

MODE OF GYPSUM PRECIPITATION IN VERTICAL FLOW PONDS¹

Arthur W. Rose, Terry Morrow, Margaret Dunn, and Clifford Denholm²

Abstract: Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitates were observed in limestone beds at four vertical flow ponds (VFP) treating acid mine drainage, but the textures and localization show that it precipitated within other materials, not in contact with the open solution.

At the Filson 1 VFP, gypsum was found within clay and organic matter left as residues on the surface of partly dissolved fragments of impure limestone. It was also found in the contact zones between fragments. At the Tangascootack 1 VFP, gypsum coated limestone and was overlain by amorphous Al precipitate. At the Jennings VFP, gypsum was present in limestone-bearing compost and within Al-rich gel occupying pores in limestone gravel. At Middle Branch, Kettle Creek, gypsum occurred in Al-rich gel and on limestone. At all sites, the effluent water was undersaturated with gypsum.

Gypsum at these sites is interpreted to have formed in situations where limestone dissolution was characterized by diffusive transport of Ca away from the limestone surface. In this situation, the Ca concentration near the limestone surface is considerably higher than in the open solution, so that gypsum was oversaturated and precipitates, even though the open solution was undersaturated.

The occurrence of gypsum as coatings or as a component of an impurity layer probably slows the dissolution of limestone, and makes the VFP less effective in neutralizing acidity.

Additional Key Words: Acid mine drainage, passive treatment, limestone dissolution

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Introduction

Vertical flow ponds (VFPs, also known as SAPS, Successive Alkalinity Producing Systems, Kepler and McCleary, 1994) are a major method for passively treating net acidic mine drainage (AMD). In these passive treatment systems, AMD in a pond flows downward through a layer of compost that reduces Fe, then into a layer of limestone that neutralizes acidity, and out through perforated pipes. In some situations, the limestone layer in these systems loses effectiveness. One possible reason for loss of effectiveness is precipitation of solids that coat limestone or fill interstices between fragments. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one potential precipitate, created by interaction of high SO_4 in AMD with CaCO_3 in the limestone.

The purpose of this paper is to report observations of gypsum at vertical flow ponds, and to suggest mechanisms promoting its formation. The observations have been the result of investigations and “autopsies” at several “failed” vertical flow ponds.

Several workers have previously reported the occurrence of gypsum coatings on limestone exposed to acid mine drainage. Hammerstrom et al. (2003) described gypsum coatings overlain by Fe and Al precipitates on sand-size limestone in an experimental treatment system. Booth et al. (1997), Wilkins et al. (2001), Huminicki (2006) and Huminicki and Rimstidt (in press) conducted lab experiments showing formation of gypsum coatings on limestone exposed to sulfuric acid (0.01 m to 1 m) and elevated SO_4 concentrations. Thomas and Romanek (2002) observed gypsum replacing limestone in experimental columns treating extremely acid solutions with about 1500 mg/L SO_4 .

Chemistry of Gypsum Formation

The dissolution and precipitation of gypsum can be expressed by the following chemical reaction:



The solubility as expressed by the solubility product is:

$$K_{\text{gyp}} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} a_{\text{H}_2\text{O}}^2 / a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})} \quad (2)$$

where “a” indicates the chemical activity of the subscripted species. At 25°C, $\log K_{\text{gyp}}$ is -4.58 (PHREEQC database, Parkhurst, 1995). Although in simple situations one can approximate solubility by assuming activities are equal to concentrations in moles/liter, in AMD a speciation calculation is desirable because of extensive complexing and high ionic strength. The high concentrations of many solutes in AMD lead to complexing of appreciable Ca by SO_4 (CaSO_4^0), and considerable complexing of SO_4 by Fe, Al, Mg and other cations. The ionic strength is high enough that activities are much less than concentrations.

Figure 1 indicates saturation conditions for simple dissolution of gypsum into water with various initial Ca and SO_4 concentrations at 25°C. For gypsum dissolving in pure water, the equilibrium concentrations are 626 mg/L Ca and 1501 mg/L SO_4 . For other conditions, Na or Cl is used to balance charge in the calculations of Fig. 1. The hyperbolic character of the diagram shows that SO_4 exceeding about 1000 mg/L is required to reach saturation for reasonable Ca concentrations, and at least 400 mg/L Ca for reasonable SO_4 concentrations. The calculations also show that 20 to 45% of the Ca in these solutions is complexed by SO_4 .

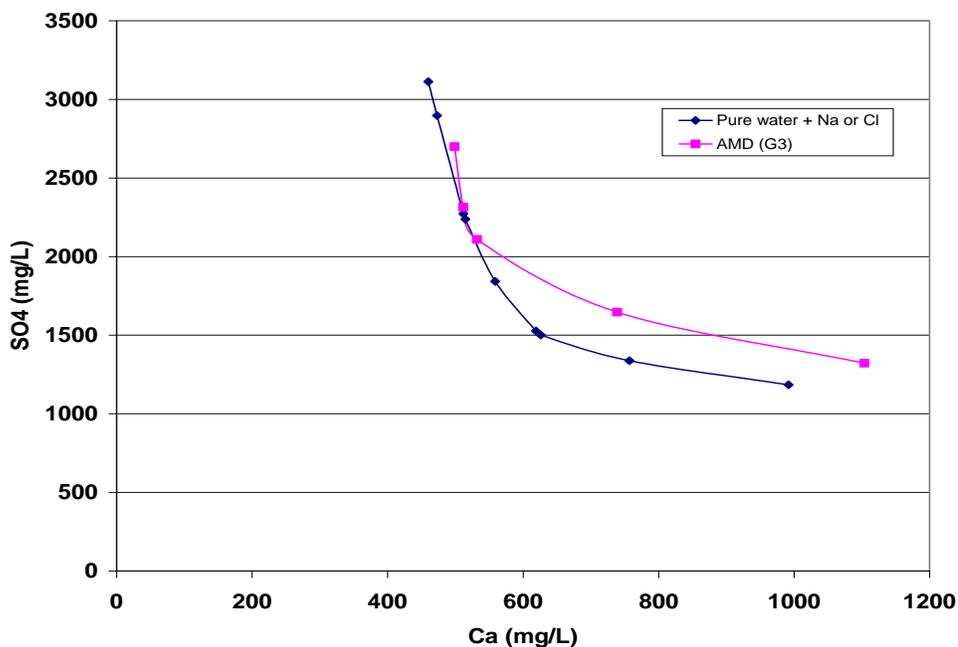


Figure 1. Concentration of Ca and SO_4 at gypsum saturation. The lower line is for gypsum dissolving in pure water, with charge balance by Na or Cl as necessary. The upper line is for gypsum dissolving in AMD from site G3 at Pot Ridge, Somerset County, PA.

In acid mine drainage solutions containing additional elements, the concentrations at saturation are somewhat different because of increased complexing by Al, Mg and other species. A second set of calculations plotted on Fig. 1 uses water influent into the Pot Ridge G-3 VFP (Rose et al., 2001, Table 3). In this case, Mg and Cl are used to balance charge when influent Ca and SO_4 are varied. The SO_4 concentrations at low Ca are markedly higher, apparently because of additional complexing of SO_4 by Al and Mg. The difference from the first case emphasizes the need to do a calculation for each specific water in order to evaluate gypsum saturation.

Methods of Investigation

Samples were collected from the VFPs immediately after trenches or holes were dug through the compost layer. The moist to wet samples were sealed into plastic bags and transported to the lab. After minor washing with deionized water, samples were examined with binocular microscope, and selected portions were scraped off for X-ray diffraction and chemical analysis. For X-ray diffraction (XRD), samples were powdered by grinding between glass slides, and mounted on a microscope slide with a drop of water. XRD patterns were made with Cu K-alpha radiation on diffractometers in the Materials Characterization Lab or Materials Research Labs at Penn State University. Minerals were identified by comparison with patterns in the Joint Committee on Powder Diffraction files, with emphasis on the strongest lines for each phase.

For chemical analysis, weighed samples from Filson were dissolved in 5 to 10 ml of boiling 1:1 HCl for about 1 minute and diluted to 25 ml for analysis. For Tangascootack, coatings were

washed off in deionized water and dissolved in pH 2 HCl. For Jennings, 2% HCl was also used. Solutions were analyzed for Al, Ca, Fe, K, Mg, Mn, Na, Si, Sr and S by ICP emission spectrometry in the Materials Characterization Lab at Penn State University. The analyses were calculated back to weight percent in the original solid.

Observations at Vertical Flow Ponds

Filson 1

The Filson 1 VFP was constructed in 1995 to treat highly acid water in the Little Mill Creek drainage near Clarion, PA. The limestone in the system is from quarries near Bellefonte, PA. By 2001, flow through the system had markedly decreased. Some information on this system is reported by Demchak et al. (2000). In late 2001, the system was largely drained and samples of limestone were removed from holes dug through the compost. The limestone fragments were covered with “mud”, possibly derived from the overlying compost and sediment in the bottom of the pond. The “mud” was gently washed off to reveal a generally gray finely crystalline surface with various types of materials in relief on the surface or as coatings. Limestone surfaces were generally smooth and appeared to have dissolved, based on local projections of insoluble materials above the general surface. Figure 2 shows the appearance of the Filson samples.

Table 1 indicates the typical chemistry of influent and effluent at the Filson 1 site. Calculations using the PHREEQC program indicate that the effluent is distinctly undersaturated with gypsum (SI = -0.57 for the average water, - 0.59 for the sample with the highest product of Ca and SO₄, and -0.33 for the combination of the highest Ca and highest SO₄ among the available samples).

At least 4 types of coatings or surface material can be identified:

1. Black material projecting 0.5 to 1 mm above the surface
2. Thin white coatings
3. Thin orangish to reddish fine-grained coatings
4. Small patches (5-10 mm diameter) with clear crystals up to 0.5 mm length, associated with medium gray platy fine-grained coatings.

The black projections are found to be mainly asphaltic material, as veins and stylolites, that were insoluble in the AMD. Tests show that this material is insoluble in acid (i.e., not Mn oxide), but on heating the black color disappears, leaving a light gray residue of quartz, illite and calcite.

The white coatings show an XRD pattern with a broad hump at 20-35° 2θ and minor peaks for quartz with possible gypsum and illite. Chemically, these coatings contain high Al with lesser SO₄, Fe and Ca. They are interpreted to be amorphous Al-OH precipitate with minor amounts of other phases. The orangish to reddish coatings appear to be the same plus minor ferric precipitate.

The clear crystals give a good XRD pattern of gypsum (Fig. 3A). The associated gray platy coating has an XRD pattern of gypsum with minor quartz and illite (Fig. 3B). These materials occur in patches up to about 1 millimeter in size.

In summary, gypsum at Filson 1 occurred mainly in patches on the surface of the limestone, and in small amounts within Al-rich coatings.



Figure 2A. Photograph of coated limestone fragment from Filson 1 VFP, sample 11. Scale in cm and mm. White coating is Al-rich, black coating is similar to organic matter in other samples. Small scale divisions are millimeters.



Figure 2B. Photo of patch and associated gypsum crystals (black and white speckled area above patch) on top of limestone. The patch is inferred to be a contact point with another fragment. Scale divisions in millimeters.

Table 1. Typical chemistry of acid mine drainage at treatment systems

Constituent	Units	Filson 1		Tangascootack		Jennings		Middle Br.		G3
		In	Out	In	Out	In	Out	In	Out	In
Fe	mg/L	27	6	1	1	69	10	7.5	7.9	135
Al	mg/L	14	10	22	11	23	0	54	23	22
Mn	mg/L	48	51	50	49	18	16	15	18	28
Ca	mg/L	134	168	189	225	105	274	48	126	109
Mg	mg/L			237	228			39	44	82
K	mg/L			6.8	6.6					3.1
Na	mg/L			5.3	5.3					2.4
Si	mg/L			13	11					11
SO ₄	mg/L	784	914	1668	1773	772	729	518	756	1071
pH		3.7	4.8	3.3	5.2	3	6.8	2.9	5.3	3.2
Acidity	mg/L CaCO ₃	241	175	282	145	272	-165	420	116	
Alkal.	mg/L CaCO ₃	0	17	0	20	0	212	0	101	0
Flow	L/min	116		232		67		52		
SI(calcite)			-0.57		-0.58		-0.46		-0.75	
Source		D		R1		W		PA		R2

Source: D, Demchak et al., 2001; PA, PA DEP unpublished data; R1, Rose et al, 2004; R2, Rose, unpublished data; W, Watzlaf et al., 2000.

SI = Saturation index = log (activity product/solubility product)

Tangascootack

An “autopsy” of this system has been described by Rose et al. (2004). The system was constructed in 1998. After an initial period during which alkaline effluent was produced, the effluent became acidic, and flow dropped off markedly. In 2003, the system was drained and samples collected from the compost and limestone layers.

The limestone for 15 to 30 cm beneath the compost layer was coated with a gelatinous white material. Analyses of the coatings dissolved in HCl showed 37 to 58 weight percent Al as Al₂O₃, 15 to 38% SO₄, 20 to 30 % CaO and lesser amounts of K, Fe, Mg, Mn and Si. XRD patterns of the white gelatinous material showed a hump at 20 to 35° 2θ, suggestive of amorphous Al precipitate, plus lines for quartz and gypsum (Rose et al, 2004, Fig. 6). XRD of a bright white coating on some washed limestone showed gypsum.

In summary, gypsum at Tangascootack occurred within gelatinous Al hydroxide precipitate on limestone, and locally coating the limestone beneath Al precipitate.

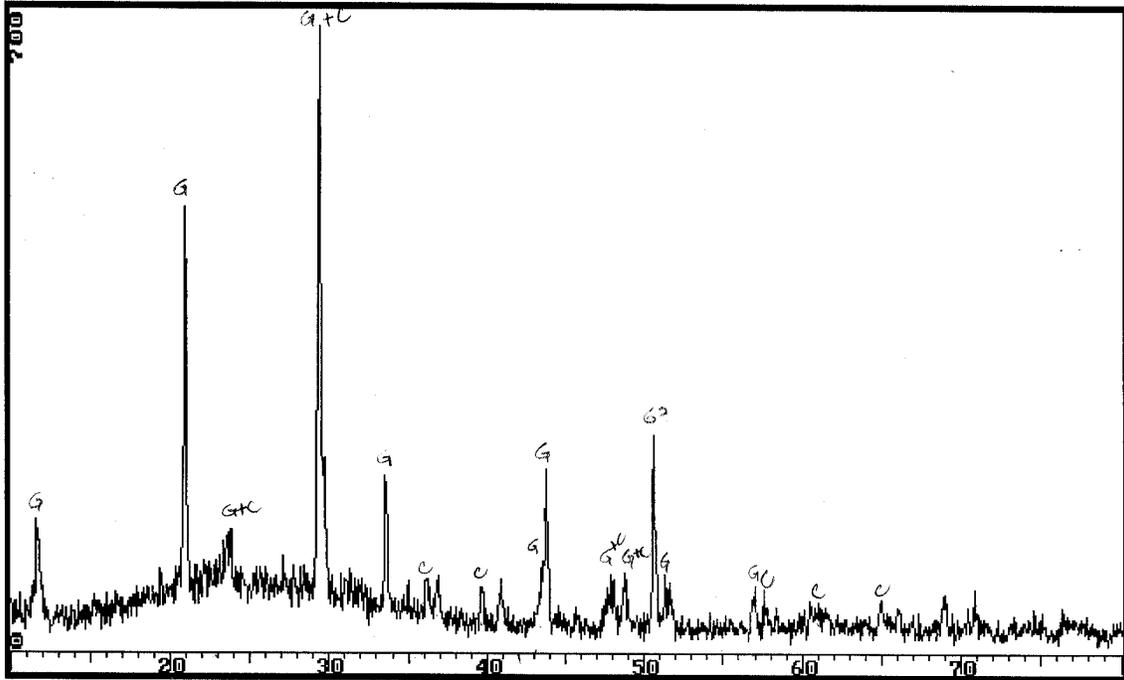


Figure 3A. X-ray diffraction pattern of gypsum crystals associated with a “patch” on Filson sample 5. G = gypsum,, C= calcite.

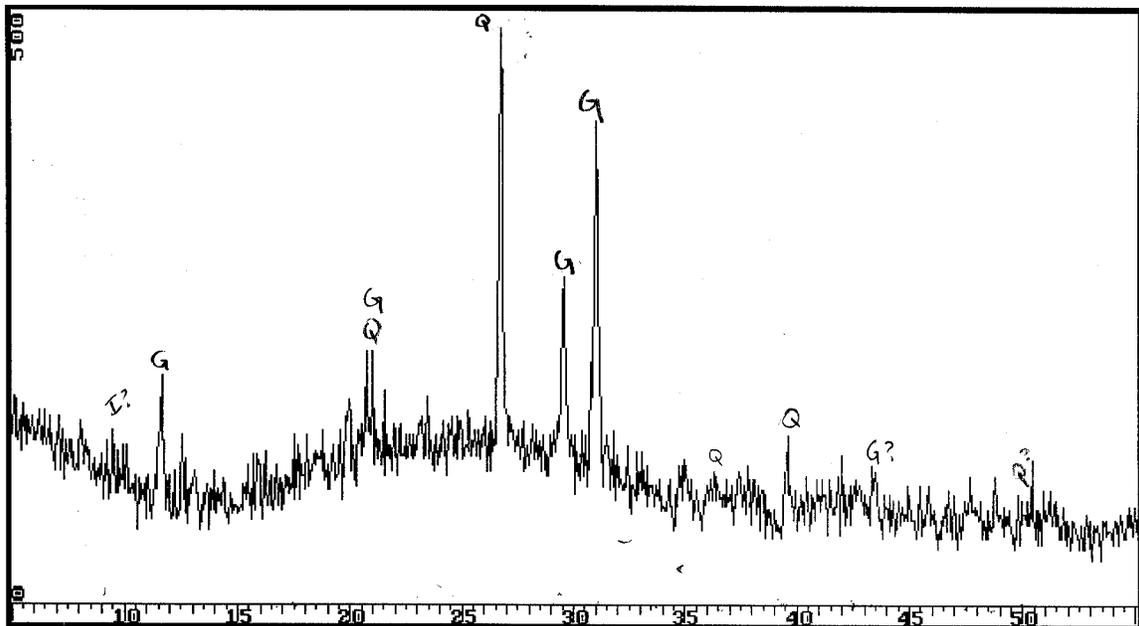


Figure 3B. X-ray diffraction pattern of a “patch” of fine-grained coating material in Filson sample. G = gypsum, Q = quartz, I = possible illite.

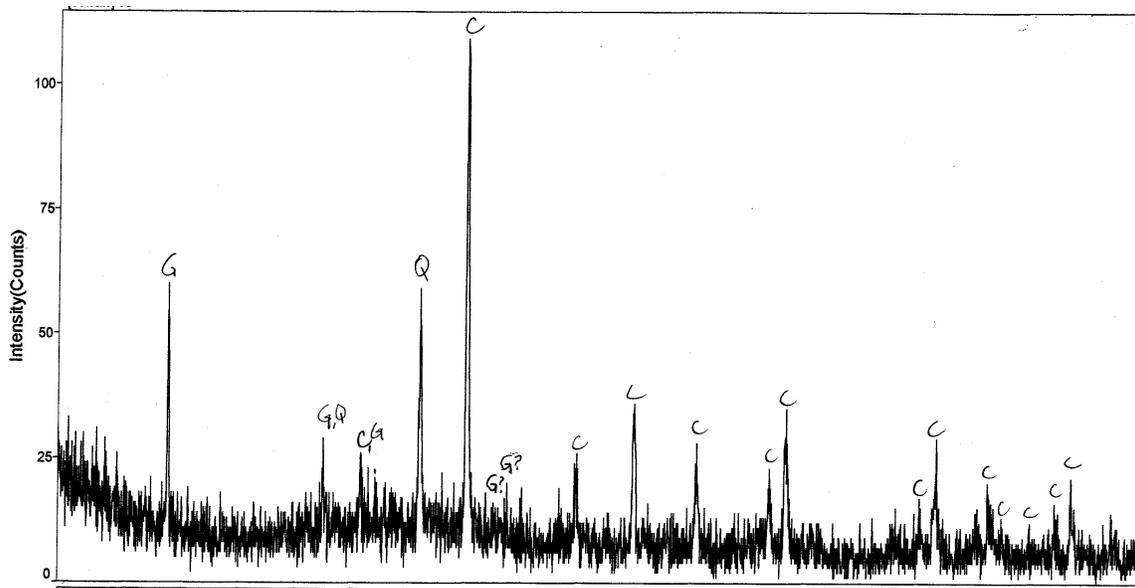


Figure 3C. X-ray diffraction pattern of white pasty material from Jennings (sample J9). G = gypsum, Q = quartz, C = calcite. Pattern from 5 to 70 degrees 2θ .

Jennings

The Jennings vertical flow system was constructed in 1997 to treat a flow of about 115 L/min with pH 3.0 and an acidity of 272 mg/L CaCO_3 (Table 1). The system consists of an approximately 0.6-m thick layer of spent mushroom compost amended with 380 tons of AASHTO#9 high-Ca limestone aggregate (1 cm mesh). This layer is underlain by 0.3 m of river gravel containing perforated underdrain pipes. The system performed well for several years, but by 2004 was overflowing part of the time and was partially plugged. In July 2004 the system was drained and trenches were excavated in the compost-limestone layer. Samples were collected from the trench walls for lab study.

The trench walls showed that the compost and limestone were incompletely mixed, so that lenses of nearly pure limestone and nearly pure compost were common. The general sequence from the surface down was (Figure 4):

1. Fe oxide precipitate
2. Light gray material composed mainly of limestone gravel with white soft pasty material in the interstices.
3. Black compost and compost-limestone mixture.

Much of the compost and limestone was compact and hard, but some was loose and soft.

Four samples of the white pasty material mixed with limestone were analyzed chemically and by XRD. Three of the four samples contained appreciable Al (2-9%, or 6 to 26% $\text{Al}(\text{OH})_3$) but lack any XRD peaks of an Al-rich phase. If the Al occurs as an amorphous Al hydroxysulfate similar to hydrobasaluminite ($\text{Al}_4\text{SO}_4(\text{OH})_{10}\cdot 36\text{H}_2\text{O}$), then the Al material would compose an even higher proportion of the sample. Loop (2003) found Al-rich material of similar chemistry, including presence of Si, in samples from other AMD sites. Gypsum peaks are

present in the XRD pattern of the white pasty material at Jennings, indicating presence of gypsum within the Al gel (Fig. 3C).



Figure 4. Photo of a trench wall in the Jennings vertical flow pond, showing red Fe oxide zone at top, white Al precipitate in limestone in the middle, and FeS-bearing compost at the bottom.

In summary, gypsum is detected at Jennings within an amorphous Al precipitate.

Middle Branch

The Middle Branch system on the Middle Branch of Kettle Creek, Clinton Co., PA, was constructed in 2001. Influent and effluent chemistry are listed in Table 1. After about 1.5 years of reasonably satisfactory treatment, the effluent became acidic. An autopsy was conducted in June 2004. The system was drained and several trenches were excavated into the limestone. The limestone beneath the compost layer for about 15 to 30 cm was covered with white pasty precipitate. Chemical analysis of this material showed high Al, but no Al phase was detected by XRD. The 020 peak of gypsum was strong in this XRD pattern. Gypsum was also observed as visible crystals at the compost-limestone interface, but may have formed by evaporation in the several hours between exposure and examination.

In summary, gypsum was found at Middle Branch within amorphous Al-rich precipitate.

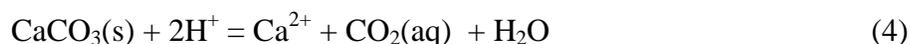
Interpretation

None of the effluents at these four sites is saturated with gypsum (Table 1), so the occurrences must be explained in some way that does not require gypsum saturation of the effluent. The observation that gypsum is always within Al precipitate, or covered by some other material, or in patches on the surface of limestone suggests an interpretation involving diffusive chemical gradients during limestone dissolution. Hammerstrom et al (2003) and Huminicki and Rimstidt (in press) have described this process for other sites.

When limestone dissolves in acid mine drainage, the H^+ migrates from the open solution to the calcite surface, and $CaCO_3$ dissolves:



or if pH is lower than about 6.4:



If the solution is flowing relatively rapidly, as by stirring or agitating in lab experiments, then the Ca^{2+} and SO_4^{2-} concentrations are nearly uniform everywhere and equal to the bulk solution, and gypsum will not precipitate unless the bulk solution is saturated in gypsum. However, if flow past the $CaCO_3$ surface is very slow, then Ca will build up at the surface, and may be carried away only very slowly by diffusion (Figure 5). Sulfate is not involved in calcite dissolution (except as a complexer of part of the released Ca), so its concentration throughout will be essentially that of the open solution. In this situation, gypsum saturation can be exceeded because of elevated Ca near the surface, and gypsum can be precipitated.

Several workers have reported gypsum coatings on calcite formed under diffusive transport conditions. Huminicki and Rimstidt (in press) observed gypsum growth on calcite at pH 2 and lower, and SO_4 concentrations of 0.1 m (9600 mg/L) in strongly agitated solutions. Wilkins et al. (2001) observed decreased dissolution rates and gypsum coatings on calcite exposed to 0.01 M H_2SO_4 (pH~2, 960 mg/L SO_4) for 1 hour, apparently under quiescent conditions. No experiments appear to have investigated the lower Ca- SO_4 limit of gypsum coating in very

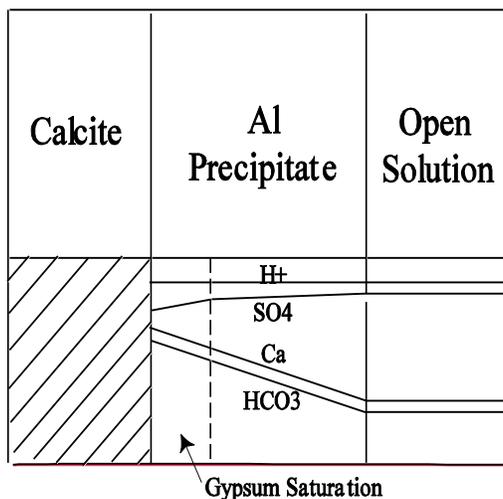


Figure 5. Schematic diagram showing concentration gradients within Al precipitates leading to gypsum saturation near dissolving calcite.

flowing solutions as would occur in a VFP.

For transport to occur by diffusion, a concentration gradient must exist to drive elements through the diffusive zone:

$$F = -D \, dC/dx \quad (5)$$

where F is the flux of the diffusing substance (mass per unit area per unit time), C is concentration, x is distance and D is the diffusion coefficient ($\text{length}^2/\text{time}$). For calcite dissolution, F is the flux of Ca , H^+ , or HCO_3^- generated by dissolution at the calcite surface. The Ca concentration at the calcite surface must be high enough to create a gradient large enough to transport the released Ca to the open solution.

In the case at hand, diffusion may occur either in a thin zone of stagnant solution near solid surfaces, or through some medium like the gelatinous Al precipitate. Inferred gradients in concentration across a zone of Al precipitate coating a limestone fragment are illustrated in Fig. 5. Ca and HCO_3^- (or H_2CO_3) are liberated from CaCO_3 and show a marked decrease in concentration across the diffusion zone from the reacting solid to the open solution. Conversely, hydrogen ion is consumed at the calcite surface and shows only a small decrease in concentration from the solution to the calcite surface. Because of its small size, H^+ has a more rapid diffusion rate (higher diffusion coefficient) than other species so the gradient in concentration is smaller. Small amounts of SO_4 are consumed in forming gypsum, so it has a small gradient inward toward the zone of gypsum precipitation. As a result of these varying concentrations in Ca and SO_4 , a zone near the calcite surface can be saturated (or slightly supersaturated) with gypsum, and contains this phase. The size of this saturated zone is dependent on H^+ , Ca , SO_4 and $\text{CO}_2(\text{aq.})$ concentrations in the solution, on diffusion coefficients for these species in the Al -rich gel or other material and on the thickness of the diffusion-controlled zone. Lower pH will increase the rate of calcite dissolution, thereby increasing Ca concentration at the calcite surface. The Al -rich gel has a high water content, and allows ready diffusion in the above manner.

Another site where diffusion can dominate is where two limestone fragments are in contact. In this contact zone, the solution occurs as only a thin film and is essentially stagnant. Diffusion can dominate transport in this zone as well. The patches containing gypsum and other precipitates at Filson 1 are considered to be caused by this situation. Concentrations of Ca are higher in the contact zone than in the open solution, as a result of calcite dissolution, and allow gypsum saturation.

Similar chemical and mineralogical studies were conducted at a test site at Jonathan Run on I-80 near Snowshoe, PA. At this site, limestone was placed in a large dumpster and provided with an automatic flushing device as part of an experiment by Hedin Environmental. The limestone in much of the dumpster was coated with white Al -rich precipitate, but no gypsum was detected in several XRD patterns. Available data indicates that the SO_4 concentration is about 400 mg/L at Jonathan Run, appreciably lower than at the sites discussed above. Evidently Ca concentration does not get high enough to form gypsum from this influent water. However, Al precipitate was concentrated in patches where limestone fragments were in contact, possibly because flow velocity at these sites was relatively low during flushing episodes.

The data suggest several implications for design of limestone treatment systems. At most of the sites, the Al precipitate is clearly the major impediment to neutralization of AMD. The gypsum within the Al gel may further decrease the diffusive flux, because of its dense structure,

but it is not a major factor in decreasing reaction rate. However, if the gypsum occurs as a coating on the limestone, beneath the Al precipitate, then it can strongly decrease the reactivity of the limestone. This situation, observed at Tangascootack, possibly reflects the very high SO_4 in the AMD at that site (1773 mg/L). The sites with 700 to 900 mg/L SO_4 did not appear to have a coating of gypsum on the limestone surface but did have gypsum within the Al precipitate, and at Jonathan Run, with 400 mg/L SO_4 , gypsum was not observed at all.

The lower limits of SO_4 -Ca activity product to form a coating of gypsum on limestone (as contrasted to gypsum within Al precipitate) are not clear. Coatings apparently occurred at pH 2 H_2SO_4 in experiments by Wilkins et al. (2001) and were observed at Tangascootack at 1773 mg/L SO_4 , 225 mg/L Ca and pH 3.3 beneath Al precipitate. Experiments by Huminicki and Rimstidt (in press) were conducted with appreciable agitation, so are not directly relevant to conditions of slow flow in a VFP. Coatings were not observed at the other three VFPs of this study, though thin coatings might have been present. In any case, coating effects may decrease reaction rates in VFPs with influent AMD approaching the Tangascootack water. For such sites, high limestone purity should be required, and slowed reaction rate may be expected.

The data from Filson suggest that the nature of impurities in limestone may be significant. The organic-rich zones resisted dissolution and stood above the surface of the adjacent limestone. These insoluble residues contained small amounts of gypsum along with quartz and illite from the limestone. Such zones are not effective in neutralizing AMD. The phenomenon suggests that limestone purity can be a factor in effectiveness. A limestone with clay or quartz impurities may accumulate these residues on its surface. Further dissolution of the limestone may be impeded because the diffusive transport in this coating is relatively slow. Gypsum may form in this zone if SO_4 is high, further slowing reaction. The level of clay-quartz impurities that will form a layer cohering to the surface is unclear, but might be only 10-20%. Thus, 10% clay impurities in a limestone might be much more deleterious than 10% dolomite, which would dissolve, but at a slower rate than calcite.

If the impurities occur in thin layers within the limestone fragments, then coating may occur on the surface exposures of these layers, but not on the pure limestone. The effectiveness of the limestone will be reduced by the percentage of the surface occupied by the impurity-bearing layers.

The observation of gypsum at the contact points between limestone fragments indicates that this phenomenon can be significant. Precipitation of gypsum at these sites decreases the pore space in which diffusion takes place, and decreases the dissolution rate of the limestone from the initial rate in un-reacted limestone. This effect may be responsible for some of the decrease in effectiveness of VFPs with time.

In high- SO_4 AMD, it may be beneficial to use dolomite instead of limestone in order to decrease Ca concentrations and avoid formation of a gypsum coating on the limestone, as was found at Tangascootack.

Conclusions

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) occurs in the limestone bed of some VFPs, but it does not normally appear to precipitate in the open solution flowing through the system. At all four of the systems studied, gypsum is undersaturated in the effluent. The gypsum has precipitated within gelatinous

Al precipitate and other materials, or at contacts between limestone fragments. The occurrence in these sites is attributed to formation in a diffusion gradient, due to elevated Ca in a zone adjacent to the dissolving limestone.

Gypsum precipitation may decrease the effectiveness of limestone dissolution in some VFPs, especially those with SO₄ exceeding about 1200 mg/L. Many VFPs treating high-Al AMD and precipitating Al in the limestone bed contain some gypsum within the gelatinous Al precipitate. Also, gypsum may contribute to decreasing reaction rate if the limestone contains clays or other impurities. Gypsum coatings on limestone may form in some high-SO₄, low pH conditions.

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