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Total and Soluble Aluminium Concentration and Suspended Particles Size Distribution Impacted by Sulphate and Silica After the NaOH Neutralization of Al-bearing Acid Mine Drainage

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ABSTRACT

A laboratory study was conducted to evaluate the effect of sulphate and silica on both, total and soluble aluminium concentrations in Al-bearing acidic rock discharge (ARD) treatment by NaOH. Independent variables included pH and different molar $Al:SO_4$ and $Al:Si:SO_4$ ratios. The experimental results showed that either sulphate or silica or both in combination influenced discharge of total and suspended Al concentrations. Sulphates reduced the soluble Al concentration by forming basaluminite, which is more insoluble than amorphous aluminium hydroxide. Particle size distributions after settling showed that the fraction and diameters of particles decreased with increasing sulphate concentration. Elevated silicate results in increasing the total aluminium level in the supernatant after 48 hours of settling. The co-presence of sulphate with silica encouraged the formation of $Si(OH)_4$, rather than Al-silica precipitates. However, the silica decreased the size of particles in the supernatant after settling, thus increasing the effluent particulate-bound Al concentration.

INTRODUCTION

Acid mine drainage (AMD) is a major source of water contamination in both coal and hard rock mining regions throughout the world (Sasowsky et al. 2000, Bunce et al. 2001). 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), Al ions could enter the surface or groundwaters from soil/sediment by cation-exchange, dissolution, or decomposition/mineralization (Cravotta 1994, Blowes & Ptacek 1994, Yucel & Baba 2013, Waters & Webster-Brown 2013). Aluminium, as an environmentally toxic contaminant, is found in many AMD locations. Data reported from over 150 different mine drainage samples across USA showed that over 30% of these locations presented minimum soluble aluminium concentrations of 50 mg/L (Watzlaf et al. 2004). Cravotta (2008) reported that over 50% of 140 abandoned coal mines in Pennsylvania showed the median of soluble aluminium concentrations over 1 mg/L which exceed the water quality criteria for the protection of aquatic life in surface water for Al [0.75 mg/L (acute) and 0.087 mg/L (chronic)] (USEPA 2009).

Theoretically, the primary reaction of aluminium removal in ARD treatment processes is considered as the for-mation of gibbsite or amorphous (am) $Al(OH)_3$ (Nordstrom & Ball 1986):

$$Al^{+3} + 3H_2O \leftrightarrow Al(OH)_3\downarrow + 3H^+ \qquad ...(1)$$
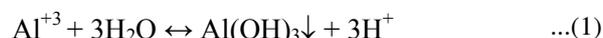
However, the precipitation of aluminium from natural AMD containing elevated sulphate and silicate levels is complex. These latter substances impact the composition and size of precipitates. The possible aluminium precipitates formed as a consequence of pH adjustment of AMD are not only aluminium hydroxides, but also Al-hydroxyl-sulphate and others. Taylor et al. (1997) and Bigham & Nordstrom (2000) reported that although the solubility of aluminium appeared corresponding to aluminium hydroxides, analysis of the compositions of formed precipitates suggested that amorphous basaluminite and aluminium hydroxysulphates were in solution, the proportions of which were pH dependent. Previous studies also reported that jurbanite-like mineral might control the activity of Al^{3+} in SO_4^- rich acidic liquid (Karathanasis et al. 1988, Sullivan et al. 1988, Van Breeman 1973). Herrmann & Baumgartner (1992) and Kim & Kim (2003a) have also reported that aluminium precipitates with other compositions can also be formed in the presence of other anions. Nordstrom et al. (2000) also found that the precipitates of basaluminite $(Al_4(OH)_{10}SO_4)$/hydrobasaluminite $(Al_4(OH)_{10}SO_4·12-$

36(H_2O)) significantly delayed the formation and equilibration of stable minerals in both field and laboratory experiments.

Soluble silica also impacts the precipitation of aluminium in water. "Soluble silica" is defined as silica that is monomeric, containing only one silicon atom and formulated as $Si(OH)_4$. The reported solubility of silica varies from reports to reports. The concentration of silica (as SiO_2) reported by investigators is typically in the range of 1-150 mg/L (Alexander et al. 1954, Stoeber 1967, Brace & Matijevic 1977 and Clesceri et al. 1989). Some researchers (Exley & Birchall 1992, Farmer & Lumsdon 1994) have reported the formation of hydroxyaluminosilica (HAS) species or co-precipitates in the conditions of diluted solution with silica. Exley & Birchall (1992, 1993) have studied the interaction between silica acid and aluminium at low aluminium concentrations. They found that HAS can be formed in such solutions, depending on silica acid concentration and pH values. At higher aluminium concentration (10^{-4} M), Birchall (1990) found that the interaction between aluminium and silica acid gives higher aluminium solubility at around neutral pH values. However, other researchers (Reiber et al. 1995) are not entirely consistent with these findings. Research reports are not conclusive and suggest that when silica is present, the predominant mineral phases acting on Al solubility control could be aluminium in equilibrium with (1) gibbsite (crystalline $Al(OH)_3$) (Sullivan & Cosby 1998), (2) a mixed phase of amorphous $Al(OH)_3$ and aluminosilicate (Gustafsson et al. 1998), (3) a metastable aluminosilicate phase (Neal & Williams 1988).

Numerous reports have focused on the soluble product of aluminium compounds in dilute and equilibrium conditions (Shah Singh & Brydon 1969, May et al. 1979, Xiao et al. 1998). However, the actual chemistry of AMD is complex and the water could likely be in a nonequilibrium condition. Many researchers have reported that amorphous $Al(OH)_3$ was the primary species of Al-precipitates (Nordstrom et al. 1984, Nordstrom & 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-sulphate and hydroxyaluminosilicate. Other researchers have reported that Al-sulphate precipitates were detected in field (Taylor et al. 1997, Bigham & Nordstrom 2000, Kim & Kim 2003a and 2003b). HAS was also formed in laboratory after long detention time (Exley & Birchall 1992, Exley & Birchall 1993, and Doucet et al. 2001).

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 aluminium concentration that likely to be achieved. The total effluent concentration will be the sum of all soluble aluminium species, plus particulate-containing aluminium species that have not settled. While the literature has many reports of aluminium containing precipitates, few report the nature and associated speciation of aqueous dissolved aluminium.

STUDY OBJECTIVES

The objectives of this study were to evaluate the effect of sulphate and silica on both suspended and soluble Al concentrations in an Al-bearing acidic discharge treatment system and on the suspended particles size distribution after settling. In order to achieve these goals, two groups of experiments were conducted with calibrated sulphate and silica concentrations. The experiments without silica examined the influence of sulphate on the soluble and suspended Al concentrations. The experiments containing silica focused on the effect of silica on aluminium concentrations. The suspended aluminium concentrations after settling were measured and suspended particulate size distributions were determined to investigate the impact of sulphate and silica on the settling of "fine" particulate aluminium solids at different pH values and water chemistries.

MATERIALS AND METHODS

Batch neutralization experiments were conducted in a 20 L glass jar with a diameter of ~30 cm. Fifteen litres of synthetic AMD was used in each experiment. A prepared solution of 5% NaOH (wt/wt) was added to synthetic AMD, and stirred for 5 minutes to assure complete mix. Stirring was then stopped to allow precipitates to form and settle. Supernatant samples were collected at a position about 10 cm under water surface after 30 minutes, and after 48 hours of settling. After the water samples (~150-200 mL each time) were collected, half of samples were immediately filtered with 0.45 μm millipore filter. HNO_3 was added to both filtered and unfiltered samples immediately to preserve for later analysis. The filtered samples were used to determine the soluble concentration, while the unfiltered samples for total concentration determination of aluminium. The distribution of supernatant suspended particle size was measured with Microtrac S3500, which use a tri-laser technology to measure the particle size. The measurement range of Microtrac S3500 is from 0.024 to 2800 μm, which can cover most of the particle sizes in supernatant of this study. During the experiments, the headspace of solution was open to the atmosphere as would be the case in the field. The pH of solution was measured by a Fisher Accumet 25, which was equipped with a Fisher Scientific Accumet pH electrode.

Table 1: The constituents of synthetic ARD and field water in Jonathan Run (mg/L).

	pH	Al	Ca	Mg	Mn	Zn	Fe	SO$_4$
Field ARD[1]	3.3 ± 0.42	47.0 ± 7.2	9.7 ± 5.8	11.9 ± 2.1	7.2 ± 0.99	0.70 ± 0.25	1.05 ± 0.38	457.1 ± 47.7
Synthetic ARD	3.5	50	10	12	7.4	NA[2]	NA	0, 180, 889

1: Monthly average concentrations of field ARD in Jonathan Run from November 2007 to July 2008
2: Not added

Table 2: The constituents of synthetic ARD water in the simulation experiments of the effect of silica on the aluminum removal (mg/L).

pH	Al	Mn	Fe	Ca	Mg	Silica (as Si)	SO$_4$
3.5	25	7.4	NA	10	12	25 or 65	0 or 450

Table 3: Soluble and total aluminium concentrations impacted by silica after ½ or 48 hours of settling at pH=6.0 and 8.0 mg/L.

Al:Si:SO$_4$	pH	Experimental results				Mineql+ model (species of precipitates)		
		0.5 hour		48 hour		Al(OH)$_3$	Al(OH)$_3$(am)+ basaluminite+ kaolinite	Al(OH)$_3$(am)+ basaluminite
		Total	Soluble	Total	Soluble (am)			
1:0:5	6.0	2.02	0.43	0.31	0.03	0.46	0.01	0.01
	8.0	4.56	3.20	1.81	1.32	3.08	0.49	0.49
1:1:0	6.0	1.40	0.30	0.21	0.02	0.46	0.01	0.46*
	8.0	3.51	2.42	1.07	0.80	3.08	0.58	3.08*
1:1:5	6.0	1.58	0.45	0.24	0.02	0.46	3.48E-04	0.01
	8.0	3.81	3.4	0.64	0.31	3.08	2.01E-03	0.49
1:2.5:5	6.0	1.86	0.41	1.35	0.14	0.46	2.39E-05	0.01
	8.0	4.27	2.14	1.32	0.12	3.08	1.39E-04	0.49

*: No basaluminite was formed in these cases

All experiments were conducted at laboratory room temperature (20°C ± 2°C).

To study the effect of sulphate on the total and soluble Al concentrations in Al-bearing AMD treatment three different experiments with molar ratios of Al:SO$_4$ of 1:0, 1:1, and 1:5 were conducted. The composition of synthetic AMD was shown in Table 1, which is based on the components of field acidic discharge in Jonathan Run located in Center County, Pennsylvania (Table 1). The pH of synthetic AMD was adjusted by HNO$_3$ to be about 3.5. The initial Al concentration was about 50 mg/L and the initial molar ratios of Al:SO$_4$ was 1:0, 1:1, and 1:5, therefore the sulphate concentrations were 0, 180 and 889 mg/L, respectively. NaCl was added in the solution at levels of 866.4 and 1082.8 mg/L when the molar ratios of Al:SO$_4$ equal 1:1 and 1:0, respectively, to make sure the ionic strength of solution was constant.

A set of experiments was conducted to evaluate the effects of silica (molar ratios of Al: silica: sulphate = 1:1:0, 1:1:5, and 1:2.5:5) on total and soluble Al concentration during Al-bearing AMD treatment with NaOH. The main

components of the synthetic AMD used in the experiments are presented in Table 2. The initial Al concentration of synthetic AMD was about 25 mg/L. Three molar ratios of Al:Si:SO$_4$ of synthetic ARD were used as 1:1:0, 1:1:5 and 1:2.5:5. The SiO$_2$ stock was prepared from Na$_2$O-SiO$_2$ by using a method designed to minimize the likelihood silica polymers or precipitates (Davis et al. 2001). During the experiments, the silica stock solution was added into synthetic AMD at the same time as addition of NaOH solution. The experimental procedure was also the same as that one described above.

Sample Handling

Water samples were digested with 5 mL of concentrated HNO$_3$ and 2 mL of concentrated HCl for 30 min at 170°C in a CEM-MARS (Matthews, N.C.) microwave digester following USEPA method 3015 (USEPA 1994). Aluminium concentrations were measured in one of two ways depending on their concentrations. The Aluminon technique, with reagents obtained from Hach Chemical Company (Hach Company, 2003) was used for aluminium levels in the range
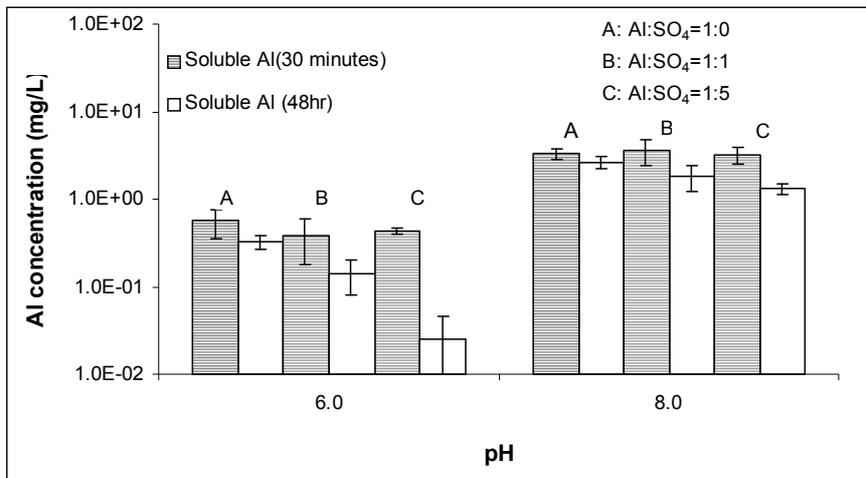
Fig. 1: Soluble Al concentration after 30 minutes and 48 hours of settling at pH=6.0 and 8.0 as influenced by sulphate (error bars represent standard deviation).
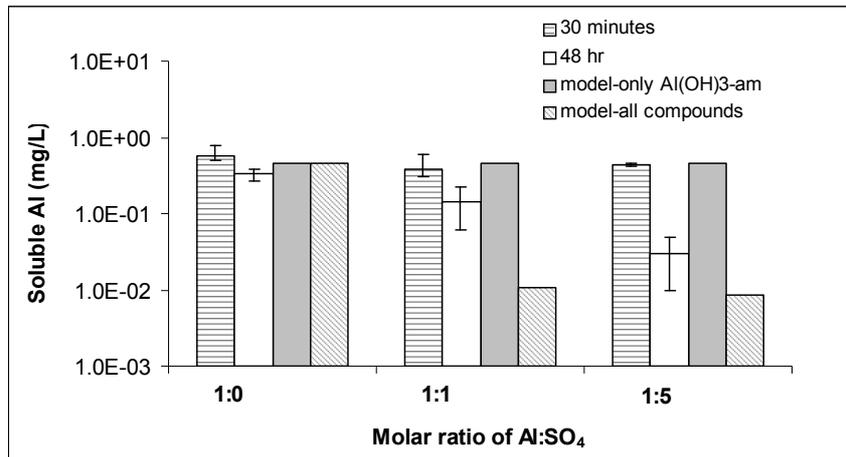

Fig. 2: Measured and calculated soluble Al concentrations from Mineql+ (with different sulphate concentrations) at pH=6.0.
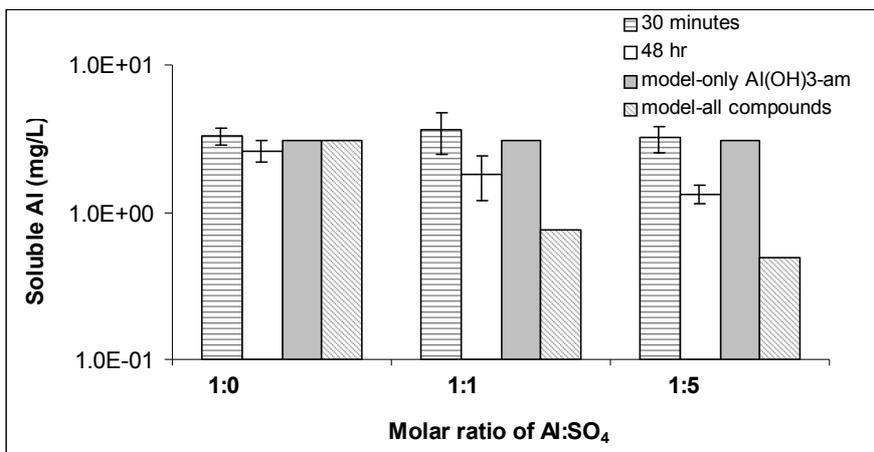

Fig. 3: Measured and calculated soluble Al concentrations from Mineql+ (with different sulphate concentrations) at pH=8.0.

of 0.008~0.8 mg/L. Aluminium concentrations over 2 mg/L were measured using a Perkin Elmer Model 1100B (Norwalk, CT) flame atomic absorption spectrometry (AAS). When the Al concentration was between 0.8-2.0 mg/L, samples were analysed with the Aluminon method after appropriate dilution. The sulphate concentration was measured with turbidimetric method (Hach 2003). The metal concentrations, such as Ca, Mn, Mg, etc. were measured by using an atomic absorption spectrometer (AA) (Perkin Elmer Model 1100B, Norwalk, CT) in accordance with Standard Method 3111 (APHA 2005). The concentration of sulphate was measured by turbidimetric method (APHA 2005). Silicate was measured by the silicomolybdate method (Hach 2003).

Data Analysis

Mineql+ chemical equilibrium modelling software is a chemical equilibrium model that is used for calculating aqueous speciation, solid phase saturation states, and precipitation-dissolution at low temperatures (0-50°C) 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 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.

RESULTS AND DISCUSSION

Aluminium Concentrations Impacted by Sulphate and Silica

The effect of sulphate concentration on Al concentration (pH =6.0 and 8.0): Experiments with three sets were conducted with calibrated Al:SO_4 molar ratios of Al:SO_4=1:0, 1:1 and 1:5. The process of this experimental series was to study the effect of sulphate on Al levels that can exist after NaOH treatment and subsequent settling of waters. Samples of supernatants were taken in the manner described above after 30 minutes, and extended 48 hours of settling.

Fig. 1 shows soluble Al concentrations as the supernatant pH was maintained at 6.0 and 8.0 respectively. After 30 minutes of settling, the soluble Al concentration was 0.46, 0.39 and 0.43 mg/L at pH=6.0, and 3.31, 3.60 and 3.20 mg/L at pH=8.0 when Al:SO_4 were equal to 1:0, 1:1 and 1:5, respec-

tively. After 48 hours of settling, soluble Al concentrations were reduced to 0.33, 0.14 and 0.03 mg/L at pH=6.0, and 2.62, 1.80 and 1.32 mg/L at pH=8.0 when Al:SO_4 ratios were equal to 1:0, 1:1 and 1:5, respectively. In both short and longer settling times, the soluble Al concentrations at pH=6.0 were lower than those at pH=8.0 in both high and low sulphate conditions. This implies that pH is a critical parameter on soluble Al concentration during neutralization of Al-bearing ARD.

Elevated sulphate level (Al:SO_4=1:5) reduced the soluble Al discharge at pHs. However, this effect was margined at pH=8.0. This figure illustrates that the influence of sulphate alone on soluble aluminium appeared to be of secondary importance as compared to the overall influence of pH since the sulphate reduced the soluble Al concentrations after 48 hours of settling.

The saturation index (SI) values of different species of Al-precipitates after 30 minutes and 48 hours settling were calculated with Mineql+ base-data and computerized equilibrium model. The input data were solution components measured after 30 minutes and 48 hours of settling, respectively.

The SI value of amorphous Al(OH)_3 was 0.07 at pH=6.0, and 0.03 at pH=8.0 when sulphate was absent after 30 minutes of settling. The SI values of amorphous Al(OH)_3 were close to 0 indicating that the solution was in equilibrium with amorphous Al(OH)_3 after 30 minutes settling. After 48 hours of settling, the SI value was -0.02 at pH=6.0 and -0.001 at pH=8.0, suggesting that the solutions were still in equilibrium with amorphous Al(OH)_3. Additional possible species of Al-precipitates include crystalline Al(OH)_3 (gibbsite) in the experiments without sulphate. The SI value of gibbsite was 2.63 and 2.53 at pH=6.0, and 2.59 and 2.55 at pH=8.0 after 30 minutes and 48 hours settling, respectively, indicating that the solutions would have been supersaturated with gibbsite. These SI data suggest that the solutions were not in theoretical equilibrium condition after 48 hours, although they would have been stable. Furthermore, the soluble Al concentration was much higher than the theoretical solubility of gibbsite also implying that gibbsite was not formed within 48 hours of settling.

When sulphate was present in solution, the possible Al-precipitates included Al-sulphate compounds, such as jurbanite and basaluminite besides amorphous Al(OH)_3. After 30 minutes of settling, SI values of amorphous Al(OH)_3 were -0.12 and -0.02 at pH=6.0, and 0.07 and 0.02 at pH=8.0 when Al:SO_4 ratios were equal to 1:1 and 1:5, respectively. All the SI values of amorphous Al(OH)_3 were close to zero in experiments with both high and low initial sulphate concentrations, indicating that the solutions were in equilib-
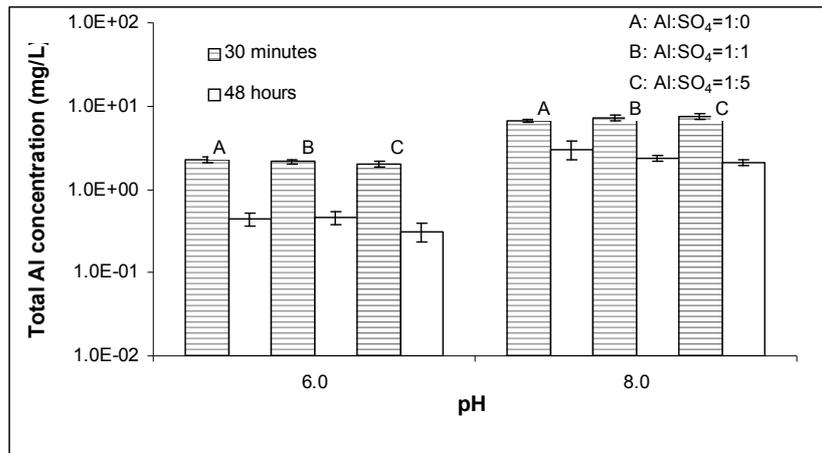
Fig. 4: Total Al concentration after 30 minutes and 48 hours of settling at pH=6.0 and 8.0 as influenced by sulphate (error bars represent standard deviation).
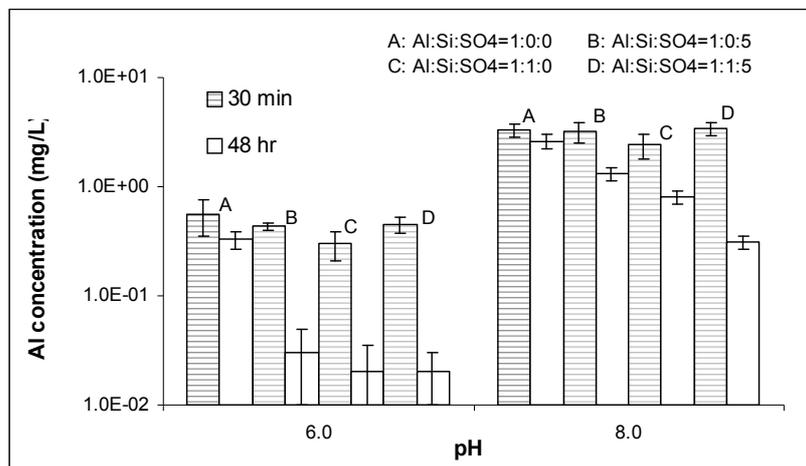

Fig. 5: Soluble Al concentration after 30 minutes and 48 hours of settling at pH=6.0 and 8.0 as influenced by sulphate and silica (error bars represent standard deviation).
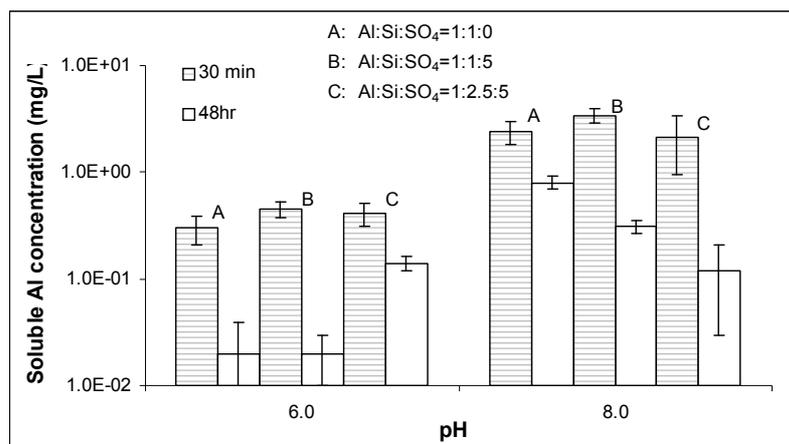

Fig. 6: Soluble Al concentration after 30 minutes and 48 hours of settling at pH=6.0 and 8.0 as influenced by sulphate and silica (error bars represent standard deviation).

rium with amorphous $Al(OH)_3$ after 30 minutes of settling. The SI values of jurbanite, which was another possible species of Al-sulphate precipitates, were -0.77 and -0.67 at pH=6.0, and -4.80 and -4.16 at pH=8.0 when $Al:SO_4$ ratios were equal to 1:1 and 1:5 after 30 minutes of settling, respectively. The negative SI values indicated that jurbanite was not produced after 30 minutes of settling. SI values of basaluminite were 6.33 and 6.79 at pH =6.0, and 2.85 and 3.35 at pH=8.0 when $Al:SO_4$ was equal to 1:1 and 1:5, respectively. All SI values of basaluminite were positive and higher than 2, which indicate that solutions were supersaturated with basaluminite in these experiments. The SI data showed that the main reaction of Al-precipitation was the formation of amorphous $Al(OH)_3$ within 30 minutes settling.

After 48 hours of settling, SI values of amorphous $Al(OH)_3$ were -0.56 and -1.23 at pH=6.0, and -0.33 and -0.37 at pH=8.0, whereas the SI values of basaluminite reduced to 4.56 and 2.17 at pH=6.0, and 1.67 and 1.81 at pH=8.0 when $Al:SO_4$ was equal to 1:1 and 1:5, respectively. The reduction of SI values was due to the decrease of both soluble Al and sulphate concentrations. All the SI values of amorphous $Al(OH)_3$ became negative after 48 hours settling, indicating that the reduction of soluble Al concentrations was not due to the formation of $Al(OH)_3$ from 30 minutes to 48 hours of settling, since the solutions were unsaturated with amorphous $Al(OH)_3$. Since the solutions were in approximately equilibrium with amorphous $Al(OH)_3$ and unsaturated with jurbanite after 30 minutes of settling, the reduction of soluble Al concentrations should be due to the formation of basaluminite. The soluble Al concentration reduced from initial 50 mg/L to less than 4.0 mg/L and the Al removal was mainly due to the formation of amorphous $Al(OH)_3$

within 30 minutes of settling, so it can be concluded that the primary sludge formed in experiments was $Al(OH)_3$ and with part of Al-sulphate precipitates. This result is similar to observations made in the field (Pu et al. 2010) in which similar conclusions were found when examining samples taken from the field for the possible presence of jurbanite and basaluminite.

Figs. 2 and 3 show elevated sulphate levels and reduced soluble Al levels at both pH=6.0 and 8.0. Actual measured Al values fell in between predicted Mineql+ values when model input information contained amorphous $Al(OH)_3$ or basaluminite in the solid phase.

While soluble Al levels are reduced by elevated sulphates, this is not the case for total aluminium concentration even after 48 hours of settling. This is shown in Fig. 4. The total Al concentration is lowered after 48 hours of settling, and increased as the pH excursion goes from 6.0 to 8.0. After 48 hours of settling, the elevated sulphate levels in the water matrix caused an increase in suspended Al-containing solids in the effluent, although the soluble Al concentration reduced.

The effect of silica concentration on Al concentration: Three different sets of batch experiments have been conducted to study the influence of silica on soluble and total Al concentrations that could exist in Al-bearing ARD 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. As mentioned above, samples of supernatant were taken after 30 minutes and 48 hours.

Fig. 5 shows the soluble Al concentrations at pH = 6.0 and 8.0 in different molar ratios of $Al:Si:SO_4$ after 30 min-
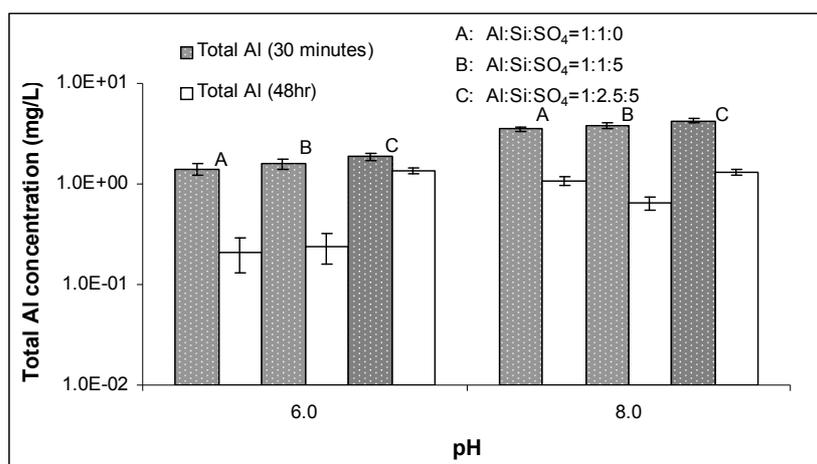

Fig. 7: Total Al concentration after 30 minutes and 48 hours of settling at pH=6.0 and 8.0 as influenced by sulphate and silica (error bars represent standard deviation).

Table 4: Suspended Al and sulphate concentration at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling.

Al:SO$_4$	Setting time	pH=6.0			pH=8.0		
		Al (mg/L)	SO$_4$ (mg/L)	Al:SO$_4$ (molar ratio)	Al (mg/L)	SO$_4$Al: (mg/L)	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	24.1	1.01	0.26	13.8
	48 hr	0.32	0.26	4.4	0.35	0.32	3.9
1:5	30 min	1.59	0.31	18.2	1.36	0.34	14.2
	48 hr	0.28	0.28	3.6	0.49	0.42	4.1

utes and 48 hours of settling. It can be seen that soluble Al concentrations were lower when silica was present than those when silica was absent after 48 hours of settling, although there was no significant difference after 30 minutes of settling. The presence of silica in an active ARD treatment site could slightly reduce the effluent soluble Al concentration from the site discharge.

Fig. 6 shows data similar to Fig. 5, except that both silica and sulphate are included. Results show that the reduction of soluble Al concentration was not only due to the formation of amorphous Al(OH)$_3$, but also the formation of Al-silica 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 were equal to 1:1:0, 1:1:5, and 1:2.5:5, respectively. 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)$_3$ at 30 minutes of settling, the reduction of soluble Al concentrations was due to the formation of Al-sulphate and/or Al-silica precipitates.

Fig. 7 shows the total Al concentrations under different silica concentrations at pH=6.0 and 8.0 after 30 minutes and 48 hours of settling (data in Table 3). After 30 minutes of settling, total Al concentration was in the range of 1.40 to 1.86 mg/L at pH=6.0, and 3.51 to 4.27 mg/L at pH=8.0. After 48 hours of settling, the total Al concentration was in the range of 0.21 to 1.35 mg/L at pH=6.0, and 0.64 to 1.32 mg/L at pH=8.0. Compared with the values under different molar ratios of silica, the total Al concentrations were the highest in the supernatants that contained highest silica concentration (Al:Si:SO$_4$=1:2.5:5). This result indicates that elevated silica in solution increases the effluent Al concentration. For comparison, Table 3 shows the total and soluble Al concentrations after 30 minutes and 48 hours of settling in experiments with the Al:Si:SO$_4$ ratios used. Results show that the soluble Al concentrations after 48 hours of settling were lower than the soluble Al concentrations in the experiments that contained silica, although there was no significant difference after 30 minutes of settling. The overall ef-

fect of silica on ARD treatment is to slightly reduce the effluent soluble Al concentration that increase the Al bound particulates in the effluent after settling.

Particles Size Distributions

The effect of sulphate on suspended particle size: Particle sizes and size distributions in supernatants were measured in order to understand the influence of suspended particulate Al solids on effluent Al concentrations after ARD/AMD NaOH treatment.

Fig. 8 shows the suspended particles size distributions in the supernatant at different sulphate concentrations after 48 hours of settling at pH=6.0. After 48 hours of settling, the median diameter of supernatant suspended particles in experiments without sulphate was about 25 µm, whereas the median diameter of suspended particles was about 2 µm when Al:SO$_4$ ratios were equal to 1:1 and 1:5, respectively. In the experiments when sulphate was present, most of the suspended particles (>60%) were in the range of 1.0 to 3.0 µm, whereas without sulphates, about 80% of the particles were larger than 10 µm in experiment without sulphate. This indicates that the presence of sulphate reduced the particle size after longer settling time (48 hours).

Table 4 shows the suspended Al and sulphate concentration at 30 minutes and 48 hours of settling. As indicated above, the suspended Al concentration was lowest when there was no sulphate in the supernatant. The particle size distribution showed that more large particles appeared in the supernatant when sulphate was absent in the solution.

From Table 4, it can be seen that the molar ratio of Al:SO$_4$ of suspended particles was from 13.8 to 24.1 after 30 minutes of settling, whereas the molar ratio became 3.6 to 4.4 after 48 hours of settling, which is close to the theoretical molar ratio (= 4) of Al:SO$_4$ of basaluminite.

The reduction of soluble Al concentration when sulphate was present suggests that Al-sulphate precipitates are being formed during the course of settling. It is reasonable to conclude that the formed Al-sulphate precipitates might
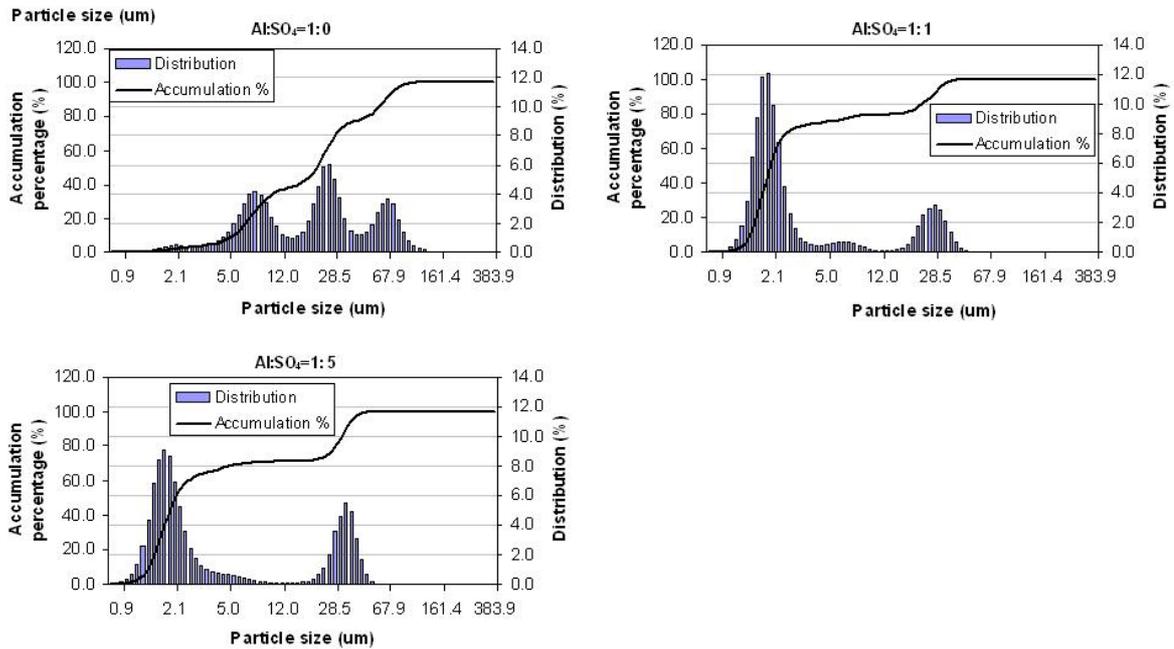
Fig. 8: Particle size distributions in the supernatant after 48 hours of settling at pH=6.0 as influenced by sulphate.
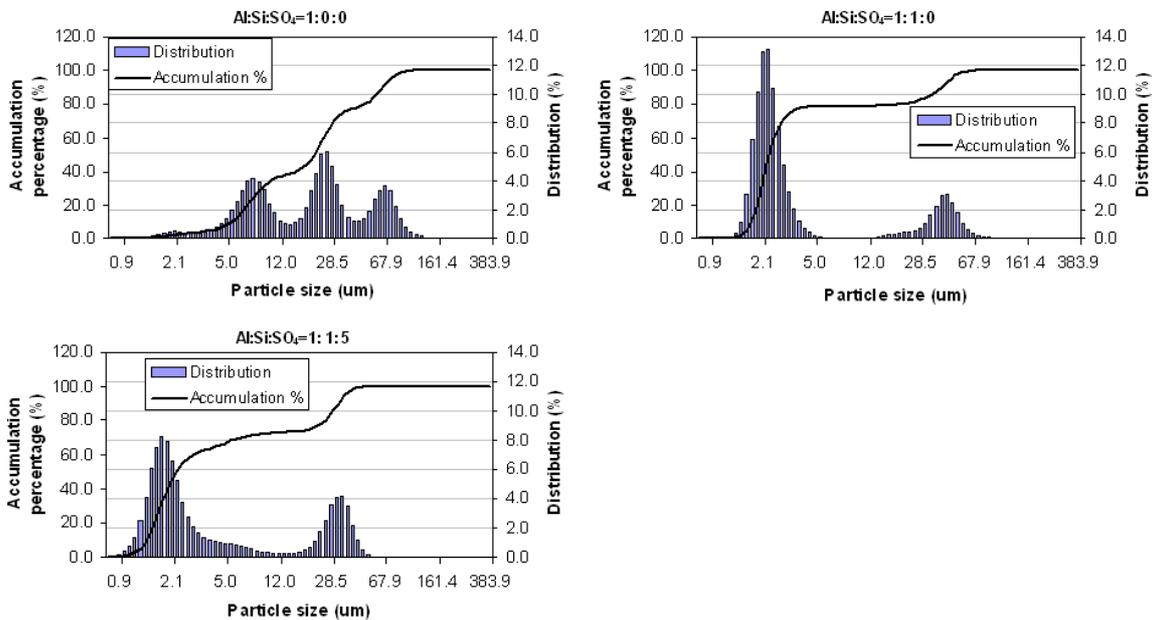

Fig. 9: Suspended particle size distribution in the supernatant at pH=6.0 after 48 hours of settling in experiments with different molar ratios of Al:Si:SO$_4$.

maintain a relatively small particle size. Since the small particles are more difficult to be removed by gravity settling, the presence of sulphate may increase the suspended particles in effluent and resulting in a higher effluent aluminium concentration.

The effect of silica on suspended particle size: Fig. 9 shows the suspended particle size distributions in experiments with different Al:Si:SO$_4$ ratios after 48 hours of settling at pH=6.0. After 48 hours of settling, the median diameter of suspended particles was about 2 μm at pH=6.0 when silica was present
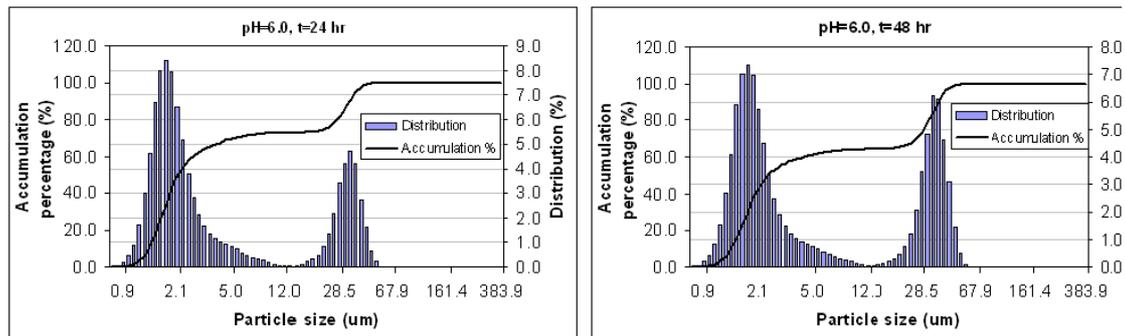
Fig. 10: Suspended particle size distribution in the supernatant at pH=6.0 after 24 and 48 hours of settling in experiment with molar ratio of Al:Si:SO$_4$=1:2.5:5.

and sulphate was absent in solution, whereas the median size was about 25 μm in experiment without both silica and sulphate. At pH=6.0, about 80% of suspended particles was smaller than 5 μm after 48 hours of settling when silica was present and sulphate was absent, whereas about 80% of particles were larger than 10 μm in experiment without both silica and sulphate. The data indicate that silica reduced the supernatant particle size after 48 hours of settling.

The suspended Al concentration was 0.19 mg/L at pH=6.0 after 48 hours of settling in experiment with Al:Si:SO$_4$ ratio equal 1:1:0, whereas the suspended Al concentration was 0.11 mg/L in experiment without both silica and sulphate. This result shows that more small suspended Al particles were in supernatant when silica was present. These small Al particles reduced the ability of suspended particulate Al solids to settling and lead to a relative higher effluent Al concentration from an NaOH active treatment ARD/AMD system.

In the experiment with molar ratio of Al:Si:SO$_4$ equal to 1:0:1 (with sulphate present and silica absent), the median diameter of suspended particles was about 2 μm (Fig. 8) and the suspended Al concentration was 0.32 mg/L after 48 hours of settling at pH=6.0. This value was slightly higher than found from experiments when silica was present and sulphate was absent (Al:Si:SO$_4$=1:1:0). These data indicate that the presence of sulphate will allow higher levels of Al precipitates to remain in the supernatant. Therefore, sulphate has a negative effect on effluent Al concentration by reducing the suspended particle size, and silica also decreased the settling ability of Al-particles.

When the solution contained a high sulphate concentration (Al:SO$_4$=1:5), the particles size distributions were similar as with experiment with low silica (Al:Si:SO$_4$ = 1:1:5) (Fig. 9) and without silica (Al:Si:SO$_4$=1:0:5) (Fig. 8) at pH = 6.0 after 48 hours of settling. For reference, at pH =6.0, the suspended Al concentration was 0.28 mg/L in experiments

without silica and 0.22 mg/L in experiments with low silica. This indicates that at pH = 6, silica and sulphate have no significant effect on suspended Al concentration. Since the particle size in both the cases was small, at pH = 6, both silica and sulphate can reduce the particle size and increase the relative amounts of non-settleable Al suspended solids.

Fig. 10 shows the particle size distributions in experiments with high silica and sulphate concentrations (molar ratio of Al:Si:SO$_4$ equal to 1:2.5:5) at pH = 6.0 at 24 and 48 hours of settling. With the increase of settling time (24 hours to 48 hours), the median diameter of particle size decreased from 27 μm to 2.5 μm, and 60% of aluminium-bound suspended particles were smaller than 5 μm. The suspended Al concentration was 1.21 mg/L after 48 hours of settling, which was much higher than in experiment with low silica (0.22 mg/L). At the highest combination of sulphate and silica, the particle size distribution was virtually unchanged between 24 hours and 48 hours of settling and the majority of the particle sizes were less than 6 μm. These data reveal that poor settleable particles and elevated suspended aluminium appeared in experiments with high silica concentration.

CONCLUSIONS

A laboratory study was conducted to evaluate the effects of sulphate and silica on both suspended and soluble Al concentrations in a laboratory synthesized Al-bearing acidic rock discharge using different Al:SO$_4$ molar ratios (1:0, 1:1, and 1:5) and Al:Si:SO$_4$ molar ratios (1:1:0, 1:1:5, and 1:2.5:5). The results suggested that pH is a critical parameter during Al-bearing ARD treatment and increasing pH would result in increase of total soluble aluminium concentrations even after extended (48 hour) settling times. The influence of sulphate and silica alone on total soluble aluminium appeared to be of secondary importance as compared to the overall influence of pH, however, both silica and sulphate in discharge waters can affect particle size dis-

tribution and effluent aluminium after settling.

Synthetic ARD experiments showed that either sulphate or silica or both in combination impacted Al concentrations in both soluble and suspended Al phases. Sulphates can decrease the soluble Al concentration in the treatment process by forming basaluminite that is more insoluble than amorphous aluminium hydroxide. Silicates at higher molar ratios in solution (Al:Si=1:2.5) result in increasing the total aluminium level in the supernatant even after 48 hours of settling. It is clear from this study that sulphate and silica have effects on both soluble and suspended Al concentration during neutralization of Al-bearing ARD.

Saturation index (SI) values showed that solution could be in equilibrium with amorphous $Al(OH)_3$ within the first 30 minutes of settling after pH adjustment. Comparing Al concentrations from different experiments, it is concluded that the formation of amorphous $Al(OH)_3$ is the primary reaction product for Al removal during Al-bearing ARD treatment with NaOH, and the formation of Al-sulphate can reduce the soluble Al concentration after long (48 hours) settling times. The latter situation can occur in AMD and ARD discharges with high sulphate levels.

Suspended particles size distribution studies revealed that the presence of sulphate reduces the mean particle size in the supernatant yielding a relative higher suspended Al concentration. Particles which are larger than 30 μm can be removed after 48 hours of quiescent settling. By comparing the particle size distribution at 30 minutes and 48 hours of settling, it is found that the pH alone does not affect the particle size in supernatant. Suspended particle size reduction resulted with increases of SO_4. The presence of sulphate can actually increase the total effluent Al concentration from active ARD treatment system due to the low settling efficiency, despite the soluble Al concentration being reduced by sulphate.

Sulphate and silica can reduce the suspended particle sizes both individually and in combination. High levels of silica could increase the effluent Al concentration by forming numerous small diameter particles. Co-presence of sulphate and silica, however, can also form particles containing $Si(OH)_4$.

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REFERENCES

Alexander, G.B., Heston, W.M. and Iler, R.K. 1954. The solubility of amorphous silica in water. J. Phys. Chem., 58: 453.

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

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, 40: 351-403.

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

Blowes, D.W. and Ptacek, C.J. 1994. Acid-neutralization mechanisms in inactive mine tailings. In: Jambor, J.L. and Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Mine-wastes, 22: 271-292.

Brace, R. and Matijevic, E. 1977. Coprecipitation of silica with aluminum hydroxide. Colloid and Polymer Science, 255(2): 153-160.

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., 35(18): 4410-4416.

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, Washington DC.

Cravotta, 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 min in Pennsylvania. In: Alpers, C.N. and Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation, pp. 345-364.

Cravotta, Charles A., III 2008. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations. Applied Geochemistry, 23(2): 166-202.

Davis, C.C., Knocke, W.R. and Edwards, M. 2001. Implications of silica sorption to iron hydroxide: mobilization of iron colloids and interference with sorption of arsenate and humic substances. Environ. Sci. Technol. 35(15): 3158-62.

Doucet, F.J., Rotov, M.E. and Exley, C. 2001. Direct and indirect identification of the formation of hydroxyaluminosilicates in acidic solutions. Journal of Inorganic Biochemistry, 87(1-2): 71-79.

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

Exley, C. and Birchall, J. D. 1993. A mechanism of hydroxy aluminosilicate formation. Polyhedron, 12(9): 1007-17.

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): 3331-3334.

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

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

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

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

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: 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.

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, 7(5): 569-581.

May, H.M., Helmke, P.A. and Jackson, M.L. 1979. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. Geochimica et Cosmochimica Acta, 43(6): 861-868.

Neal, C. and Williams, R. J. 1988. Towards establishing aluminium hydroxyl silicate solubility relationships for natural waters. J. Hydrology, 97: 347-352.

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. Environmental Science and Technology, 34: 254-258.

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): 611.

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

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. Sci., 27(2): 169-180.

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

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

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., 107: 12-16.

Stoeber, Werner 1967. Formation of silicic acid in aqueous suspensions of different silica modifications. Advan. Chem. Soc., 67: 161-82.

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

Sullivan, P.J., Yelton, J.L. and Reddy, K.J. 1988. Iron sulfide oxidation and the chemistry of acid generation. Environ. Geol. Water Sci., 11: 289-295.

Taylor, P.D., Jugdaohsingh, R. and Powell, J.J. 1997. Soluble silica with high affinity for aluminum under physiological and natural conditions. J. Am. Chem. Soc., 119(38): 8852-8856.

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

USEPA 2009. National Recommended Water Quality Criterias. U.S. Environmental Protection Agency. At www.epa.gov/waterscience/criteria/wqctable/index.html, accessed September 9, 2010.

Waters, A.S. and Webster-Brown, J.G. 2013. Assessing aluminium toxicity in streams affected by acid mine drainage. Water Sci. Technol., 67(8): 1764-1772.

Watzlaf, K. Schroeder, R. Kleinmann, C. Kairies and Nairn, R. 2004. The passive treatment of coal mine drainage. National Energy Technology Laboratory, US Department of Energy (2004) Information circular.

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

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

Yucel, Deniz Sanliyuksel, Baba, Alper 2013. Geochemical characterization of acid mine lakers in northwest Turkey and their effect on the environment. Archives of Environmental Contamination and Toxicology, 64(3): 357-376.