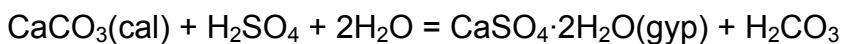


The effect of gypsum coatings and hydrodynamic factors on ALD performance

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Anoxic limestone drains (ALD) are increasingly used as a cost effective treatment of acid mine drainage. However, ALD performance can be compromised by the formation of coatings on the limestone grains and the overall ALD effectiveness is controlled by hydrodynamic processes in the packed bed. We have combined laboratory studies of these processes with chemical engineering principles to create models of ALD performance that can guide the construction of more effective ALDs.

ALD's have been reported to fail after a period of time because the limestone grains become coated with secondary precipitates. Although these coatings are often iron and aluminum hydroxides and hydroxysulfates, gypsum coatings can also form by the reaction:



We used an array of batch reactor experiments to measure the dissolution rates of Iceland spar calcite ($A_{\text{sp}} = 0.015 \text{ m}^2/\text{g}$, 40-60 mesh fraction) at room temperature in up to 1.0 M sodium sulfate solutions with pH ranging from 1.5 to 3.5. Scanning electron microscopy (SEM) showed that gypsum coatings formed on calcite at low pH where sulfate concentrations were high. Gypsum coating formation is controlled by the saturation of gypsum at the calcite surface.

The growing gypsum layer on the calcite surface slows the rate of acid neutralization both by physically covering the surface and by creating a static layer of solution adjacent to the calcite so that the dissolution rate is controlled by the transport of hydrogen ions through this layer. This effect was modeled using Fick's first law of diffusion, which when solved using appropriate boundary conditions predicts that the rate of neutralization of acid declines as the square root of time. Our experimental data fit the following equation

$$r = -10^{-1.96} t^{-0.53} .$$

Our experiments predict that the diffusion coefficient for H^+ through this growing gypsum layer lies between 1.71×10^{-15} and $4.54 \times 10^{-14} \text{ m}^2/\text{sec}$. The gypsum coatings are strongly adherent because they form by epitaxial nucleation whereas iron and aluminum oxyhydroxide coatings are not. This means that the gypsum coatings cannot be removed by flushing so the best strategy for controlling them is to avoid supersaturating the solution with gypsum either by limiting the amount of reaction between the solutions and the limestone or by using dolomite in place of limestone.

Laboratory studies have shown that calcite dissolution in acid solutions is limited by the transport of hydrogen ions from the solution to the mineral surface.

Fitting data from Alkattan et al. (1998) shows that the calcite dissolution rate (r) can be expressed as

$$r = -10^{-2.61} \text{Re}^{0.31} m_{H^+}^{0.87}$$

where Re is the Reynolds number and m_{H^+} is the hydrogen ion concentration. We have combined this relationship with a function that expresses Re as a function of particle size (r_p) and specific discharge (q) to show that the rate of neutralization (r) of acid solutions by calcite is

$$r = 10^{-2.97} q^{0.31} r_p^{-0.69} m_{H^+}^{0.87}$$

This analysis shows that the effectiveness of ALD's increases with decreasing specific discharge and decreasing particle size. However, decreasing the particle size decreases the pore size and increases the tendency for the flow paths to become plugged by secondary precipitates. Decreasing the specific discharge reduces the rate at which AMD can be processed. Field tests are needed to identify the best combination of particle size, flow rate, and extent reaction.

Our results show that laboratory data can be scaled up to create useful models of field behaviors. Even though the coefficients of these models require further refinement by field-testing, their mathematical forms help to clarify how various design choices can affect ALD effectiveness.

Alkattan M., Oelkers E.H., Dandurand J.-L., and Schott J. (1998) An experimental study of calcite and limestone dissolution rates as a function of pH from -1 to 3 and temperature from 25 to 80°C. *Chemical Geology*, 151, 199-214.