

Iron and Aluminum Reaction with Limestone

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Abstract

The treatment of Acid Mine Drainage (AMD) with Anoxic Limestone Drains (ALDs) has been the subject of ongoing research and discussion within the coal mining industry. Many field ALDs have been constructed, but few have been able to successfully treat AMD for the time period that they were intended. Complications develop when oxygen, Fe^{2+} , and Al^{3+} exist as aqueous species within AMD. Dissolved oxygen acts as an electron acceptor for Fe^{2+} oxidation and Fe^{2+} and Al^{3+} precipitate as hydroxide solid phases. Once the metal hydroxides precipitate onto the limestone, dissolution slows to a point where base generation is not sufficient to neutralize acidity and totally remove dissolved metals within the AMD. Due to coating, the integrity of the ALD may be compromised, rendering it ineffective for AMD treatment. The time frame for coating of the limestone surfaces as well as the ability of the limestone to continue to dissolve under conditions of hydroxide coating is currently unclear. A laboratory study using 15.2 cm diameter by 91.4 cm length (6 inches by 3 feet) polyvinyl chloride columns filled with limestone was undertaken in order to determine: 1) rate of limestone dissolution over time and space within a simulated ALD where $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ precipitation is occurring, 2) dominant chemical reactions and 3) effects of diffusion on reaction rate (H^+ to limestone surfaces or Ca^{2+} and/or CO_2 away from limestone surfaces).

Results indicate that Ca^{2+} generation can be modeled for the initial experimental concentrations by a power function:

$$\text{Ca}^{2+}_{(x,t)} = bt^m$$

Where:

$\text{Ca}^{2+}_{(X,t)}$ ~ calcium concentration at any distance x (cm)

or any residence time t (hr)

t = contact time (hr)

b and m = empirical constants

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Calcium concentration can be modeled at any position along the flow path within the ALD using this model. Data indicate that the majority (~ 80%) of dissolution takes place within 1.2 hr of contact time, with only minor dissolution occurring during the remaining contact time (3.6 hr). This suggests that only the front section of an ALD is responsible for producing the majority of base necessary to achieve equilibrium conditions. The remainder of the ALD adds a disproportionately lower amount of base even though contact time is greater.

Calculations from aqueous ion concentration data indicate that the AMD is at equilibrium with respect to the solid phase precipitates $Fe(OH)_3$ and $Al(OH)_3$, throughout the length of the experiment. Calcium carbonate within the bulk solution remains at least 2 orders of magnitude undersaturated, therefore dissolution should continue during the whole length of the column with a continual decrease in Fe^{3+} and Al^{3+} throughout the experiment. However, total amounts of Fe^{3+} and Al^{3+} being removed from solution lessens during the length of experiment indicating that inadequate amounts of base are being input to the water to precipitate metals. Alternatively, limestone dissolution is hindered so metals cannot be scavenged from solution as the thickness of the coating around the limestone increases. This indicates that limestone dissolution and hence neutralization of AMD is controlled by either diffusion to or away from the limestone surface. As metals precipitate on limestone surfaces, a barrier is created between the bulk solution and the limestone surface. It is hypothesized that one of two scenarios is taking place that may explain the lack of neutralization of AMD. In the first scenario, H^+ are unable to diffuse through the metal hydroxide coating to the limestone surface. In this case, the lack of H^+ would not allow dissolution at the limestone surface because the solution would be at equilibrium with respect to $CaCO_3$. The second scenario would be that Ca^{2+} and/or CO_2 as $H_2CO_3^*$ is unable to diffuse away from the limestone surface. In this case, H^+ penetrate the coating and dissolve $CaCO_3$, but the disassociation products (Ca^{2+} and $H_2CO_3^*$) remain at the surface. Equilibrium with respect to $CaCO_3$ will be established and pCO_2 will be extremely high ($>10^{-1}$). Presently, the diffusion models are hypotheses to be tested, but diffusion of aqueous species to or from limestone surfaces appear to be the rate limiting step.