of precipitates should be in the form of amorphous $Al(OH)_3$, and the solution was unsaturated with amorphous $Al(OH)_3$ and supersaturated with kaolinite. The soluble Al concentration was possible controlled by kaolinite.

Comparing the theoretical solubility with measured concentration, it is noted that the soluble Al concentration in experiments with silicate was less than the solubility of amorphous $Al(OH)_3$ even if the settling time was short. Furthermore, the soluble Al concentration reduced to very low after 48 hours of settling. It was reasonable to conclude that the low soluble Al concentration was caused by the formation of Al-silicate precipitates. However, the sludge analysis did not provide any evidence to support this conclusion. The sludge analysis showed that the silicon content in sludge was not a significant difference between short (30 minutes) and long (48 hours) of settling. This phenomenon could be studied more in the future work to evaluate the main reaction that reduced the soluble Al concentration when both silicate and sulfate were present in the neutralization of Al-bearing ARD/AMD.

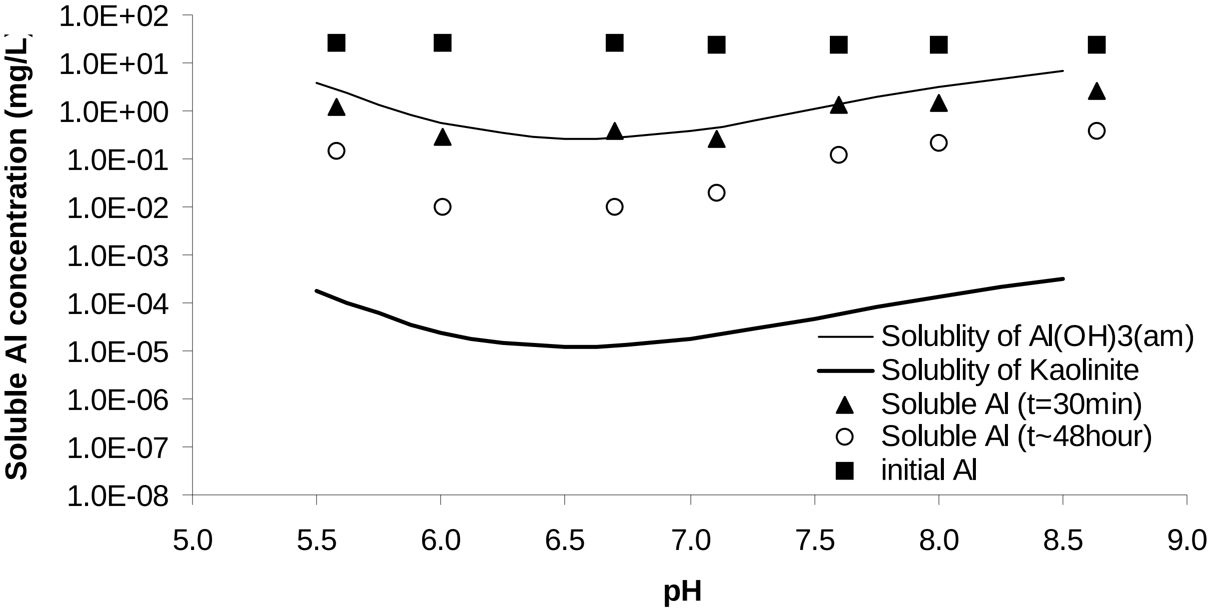


Figure 5.22 Soluble aluminum concentrations at different detention time vs. pH values when the molar ratio of Al:Si:SO_4=1:2.5:5 and theoretical solubility of $Al(OH)_3$(am) and kaolinite.

5.5 SUSPENDED PARTICLES SIZE DISTRIBUTION OF ALUMINUM-SILICATE PRECIPITATES IN THE SUPERNATANT

Suspended Al-containing particulate solids are the primary Al source in the effluent from active treatment system especially in the range of pH values greater than 6. In order to better understand the influence of silicate in suspended Al solids during Al-bearing ARD/AMD treatment, the particle size in the supernatant was measured. As mentioned above, particle size and its distribution were measured with a Microtrac S3500.

5.5.1 The particles size distribution in experiments with low silicate concentration and without Sulfate (Al:Si:SO_4=1:1:0)

Figure 5.23 is a set of four plots showing Al-containing suspended particle solid size distribution in experiments with molar ratio of Al:Si:SO_4=1:1:0 at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling. In these figures, the median diameter of suspended particles in the supernatant was similar at pH=6.0 and 8.0 and both were 20 µm after 30 minutes of settling. The particle size distribution was also similar at these two pH values, where the most suspended particular solids were in the range of 10 to 30 µm.

After 48 hour of settling, the median size of particles decreased to about 2.0 µm at pH=6.0, and about 10 µm at pH=8.0. At pH=6.0, most of suspended particles were in the range of less than 5.0 micrometer. At pH=8.0, the most particles were in range of 5.0 to 20 µm. The particles size distribution showed that suspended particle size was smaller at low pH (~6.0).

The suspended Al concentration was 0.19 and 0.27 mg/L at pH=6.0 and 8.0 after 48 hours of settling, which indicated that more suspended particulate Al solids were in the supernatant at pH=8.0. Comparing with the suspended particle size distribution in experiments without both silicate and sulfate (median size were 20 and 40 um at pH=6.0 and 8.0, respectively, in Figure 4.42), it can be found that the presence of silicate reduced the suspended particle size. The suspended Al concentration after 48 hours of settling in experiments without both silicate and sulfate was 0.11 and 0.25 mg/L at pH=6.0 and 8.0, respectively. Since the suspended Al concentration after 48 hours of settling in experiments with low silicate and without sulfate concentration was not significant difference from those in experiments without both silicate and sulfate, it appeared that smaller suspended particles in the supernatant were more in experiments when silicate was present. These small Al particles could reduce the settleable ability of suspended Al containing solids and lead to a relative high effluent Al concentration after long settling time in the discharge from an ARD/AMD treatment system. Therefore, the presence of silicate can reduce the suspended particles size and cause the colloids in solution to become "stable" and virtually non-settleable thus leading to a higher total aluminum containing discharge from settling basins.

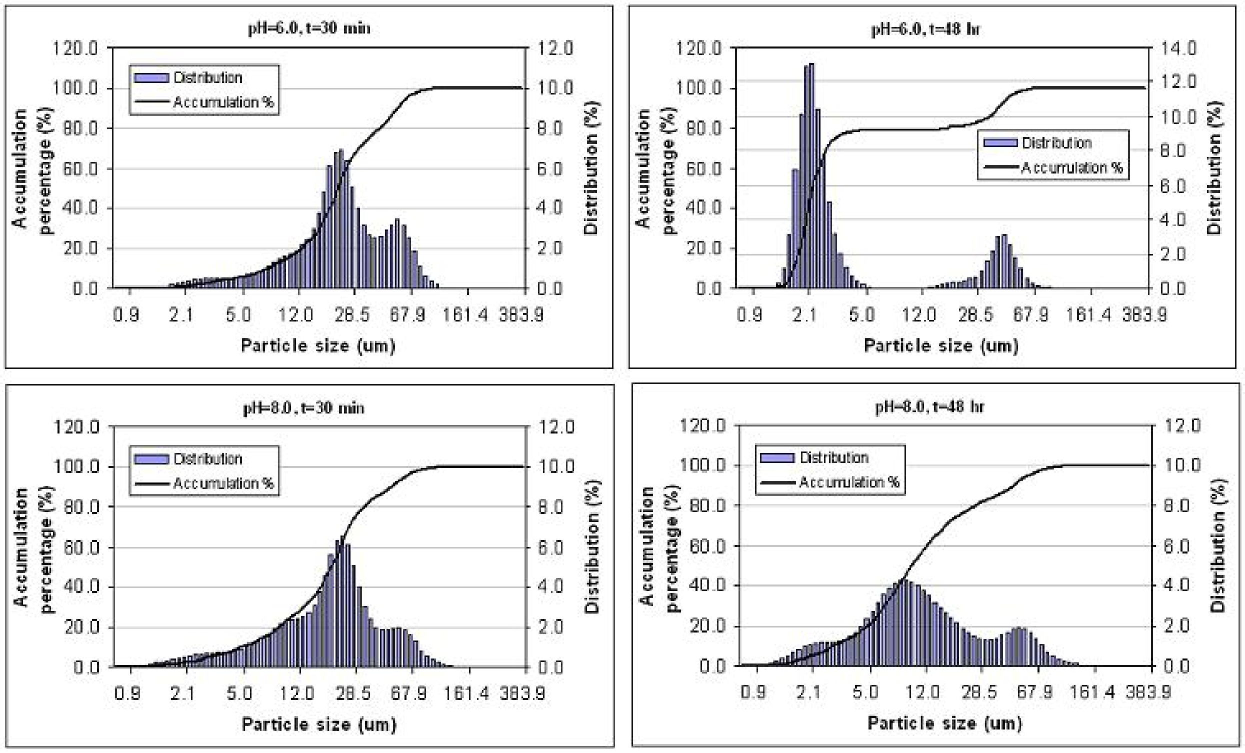


Figure 5.23 Suspended particle size distribution in supernatant at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling in experiment with molar ratio of Al:Si:SO_4=1:1:0

In experiments with molar ratio of Al:Si:SO_4=1:0:1 (*sulfate present and silicate absent*), the median size of particles was about 2.0 μm at both pH=6.0 and 8.0 (Figure 4.43) after 48 hours of settling. At pH=8.0, the particle size in experiments with sulfate was smaller than that in experiments with silicate. The suspended Al concentration was 0.32 and 0.55 mg/L in experiments with sulfate after 48 hours of settling at pH=6.0 and 8.0, respectively, which was higher than that in experiments with silicate. These data indicated that the presence of sulfate reduced the size of suspended Al solids and remained more Al precipitates suspended in the supernatant. In summary, both silicate and sulfate reduced the median diameter and overall size distribution of Al-bound suspended particles resulting in elevated suspended aluminum levels in settling tank supernatant discharges after NaOH neutralization.

5.5.2 The particle size distribution in experiments with low silicate and high sulfate concentrations (Al:Si:SO_4=1:1:5)

Figure 5.24 is a set of 4 plots showing the particle size distribution in experiments with molar ratio of Al:Si:SO_4=1:1:5 at pH =6.0 and 8.0 after 30 minutes and 48 hours of settling. The median diameter of suspended particles was about 20 µm after 30 minutes of settling at both pH values. After 48 hours of settling, the proportion of small particles increased at both pH values. The median diameter of suspended particles reduced to about 2.0 µm at pH=6.0, whereas the median size was about 7.0 µm at pH=8.0. Also most particles were less than 4.0 µm at pH=6.0. At pH=8.0, most suspended particles were less than 10 µm, although some particles were in the range of 10 to 30 µm.

Comparing with the particle size distribution in experiments that contained the same sulfate concentration and no silicate (Figure 4.44), it can be seen the particle size distribution was similar in both experiments with or without silicate at pH=6.0 after long setting time. At pH=8.0, the median diameter of suspended particles in experiments without silicate was about 4.5 µm and almost all particles was less than 10 µm, which was smaller than that in experiments with silicate. These data indicated that the suspended particles were smaller in experiments if only sulfate was present in solution.

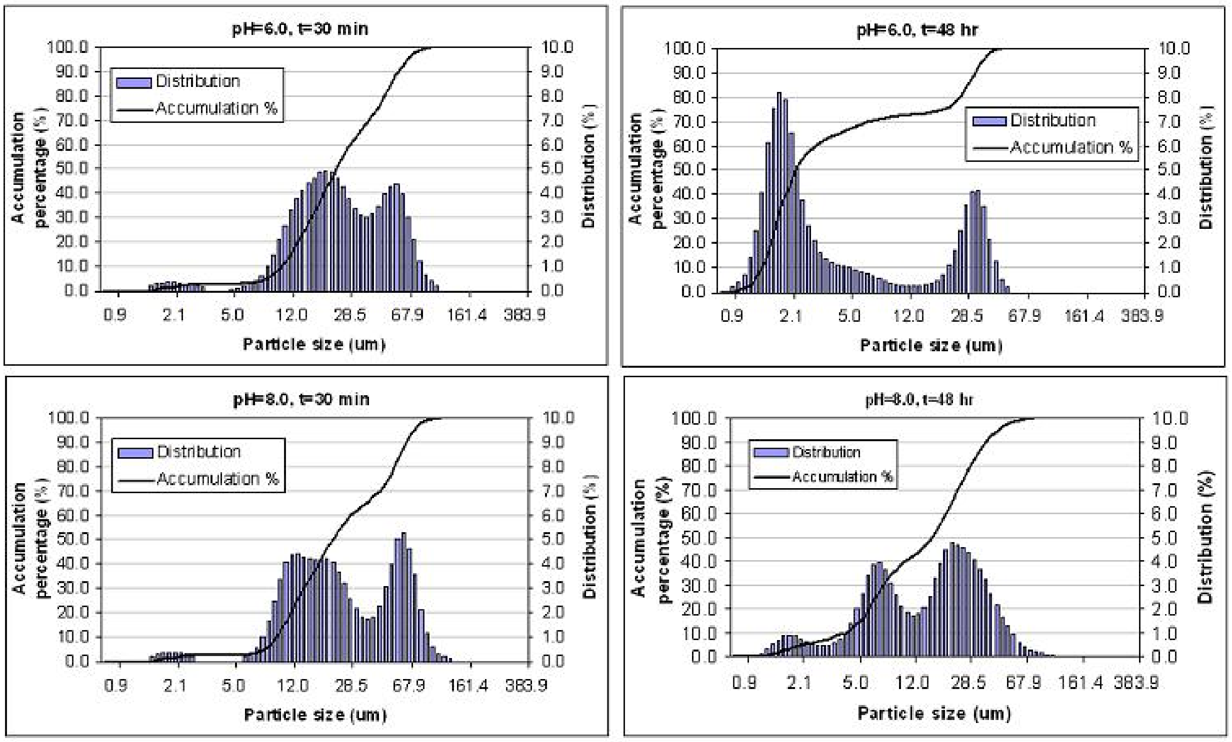


Figure 5.24 Suspended particle size distribution in the supernatant at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling in experiment with molar ratio of Al:Si:SO$_4$=1:1:5

The suspended Al concentration was 0.28 and 0.49 mg/L in experiments without silicate (Al:Si:SO$_4$=1:0:5) and 0.22 and 0.33 mg/L in experiments with silicate (Al:Si:SO$_4$=1:1:5) at pH=6.0 and 8.0, respectively, whereas the suspended Al concentration was 0.11 and 0.25 mg/L in experiments without both sulfate and silicate. In confirmation of the first set of experiments, both silicate and sulfate and combination of them reduced the particle size and increased the amount of non-settleable Al suspended solids in the supernatant discharge.

5.5.3 The particle size distribution in experiments with high silicate and high sulfate concentrations (Al:Si:SO_4=1:2.5:5)

Figure 5.25 is a set of 4 plots that show the particles size distribution in experiments with molar ratio of Al:Si:SO_4=1:2.5:5 at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling. After 30 minutes of settling, the median diameter of suspended particles was about 27 and 30 µm at pH= 6.0 and 8.0, respectively. At both pH values, most of suspended particles were in the range of 20 to 100 µm after 30 minutes of settling.

The mean and median particle size became smaller with the increase of settling time from 30 minutes to 48 hours. The median diameter was 2.5 and 2.0 µm at pH=6.0 and 8.0 after 48 hours of settling, respectively. Particle size distribution was similar in experiments at pH=6.0 to at pH= 8.0. Although the particle size was smaller in the experiment with high silicate concentration, the suspended Al concentration was high at both pH=6.0 and 8.0. The suspended Al concentration was 1.21 and 1.28 mg/L at pH=6.0 and 8.0 after 48 hours of settling, respectively, which was similar to (*but somewhat less than*) the suspended Al concentration after 30 minutes of settling (1.45 and 2.16 mg/L, respectively). These data revealed that the poorly settleable particles resulted in experiments with high silicate concentration.

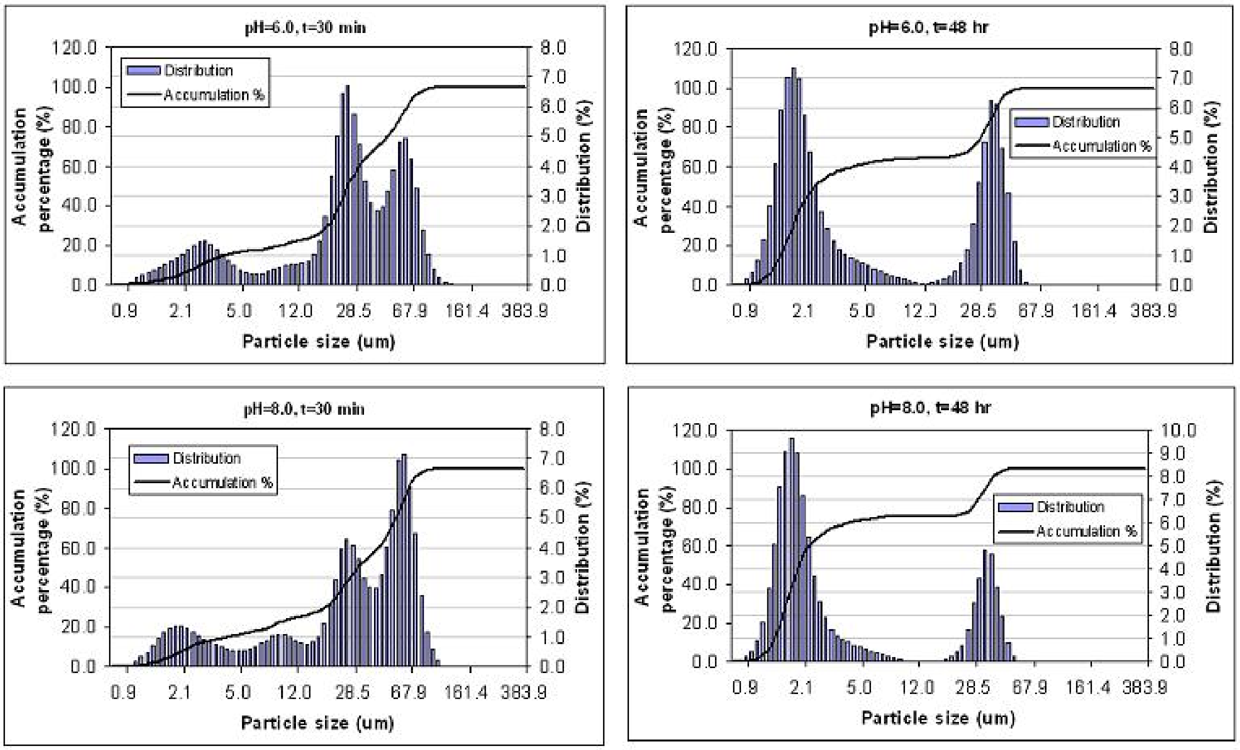


Figure 5.25 Suspended particle size distribution in the supernatant at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling in experiment with molar ratio of Al:Si:SO_4=1:2.5:5

Furthermore, the particle size distribution at the highest combination of sulfate and silicate molar ratios (Figure 5.26) showed that the particle size distribution was virtually unchanged between 24 and 48 hours of settling, and the majority of the particle size was less than 6.0 µm. The distribution of particle sizes showing the majority of the particles as being "small" indicated that the colloids in solution were "stable" and virtually nonsettleable.

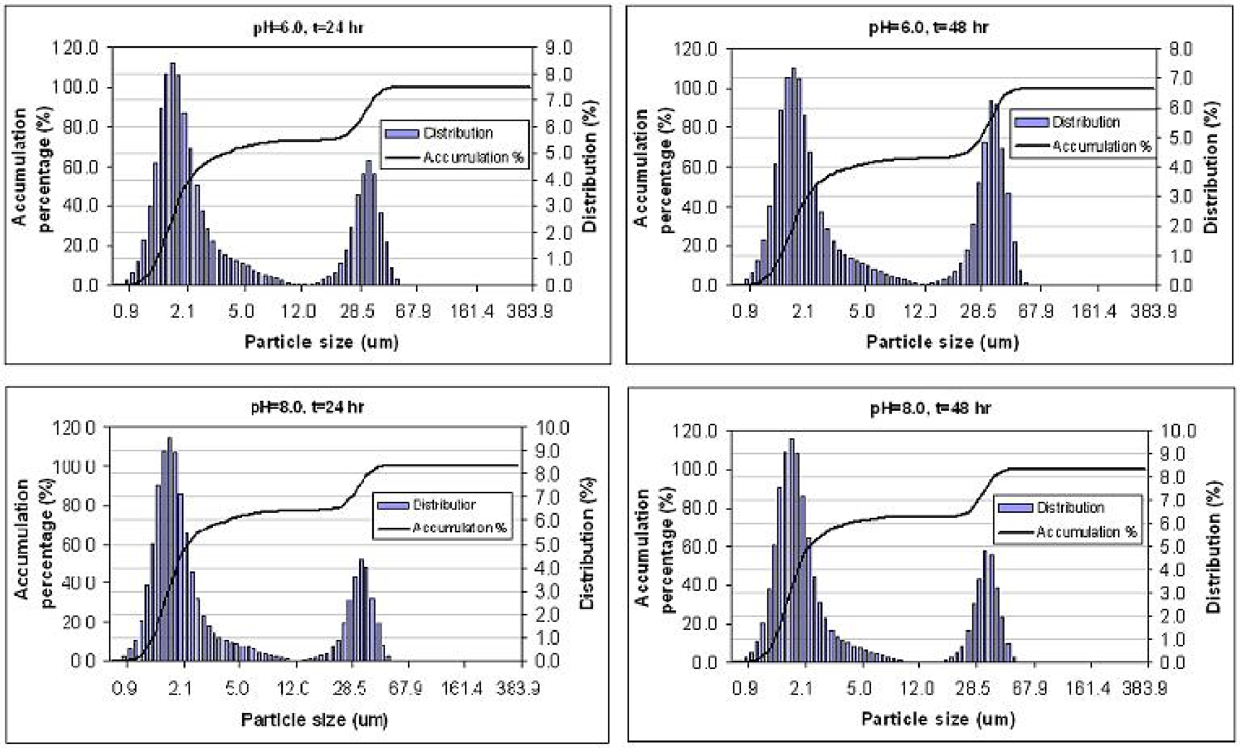


Figure 5.26 Supernatant particle size distribution in experiments with high silicate and sulfate concentrations (Al:Si:SO_4=1:2.5:5)at pH = 6.0 and 8.0 after 24 and 48 hours of settling,

5.5.4 Effect of suspended particle size on Al concentration

In Figure 5.10, it can be seen that suspended Al concentration in experiment with low silicate concentration was higher than that in experiment without silicate and sulfate at pH=6.0 after 48 hours of settling. However, at pH=8.0, the suspended Al concentration did not show a significant difference between the experiments with low silicate and without silicate and sulfate. In Figure 5.11, it can be seen that the suspended Al concentration in experiments with very high silicate concentration (Al:Si=1:2.5) was much higher than in experiments without silicate at both pH=6.0 and 8.0.

Figure 5.27 shows the relationship of the suspended Al concentration to the suspended particle size in experiments with silicate. From Figure 5.27, it can be seen that the low suspended Al concentration corresponded to the larger suspended particle size, whereas the higher suspended Al concentration corresponded to smaller size of suspended particles.

At pH=6.0, it can be seen that the suspended Al concentrations in experiments with silicate were higher than that in experiment without silicate and sulfate. Assuming the density of suspended particles did not change with settling time and with the size of suspended particles, the contribution of smaller suspended particles to suspended Al concentration was calculated. After 30 minutes of settling, the smaller suspended particles (< 5µm) contributed about 0.07 and 0.03 mg/L suspended Al concentration in experiments with molar ratio of Al:Si:SO_4=1:1:0 and 1:1:5, respectively, whereas the small particles contributed 0.15 mg/L and 0.15 mg/L after 48 hours of settling, respectively. These data indicate that small suspended particles increased from 30 minutes to 48 hours when solution contained silicate at pH=6.0.

At pH=8.0, the contribution of small particles was 0.11 and 0.02 mg/L after 30 minutes of settling in experiments with molar ratio of Al:Si:SO_4=1:1:0 and 1:1:5, respectively, whereas the small suspended particles contributed 0.05 mg/l and 0.05 mg/L of suspended Al concentration after 48 hours of settling, respectively. In experiment without silicate and sulfate, the small suspended particles contributed 0.03 mg/L suspended Al concentration after 48 hours of settling at pH=8.0, which was close to the amount in experiments with low silicate concentration. In Figure 5.27, it can be seen that the suspended Al concentrations was close at pH=8.0 after 48 hours of settling in experiments with low silicate and without silicate. Therefore, it is concluded that the small suspended particles is the key factor to affect the suspended Al concentration after a long settling time (48 hours). At pH=6.0, the presence of silicate (low concentration) increased the suspended Al concentration was due to the formation of small suspended particles (most probable Al-silicate precipitates), which can remain in solution for a long time (> 48 hours).

When solution contained very high silicate concentration (Al:Si:SO_4=1:2.5:5), the contribution of small suspended particles was 0.24 and 0.35 mg/L of suspended Al concentration after 30 minutes at pH=6.0 and 8.0, respectively. However, after 48 hours, the small suspended particles contributed 0.74 mg/L, and 0.94 mg/L suspended Al concentration at pH=6.0 and 8.0, respectively, which was much higher than at 30 minutes. These results indicate that the number of small suspended particles (<5µm) has been greatly increased from 30 minutes to 48 hours. Therefore, it can be concluded that the increase of small suspended particles caused the increase of suspended Al concentration when solution contained very high silicate concentration.

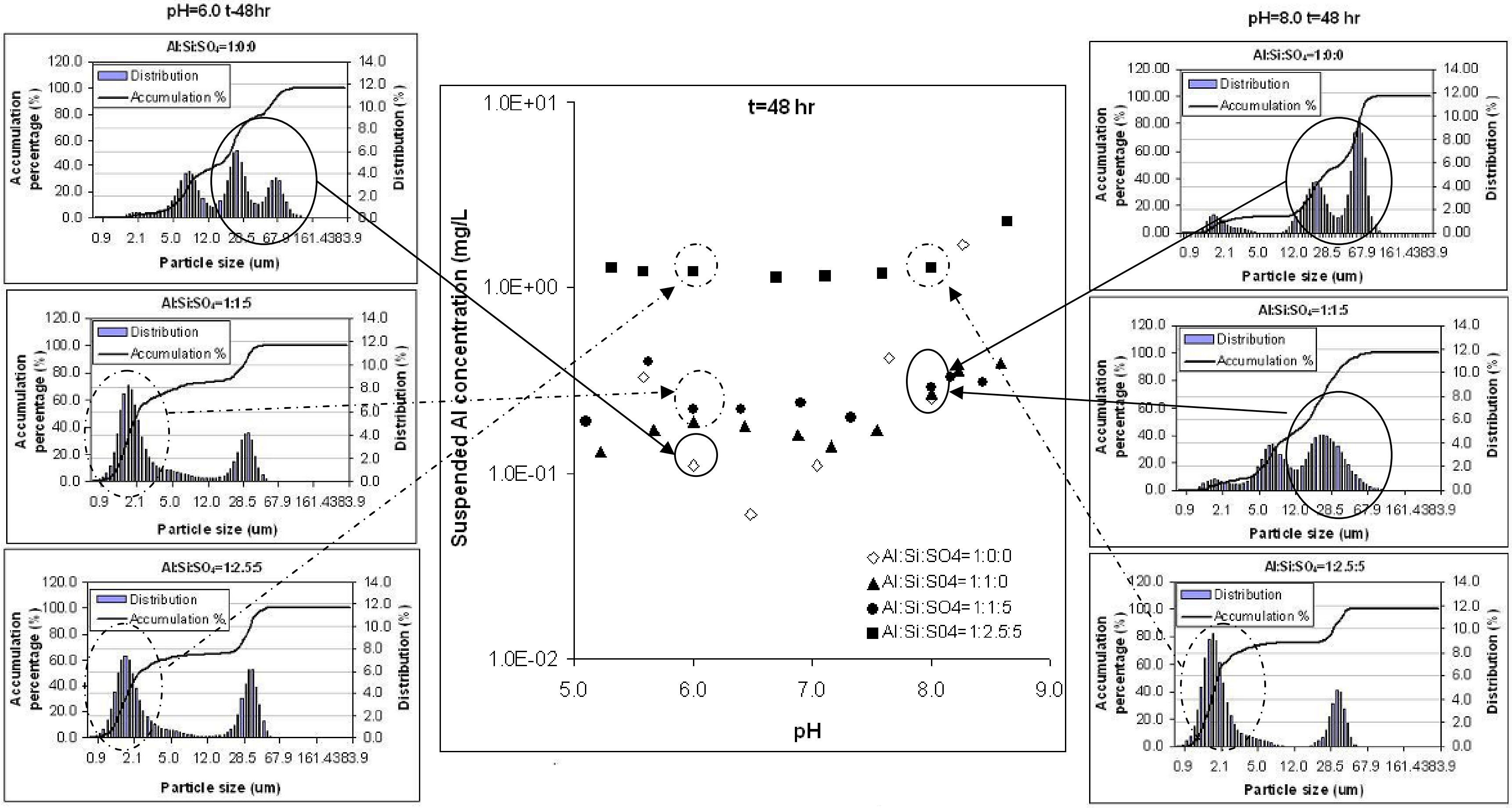


Figure 5.27 Suspended Al concentration at different pH values after 48 hours of settling

5.6 SUMMARY AND CONCLUSIONS

1 Laboratory study was conducted to evaluate the effects of silicates alone and/or the combination of silicates and sulfates on both suspended and soluble Al concentrations in a synthesized Al-bearing acidic rock discharge with different Al:Si:SO_4 molar ratios (1:1:0, 1:1:5, and 1:2.5:5). Results showed that pH is the critical parameter for soluble Al concentration controlling in Al-bearing ARD treatment. The influences of silicate alone and/or the combination with sulfate on soluble aluminum concentration appeared to be of secondary importance as compared to the overall influence of pH.

2 Synthetic ARD experiments showed that silicate and/or the combination of silicate and sulfate influenced Al concentration in both soluble and suspended Al phases. Silicates at higher molar ratios in solution (Al:Si=1:2.5) resulted in increasing the total aluminum level in the supernatant even after 48 hours of settling. It is clear from this study that sulfate and silicate have effects on both soluble and suspended Al concentration in neutralization of Al-bearing ARD.

3 The presence of silicate reduced the soluble Al concentration immediately after pH adjustment. The reason was the formation of Al-silicate precipitates which have a lower solubility than amorphous $Al(OH)_3$. However, the sludge analysis showed that most of the precipitates formed in experiments were amorphous $Al(OH)_3$. The sludge analysis also showed that some silicate can settle down in the form of $Si(OH)_{4(s)}$. The presence of sulfate can reduce the soluble Al concentration at $pH > 8.0$, when silicate concentration was low. Furthermore, sulfate can enhance the precipitation of silicate in the form of $Si(OH)_4$ instead of Al-silicate precipitates.

4 Sludge analysis showed that no crystalline precipitates were formed in the experiments. the SEM analysis showed that the silicon contents in sludge did not show a significant difference after a long settling time (48 hours). The elevated silicate levels resulted in a higher silicon content in sludge.

5 The presence of silicate reduced the suspended particle sizes both individually and in combination with sulfate. High levels of silicate could increase the effluent Al concentration by forming numerous small diameter particles. Co-presence of sulfate and silicate, however, can also form particles containing $Si(OH)_{4(s)}$.

6.0 PREDICTION OF EFFLUENT AL CONCENTRATION AND CHARACTERISTICS OF SLUDGE FROM THE JONATHAN RUN ACTIVE TREATMENT SYSTEM

6.1 INTRODUCTION

Jonathan Run is a tributary to the South Fork of Beech Creek, located near the intersection of State Route 144 and I-80 in Centre County, Pennsylvania (shown in Figure 6.1). The headwaters of Jonathan Run are located east of Snow Shoe in Centre County, Pennsylvania. It was once a quality stream used as a trout fishery for the local public and was used to support breeding ponds for the Snow Shoe Summit Lodge Corporation. The pH of water of Jonathan Run has been declined after the construction of I-80, and aluminum is elevated as toxic to aquatic life because of its ability to clog the gills of fish.

These water quality changes in Jonathan Run occurred in the 1960’s during the construction of I-80. The headwaters were filled and used for staging during the highway’s construction. A large amount of excess sandstone, produced by several large road cuts, was piled on the site and was used to construct a 60-80 foot high embankment that supports both lanes of I-80. After the construction of I-80 in the 1960’s by the Pennsylvania Department of Transportation (PennDOT), Jonathan Run was no longer able to support aquatic life. Previous research determined that the primary source of contamination originated from the acidic sandstone fill that was placed across the stream valley to support the interstate. The interstate platform, which was built directly over the stream channel was constructed using outcrops from nearby road cuts that contained high amounts of sulfide in the form of pyrite. When these minerals are exposed to oxygen and water they oxidize and generate acidity (Hedin Environmental, 2003.). The acidic discharge in Jonathan Run contains high aluminum concentration that is different from other acidic drainage. It is assumed when the acidic water generated by the acidic sandstone running over the alumino-silicatete (clay) soil, clay is disrupted and aluminum (Al^{3+}) is replaced by hydrogen ions (H^+) (Tan, 2000; Feng *et al*, 2000*;* Vazquez *et al.*, 2010a and 2010b).

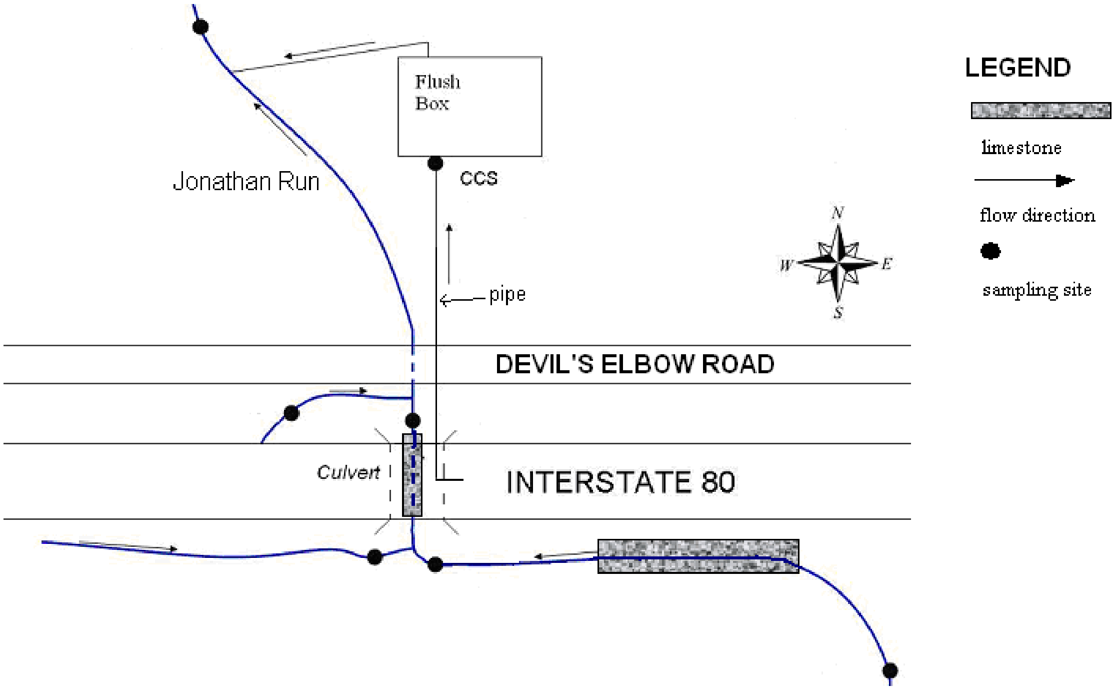


Figure 6.1 Sketch map of Jonathan Run location

Previous reported work stated that low pH and high aluminum concentration are the main pollutants in the Jonathan Run (Hedin Environmental, 2003; Neufeld *et al*. 2007). Water from the culvert collection system (called "CCS") flows coming through the embankment and platform supporting I-80. The components of acidic discharge in Jonathan Run are listed in Table 6.1. This water becomes the main contributor of aqueous aluminum (~ 40-60 mg/L) to the Jonathan Run site discharge and the point source of aluminum contamination. This water also contains relative high sulfate (~400mg/L) and about ~25 mg/L Si.

6.2 CHEMICAL COMPONENTS OF FIELD ARD IN JONATHAN RUN

Water collected from culvert "CCS" of Jonathan Run was used in the laboratory to simulate the NaOH precipitation treatment process. The chemistry of field water from CCS is shown in Table 6.1. In Table 6.1, it can be seen that the total aluminum concentration was about 41 mg/L, whereas the sulfate concentration was about 421 mg/L. This ARD contained only 0.86 mg/L Fe. Additional metal ions include 10.4 mg/L Ca, 12.4 mg/L Mg, 104 mg/L Na, 3.5 mg/L K, 7.1 mg/L Mn, 0.50 mg/L Zn, and about 25 mg/L Si.

The NaOH solution used in the laboratory experiments was 5% (wt). The goal of the laboratory experiments with field water from Jonathan Run was to compare some of the prior results using synthetic ARD waters with actual ARD waters. The laboratory experimental procedure was the same as experiments with synthetic ARD described in Chapter 3. Outcomes of concern include the effect of pH on the final aluminum concentration (both soluble and total) and the effect of settling time on the effluent aluminum concentration. pH values evaluated were in the range of 6.0 to 8.0, which may be typical value of the actual pH range that will be found during the operation of the field treatment plant.

Table 6.1 ARD composition of culvert (CCS) discharge (mg/L)

	Total		Dissolved	
	Average	Stdev	Average	Stdev
Al	41.1	0.12	40.5	0.48
Iron	0.86	0.01	0.84	0.01
Ca	10.4	0.1	10.1	0.13
Mg	12.48	0.05	11.55	0.44
Na	104.0	0	101	1.0
K	3.52	0.07	3.30	0.09
Mn	7.05	0.03	6.75	0.12
Zn	0.50	0.01	0.50	0.01
SO_4	420.9	13.2	413.7	3.0
Si	25.5	0.52		
pH*	3.6	0.02		
TSS*	3.8	0.35		

*: only the unfiltered samples were measured

6.3 Al CONCENTRATIONS AT DIFFERENT pH VALUES AND SETTLING TIME IN LABORATORY EXPERIMENTS WITH FIELD WATER FROM JONATHAN RUN

6.3.1 Total and soluble Al concentrations at different pH values after different settling time in laboratory experiments with field ARD

The aluminum concentrations have been measured after different settling time (settling time= 2hr, 24 hr, 48hr). Figure 6.2, 6.3, and 6.4 present the change of total and soluble Al concentrations with supernatant pH values from treatability experiments of field ARD. These data were collected after 2 hours, 24 hours, and 48 hours of settling, respectively. The data is also presented in Table 6.2.

From these figures, it can be found that the lowest soluble aluminum concentration occurred at pH value among 6 to 6.5. When pH was higher than 6.5, the soluble aluminum concentration increased quickly with the increasing of pH. On the other hand, the total aluminum concentration did not change much from pH =5.3 to 7 because the soluble fraction of the total aluminum in this pH range was negligible compared with the suspended aluminum concentration (difference between total and soluble aluminum as shown on Figures 6.2, 6.3, and 6.4) thus the vast majority of the total discharged aluminum in this pH range was suspended.

Soluble aluminum concentration increased dramatically outside of this pH range, thus causing soluble aluminum to become the controlling parameter for total aluminum discharge. This information substantiates prior work done with synthetic ARD wastes, and confirms the importance of good pH control at Jonathan Run.

Table 6.2 Treatability results with Jonathan Run culvert discharge water showing total and soluble Al concentrations after pH adjustment and settling times

pH	2 hours		24 hours		48 hours	
	total	soluble	total	soluble	total	soluble
5.3	1.12	0.31	0.34	0.13	0.33	0.12
5.5	1.13	0.27	0.41	0.12	0.3	0.08
6.0	0.91	0.1	0.24	0.05	0.25	0.03
6.1	1.45	0.08	0.27	0.04	0.26	0.05
6.6	1.37	0.11	0.25	0.05	0.22	0.02
7.0	1.67	0.2	0.47	0.09	0.35	0.14
7.5	1.79	1.33	1.11	0.57	1.00	0.46
7.9	2.57	2.39	1.99	1.32	1.56	0.91
8.3	5.46	5.29	4.22	3.66	2.78	1.95

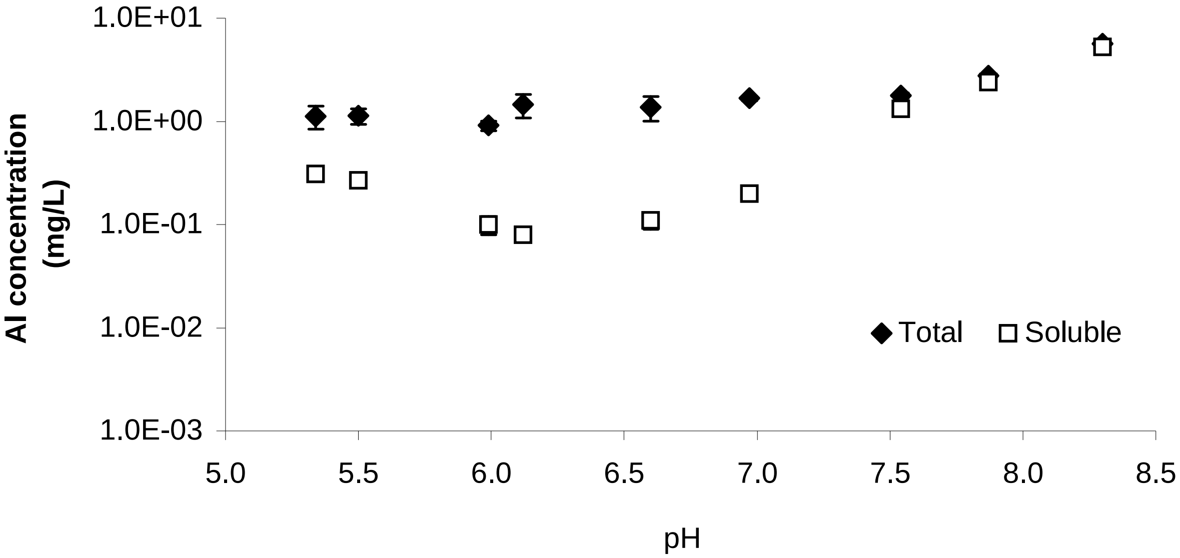


Figure 6.2 Total and soluble aluminum concentrations at different pH values in experiments with field ARD from Jonathan Run (settling time =2 hr)

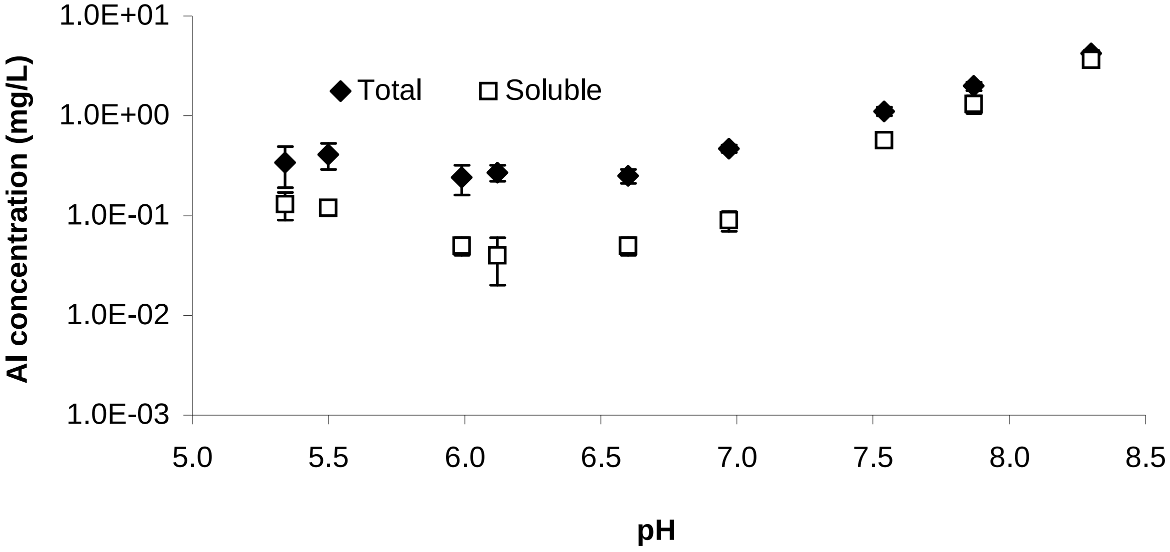


Figure 6.3 Total and soluble aluminum concentration at different pH values in experiments with field ARD from Jonathan Run after 24 hours of settling

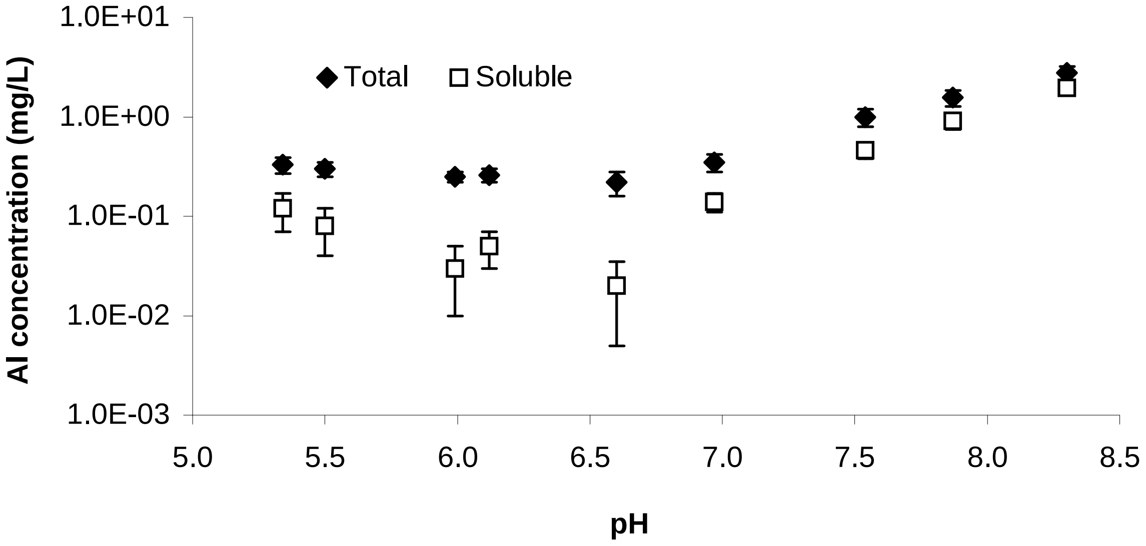


Figure 6.4 Total and soluble aluminum concentrations at different pH values in experiments with field ARD from Jonathan Run after 48 hours of settling

6.3.2 Suspended Al concentrations at different pH values after different settling time in laboratory experiments with field ARD

Figure 6.5 presents the suspended Al concentration at different pH values after 2, 24, and 48 hour of settling in the pH range of 5.3 to 8.3. The data showed that aluminum containing suspended solids was at a relatively constant level after 48 hours of settling in the pH range of 5.3 to 7.0. Higher pH values and shorter settling time (as would occur during wet weather events) will likely lead to higher levels of aluminum-containing suspended solids in the Jonathan Run discharge.

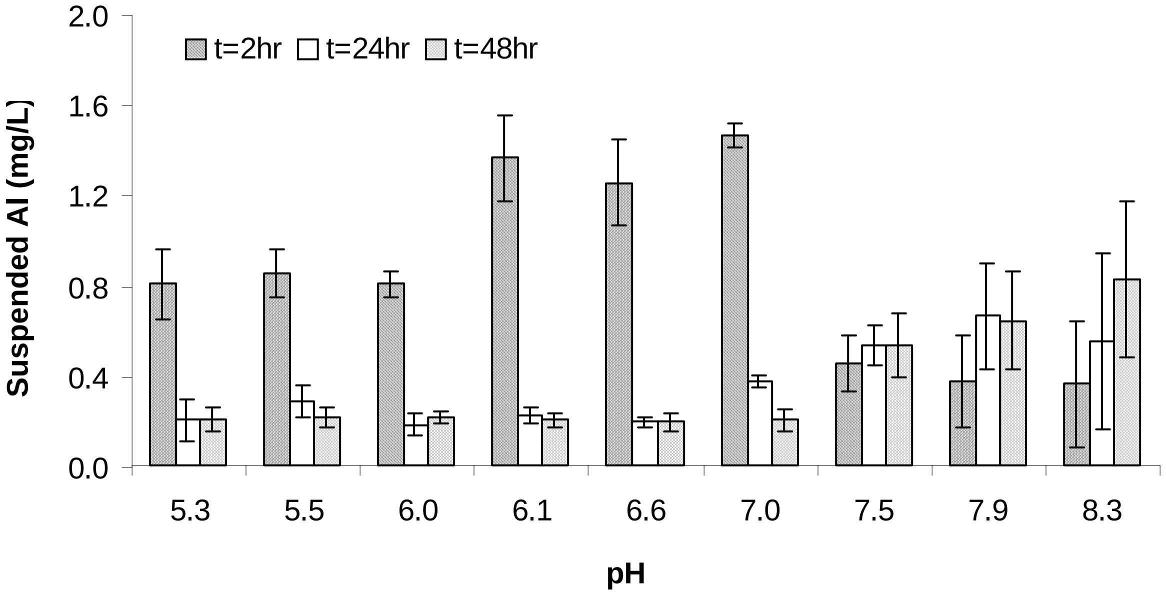


Figure 6.5 Treatability studies after settling: Suspended Al concentrations at different pH values and settling time

6.4 PREDICTION OF EFFLUENT Al CONCENTRATION IN ACTIVE TREATMENT SYSTEM OF ARD IN JONATHAN RUN

6.4.1 The prediction of soluble Al concentration with computer model (Mineql+ equilibrium computer model)

Traditionally, aluminum hydroxide is usually considered as the aluminum precipitates formed during neutralization processes. There are two different construction $Al(OH)_3$, amorphous $Al(OH)_3$ and gibbsite (crystalline $Al(OH)_3$). Since the solubility product of amorphous aluminum hydroxide and gibbsite is $10^{-31.8}$ and $10^{-33.2}$, respectively, the theoretical aluminum precipitates should be gibbsite. Therefore, the prediction with theoretical constant of aluminum hydroxide always shows the solubility of gibbsite (crystalline $Al(OH)_3$). However, in our study, it was found that the soluble Al concentration was higher than the calculated solubility of gibbsite. Furthermore, the analysis of precipitates collected in Jonathan Run field (Pu *et al*., 2010) also shows that the crystalline $Al(OH)_3$ was not detectable. Therefore, based on our study, in the prediction of the possible effluent Al concentration from active treatment system in Jonathan Run, amorphous $Al(OH)_3$ is a possible species of Al-precipitates, but gibbsite is not, even though the solubility of gibbsite is lower.

In actual conditions, the chemistry of ARD is complex. Not only aluminum hydroxides, but also other aluminum compounds, such as jurbanite, basaluminite, and Al-silicate (such as alunite and kaolinite), are the possible species of aluminum precipitates. The species of aluminum precipitates could be more complex in the presence of both sulfate and silicate. On the basis of the theoretical value for the solubility product of jurbanite (($A1(OH)SO_4$), the precipitation of this mineral has been hypothesized by several authors (Nordstrom, 1982a and

1982b; Prenzel, 1983; Khanna *et al*., 1987 Levy et al. 1997). On the other hand, close inspection of solution data and the lack of evidence for coupled mass transfers of A1 and SO_4 between solid phases and soil solution has led others to disagree the jurbanite hypothesis (Mulder *et al*., 1987). In many cases, the theoretical calculation by different models has hypothesized that jurbanite, or basaluminite, and or alunite are the possible species of aluminum precipitates (Williams and Smith, 2000; Ferna´ndez-Caliani et al. 2008).

Based on the previous study and the varies of soluble Al concentrations at pH=6.0 and 8.0 in different experiments with synthetic ARD, it has been concluded that the possible Al-sulfate precipitates formed in Al-bearing ARD neutralization processes are basaluminite ($Al_4(OH)_{10}SO_4$). Therefore, basaluminite is also considered as the possible Al-precipitates in the prediction with Mineql+ model.

In order to verify these conclusions, Mineql+ model was used to calculate the soluble Al concentration in experiments with field ARD from Jonathan Run after pH adjustment. In the calculation, as mentioned above, the possible Al-precipitates were selected as amorphous $Al(OH)_3$ and basaluminite ($Al_4(OH)_{10}SO_4$), respectively. The input data is the components of ARD used in the experiments (showed in Table 6.1).

Figure 6.6 presents the experimental soluble aluminum concentration at different settling time and the calculated soluble aluminum concentration at pH =6.0 and 7.9. All pH are listed in Table 6.3. In Figure 6.6, it can be seen that the trend of soluble aluminum concentration of experiments was similar to the soluble aluminum concentration calculated with Mineql+ model. Meanwhile, the figure shows that the calculated aluminum concentrations were lower than the soluble aluminum concentrations in the experiments when settling time was 48 hours. The reason is that the filter paper size used in the experiments was 0.45 µm, therefore some precipitates could pass the filter paper, and the soluble aluminum concentration in the experiments became higher than it should be. Comparing the soluble aluminum concentration at different settling time, it can be found that the value decreased as the increase of settling time. Therefore, the calculated aluminum concentration could be considered as the final soluble aluminum concentration when the settling time is long enough. The figure confirms information gathered from synthetic samples in that the actual precipitates appeared to be a combination of both amorphous $Al(OH)_3$ and other Al-containing precipitates that can be represented by basaluminite.

Table 6.3 Calculated and experimental soluble aluminum concentration at different pH (mg/L)

	Experimental results			Calculated results		
pH	t* = 2 hr	t = 24 hr	t = 48 hr	$Al(OH)_3$ (am)	basaluminite	Theoretical
5.3	0.31	0.13	0.21	12.26	0.14	0.14
5.5	0.27	0.12	0.08	4.05	0.05	0.04
6.0	0.10	0.05	0.03	0.55	0.01	0.01
6.2	0.08	0.04	0.05	0.43	0.01	0.01
6.6	0.11	0.05	0.02	0.27	0.01	0.01
7.0	0.2	0.09	0.14	0.4	0.07	0.07
7.5	1.33	0.57	0.46	1.08	0.25	0.24
7.9	2.39	1.32	0.91	2.54	0.49	0.49
8.3	5.29	3.66	1.95	5.24	1.19	1.16

*: t: settling time

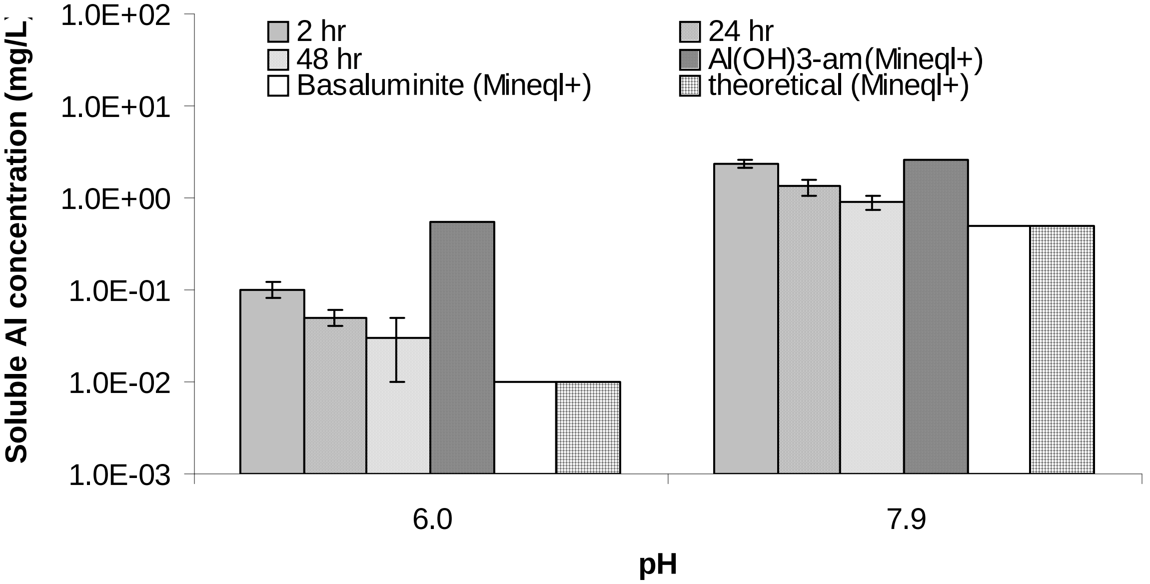


Figure 6.6 Treatability and modeled soluble Al concentrations at pH=6.0 and 7.9 and settling times of 2 hours, 24 hours, and 48 hours.

(Theoretical represent the soluble Al concentration when $Al(OH)_3$(am), basaluminite, and kaolinite were considered as possible Al-precipitates. Mineql+ model provides equilibrium values only.)

The simulation with Mineql+ model shows that the calculated soluble Al concentration was lower than the experimental results. As discussed above, the reason is that the calculated soluble Al concentration is in equilibrium conditions. Therefore the soluble Al concentration in experiments was a litter higher than the calculation results. In Jonathan Run active treatment, the actual settling time might be longer than two days in our experiments. So the actual effluent soluble Al concentration will be lower than the experimental soluble Al concentration and close to the calculated soluble Al concentration. Prior study showed that the silicate could also influence the soluble Al concentration and the settlement of precipitates in ARD treatment. In Jonathan Run, the investigation of water quality showed that the discharge water from CCS, which is the main influent water of active treatment system, contained about 25 mg/L Si. The silicate level is relative low to the Al level. Therefore, the effluent soluble Al concentration cannot be controlled by Al-silicate precipitates. In other words, although the Al-silicate precipitates might be a composition of sludge in the prediction, it will not influence the calculated soluble Al concentration. However, the Al-silicate precipitates were also considered as the possible species of Al precipitates as we found in the prior study.

In summary, in the prediction with Mineql+ model, the possible Al precipitates formed in the treatment processes are amorphous $Al(OH)_3$, basaluminite ($Al_4(OH)_{10}SO_4$), and Al-silicate (considered as kaolinite) based on our study. Of course, the amount of these compounds formed varies with the influent components, pH values, and temperature. The following section is the effect of temperature on the effluent Al concentration.

6.4.2 The effect of temperature on effluent Al concentration from Al-bearing ARD/AMD treatment system in Jonathan Run

The temperature is a factor that can influence either the soluble Al concentration or the settling characteristics of Al-precipitates. In actual ARD treatment systems, the temperature of water varies with seasons. Therefore, to understand the effect of temperature on effluent Al concentration is also important.

In the prediction of effluent Al concentration influenced by temperature, similar to the above calculation, the soluble Al concentration at different temperature was calculated by Mineql+ model. In calculation with Mineql+ model, the input data is the components of field ARD collected in Jonathan Run (Table 6.1). The possible species of Al-precipitates are also selected as amorphous $Al(OH)_3$, basaluminite, and kaolinite.

Temperature might also influence the suspended Al solids. The Stocks Law indicates that the primary reason that would influence suspended aluminum solids settling rate at different temperatures is water viscosity (MWH, 2005). However, temperature could also influence the suspended Al solids in size, strength etc. (Fitzpatrick *et al*., 2004). Furthermore, variations in wind speed which would cause a stirring in the settling tanks is likely to be more significant on effluent suspended Al solids than temperature. Therefore, the difference of suspended Al concentration among different temperature is neglected and considered as a constant.

The prior data showed that the suspended Al concentration remained about 0.2 mg/L after 24 hours when pH=6.0 and about 0.55 mg/L at 48 hours when pH=8.0 in experiments with field ARD from Jonathan Run. In the experiments with Al:Si:SO_4 ratios equal to 1:1:5, which was close to the molar ratio of ARD in Jonathan Run, the suspended Al concentration was from 0.2 to 0.3 mg/L in pH range of 6.0 to 8.0. As mentioned above, the suspended Al concentration varies with settling time. In actual treatment system, the settling time changes with influent rate. In Jonathan Run, the influent rate varies with seasons and precipitation. In storm weather, the settling time decreases, then the suspended Al concentration increases in effluent. Since the actual settling time in settling tank is usually longer than 48 hours, it is reasonable to assume the suspended Al concentration is 0.2 mg/L in effluent from the active treatment system in Jonathan Run.

Figure 6.7 shows the prediction of the effluent Al concentration from active treatment system of ARD in Jonathan Run at different water temperature and the data are listed in Table 6.4. The simulated soluble Al concentration shows that the higher the temperature, the higher the soluble Al concentration. The data also show that in the conditions of pH<=7.5 and temperature <=25˚C, the effluent Al concentration should be less than 0.6 mg/L if settling time is long enough. From Figure 6.7, it can be seen that both soluble and total Al concentrations at pH=6.0 are almost independent on temperature, however, at pH=8.0, the higher the temperature of water, the higher the Al concentrations (both soluble and total Al concentrations). The data indicate that the pH value is a critical parameter for controlling the effluent Al concentrations when water's temperature is high (30ºC). In other words, during summer season, the pH control of treatment system is very important to control the effluent Al concentrations from treatment system of Jonathan Run.

Table 6.4 Predicted effluent Al concentration at different temperature in active ARD treatment system in Jonathan Run (Mineql+ modeling)

	Soluble Al (mg/L)					**Total Al (mg/L)**				
	10˚C	**15˚C**	**20˚C**	**25˚C**	**30˚C**	**10˚C**	**15˚C**	**20˚C**	**25˚C**	**30˚C**
6.0	0.008	0.008	0.009	0.010	0.014	0.21	0.21	0.21	0.21	0.21
6.5	0.005	0.006	0.008	0.014	0.032	0.21	0.21	0.21	0.21	0.23
7.0	0.007	0.011	0.022	0.060	0.18	0.21	0.21	0.22	0.26	0.38
7.5	0.017	0.040	0.12	0.37	1.15	0.22	0.24	0.32	0.57	1.35
8.0	0.054	0.17	0.56	1.87	5.99	0.25	0.37	0.76	2.07	6.19

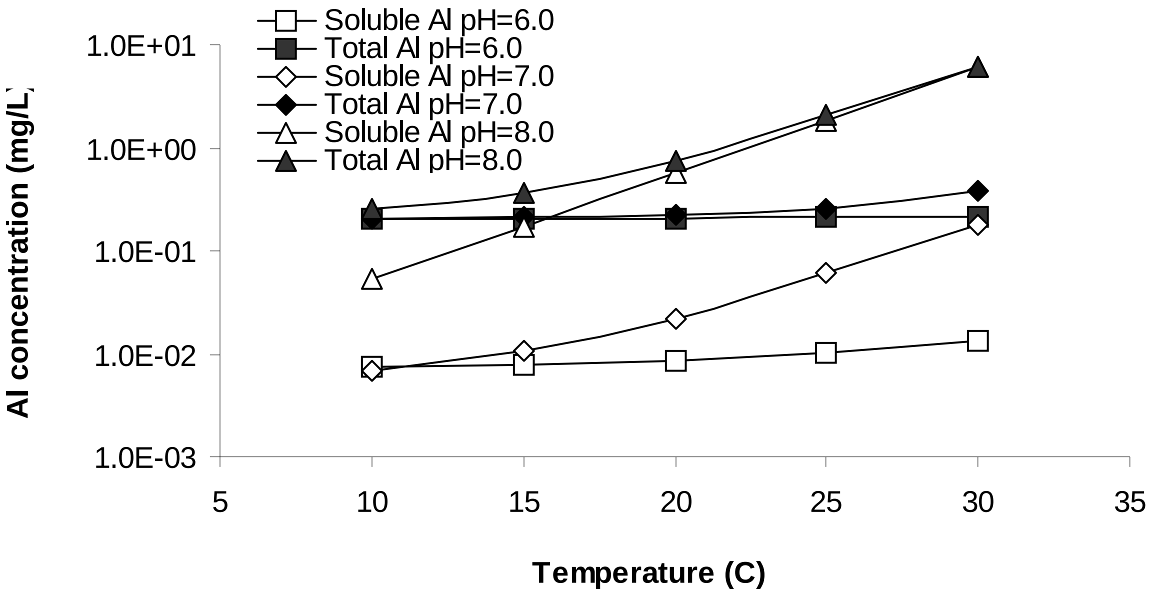


Figure 6.7 Influence of temperature on total effluent Al concentration from active treatment system of Al-bearing ARD/AMD with NaOH in Jonathan Run.

6.5 SUMMARY AND CONCLUSIONS

In general, treatability experiments with culvert collection system (CCS) ARD from Jonathan Run suggested that settling detention time of at least 24 hours is necessary to minimize (but not eliminate) aluminum-containing particulate matter. In the pH range of 6 to about 7, aluminum-bound particulate matter was the predominant form of aluminum in the supernatant even after 48 hours of settling. However, as the pH increased beyond 7, the soluble forms of aluminum quickly increased in concentration and became predominant in the supernatant. This indicates that pH control can manage soluble aluminum only while settling tank operation has a significant influence on aluminum-containing suspended particulate matter in the supernatant. This further suggests the importance of pH control, particularly during wet weather events when the detention time in the field-settling basin is shortened and aluminum discharges from the Jonathan Run site are likely to become elevated.

Modeling of the field ARD discharge with the Mineql+ computerized equilibrium model sheds light on and provides an explanation for the chemical speciation of aluminum that is likely to exist after NaOH pH adjustment and precipitation at Jonathan Run. The solubility of amorphous $Al(OH)_3$ is higher than the solubility of basaluminite, and the measured levels of soluble aluminum are somewhere in between those solubilities even after 48 hours of settling. This could imply that the solution is not in equilibrium even after 48 hours of settling, or that additional aluminum species exist in this complex solution.

Water temperature will influence the effluent Al concentration of ARD treated by an active treatment system. Calculations with the MINEQL+ model for the field water from a field ARD site in Centre County Pennsylvania show that the soluble Al concentration significantly increases at all pH values with increase of temperature, which could exist during warm summer temperatures. The minimum effluent total Al concentrations is about 0.5 mg/L in the range of pH =6.0 to 7.0. The total Al concentration would be higher when the pH values are greater than 7.0 during warm temperature conditions in summer, since the soluble Al concentration increase sharply with temperature at pH >7. Calculations with Mineql+ model suggest that pH control is more important during summer months to ensure the effluent Al concentration than during colder winter months.

It is suggested that further research can be conducted once the settling basins are operational to evaluate better means to reduce the zeta potential of colloids formed in the supernatant.

7.0 OVERALL SUMMARY AND CONCLUSIONS

1 This study has evaluated the effects of sulfates and silicates on Al removal during the active treatment of ARD discharge. Laboratory experiments of NaOH neutralization of aqueous aluminum with different levels of sulfates and silicates were conducted at different pH values. Experiments showed that pH is the critical factor to control the effluent soluble Al concentration during Al-bearing ARD/AMD treatment. Results showed that the presence of sulfates and/or silicates decreased soluble Al concentration due to the formation of Al-sulfates and/or Al-silicates precipitates. Therefore, based on the prediction of probable effluent soluble Al concentration from a treatment system of ARD/AMD, not only $Al(OH)_3$, but also Al-sulfate and Al-silicates should be considered as the likely species of Al-precipitates.

2 Results showed that either sulfates or silicates and combination of them affected both soluble and suspended aluminum in the supernatant of active treatment with NaOH neutralization. The presence of sulfates in solution reduced the soluble aluminum concentration, with concomitant formation of small size particles, which were mainly basaluminite. The reduction of soluble aluminum by the formation of basaluminite appeared after a long settling time (48 hours). However, elevated sulfates levels increased the formation of small suspended Al particles, which could remain in the supernatant for long time and thus increase the total level of aluminum in the discharge. Similar observations were made with the presence of silicates. Silicates can also reduce soluble Al concentration immediately after pH adjustment due to the

formation of Al-silicate precipitates. As with the case of sulfates, the presence of silicates increased the suspended Al concentration also, especially when silicates concentration was high. Both elevated sulfate and silicate levels result in aluminum complexation and formation of small particles that do not settle well. The increase of remaining small particles leads to the increase of total aluminum levels (soluble + suspended) if settling time is insufficient in the settling tanks, which may occur during wet weather events. Therefore, detention time is also important for ARD/AMD active treatment design, which can be short during wet-weather events.

3 The study of reduction of aqueous aluminum and sulfates with settling time revealed that the formation of amorphous aluminum hydroxide was the main precipitate product occurring after NaOH neutralization. However, when sulfates were present, product was basaluminite after 4 hours of settling. The formation of basaluminite caused the reduction of soluble aluminum concentration after a long settling time (48 hours).

4 The calculated values using the MINEQL+ computerized equilibrium model confirmed that solution reached equilibrium with amorphous $Al(OH)_3$ within the first 30 minutes after pH adjustment.

5 Sludge analysis with XRD revealed that no crystalline precipitates were produced during experiments. The XRD results indicated that the reduction of soluble Al was not due to the formation of gibbsite (crystalline $Al(OH)_3$). Furthermore, TGA and SEM analysis showed that sulfate content in sludge increased with settling time and the sulfate levels.

6 The molar ratio of $Al:SO_4$ of suspended particles showed that the composition of suspended particles became unchanged after 24 hours of settling and the value of molar ratio of $Al:SO_4$ of suspended particles in the supernatant was close to the theoretical molar ratio of $Al:SO_4$ of basaluminite. Based on these results, it is concluded that the formation of basaluminite was the

key reaction to reduce the soluble Al concentration and the main species of suspended Al solids was basaluminite after 24 hours of settling.

7 Suspended particle size distributions revealed that the presence of sulfates and/or silicates reduced the suspended particle size in the supernatant, with the increase in mass of suspended Al concentration in the supernatant. By comparing the particle sizes after 30 minutes and 48 hours of settling, it was found that pH alone did not influence the particle size. The reduction of suspended particle sizes was accompanied with the increase of sulfate in the suspended solids. Furthermore, the molar ratio of Al/SO_4 of suspended particles was close to the theoretical ratio of basaluminite. It is concluded that the reduction of suspended particle size was due to the change of species of suspended particles to become suspended basaluminite solids. .

8 The particle size analysis showed that the presence of silicates also decreased the mean size of suspended particles and increased the fraction of small-suspended solids in the supernatant. Therefore, the presence of sulfate and/or silicates will increase the effluent suspended Al concentration in a treatment system due to the small particle formation, although the soluble Al concentration can be reduced after long settling time.

9 In general, treatability experiments with ARD from a field ARD site in Centre County Pennsylvania suggested that settling detention time of at least 24 hours is necessary to minimize (but not eliminate) aluminum-containing particulate matter. In the pH range of 6 to about 7, aluminum-bound particulate matter was the predominant form of aluminum in the supernatant even after 48 hours of settling. However, as the pH increased beyond 7, the soluble forms of aluminum quickly increased in concentration and became predominant in the supernatant, which indicates that pH control can manage soluble aluminum only while settling tank operation has a significant influence on aluminum-containing suspended particulate matter in the supernatant.

The further suggests the importance of pH control, particularly during wet weather events when the detention time in the field-settling basin is shortened and aluminum discharges from the site are likely to become elevated.

10 Modeling of the field ARD discharge with the Mineql+ computerized equilibrium model sheds light on and provides an explanation for the chemical speciation of aluminum that is likely to exist after pH adjustment. The measured levels of soluble aluminum were somewhere in between the solubility of amorphous $Al(OH)_3$ and basaluminite even after 48 hours of settling, which imply that the solution was not in equilibrium even after 48 hours of settling, or that additional aluminum species existed in this complex solution.

11 Calculations with the MINEQL+ model for the field water from a field ARD site in Centre County Pennsylvania show that the soluble Al concentration significantly increases at all pH values with increase of temperature, which could exist during warm summer temperatures. The minimum effluent total Al concentrations is about 0.5 mg/L in the range of pH =6.0 to 7.0. The total Al concentration would be higher when the pH values are greater than 7.0 during warm temperature conditions in summer, since the soluble Al concentration increase sharply with temperature at pH >7. Calculations with Mineql+ model suggest that pH control is more important during summer months to ensure the effluent Al concentration than during colder winter months.

8.0 FUTURE RECOMMENDED RESEARCH

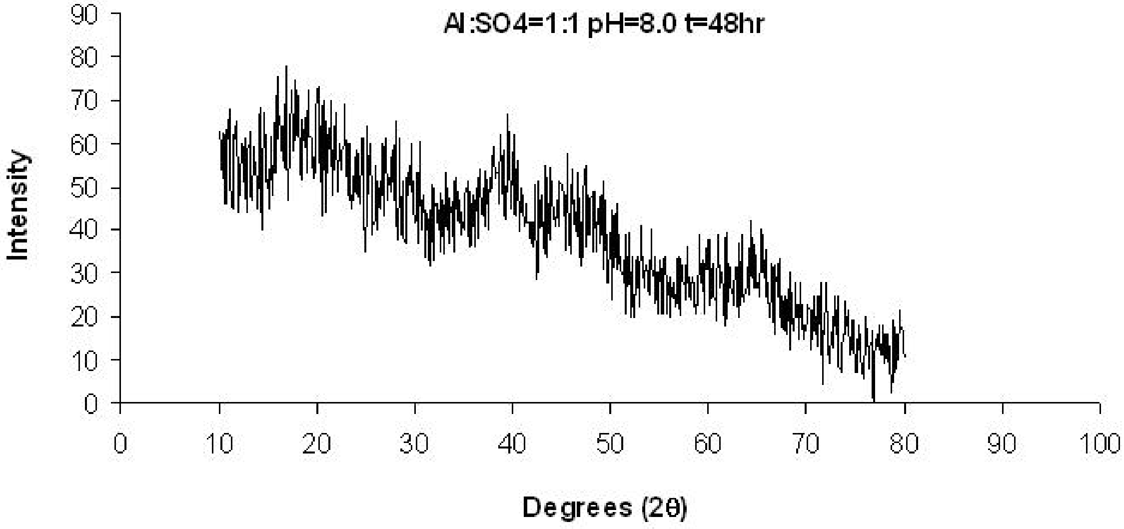
The following suggestions are presented as areas of future research on ARD/AMD treatment:

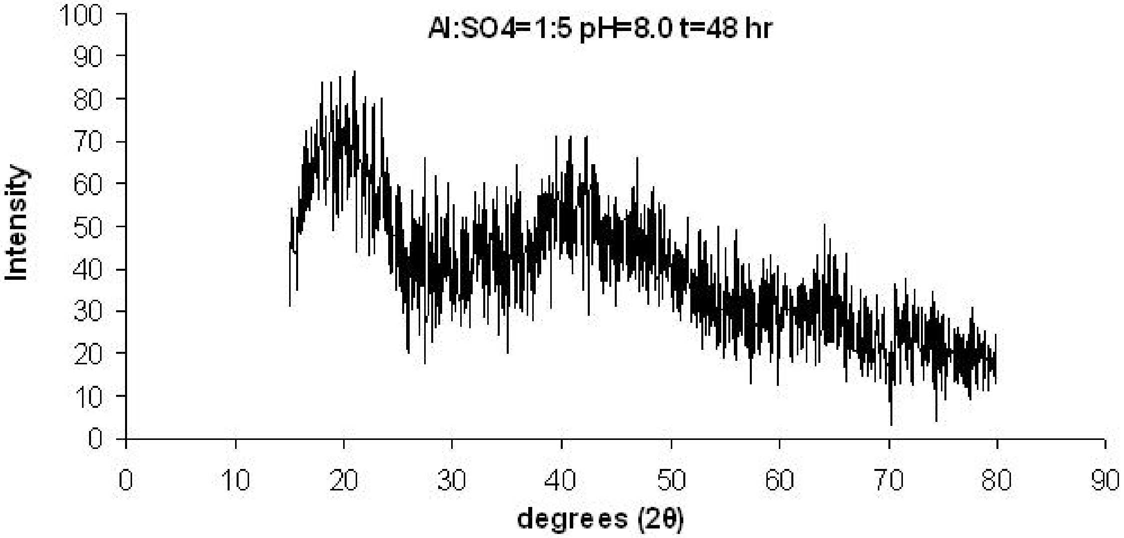
1. The variation of temperature from summer to winter is great, which could lead to a significantly different effluent Al concentration from a treatment system due to the effect of temperature on both soluble and suspended Al phases. The effect of temperature on soluble Al concentrations could be evaluated with a computer model. However, there is a lack of information of suspended solids with temperature in active AMD/ARD treatment systems.
2. The change of suspended particulate aluminum size with elevated sulfate levels might be due to the sorption of sulfate on $Al(OH)_3$ particles or the change of species of suspended Al particles (becoming aluminosulfate compounds). This study evaluated the main mechanisms that caused the reduction of Al particle size. It is suggested that a future study can isolate the effects of sorbed and reacted sulfate on the size distribution of suspended Al particles during AMD/ARD treatment.
3. Sodium and potassium are common solutes in AMD/ARD and the presence of potassium might affect the species of Al-precipitates when sulfates or silicates are present.

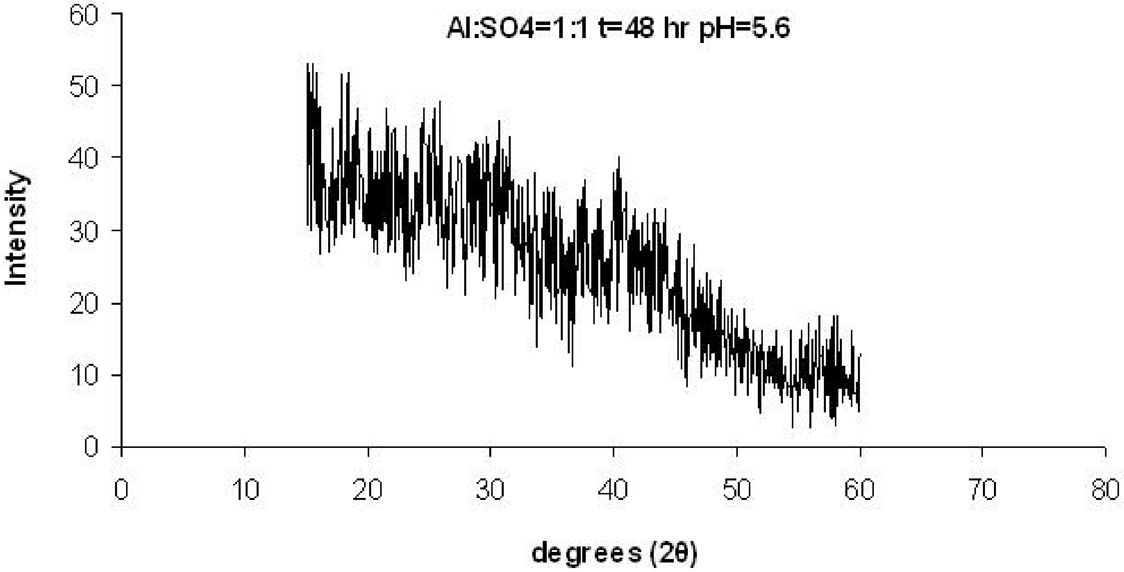
APPENDIX A

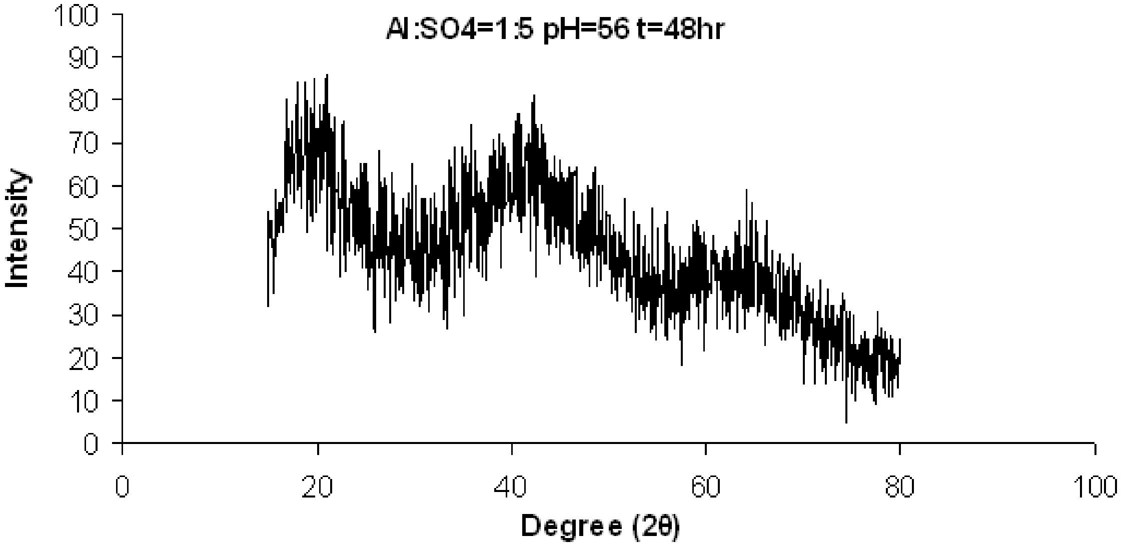
XRD PATTERNS OF SLUDGE

XRD patterns of sludge formed in experiment with low and high sulfate




Al:SO4=1:5 pH=8.0 t=48 hr
Intensity
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80
90
degrees (2θ)


Al:SO4=1:1 t=48 hr pH=5.6
Intensity
0
10
20
30
40
50
60
0
10
20
30
40
50
60
70
80
degrees (2θ)

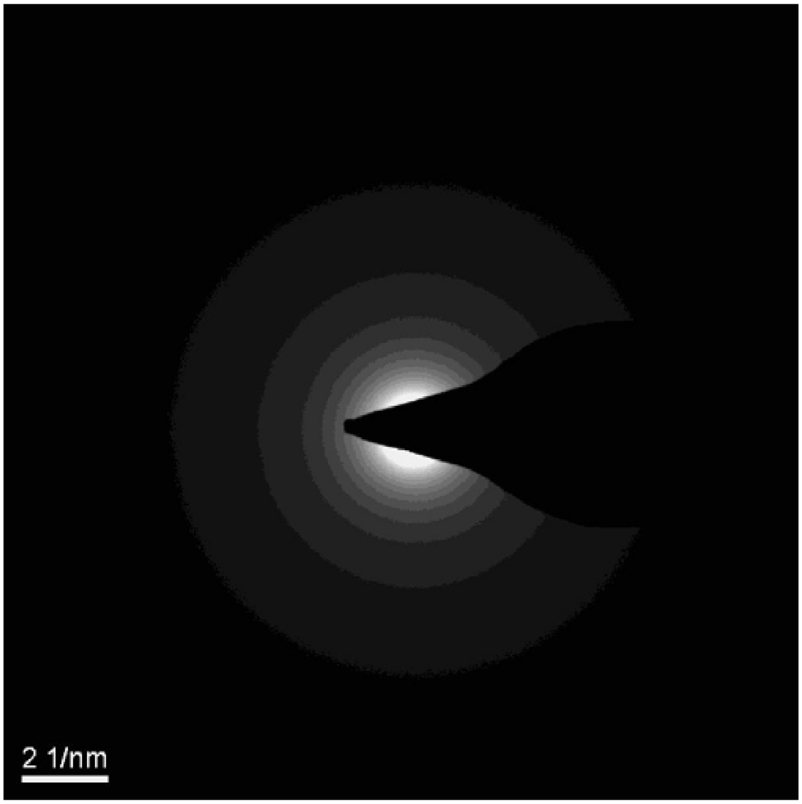

Al:SO4=1:5 pH=56 t=48hr
Intensity
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Degree (2θ)

APPENDIX B

SEM IMAGES OF SLUDGE AND THE CHEMICAL COMPONENTS

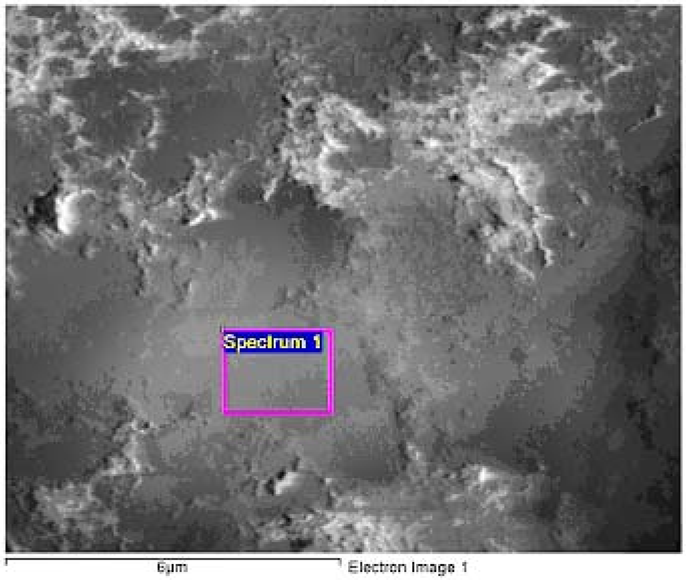
B.1 TEM DIFFRACTION PATTERN OF PRECIPITATES

Sulfate concentration (AL:SO_4=1:1), pH=6.6, t=48 hours



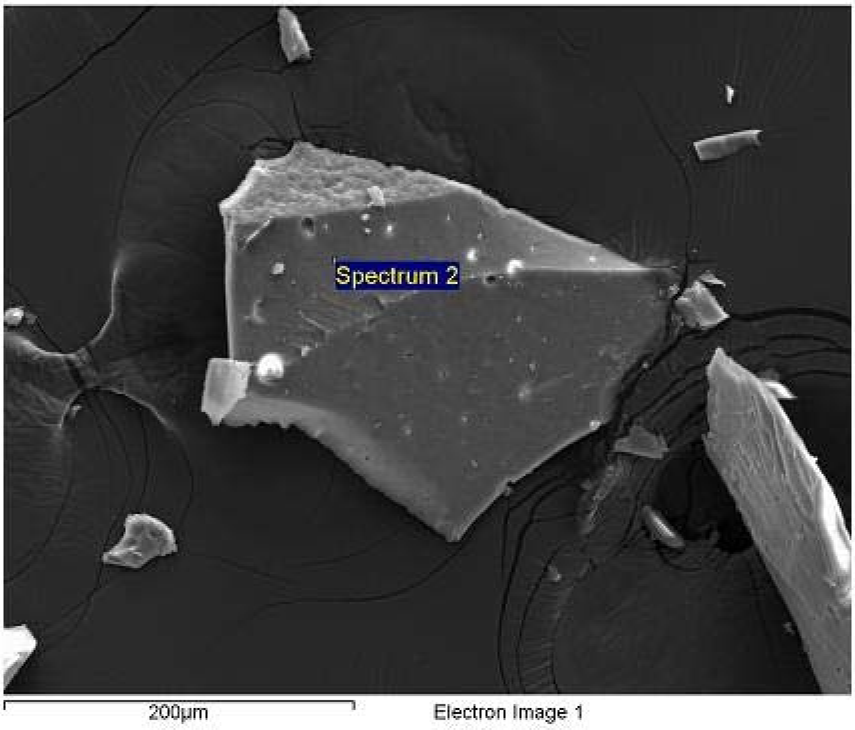
B.2 SEM IMAGES OF SLUDGE FORMED IN EXPERIMENTS WITH LOW SULFATE CONCENTRATION (Al:SO$_4$=1:1)

pH= 5.6 t=30min



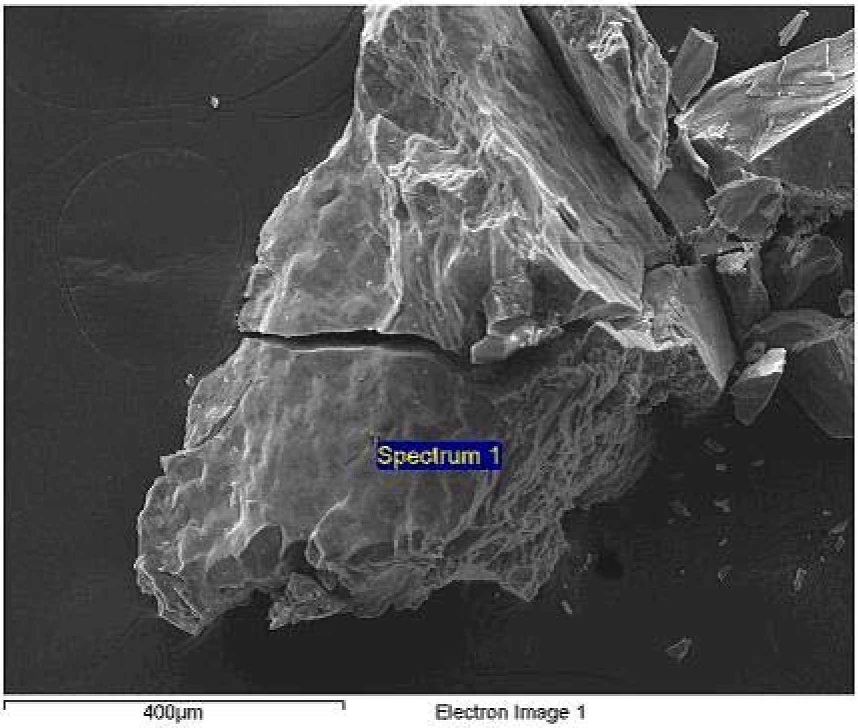
	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic %	Weight%	Weight %	Atomic%	Atomic %	Weight %	Atomic%
C K	1.78	2.69	0.94	4.18	6.42	1.46	2.30	3.52
O K	68.19	77.39	63.79	60.51	69.71	74.36	64.16	73.82
Mg K	ND	ND	ND	ND	ND	ND	ND	ND
Al K	28.66	19.28	34.13	33.33	22.75	23.57	32.04	21.87
Mn K	0.59	0.20	0.24	0.10	0.04	0.08	0.31	0.11
S K	0.78	0.44	0.91	1.88	1.08	0.53	1.19	0.68
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 5.6 t=48 hours



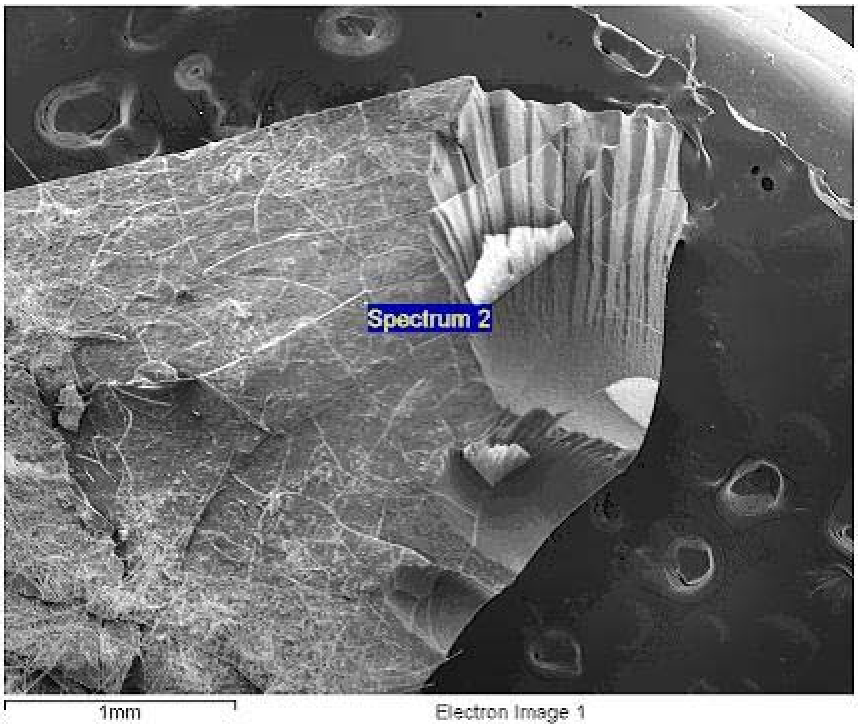
	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	3.78	5.64	2.48	3.78	3.58	5.50	3.28	4.97
O K	67.16	75.18	64.99	74.31	61.68	71.01	64.61	73.50
Mg K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al K	28.06	18.61	31.34	21.23	32.76	22.35	30.72	20.73
S K	1.01	0.57	1.19	0.68	1.98	1.14	1.39	0.80
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.01	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 6.0 t=30 minutes



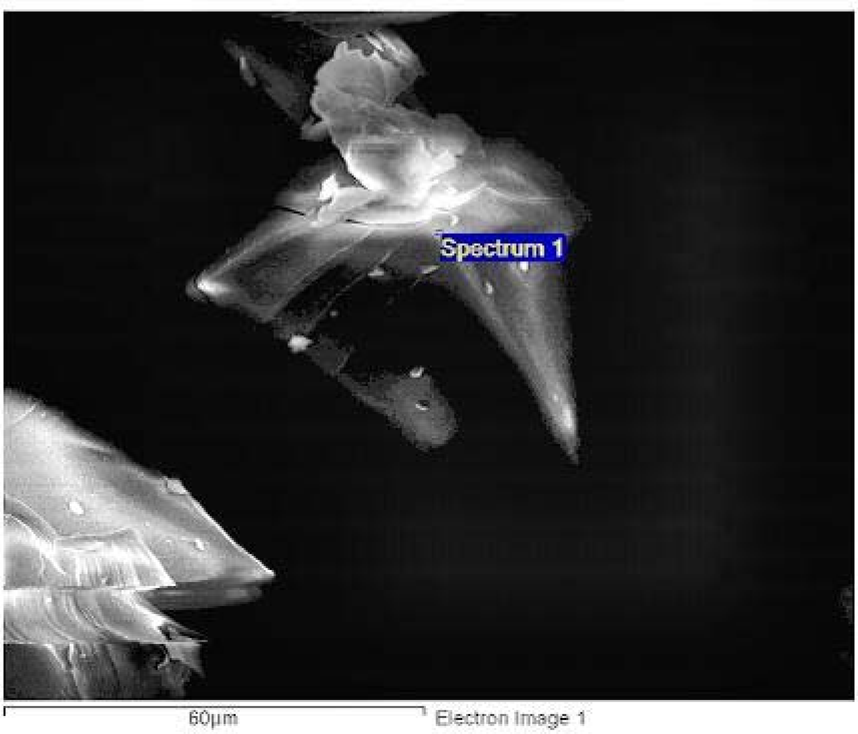
	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	1.68	2.62	4.65	7.03	1.16	1.78	2.50	3.81
O K	61.92	72.38	63.41	71.87	66.86	76.66	64.06	73.63
Mg K	0.42	0.33	0.13	0.10	0.13	0.10	0.23	0.17
Al K	34.63	23.99	29.79	20.01	30.80	20.93	31.74	21.64
S K	0.74	0.43	1.02	0.58	0.67	0.38	0.81	0.47
Ca K	0.35	0.16	0.72	0.33	0.22	0.10	0.43	0.20
Mn K	0.26	0.09	0.27	0.09	0.17	0.06	0.23	0.08
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 6.0 t=48 hours



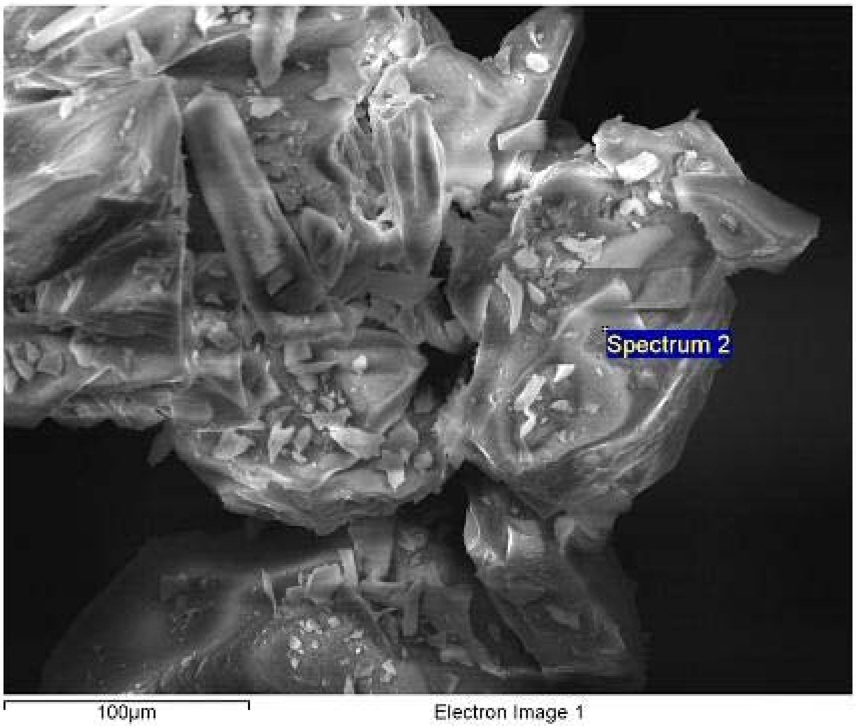
	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	5.09	7.52	5.58	8.45	2.90	4.37	4.52	6.78
O K	66.80	74.03	60.63	68.87	66.84	75.45	64.75	72.79
Mg K	0.72	0.53	1.05	0.80	0.63	0.47	0.80	0.60
Al K	26.68	17.52	31.25	21.03	28.46	19.04	28.79	19.20
S K	0.73	0.40	1.49	0.85	1.17	0.66	1.13	0.64
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 7.5 t=30 minutes



	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	4.18	6.27	2.79	4.23	3.94	6.00	3.64	5.50
O K	65.55	73.75	65.48	74.51	63.11	72.03	64.71	73.43
Mg K	ND	ND	ND	ND	ND	ND	ND	ND
Al K	29.26	19.51	30.73	20.72	30.93	20.92	30.31	20.38
S K	0.6	0.34	0.88	0.50	1.58	0.90	1.02	0.58
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	0.41	0.13	0.12	0.04	0.44	0.15	0.32	0.11
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

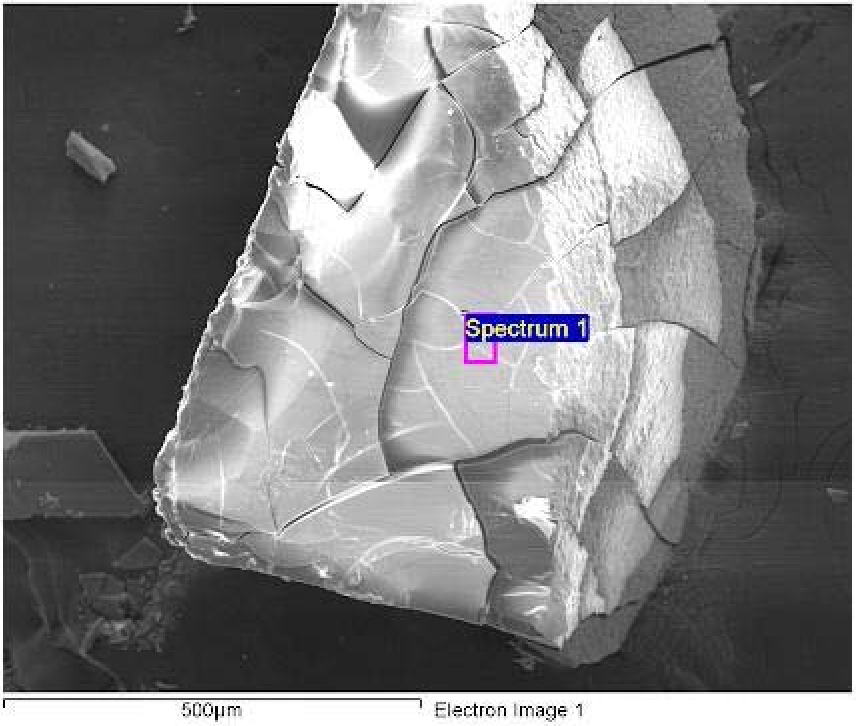
pH= 7.5 t=48 hours



	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	2.30	3.51	2.93	4.55	2.98	4.53	2.74	4.20
O K	65.80	75.25	60.68	70.84	64.90	74.07	63.79	73.39
Mg K	0.08	0.06	0.59	0.46	0.18	0.14	0.28	0.22
Al K	28.66	19.42	30.97	21.43	28.88	19.53	29.51	20.13
S K	2.76	1.58	3.99	2.33	2.93	1.67	3.22	1.86
Ca K	0.40	0.18	0.85	0.40	0.14	0.06	0.46	0.21
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

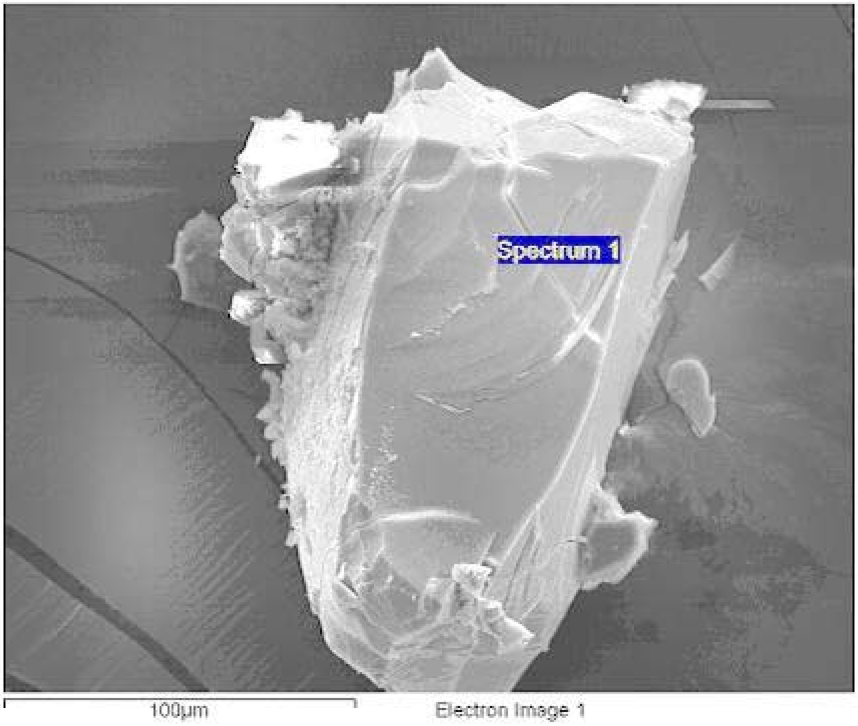
B.3 SLUDGE FORMED IN EXPERIMENT OF LOW SULFATE (AL:SO_4=1:5)

pH= 5.5 t=30min



	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	1.67	2.55	2.98	4.51	3.71	5.70	2.79	4.25
O K	66.32	75.94	65.41	74.35	61.75	71.01	64.50	73.77
Mg K	ND	ND	ND	ND	ND	ND	ND	ND
Al K	30.38	20.61	30.32	20.42	32.71	22.29	31.14	21.11
S K	1.48	0.85	1.19	0.68	1.66	0.96	1.45	0.83
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	0.15	0.05	0.09	0.03	0.16	0.05	0.13	0.04
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 5.5 t=48 hours

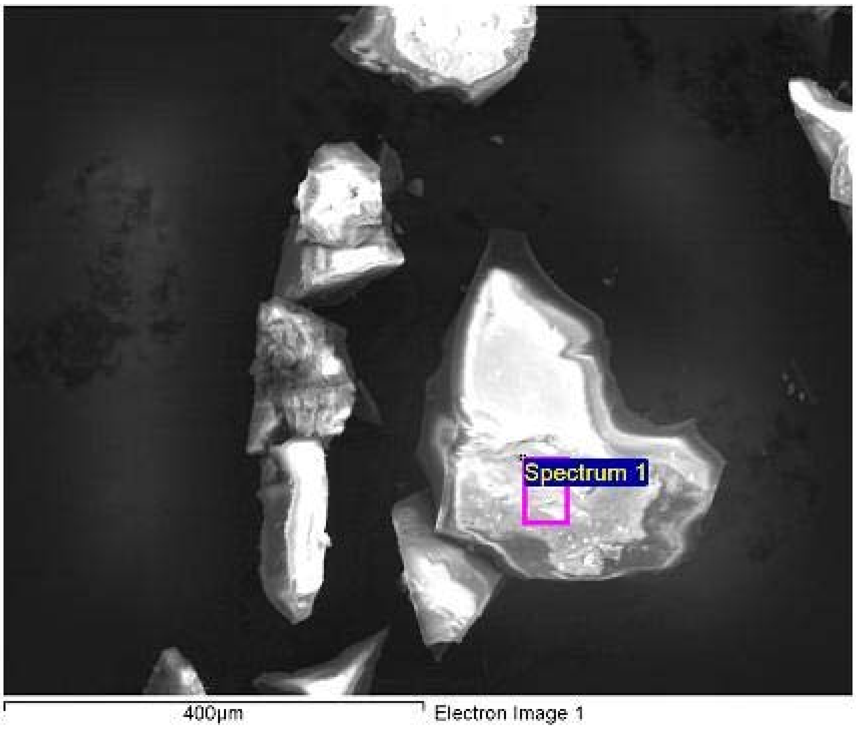


	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	0.80	1.25	0.53	0.82	0.94	1.47	0.75	1.18
O K	62.73	73.68	65.36	75.97	61.07	72.12	63.05	73.92
Mg K	ND	ND	ND	ND	ND	ND	ND	ND
Al K	33.60	23.39	31.53	21.71	36.32	25.42	33.82	23.51
S K	2.88	1.69	2.58	1.50	1.68	0.99	2.38	1.39
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 6.0 t=30 minutes

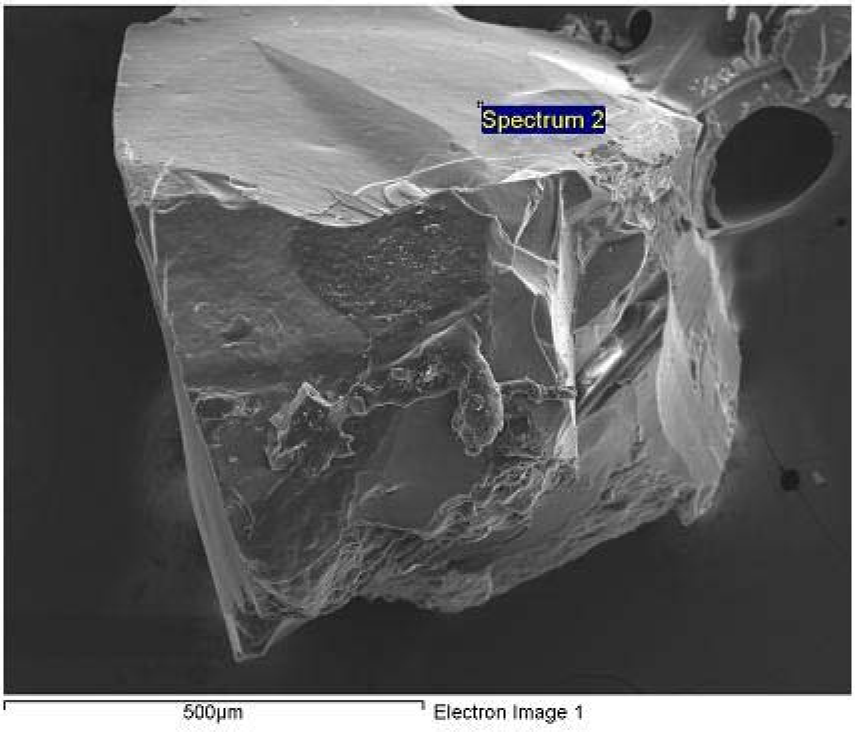
	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	1.82	2.80	3.00	4.65	2.99	4.52	2.60	3.99
O K	65.13	75.13	61.27	71.31	65.29	74.19	63.89	73.54
Mg K	0.26	0.20	0.55	0.43	0.35	0.26	0.39	0.30
Al K	30.06	20.55	32.09	22.13	30.81	20.75	30.99	21.14
S K	1.42	0.82	1.34	0.78	0.17	0.10	0.97	0.56
Ca K	0.49	0.22	0.87	0.41	0.39	0.18	0.58	0.27
Mn K	0.83	0.28	0.89	0.30	0.00	0.00	0.57	0.19
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 6.0 t=48 hours



	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	1.71	2.63	3.29	5.09	3.38	5.09	2.79	4.27
O K	64.95	74.85	60.68	70.45	66.11	74.66	63.91	73.32
Mg K	0.07	0.06	0.59	0.45	0.18	0.14	0.28	0.22
Al K	31.10	21.24	32.44	22.32	28.68	19.19	30.74	20.92
S K	1.97	1.14	2.52	1.46	1.51	0.85	2.00	1.15
Ca K	0.20	0.09	0.49	0.23	0.14	0.06	0.27	0.13
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH= 7.5 t=30 minutes



	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	4.96	7.39	5.01	7.60	3.56	5.34	4.51	6.78
O K	65.62	73.32	62.15	70.71	66.85	75.25	64.87	73.09
Mg K	ND	ND	ND	ND	ND	ND	ND	ND
Al K	28.30	18.74	30.50	20.56	27.97	18.65	28.92	19.32
S K	0.80	0.45	1.47	0.84	0.97	0.54	1.08	0.61
Ca K	ND	ND	ND	ND	ND	ND	ND	ND
Mn K	0.32	0.10	0.87	0.29	0.66	0.22	0.61	0.20
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

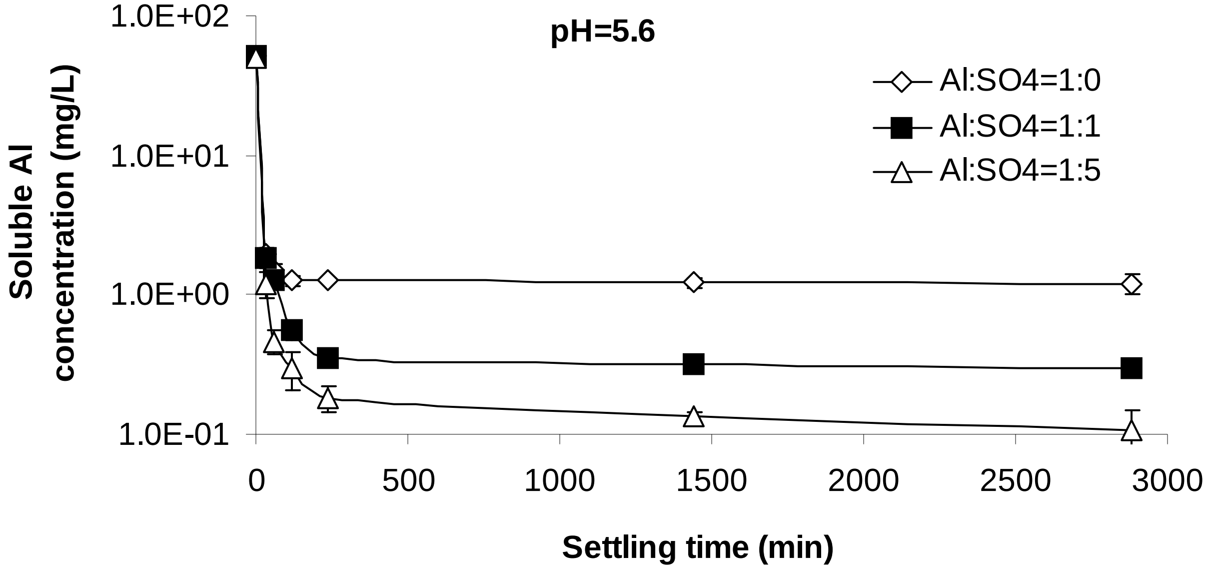
pH= 7.5 t=48 hours

	Spectrum 1		Spectrum 2		Spectrum 3		Average	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C K	5.15	7.69	1.97	3.12	3.14	4.75	3.42	5.19
O K	64.71	72.50	59.54	70.59	65.83	74.67	63.36	72.58
Mg K	0.26	0.19	1.17	0.93	0.36	0.27	0.60	0.46
Al K	27.89	18.52	31.60	22.20	27.88	18.74	29.12	19.82
S K	1.87	1.05	3.84	2.28	2.74	1.55	2.82	1.63
Ca K	0.11	0.05	1.88	0.89	0.05	0.02	0.68	0.32
Mn K	ND	ND	ND	ND	ND	ND	ND	ND
Totals	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

APPENDIX C

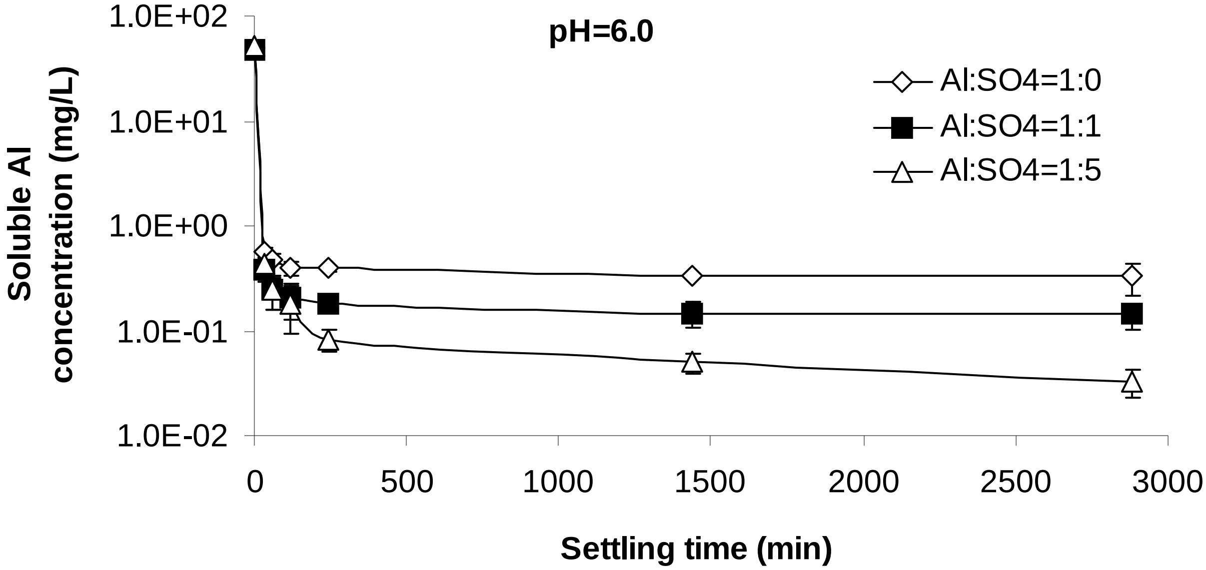
Al CONCENTRATION WITH SETTLING TIME AT DIFFERENT pH VALUES

Soluble Al concentration with settling time at different pH

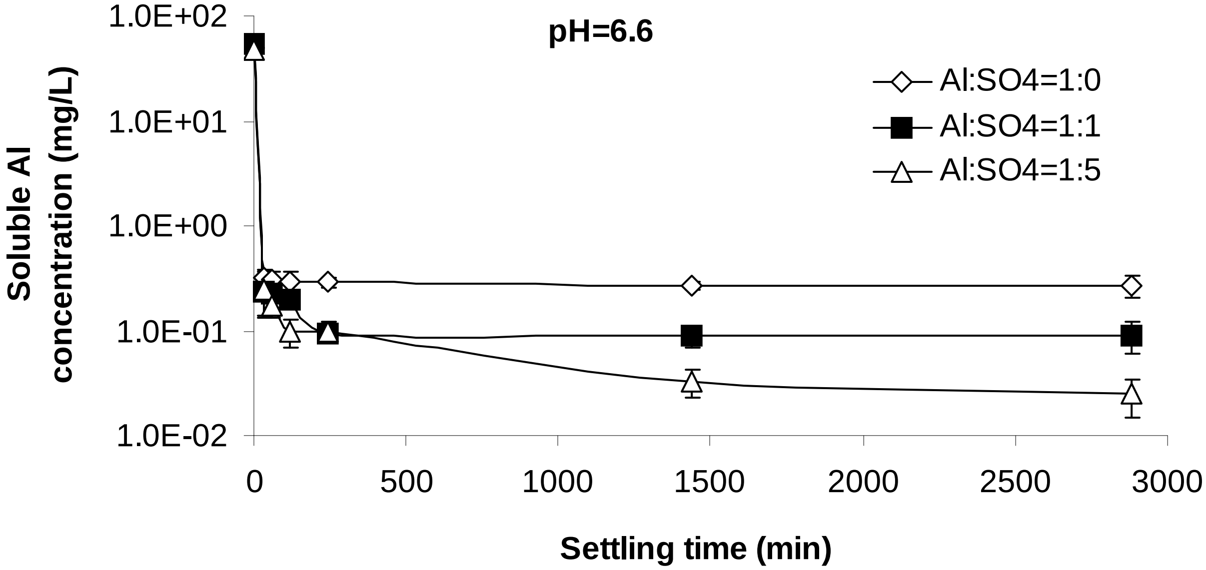


Soluble Al concentration change with settling time at pH=5.6

(note: the final pH value in experiment of high sulfate concentration (1:5) was 5.5)

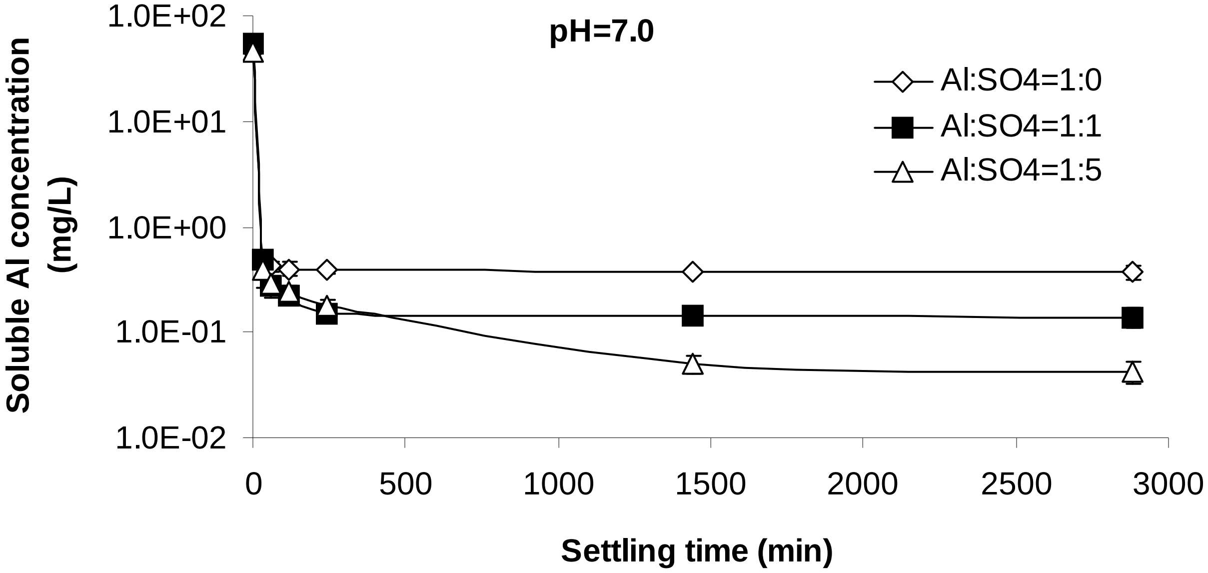


Soluble Al concentration change with settling time at pH=6.0



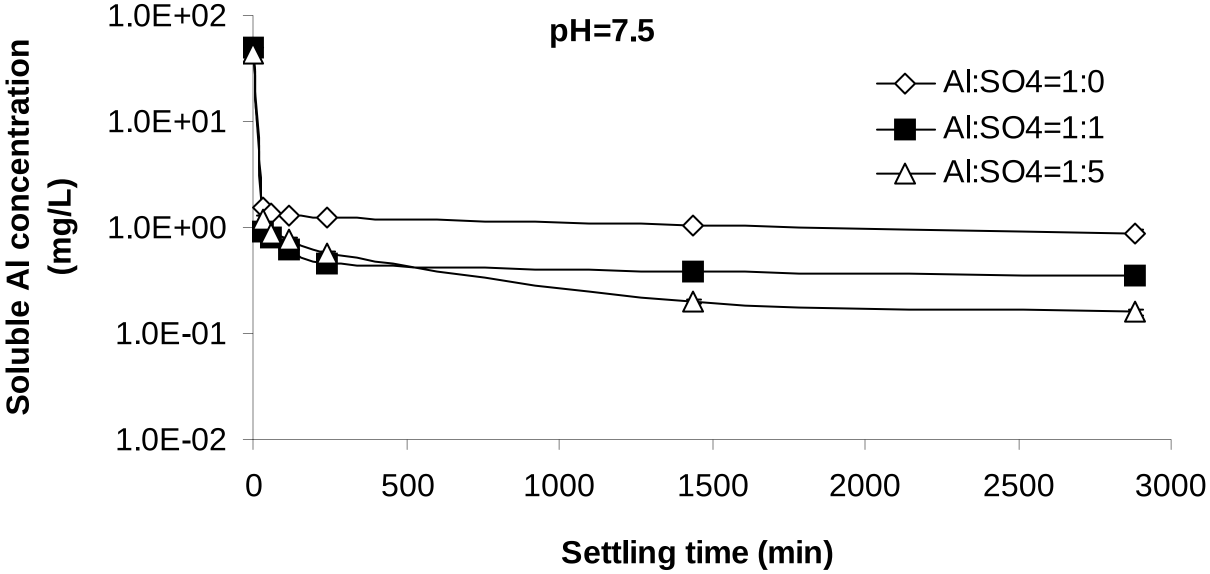
Soluble Al concentration change with settling time at pH=6.6

(Note: the final pH value in experiment without sulfate (Al:SO_4=1:0) was 6.5)



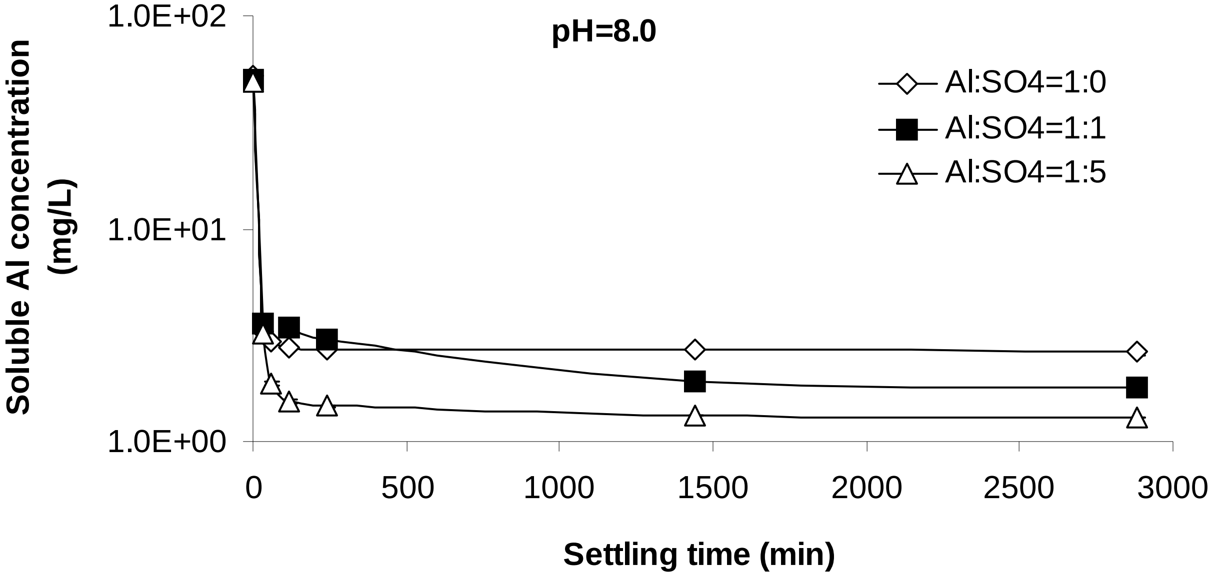
Soluble Al concentration change with settling time at pH=7.0

(Note: the final pH values in experiment of low sulfate (Al:SO_4=1:1) and high sulfate (Al:SO_4= 1:5) concentrations were 7.2 and 7.1, respectively)

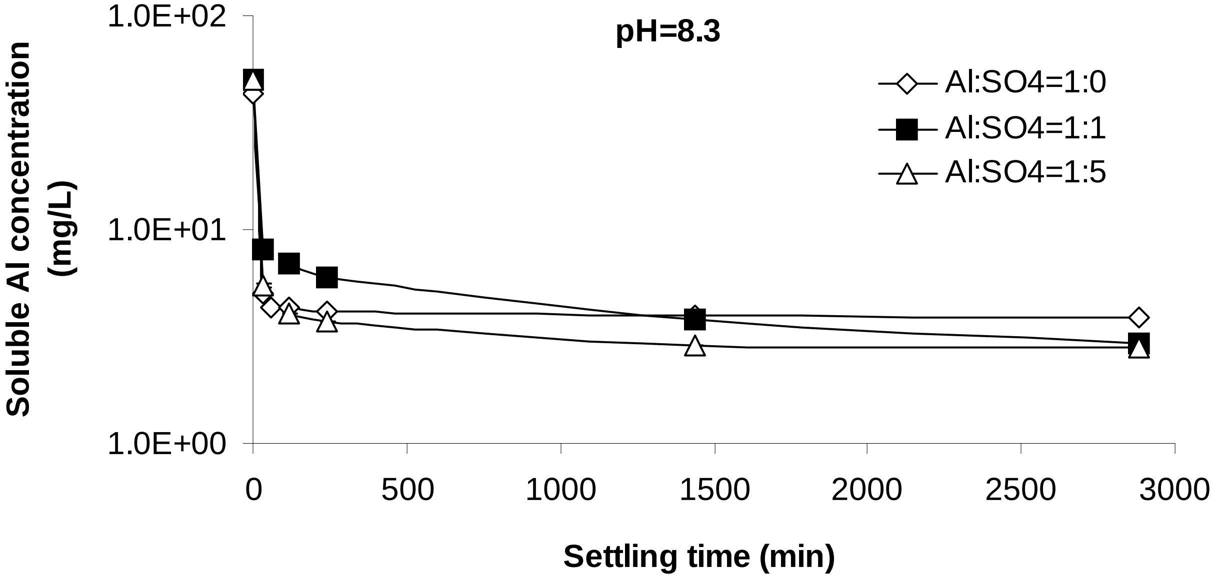


Soluble Al concentration change with settling time at pH=7.5

(the final pH value in experiment without sulfate (Al:SO_4=1:0) was 7.**7)**



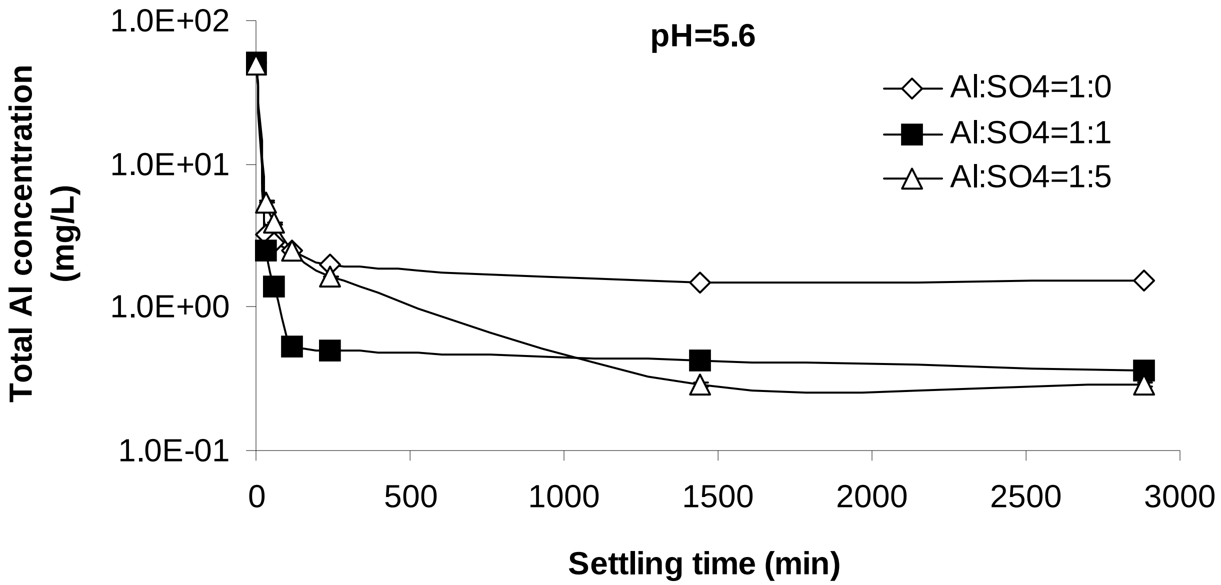
Soluble Al concentration change with settling time at pH=8.0



Soluble Al concentration change with settling time at pH=8.3

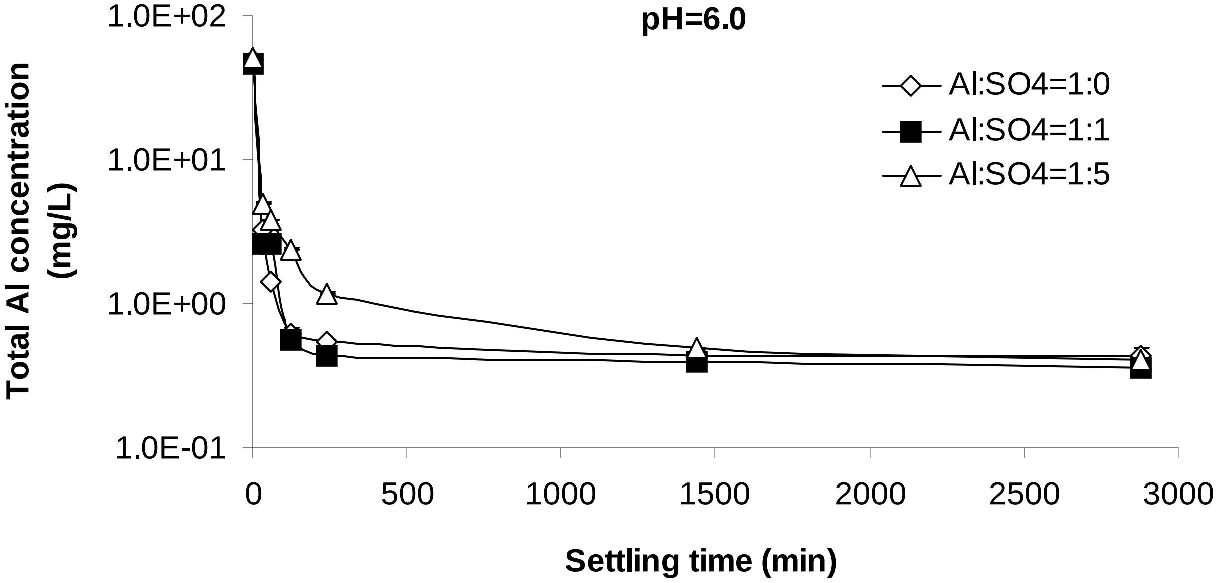
(the final pH values in experiment of high sulfate concentration (Al:SO_4=1:5) was 8.4)

The Total Al concentration with settling time at different pH values

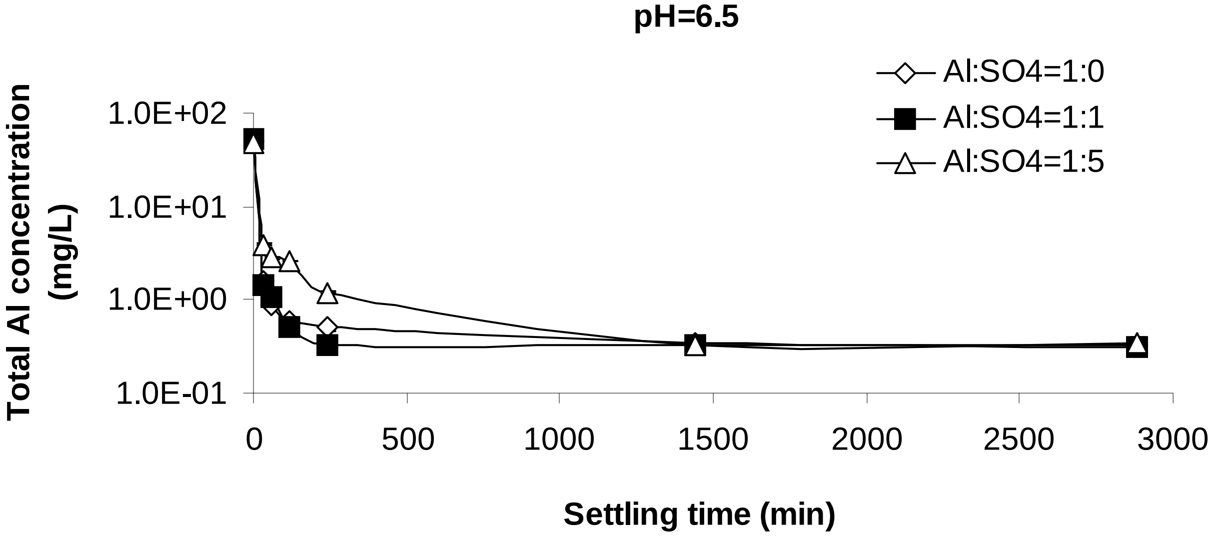


Total Al concentration change with settling time at pH=5.6

(note: the final pH value in experiment of high sulfate concentration (Al:SO_4=1:5) was 5.5)

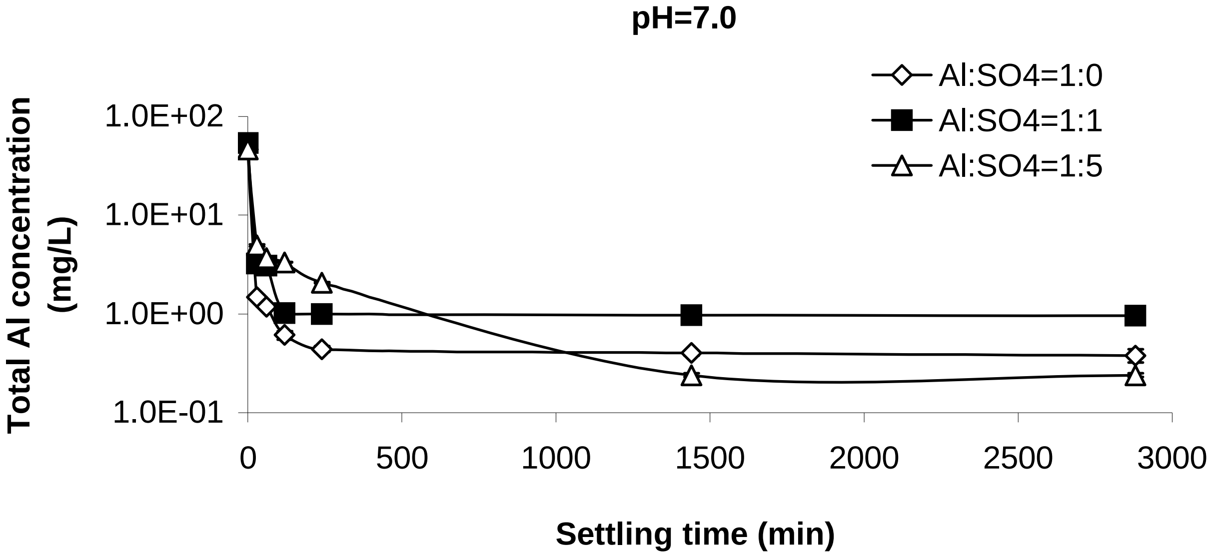


Total Al concentration change with settling time at pH=6.0



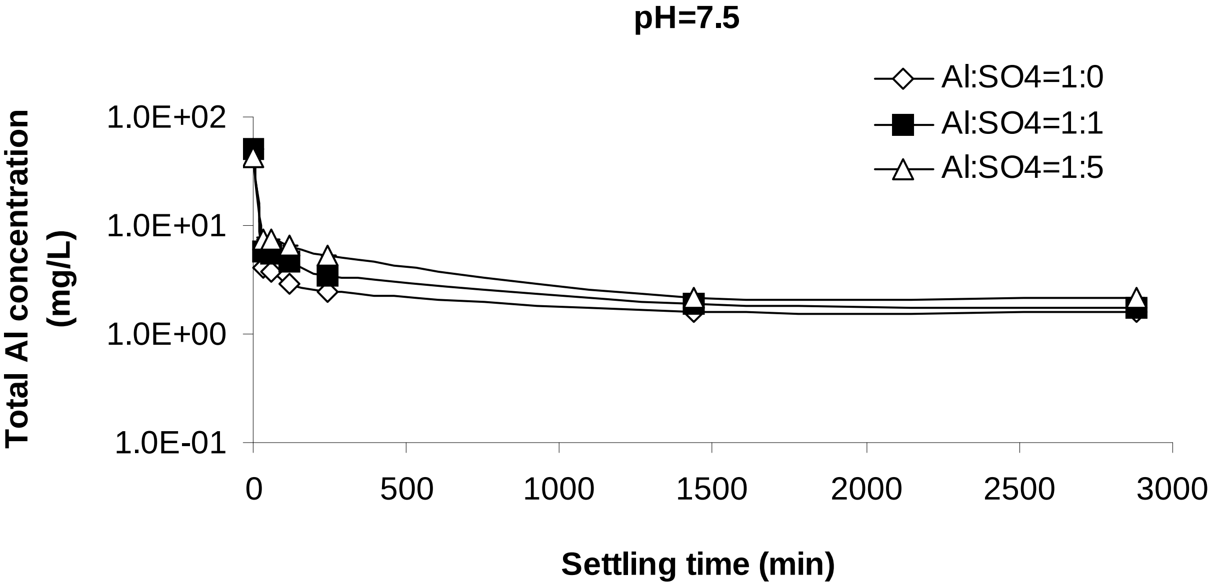
Total Al concentration change with settling time at pH=6.6

(Note: the final pH value in experiment without sulfate (Al:SO_4=1:0) was 6.5)



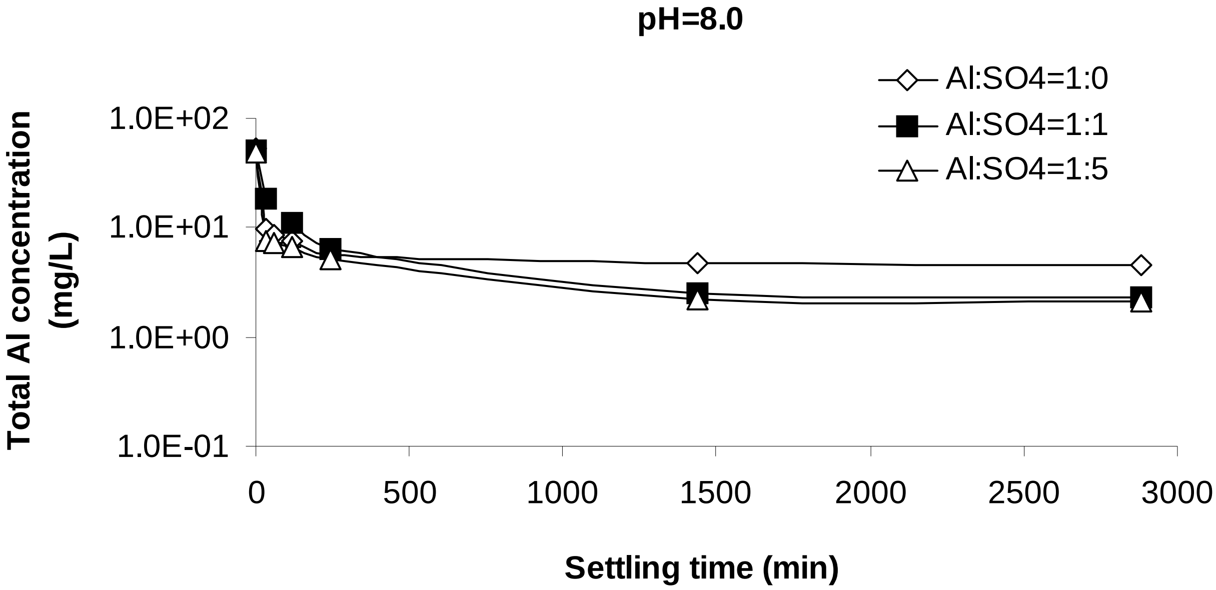
Total Al concentration change with settling time at pH=7.0

(Note: the final pH values in experiment of low sulfate (Al:SO_4=1:1) and high sulfate (Al:SO_4=1:5) concentrations were 7.2 and 7.1, respectively)

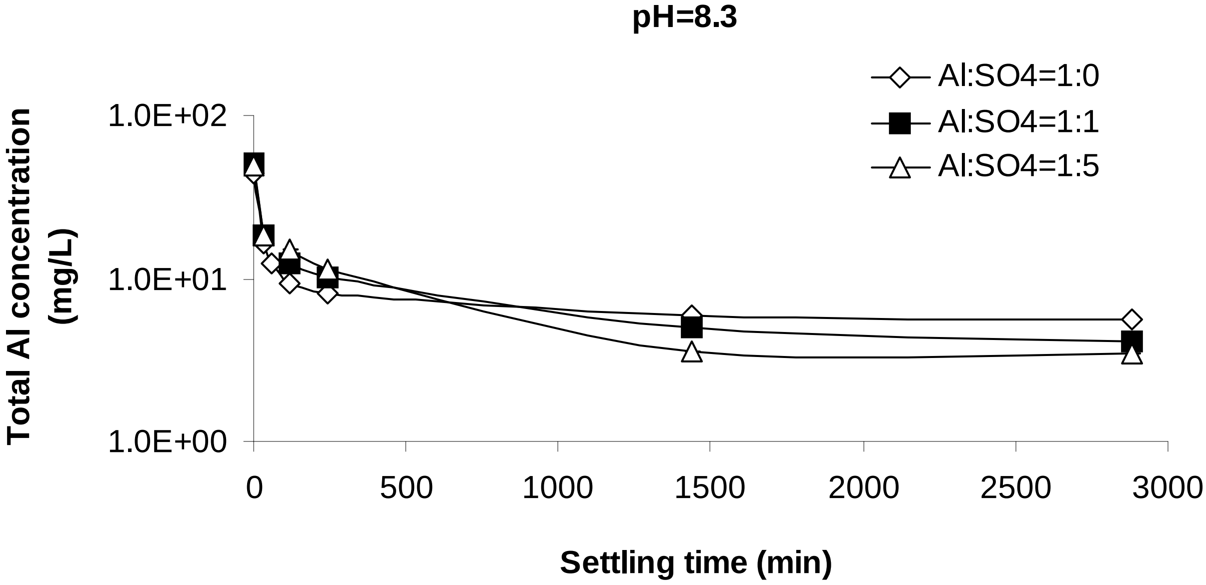


Total Al concentration change with settling time at pH=7.5

(the final pH value in experiment without sulfate (Al:SO_4=1:0) was 7.7)



Total Al concentration change with settling time at pH=8.0



Total Al concentration change with settling time at pH=8.3

(the final pH values in experiment of high sulfate concentration (Al:SO_4=1:5) was 8.4)

APPENDIX D

SATURATION INDEX VALUES OF Al-COMPOUNDS (CALCULATION WITH MINEQL+ MODEL)

Saturation index values of Al-compounds in experiments with molar ratio of Al:SO_4=1:0

	30 minutes		**48 hours**	
SI	$Al(OH)_3$am	Gibbsite	$Al(OH)_3$am	Gibbsite
5.6	0.075	2.63	-0.086	2.464
6.0	0.027	2.58	-0.12	2.43
6.5	0.082	2.63	-0.09	2.46
7.0	0.006	2.56	0.065	2.615
7.7	-0.033	2.52	-0.174	2.376
8.0	0.03	2.58	0.072	2.622
8.3	0.32	2.87	0.082	2.632

Saturation index values of Al-compounds in experiments with molar ratio of Al:SO_4=1:1

Settling time =30 minutes

SI	$Al(OH)_3$ am	Basaluminite	Gibbsite
5.6	-0.15	5.8	2.4
6	-0.14	4.58	2.41
6.6	0.039	5.34	2.589
7.2	-0.075	3.84	2.475
7.5	-0.11	1.83	2.44
8	0.066	2.81	2.616
8.3	0.186	2.97	2.736

Settling time =48 hours

SI	$Al(OH)_3$ am	Basaluminite	Gibbsite
5.6	-0.74	4.45	1.4
6.0	-0.56	4.36	1.41
6.6	-0.48	3.48	1.589
7.2	-0.64	1.5	1.475
7.5	-0.48	1.52	1.44
8	-0.23	1.6	1.616
8.3	-0.25	1.18	1.736

Saturation index values of Al-compounds in experiments with molar ratio of Al:SO_4=1:5

Settling time =30 minutes

SI	$Al(OH)_3$ (am)	Basaluminite	Gibbsite
5.5	-0.18	5.93	2.37
6	-0.14	6.72	2.41
6.6	-0.046	5.88	2.504
7.1	-0.098	4.68	2.452
7.5	0.04	4.29	2.59
8	0.018	3.3	2.568
8.4	-0.04	2.64	2.51

Settling time =48 hours

SI	$Al()H)_3$ (am)	Basaluminite	Gibbsite
5.5	-1.63	1.73	1.37
6	-1.34	1.91	1.41
6.6	-1.16	1.44	1.504
7.1	-1.1	0.72	1.452
7.5	-0.83	0.79	1.59
8	-1.02	1.46	1.568
8.4	-0.34	2.57	1.51

APPENDIX E

DETERMINING WHETHER THE SLUDGE CONTAINS KAOLINITE AND $Si(OH)_4$

Assuming All Al-silicate precipitates formed in experiments with silicate are kaolinite: $Al_2Si_2O_5(OH)_4$.

According to the composition of sludge (EDS results): the molar percentage of O, Si, and Al was known. In sludge, there are three kinds of compounds (Al-sulfate was not considered since the amount of sulfate is very little): $Al(OH)_3$, $Al_2Si_2O_5(OH)_4$., and $Si(OH)_4$. Assuming there are x, y, and z molar of $Al(OH)_3$, $Al_2Si_2O_5(OH)_4$., and $Si(OH)_4$ in sludge, then:

Total molar of O is: $O_{total} = 3x + 9y + 4z$

Total molar of Al is: $x + 2y$

Total molar of Si is : $2y + z$

Then the actual molar of O/Al in sludge except Al-silicate is:

$$[{}^{O}\!/_{Al}]_{correct} = \frac{(3x + 9y + 4z) - 9y - 4z)}{(x + 2y) - 2y} = 3$$

If it is assumed that all Silicate is in the form of $Si(OH)_4$ in sludge, then the molar ratio of O/Al is:

$$[{}^{O}\!/\!{}_{Al}]_{Si(OH)4} = \frac{(3x+9y+4z)-4*(x+2y)}{x+2y} = \frac{3x+5y}{x+2y}$$

If there is any amount of Al-silicate (as kaolinite), the value of $[O/Al]_{Si(OH)}$ will be less than 3. Therefore, according to the composition of sludge measured by EDS, assume all the silicon content as $Si(OH)_{4,}$ the correct oxygen is subtracted C(as CO2), S(as SO4) and Si(as Si(OH)4). If the correct O/Al value is less than 3, it indicates that some Si is in form of kaolinite.

If it is assumed that all silicon as kaolinite in sludge, then the corrected O/Al molar is :

$$[O/Al]_{kao} = \frac{(3x+9y+4z)-4.5*(2y+z)}{(x+2y)-(2y+z)} = \frac{3x-0.5z}{x-z}$$

If there is any amount of $Si(OH)_4$ in sludge, the correct O/Al value is not 3.

BIBLIOGRAPHY

Adams, F. and Z. Rawajfih, 1977, Basaluminite and alunite: a possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Am. J.* , 41, pp. 686–692.

Akit, J.W., Fransworth, J.A., and Letellier, P., 1985, Nuclear magnetic resonance and molar-volume studies of the complex formed between aluminum (III) and the sulfate anion. *J. Chem. Soc. Faraday Trans. I*, 85, pp-193

Alexander, G.B., Heston, W.M., and Iler, R.K., 1954. The Solubility of Amorphous Silicate in Water. *J.Phys. Chem.,* 58, pp: 453

Alpers, C.N., Blowes, D.W., Nordstrom, D.K., Jambor, J.L., 1994. Secondary minerals and acid mine water chemistry. In: Jambor, J.L., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Mine-Wastes. Mineralogical Association of Canada, Short Course Handbook, vol. 22, pp: 247 – 270

APHA (American Public Health Association), American Water Works Association, Water Environment Federation, 2005, *Standard Methods for the Examination of Water and Waste Water*, 21st Ed., Washington, D.C.

Berger A. C., Bethke C. M., and Krumhans J. L., 2000. A process model of natural attenuation in drainage from a historic mining district. *Appl. Geochem.* 15, 655 – 666

Berkowitz, J., Anderson, M.A., and Graham, R.C., (2005). Laboratory investigation of aluminum solubility and solid-phase properties following alum treatment of lake waters. *Water Res.* 39(16). 3919-3928

Bertsch, P. M. and Parker, D. R. 1996. Aqueous polynuclear aluminum species. In: *The Environmental Chemistry of Aluminum,* pp. 117–168. (Sposito, G., Ed.) New York, Lewis Publishers.

Bi, S.P., 2001, Speciation of aluminum in the stream waters from the Susquehanna River watershed, Chesapeake Bay, *Environmental Geology*, 40 (3), pp:300-304,

Bi, S.P., An, S.Q., Yang, M., and Chen, T., 2001. Dynamics of aluminum speciation in forest-well drainage waters from the Rhode River watershed, Maryland. *Environmental International* 26 (5-6), 377-380.

Bigham, J.M., and Nordstrom, D.K., 2000. Iron and aluminum hydroxyl-sulfates from acid sulfate waters. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.), Sulfate Minerals, Reviews in Mineralogy and Geochemistry, Vol. 40. Mineralogical Society of America, Washington, DC, pp. 351–403.

Birchall, J.D., 1990, Role of silicon in biology, *Chemistry in Britain*, 26, pp:141-144.

Birchall, J. D., Exley, C., Chappell, J. S., and Phillips, M. J., 1989, Acute toxicity of aluminum to fish eliminated in silicon-rich acid waters, *Nature* (London, United Kingdom), 338, pp: 146-148

Brace, R. and Matijevic, E., 1977, Coprecipitation of silicate with aluminum hydroxide. *Colloid Polym Sci* 255, pp:153-60

Brown, A.D., Jurinak, J.J., 1989. Mechanism of pyrite oxidation in aqueous mixtures. *J. Environ. Qual*. 18, pp:545–550.

Browne, A. and Driscoll, C.T., 1992, Soluble aluminum silicates: stoichometry, stability and implications for environmental geochemistry, *Science*, 256, pp: 1667.

Brydon, James E.; Shah Singh, S., 1969. Nature of the synthetic crystalline basic aluminum sulfates as compared with basaluminite. *Canadian Mineralogist* , 9(5), pp: 644-54

Bunce,N.J., Chartrand, M., and Keech, P. 2001. Electrochemical treatment of acidic aqueous ferrous sulfate and copper sulfate as models for acid mine drainage. *Water Res.* Vol.35(18), 4410-4416

Campbell, P. G. C., and Stokes, P. M. 1985. Acidification and toxicity of metals to aquatic biota. *Can. J. Fish. Aquat. Sci.* 42**,** 2034–2049.

Chadwick, D. J. and Whelan, J.,(Editors). 1992, Secondary Metabolites: Their Function and Evolution, Proceedings of a Symposium held at the Ciba Foundation, London, England [In: Ciba Found. Symp.,

Chapman, B.M., Jones, D.R., Jung, R.F., 1983. Processes controlling metal ion attenuation in acid mine drainage streams. *Geochim. Cosmochim. Acta* 47, pp:1957-1973.

Chappell, J. S. and Birchall, J. D. 1988. Aspects of the interaction of silicic acid with aluminium in dilute solution and its biological significance. *Inorg. Chim. Acta* 153**,** 1–4.

Charles, D. F. (Ed.), 1991. *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies.* New York, Springer-Verlag

Clesceri, L.S., Greenberg, A.E., and Trussell, R.R., 1989. Standard Methods For The Examination of Water and Wastewater, 17th ed., APHA-AWWA-WPCF;

Cooke, G. D., Welch, E. B., Martin, A. B., Fulmer, D. G., Hyde, J. B., and Schrieve, G. D. 1993. Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. *Hydrobiologia* 253**,** 323–335.

Cravotta III, C.A., 1994. Secondary iron-sulfate minerals as sources of sulfate and acidity – the geochemical evolution of acidic ground water at a reclaimed surface coal mine in Pennsylvania. In, Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation. American Chemical Society of Symposium Series, vol. 550, pp. 345–364.

Cravotta III, C.A., Dugas, D.L., Brady, K.B.C., Kovalchuk, T.E., 1994. Effects of selective handling of pyritic, acidforming materials on the chemistry of pore gas and ground water at a reclaimed surface coal mine in Clarion County, PA, USA. U.S. Bureau of Mines Spec. Publ. SP 06A, pp. 365–374.

Cravotta, C.A., 1998. Effect of sewage sludge on formation of acidic groundwater at a reclaimed coal mine. *Ground Water*. 36, pp:9-19.

Cravotta III, C.A., and Trahan, M.K., 1999, Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Application of Geochemistry*. 14, pp:581–606

Cravotta, Charles A., III. 2008. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: Geochemical controls on constituent concentrations. *Applied Geochemistry*. Vol.23(2), 203-226

Cronan, C. S. and Schofield, C. L. 1979. Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in Northeast. *Science* 204: 304-306;

Davis, Christina C., Knocke, William R., and Edwards, Marc, 2001. Implications of silicate sorption to iron hydroxide: mobilization of iron colloids and interference with sorption of arsenate and jumic substances. *Environ Sci Technol. Vol* 35(15): 3158-62

Dillon, P. J., Yan, N. D., and Harvey, H. H. 1984. Acidic deposition: Effects on aquatic ecosystems. *CRC Crit. Rev. Environ. Control* 13**,** 167–194.

Drablos, D. and Tollan, A. (Eds.) 1980. Ecological influence of acid precipitation. Proceedings of an International Conference, Sandfjord, Norway, March 11–14, 1980. Oslo, Norway, SNSF Project.

Driscoll, C. T. and Schecher, W. D. 1990. The chemistry of aluminum in the environment. *Environ. Geochem. Health* 12**,** 28–49.

Driscoll, C. T. and Newton, R. M. 1985. Chemical characteristics of Adirondack lakes. *Environ. Sci. Technol.* **19,** 1018–1024.

Driscoll, C.T. and Postek, K.M., 1996, The chemistry of aluminum in surface water, in *The Environmental Chemistry of Aluminum (2^{nd} Ed)*, Spostto, Garrison Ed. Lewis Publishers , pp:363-418

Duan, Jinming and Gregory, John, 1996. Influence of soluble silicate on coagulation by aluminum sulfate. *Colloids and Surfaces*, A: Physicochemical and Engineering Aspects, 107, pp: 309-19

Duan, Jinming and Gregory, John, 1998. The influence of silicic acid on aluminum hydroxide precipitation and flocculation by aluminum salts. *J. of Inorganic Biochemistry* , 69(3), pp: 193-201

Dubikova, M., Cambier, P., Šucha, V., Čaplovičova, M. 2002. Experimental soil acidification. *Applied Geochemistry*, Vol.17, 245-257

Essington, Michael E., 2004. Soil and Water Chemistry: An integrative Approach**.** Boca Raton: CRC Press,C2004

Exley, C., 1996. Aluminium in the brain and heart of the rainbow trout. *Journal of Fish Biology* 48(4), 706-713.

Exley, C., and Birchall, J.D., 1992, Hydroxyaluminosilicate formation in solutions of low total aluminum concentration, *Polyhedron*, 11(15), pp: 1901-1907

Exley, C.; Birchall, J. D., 1993. A mechanism of hydroxyaluminosilicate formation. *Polyhedron.* Vol 12(9), pp:1007-17.

Exley, C., Chappell, J. S., and Birchall, J. D. 1991. A mechanism for acute aluminium toxicity in fish. *J. Theor. Biol.* 151, pp: 417–428

Farmer, V. C.,and Lumsdon, D. G. 1994, An assessment of complex formation between aluminum and silicic acid in acidic solutions. *Geochimica et Cosmochimica Acta,* 58(16), pp: 3331-4.

Feng, D., Aldrich, C., and Tan, H., 2000. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. Minerals Engineering 13 (6), 623–642

Ferna´ndez-Caliani, J. C.; Barba-Brioso, C.; Perez-Lopez, R., (2008). Long-term interaction of wollastonite with acid mine water and effects on arsenic and metal removal. *Applied Geochemistry* , 23(5), pp:1288-1298

Filipek, L.H., Nordstrom, D.K., Ficklin, W.H., 1987. Interaction of acid mine drainage with waters and sediments of West Shaw Creek in the West Shasta Mining District, California. *Environ. Sci. Technol*. 21, pp: 388 ‐ 396

Findlay, D. L. and Kasian, S. E. M. 1986. Phytoplankton community responses to acidification of Lake 223, Experimental Lakes Area, northwestern Ontario. *Water Air Soil Pollut.* 30**,** 719–726.

Fitzpatrick, C. S. B.; Fradin, E.; Gregory, J., (2004). Temperature effects on flocculation, using different coagulants. *Water Science and Technology*, 50(12), pp: 171-175

Golub, M. S. and Domingo, J. L.,1996, What we know and what we need to know about developmental aluminum toxicity, *Journal of Toxicology and Environmental Health*, 48(6), pp: 585-597

Gostomski, F. 1990. The toxicity of aluminum to aquatic species in the US. *Environ. Geochem. Health* 12, 51–54.

Gray, N.F. 1998. Acid mine drainage composition and the implications for its influence on Lotic Systems. *Water Research*. Vol.32 (7), 2122-34

Guesek, James J., and Wildeman, Thomas R, 2002, Passive Treatment of Aluminum-Bearing Acid Rock Drainage, 23rd Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Gustafsson, J. P., Lumsdon, D. G., and Simonsson, M., 1998, Aluminum solubility characteristics of spodic B horizons containing imogolite-type materials. *Clay Miner*. 33, pp: 77–86.

Hach Company, 2003, *Water Analysis Hand Book*, 4th Ed, Hach Company, Loveland, CO.

Handy, R. D. 1993. The accumulation of dietary aluminum by rainbow trout, *Oncorhynchus mykiss*, at high exposure concentrations. *J. Fish. Biol.* 42, pp:603–606

Hedin, R.S., Watzlaf, G.R., 1994. The effects of anoxic limestone drains on mine water chemistry. U.S. Department of Interior Bureau of Mines Special Publication SP 06A-94, Pp: 185-194.

Hedin Environmental, 2003, Assessment of Pollution Sources to the Headwaters of Jonathan Run and Recommended Remediation Actions, Final Report, *in cooperation with* Department of Environmental Protection (Hawk Run District Mining Office) and Pennsylvania Department of Transportation (PennDOT District 2-0), June 30,

Hem, J.D., 1985, Study and interpretation of chemical characteristics of natural water, 3rd ed., U.S. Geological Survey Water-Supply. Alexandria VA: U.S. Government Printing office

Hendershot, W. H., Courchesne, F., and Jeffries, D. S. 1996. Aluminum geochemistry at the catchment scale in watersheds influenced by acidic precipitation. In: *The Environmental Chemistry of Aluminum* (2nd ed.), pp. 419-449. (Sposito, G., Ed.) New York, Lewis Publishers.

Herrmann, R., and Baumgartner, I., 1992. Aluminum species distribution during mixing of acid coal and slate mine drainage with neutral stream waters, *Geologische Rundschau*, Vol.81(3), pp: 759-67

Howells, G. D., Brown, D. J. A., and Sadler, K. 1983. Effects of acidity, calcium, and aluminium on fish survival and productivity: a review. *J. Sci. Food Agric.* 34**,** 559–570.

Huang, P., Wang, M., Kampf, N., Schultze, D., 2002. Aluminum hydroxides. In: Dixon, J.B., Schulze, D.G. (Eds.), Soil Mineralogy With Environmental Applications. Soil Science Society of America, Madison, WI, pp. 261 – 289

Jardine, P. M. and Zelazny, L. W. 1996. Surface reactions of aqueous aluminum species. In: *The Environmental Chemistry of Aluminum* (2nd ed.), pp: 221–270. (Sposito, G., Ed.) New York, Lewis Publishers

Karathanasis, A.D., Evangelou, V.P., Thompson, Y.L., 1988. Aluminum and iron equilibria in soil solutions and surface waters of acid mine watersheds. *J. Environ. Qual.* Vol(17), pp:534-543

Karathanasis, A., Harris, W., 1994. Quantitative thermal analysis of soil minerals. In: Amonette, J.E., Zelazny, L.W. (Eds.), Quantitative Methods in Soil Mineralogy. Soil Science Society of America, Madison, WI, pp. 360 – 411

Khanna, P. K.; Prenzel, J.; Meiwes, K. J.; Ulrich, B.; Matzner, E., (1987). Dynamics of sulfate retention by acid forest soils in an acidic deposition environment. *Soil Science Society of America Journal* , 51(2), pp:446-52.

Kim, J.J. and Kim, S.J., 2003a, Seasonal factors controlling mineral precipitation in the acid mine drainage at Donghae coal mine, Korea, *Science of the Total Environment*, 325, pp: 181–191

Kim, J.J. and Kim, S.J., 2003b, Environmental, Mineralogical, and Genetic Characterization of Ochreous and White Precipitates from Acid Mine Drainages in Taebaeg, Korea, *Environmental Science and Technology*, 37 (10), 2120-2126

Krauskopf, Konrad B. and Bird, Dennis K., 1995, *Introduction of Geochemistry*, Third Edition, McDraw-Hill, pp:86-106

LaZerte, B. D., van Loon, G., and Anderson, B. 1997. Aluminum in water, In: *Research Issues in Aluminum Toxicity,* pp. 17–45. (Yokel, R. A. and Golub, M. S., Ed.) Washington, DC, Taylor and Francis

Lee, G., Bigham, J. M. and Faure, G., 2002, Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry*, Vol 17(5), pp: 569-581

Leonard, G., 1973. Selected Powder Diffraction Data for Minerals. Joint Committee on Powder Diffraction Standards, Swarthmore, PA

Levy, D. B.; Custis, K. H.; Casey, W. H.; Rock, P. A., (1997). A comparison of metal attenuation in mine residue and overburden material from an abandoned copper mine**.** *Applied Geochemistry*, 12(2), pp:203-211

Luciuk, G.M. and Huang, P.M., 1974, Effects of monosilicic acid on hydrolytic reaction of aluminum, *Soil Sci. Soc. Am.J.,* 38, pp: 235

Maree, J. P. and Plessis, P., 1994, Neutralization of acid mine water with calcium carbonate, *Water Science and Technology*, 29(9), pp: 285-96

Marsh, D. E. 1999. Photokinetics: a new approach to assessment of biologically significant influences in aquatic systems. M.Sc. Thesis, Boston University, Boston, MA.

May, H.M., Helmke, P.A., and Jackson, M.L., 1979, Gibbsite solubility and thermodynamic properties of hydroxyl-aluminum ions in aqueous solution at 25°C, *Geochim. Cos. Mochim. Acta,* 43, pp:861

Moses, C.O., Nordstrom, D.K., Herman, J.S., Mills, A., 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochim. Cosmochim. Acta* 54, pp:395–402.

Moses, C.O., Herman, J., 1991. Pyrite oxidation at circumneutral pH. *Geochim. Cosmochim. Acta*. 55, pp:471–482.

Mulder, J.; Van Grinsven, J. J. M.; Van Breemen, N., (1987) Influences of acid atmospheric deposition on woodland soils in the Netherlands: III. Aluminum chemistry. *Soil Science Society of America Journal*, 51(6)

Muniz, I. P. and Leivstad, H. 1980. Acidification — effects on freshwater fish. In: Ecological Influence of Acid Precipitation: Proceedings of an International Conference, Sandfjord, Norway, March 11–14, 1980, pp. 84–92. (Drablos, D. and Tollan, A., Eds.) Oslo, Norway, SNSF Project.

MWH, (2005). Water treatment principles and design. Revised by John Crittenden et al. 2nd edition. Hoboken, N.J. Wiley, c2005. pp: 780-797

Neal, C., Skeffington, R. A., Williams, R., and Roberts, D. J. 1987. Aluminium solubility controls in acid waters: the need for a reappraisal. *Earth Planet. Sci. Lett.* 86**,** 105–112.

Neal, C. and Williams, R. J., 1988, Towards establishing aluminium hydroxyl silicatete solubility relationships for natural waters. *J. Hydrology*. 97, pp: 347–352.

Neufeld, R.D., Gray, T.A., Monnell, J., Smoke, J., and Hedin, R., 2007. Jonathan Run Acid Rock Discharge Mitigation Strategies, Report (Project number 04-01 (C11)) for Pennsylvania Department of Transportation

Neufeld, R.D., Gray, T., Monnell, J., Smoke, J. "Jonathan Run Acid Rock Discharge Mitigation Strategies" FHWA-PA-2007-010-04011 March, 2007 (available from NTIS as PB2007-107284) 134 pages

Nicholson, R.V., Gillham, R.W., Reardon, E.J., 1989a. Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. *Geochim. Cosmochim. A*cta, 52, pp:1077–1085.

Nicholson, R.V., Gillham, R.W., Reardon, E., 1989b. Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. *Geochim. Cosmochim. Acta,* 54, pp: 395–402.

Nordstrom, D.K., 1982a. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: Hossner, L.R., Kittrick, J.A., Fanning, D.F. (Eds.), Acid Sulfate Weathering, Pedogeochemistry and Relationship to Manipulation of Soil Minerals. Soil Science Society of America Press, Madison, pp: 46.

Nordstrom, D.K., 1982b, The effect of sulfate on aluminum concentration in natural waters: some stability relations in the system Al_2O_3-SO_3-H_2O at 298K, *Geochim. Cos. Mochim. Acta*, 46, pp:681

Nordstrom, D.K., Ball, J.W. , Robertson, C.E., and Hanshaw, B.B., 1984, The effect of sulfate on aluminum concentrations in natural waters: II. Field occurrences and identification of aluminum hydroxysulfate precipitates. *Geol. Soc. Am. Program Abstr.* 16 (6), pp: 611

Nordstrom, D.K. and Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters, *Science,* 232, pp. 54–56.

Nordstrom, D.K. and May,H.M.,1996， Aqueous equilibrium data for mononuclear aluminum species, chap 2., in *The Environmental Chemistry of Aluminum (2nd Ed)*, Spostto, Garrison Ed. Lewis Publishers, pp:39-80

Nordstrom, D.K., and Alpers, C.N., 1999, Geochemistry of acid mine waters. pp: 133–160. *In* G. S. Plumlee and M. J. Logsdon (ed.) The environmental geochemistry of mineral deposits. Part A. Processes, methods, and health issues. Reviews in Economic Geology 6A. *Soc. of Econ. Geol*., Littleton, CO.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D., 2000, Negative pH and extremely acidic mine waters at Iron Mountain Mine, California. *Environ.l Sci. and Tech.*, Vol.34, 254-258

Nordstrom, D.K., Ball, J.W., McCleskey, R.B., 2006. Geochemistry of aluminum in surface and ground waters affected by acid rock drainage (abs.): Geological Society of America, GSA Abstracts with Programs, abstract 134-10.

Perry, E.F., 2001. Modelling rock-water interactions in flooded underground coal mines. Geochem. Explor. *Environ. Anal.* 1, pp: 61-70

Peterson, S.A., Sanville, W.D., Stay, F.S. and Powers, C.F. 1974. Nutrient inactivation as a lake restoration procedure. Laboratory investigations. EPA-660/3-74-032. National Technical Information Service, Springfield, VA

Poston, H. A. 1991. Effects of dietary aluminum on growth and composition of young Atlantic salmon. *Progress. Fish-Cultur.* 53, pp:7–10

Prenzel, J..(1983). A mechanism for storage and retrieval of acid in acid soils**.** Eff. Accumulation Air Pollut. For. Ecosyst., Proc. Workshop , Meeting Date 1982, pp:157-70

Pu, Xunchi, Vazquez, Oscar; Monnell, Jason D., and Neufeld, Ronald D., 2010. Speciation of aluminum precipitates from acid rock discharges in Central Pennsylvania. *Environ. Eng. Sc*i., Vol.27(2), pp: 169-180

Reiber, S., Kukull, W., and Standish-Lee, P., 1995. Drinking water aluminum and bioavailability. *J. Am. Wat. Works Assoc*. 87, pp: 86–100

Robbins, E.I., Nord, G.L., Savela, C.E., Eddy, J.I., Livi, K.J.T., Gullett, C.D., Nordstrom, D.K., Chou, I.-M., Briggs, K.M., 1996. Microbial and mineralogical analysis of aluminum-rich precipitates that occlude porosity in a failed anoxic limestone drain, Monongalia County, West Virginia. In: Chiang, Shiao-Hung (Ed.), Proceedings of the 13th Annual Internation Pittsburgh Coal Conference. *Coal-Energy and the Environment*, vol. 2. Reed & Witting Company, Pittsburgh, PA, pp:761 – 767.

Robbins, E.I., Cravotta III, C.A., Savela, C.E., Nord, G.L., 1999. Hydrobiogeochemical interactions in “anoxic” limestone drains for neutralization of acidic mine drainage. *Fuel* 78, pp:259 – 270

Roberson, C.E. and Hem, J.D., 1967, Solubility of aluminum in the presence of hydroxide, fluoride, and sulfate, *U.S. Geol. Surv. Water-Supply Pap*., 1827-C,

Rodushkin, I., Moiseenko, T., Kudravsjeva, L., 1995. Aluminium in the surface waters of the Kola Peninsula, Russia. *The Science of the Total Environment* 163(1-3), 55-59

Rose, A.W., and Cravotta III, C.A. , 1998. Geochemistry of coal-mine drainage. In K. B. C. Brady, M. W. Smith, and J. Schueck (Ed.) Coal mine drainage prediction and pollution prevention in Pennsylvania. pp: 1.1–1.22

Rose, S. and Ghazi, A.M., 1998, Experimental study of the stability of metals associated with iron oxyhydroxides precipitated in acid mine drainage, *Environmental Geology*, 36 (3–4), pp: 364-370

Rosseland, B. O., Eldhuset, T. D., and Staurnes, M. 1990. Environmental effects of aluminium. *Environ. Geochem. Health* 12**,** 17–27.

Rosseland, B. O., Blakar, I. A., Bulger, A., Kroglund, F., Kvellstad, A., Lydersen, E., Oughton, D. H., Salbu, B., Staurnes, M., and Vogt, R. 1992. The mixing zone between limed and acidic river waters: complex aluminium chemistry and extreme toxicity for salmonids. *Environ. Pollut.* 78**,** pp:3-8.

Rosseland, B. O., and Stuarnes, M., 1994. Physiological mechanisms for toxic effects and resistance to acidic water: an ecophysiological and ecotoxicological approach. In: *Acidification of Freshwater Ecosystems: Implications for the Future.* (Steinberg, C. E. W. and Wright, R. F., Eds.) New York, Environ. Sci. Rep. ES 14, John Wiley & Sons.

Sanchez Espana, Javier; Lopez Pamo, Enrique; Santofimia, Esther; Aduvire, Osvaldo; Reyes, Jesus; Barettino, Daniel., 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel River watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry* , 20(7), pp:1320-1356

Sanchez Espana, J.; Lopez Pamo, E.; Santofimia Pastor, E.; Reyes Andres, J.; Martin Rubi, J. A., 2006. The removal of dissolved metals by hydroxysulphate precipitates during oxidation and neutralization of acid mine waters, Iberian Pyrite Belt. *Aquatic Geochemistry*, 12(3), 269-298.

Sanchez Espana, Javier; Lopez Pamo, Enrique; Santofimia Pastor, Esther; Diez Ercilla, Marta., 2008. The acidic mine pit lakes of the Iberian Pyrite Belt: An approach to their physical limnology and hydrogeochemistry. *Applied Geochemistry*, 23(5), pp:1260-1287

Sasowsky, I., Foos, A., and Miller, C., 2000. Lithic controls on the removal of iron and remediation of acidic mine drainage. *Water Res.* Vol.34(10), 2742 – 2746

Schecher, W. D., and McAvoy, D. D., 1998, "*MINEQL+ A Chemical Equilibrium Modeling System: Version 4.0 for Windows*," User's Manual, Environmental Research Software, Hallowell, Maine

Scheuhammer, A. M.,1987. Acidification-related changes in the biogeochemistry and ecotoxicology of mercury, cadmium, lead and aluminium: overview. *Environmental pollution*, 71(2-4), pp:87-90

Scheuhammer, A. M., 1991. Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. *Environmental Pollution* (Oxford, United Kingdom), 71(2-4), pp: 329-75

Schindler, D. W., Mills, K. H., Malley, D. F., Findlay, D. L., Shearer, J. A., Davies, I. J., Turner, M. A., Linsley, G. A., and Cruikshank, D. R. 1985. Long-term ecosystem stress: the effects of years of experimental acidification on a small lake. *Science* 228**,** 1395–1401

Shah Singh, S. and Brydon, J.E., 1969. Solubility of basic aluminum sulfates at equilibrium in solution and in the presence of montmorillonite. *Soil Sci*., Vol(107), pp: 12-16

Siever, Raymond. 1953. Petrology and sedimentation of upper Chester sandstones. *J. of Sedimentary Petrology*. 23, pp: 207-19

Singer, P.C., and Stumm, W., 1970. Acidic mine drainage: therate-determining step. *Science* 167, pp:1121–1123.

Skousen, J.; Sencindiver, J.; Owens, K.; Hoover, S., 1998. Physical properties of minesoils in West Virginia and their influence on wastewater treatment. *J. of Environmental Quality*, 27(3), pp: 633-639

Skousen, J.G., Sexstone, A., Ziemkiewicz, P.F., 2000. Acid mine drainage control and treatment. Agronomy, 41(Reclamation of Drastically Disturbed Lands), pp:131-168.

Spry, D. J., and Wiener, J. G., 1991. Metal bioavailability and toxicity to fish in low-alkalinity lakes: a critical review. *Environ. Pollut.* 71**,** 243–304.

Stoeber, Werner. 1967. Formation of silicic acid in aqueous suspensions of different silicate modifications. *Advan. Chem. Soc.* , No. 67, pp:161-82.

Sullivan, T. J. and Cosby, B. J., 1998. Modeling the concentration of aluminum in surface waters. *Water Air Soil Pollution*. 105, pp: 643–659.

Sullivan, A. B., and Drever, J. I., 2001. Geochemistry of suspended particles in a mine-affected mountain stream. *Applied Geochemistry*. 16(15), pp: 1663-1676

Taylor, P.D., Jugdaohsingh, R., and Powell, J.J., 1997. Soluble Silicate with High Affinity for Aluminum under Physiological and Natural Conditions, *J. Am. Chem. Soc.*, *119* (38), pp: 8852–8856

Tan, Kim H., 2000, Environmental Soil Science, Second Edition, Marcel Dekker, Inc, New York, pp: 187-191,

Thomas, R.C., Romanek, C.S., 2002. Passive treatment of low pH, ferric dominated acid rock drainage in a vertical flow wetland – II. Metal removal. In: Proceedings of the 19th Annual Meeting of American Society of Mining and Reclamation, Lexington, Kentucky, June 9 – 13, 2002. American Society of Mining and Reclamation, pp. 752 – 775

Totsche, O., Pothig, R., Uhlmann, W., Buttcher, H. and Steinberg, E. W., 2003. Buffering mechanisms in acidic mining lakes - A model-based analyses. *Aquat. Geochem*. 2003, 9, 343 – 359

USEPA, 1994. Method 3015, Microwave Assisted Acid Digestion for Aqueous Samples and Extracts. At www.epa.gov/epaoswer/hazwaste/test/pdfs/3015.pdf , accessed February 17, 2007.

USEPA, 2005, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods." Microwave Assisted Acid Digestion of Aqueous Samples and Extracts. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3015.pdf

USEPA, 2009. National Recommended Water Quality Criteria. At www.epa.gov/waterscience/criteria/wqctable/index.html , accessed September 9, 2010.

Van Breemen, N. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. *Soil Sci. Soc. Am. Proc.,* 1973, 37**,** pp. 694–697

Vazquez, O., Pu, Xunchi., Monnell, J., Neufeld, R., 2010a, "Release of Aluminum from Clays in an Acid Rock Drainage Environment", *Mine Water and the Environment*, June 2010, pp:1-7

Vazquez, Oscar, Monnell, Jason D., Pu, Xunchi, and Neufeld, Ronald D., 2010b, Major processes dominating the release of aluminum from smectite clays when leached with Acid Rock Drainage, *Environmental Engineering Science*, Vol 27(12)

Watzlaf, G.R., Schroeder, K.T., and Kleinmann, R.L.P., *et al*., 2004, The Passive treatment of coal mine drainage, DOE/NETL-2004/12/02

Weaver, Kimberly R., Lagnese, Kathleen M., and Hedin, Robert S., 2004. Technology and design advances in passive treatment system flushing, National Meeting of the American Society of Mining and Reclamation and The 25th West Virginia Surface Mine Drainage Task Force, April 18 – 24,2004. Published by ASMR, 3134 Montavesta Road, Lexington, KY 40502.

Williams, D.J., Bigham, J.M., Cravotta III, C.A., Traina, S.J., Anderson, J.E., Lyon, G., 2002. Assessing mine drainage pH from the color and spectral reflectance of chemical precipitates. *Appl. Geochem*. 17, pp:1273 – 1286

Williams, T. M.; and Smith, B., (2000). Hydrochemical characterization of acute acid mine drainage at Iron Duke mine, Mazowe, Zimbabwe. *Environmental Geology* (Berlin), 39(3/4), pp: 272-278

Xiao, F., Zhang, B., and Lee, C., 1998. Effects of low temperature on aluminum(III) hydrolysis: Theoretical and experimental studies. *J. of Environ. Sci*., Vol 20(8), pp: 907-914