Release of Aluminum from Clays in an Acid Rock Drainage Environment

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Abstract Aluminum concentrations in low pH acid rock drainage (ARD) commonly exceed the freshwater aquatic toxicity threshold. An Al-containing ARD released from pyritic sandstone and shale fill along US. Interstate 80 in Center County, Pennsylvania has adversely impacted a former fishing stream. This ARD consistently contains low concentrations (<2 mg/L) of Fe and high concentrations (≈ 48 mg/L) of Al. Batch experiments conducted with kaolinite and H/Al-bentonite clays and clay soils collected from the Centre County, PA area suggests that synthetic brackish ARD enhances the release of Al from these clays, compared to synthetic acid (sulfuric) only and non-brackish ARD. This implies that highway deicing salts in road runoff could aggravate the leaching of Al from pyritic rocks used as fill or exposed in road cuts. Likewise, the use of ARD to enhance the production of natural gas from tight shales could result in the leaching of Al. Quantification of levels of Al released from field clays could be critical when considering remediation strategies.

Keywords Acid rock drainage · Aluminum · Clay · Exchange reactions · Mine drainage

Introduction

Aluminum concentrations in low-pH acid rock drainage (ARD) commonly exceed the freshwater aquatic toxicity threshold of 0.087 mg/L (US Environmental Protection Agency 2002). Data reported for over 150 different mine drainage samples across USA showed that over 30% of these locations have dissolved Al concentrations no lower than 50 mg/L (Watzlaf et al. 2004). Data reported for 140 abandoned coal mines in Pennsylvania shows that over 50% of these locations present median dissolved Al concentrations over 1 mg/L. The highest concentrations of Al (between 1 and 108 mg/L) were found in the acidic range of pH 2.7–5 (Cravotta 2008a, b).

Aluminum, the third most abundant rock-forming element of the Earth's crust, is commonly present in clays and other aluminosilicate minerals (Drever 1997). Aluminum in ARD results from the dissolution of aluminosilicate minerals at low pH. Typical clay minerals found in USA soils include kaolinite [$Al_2Si_2O_5(OH)_4$], (Sidenko and Sherriff 2005; Smoke 2007) and smectite, $M_x[Mg_{0.66}Al_{3.34}]^{VI}[Si_8]^{I-V}O_{20}(OH)_4$ ($H2O$)$_n$, where $x = 0.33$ when M represents exchangeable divalent cations (generally Ca) or $x = 0.66$ when M represents monovalent cations (generally Na or K) (Astudillo 2004; Metz et al. 2005). Kaolinite, which is a major component of shale and claystone, occurs in enormous quantities in the sedimentary sequences that host coal deposits (Shaw 1928). Galan et al. (1999) showed that kaolinite is a possible reaction product of the dissolution of unstable smectite under acidic conditions. Mining areas in the USA frequently generate ARD with high Al concentrations due to the abundance of kaolinite, smectite, and other Al-bearing minerals in these areas. The literature abounds with studies on the release of Al from these and other clays within a broad range of pH values from 1 to 11 (Sondi et al. 2008; Walther 1996). These studies generally focus on processes such as proton-promoted dissolution of clays and exchange reaction involving clays in saline environments. Their research has shown that pH is a chief factor in the release of Al from clays. It has also been reported that interactions of acidic red mud and seawater may release Al at

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concentrations over 50 mg/L, concomitant with a decrease of cation concentrations in seawater, at pH values around 4 (Kombo et al. 2003). The presence of anions, such as SO_4^{2-}, in the soil solution, may also increase the concentrations of Al, due to aqueous complexation reactions between Al and these anions (Cravotta 2008b; Pu et al. 2010). However, the effect of cations such as Fe^{2+}, Na^+, and K^+ in ARD on the release of Al from clays has been barely addressed. It was hypothesized that the elevated concentrations of SO_4^{2-} and cations such as Fe^{2+}, Na^+, and K^+, in many ARD environments could significantly affect the release of Al from clays.

Problem

A significant ARD discharge exists in Centre County, Pennsylvania, where rock cuts were used to construct an embankment along US Interstate 80 directly over a local stream (Smoke 2007; Waddell et al. 1980). The stream was redirected to flow through a concrete culvert under this embankment. Exploratory drilling through the highway embankment and areas around it showed the presence of pyritic sandstone and clay material. Secondary aluminum precipitates $(Al(OH)_3)$, which are formed by neutralization of the ARD, are present at the exit and downstream of the concrete culvert. Groundwater samples collected from the boreholes throughout the embankment and near the culvert show the presence of groundwater Al and Fe concentrations as high as 160 and 173 mg/L, respectively (GAI Consultants 2007; Hedin Environmental 2003; Neufeld et al. 2007). These data confirm this area as the main source of Al-containing ARD discharging into the local stream (Smoke 2007).

The monthly Al and Fe concentrations in the surface water seepage from the highway embankment, prior to the discharge into the stream, from November 2007 to July 2008, are shown in Fig. 1. While borehole waters contained high Al and Fe concentrations (160 and 173 mg/L, respectively), surface seep waters discharged from the affected site consistently had elevated Al ($\approx$ 48 mg/L), but low Fe concentrations (1 mg/L) (Table 1).

The highway embankment is raised 18–24 m off the valley floor and presents numerous soft spots or voids of 0.3 m or less through its depth. This provides an opportunity for infiltrating rainfall and oxygen to interact with exposed pyrite, resulting in the oxidation reaction:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$
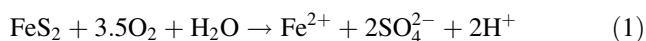
Ferrous iron may be further oxidized, as follows (Letcher 2007):

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (pH < 3) \qquad (2)$$
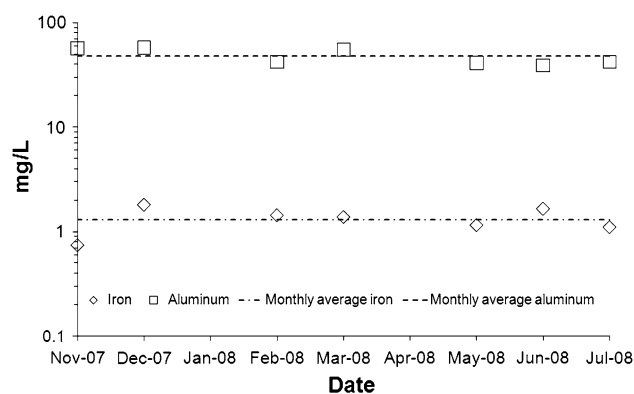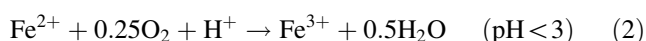

Fig. 1 Monthly total aluminum and iron concentrations in ARD surface water samples collected from November 2007 to July 2008 in a Centre County site, PA affected by ARD. Monthly averaged Al for this period = 47.7 mg/L; Monthly averaged Fe for this period = 1.3 mg/L

Table 1 Measured monthly averaged dissolved components of the ARD discharging into the local stream in Centre County, PA, November 2007 to July 2008; concentrations in mg/L

pH	Total Al	Total Fe	Mg	Mn	Ca	Zn	SO₄
3.3	47.7	1.3	11.8	7.2	9.6	0.66	460

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_{3(S)} + 2H^+$$
$$(pH > 3) \qquad (3)$$
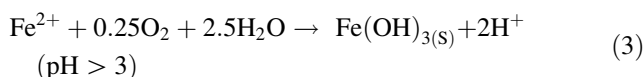
The protons (H^+) generated by these oxidation and hydrolysis reactions can react with aluminosilicate minerals, releasing Al to the solution, as follows:

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightarrow 2Al^{3+} + 2SiO_2 + 5H_2O \qquad (4)$$
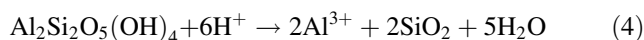
Ocherous precipitates observed upstream of the concrete culvert suggest that ferrous iron contained in the underground ARD is quickly oxidized and precipitated in the stream channel. The expected ferrous iron concentrations in this underground Centre County ARD can be estimated based on the pyrite oxidation reaction shown in Eq. 1 coupled with measured sulfate concentrations. Given the average sulfate concentration of 460 mg/L, the corresponding concentration of iron based on the stoichiometry of Eq. 1 would be 134 mg/L, which is 100 times greater than the observed concentration of 1.3 mg/L (Table 1). It therefore follows that iron is being retained within the sandstone embankment.

Objective

The objective of this study was to investigate the leaching of aged acid clays with ARD typically found in the Pennsylvanian and Appalachian region. A secondary

objective was to develop information supporting the phenomena of the release of elevated Al from such interactions. Our study focused on the release of Al from kaolinite, H/Al-bentonite, and clay soil collected from the ARD-affected site in Centre County, PA. H/Al-bentonite species are part of the main group of smectite clays and are frequently found with kaolinite in most ARD-affected clay soils. Aged acid kaolinite and H/Al-bentonite better approach conditions found in most ARD-affected clay soils where the H/Al composition of the adsorption complex is typically above 20% of its cation exchange capacity (CEC) and where Al is the dominant species on the exchange phase of these clays (Bolt and Bruggenwert 1976; Coleman and Craig 1961; Essington 2004).

To accomplish these objectives, exchange reactions between ferrous iron and exchangeable Al on the surfaces of clays were considered as a possible explanation for the observed low iron concentrations in some ARDs. The influence of brackish ARD groundwater with Na and K salts on the observed release of Al from these clays was investigated as well. The results of this study built on existing field data from the Centre County, PA ARD seepage.

Methods and Materials

To accomplish the objectives of this study, the following aged acid clays were used: acid-washed kaolinite, prepared H/Al-bentonite (smectite group), and clay soil collected downstream of the main source of ARD in this Centre County ARD-affected area.

Preparation of H/Al-bentonite

An acid-bentonite slurry suspension was prepared from Na-bentonite supplied by Fisher Scientific (Pittsburgh, PA) by adding 60 g of this clay to 1 L of 0.05 N HCl. During the stirring of this suspension, an additional 4 mL of 12.1 N HCl was added to stabilize the pH over time. After the pH became stable, the suspension was concentrated by heating it. The concentrated suspension was cooled at room temperature, 25°C, transferred to centrifuged tubes and centrifuged at 8,500 G for 15 min in a Fisher Scientific AccuSpin Model 400 Benchtop Centrifuge. After centrifugation, supernates were collected and pH, Na, and total Al were determined by flame atomic absorption spectrometry (AAS). Then, 30 mL of 0.05 N HCl were added to the remainder of the clay in the 50 mL centrifuge tubes and the mixture was shaken for 1 min to keep the clay in suspension. After that, the tubes were centrifuged a second time and the pH, Na, and total Al were measured again. The procedure was repeated until the Na concentration in the supernatant was below 5 ppm. After that, the same procedure was repeated 3 more times with distilled water to minimize excess Na and Al in the pore water.

Batch Experiments

Batch experiments were conducted at gram/gram (wt/wt) clay to stock solution ratios of 4:40 (10% wt/wt) and at room temperature, 25°C. The predetermined amounts of clay were mixed with calibrated volumes of 3 different synthetic stock solutions: sulfuric acid solutions (labeled 'sulfuric acid'), a leaching solution simulating underground ARD (labeled 'ARD 1'), and a third leaching solution simulating underground and brackish ARD (labeled 'ARD 2'), as shown in Table 2. The chemicals used in the preparation of these synthetic stock solutions were reagent grade and are shown in Table 2. The leaching solution labeled sulfuric acid was prepared adding 2.7 mL of 0.36 N H_2SO_4 to 2 L of deionized water. A predetermined volume (1 L) of this solution was transferred to a different glass beaker, where 2.5 g of $FeSO_4 \cdot 7H_2O$ were added to prepare the ARD 1 leaching solution. Finally, a predetermined volume of ARD 1 (500 mL) was transferred to a third glass beaker, where 0.48 g of KCl and 1.3 g of NaCl were added to prepare ARD 2.

Acid-washed kaolinite, $(Al_2Si_2O_5(OH)_4)$, provided by Fisher Scientific, was used in powdered form. Prepared

Table 2 Synthetic stock solution compositions (as prepared) to conduct the batch experiments with clays at predetermined gram/gram (wt/wt) ratios of 4:40; all concentrations in mg/L

Stock solutions	Chemical reagents used	pH	Total Al[d]	Fe^{2+}	K$^+$	Na$^+$
Sulfuric acid	H_2SO_4	2.6–2.7	<1[a]	<2[b]	<2[b]	<5[c]
ARD 1	H_2SO_4, $FeSO_4 \cdot 7H_2O$	3.1–3.2	<1[a]	506–673	<2[b]	<5[c]
ARD 2	H_2SO_4, $FeSO_4 \cdot 7H_2O$, NaCl, KCl	3.3–3.4	<1[a]	518–621	511–568	821–992

[a] Below practical quantitation limit (PQL) of 1 ppm

[b] Below PQL of 2 ppm

[c] Below PQL of 5 ppm

[d] Determination of aluminum with non-digested samples

H/Al-bentonite and clay soil from Centre County were dried overnight at 105°C, gently ground, and sieved using a #20 mesh, before being used in the batch experiments. The reactors in these experiments, 50 mL centrifugation tubes, were continuously shaken to maintain the solid phase in suspension. All batch experiments were carried out in duplicate.

Samples were collected after 67 h of reaction time. Preliminary data (not shown) suggested that an asymptotic approach to true equilibrium was not achieved, even after 6 months of reaction time; however, reaction times over 60 h were considered sufficiently close to the apparent equilibrium point for purposes of quantifying the release of Al from these clays after interaction with the different leaching stock solutions shown in Table 2.

After 67 h of reaction, the clay suspensions were centrifuged at 8,500 G for 15 min in a Fisher Scientific AccuSpin Model 400 Benchtop Centrifuge to separate the clays from the aqueous portion. The pH was measured after centrifugation using a previously calibrated Fisher Accumet 25 benchtop electrode pH meter equipped with a Fisher Scientific Accumet pH electrode. Subsequently, the supernatants were filtered through 0.45 μm HA Isopore™ membrane filters supplied by Millipore. Filtered extracts were stored at 4°C for further analysis. Prior to heavy metal analysis, the filtered extracts were digested with concentrated HNO_3 and HCl in a CEM-MARS microwave digester. The concentrations of total Al, Fe, K, and Na were determined by AAS (APHA 2005). Analysis for Al used filtered non-digested samples to prevent the dilution of samples during the digestion procedure and to enhance the detectability of this cation. In preliminary experiments, determination of Al concentrations from both microwave digested and non-digested filtered extracts were equivalent, so microwave digestion for Al in the leachate samples was discontinued. Samples of each leachate were analyzed in triplicate. This resulted in six samples being analyzed for each experimental condition: duplicated experiments each generated leachate samples measured in triplicate. Resultant analyses were averaged.

Preliminary determination of ferrous iron concentrations on stock solutions show that over 98% of the initial iron remained in the ferrous form after more than 67 h. This was expected since the pH of the stock solutions was in the range of 3.1–3.4. The colorless 67 h supernatants observed after centrifugation implied an absence of $Fe(OH)_3$, which is consistent with these results. Consequently, Fe^{3+} can be considered a minor component in the total iron concentrations (Fe^{2+} and Fe^{3+} species) determined by AAS.

Results and Discussion

The experimental data obtained for kaolinite, H/Al-bentonite, and clay soil from Centre County, PA, at a wt/wt soil to solution ratio of 4:40 (10% wt/wt), are summarized in Table 3. The decrease of Na after 67 h of leaching remained below 5% of the initial concentrations of Na in brackish ARD (ARD 2) (Table 3), suggesting negligible Na sorption onto kaolinite and clay soil from Centre County, PA. Figure 2 and Table 4, respectively, show the release of Al and cation sorption per unit mass of each of these clays.

The data indicate that brackish waters in an ARD environment (ARD 2) enhance the release of Al from these clays, compared to acidic (sulfuric acid) or non-brackish ARD environments (ARD 1). This implies that highway deicing salts in road runoff could exacerbate the leaching of aluminum by ARD. The combination of saline subterranean ARD with clays would introduce elevated amounts of Al into surface seepage water. Other research at the University of Pittsburgh suggests that if not abated or accommodated during earth-moving activities, this Al release can continue for more than 40 years (Smoke 2007).

Sorption/Exchange of Cations

From Fig. 2 and Table 4, it can be seen that release of Al and sorption of cations on these clays, expressed as μeq/g of clay, are higher for H/Al-bentonite than for kaolinite clays. These results are consistent with the reported higher chemical degradation of H/Al-bentonites (smectite group), relative to other clays, under acidic conditions (Galan et al. 1999) and the higher cation exchange capacity of the H/Al-bentonites (smectite group) compared to the kaolinites (Angove et al. 1997; Chukwudi 2008; Giese and van Oss 2002).

Sorption of ferrous cations per gram of selected clays varied from around 8% (kaolinite) to a maximum of 63% (H/Al-bentonite) of the initial ferrous iron in the synthetic ARD solutions, as inferred from Table 4. Sorption of potassium cations per gram of selected clays varied from 4% (kaolinite) to 26% (H/Al-bentonite) of the initial K in the brackish ARD 2. Sorption of sodium cations per gram of selected clays varied from near 0% (kaolinite and field-collected clay soil) to 12% (H/Al-bentonite) of the initial Na in ARD 2. It therefore appears that this cation did not influence the release of Al from kaolinite. On the other hand, sorption of ferrous and K cations in addition to the Na present on the H/Al-bentonite suggests that all of these cations can enhance the release of Al from H/Al-bentonite. Cation sorption on clay soil from Centre County, PA was between that for kaolinite clays (Na sorption was negligible) and H/Al-bentonite, as shown in Table 4.

Aluminum released per gram of Centre County clay soil, 17.9 μeq/g, was within the range of Al released from kaolinite and H/Al-bentonite clays, 2.6 and 29.4 μeq/g, respectively, when these clays were leached with synthetic

Table 3 Results from batch experiments when kaolinite and clay soil from Centre County, PA and H/Al-bentonite were leached with synthetic sulfuric acid, ARD 1, and ARD 2 leaching solutions for about 67 h; experiments were conducted at wt/wt solution ratios of 4:40 (10% wt/wt); all concentrations in mg/L

Kaolinite		pH ± stdev[e]	Total Al ± stdev[d,e]	Fe^{2+} ± stdev[e]	K$^+$ ± stdev[e]	Na$^+$ ± stdev[e]
Sulfuric acid	Initial conc.	2.7 ± 0.0	<1[a]	<2[b]	<2[b]	<5[c]
	Final conc.	3.3 ± 0.1	<1[a]	<2[b]	5.0 ± 0.5	5.5 ± 1.3
ARD 1	Initial conc.	3.2 ± 0.0	<1[a]	673 ± 0	<2[b]	<5[c]
	Final conc.	3.4 ± 0.0	2.3 ± 0.1	620 ± 2	6.8 ± 0.1	5.7 ± 0.3
ARD 2	Initial conc.	3.4 ± 0.0	<1[a]	621 ± 14	529 ± 5	992 ± 25
	Final conc.	3.7 ± 0.0	3.2 ± 0.1	596 ± 0	507 ± 7	978 ± 4
Clay soil						
Sulfuric acid	Initial conc.	2.7 ± 0.1	<1[a]	<2[b]	<2[b]	<0.2[f]
	Final conc.	3.1 ± 0.1	2.9 ± 0.1	<2[b]	<2[b]	1±0.3
ARD 1	Initial conc.	3.2 ± 0.1	<1[a]	547±1.4	<2[b]	<0.2[f]
	Final conc.	3.4 ± 0.1	16.1 ± 0.5	464 ± 2.8	<2[b]	<1[a]
ARD 2	Initial conc.	3.3 ± 0.1	<1[a]	518 ± 8.5	511 ± 9.9	949 ± 4.2
	Final conc.	3.6 ± 0.1	20.2 ± 0.7	458 ± 2.8	486 ± 14.1	921 ± 4.2
H/Al-bentonite						
Sulfuric acid	Initial conc.	2.6 ± 0.0	<1[a]	<2[b]	<2[b]	<1[a]
	Final conc.	2.5 ± 0.0	<1[a]	<2[b]	4.8 ± 1.4	6.2 ± 0.3
ARD 1	Initial conc.	3.1 ± 0.0	<1[a]	506 ± 19	<2[b]	<1[a]
	Final conc.	2.5 ± 0.0	26.5 ± 1.0	186 ± 0.0	4.0 ± 0.3	7.6 ± 0.0
ARD 2	Initial conc.	3.3 ± 0.0	<1[a]	540 ± 14	568 ± 2.8	821 ± 12.7
	Final conc.	2.5 ± 0.0	48.1 ± 1.3	252 ± 6	421 ± 18	721 ± 1.4

[a] Below practical quantitation limit (PQL) of 1 ppm

[b] Below PQL of 2 ppm

[c] Below PQL of 5 ppm

[d] Determination of aluminum with non digested samples

[e] Stdev = standard deviation

[f] Below PQL of 0.2 ppm
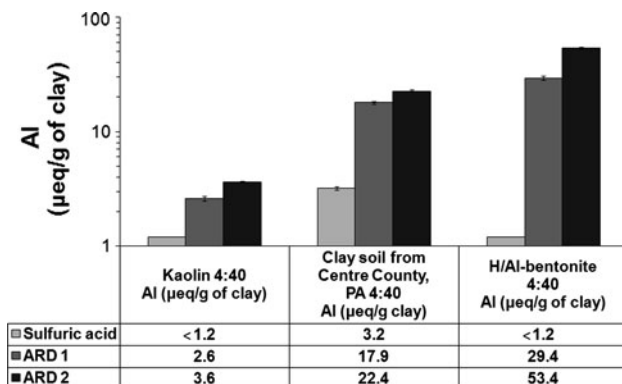
Fig. 2 Total aluminum leached, expressed as μeq/g of clay, from kaolin, clay soil from Centre County, PA and H/Al-bentonite and after 67 h of reaction time with synthetic leaching solutions. Experiments conducted at wt/wt soil to solution ratio of 4:40. Initial concentrations of synthetic leaching solutions in reactors: sulfuric acid: pH = 2.6−2.7; ARD 1: Fe^{2+} = (506−673) mg/L, and pH = 3.1−3.2; ARD 2: Fe^{2+} = (518−621) mg/L, K$^+$ = (511−568) mg/L, Na$^+$ = (821−992) mg/L, and pH = 3.3−3.4

non-brackish ARD 1 (Fig. 2). Similarly, when the clays were leached with the brackish ARD 2 (Fig. 2), the Al released per gram of Centre County clay soil, 22.4 μeq/g, was within the range of Al released from kaolinite and H/Al-bentonite clays, 3.6 and 53.4 μeq/g.

An exception was the Al released from the H/Al-bentonite into the relatively pure sulfuric acid leaching solution. When leached with this solution, the release of Al from the Centre County clay soil was higher than that from the H/Al-bentonite. We believe this is an artifact of the dissolved Al present in the pore water that was collected along with the Centre County clay soil sample. Thus, we believe that the measured Al in this case does not entirely represent Al released from the clay soil.

Summary

Aluminum released per gram of H/Al-bentonite to synthetic brackish ARD waters containing Na and K salts was

Table 4 Cation sorption onto kaolinite, clay soil from Centre County, PA and H/Al-bentonite, in μeq/g, after 67 h of reaction time with synthetic sulfuric acid, ARD 1, and ARD 2 leaching solutions

Kaolinite	Sorbed H^+	Sorbed Fe^{2+}	Sorbed K^+	Sorbed Na^+	Overall cation sorption $(H^+ + Fe^{2+} + K^+ + Na^+)$	Released Al
Sulfuric acid	14.9	N.D.	N.D.	N.D.	14.9	<1.2
ARD 1	2.3	19	N.D.	N.D.	21.3	2.6
ARD 2	2.0	N.D.	5.6	N.D.	7.6	3.6
Clay soil						
Sulfuric acid	12.0	N.D.	N.D.	N.D.	12.0	3.2
ARD 1	2.3	29.7	N.D.	N.D.	32	17.9
ARD 2	2.5	21.5	6.4	N.D.	30.4	22.4
H/Al-bentonite						
Sulfuric acid	N.D.	N.D.	N.D.	N.D.	N.D.	<1.2
ARD 1	N.D.	115	N.D.	N.D.	115	29.4
ARD 2	N.D.	103	37.6	43.5	184.1	53.4

Experiments conducted at wt/wt soil to solution ratio of 4:40. Initial characteristics of synthetic solutions in reactors: sulfuric acid: pH = 2.6−2.7; ARD 1: Fe^{2+} = 506−673 mg/L and pH = 3.1−3.2; ARD 2: Fe^{2+} = 518−621 mg/L, K^+ = 511−568 mg/L, Na^+ = 821−992 mg/L and pH = 3.2−3.4

N.D: not detected or negligible (cation concentration decrease was within 5% of the initial cation concentration in the leaching solution (ARD 1 or ARD 2)

no less than 48 times higher than Al released to sulfuric acid leaching solutions and was about 1.8 times higher than Al released to synthetic non-brackish ARD with similar ferrous concentrations (about 500 ppm).

The release of Al per gram of clay was around 14.8 times higher for H/Al-bentonites than for kaolinites when both clays were leached with the same leaching solutions, simulating brackish and underground ARD, with initial high concentrations of Fe^{2+}, K, and Na. The corresponding overall cation sorption per gram of clay was about 24 times higher for H/Al-bentonites than for kaolinites.

Sorption of ferrous cations per gram of kaolinite, H/Al-bentonite, and field-collected clay soil varied from 8% (kaolinite) to a maximum of 63% (H/Al-bentonite) of the initial ferrous iron in synthetic ARD.

Sorption of K cations per gram of kaolinite, H/Al-bentonite, and field-collected clay soil varied from 4% (kaolinite) to 26% (H/Al-bentonite) of the initial K in synthetic brackish ARD.

Sorption of Na cations per gram of kaolinite, H/Al-bentonite, and field-collected clay soil varied from 0% (kaolinite and field-collected clay soil) to 12% (H/Al-bentonite) of the initial Na in synthetic brackish ARD. The fact that sorption of Na into kaolinite and clay soil from Centre County, PA was negligible under the experimental conditions indicates that Na does not influence the release of Al from kaolinite or clay soil from Centre County, PA.

Aluminum released per gram of Centre County clay soil, 17.9 μeq/g, was within the range of Al released from kaolinite and H/Al-bentonite clays, 2.6–29.4 μeq/g, when these clays were leached with the same synthetic non-brackish ARD. Similarly, when the leaching solution was synthetic brackish ARD, the Al released per gram of Centre County clay soil, 22.4 μeq/g, was within the range of Al released from kaolinite and H/Al-bentonite clays, 3.6–53.4 μeq/g.

Conclusions

Kaolinite and smectite clays are important families of clays that are often associated with the presence of acidic-sulfide containing minerals and mining areas. Field Al-bearing clay soils, such as those existing in the Centre County ARD site, are frequently mixtures of these clays, along with other weathered minerals. Experimental and field observations show that Al release from kaolinite and H/Al-bentonite (smectite group) clays is enhanced by potassium salts (KCl) in ARD. Sodium salts (NaCl) in ARD enhanced the release of Al from H/Al-bentonite clays but had a negligible effect on the release of Al from kaolinite. Overall, it is likely that the extent of iron retention within this Centre County subsurface environment is controlled by the overall cation exchange capacity of the clay mineralogy in this pyritic sandstone and shale fill.

This work offers preliminary insight into some other issues of possible significance. The observation of greater concentrations of Al in leachate produced by brackish ARD implies that highway deicing salts in road runoff could aggravate the leaching of Al from pyritic rocks used as fill or exposed in road cuts. Likewise, it has been proposed that ARD could be used as a source of 'fracing' fluid

to enhance the production of natural gas from tight shales, but our research indicates that this could result in the leaching of Al. Additional investigations to document such potential interactions are warranted.

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