



Laboratory and Field Evaluation of Solubility Control of Aluminium During Al-Bearing Acid Rock Discharge Treatment

Xunchi Pu, Ran Li, Kefeng Li and Ruifeng Liang[†]

State Key Laboratory of Hydraulics and Mountain River Engineering, Sichuan University, Chengdu, 610065, China

[†]Corresponding author: Ruifeng Liang

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 03-11-2017
Accepted: 19-12-2017

Key Words:

Basaluminite
Jurbanite
Amorphous Al(OH)₃ solubility
Al-bearing acid rock discharge
Al-precipitates

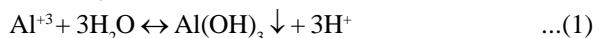
ABSTRACT

Potential control of soluble aluminium in Al-bearing acidic discharge neutralization by formation of precipitates other than Al(OH)₃ was studied. At pH around 5.5, precipitates formed in field and laboratory showed that Al-solids contained sulfate and silicon. Although the soluble aluminium concentration do not match each of the solubility of species of Al-precipitates, the reason that soluble aluminium concentrations were less than solubility of amorphous Al(OH)₃ was due to the formation of Al-sulfate. The laboratory experiments of synthetic ARD showed that basaluminite was formed and this was the reason that soluble Al concentration became less than the solubility of amorphous Al(OH)₃. The change of sulphur contents in the sludge with pH revealed that more Al-sulfate (basaluminite) was formed at high pH (~8.3). The atomic ratio of Al/OH at different pH values suggested that the sludge formed at neutral pH conditions contained the most proportion of Al(OH)₃. The formation of these precipitates provides a possible mechanistic explanation for the decrease of soluble Al concentration in neutralization of ARD.

INTRODUCTION

Acid rock discharge (ARD) or acid mine drainage (AMD) formed through the oxidation of sulfide minerals (usually pyrite) is a major source of water impairment in both, coal and hard rock mining regions throughout the world (Sasowsky et al. 2000, Bunce et al. 2001). Usually, the primary contaminants in ARD are iron and sulfate, which come from the oxidation of pyrite. Other metals, such as Al, Mn, Mg, etc. could also be present in ARD as the principal contaminants (Cravotta 2008, Nordstrom & Alpers 1999, Neufeld et al. 2007). Al concentration changes widely in ARD/AMD. Data reported from over 150 different mine drainage samples across USA showed that over 30% of these locations presented minimum soluble Al concentrations of 50 mg/L (Watzlaf et al. 2004). Cravotta (2006, 2008) reported that in over 50% from 140 abandoned coal mines in Pennsylvania were present median soluble Al concentrations over 1.3 mg/L and the maximum concentration was 108 mg/L. Researches also reported that the Al concentration was up to 1,100 mg/L in AMD in Sobov, Slovakia (Dubikova et al. 2002). In Spain, Galan et al. (1999) reported the Al concentration of about 50 mg/L in AMD at Huelva. Al pollutant due to AMD/ARD is an environmental problem over the world (Gray 1998), since Al is highly toxic to aquatic organisms, and can destroy the benthic habitat and degrade the aesthetic qualities of stream (Koryak et al. 1972, Evangelou & Zhang 1995).

Theoretically, the primary reaction of Al precipitation is considered as the formation of gibbsite or amorphous (am) Al(OH)₃:



However, the precipitation of Al from natural ARD and/or AMD is complex. ARD/AMD often contains sulfate and silicate, which could impact the composition of precipitates. While Al(OH)₃ is usually the primary species of Al-precipitates found in field, the presence of sulfate could dramatically impact the solubility of Al. The strong affinity that Al has for sulfate in the form of basaluminite and alunite has been observed by Taylor et al. (1997) and Bigham & Nordstrom (2000). They reported that although the solubility of Al appeared corresponding to aluminium hydroxides, analysis of the composition of formed precipitates suggested that amorphous basaluminite and Al hydroxysulphates were in solution, the proportions of which were pH dependent. Several previous studies (Karathanasis et al. 1988, Sullivan et al. 1988, Van Breeman 1973) have reported that a jurbanite-like mineral, having a molar stoichiometry of Al:OH:SO₄=1:1:1, might control the activity of Al³⁺ in acidic, SO₄-rich waters. Adams & Rawajfih (1977) found that amorphous basaluminite (Al₄(SO₄)₁₀(OH)₁₀) was precipitated during titration of Al 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 hydroxysulphate with basaluminite

stoichiometry. Herrmann & Baumgartner (1992) and Kim & Kim (2003a) have also reported that other compositions of Al precipitates can also be formed in the presence of other anions. Nordstrom et al. (2000) also found in both field and laboratory experiments that the precipitates of basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$)/hydrobasaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 12\text{H}_2\text{O}$) significantly delayed the formation and equilibration of stable minerals. Numerous researches have investigated the solubility product of Al compounds in dilute and equilibrium conditions (Shah Singh & 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 researches have reported that the amorphous $\text{Al}(\text{OH})_3$ 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 species of Al-precipitates should be gibbsite and/or Al-sulfate. Meanwhile, some researches have reported that Al-sulfate precipitates were detected in field (Taylor et al. 1997, Bigham & Nordstrom 2000, Kim & Kim 2003a, 2003b). It has long been known that anions, such as sulfate and silicate, can impact the composition of Al-precipitates (Adam & Rawajfih 1977, Nordstrom et al. 1984, Bigham & Nordstrom 2000 and Kim & Kim 2003b). Relatively, little work has focused on the influence of alternative species of Al-precipitates on the concentration of residual soluble Al during ARD/AMD treatment, but previous works showed several Al-precipitate species, such as basaluminite and jurbanite, that might be important under low and high pH conditions (Nordstrom & Ball 1986, Nordstrom et al. 2000). Understanding of the relation of species of Al-precipitates and soluble Al concentration in different pH values may help elucidate observed difference in the species of Al-precipitates in field.

The objective of this study was to quantify, in controlled laboratory experiments, Al solubility and solid species in field ARD over time in neutralization with NaOH. The laboratory results were compared with the field observation. Meanwhile, synthetic ARD was used in this study to identify the possible species of Al precipitates formed in neutralization of ARD with NaOH. This study focused on the species of Al-precipitates and the relationship of soluble Al concentrations to the species of precipitates. The results of this study provide insight into soluble Al concentration and solid-phase speciation in Al-bearing acidic discharge treatment processes.

SITE DESCRIPTION

Al-bearing ARD has been an environmental problem in Jonathan Run located in Centre County, Pennsylvania (Hedin Environmental 2003). Water quality changes in

Jonathan Run occurred in the 1960's during the construction of I-80. Previous research determined that the primary source of contamination originated from the acidic sandstone fill that was used to construct the embankment of I-80. The stream flows through a culvert under this embankment and Al precipitates were found downstream of this culvert (Neufeld et al. 2007).

The surface seep from the embankment of I-80 contained high Al concentration (~48 mg/L) and low concentration of iron (<2.0 mg/L) (Neufeld et al. 2007, Hedin Environmental 2003). Two pilot-scale flush boxes that contained limestone were installed in North of I-80 near Jonathan Run to treat the Al-bearing acidic discharge. The flush boxes are pilot systems to treat acid water from the I-80 culvert in the culvert collection system (CCS). Flush boxes in Jonathan Run consists of two 30 CY metal roll-off boxes that contain limestone aggregate and receive flow from the CCS. The two boxes are completely independent of each other and operate parallel. Acidic water enters the top of the roll-off, spills onto the limestone aggregate, and fills the container. Each box contains an automatic self-flushing siphon device. The siphon is triggered and the effluent from flush boxes discharges into a small sediment basin when the water level in the container reaches the top of the limestone (Hedin Environmental 2008). The flush boxes were 6060 gallon roll off containers which contained limestone. The actual bulk porosity of flush boxes was 2537 and 2153 gallon for Box 1 and Box 3, respectively (Hedin Environmental, 2008). According to the influent flow rates (1.1 to 2.0 gpm), the interval of siphon triggered was from 21.1 to 32.6 hours. These flush boxes operated from May 2003. The flush boxes treated Al-bearing acidic water that was collected from I-80 culvert. This flow has low pH, high Al concentration and low iron concentrations. The sulfate concentration of this acidic discharge was about 400-500 mg/L. From 2003 to 2006, the effluent quality from flush boxes had considerably deteriorated. The decline of efficiency was due to armoring of precipitates on the surface of limestone (Hedin Environmental 2008).

The sludge on limestone surface in flush boxes had been collected in 2007 and analyzed by XRD and SEM. The results showed that most of the sludge was amorphous $\text{Al}(\text{OH})_3$ mixed with a little amount of Al-sulfate (Pu et al. 2010).

MATERIALS AND METHODS

Laboratory neutralization experiments: Laboratory experiments were conducted to study the relation of solubility of aluminium to species of Al-precipitates formed in different conditions. The neutralization of Al-bearing ARD used NaOH (5% wt). The experiments were conducted in a

20 L glass jar with a diameter of ~30cm. During the experiments, 5% NaOH (Wt/Wt) solution was added into 15 L ARD (field ARD water or synthetic ARD) to obtain the expected pH value. The pH of solution in experiments was measured by a Fisher Accumet 25 benchtop pH electrode meter with Fisher Scientific Accumet pH electrode. After addition of NaOH, the reactor was stirred for 5 minutes to let the solution completely mixed. Then stirring was stopped to allow the formed precipitates to settle down. The headspace of solution was open to the atmosphere. All experiments were conducted at room temperature ($20^{\circ}\text{C} \pm 3^{\circ}\text{C}$).

Supernatant fluids were collected for subsequent analysis from a location of about 10 cm under the water surface. After the water samples (~150–200 mL each time) were collected, they were immediately filtered with 0.45 μm millipore filter (Billerica, MA) and added 1 drop of HNO₃ (1+1) and stored at 4°C in refrigerator for subsequent analysis. Duplicate samples were collected each time. The filtered samples represent soluble concentration. The sludge was collected after 48 hours settling and separated from water by centrifuging at 8500 g for 15 minutes in a Fisher Scientific AccuSpin Model 400 benchtop centrifuge and washed by DI water for three times.

Two kinds of water, field water and synthetic ARD, were used in laboratory experiments. The field water was collected from the influent of flush boxes in Jonathan Run located in Centre County, Pennsylvania in May 2008. The components of field water are given in Table 1. The concentrations of main contaminants (Al, Ca, Mg, SO₄) of field water sample were almost the same as the monthly average concentrations of influent samples from November 2007 to July 2008. Synthetic acidic water, which was used to study the effect of sulfate on precipitate species and soluble Al, was prepared according to the components of field water, but with different sulfate concentrations. The molar ratios of sulfate to Al in synthetic ARD were 1:1 and 5:1, respectively. Synthetic ARD contained Na⁺, Ca²⁺, Mg²⁺, Mn³⁺,

Al³⁺, Cl⁻, and SO₄²⁻. The pH value was adjusted by addition of HNO₃ (1+1) to about 3.5. When molar ratio of Al:SO₄ was 1:1, NaCl was added to make the same liquid ionic strength. The concentration of Al was about 50 mg/L. The molar ratio of Al/SO₄ was 1:1, and 1:5, therefore the sulfate concentrations were 180 and 889 mg/L, respectively.

Analysis methods: Al concentration was measured by Aluminon method (Hach company 2003), for which the measure limits are from 0.008–0.8 mg/L, when the Al concentration was less than 2 mg/L. If the Al concentrations were more than 0.8 mg/L and less than 2 mg/L, samples were diluted to suitable Al concentrations and analyzed with Aluminon method. 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. The field sludge in the flush box of Jonathan Run was collected in November 2006. The method has been described earlier by Pu et al. (2010).

The mineralogy of precipitates was analyzed by X-ray powder diffractometer (Rigaku GeigerflexRAD3-C Model, Tokyo, Japan) from 15 to 80° in step interval of 0.05 2θ and 10s scanning time because most of them are non-crystal. The composition of precipitates was measured by a Philips XL30 scanning electron microscope (SEM). The energy-dispersive X-ray microanalysis system, Oxford Instruments INCA (Abingdon, UK), was used to perform energy-dispersive spectrometry (EDS) analysis. In order to remove the effect of absorbed water, the precipitates were dried at about 85°C for two hours before SEM analysis.

RESULTS AND DISCUSSION

Laboratory Neutralization of ARD with NaOH

Laboratory simulation experiments of neutralization ARD were conducted with both field water and synthetic water. Field water was collected from Jonathan Run and the components are given in Table 1. The soluble Al concentrations

Table 1: Components of waters used in neutralization experiments and average monthly quality of ARD in Jonathan Run (mg/L).

	pH	Al	Ca	Mg	Mn	Zn	iron	K	Na	Si	Cl	SO ₄
Field water ¹	3.6±0.02	46.5±0.48	10.1±0.13	11.5±0.44	6.7±0.12	0.5±0.01	0.8±0.01	3.3±0.09	101.0±1.0	25.5±0.52	NM ³	413.7±3.0
Average of monthly ²	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	NM	NM	NM	NM	457.1±47.7
Synthetic ARD	3.5	50	10	12	7.4	NA ⁴	NA	NA	362 or 106	NA	807 or 282	180 or 889

1: Field water was collected from influent of flush boxes in Jonathan Run located Centre County, Pennsylvania in May 2008.

2: Average of monthly quality of flush boxes influent from November 2007 to July 2008.

3: Not measured

4: Not added

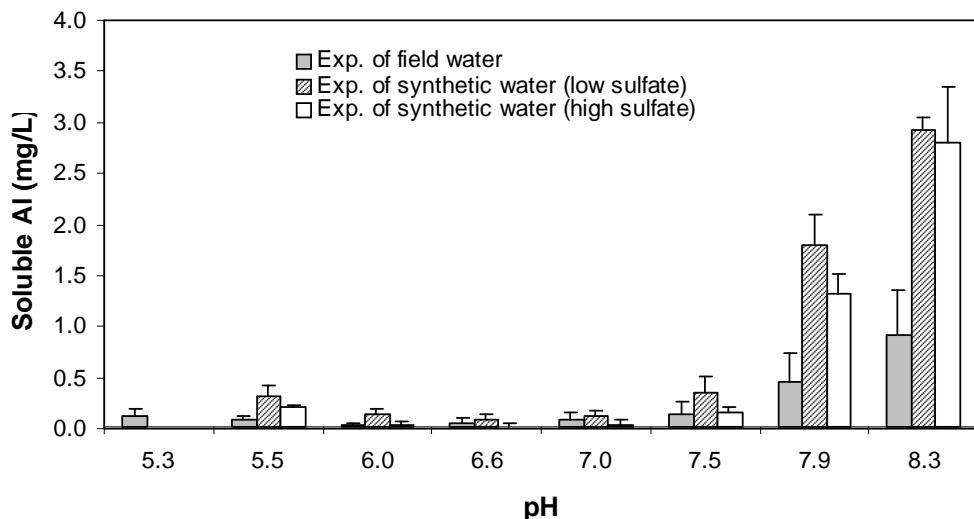


Fig. 1: Soluble Al concentrations at different pH values after 48 hours settling in the simulation experiments in laboratory.

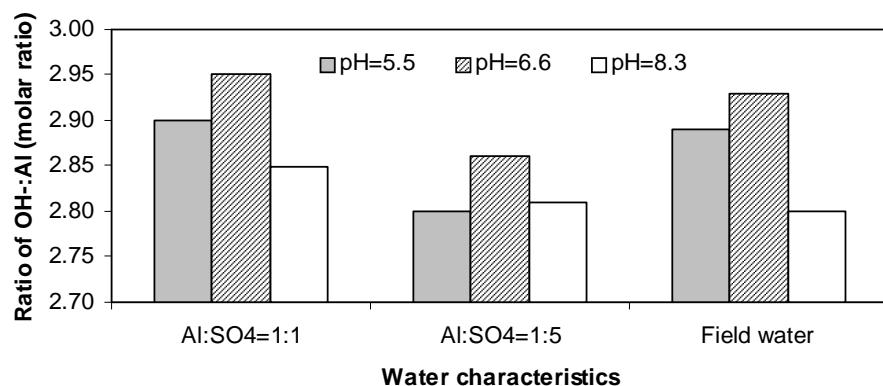


Fig. 2: Molar ratios of OH/Al of sludge at different pH values in laboratory experiments.

in the experiments changed with pH and settling time. The Al concentration rapidly decreased after addition of NaOH during the first hour and thereafter gradually approached “steady-state” conditions (data are not shown). The “final” soluble Al concentrations (48 hours settling) were from 0.03 to 0.91 mg/L with pH = 5.3 to 8.3 (Fig. 1). The lowest soluble Al concentration occurred at pH value among 6.0 to 7.0. When pH was higher than 7.0, the soluble Al concentration increased quickly with the increasing of pH.

In the experiments of synthetic water, the synthetic water contained different sulfate concentrations. In experiments with lower sulfate concentration (sulfate = 180 mg/L and Al:SO₄=1:1), soluble Al concentrations were from 0.09 to 2.92 mg/L (pH value from 5.6 to 8.3) (Fig. 1). In experiments with higher sulfate concentrations (sulfate = 889 mg/L and Al:SO₄=1:5), soluble Al concentrations were from 0.02 to 2.81 mg/L (Fig. 1). Similar to the experiments of field water, the lowest soluble Al concentrations occurred at pH from

6.0 to 6.6. However, compared with field water, soluble Al concentrations in the experiments of synthetic water were relatively higher at the higher pH values at pH above 7.5.

The Chemistry of Precipitates Formed in the Laboratory Experiments

SEM analysis was performed on the precipitates formed in experiments with different sulfate concentrations, along with the respective EDS. The samples were dried at 85°C for two hours to remove the adsorbed H₂O (Shah Singh & Brydon 1969). The chemical components of precipitates at pH values are presented in Table 2 (measured by EDS). It can be found that precipitates contained different elements, including Al, Mg, Ca, Si, O, C, and S, in different conditions.

The oxygen contents of precipitates included the oxygen combined with C (as CO₂), S (as SO₄²⁻), Si (as Si₂O₅²⁻), and as OH. In order to calculate the atomic ratio of Al/OH of samples, the corrected atomic OH⁻ percentage was calcu-

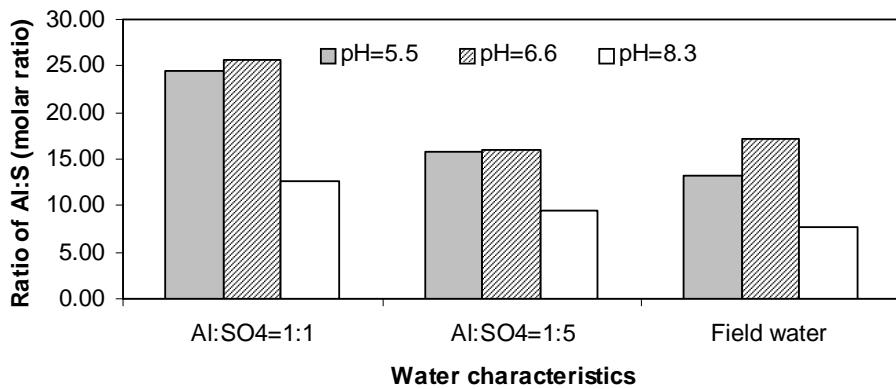


Fig. 3: Molar ratios of Al/S in sludge at different pH values in laboratory experiments.

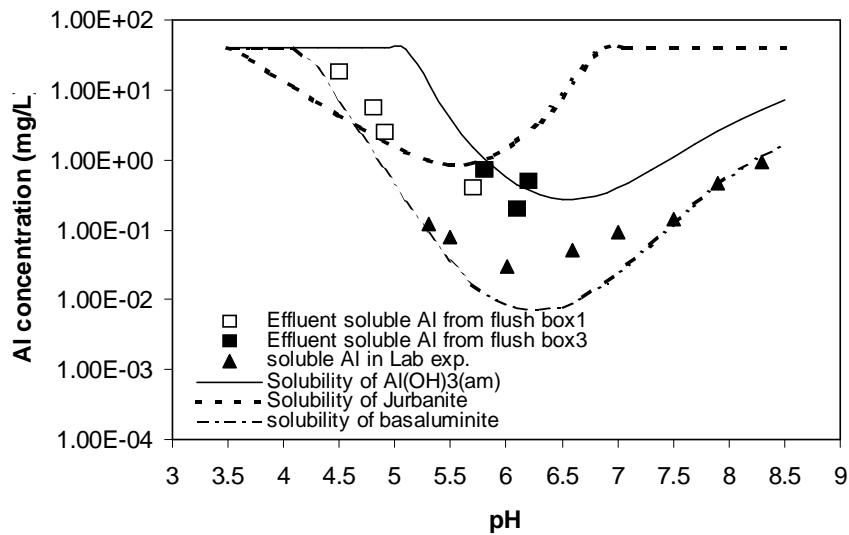


Fig. 4: Soluble Al concentrations of effluent from flush boxes located in Jonathan Run and in laboratory experiments. Theoretical curves of solubilities calculated using Mineql+ model; □ and ■: effluent soluble Al concentrations from flush boxes located in Jonathan Run (after Weaver et al. 2004); ▲: soluble Al concentration in laboratory experiments with field water.

lated by subtracting the oxygen that combines with C, S, and Si. In experiments of field water, the molar ratios of Al/OH of the sludge were 1:2.89, 1:2.93, and 1:2.80 at pH=5.5, 6.6, and 8.3, respectively (Fig. 2). The Al/OH ratio of precipitates in experiments of low sulfate concentration (Al:SO₄=1:1) were 1:2.90, 1:2.95, and 1:2.85 at pH=5.6, 6.6, and 8.3, respectively, and were 1:2.80, 1:2.86, and 1:2.81 in experiments of higher sulfate conditions (Al:SO₄=1:5), respectively (Fig. 2). It can be found that the ratio of OH:Al in sludge was the highest at neutral pH. This indicated that Al(OH)₃ likely produced at neutral pH compared with low and high pH conditions, since the ratio of OH:Al was 1:1 (jurbanite) and 2.5:1 (basaluminite).

Molar ratios of Al/S are shown in Fig. 3. At neutral pH (~6.6), Al/S ratio was 25.7, 16.0, and 17.2 in sludge formed

in laboratory experiments of low sulfate, high sulfate synthetic ARD, and field water, respectively. The Al/S ratio of sludge formed at neutral pH was higher than that at low (~5.5) and high pH (~8.3). The high Al/S ratio indicated the low proportion of Al-sulfate precipitates in sludge. At high pH condition (~8.3), Al/S ratios in sludge, were 12.7, 9.4, and 7.7 in sludge formed in experiments of low sulfate, high sulfate synthetic ARD, and field water, respectively, were the lowest compared with other pHs. The low Al/S ratio at high pH values revealed that more Al-sulfate formed at relatively high pH conditions.

Discussion and Modelling with Mineql+ Model

Simulation effluent soluble Al concentration from flush boxes and neutralization experiments in laboratory: In

Table 2: Composition of precipitates formed in the experiments (atomic percentage).

	Al:SO ₄ =1:1		Al:SO ₄ =1:5		Field water	
	pH= 5.6	pH= 6.6	pH= 5.5	pH= 6.6	pH= 8.4	pH= 8.3
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
C	5.0	1.1	6.8	2.1	4.3	0.6
O	73.5	2.4	72.8	3.5	73.4	3.2
Mg	ND	ND	0.6	0.7	0.2	0.2
Al	20.7	1.7	19.1	1.7	20.1	1.2
S	0.8	0.3	0.7	0.2	1.8	0.4
Ca	ND	ND	ND	ND	0.3	0.2
Mn	ND	ND	ND	ND	ND	ND
Al:SO ₄ =1:5						
	pH= 5.5	pH= 6.6	Ave.	Stdev.	Ave.	Stdev.
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
C	1.2	2.3	4.3	1.4	6.2	3.6
O	73.9	3.6	73.3	3.5	72.6	1.9
Mg	ND	ND	0.2	0.22	0.4	0.7
Al	23.5	1.8	20.8	1.6	18.6	2.1
S	1.5	0.4	1.4	0.3	2.0	0.6
Ca	ND	ND	0.1	0.1	0.3	0.5
Mn	ND	ND	ND	ND	ND	ND
Field water						
	pH= 5.5	pH= 6.6			pH= 8.3	
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
C	2.9	0.5	4.4	0.7	2.5	0.4
O	73.9	1.4	73.5	3.6	73.1	1.9
Mg	ND	ND	0.2	0.1	0.5	0.3
Al	19.9	0.2	18.9	0.7	19.2	1.0
S	1.5	1.0	1.1	0.7	2.5	0.8
Ca	ND	ND	0.07	0.1	0.4	0.3
Mn	ND	ND	ND	ND	ND	ND
Si	1.8	0.7	1.9	0.6	1.8	0.5
K	ND	ND	ND	ND	0.1	0.1

1 Al:OH: atomic ratio of Al:OH. In this atomic ratio, the OH atomic % was the total oxygen subtracted the oxygen that was combined with C (as CO₂), S (as SO₄²⁻), and Si (as Si₂O₅);

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

3 ND: not detected

4 Al:Si: the atomic ratio of Al:Si

2003, the monitor of the operation of flush boxes in Jonathan Run showed that the effluent soluble Al concentration was 0.4 to 18.1 mg/L and pH increased from 4.5 to 5.9 in Box 1. In Box 3, the effluent soluble Al concentration was 0.2 to 0.7 mg/L and pH was from 4.7 to 6.2 (Weaver et al. 2004). The components of influent of flush boxes were almost the same from 2003 and 2008 (Vazquez et al. 2011) and the Al concentration was around 48 mg/L. Therefore, it is reasonable to consider the influent components of flush boxes as the same as the components of field water collected in May 2008 which was used as the input data of Mineql+ model to simulate the neutralization processes in laboratory simulation experiments and flush boxes. Based on the components of field water, it contained silicate, sulfate, Al, Mg, Ca, Mn, and low concentration of iron and potassium (Table 1). There-

fore, the possible species of Al precipitates formed in the neutralization processes included: gibbsite (crystalline Al(OH)₃), amorphous Al(OH)₃, spinel (MgAl₂O₄), basaluminite (Al₄(OH)₁₀SO₄), jurbanite (AlOHSO₄), alunite (KAl₃(SO₄)₂(OH)₆), and kaolinite (Al₂Si₂O₅(OH)₄). Since Mg and potassium were not detected in sludge collected in flush boxes (Pu et al. 2010) and the sludge in laboratory experiments contained little (or was not detected) Mg and potassium (Table 2), spinel (MgAl₂O₄) and alunite (KAl₃(SO₄)₂(OH)₆) were not considered as the possible precipitates. Since XRD analysis revealed that no crystalline was formed in both flush boxes and laboratory experiments, gibbsite was not considered as the possible species of Al-precipitate also. Therefore, four species of Al-precipitates were considered as the possible Al-precipitates in

Mineql+ model simulation. They were, Al(OH)_3 (amorphous), basaluminitite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$), jurbanite (AlOHSO_4), and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

The molar ratio of Al:Si in acidic rock discharge was about 2:1 that was higher than the theoretical molar ratio of kaolinite (Al:Si=1:1). This indicated that other species of Al-precipitates, which might control the solubility of Al, were formed even if all silicate ions had been combined with Al ions to form kaolinite. The calculation with Mineql+ model showed that the presence of silicate in this study did not impact the solubility of other species of Al-precipitates if it was assumed that all silicate had been combined with Al to form kaolinite. Therefore, the primary species of Al-precipitates that controlled soluble Al concentrations in the experiments were basaluminitite, amorphous Al(OH)_3 and jurbanite.

In 2003, the effluent soluble Al concentration from flush boxes was from 0.4 to 18.1 mg/L at pH range from 4.5 to 5.9 from Box 1, and 0.2 to 0.7 mg/L at pH range from 4.7 to 6.2 from Box 3 (Weaver et al. 2004). The effluent soluble Al concentrations from flush boxes in Jonathan Run were less than the calculated solubility of amorphous Al(OH)_3 (with Mineql+model), and higher than the solubility of basaluminitite (Fig. 4). Comparison with the calculated results, the effluent soluble Al concentrations from flush boxes were higher than the solubility of jurbanite at pH <5.5 and lower at pH >5.5. These results indicated that some reactions of formation of Al-sulfate precipitates might be occurred in flush boxes, although the reactions were not at equilibrium.

In neutralization experiments of field water in laboratory, the pH varied from 5.3 to 8.3, and soluble Al concentrations from 0.03 mg/L to 0.91 mg/L after 48 hours settling down. Comparison with calculated solubilities of amorphous Al(OH)_3 , jurbanite, and basaluminitite, soluble Al concentration in experiments were always lower than the simulation solubilities of both amorphous Al(OH)_3 and jurbanite and higher than that of basaluminitite (Fig. 4). The possible reason was the formation of basaluminitite. In Fig. 4, it can be found that soluble Al concentration in laboratory experiment were usually lower than the effluent soluble Al concentration from flush boxes. Since, the effluent from flush boxes was "pulse" drainage, the detention time of part of the influent was not long enough for reaction. In laboratory experiments, the detention time was 48 hours and the solution was mixed completely at the beginning of experiments. Since, it is usually considered that jurbanite cannot be formed at high pH values (>5.5) (Nordstrom et al. 2006), the lower soluble Al concentrations could be due to the formation of basaluminitite. However, the fraction of element in

sludge of experiments indicated that basaluminitite was not the predominated species of precipitates. The proportion of sulphur/Al in sludge was 1/7.7 to 1/17.2 and the theoretical proportion is 1/4 (not considered hydrogen). The less of sulphur fraction in precipitates indicated that the sludge was also mixture of precipitates.

The EDS results indicated that the sludge in field water experiments contained silicon and the proportion of Al/Si was from 9.91 to 11.06. This result indicated that only part of silicate had combined with Al to form kaolinite, since the molar ratio of Al/Si was 2:1 in field water. The low sulphur and silicon contents in sludge indicated that most of sludge was amorphous Al(OH)_3 in field water experiments. The simulation solubility also implied that the liquid phase in experiment was not at equilibrium, although the experiments were in "steady-state".

Simulation the effect of sulfate on neutralization of Al-bearing ARD with NaOH: In experiments of synthetic ARD, sulfate concentration was 180 mg/L and 889 mg/L, which was one time and five times as Al molar concentration in water, respectively. The final soluble Al concentrations after 48 hours settling are shown in Fig. 1. Comparing soluble Al concentrations in the two experiments, it can be seen that the final soluble Al concentration in the experiments with high sulfate concentration were slightly lower than in the experiment with low sulfate concentrations. The XRD results showed that no crystalline was detected in sludge formed in these experiments (not shown). These results implied that gibbsite was not produced during the laboratory experiments.

Mineql+ model was also used to simulate the experiment of synthetic ARD. The input data were the composition of synthetic ARD. The synthetic ARD contained Al, Ca, Mn, Mg, Na, Cl, and SO_4 . The EDS analysis showed that sludge in synthetic ARD experiments contained Mg. Then the possible precipitates in modelling simulation were basaluminitite, jurbanite, amorphous Al hydroxide, and spinel (MgAl_2O_4). However, calculation showed that the solubility of spinel was higher than the initial Al concentration in these experiments. Therefore, the possible Al-precipitates were selected as basaluminitite, jurbanite, and amorphous Al(OH)_3 . In experiments of synthetic ARD, soluble Al concentrations were lower than the calculated solubility of amorphous Al(OH)_3 in both low and high sulfate concentration (Fig. 5). Since, synthetic ARD did not contain silicate, the low soluble Al concentrations in the experiments were due to the formation of Al-sulfate precipitates. This indicated that the presence of sulfate could decrease the soluble Al concentration. Kvech & Edwards (2002) reported the similar experimental results in drinking water at low pHs (<

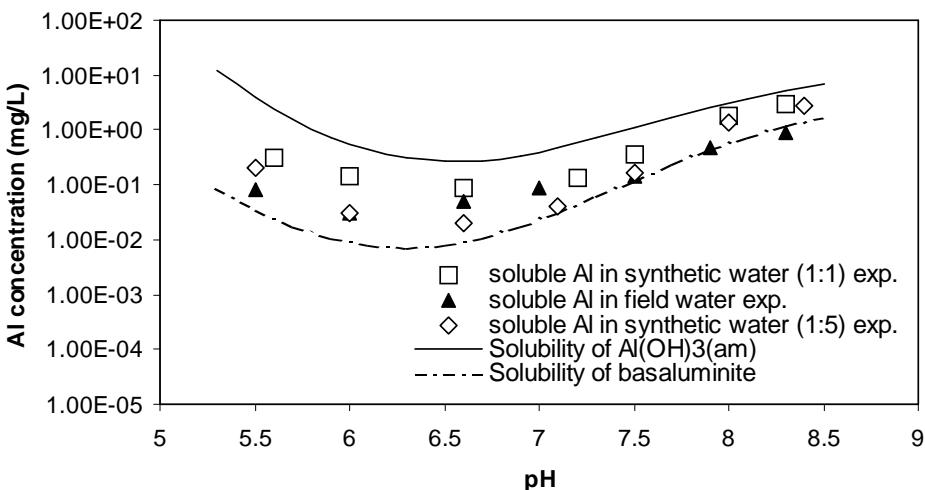


Fig. 5: Soluble Al concentrations in experiments of field water and synthetic ARD. □: soluble Al concentrations in experiments of low sulfate concentration ($\text{Al}:\text{SO}_4=1:1$); ▲: soluble Al concentrations in experiments of field water; ◇: soluble Al concentrations in experiments of high sulfate concentration ($\text{Al}:\text{SO}_4=1:5$).

6.0). Since, jurbanite is not formed at $\text{pH} > 5.5$ (Nordstrom et al. 2006), it is reasonable to assume that the soluble Al concentration lower than solubility of amorphous Al(OH)_3 was due to the formation of basaluminite. However, the soluble Al concentrations in the experiments were higher than the solubility of basaluminite. This indicated that the solution was not at equilibrium for basaluminite after 48 hours in the laboratory experiments.

Interestingly, in Fig. 5, it can be seen that the soluble Al concentrations in the experiments of high sulfate concentrations were lower than others at pH range from 6.0 to 7.0. However, at pH below 6.0 and above 7.5, the soluble Al concentrations were lowest in the experiments of field water. Since, the synthetic ARD of high sulfate concentration contained about 890 mg/L, which was about two times higher than field water (~420 mg/L). The decrease of soluble Al concentration in field water experiments was possible due to the effect of silica. Kvech & Edwards (2002) reported that the presence of silica could decrease the soluble Al concentration at pH above 9.5. This indicated that the presence of silica could decrease the soluble Al concentration also, even if the silica concentration was less than the Al concentration based on the stoichiometry of kaolinite.

At neutral pH value (~6.6), the EDS analysis showed that the Al/S ratio was 25.7, 16.0 and 17.2 in sludge formed in experiment of low sulfate, high sulfate synthetic ARD, and field water, respectively. The Al/S ratio of sludge at neutral pH values (~6.6) was higher than at low (~5.5) and high pH values (~8.3) (Fig. 3). The high Al/S ratio indicated the low proportion of Al-sulfate precipitates in sludge. These results showed that most of Al formed Al(OH)_3 at neutral pH

conditions during the neutralization. In Fig. 3, it can be seen that the Al/S ratios of sludge were the lowest at high pH (~8.3), the Al/S ratio was 12.7, 9.4, and 7.7 in sludge formed in experiments of low sulfate, high sulfate synthetic ARD, and field water, respectively. The lowest ratio of Al/S indicated that the highest proportion of Al-sulfate precipitates in sludge. The data of Al/S ratios in sludge formed at different pH values revealed that more Al-sulfate formed at high pH conditions (~8.3). Kim & 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.

Meanwhile, the Al/OH ratio of sludge at neural pH (~6.6) was the lowest in all experiments, which was 1/2.95, 1/2.86, and 1/2.93 in low sulfate, high sulfate and field water, respectively (Fig. 2). The theoretical molar ratio of Al/OH of Al(OH)_3 , jurbanite, and basaluminite was 1:3, 1:1, and 1:2.5, respectively. The Al/OH ratio closed to theoretical ratio of Al(OH)_3 indicated that the sludge formed at neutral pH contained more proportion of Al(OH)_3 than at low (~5.5) and high pHs (~8.3). In other words, more Al in ARD was removed by the formation of amorphous Al(OH)_3 at neutral pH (~6.6) compared with at high pH (~8.3).

CONCLUSIONS

The soluble Al concentration was lower than the solubility of amorphous Al(OH)_3 in both low ($\text{pH} < 5.5$) and high pH conditions ($\text{pH} > 7.5$) in both laboratory experiments and flush boxes, which was the field passive treatment systems located in Jonathan Run in center county, Pennsylvania. The sludge analysis showed that the Al-sulfate precipitates were

formed in neutralization of Al-bearing ARD. The simulation with Mineql+ model indicated that soluble Al concentration lower than solubility of amorphous Al(OH)_3 was due to the formation of Al-sulfate precipitates. The data of soluble Al concentrations under different sulfate concentration showed that the presence of sulfate in ARD impacted the soluble Al concentration in neutralization of Al-bearing ARD.

The laboratory experiments of synthetic ARD showed that basaluminite was formed in neutralization of ARD. The formation of basaluminite caused the decrease of the soluble Al concentration and became less than the solubility of amorphous Al(OH)_3 . However, the soluble Al concentration was higher than the solubility of basaluminite. This indicated that the solution was not at equilibrium for basaluminite in laboratory experiments after 48 hours settling. Furthermore, the presence of silica could also decrease the soluble Al concentration, although the silica concentration was less than the soluble Al concentration in stoichiometry of kaolinite.

The sludge analysis showed that most of Al was removed by the formation of Al(OH)_3 precipitates at neutral pH, whereas, the proportion of basaluminite in sludge increased at relative high pH (~8.3).

ACKNOWLEDGEMENT

National Key R & D Program of China (Grant No. 2016YFC0401710).

REFERENCES

- Adams, F. and Rawajfih, Z. 1977. Basaluminite and alunite: a possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Am. J.*, 4: 686-692.
- 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*, Mineralogical Society of America, Washington, DC, 40: 351-403.
- 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.
- Cravotta, C.A. 2006. Relations among pH, sulfate, and metals concentrations in anthracite and bituminous coal-mine discharges, Pennsylvania. International Conference of Acid Rock Drainage, St. Louis, MO.
- 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.
- Dubikova, M., Cambier, P., Šucha, V. and Ěaplovičová, M. 2002. Experimental soil acidification. *Applied Geochemistry*, 17: 245-257.
- Evangelou, V.P. and Zhang, Y.L. 1995. A review: pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Reviews in Environmental Science and Technology*, 25(2): 141-199.
- Galan, E., Carretero M.I. and Fernandez-Caliani, J.C. 1999. Effects of acid mine drainage on clay minerals suspended in the Tinto River (Rio Tinto, Spain): an experimental approach. *Clay Minerals*, 34: 99-108.
- Gray, N.F. 1998. Acid mine drainage composition and the implications for its impact on Lotic Systems. *Water Research*, 32(7): 2122-34.
- Hach Company 2003. Water Analysis Hand Book, 4th Ed., Hach Company, Loveland, CO.
- Hedin Environmental 2003. Assessment of pollution sources to the headwaters of Jonathan Run and recommended remediation actions. Prepared for the Beech Creek Watershed Association.
- Hedin Environmental 2008. Optimizing the design and operation of self-flushing limestone systems for mine drainage treatment. Final Report for Western Pennsylvania Coalition for Abandoned Mine Reclamation, Dec. 2008.
- 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. *Environ. Sci. and Tech.* 37(10): 2120-2126.
- Koryak, M., Shapiro, M.A. and Sykora J.L. 1972. Riffle zoobenthos in stream receiving acid mine drainage, *Water Res.*, 6: 1239-1247.
- Kvech, Steve and Edwards, Marc 2002. Solubility controls on aluminum in drink water at relative low and high pH. *Water Research*, 36: 4356-4368.
- 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*, 17(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.
- Neufeld, R.D., Gray, T., Monnell, J. and Smoke, J. 2007. Jonathan Run Acid Rock Discharge Mitigation Strategies, FHWA-PA-2007-010-04011 March, 2007 (available from NTIS as PB2007-107284) 134 pages.
- Nordstrom, D.K. and Alpers, C.N. 1999. Geochemistry of acid mine waters. In: Plumlee, G.S., and Logsdon, M.J., eds., *The Environmental Geochemistry of Mineral Deposits-Part A. Processes, Methods, and Health Issues: Reviews in Economic Geology*, 6A: 1333-60.
- 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. Sci. and Tech.*, 34: 254-258.
- Nordstrom, D.K. and Ball, J.W. 1986. The geochemical behavior of aluminum in acidified surface waters. *Science*, 232: 54-56.
- Nordstrom, D.K., Ball, J.W. and 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.
- 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.

- 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.
- 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.
- 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.
- Watzlaf, K., Schroeder, R., Kleinmann, C., Kairies and R. Nairn, 2004. The passive treatment of coal mine drainage. National Energy Technology Laboratory, US Department of Energy (2004), Information circular.
- 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.
- 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.
- Van Breemen, N. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. *Soil Sci. Soc. Am. Proc.*, 37: 694-697.
- Vazquez, O., Monnell, J.D., Pu, X. and Neufeld, R.D. 2011. Major processes dominating the release of aluminum from smectite clays when leached with acid mine drainage. *Environmental Engineering Science*, 28(3): 163-169.