Improving the performance of constructed wetlands for treatment of acid mine drainage: a pilot-scale study of the use of dolostone instead of limestone for anoxic drains

J. Barry Maynard (barry.maynard@uc.edu)
Ashley McKendree Helton (amhelton@uga.edu)
Department of Geology, University of Cincinnati, Cincinnati OH 45221-0013
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Summary

To be effective, mine drainage wetlands must receive net alkaline waters with pH values above 6. Anoxic limestone drains are commonly used ahead of the wetlands to generate this needed alkalinity. Dissolution of the limestone neutralizes the acidity of the mine drainage, and anoxic conditions within the drain prevent precipitation of ferric oxides, which would clog the drain and stop the flow. Anoxic conditions, however, cannot prevent precipitation of gypsum, formed from the calcium released by the dissolving limestone combining with the sulfate in the mine drainage. Dolostone could be used in place of limestone to provide equal alkalinity generation with one-half the calcium release, but standard practice and EPA guidelines specify high-calcium limestone for the drain fill.

We evaluated the performance of dolostone relative to limestone for neutralization of mine drainage using stirred reaction vessels with limestone or dolostone particles suspended in sulfuric acid solution. On the time scale of a few hours, limestone reacts faster to neutralize the sulfuric acid, and it is this initially faster reaction that has favored the use of limestone. Anoxic drains, however, are designed for 15 to 20 hour retention times, and on this time scale, dolostone reaction rates are the same as those of limestone.

To test long-term behavior under conditions more closely simulating those in the field, column experiments using solutions containing sulfate, iron and aluminum in concentrations typical of southwest Indiana mine drainage were run for 24-hour cycles of filling. Most of the columns with limestone fill began to fail after about 80 cycles, whereas none of the dolostone columns failed on times of up to 120 cycles. Thin-section study of the run products showed extensive cementation of the limestone by gypsum, but only slight cementation of the dolostone. The dolostone also was less affected by armoring by iron oxide.
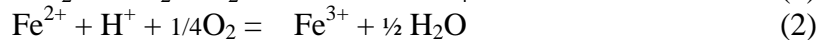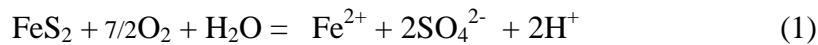
We conclude that dolostone offers significant advantages over limestone as the fill material for anoxic drains. It provides equal alkalinity generation, is largely free of gypsum clogging, and is less subject to iron clogging.

Introduction

Untreated acid mine drainage (AMD) is a widespread environmental problem in areas of active and abandoned coal and hard rock mining. The EPA (1994) reported mining and petroleum activities as the most common source of pollution impairing rivers and streams of the Ohio and Tennessee River Basin. AMD severely degrades both surface and ground water, and its deleterious effects on aquatic ecosystems are also extensive.

Acid mine drainage is formed when sulfides (commonly pyrite) from coals and from shales associated with coal beds oxidize by coming in contact with oxygenated water, releasing acid, sulfate, and metals such as Fe, Mn, and Al into the water. The acidic conditions and elevated dissolved metals associated with mine drainage can be toxic to aquatic life and, if introduced into residential wells, potentially harmful to humans. Surface and ground waters in areas with abandoned coal mines commonly exceed Secondary Maximum Contaminant Limits set by the USEPA for acidity, Fe, Mn, and sulfate.

The processes of pyrite oxidation have been reviewed extensively by Nordstrom et al. (1987) and by Stumm and Morgan (1996). The dominant reactions that take place are

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$
$$Fe^{2+} + H^+ + 1/4O_2 = Fe^{3+} + \tfrac{1}{2} H_2O \qquad (2)$$
$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad (3)$$

These reactions show that both the iron and the sulfide in pyrite oxidize and release acidity. The breakdown of pyrite is one of the most acidic of all weathering reactions because the oxidation of one mole of pyrite releases four moles of H+ (Webb and Sasowsky, 1994). In addition to reacting with oxygen and water, pyrite can be oxidized by dissolved ferric iron according to the following reaction (Stumm and Morgan, 1996):

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$
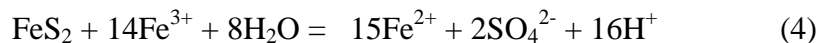
In equation 4, free oxygen is not needed so that pyrite can continue to be oxidized by ferric iron alone. Even if the supply of atmospheric oxygen is completely cut off, the dissolution of any solid $Fe(OH)_3$ can supply the necessary ferric iron (Stumm and Morgan, 1996; Moses et al., 1987). Thus if the oxygen supply is eliminated by flooding or sealing mines, the production of acid mine drainage can still continue once reactions have begun (Webb and Sasowsky, 1994). Accordingly acid production from old mines is a persistent problem. Moreover, many of these mines have been abandoned and it has fallen to the public sector to provide remediation of the acid drainage problems they cause.

Traditionally, acid mine drainage was treated chemically, but chemical processes are expensive and chemical byproducts may themselves be damaging to aquatic life. Limestone treatment, which raises alkalinity, is popular because of its lower cost, good buffering ability, and lower potential for overdosing. However, if conditions are aerobic,

iron and aluminum can precipitate and coat the limestone, hindering its dissolution and rendering it useless (Brodie et al., 1993). Cost-effective remedies for long-term control of acid drainage are called for.

In the 1970s, it was observed that some natural wetlands, rather than being degraded by acid drainage, actually exhibited some cleanup of the water (EPA, 2000). Using this observation, the Tennessee Valley Authority (TVA) began experimenting with artificial *Typha* (cattail) marshes to treat acid mine drainage. Most designs of the wetlands subsequently constructed to treat acid mine drainage have used *Typha* surface-flow marshes (e.g. Kleinmann, 1986; Girts, 1986; Bastian and Hammer, 1993; Wieder, 1993). Interest in using wetlands for the remediation of polluted waters (acid mine drainage, sewage, industrial and agricultural runoff) has been increasing because of their natural and economical way of providing a sink for heavy metals, raising the pH, and filtering suspended materials (Hedin, and Nairn, 1990; Brix, 1993; Witthar, 1993; Berezowsky, 1995). Constructed wetlands can retain iron (Stark et al., 1994) and other heavy metals (Mungur et al., 1997), but can be ineffective in controlling acidity of AMD (Mitsch and Wise, 1998).

One favorable geochemical property of wetlands is that they foster bacterial sulfate reduction, which not only removes sulfate, but also increases alkalinity and removes some iron. Sulfate-reducing bacteria use electrons to reduce SO_4^{2-} while oxidizing an organic substrate (Singleton, 1993). The oxidation of organic compounds, using CH_2O as a model, coupled with sulfate-reduction and the precipitation of sulfides is shown in the following equations, where Me^{2+} are metal cations such as Fe^{2+} (Hedin et al., 1989; McIntire and Edenborn, 1990; Bjorn et al, 1996):

$$2CH_2O + SO_4^{2-} + H^+ = 2CO_2 + 2H_2O + HS^-$$

$$Me^{2+} + HS^- = MeS + H^+$$
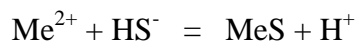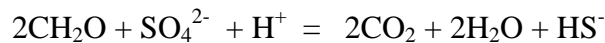
Certain conditions are necessary for significant sulfate reduction in a wetland: (1) absence of dissolved oxygen in the substrate, (2) a source of sulfate, (3) a source of organic carbon, (4) the presence of sulfate-reducing bacteria, (5) a way to physically retain metal sulfide precipitates, and (6) a pH above 5 (Dvork et al, 1992). If it meets these requirements, a wetland should be able to promote sulfate reduction. The acid mine drainage itself provides an abundant source of sulfate; *Typha* wetlands can provide anaerobic conditions, a source of organic carbon, and the sulfate-reducing bacteria. The cattail stalks also provide baffling of water flow and physical retention of metal precipitates.

The critical remaining condition is then a relatively high inlet pH. Current practice is to use an anoxic limestone drain (ALD) ahead of the wetland, which can typically provide a net alkaline water with an initial pH of ~5-6 (Kleinmann et al., 1998). An ALD is a buried bed of limestone capped with clay or plastic to ensure an anoxic system (EPA, 2000). The drainage is intercepted by the ALD before it flows through constructed wetlands. The alkalinity and pH of AMD are increased in an ALD before mine water

enters a wetland and dissolved metals are oxidized and precipitated (EPA, 2000). Keeping the limestone isolated from the atmosphere prevents coating by iron-oxide scale and allows the limestone to continually add alkalinity. Other minerals, however, can still form under these conditions. For example, aluminum oxides are not affected by dissolved oxygen and high Al drainage cannot be treated with the ALD approach because of clogging of the drain by Al compounds. Similarly, the calcium released from dissolution of the limestone can react with the sulfate in the inlet water to produce gypsum, which will again clog the drain.

Although many constructed wetlands have a design life of up to 30 years (Watzlaf et al., 2000), these systems tend to fail prematurely because of the failure of the ALD to sufficiently raise the alkalinity of the mine water. Failure of ALDs may be attributed to clogging of the drains by precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), or of iron or aluminum hydroxides. Hedin and Watzlaf (1994) evaluated twenty-one drains in which large changes in acidity generally resulted from retention of ferric iron and aluminum, which indicated precipitation of iron and aluminum compounds within the drain. Also, sulfate was retained and gypsum was supersaturated at two drains, which received water with more than 4000mg/L of sulfate. Evaluation of ten ALDs over a decade by Watzlaf et al. (2000) identified aluminum hydroxides as clogging agents of the only failed ALD. Robbins et al. (1999) attributed the clogging of two ALDs to the precipitation of iron and aluminum compounds within the drain, combined with low flow rates; however, in one of the clogged drains, gypsum saturation was reached and gypsum crystals formed on submerged calcite. Barton and Karathanasis (1999) also blame the failure of a Kentucky ALD on clogging by aluminum compounds, and attribute sulfate removal to gypsum precipitation.

The formation of gypsum on the surface of limestone when exposed to sulfuric acid has been well documented (Wilkins et al., 2001; Booth et al., 1997; and Hammarstrom et al., 2003). Furthermore, when gypsum coats limestone, the dissolution reaction rate decreases (Wilkins et al., 2001). When calcite, the mineral limestone is mainly composed of, dissolves forming the bicarbonate alkalinity that raises the pH of the mine drainage, calcium released into solution can combine with sulfate already present in AMD to form gypsum. Hammarstom and others (2003) found that a layer of gypsum formed around each limestone particle, between the limestone core and the outer aluminum and iron armor, in a constant flow experiment designed to imitate an ALD. Wilkins and others (2001) also found that as gypsum coverage of calcite became more substantial, calcite dissolution decreased from 0.035 cm/s to 0.004 cm/s when exposed to 0.1M sulfuric acid for 21 hours in channels with flow rates of 0.25-0.0065cm^3/s. So, if gypsum forms and precipitates within the ALD, it may coat the limestone and decrease dissolution rate, which may contribute to failure of the ALD to sufficiently raise AMD alkalinity. An initial gypsum rind on the ALD particles may also enhance later precipitation of Fe and Al compounds.

One way to mitigate this problem may be the use of dolostone instead of limestone as drain fill material. When dolostone dissolves, releasing bicarbonate alkalinity, an equal amount of magnesium and calcium is released into solution. Since the sulfate of

magnesium, epsomite, is very soluble, its precipitation is unlikely. Furthermore, since only half as much calcium is released in dolomite dissolution as in calcite dissolution, the formation and precipitation of gypsum would also be reduced. However, since the EPA (2000) recommends use of a high calcium limestone, and since dolostone is generally thought to react much slower than calcite; dolostone is not used as anoxic drain fill, even though it may increase the longevity of the anoxic drains.

In our previous work on constructed wetlands (Hsu and Maynard, 1999; Flege, 2001), we used measurement of the stable isotopes of sulfur to evaluate the extent of sulfate reduction in three wetlands in Indiana and three in Ohio. We found that only two out of these 6 wetlands was still properly functioning, and one of these has subsequently failed. All of the failures could be traced to a failure to control input acidity, usually resulting from clogging of the anoxic limestone drains.

Midwestern
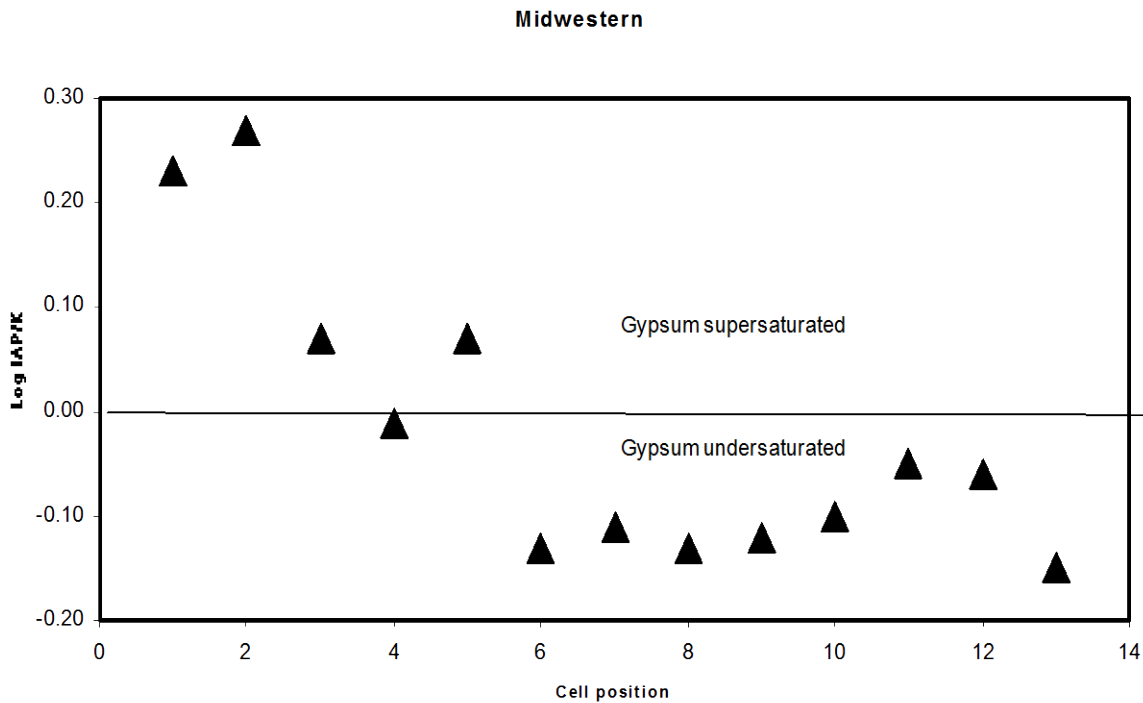
Figure 1. Water in the first few wetland cells is supersaturated with gypsum, indicating that gypsum is a likely precipitate in the ALD. About a third of the way through the wetlands, sulfate has decreased to the point that gypsum no longer can precipitate.

Based on our experience with the Wills Creek Wetland in Ohio and the Midwestern Wetland in Indiana (Hsu and Maynard, 1999; Flege, 2001), a likely source of clogging in Indiana ALDs is solid gypsum. Thermodynamic calculations on the water downstream from the ALDs at the Wills Creek and Midwestern sites showed that gypsum was supersaturated almost everywhere (Figure 1). The presence of gypsum in the soils of the Wills Creek wetland was confirmed by X-ray diffraction. We did not have access to the

ALDs to test directly for the presence of gypsum clogging the drains, but the indirect evidence is strong.

Our earlier work shows that some wetland systems fail in the first 5 years after construction, and that this failure is generally attributable to failure of the anoxic limestone drain. Therefore a knowledge of what mineral precipitates are causing this failure is essential to developing better strategies. There are three classes of likely culprits: Fe oxides and hydroxides, Al hydroxides, and Ca sulfates. The chemical data points to Ca sulfates as the most likely. If so, a change from limestone to dolomite as the fill for the drains might cure the problem. We have tested this hypothesis with excavation of a set of drains to determine which minerals are indeed forming and with a series experiments at the bench scale using two designs: stirred reactors and flow-through columns.

Part I. Field Investigations

In the fall of 2003 we excavated several anoxic limestone drains in Pike County, Indiana that were experiencing flow problems. One set was at the Tecumseh site and one set at Midwestern. The anoxic drains at Tecumseh have not been flowing for several years and the AMD has diverted around the drains directly into the wetlands, where it has severely degraded the vegetation (Flege, 2001). When excavated, the drains at Tecumseh were found to be completely cemented with a white mineral. At the Midwestern site, there are two sets of wetlands that we have referred to as South (studied in detail by Flege, 2001) and North. The South wetland system is functioning normally, but several of the North set are experiencing flow problems. When excavated, these drains proved to be largely free of cementing material and to contain waters with pH values in the 6-7 range. Their flow problems were being caused by precipitation of Al and Fe hydroxides at the exit of the drains.

Investigation of the cementing material at Tecumseh by polarized light microscopy of thin sections shows the dominant mineral to be gypsum with significant amounts of the Fe carbonate, siderite. In Figure 2 we show a thin section photomicrograph with clear white gypsum cementing two pieces of Indiana Limestone, distinguished by the micritic brown peloids.
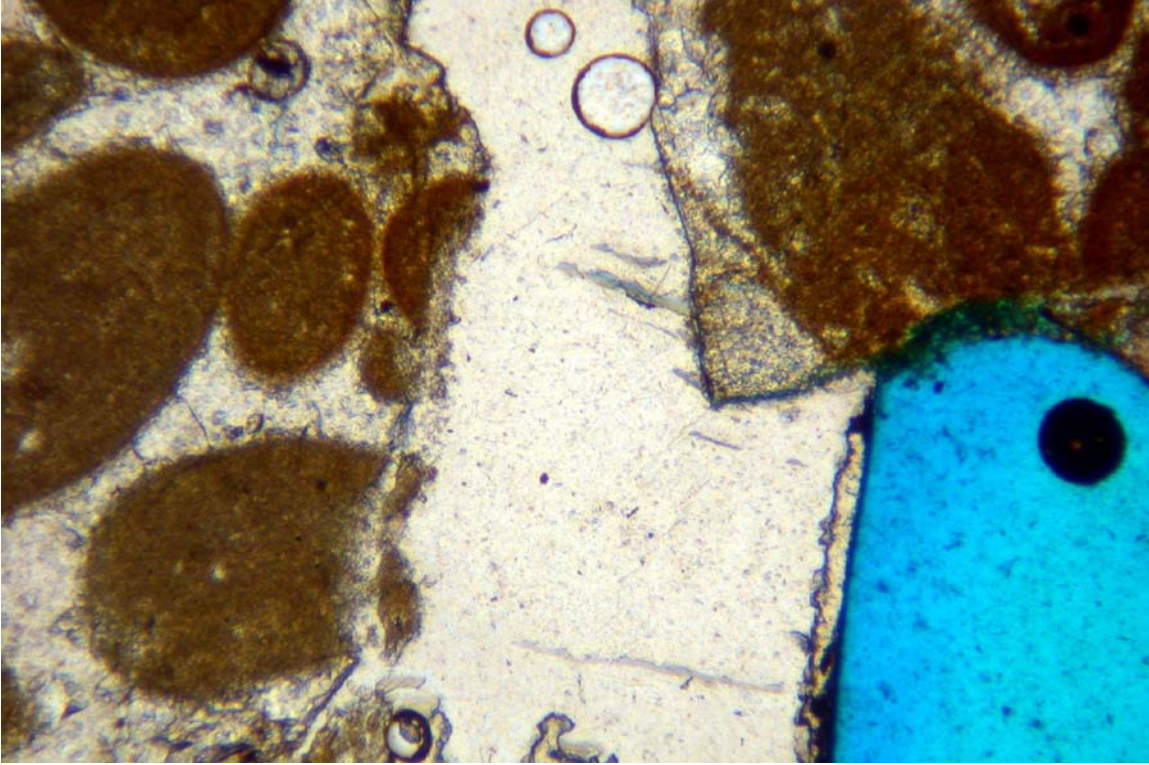
Figure 2. Material excavated from the Tecumseh ALD shows particles of Indiana Limestone (the dark peloidal grains in a finer white matrix) cemented by water-clear white gypsum. The blue is dyed epoxy in which the particles were embedded.
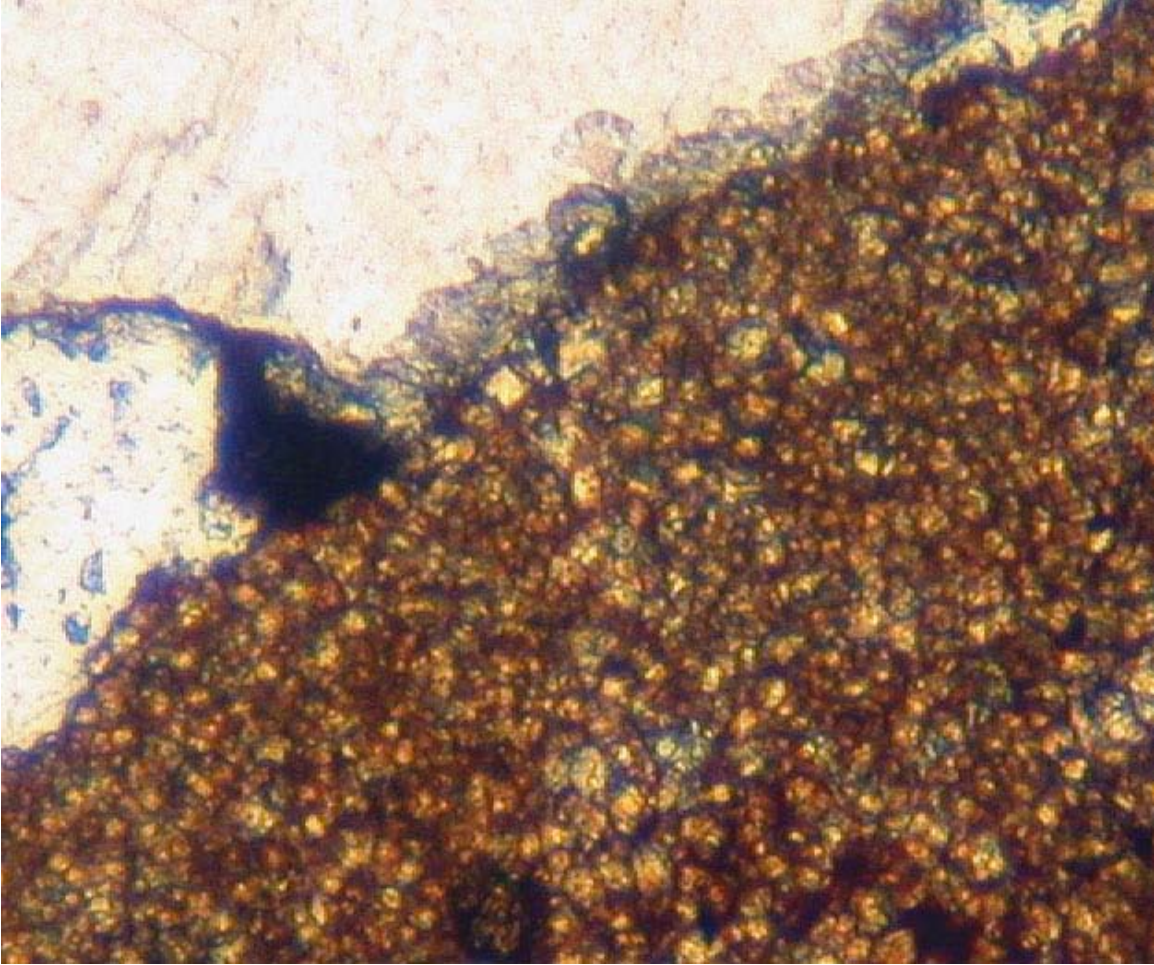
Figure 3. Also present in the cementing material is siderite, $FeCO_3$, the fine brownish crystals. The white mineral at the top is gypsum again.

An important difference in the two wetland systems is that at Tecumseh the ALDs were filled with fine-grained limestone particles, about 1 cm across. These would have a high surface area that would give the drain a faster reaction time for acid neutralization, but also for gypsum growth. At Midwestern, the limestone was in clasts about 20 cm across, and there was minimal growth of new material.

## Part II. Stirred-reactor Experiments

A series of batch experiments were undertaken in which limestone and dolostone particles were stirred in a sulfuric acid solution and the reaction progress monitored. These experiments differ from field conditions in having much higher water-to-rock ratios. On the other hand, they offer the advantage of greater simplicity and manageability of conditions, which allows for unambiguous determination of critical parameters.

Materials

Limestone was obtained from Liter's Quarry in Clark County, Indiana and dolostone was obtained from Melvin Stone Quarry in Clinton County, Ohio (Maynard et al. 2000). Limestone and dolostone rock were evaluated by X-ray diffraction and X-ray fluorescence to verify that they were mainly composed of calcite and dolomite, respectively. Batches of the quarry run material were sieved to constant grain size range and then washed repeatedly with distilled water until no cloudiness resulted. Figures 4 and 5 illustrate the microscopic characteristics of the two rock types. Note that the Melvin dolostone comprises dominantly dolomite, but also has some calcite present, whereas the Liter limestone comprises entirely calcite.

calcite   Shell fragment

10 μm
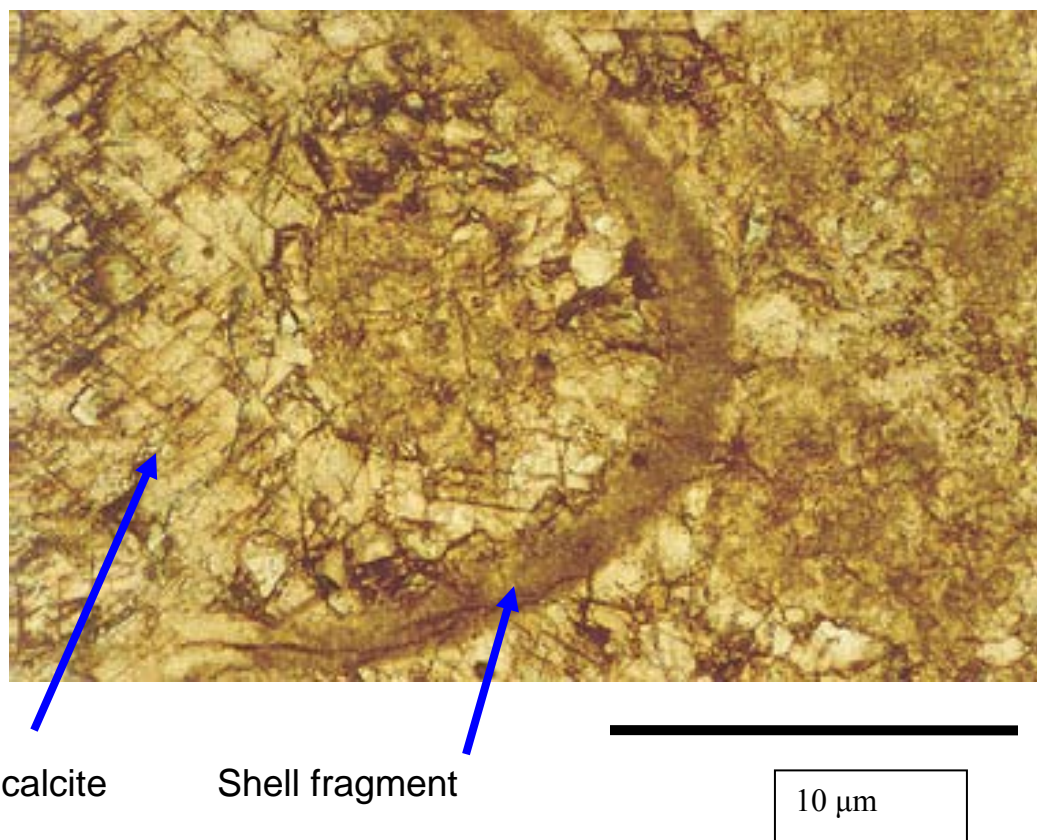
Figure 4. Typical limestone from the Liter Quarry
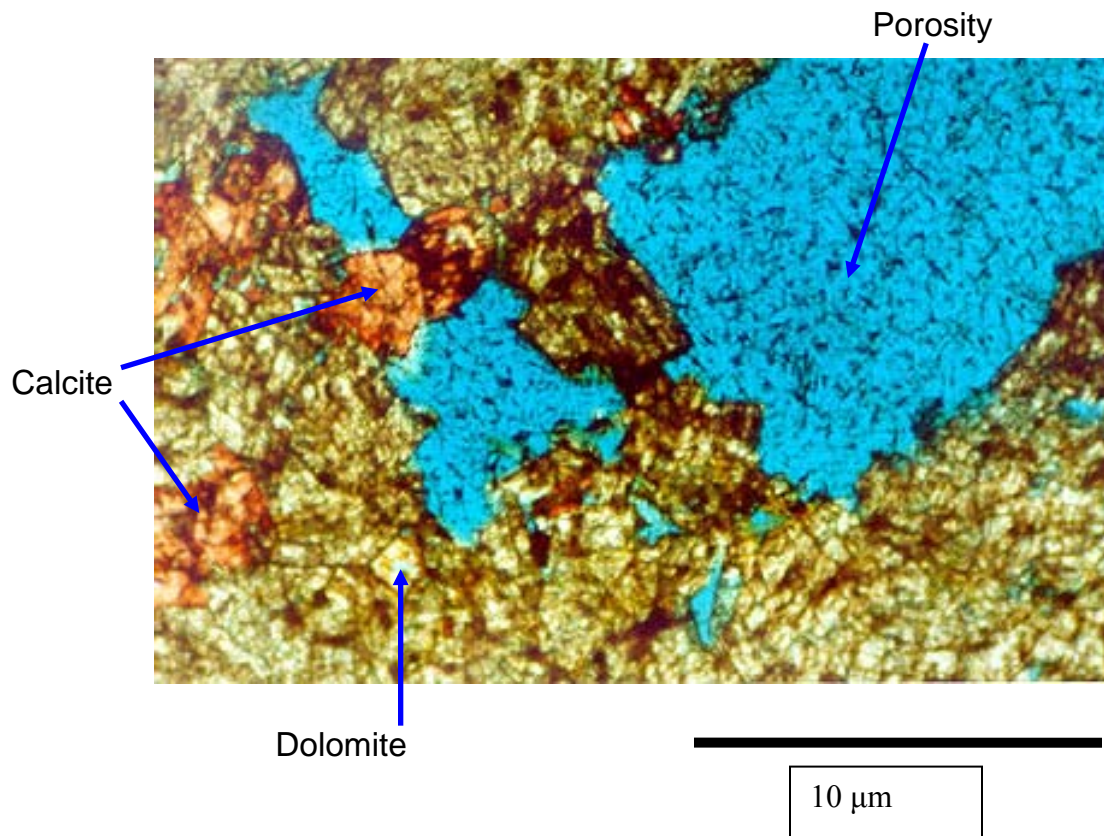
Figure 5. Typical dolostone from the Melvin Quarry. Note the large amount of primary porosity.

Experimental Conditions

The experiments were performed in two double-walled reaction vessels connected to tap water to control temperature (Figure 6). Limestone and dolostone of various average grain sizes (390 μm, 630μm, 920μm, and 1210μm) were reacted with sulfuric acid at a starting pH of 1.5. For most runs, 0.79 g of rock were reacted in 500 ml of solution, giving a water/rock ratio of 1700 to 1800 v/v. Although stirring rate was held constant for all experiments, one reaction vessel had a flatter bottom than the other, producing a difference in effective agitation. The resulting reaction rates were different, and below we distinguish these two designs as the round and the flat reaction vessel (Figure 6). pH, conductivity and temperature were monitored during each experiment. pH was measured with a Corning pH meter and Fisher combination pH electrode with Ag/AgCl reference. Conductivity and temperature were measured with an Orion conductivity meter. After each batch experiment, the solution was filtered through cellulose nitrate membrane filers (0.45μm), and the filtrate and solution were analyzed for sulfate and for Ca, Mg, and Fe concentrations.

Figure 6. Experimental set-up for batch experiments. pH and conductivity continuously monitored. Flat vessel on the left and round vessel on the right.

Analytical Methods

X-Ray Fluorescence (XRF). Unreacted samples of limestone and dolostone were analyzed by XRF using a Rigaku 3070 spectrometer, located in the Department of Geology, University of Cincinnati. Samples of the raw limestone and dolostone were ground in a ball mill and pressed with a binding agent (polyvinyl alcohol) before analysis.

X-Ray Diffraction (XRD). Minerals were identified by XRD using a Siemens D500 X-ray diffractometer. The samples of unreacted limestone and dolostone prepared for XRF were also used for XRD analysis. The filtrate from final batch experiments was also analyzed by XRD. All Step scans were run over a 2-θ the range of 10°-55°, with a 0.05^o interval and a 1.0 second count time. Patterns were interpreted with tables of lines in X-ray diffraction from two sources (Chen, 1977; Brindley and Brown, 1980).

Atomic Absorption. Acidified solute from batch and vertical column solutions were analyzed by atomic absorption. Samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}) and iron (Fe^{2+}) using standard methods (APHA, 1995).

Dissolved Sulfate. Acidified solute final batch and vertical column solutions was analyzed by the gravimetric method as described in standard methods (APHA, 1995).

Results and Discussion

Figure 7 is a plot of pH versus time of limestone and dolostone of the same particle size reacted in the round reaction vessel. The overall reaction rates of the limestone and dolostone are very similar, both beginning at pH 1.5 and reaching a pH of 6 at about 100 minutes. Initially, however, limestone reacts faster. Figure 7 shows that the dolostone reaction has a lag of about 50 minutes, after which it proceeds at a rate similar to the limestone. On the 15 hour time frame of an ALD, it is safe to say that the two materials have the same reaction rate and raise the pH to the same final level.
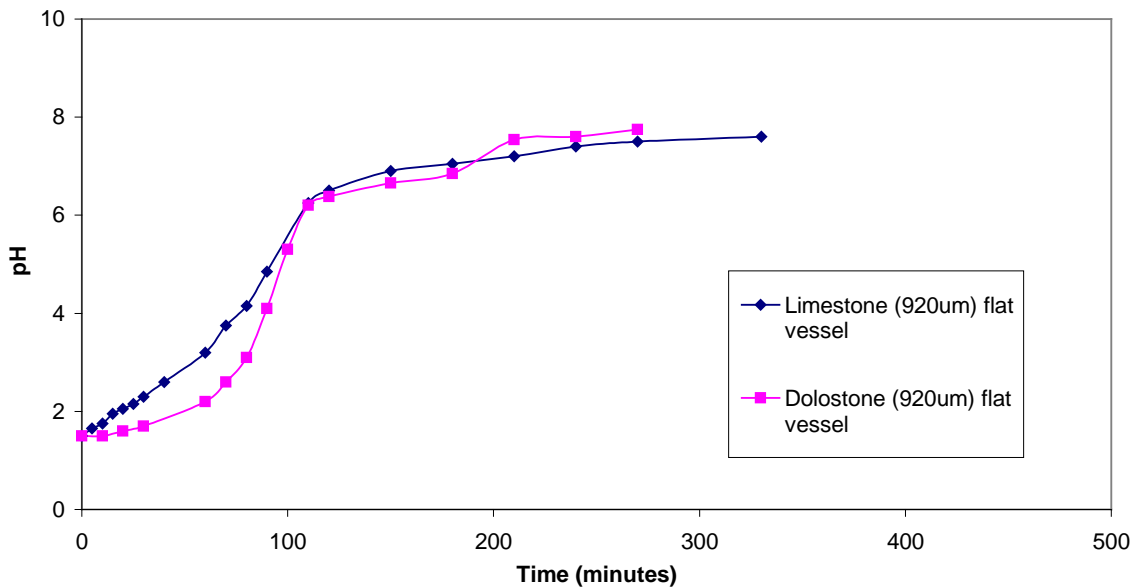

Figure 7: pH versus time (minutes) of limestone and dolostone batch experiments with a grain size of 920μm, reacted in flat-bottom reaction vessel.

We discovered that reaction rates were different in the two vessels for dolostone, but not for limestone. Figure 8 is a plot of pH versus time of limestone and dolostone of the same particle size reacted in the flat reaction vessel and the round reaction vessel. The two limestone experiments follow a very similar course, suggesting that the limestone reaction is largely independent of stirring conditions. However, this was not the case for dolostone. Dolostone dissolution proceeded much faster in the flat cell than it did in the round cell, although the initial rate is still slower than that for limestone. It was observed that stirring was more thorough in the flat vessel so that particles stayed in suspension better.
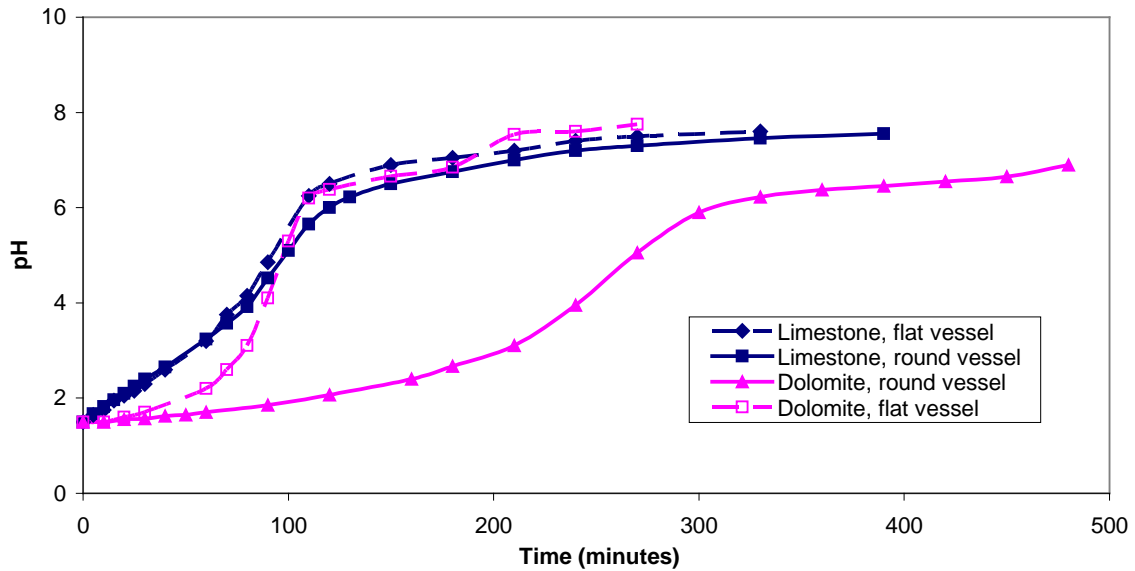
Figure 8. Effect of vessel shape on dolostone and limestone reaction rates

Batch experiments were also performed to compare reaction rates among various particle sizes. Figure 9a is a plot of pH versus time for dissolution of limestone of three different particle sizes (390 µm, 630µm, and 920µm), reacted in the round reaction vessel. The reaction rates decrease with increasing particle size (and thus decreasing specific surface area). Figure 9b compares dolostone of the same three particle sizes, also reacted in the round vessel. Again, the reaction rates decrease with increasing particle size, but the difference in reaction rate between the small particle size and the large particle size is much more pronounced.
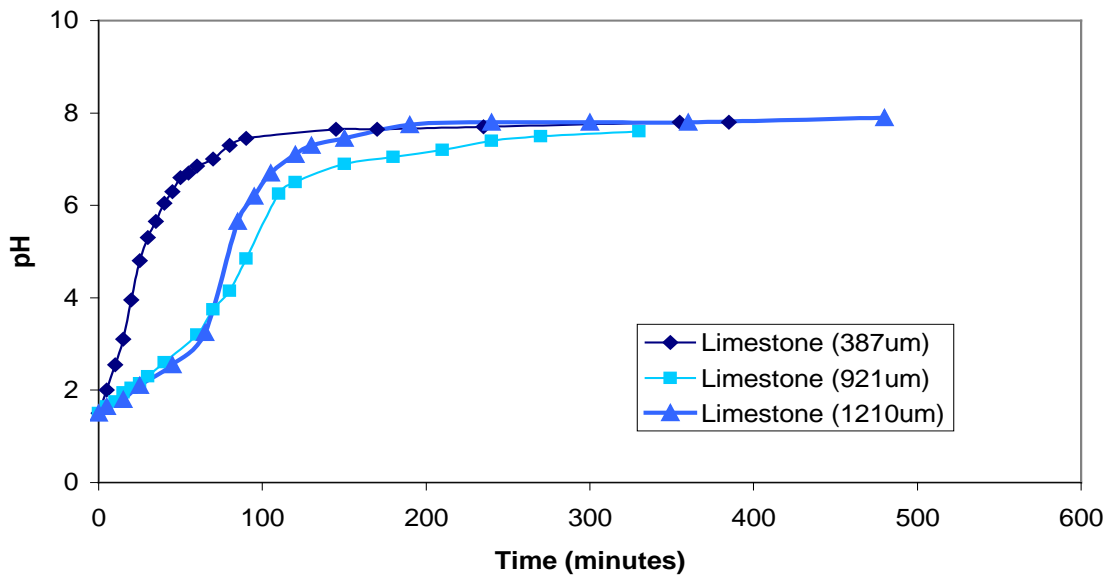
Figure 9a. Effect of grain size on limestone reaction rates
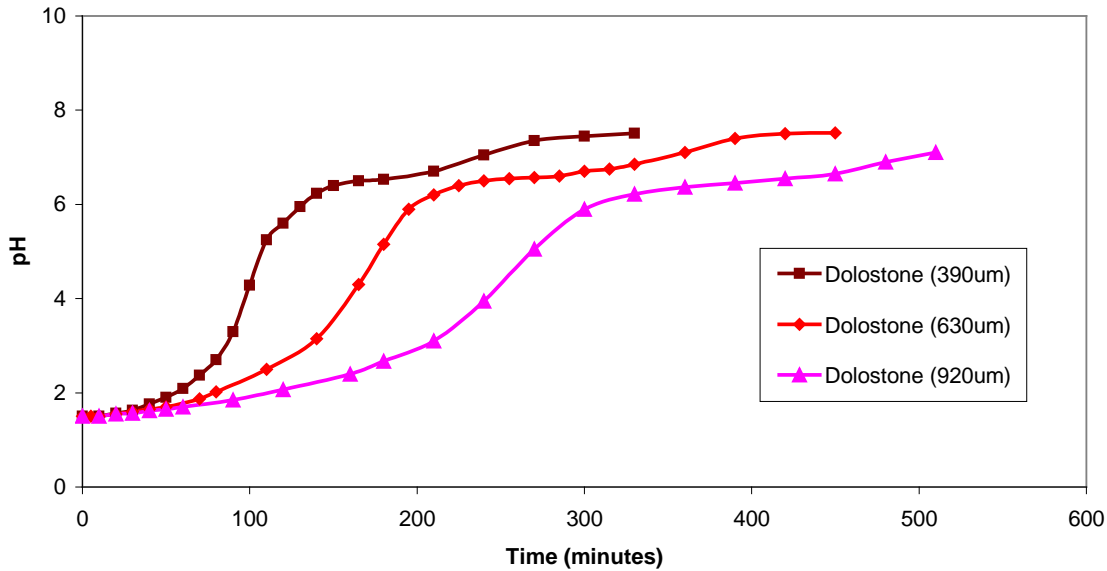
Figure 9b. Effect of grain size on dolostone reaction rates

Discussion of the Stirred-reactor results

These batch experiments show that the reaction rates of limestone and dolostone are not appreciably different in the context of contact time in an anoxic drain system. However, the distinct shapes of the reaction curves indicate that the reactions are controlled by different reaction mechanisms. For all carbonate minerals dissolving at low pH, far from equilibrium, the rate of reaction is thought to be controlled by diffusion through a layer of still water at the grain surface (Morse and Arvidson, 2002). The nature of this layer may, however, be different for the two rock types. For example, previous research has shown that dissolution of dolomite is more complicated than dissolution of calcite (Chou et al., 1989). Topography develops on dolomite mineral surfaces when dissolution takes place in solution at low pH, so surface area may increase with reaction progress (Gautelier and others, 1999). In our experiments, the dolostone surface became rougher and more pitted after partial reaction, but the surface of the limestone became smoother. So, surface roughness increased for the dolostone but decreased for the limestone. We suggest that stirring rate has a much stronger effect on the stagnant surface layer on the rough dolostone particles than it does on the smoother limestone particles. Hence the strong effect of reaction vessel shape for the dolostone but not the limestone dissolution and also the much greater influence of grain size on dissolution rate for the dolostone.

Conclusions

The stirred reaction vessel experiments clearly demonstrate the similarity of the overall limestone and dolostone reaction rates. A pH of between 6 and 7 is achieved by 400 minutes in all of the runs. However, the reaction vessel experiments also suggest that the reaction mechanism for limestone and dolostone is different: dolostone is more sensitive to the degree of agitation and to variation in grain size. The implication for ALD design is that dolostone is equally effective at acid neutralization as is limestone on the time scale of hours.

Part III. Column Experiments

A second set of experiments were performed in vertical columns packed with limestone or dolostone particles (Figure 10). These experiments were designed to test the relative behaviors of the two rock types at low water/rock ratios more typical of ALDs. For these experiments, the sulfuric acid solution (pH 1.5) was poured into the column to just cover the particles. After various reaction times, the solution was drawn off the bottom of the column and analyzed. The porosity of the sediment plug in these columns is 35%. Thus the water/rock ratio (v/v) is 35/65 or 0.54. Other analytical conditions were the same as for the stirred reactor experiments.

We used five limestone and five dolostone columns. Each pair of columns was designed to observe the reactions of limestone and dolostone in a sulfuric acid solution (pH=1.5) and to analyze possible precipitates formed by adding sulfate, aluminum and iron in concentrations similar to those found in acid mine drainage in SW Indiana. However, the experiments were not designed to exclude dissolved oxygen. That is, these systems are not anoxic, whereas functioning ALDs are. The neutralization reaction proceeds much faster under these conditions, and pH values > 6 were achieved after only 10 minutes of reaction time.

Materials and Methods
Two sets of glass cylindrical columns were set up, one with limestone and one with dolostone. The columns contained the same volume of limestone (volume=30ml, mass=39.072grams) and dolostone (volume=30ml, mass=39.518grams). Porosity for the limestone and dolostone set-ups was approximately 35%. Sulfuric acid solution (pH=1.5) was poured into the glass columns over the rock, drained and replaced every 22 to 26 hours, which is comparable to the normal 15-hour detention time for ALDs. Final pH was measured each day and effluent solution was collected and analyzed for Ca^{2+}, Mg^{2+}, SO_4^{2-}, and alkalinity once a week.

Five solutions were used in these experiments, in which additional concentrations of sulfate, iron or aluminum were added to the sulfuric acid solution (pH=1.5) before it was poured over the limestone and dolostone. These were:

1)   sulfuric acid in water (pH = 1.5)
2)   2500mg/L of added sulfate
3)   2500mg/L of sulfate and 500mg/L of ferrous iron
4)   2500mg/L of sulfate and 20mg/L of aluminum
5)   2500mg/L of sulfate, 500mg/L of ferrous iron, and 20mg/L of aluminum.

Additional sulfate was added using sodium sulfate (Na_2SO_4). Iron and sulfate were added as iron ammonium sulfate ($Fe(NH_4)_2(SO_4)2*6H_2O$). Aluminum was added as aluminum nitrate ($Al(NO_3)_3*9H_2O$). The final influent solutions were adjusted back to a pH of 1.5 using hydrochloric acid.

Figure 10. Experimental set-up for column experiments.

Alkalinity was measured by the standard potentiometric titration method (APHA 1995) to a pre-selected pH of 4.3 using 0.01N HCl as a titrant. Effluent was analyzed for sulfate once per week by the standard gravimetric method of drying of residue from $BaSO_4$ precipitation (APHA 1995). To remove interference by ferrous iron in the barite precipitation, iron was first removed by precipitation using sodium hydroxide in those setups that used added iron. Then, the pH of the effluent of these treatments was readjusted to < 4 using nitric acid to eliminate any possibility of $BaCO_3$ precipitation during the sulfate analysis. Mg2+ and Ca2+ levels in the solutions were measured by Atomic Absorption Spectroscopy at Brookside Labs, New Knoxville, OH.

**Results and Discussion for Column Experiments**
For every case, dolostone outperformed limestone over long time periods. Figures 11a-e display the results for the various solutions as pH versus time in cycles. One cycle (22 to 26 hours) is roughly equivalent to the design detention time of acid mine drainage in an ALD, which is usually 15 to 20 hours according to Watzlaf et al (2000).

In the simplest experiment, with only sulfuric acid, the limestone and dolostone behavior is identical (Figure 11a), and both columns were still functioning after 180 cycles. This system is far from the field compositions, however, because acid mine drainage has much higher total sulfate and also contains appreciable Fe and Al. The subsequent experiments

(Figure 11b-e) were designed to test each of these components separately and then in combination.


a.

b.

c.

d.
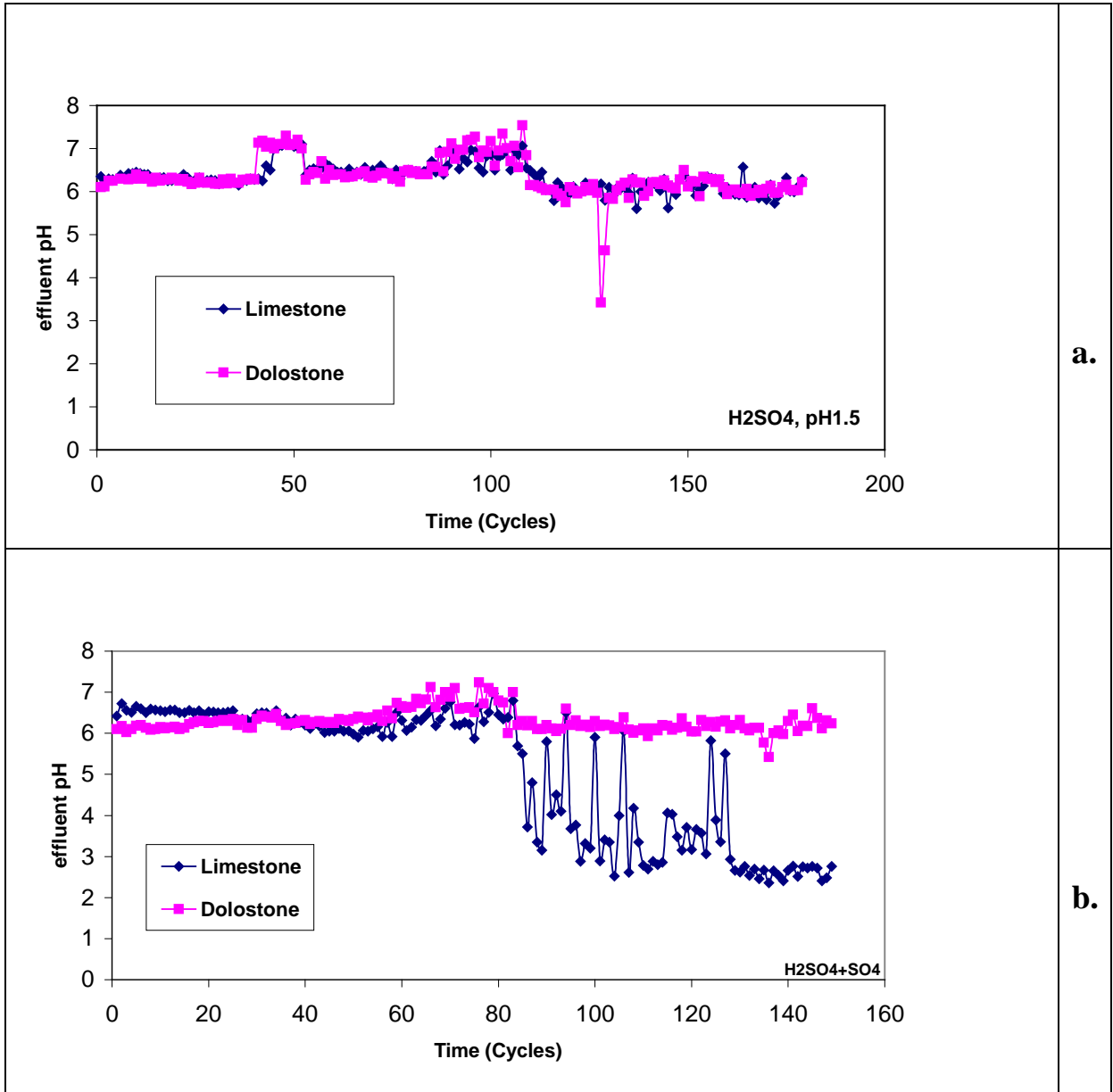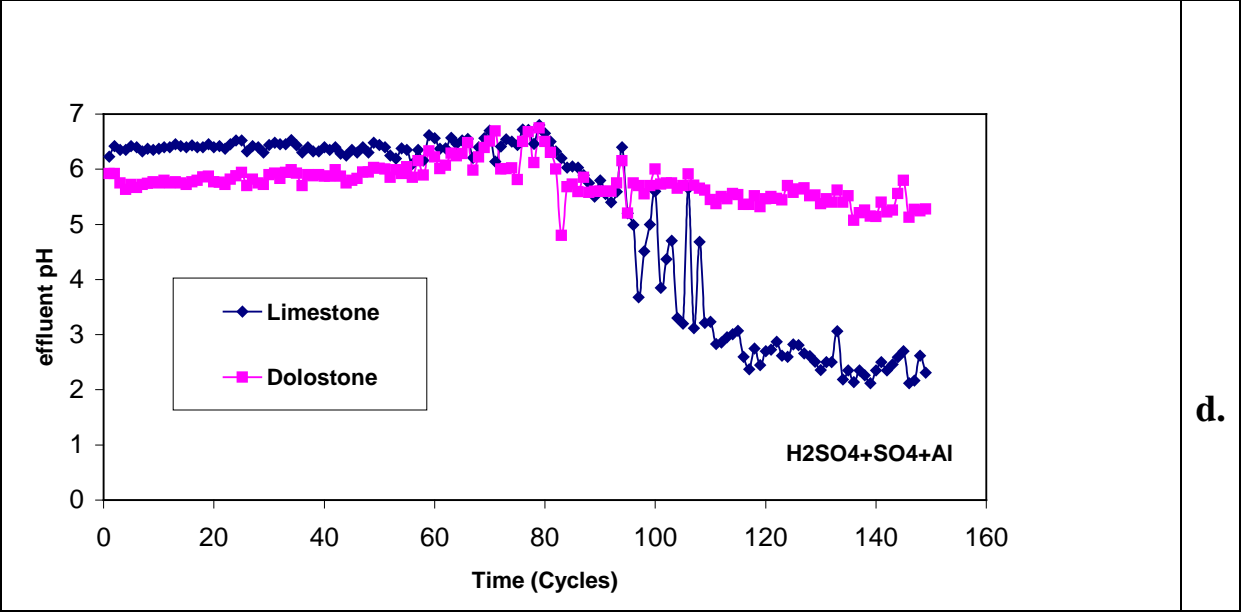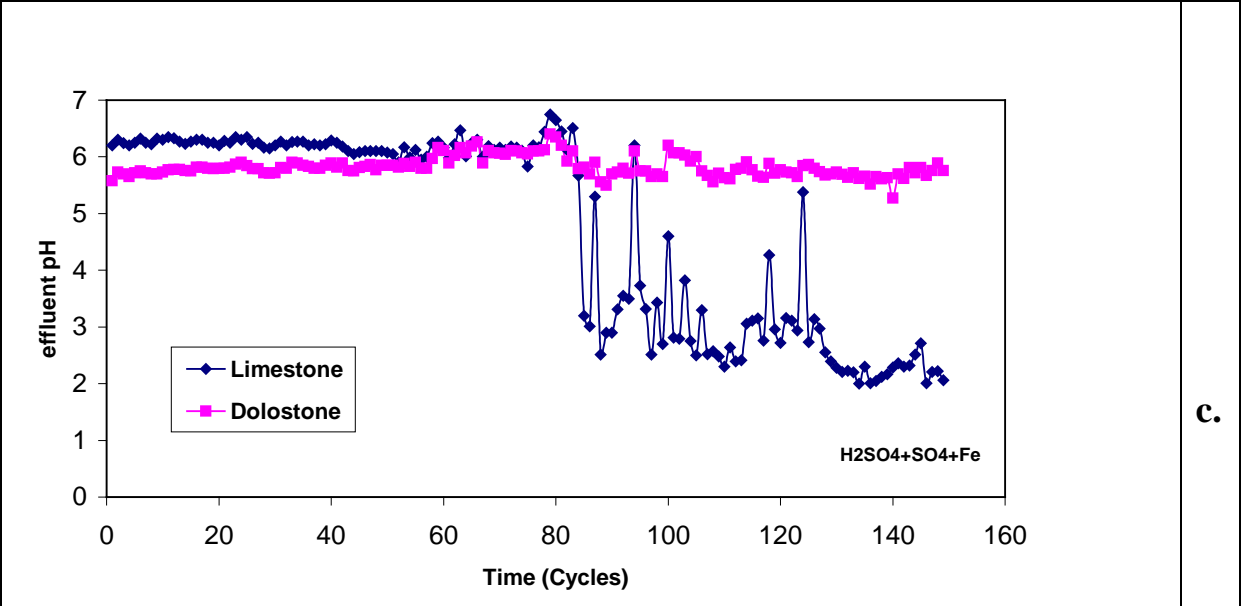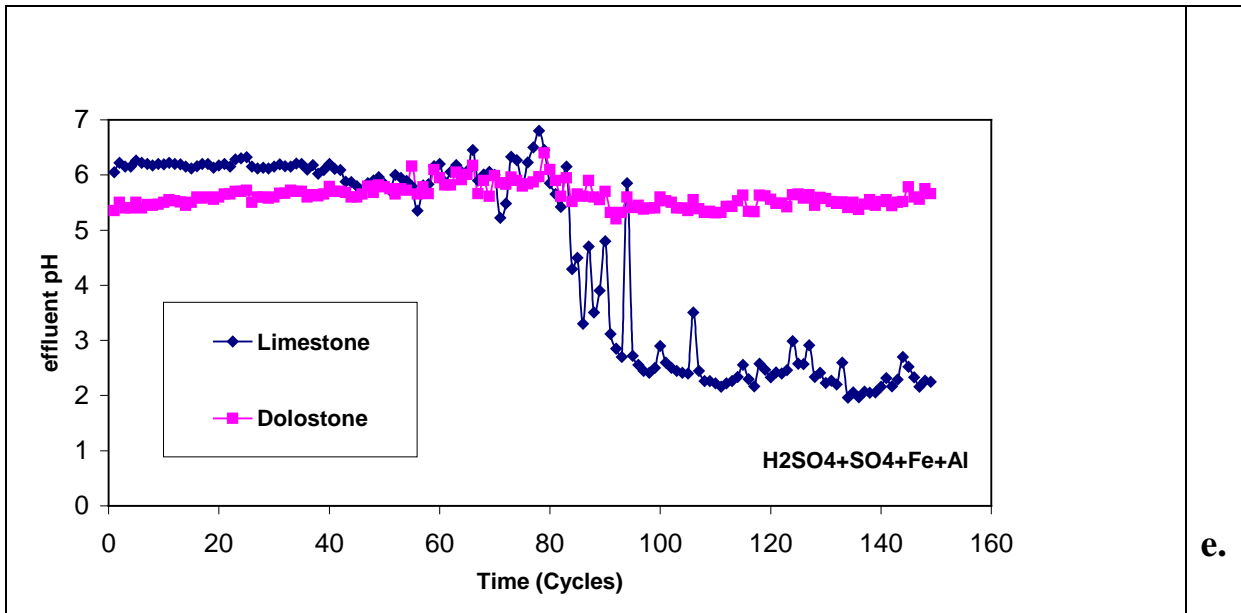
Figure 11. Time progression of reaction of limestone and dolostone packed columns with synthetic acid mine drainage of varying compositions

For the simple sulfuric acid solution (Figure 11a), the limestone and dolostone systems reach approximately the same pH almost immediately. In contrast, the other experiments show that as additional sulfate, iron and aluminum are added, the ability of dolostone to raise the pH to the same levels as limestone is decreased in initial cycles (Figure 11b-e). Over time, however, the ability of dolostone to increase pH improves. Somewhere between 40 and 60 cycles there is in every case a cross-over point beyond which dolostone is superior in acid neutralization. At 80 to 90 cycles, each of the limestone experiments began to exhibit failure.

The same behavior can be seen in measurements of alkalinity, the prime parameter for evaluation of wetland performance. For most experiments, alkalinity generation was initially higher for limestone, but fell steadily. Figure 12 is typical. Effluent alkalinity from the limestone column declines linearly, ending with zero alkalinity generation by cycle 85. Dolostone, by contrast, maintains a steady, albeit lower alkalinity generation throughout the course of the experiments.
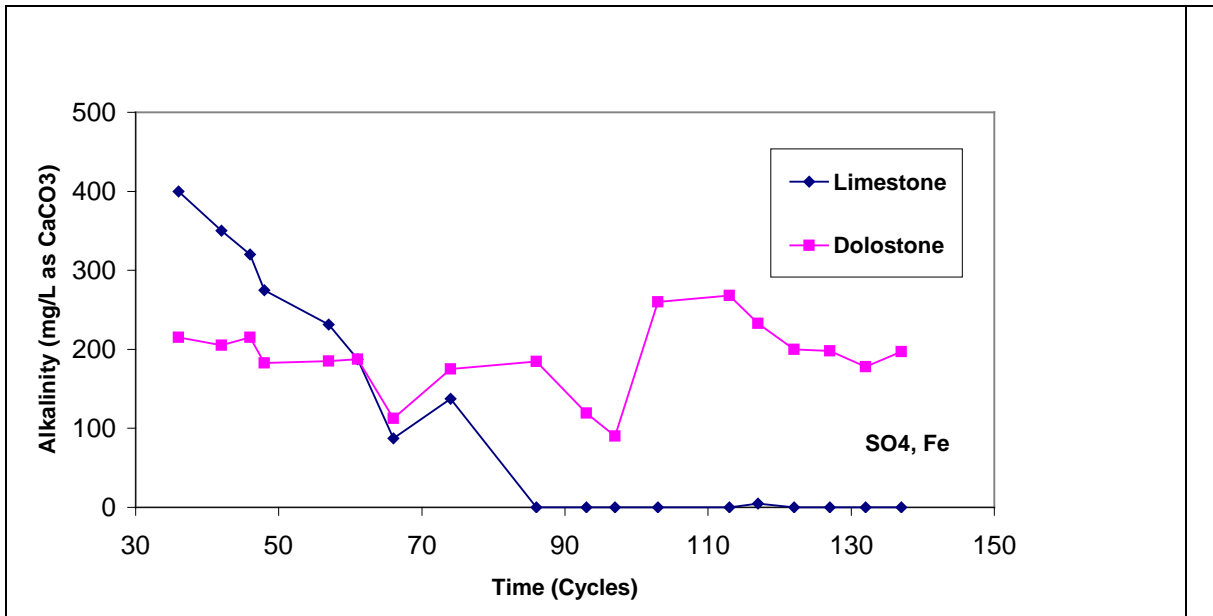
Figure 12. Effluent alkalinity for limestone and dolostone compared.

Insight into the mechanism of these failures can be gained by examining effluent sulfate concentrations. In each case, effluent SO_4^{2-} is higher for the dolostone than for the limestone, which indicates that a sulfate mineral is forming within the limestone columns. A comparison of input and output SO_4^{2-} shows that there is significant retention within both the limestone and the dolostone, but that the amounts are greater in the limestone (Figure 13). To save space we only show one example, but the other runs are similar.

The amounts of sulfate retained in the limestone columns are invariably greater than the amounts retained in the dolostone columns (Table 1). Retention is greatest in the SO_4^{2-} only experiments. The much lower retentions for the Fe + SO_4^{2-} and the Al + SO_4^{2-} experiments suggest that a protective layer of Fe or Al hydroxide forms on the particles that partially blocks the attachment of gypsum to the limestone or dolostone particles. The mixed Fe + Al + SO_4^{2-} experiment, which is closest to the field composition of AMD, approaches the pure SO_4^{2-} case in the amounts retained. It would appear that the protective Fe and Al layers do not form as easily in this more complex solution.
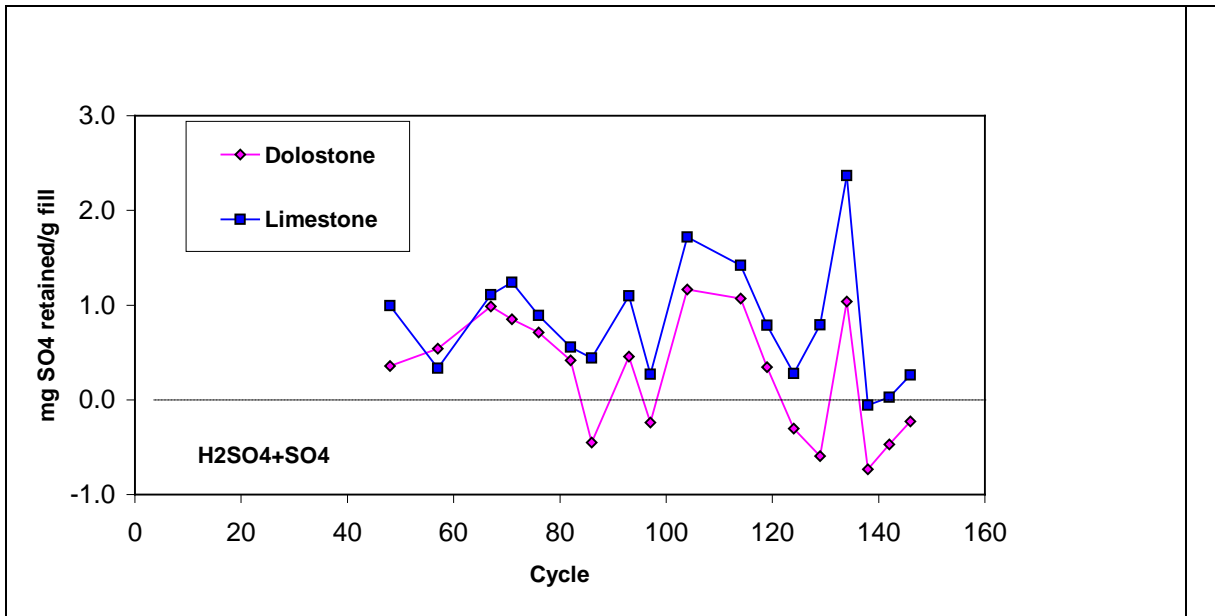
Figure 13. Mass of SO_4^{2-} retained by dolostone and limestone columns per gram of fill particles.

Table 1. Amounts of sulfate retained in column experiments		
Experiment	Limestone	Dolostone
	SO_4^{2-} accumulated (mg/g fill)	SO_4^{2-} accumulated (mg/g fill)
H_2SO_4, pH 1.5	56.8	12.5
$H_2SO_4 + SO_4 + Al$	78.3	6.1
$H_2SO_4 + SO_4 + Fe$	86.5	12.2
$H_2SO_4 + SO_4 + Fe + Al$	120.5	36.3
$H_2SO_4 + SO_4$	133.1	57.2

Insight into the dissolution of the limestone and dolostone particles in the columns can be gained from plots of Mg^{2+} and Ca^{2+} through time. On a molar basis, Mg and Ca are about equal in release rates (Figure 14a), demonstrating that there is no preferential attack on the Ca sites in the dolomite mineral and that dissolution is congruent. The release of Ca from dolostone is about equal to the release rate from limestone (Figure 14b). Because equal moles of Mg are also being released from the dolostone, the release of cations is much greater from the dolostone and therefore the acid neutralization is greater. We attribute this to a surface area effect. The dolostone particles were found to have considerable internal porosity when studied in thin section, whereas the limestone particles are solid. This internal porosity would contribute considerable internal surface

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area, so total surface area is much greater for the dolostone compared with the limestone despite their identical particle sizes. This factor provides an additional advantage to the use of dolostone, because this greater porosity is typical, and would contribute to faster reaction rates for dolostones.


a

b
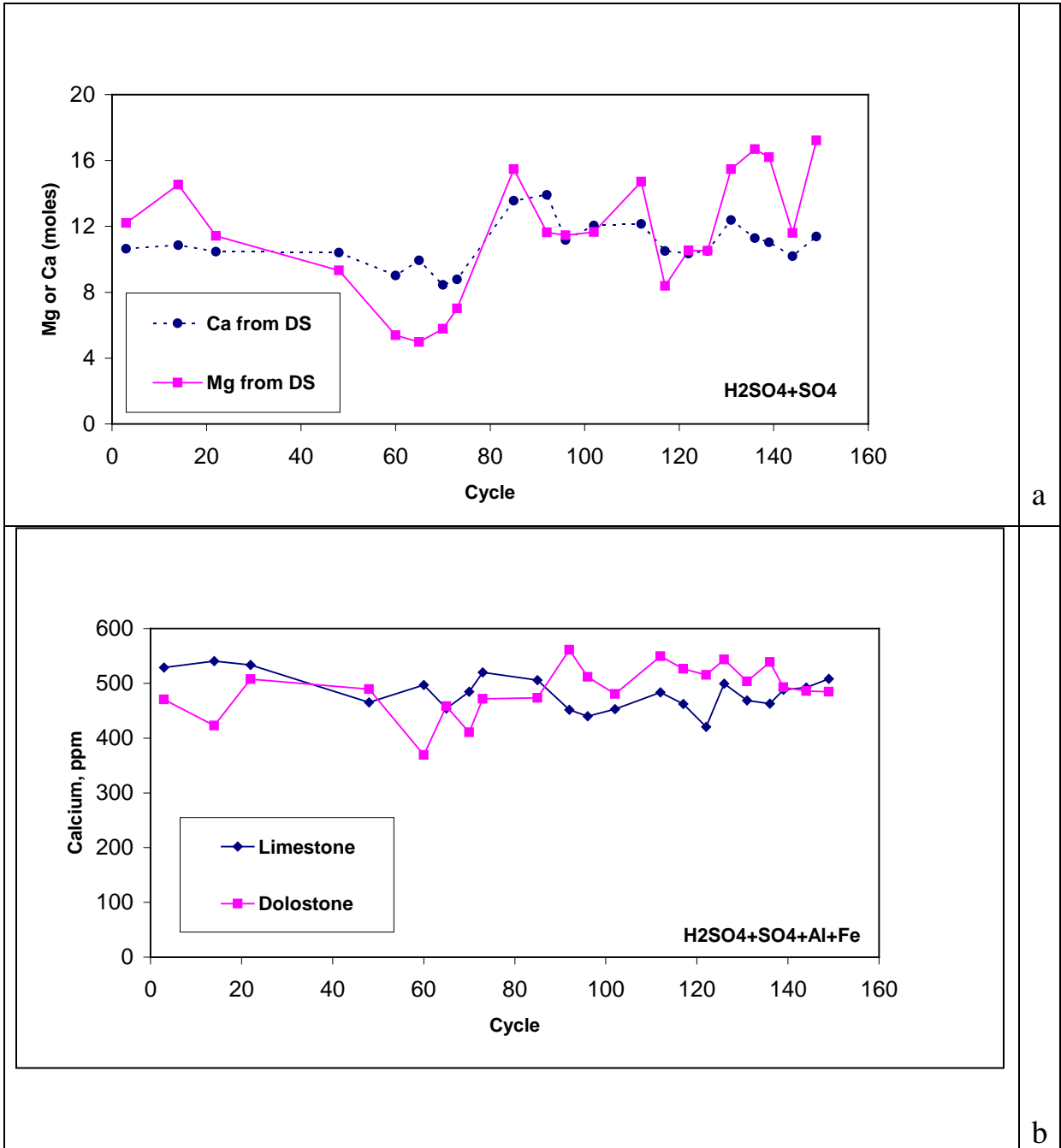
Figure 14. Release of Mg^{2+} and Ca^{2+} from dolostone (a) and release of Ca^{2+} from limestone compared with dolostone (b).
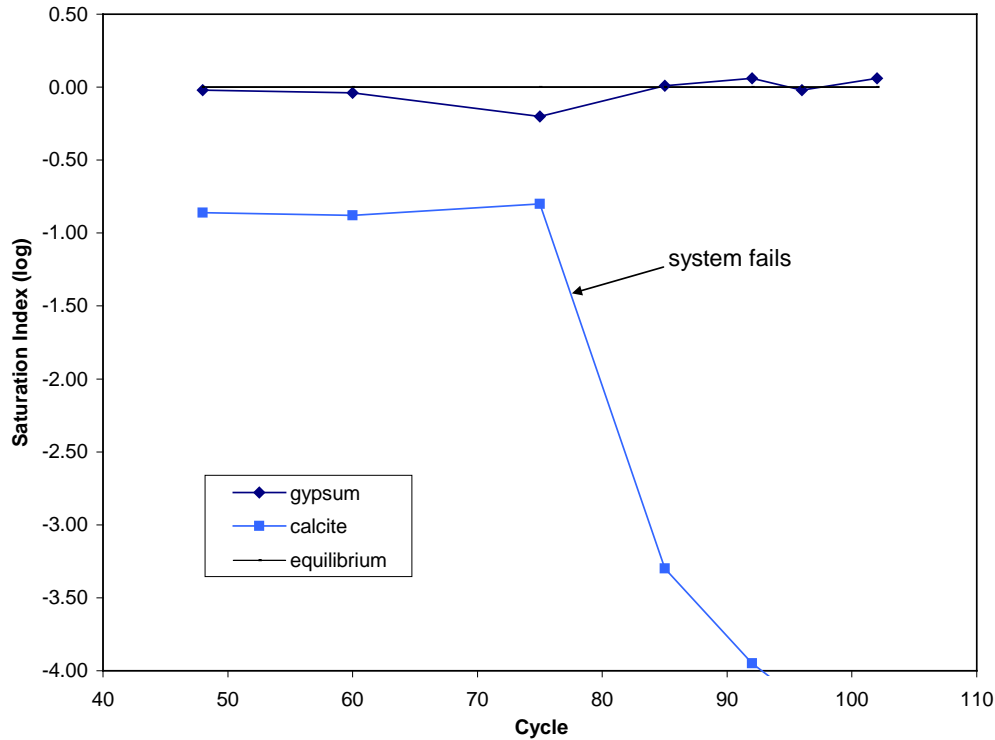
Saturation state

The degree of saturation of the solutions with respect to various minerals of interest can be estimated by the use of computer codes such as PHREEEQC (from the US Geological Survey). This code generates an equilibrium model for solution species and shows which minerals are likely to precipitate (Saturation Index greater than zero) and which are likely to dissolve (Saturation Index less than zero).

In all of the column experiments, solutions approached gypsum supersaturation after minimal contact time. In Figures 14 and 15 we show the results for the experiments with SO_4^{2-} added, which are representative. Figure 14, for dolostone, suggests that the column began precipitating gypsum after cycle 80. At this point the amount of dissolution of the dolomite constituent in the rock began to diminish somewhat because of armoring, but still continued.
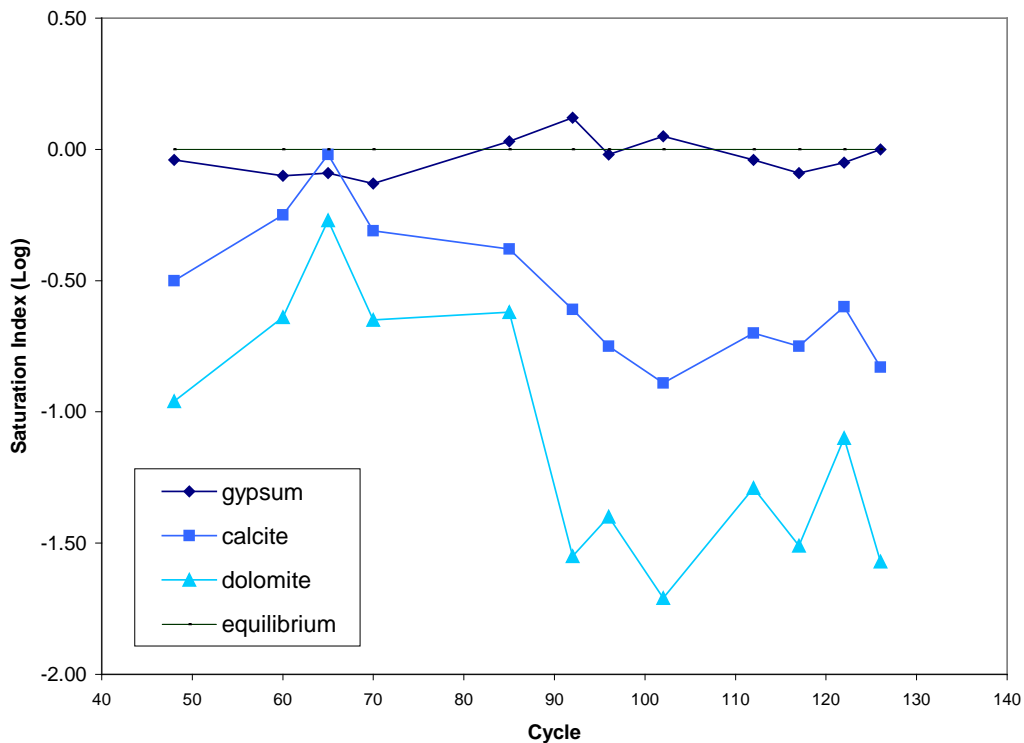
Figure 14. Saturation state of the dolostone column in the SO_4^{2-} added experiment as a function of time.

Figure 15, for limestone, shows gypsum saturation throughout, and furthermore that calcite dissolution ceased at about cycle 80. Thus both columns should have some gypsum precipitation, but it should be far more extensive in the limestone case, extensive enough to plug the pores of the fill and lead to column failure.

Figure 15. Saturation state of the limestone column in the SO$_4^{2-}$ added experiment as a function of time.
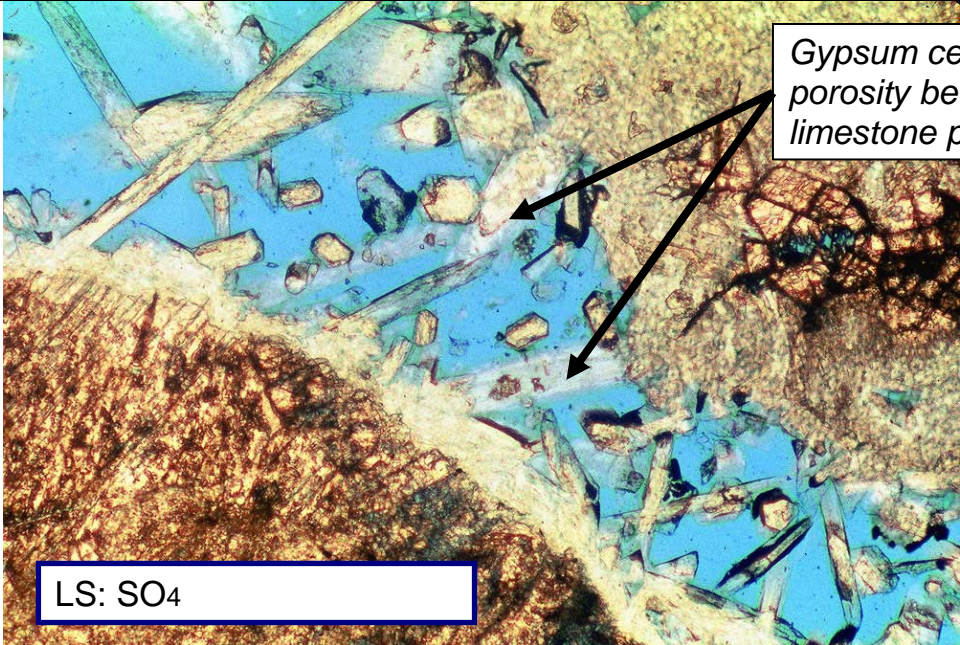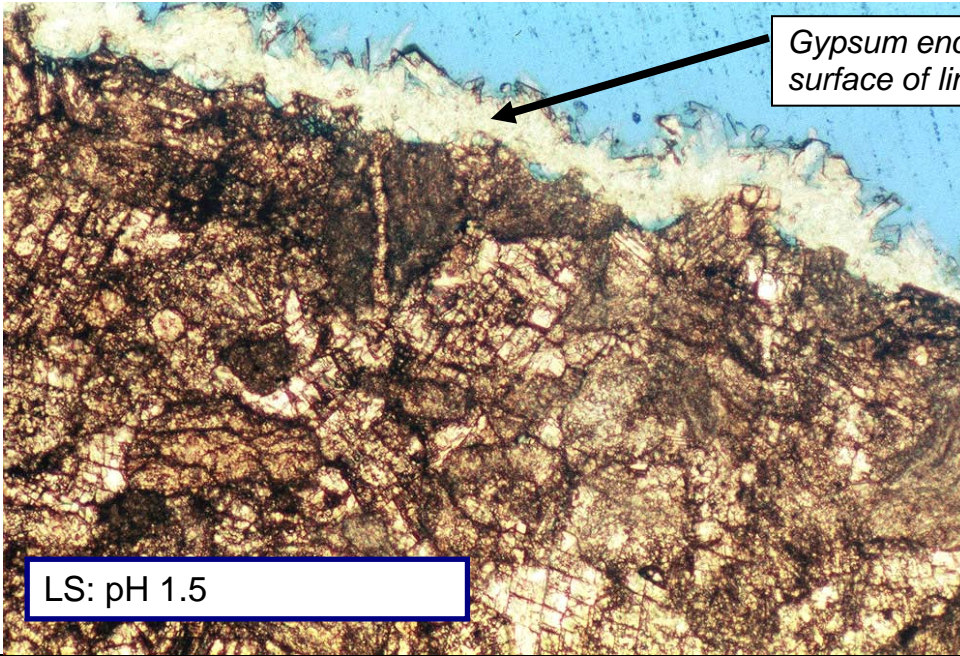
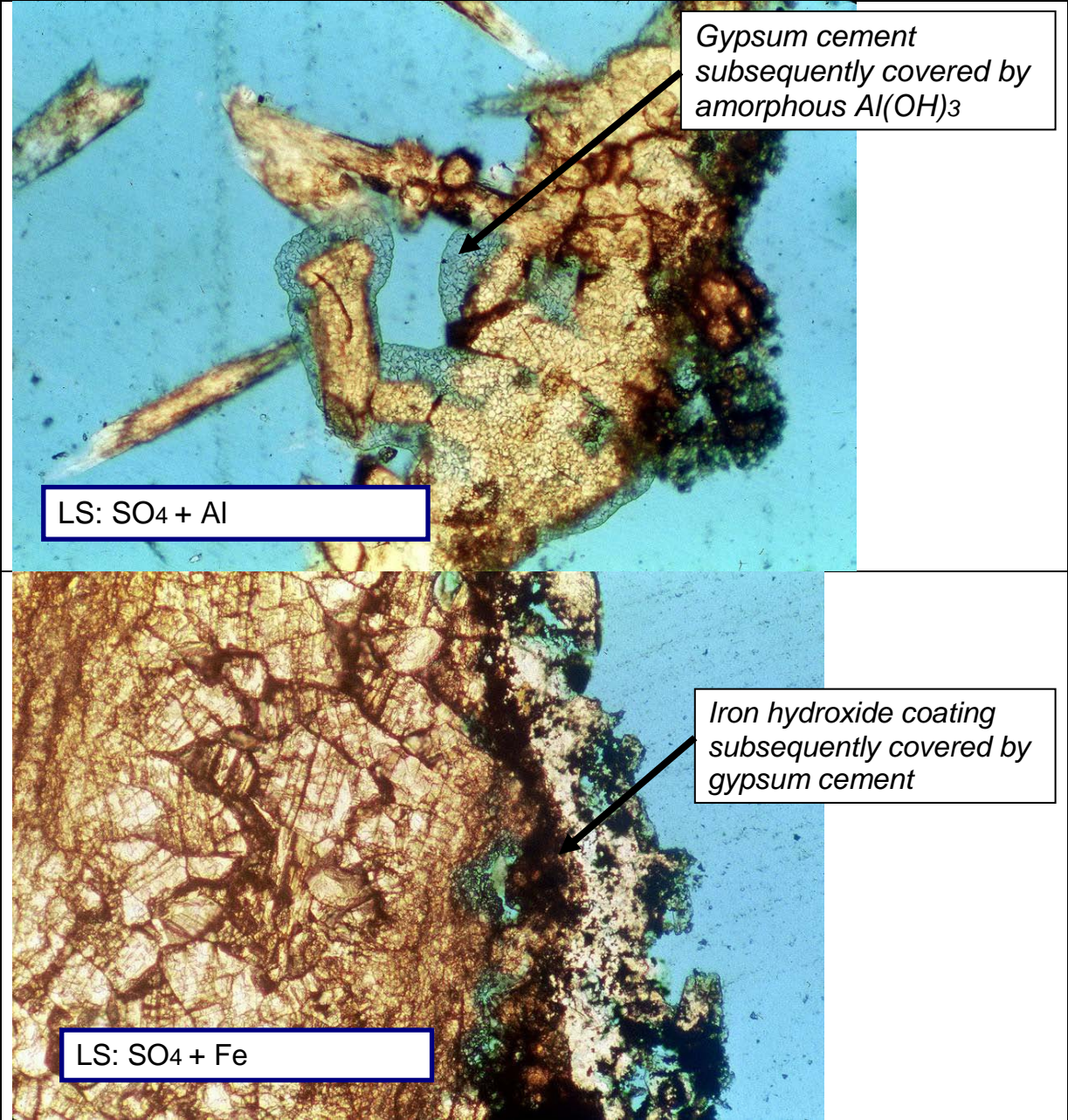<u>**Examination of Fill Material at the End of the Column Experiments**</u>
To test these interpretations, we made petrographic thin sections of the fill material at the end of the experiments. All of the limestone experiments, except the simple sulfuric acid set up, had experienced cementation, which converted the loose fill into a rock-like mass. None of the dolomite runs exhibited cementation. In Figures 16 and 17 we show a series of thin-section photomicrographs of the run products. In each case, gypsum development is far more extensive for the limestone than for the dolostone. All of the limestone runs developed thick gypsum coatings on the fill material grains and some showed bridging between the grains by gypsum. In other cases, there was intense replacement of the limestone by gypsum. When iron was present in the synthetic AMD, a coating of iron oxide formed on the grains before gypsum precipitated. Al, when present, produced an amorphous coating, probably Al(OH)$_3$, that seems to follow gypsum precipitation in time.

For the dolostone experiments, minor amounts of gypsum are seen in every case. For the Al-added run, there is good development of the Al(OH)$_3$ coatings seen in the limestone case. For the Fe-added runs, a rim of iron oxide developed early on the grains, but did not inhibit further acid dissolution of the dolomite mineral component. Skeletal remnants of these grain coats remain, indicating that the fill has maintained its structural integrity into advanced stages of dissolution.

Figure 16. Limestone experiments

Gypsum encrustation on surface of limestone particle

LS: pH 1.5

Gypsum cement bridging porosity between limestone particles

LS: SO$_4$

Gypsum cement subsequently covered by amorphous Al(OH)$_3$

LS: SO$_4$ + Al

Iron hydroxide coating subsequently covered by gypsum cement

LS: SO$_4$ + Fe

Iron hydroxide coating subsequently covered by gypsum cement. No apparent Al(OH)$_3$

LS: SO$_4$ + Al + Fe
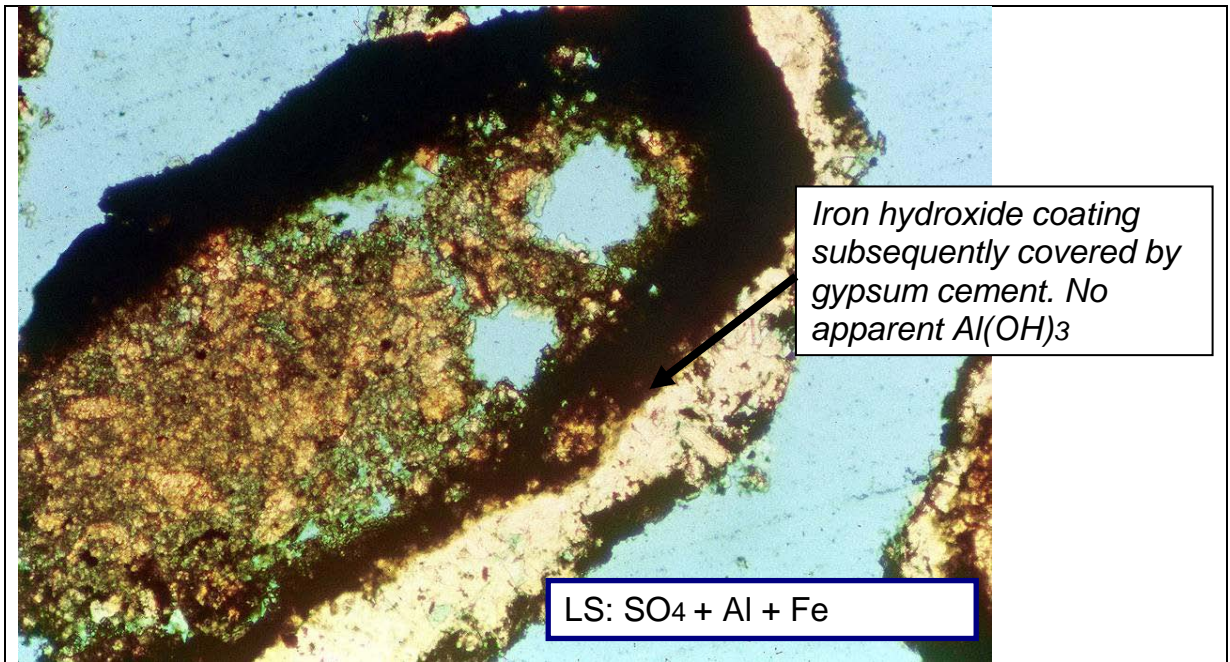
Figure 17. Dolostone experiments

Minor gypsum cement

DS: pH 1.5

Gypsum cement coating some grain surfaces

DS: SO$_4$

Rim of amorphous Al(OH)$_3$ coating grains

DS: SO$_4$ + Al

Iron hydroxide coating subsequently covered partially by gypsum

DS: SO$_4$ + Fe

DS: SO$_4$ + Al + Fe

Skeletal remnants of iron hydroxide coating from which remaining dolomite has been dissolved; some subsequent gypsum, but no apparent Al(OH)$_3$
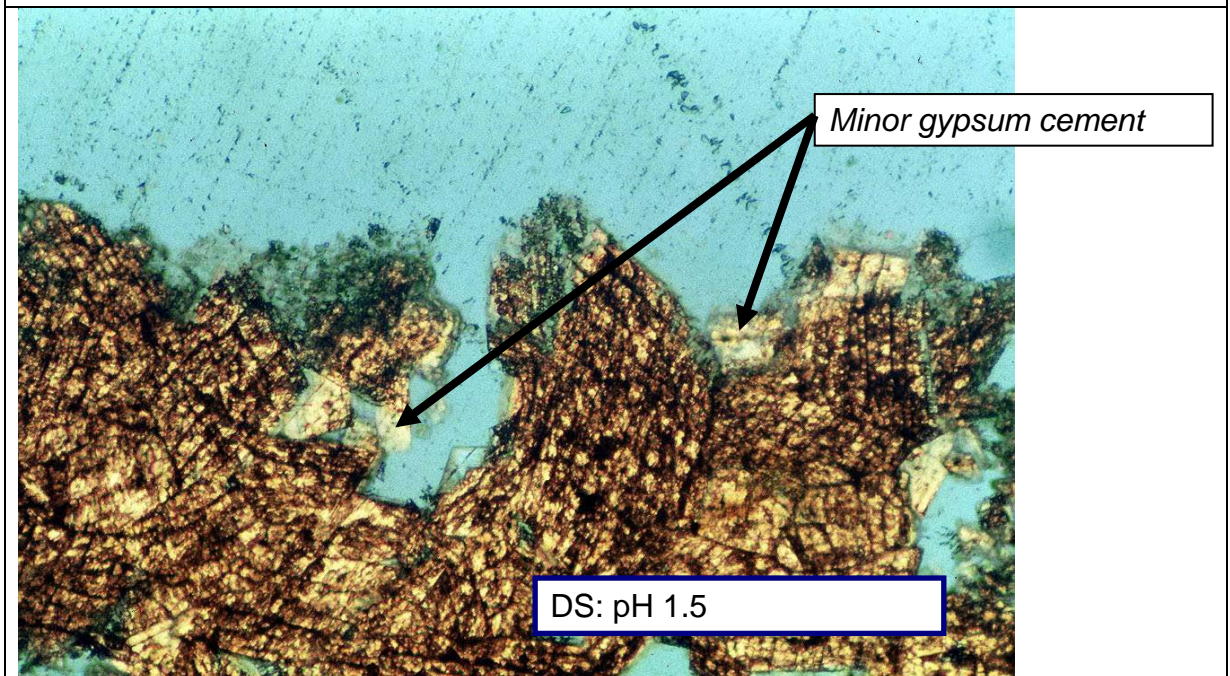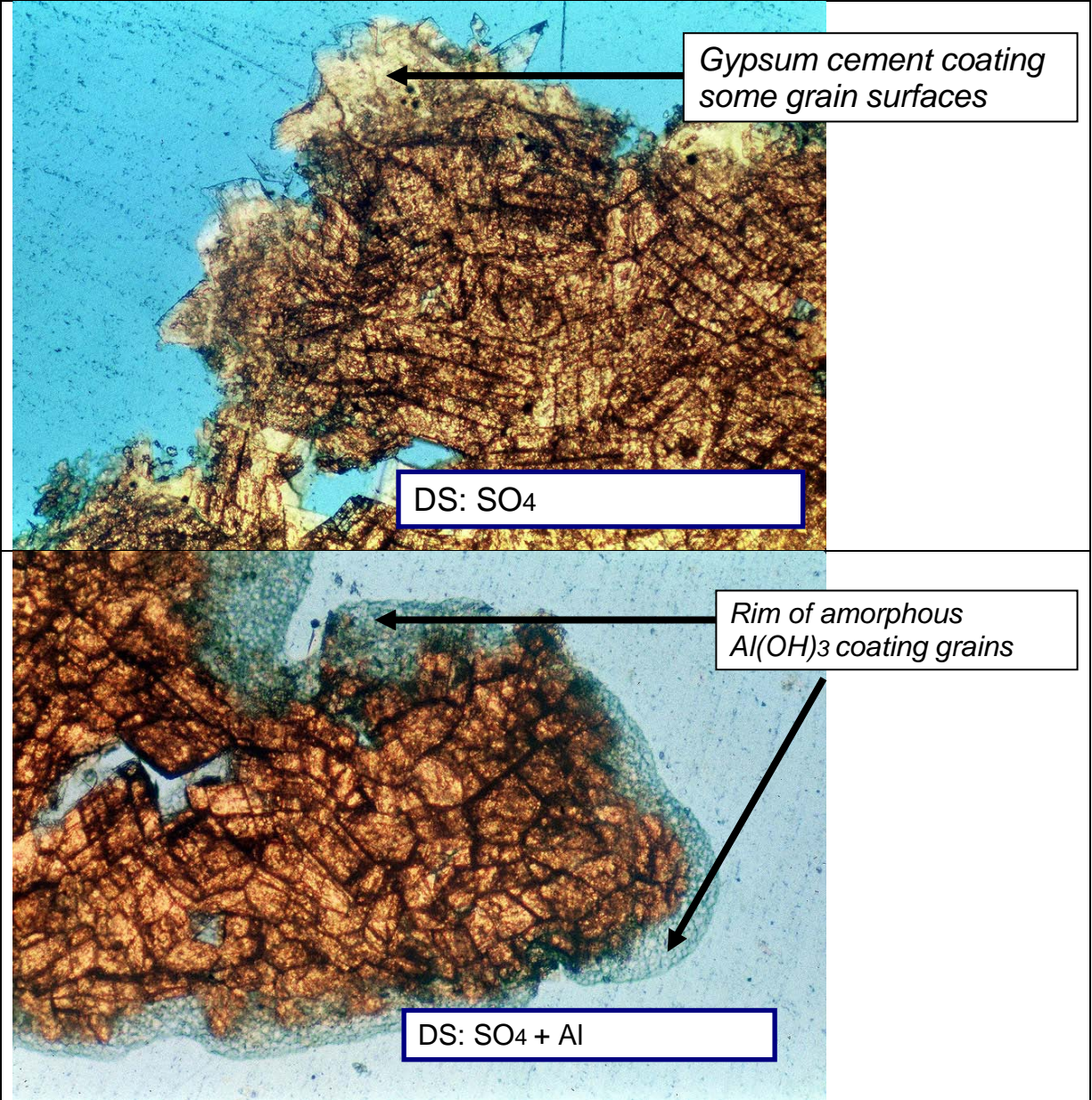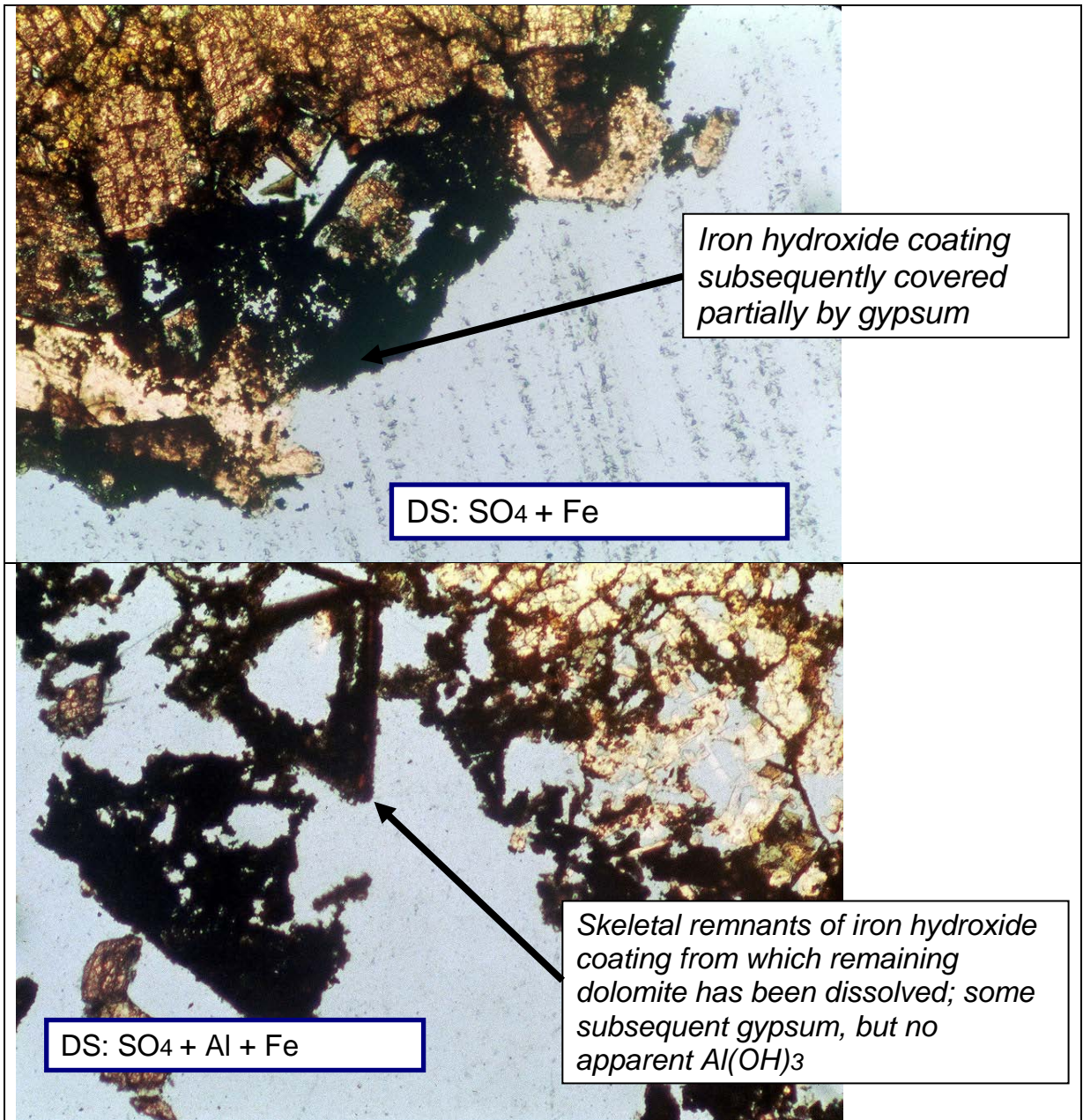
Overall Conclusions

To be effective, anoxic drains need to raise the pH of acid mine drainage to about 6.5 over the course of 15 to 20 hours (Watzlaf et al., 2000). From our experiments under all conditions of reaction vessel configuration and input solution composition, dolostone is

equal to limestone in producing final pH values in the required range. It is strongly superior to limestone in long-term performance because is does not experience clogging by gypsum. It also provides some benefits compared to limestone because of its high internal surface area. Coatings of grains by iron oxides was not as deleterious to performance in the dolostone runs compared to limestone. Acid attack on the grains still occurs, even with heavy precipitation of iron.

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