SOLUBILITY OF Fe (III) AND Al IN AMD BY MODELLING AND EXPERIMENT[1]

by

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Abstract: Studies of Fe(III) and Al species in acid mine drainage (AMD) alone and in contact with limestone were conducted by MINTEQA2 modelling and by experiments. The objectives of these studies were to: 1) determine at what pH Fe(III) and Al would be in solution in AMD such that the water would be harmful to an anoxic limestone drain (ALD), and 2) evaluate the theoretical limits to the amount of alkalinity that could be generated by an ALD. Using $Fe(OH)_3$ as the primary species and the standard values for MINTEQA2, Fe(III) precipitates at pH 2.90 when the concentration is over 453 mg/L. Al precipitates at a pH of 4.00 when the concentration is over 108 mg/L. Experiments found that over 90 % of Fe(III) and 45 % of Al were precipitated at these pH's. Experimental verification of Fe(III) concentrations of pH's from 2.90 to 4.0 found that modelling agreed with experiment when ferrihydrite is the primary solid and the log Ksp (solubility product) is -38.9. For Al, gibbsite would be the primary solid and log Ksp is -34.1. For AMD in contact with $CaCO_3$ when CO_2 is conserved, final alkalinity is higher when mineral acidity is higher even though pH of the final solution is lower. This modelling result was confirmed by experiment. Higher mineral acidity causes generation of more CO_2 that reacts with $CaCO_3$ to generate more dissolved HCO_3^-.

Additional Key Words: Anoxic Limestone Drain, Mineral Acidity, Alkalinity

Introduction

Anoxic Limestone Drains (ALD) are an important component in the arsenal of methods that can be used to passively treat acid mine drainage (AMD) (Brodie, et al., 1991; Nairn, Hedin, and Watzlaf, 1991). The function of an ALD is to add alkalinity to the water through the dissolution of calcium carbonate. The chemical reactions that govern this dissolution are:

$$CaCO_3\,(s) + 2H^+ = Ca^{2+} + CO_2\,(aq) + H_2O \quad (pH < 6.4)$$

$$CaCO_3\,(s) + CO_2\,(aq) + H_2O = Ca^{2+} + 2HCO_3^-$$

$$CaCO_3\,(s) + H^+ = Ca^{2+} + HCO_3^- \quad (pH > 6.4)$$

Alkalinity is produced in the form of HCO_3^-. Below a pH of 6.4, aqueous CO_2 is the primary carbonate species, while above pH of 6.4 HCO_3^- becomes the primary species. An oxidation pond is placed after the ALD to oxidize Fe(II) to Fe(III) and use the alkalinity generated to buffer the H^+ acidity generated

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during $Fe(OH)_3$ precipitation. The stepwise reactions are:

$$Fe^{3+} + 3\ H_2O \text{ ----> } Fe(OH)_3 + 3\ H^+$$

$$HCO_3^- + H^+ \text{ ---> } H_2O + CO_2\,(aq)$$

This gives an overall net reaction of:

$$Fe^{3+} + 3\,HCO_3^-\ (aq) \text{ -----> } Fe(OH)_3 + 3\ CO_2\,(aq)$$

In this paper, Fe(II), Fe(III), and Al(III) are used to designate all dissolved species of the metal. For example, Fe(III) could include dissolved Fe^{3+}, $Fe(OH)^{2+}$, and $Fe(OH)_2^+$.

Early in the development of ALD's it was found that dissolved Fe(III) and Al(III) impaired the function of an ALD by armoring the limestone with hydroxide precipitates. This restricted the dissolution of limestone (Brodie, et al., 1991). In addition, buildup of hydroxide precipitates caused ALD's to plug (Watzlaf et al. 1994). Brodie and others (1991) suggested 10 mg/L of Al(III) and 1.0 mg/L of Fe(III) as the maximum amount of Al and Fe in the AMD flowing into an ALD. Hedin and Nairn (1992) advised that if the concentration of Al(III) and Fe(III) exceeded 1.0 mg/L that performance could be compromised. In the latest USBM guidelines on passive treatment, Hedin, Nairn, and Kleinmann (1994) placed the maximum concentrations of Al(III) and Fe(III) that could be tolerated within an ALD at 1.0 mg/L.

Both Al(III) and Fe(III) cause this armoring because they will react with water even in fairly acidic solution to form hydroxides. The reaction for Al is:

$$Al^{3+} + 3\,H_2O \text{ ------> } Al(OH)_3 + 3\,H^+$$

For Fe(III), hydrolysis occurs at pH's between 2.75 and 3.25; for Al(III), at pH's between 4.0 and 4.5.

Because the concentrations of Al(III) and Fe(III) are so critical to determining whether an ALD can be used for treatment, the first objective of this study was to determine what concentrations of these metals were predicted by an equilibrium modelling program such as MINTEQA2 (Felmy, Girvin, and Jenne 1983, Allison, et al., 1991). The second objective was to determine whether the concentrations predicted by MINTEQA2 modelling were confirmed by Fe(III) and Al(III) solutions in the laboratory.

In addition to determining Al and Fe concentrations in AMD, another objective was to determine the maximum amount of alkalinity that can be generated by an ALD. Hedin, Watzlaf, and Nairn (1994) noted significant differences between the alkalinity in two ALD systems that received water of very similar quality. Also, Watzlaf and Hedin (1993) had developed a method for predicting the alkalinity that could be generated in an ALD using cubitainers. The same methods of modelling confirmed by laboratory experiments were used to determine the pH and alkalinity that could be theoretically generated when limestone was brought into contact with various acidic solutions containing Al(III) and Fe(III).

This paper reports on the results of modelling and laboratory studies that were performed on Al(III) and Fe(III) solutions and these solutions in contact with $CaCO_3$.

Experimental Methods

For the MINTEQA2 modelling exercises, the equilibrium pH was set at various acidic values, Al(III) or Fe(III) was added at various concentrations at the set pH to determine the minimum concentration that must be present for precipitates to form. Sulfate was used to balance charges, and no other ions were entered. For Fe, ferrihydrite ($Fe(OH)_3$) with log Ksp (solubility product) of -37.1 (with respect to Fe^{3+}) was entered as the possible solid. For Al, crystalline gibbsite ($Al(OH)_3$) with log Ksp of -33.2 (with respect to Al^{3+}) was entered as the possible solid. In separate runs, amorphous $Al(OH)_3$ with log Ksp of -31.6 was entered as the possible solid.

For modelling the interaction of $CaCO_3$ with acidic solutions, $CaCO_3$ was set as an infinite solid and the above hydroxide precipitates were set as possible solids. Initial pH and Fe(III) or Al(III) concentrations were set, and the system was allowed to come to a new equilibrium. In the calculation, CO_2 partial pressure was allowed to exceed the atmospheric value of $10^{-3.5}$. This is the case in actual ALD's where attempts are made to retain the CO_2 that is generated (Brodie, et al., 1991; Hedin, Watzlaf, and Nairn, 1994). In all cases, 100 % of the Al and Fe precipitated as hydroxides. At the new equilibrium pH, the alkalinity was calculated from the concentration of dissolved HCO_3^-.

In the laboratory experiments where the precipitation curves for Al(III) and Fe(III) were determined, solution concentrations from 1 to 1000 mg/L of the cation were used. Ferric ammonium sulfate and hydrated aluminum sulfates were used to make the stock solutions. The pH of the solution was set using NaOH and H_2SO_4. Aliquots of the solution were taken at 24, 72, and 96 hours and the pH of the solution was readjusted to the initial value after the first two aliquots were taken. The aliquots were filtered through 0.45 micrometer filters. Fe concentration was determined by flame atomic absorption and aluminum was determined colorimetrically using aluminon reagent.

In the limestone experiments, 3.8 liter collapsible, low-density polyethylene cubitainers were used in a configuration similar to that of Watzlaf and Hedin (1993). A quantity of 4.0 kg of washed limestone of greater than 90 % $CaCO_3$ in quality, of 0.3 to 1.0 cm in diameter was added to the cubitainer. Approximately 2 liters of Al(III) and Fe(III) solutions, whose pH's had been set, were added until the cubitainer overflowed and no air was present. At times of 3, 6, 12, 24, and 48 hours, aliquots of 20 mL were removed by squeezing the cubitainer. For each aliquot, alkalinity and pH were measured, then the sample was filtered and acidified and Fe and Al concentrations were determined.

Further details on the modelling and laboratory studies can be found in Mitchell (1994).

Results of the Precipitation and Limestone Equilibration Studies

The modelling results compared with the laboratory-determined, saturation concentrations of Fe(III) and Al(III) are shown in Figures 1 and 2 respectively. The modelling runs for iron were quite surprising because, out to a pH of 4.0, Fe(III) was still in solution at concentrations above 1.0 mg/L. Based on field experiences in Colorado, the rule of thumb we use is that Fe(III) should not be in solution beyond a pH of 3. The rule of thumb was confirmed in the laboratory studies. In experiments where the pH was set to approximately 3.5, the Fe(III) concentrations averaged 0.10 mg/L. In experiments where the pH ranged from 2.99 to 3.01 the concentration of Fe(III) ranged from 1.3 to 4.2 mg/L. The difference between the experimental and modelling results is probably due to the inclusion of Fe(III) complexes, such as $Fe(OH)_2^+$, in the model.

For aluminum, the experimental results generally followed the modelling concentrations when Al(III) is in equilibrium with crystalline gibbsite. In experiments where the pH was set to approximately 4.0, the Al concentrations ranged from 19 to 46 mg/L. In experiments

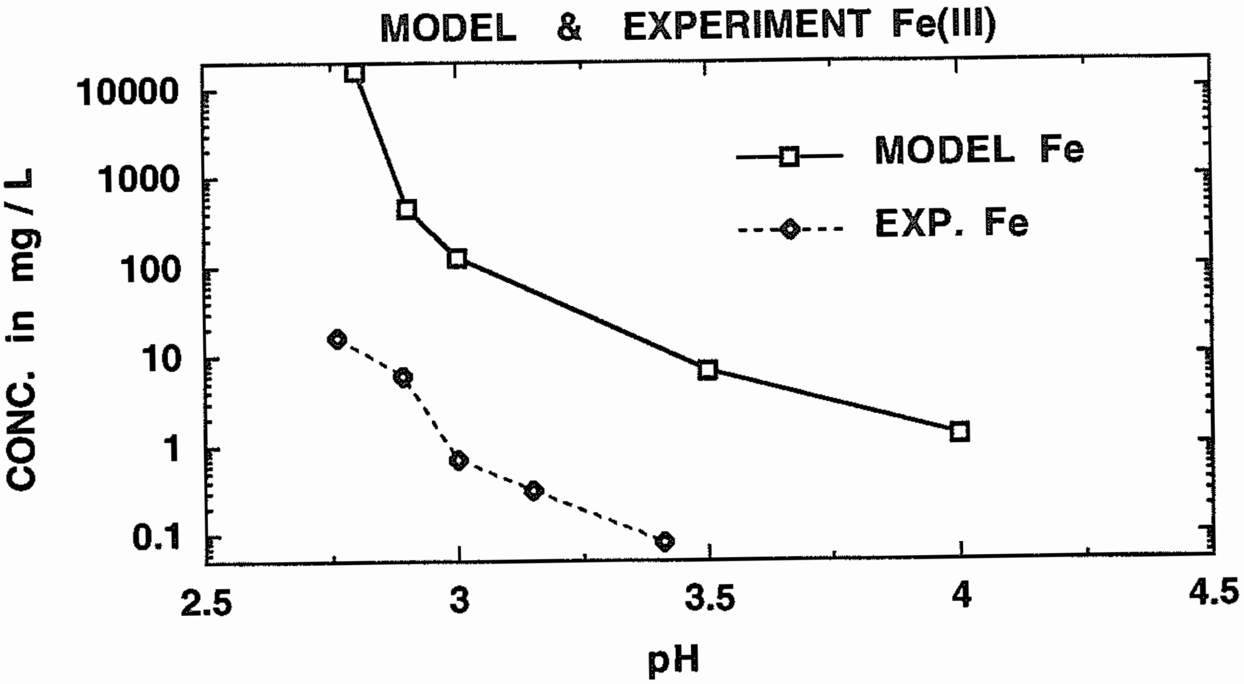

Figure 1. Model and experiment concentrations of Fe(III) in equilibrium with ferric solids at acidic pH values.

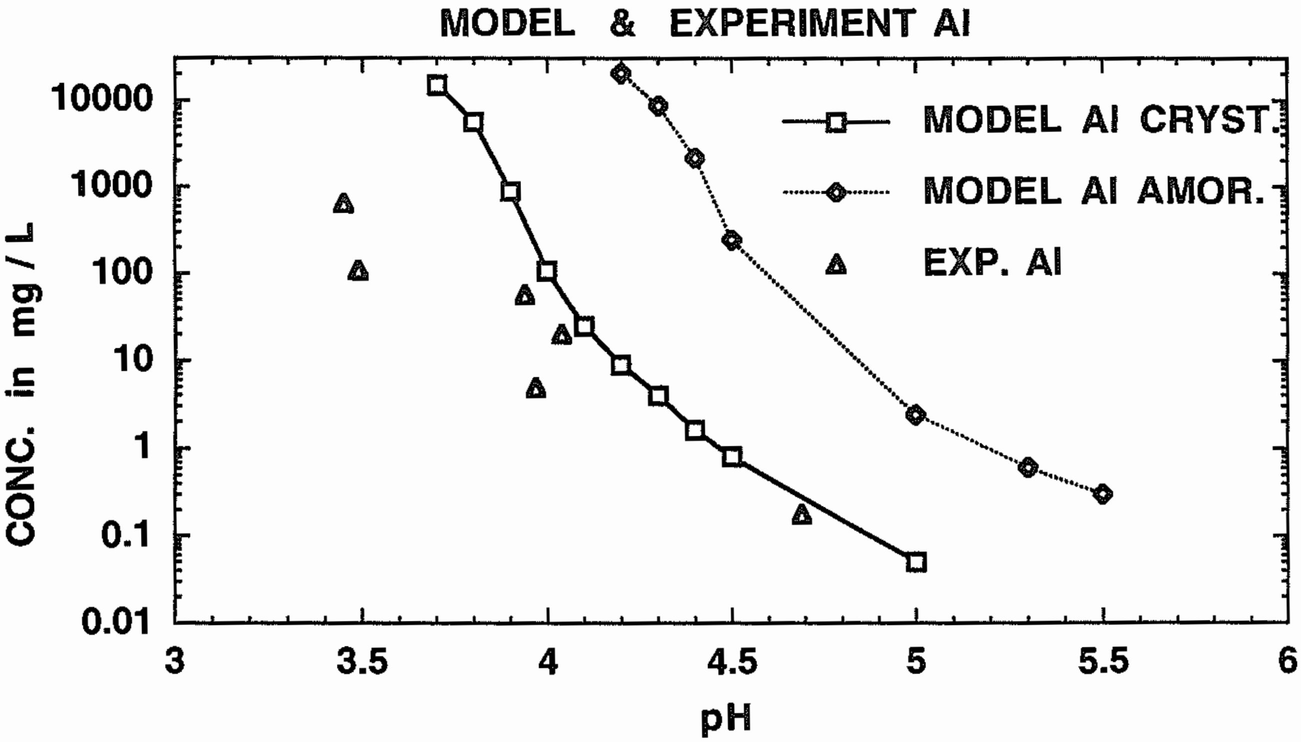

Figure 2. Model and experiment concentrations of Al(III) in equilibrium with aluminum solids at acidic pH.

Table 1. Modelling and laboratory results of limestone equilibrated with solutions of Fe(III) and Al(III) at various pH values. Alkalinity is in units of mg $CaCO_3$ / L. Laboratory results were after 48 hours of reaction.

			Modelling Results			Laboratory Results	
Initial pH	Initial Fe(III)	Initial Al	Final pH	Final Alkalinity	Log P (CO2)	Final pH	Final Alkalinity
2.9	50.0	0.0	7.16	152	-1.94	7.5	131
2.9	50.0	0.0	7.16	152	-1.94	7.5	132
2.9	100	0.0	6.87	213	-1.48	7.35	160
2.9	0.0	0.0	7.84	58	-4.41	7.55	87
4.0	0.0	50	6.93	190	-1.58	7.30	173
4.0	0.0	100	6.57	270	-1.07	7.30	173
3.5	1.0	100	6.57	277	-2.56	7.04	187
3.5	5.0	400	6.02	500	-1.78	6.66	280
3.5	5.0	400	6.02	500	-1.78	6.57	288

where the pH was set to approximately 4.7, the concentration of Al ranged from 0.12 to 0.27 mg/L.

In Table 1, the modelling and laboratory results of limestone equilibrated with waters containing various concentrations of Al(III), Fe (III), and H^+ are presented. In Figure 3, the experiment and model pH's are compared. In Figure 4, the experiment and model alkalinities are compared.

The modelling results show that when CO_2 gas is conserved, it indeed does exceed the atmospheric value of $10^{-3.5}$. In turn, this does indeed increase the alkalinity. For the laboratory samples, except for the acid solution with no Fe(III) and Al(III), the final alkalinity is lower and the pH higher than the model predictions. In Table 1, the final experimental values of the alkalinity taken after 48 hours are given. In systems with high mineral acidity, the excess CO_2 gas far exceeds the atmospheric value. In experiments with 100 and 400 mg /L of Al(III) where there was excess CO_2, the alkalinity peaked at between 12 and 24 hours and then consistently decreased. The maximum values for these experiments are also plotted in Figure 4.

Discussion

For the precipitation experiments, additional modelling was performed to test the possibility that phases other than ferrihydrite and gibbsite were controlling the Fe(III) and Al(III) concentrations. For Fe, maghemite (Fe_2O_3) gave the best fit. However, this is an unrealistic phase to form in a near surface environment. Use of lepidocrocite (FeOOH) caused the precipitation of too much iron, and use of hydrogen jarosite ($HFe(SO_4)_2(OH)_6$) caused too much Fe(III) precipitation at low pH's and not enough at high pH's. For Al, diaspore (AlOOH) and jurbanite ($AlOSO_4$) caused the precipitation of too much aluminum. When boehmite (AlOOH) and basaluminite ($Al_4(OH)_{10}SO_4$) were tried, not enough aluminum precipitated. In the study of Butte, Montana Berkeley Pit water, Davis and Ashenberg (1989) also found that the AMD was supersaturated with respect to jurbanite. Apparently, precipitation of jurbanite is kinetically hindered.

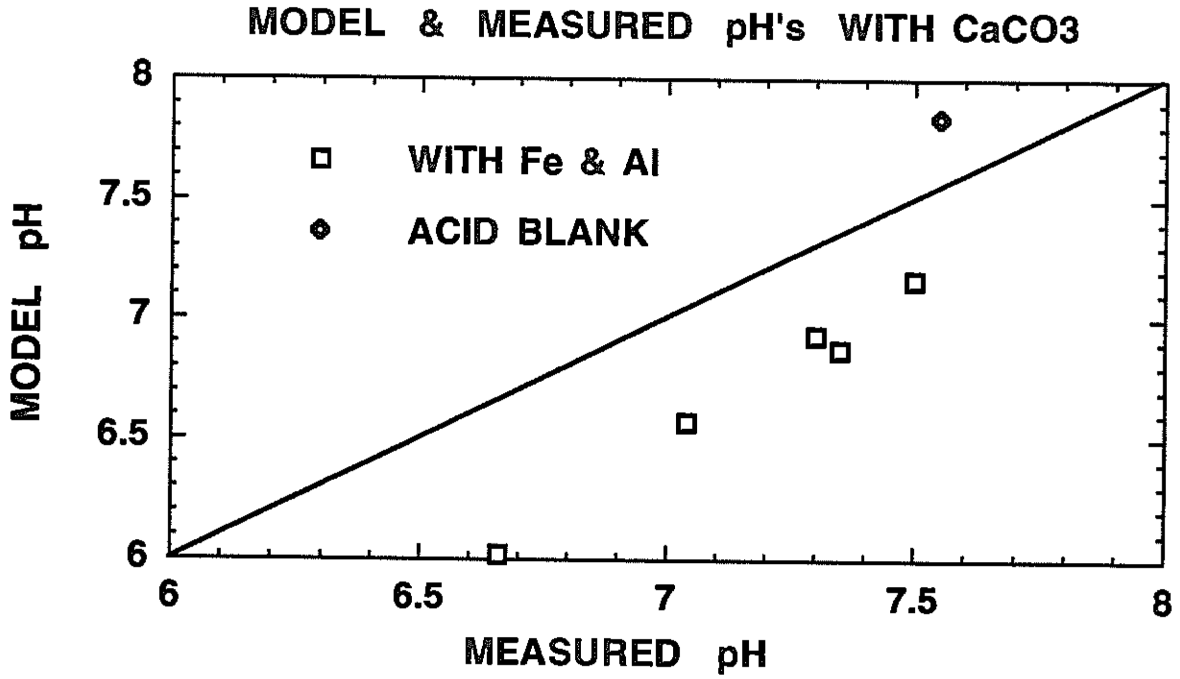

Figure 3. Model and experiment pH values from the reaction of acidic solutions of Fe(III) and Al(III) equilibrated with $CaCO_3$. In the modelling and experiments, the CO_2 generated was retained.

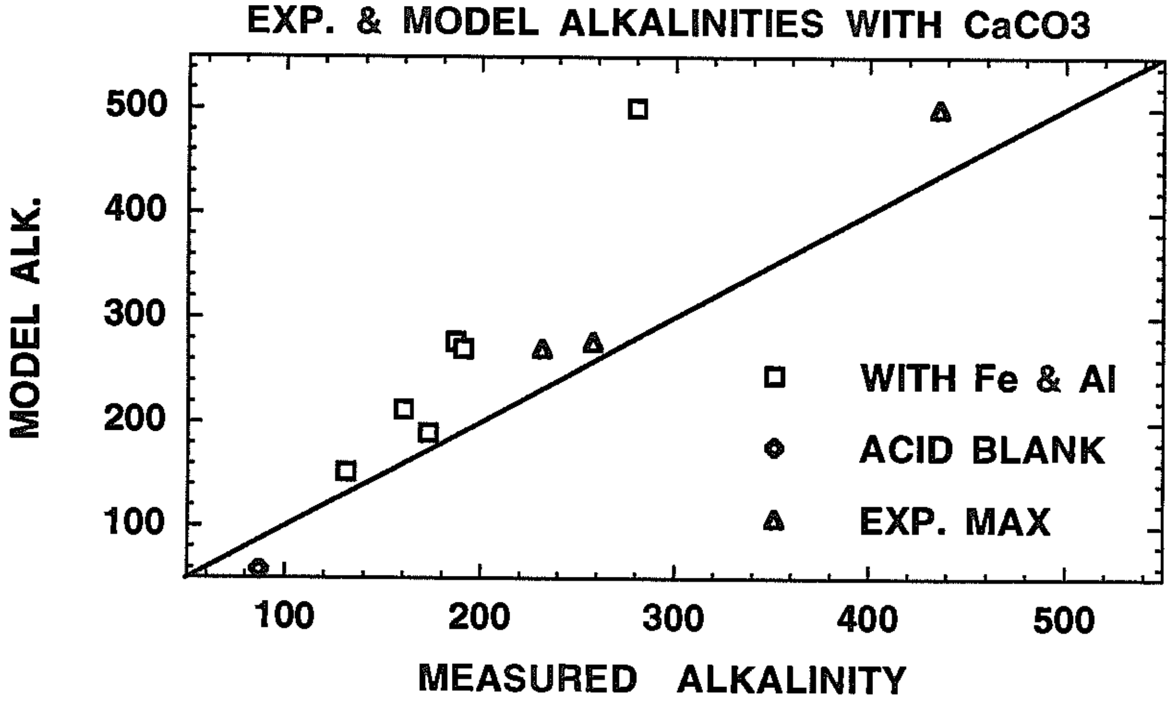

Figure 4. Model and experiment alkalinities from the reaction of acidic solutions of Fe(III) and Al(III) equilibrated with $CaCO_3$. In the modelling and experiments, the CO_2 generated was retained. The experimental maxima occurred between 12 and 24 hours. The final values were after 48 hours.

Another possibility for resolving the laboratory results with MINTEQA2 modelling is to determine the solubility product of $Fe(OH)_3$ and $Al(OH)_3$ based on the laboratory results and use this value in the model. For the 15 Fe precipitation experiments, the average solubility product on a log basis is -38.9 ± 0.3. For the 10 Al precipitation experiments the average solubility product on a log basis is -34.1 ± 0.5.

Literature values for the log Ksp for ferrihydrite range from -36 to -39 (Chapman, Jones, and Jung 1983). MINTEQA2 allows a range for ferrihydrite log Ksp of -37.00 to -40.44, and uses a default value of -37.1 if nothing is specified. Chapman, Jones, and Jung (1983) studied the processes controlling metal ion concentrations in AMD and determined that ferrihydrite was the most reasonable precipitate and a log Ksp of -39 produced the most consistent results. Based on the results from this and other studies, using ferrihydrite with a log Ksp of -39 as a possible solid phase is the most reasonable procedure for modelling the concentration of Fe(III) in AMD.

Literature values for the log Ksp for $Al(OH)_3$ range from -31.6 to -36.3 (Chapman, Jones, and Jung 1983). MINTEQA2 has maximum and minimum values for log Ksp of -32.56 to -33.51 for gibbsite, and uses a default value of -33.23 if nothing is specified. Chapman, Jones, and Jung (1983) determined that amorphous $Al(OH)_3$ was controlling the aluminum concentration, and a log Ksp of -31.6 produced the most consistent results. The value of log Ksp of -34.1 determined in this study is outside the values used in MINTEQA2 and in the Chapman, Jones, and Jung (1983) study. However it is within the range of literature values. Based on the results from this and other studies, using gibbsite as a possible solid phase is the most reasonable procedure for modelling the concentration of Al(III) in AMD. However, using the default value of log Ksp of -33.23 will produce an upper bound on aluminum concentration and a value of -34.1 will produce a lower bound.

The modelling and laboratory studies of the equilibration of acidic Fe(III) and Al(III) solutions with $CaCO_3$ do not completely parallel the reaction of AMD in an actual ALD. This is because Fe(III) and Al(III) hopefully are not present when AMD courses through an ALD, and consequently, precipitation of hydroxides is avoided. In these studies, complete precipitation of Fe(III) and Al(III) occurred. Nevertheless, certain aspects of this study apply to any time AMD reacts with limestone including the reaction of AMD in an ALD. In particular, the property of alkalinity increasing and pH decreasing with increasing mineral acidity applies whenever AMD reacts with limestone. This somewhat counter-intuitive property can be understood by considering the following equilibrium reaction:

$$CO_3^{=} + CO_2(g) + H_2O \longleftrightarrow 2\,HCO_3^-$$

The reactant CO_2 gas is generated from the reaction of AMD with $CaCO_3$ according to the first reaction in the **Introduction** and is retained in the system rather than being released. The reactant $CO_3^{=}$ comes from calcite dissolution. The greater the mineral acidity, the more CO_2 is generated to react with the calcite, and the more bicarbonate alkalinity is produced. If the water is allowed to degas and CO_2 escapes, this shifts the above reaction to the left and alkalinity is reduced. However, when the reaction shifts to the left, more $CO_3^{=}$ is produced and the pH increases.

With respect to the reaction of AMD with an ALD, the amount of alkalinity generated depends on the pH of the water entering the ALD. If the CO_2 is retained, the lower the pH, the greater the amount of alkalinity that theoretically can be generated. Greater alkalinity does not necessarily mean a higher pH. In addition, if the CO_2 is retained and reaches pressures greater than the atmospheric pressure of $10^{-3.5}$, then this CO_2 has the possibility of degassing from the water when the AMD breaches the surface after coursing through the ALD. In such a situation, the pH would rise, but there would be less alkalinity available for precipitation of $Al(OH)_3$ and $Fe(OH)_3$.

Conclusions

Modelling and laboratory experiments studying the chemistry of acidic solutions of Al(III) and Fe(III) alone and in contact with $CaCO_3$ has lead to the following observations:

- The precipitation curve for $Fe(OH)_3$ occurs at about a pH of 3 so that by a pH of 3.5, the concentration of Fe(III) is down to 0.1 mg/l. For Al, the precipitation curve for $Al(OH)_3$ occurs above a pH of 4 and at a pH of 4.7, the concentration is approximately 0.20 mg/L.
- For modelling Fe(III) chemistry in AMD, ferrihydrite with a log Ksp of -39 is the best choice for a possible phase. For modelling Al(III) chemistry in AMD, gibbsite is the best choice for a possible phase. The value of log Ksp to use is a bit more uncertain. This study suggests a value of -34.1.
- In the reaction of AMD with $CaCO_3$, if the CO_2 is retained, the higher the mineral acidity, the higher the possible alkalinity that can be generated, and the lower will be the pH at equilibrium.

- If, when AMD reacts with an ALD, the CO_2 is retained and reaches pressures far above the atmospheric value of $10^{-3.5}$, the CO_2 can dissolve from the AMD and be lost to the atmosphere when it breaches the surface. If this occurs, the pH will rise and alkalinity will be lost.

From a practical viewpoint, aluminum is not always analyzed in AMD. Consequently, its presence in water may be overlooked in assessing the appropriateness of an ALD. In a 1995 survey of AMD from metal mines in Colorado, a significant number of the waters that had pH below 4 had concentrations of Al above 1 mg/L. In the opinion of the authors, a maximum concentration of Al of 1 mg/L is presently a conservative guideline based on the fact that people are unsure of how much dissolved aluminum will plug an ALD.

The other important feature that this study reveals is how important initial acidity of the water and retention of CO_2 are to the final alkalinity of the AMD. Loss of CO_2 or precipitation of iron within the ALD could account for the alkalinity differences that Hedin, Watzlaf, and Nairn (1994) found in their study. The high alkalinity values shown in Table 1 and in Figure 4, generated when all the Fe(III) and Al(III) were allowed to hydrolyze should be carefully considered. This was caused by the generation of more CO_2 which reacted with the calcite. In an actual ALD, no precipitation can occur because it would eventually plug the structure. In Table 1, the alkalinity values for the system where no Fe(III) and Al(III) are present may be closer to what should be expected in the field. In-field alkalinity values of 300 mg/L of $CaCO_3$ may look very desirable. However, such high values may only be an indication that Fe(III) or Al(III) are precipitating in the ALD.

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