

Passive Treatment of Aluminum-Bearing Acid Rock Drainage ⁽¹⁾

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Abstract: When acid rock drainage attacks clay-bearing formations at hard rock mining sites, significant amounts of dissolved aluminum can be created. The geochemistry of aluminum is complex and this can cause problems in passive treatment systems. The formation of the mineral gibbsite $[\text{Al}(\text{OH})_3]$ is especially problematic as it is a gelatinous solid. Gibbsite tends to form in limestone-dominated passive treatment cells and the sludge tends to plug the void spaces between the limestone rock, becoming a major maintenance problem. While the precise mechanisms have not been completely identified, the precipitation of gibbsite is avoided in sulfate reducing bacteria (SRB) cells. It is suspected that unidentified alternative aluminum compounds form in the SRB cells instead of gibbsite, and these compounds are less prone to plugging. This paper will present several case histories of SRB passive treatment projects that involved treating acid rock drainage with high aluminum concentrations.

Additional keywords: sulfate reduction, acid mine drainage, aluminosilicates, aluminosulfates.

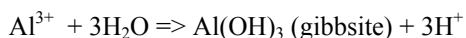
Introduction

It is ironic that many domestic drinking water treatment plants add aluminum in the form of alum as a coagulant while the mining industry works diligently to remove it from acid mine drainage/acid rock drainage (AMD/ARD). When found in a mine effluent that is actively treated using lime dosing, aluminum probably assists in the settling of iron hydroxide flocs. Conversely, the presence of aluminum in mine effluents that are passively treated typically causes maintenance headaches.

Neutralization processes that raise the pH dominate many passive treatment system components. Anoxic limestone drains (ALD's) and Successive Alkalinity Producing Systems (SAPS) are typical examples of neutralizing cell types; their ultimate goal is to add alkalinity so that iron-laden AMD/ARD is buffered against pH drops when the iron is ultimately hydrolyzed and precipitated as a hydroxide. The presence of aluminum in the AMD/ARD is problematic for SAPS and ALD's (Sternier, et al., 1997) because the geochemical conditions found in them favor the formation of the mineral gibbsite $[\text{Al}(\text{OH})_3]$, which is a gelatinous solid. The gibbsite sludge tends to fill the void spaces between the limestone rock used in a typical SAPS or ALD and becomes a major maintenance problem. Small amounts of aluminum in the AMD/ARD thus preclude the use of an ALD; aluminum can be tolerated in minor amounts by SAPS units, but periodic flushing of sludge from the unit (about once every several months) is required to maintain cell effectiveness.

Geochemistry of Aluminum

The dissolution of aluminosilicates such as clay minerals by the oxidizers (hydrogen ion and ferric ion) in AMD/ARD is the primary source of dissolved aluminum in typical AMD/ARD solutions. Coincidentally, it is also the source of any dissolved silica (SiO_2) or $(\text{H}_4\text{SiO}_4 [\text{aq}])$. The precipitation of solid-phase aluminum from AMD/ARD can be complex. The primary reaction most familiar to workers in AMD/ARD mitigation is the precipitation of gibbsite, as shown below.



This is the favored reaction when limestone dissolution or other alkalinity source abruptly raises the pH of the ARD/AMD. As previously discussed, this reaction is problematic due to sludge buildup in limestone-dominated passive treatment structures.

(1) To be presented at the 23rd Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV April 16-17, 2002.

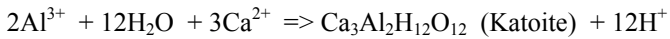
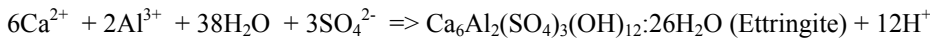
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There are many other aluminum-related reactions possible, complicated by:

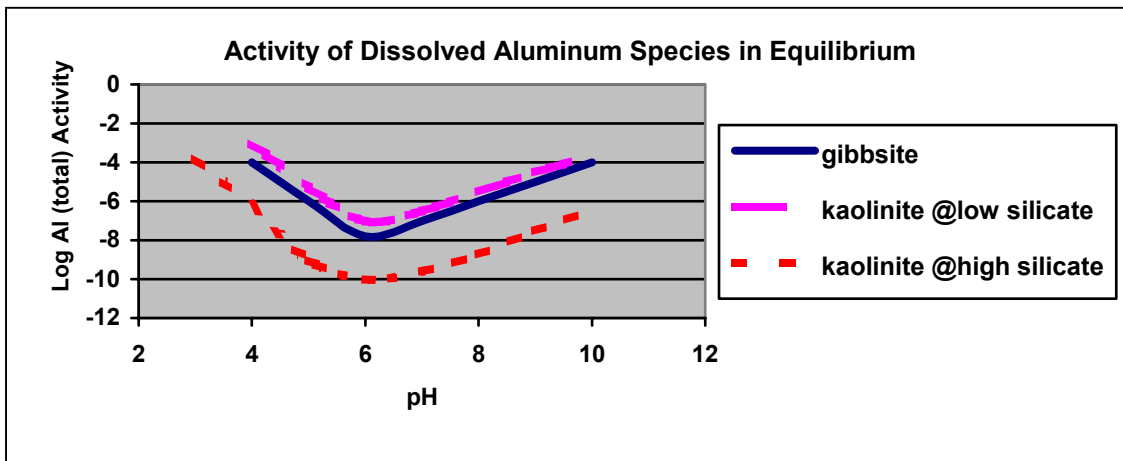
- organic matter in the form of ligands (Drever, 1988), which may tend to keep aluminum in solution through a complexation process called chelation, and
- the presence of other anions and cations.

Drever (1988) noted that the activities (or relative concentrations) of other ionic species can affect the solubility of gibbsite, particularly silica and other anions like sulfate, magnesium and potassium. The following chemical equations are offered as a sample of the over 100 potential reactions that may be possible for precipitating aluminum from the dissolved condition:



The presence of organic molecules such as humic acid, fulvic acid, formic acid or other organic and inorganic ligands have been shown to complex with aluminum and form aqueous compounds that may be mildly resistant to chemical precipitation or encourage the formation of non-gibbsite complexes (Sposito, 1996). The fluoride ion is especially notorious in creating strong ionic complexes with aluminum that are difficult to disrupt. (Drever, 1988).

To illustrate the complexity of aluminum solubility in the presence of a particular anion, the following solubility diagram for total aluminum with two dissolved silicate activities is presented. At low silicate concentrations, the formation of gibbsite is favored over kaolinite; in this instance, silicate activity was 1×10^{-5} . At a higher silicate activity (1×10^{-2}), the reverse is true and the formation of kaolinite is favored over gibbsite in the entire range of pH values. Similar trends are found in other silicate species such as pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$.



Ref: After Drever, 1988

In summary, it is well established that the solubility of various aluminum species can be controlled by factors other than pH.

Sulfate Reducing Bioreactors

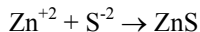
Sulfate reduction has been shown to effectively treat AMD/ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria *Desulfovibrio* in sulfate reducing bioreactors as shown in cross section below. The sulfate reducing bacterial reactions involve the generation of:

- *Sulfide ion* (S^{2-}), which combines with dissolved metals to precipitate sulfides, and
- *Bicarbonate* (HCO_3^-), which has been shown to raise the pH of the effluent.

The sulfate reducing bacteria, which appear to function best above pH 5.0, produce sulfide ion (S^{2-}) and bicarbonate (HCO_3^-) in accordance with the following reactions (Wildeman, et al., 1993):



The dissolved sulfide ion precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The geochemical behavior of aluminum in sulfate reducing bioreactors has not been documented beyond preliminary evidence as discussed below in three case histories. Suspected reasons for the observed behavior are offered subsequently in the paper.

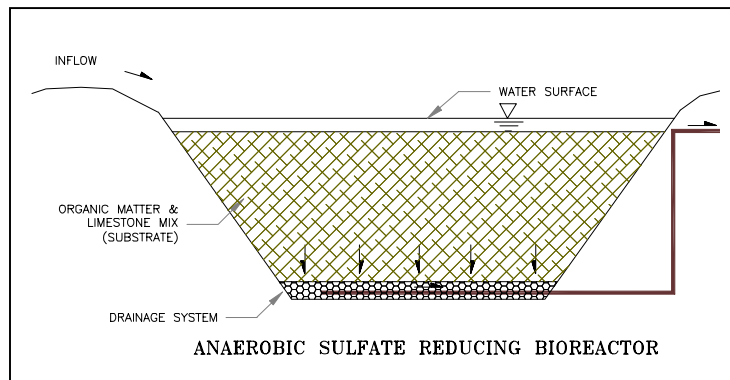
Case Histories

Knight Piésold has been involved with about two dozen AMD/ARD and mine water remediation projects, some of which have resulted in the construction of large-scale systems. Discussion of selected results from three of these sites that involved aluminum follows.

Underground Coal Mine, Pennsylvania

An underground coal mine in western Pennsylvania, closed in 1985, had mined coal from the Lower Kittanning Seam. The mine pool that developed is relatively small and its level is controlled by mine pumps that currently feed a lime dosing treatment system. The pumping rate varies with local precipitation from about 11 to over 220 gpm. The acidic drainage has a pH of about 2.8, iron of 130 mg/L, aluminum of about 30 mg/L, manganese of about 2 mg/L and acidity of 450 mg/L.

In August 2000, six bench-scale test cells were operated for 12 weeks to evaluate the application of SRB anaerobic bioreactors at the site. Bench test cell volumes were about 180 liters (32 gallons); treatment flow was about 6.5 ml/min (9.4 liters per day). The cells were filled with a mixture of chipped wood, sawdust, crushed limestone, cow manure, mushroom compost and hay in varying amounts. The results of the bench test showed similar treatment efficiencies among the test cells; typically, 99 percent of the iron and aluminum were



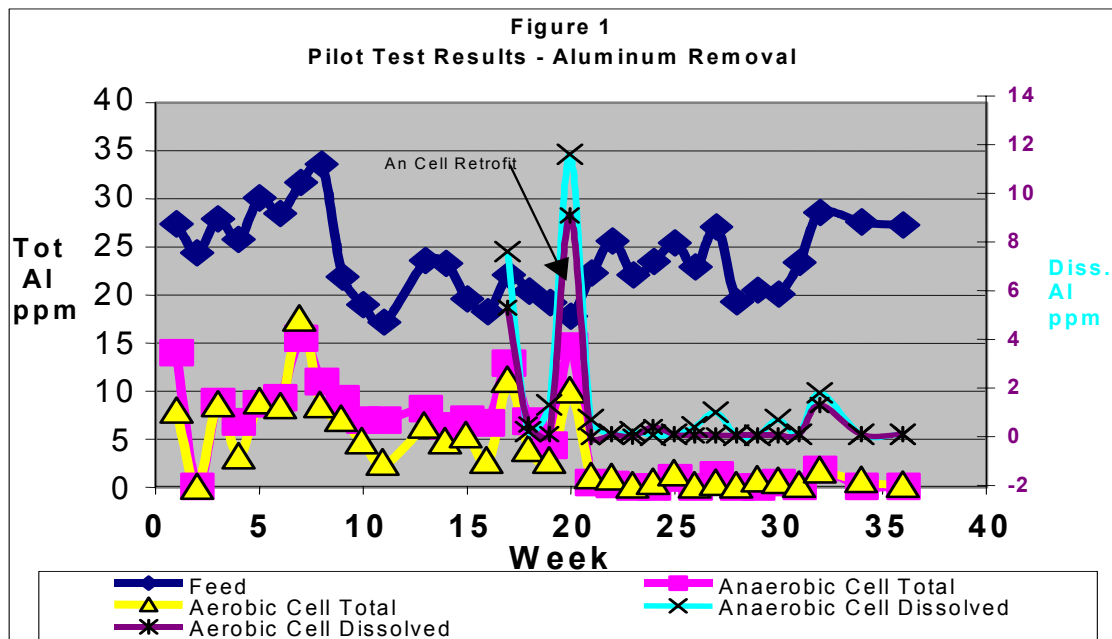
removed. Aluminum plugging was a concern, however, and one cell was sliced in half at the conclusion of the test period and no evidence of gibbsite formation was observed.

This encouraging finding supported the design of a 1.7 gpm pilot scale system (shown to the right) that was constructed in late November 2000 and operated for 14 months as of the date of this writing, March 2002. The pilot cell is about three feet deep and has a surface area of about 4,000 square feet. It feeds an aerobic polishing wetland about 120 square feet in size that discharges into a holding pond that is within the mine water management/treatment system. Data available for the first 36 weeks of operation are shown on Figure 1.



As stated earlier, the cell was commissioned in late November 2000, just as the winter season began. Incubation water temperatures were far below the ideal 10 degrees centigrade and the cell “limped” through the first 19 weeks of depressed temperature conditions. Redox and pH data suggested that conditions were favorable for sulfate reduction at anticipated design rates by Week 20. However, actual sulfate reduction rates were erratic, indicating that the cell was under stress. In early March 2001, field observations confirmed a short circuit had formed in the feed end of the cell and corrective measures were taken, which hopefully will be the topic of future paper.

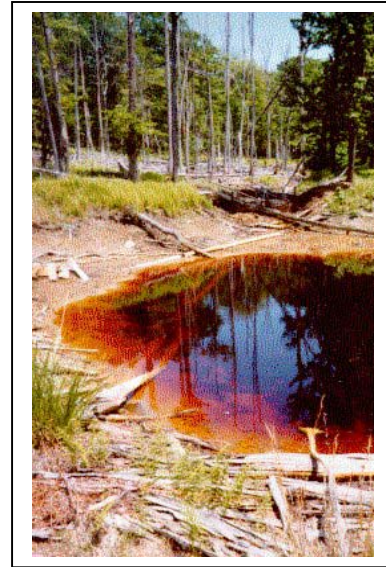
As shown on Figure 1, the aluminum removal rates improved after the retrofit and remain acceptable (less than 0.1 mg/L) despite a late-2001 increase in the feed concentration of aluminum up to 40 mg/L (Week 51) due to drought conditions.



During the operation of this SRB cell, some plugging of the effluent piping (one-inch diameter clear plastic tubing) was observed due to biological oxygen demand sludge accumulation. With the exception of the short circuiting event that required the repair, there was no other evidence of gibbsite sludge plugging during the 14 months of operation of this pilot cell.

Fran Mine, Pennsylvania

Fran Contracting mined a 37-acre surface coal mine in East Keating Township, Clinton County, Pennsylvania in Sproul State Forest. Mining of the site from 1974 to 1977 resulted in post-mining discharges of AMD that destroyed aquatic life in 2.8 miles of Camp Run, 1.3 miles of Rock Run and 2.1 miles of Cooks Run, all tributaries of the Susquehanna River. This impact occurred despite the in-situ remediation efforts that the Pennsylvania Bureau of Abandoned Mine Reclamation (BAMR) conducted in 1993. BAMR personnel have characterized the quality of discharge from this site as the “worst AMD/ARD in the entire State of Pennsylvania from a surface coal mine”. The AMD/ARD averages 2,900 mg/L of sulfate, 2,800 mg/L of acidity, 407 mg/L of iron, **237 mg/L of aluminum**, and 42 mg/L of manganese. It has a pH of about 2.3 or less and also contains heavy metals including copper, zinc, cadmium, chromium and arsenic. While the source of the AMD is a coal mine, it is comparable to AMD/ARD from an abandoned metal mine. Peak flow rate from this site is only 30 gpm, but this loading is enough to impact five miles of potential fishery downstream.

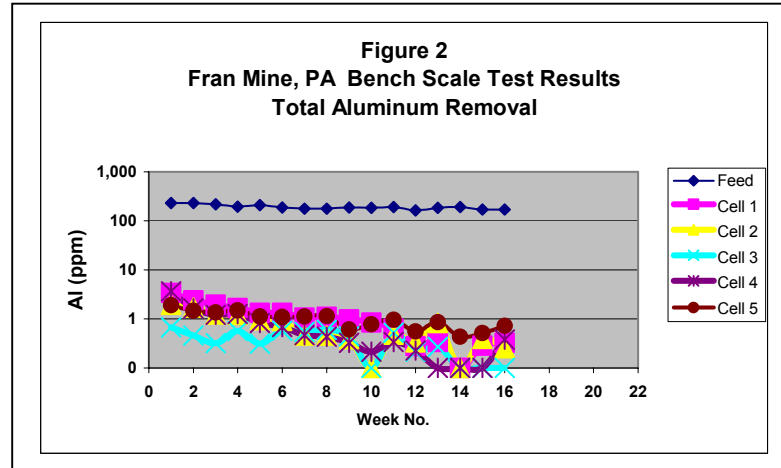


In early August 2001, Knight Piésold, supported by funding secured by the Allegheny Mountain Chapter of Trout Unlimited, constructed five bench-scale SRB bioreactors with the assistance of BAMR personnel. The five cells, built using various organic substrate mixtures, were operated for about 20 weeks. Figure 2 is a plot of the results for aluminum removal for the first 18 weeks.

Figure 2 below shows that with the exception of Cell 5, which was a cell with a high limestone content (50 percent by weight), the cells behaved similarly in removing metals and improving the pH of the Fran Mine feed water. While all the cells showed similar results, the iron removal efficiency of Cell 4 showed the best performance compared to the other four cells. In the final six weeks of sampling data, the total iron concentration in the influent to all cells averaged about 370 mg/L. Effluent from Cell 4 averaged 3.7 mg/L; Cells 1 and 2, the next best with regards to iron, averaged 20.1 and 47.5 mg/L, respectively, over the same period. Aluminum removal was excellent for all cells. The last six week average feed concentration was 178 mg/L. Effluent concentration for the cells ranged from 0.21 mg/L (Cell 4) to 0.67 mg/L (Cell 5) during this time period.

In mid-January 2002, all cells were subjected to an “autopsy” to evaluate how much, if any, plugging occurred due to the precipitation of metal sulfides and other metallic compounds during the test period. The autopsies of the cells did not reveal any visible accumulations of aluminum precipitate, even in Cell 5. The effluent pipe and limestone drainage layers were typically clean. Unfortunately, the cells were frozen, so it was not possible to closely examine the substrate for traces of aluminum deposits. Regardless, all cells operated from early August to late December without any need for “flushing” to maintain the flows.

This is encouraging from a maintenance standpoint; the full-scale sulfate reducing cells may be able to operate unattended for years, perhaps decades, without requiring flushing, major maintenance, or retrofitting. This needs to be confirmed at a pilot scale; a pilot cell is planned for construction in the spring of 2002.



Prior to the start of dissecting the bench cells, sample aliquots were recovered from the feed water holding tank, and the discharge pipes of Cells 2, 4 and 5. These samples were submitted to the Colorado School of Mines for total metals analysis using an induction coupled plasma spectrometer or ICP unit. The results of the analysis are shown on Table 1. This analysis confirms that there are other heavy metals present in the Fran Mine AMD that might impact Cook's Run, including trace amounts of cadmium, cobalt, copper, chromium nickel, and zinc. The results in Table 1 suggest that the sulfate reduction in the bench cells, especially Cell 4, was very efficient at lowering the concentration of these other heavy metals in addition to the iron and aluminum that were analyzed weekly.

Table 1
Fran Mine Bench Scale Final Samples
ICP Analysis by Colorado School of Mines Chemistry Department

Parameter	Duplicates		Bench 2	Bench 4	Duplicates		Det. Limits
	Feed Sample 1	Feed Sample 2			Bench 5A	Bench 5B	
Aluminum	382	305	0.11	BDL	0.09	0.17	0.02
Cadmium	0.12	0.10	0.01	0.00	0.03	0.03	0.00
Cobalt	2.96	2.40	0.06	0.02	0.26	0.22	0.01
Chromium	0.20	0.16	BDL	BDL	0.01	0.01	0.00
Copper	1.99	1.61	BDL	0.01	BDL	BDL	0.00
Iron	876	709.16	38.10	0.66	94.21	107.22	0.00
Manganese	97.95	79.28	21.77	2.86	38.34	38.80	0.00
Nickel	3.60	2.93	0.03	0.04	0.28	0.24	0.00
Sulfur	1,846	1,463	466	69	417	446	0.06
Sulfate (calc'd)	5,538	4,389	1,398	207	1,251	1,338	n/a
Silicon	85.22	66.96	11.36	6.83	41.70	45.67	0.01
Tin	0.22	0.17	0.04	BDL	BDL	BDL	0.02
Zinc	7.05	5.75	0.02	0.05	0.10	0.06	0.00

It is curious to note the marked decrease in silicon, from about 77 mg/L in the feed water (average of 68 and 85 mg/L) and about 7 mg/L in the Cell 4 effluent. This reduction suggests that silicate-based metal compounds, perhaps higher density aluminosilicates, might be forming in the substrate in lieu of the typical gibbsite which is so problematic in many SAPS and other limestone-based passive treatment systems.

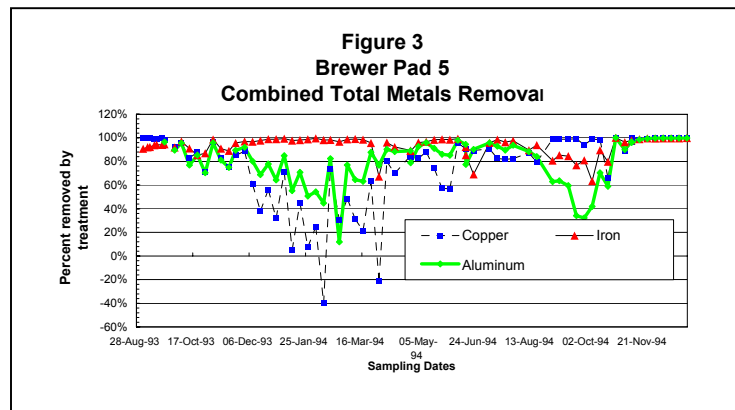
Brewer Gold Mine, South Carolina

This open pit gold mine (which has since been closed) had two AMD/ARD sites, a flooded open pit and a spent cyanide heap leach pad. Two pilot scale sulfate-reducing cells were built, one of which is shown in the photo on the right. The cells were filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. The cells treated 3.8 and 2.8 L per min (1.0 and 0.75 gpm) (pit and pad flows, respectively) for approximately 18 months. This discussion focuses on the treatment of spent heap leach pad (Pad 5) effluent. The pad had been rinsed to reduce cyanide concentrations, but its effluent had turned acidic.



This sulfate reducing cell was described in more detail elsewhere (Gusek, 2000). Throughout the testing program, Pad 5 influent concentrations fluctuated in response to rainfall events on the heap and the presumed rise of pyrite oxidation activity as buffering leach solutions were rinsed out. Iron concentration varied from 8 mg/L after a leach solution flush to about 3,950 mg/L at cell decommissioning; pH values varied from 4.7 down to 2.0 at decommissioning. Aluminum concentration in the raw feed to the Pad 5 cell averaged about 60 mg/L with a range of 4 to 220 mg/L. At the time of the pilot testing (1994-1995), there was more concern about the iron concentrations than the aluminum values.

Typical cell effluent values included a pH of 6.5, iron of 44 mg/L and aluminum of 6 mg/L. As shown in Figure 3 below, the removal of aluminum in the cell was erratic. This occurred in response to changing redox conditions that were traced to the effects of plant growth on the cell surface. Regardless, there were no indications of gibbsite formation during the 18-month pilot test.



Suspected Aluminum Behavior in Sulfate Reducing Conditions

Visual observations of organic substrates during sulfate reducing bench cell autopsies at the Fran Site failed to detect gibbsite despite being exposed to aluminum concentrations over 200 mg/L. The operation of pilot scale cells for over year at the Dixon Run No. 3 Site in Pennsylvania and the 18 month test at the Brewer Mine in South Carolina did not exhibit plugging conditions that might be attributed to gibbsite formation. It is suspected that aluminum species that are physically denser than gibbsite are being preferentially precipitated in the reduced conditions found in a typical sulfate reducing bioreactor.

Geochemical modeling may reveal likely mineral phase candidates that may be forming. These may include silicates like kaolinite or pyrophyllite or aluminum sulfates like jurbanite, diaspore, boehmite or basaluminite. Even with modeling results, however, the precise mechanisms that occur in different sulfate reducing bioreactors might be site-specific and generalizations on the phenomenon may prove to be elusive.

Mitchell and Wildeman (1996) compared the behavior of aluminum predicted by a geochemical model (MINTEQA2) with laboratory test results. Most of the mineral phases considered were either aluminum hydroxides or aluminosulfate species. They found that modeling results required some adjustments to better match their laboratory test data. In particular, it was difficult to account for all the aluminum precipitation assuming just one species; jurbanite and diaspore caused the precipitation of too much aluminum and boehmite and basaluminite caused the precipitation of too little.

The results of rudimentary stoichiometric calculations using the Fran Mine silica values presented in Table 1 suggest that there was an insufficient amount of silica present to account for all the aluminum precipitated as an aluminosilicate species. Thus, other non-silicate species such as aluminosulfates may be forming as well. Which species forms first (i.e., aluminosilicates or aluminosulfates) will be dictated by the solubility products of the respective compounds in the conditions unique to each AMD/ARD source and the local redox conditions in the sulfate reducing bioreactor.

Summary

The three case studies provide some insight into the potential for sulfate reducing bioreactors to accept and effectively treat dissolved aluminum. The mechanisms are not well understood because of the complexity of aluminum geochemistry. Future work may involve geochemical modeling and laboratory work to further understand the phenomenon. This situation should provide many future research topics. But from a practical perspective, as long as the plugging problem is solved, AMD/ARD abatement design professionals may be provided with yet another powerful tool in the passive treatment arsenal.

Acknowledgments

The authors gratefully acknowledge the following companies for contributing information or permission to publish this paper:

- Allegheny Mountain Chapter of Trout Unlimited
- Brewer Gold Company

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