Use of Calcite-bearing Volcanic Rocks to Neutralize Sulfide Mine-waste Drainage: Results from Static Reaction Vessel Experiments

Mark R. Stanton[1] and Douglas B. Yager[1]
[1]U.S. Geological Survey, Denver, CO, USA, mstanton@usgs.gov

Abstract
Results from reaction vessel experiments to determine acid neutralizing capacity (ANC) of propylitically-altered volcanic rock containing varying, minor amounts of calcite (compared to limestone) are reported here. The ANC rock was reacted with mine waste (MW) to examine changes in water chemistry and composition over time, especially changes in pH and aqueous metal concentrations. The static tests indicate that the alkalinity generated from the volcanic ANC rock is sufficient to neutralize acid drainage from MW. Decreasing aqueous metal concentrations indicate that the ANC rock dissolution improves water quality. The ratio of masses of ANC to MW rock, the water/ANC rock ratio, grain size, and the solid and aqueous compositions of the MW influence the amount of neutralization that occurs. The results suggest the volcanic ANC rock might be useful as a local source and/or substitute for limestone in acid mine drainage (AMD) treatment, despite being less effective than limestone. Other geochemical processes that were observed, such as precipitation of iron solids during alkalinity generation and sorption of metals to iron solids, also appear to be important factors in determining the ability of ANC rock to maintain water quality and pH at more desirable (near-neutral) values.

Keywords: geochemistry, alkalinity, iron oxides, metals, mineralogy, aqueous chemistry

Background
Mitigation of acid mine and acid rock drainage (AMD/ARD) involves the use of rocks that possess acid neutralizing capacity (ANC). Carbonate-bearing rocks such as limestone have the best ANC because minerals in these rocks dissolve to produce CO_3^{2-} and HCO_3^--ions. The carbonate and bicarbonate ions neutralize the acid (H_3O^+) produced by the reaction of acid-generating sulfides like pyrite (FeS_2) with water and air. The ANC is the available or reactive concentration and the solubility of acid-neutralizing minerals such as calcite ($CaCO_3$) which are both in turn related to surface area.

Transportation costs may limit or inhibit routine usage of limestone. An alternate ANC source such as the local volcanic rocks described in this paper may improve water quality. We examined the use of volcanic rock that contains some ANC to see whether it could be useful as a lower-cost option. That is, could the ANC available in these rocks sufficiently neutralize acidity from mine drainage to improve water quality? Although this work focuses on laboratory studies and results, the materials used were from the upper Animas watershed near Silverton, Colorado, and that area will be referred to as the study area.

ANC and Mine Waste Rock Compositions
The ANC rock used in this study has the composition of pyroxene andesite and has been propylitically altered (Yager *et al.* 2005). Major mineral abundances vary, but generally include (in approximate order of decreasing abundance) quartz, chlorite, epidote, calcite, K-feldspar, albite, pyrite, and Fe-oxides. The abundance of each mineral depends on the rock alteration history, and in some cases, the chlorite-epidote-calcite assemblage can dominate. In common with most country rock in the region, minor (<1 wt. %) to moderate (<5 wt. %) amounts of pyrite were usually present in the ANC rocks. Rocks that lack detectable pyrite tended to have the highest ANC values (Yager *et al.* 2005). Results from semi-quantitative x-ray diffraction (XRD) indicated calcite ranged from undetectable to as high as 18 wt. % in the ANC rock (McCafferty *et al.* 2011). However, calcite, pyrite, and other minerals were not uniformly distributed within mapped rock units, and vary greatly from sample to sample.

The mine waste rock used in this study was from the Grand Mogul mine near Silverton. The mine waste contains many of the same propylitic minerals as the ANC rock but in lower abundances. The major difference is that metal-bearing sulfides or their weathering products (usually sulfate salts) tend to be dominant solid phases. Micas, clays, and other rock-forming silicates are present in varying amounts. Previous leachate studies (Yager *et al.* 2008) showed that several potentially harmful or toxic elements are present in the solid mine waste, including aluminum (Al), iron (Fe), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb). Many of these elements were found to be readily leachable using water or weak acids and solvents (Yager *et al.* 2008). The highest abundances of these elements were found primarily in sulfide or primary Fe/Al oxide and silicate phases. Total levels of these elements in mine waste solids range from about 4 times (Al) to 1,000 times (Pb) more-concentrated than in the ANC rocks. The pH of drainage flowing from the waste pile (measured in the field) ranged from 1.9 to 2.8. The long residence time of water within the waste pile is the likely reason that field pH values were lower than lab-measured pH values (as high as 3.9) ,which were obtained by placing "dry" mine waste solids into deionized (DI) water.

Experimental Procedures

Vessel design

Both large- and small-scale vessel tests were run. The large vessels (10-20 L) were designed to mimic field conditions where larger grain sizes (boulders, cobbles, pebbles) were present. In some field settings, heavy equipment had been used to place mine waste on top of limestone (and vice versa) during remediation efforts. The large reaction vessels consisted of a 1.5m high acrylic cylinder (0.25m diameter) sealed at the bottom by a thick layer of acrylic (Figure 1). The cylinder was fitted with three valves (for withdrawing aqueous samples) located at 10, 50, and 80 cm above the base of the vessel. A 1.25-cm diameter central PVC column (slotted) was also incorporated into the vessel to facilitate initial addition of water and withdrawal of water samples.

The small vessels (<1 L) were used to examine reactions of the <2 mm fraction of both MW and ANC rock. The <2 mm fraction was obtained by sequential sieving of the same mine waste material used in the large vessel tests. The mine waste and ANC grains were mixed together for the reaction; the mass ratio of ANC to MW rock was varied to include ratios of 8.0, 4.0, 2.7, and 2.0, with a constant volume of solution. Two separate control experiments were run by: a) reacting "pure" limestone with mine waste on a 4:1 mass basis and b) allowing mine waste to dissolve in the absence of ANC material, to see whether solution acidity changed significantly. The vessel identifications, mass ratios, and initial and final pH values from these tests are shown in Table 1.

Table 1. Summary of mass ratios of ANC/MW rock, and initial and final pH values from small vessel reaction tests. LST = limestone; NA = not applicable.

Vessel ID	Mass Ratio ANC / MW	Initial pH, (t=0 hrs)	Final pH, (t=116 hrs)
A	8.0	3.54	6.91
B	4.0	3.4	6.71
C	2.7	3.35	6.51
D	2.0	3.16	6.3
E (LST+ MW)	4.0	3.48	8.21
F (MW only)	NA	3.96	3.2

In the large vessels (Figure 1), equal masses (6.0 kg) of waste rock and ANC rock were placed into the vessel. A layer (≈0.5 m) of ANC rock was placed in the vessel bottom and then overlain by an equal

mass of mine waste. In this instance, the reaction was based on a 1:1 ratio of mass of ANC to mass of MW. This arrangement of rock types was designed to allow acidic mine waters to develop and then flow through ANC material to see whether the acid was neutralized. In other tests, the positions of the layers of ANC and MW were reversed, or the materials were mixed thoroughly (small vessels). The layering of rock types was intended to examine the effect of the physical arrangement of ANC and MW rocks. In some small remediation efforts that had been performed in the study area, the positioning/layering of rocks in waste piles had not been considered in the waste pile treatment design. As a result, some waste piles seen in the field had begun to produce acid again within two years of remediation.

Figure 1. Large reaction vessel apparatus showing three water sampling valves (left side) and central sampling column. The ANC rock is the coarse-grained gray layer in the bottom; it is overlain by the fine-grained, tan-colored MW rock.

Deionized water (4.5 L) was slowly added via the central open column until the entire rock mass was saturated and covered by a 5-cm layer of water. Immediately after saturation (5 minutes), the pH, specific conductivity (SpC), and temperature (°C) of each aqueous layer (ANC and MW) were measured with the appropriate meters that were calibrated 10 minutes prior to the measurement.

Sampling and analyses

For the large vessels, two sets of water samples, consisting of three samples each, were processed after the physical and chemical parameters were measured. The two sets represented water from the mine waste (near the surface) and from ANC rock (bottom of vessel). The first sample was filtered through a 0.45µm polycarbonate filter and left unacidified for alkalinity determination by electrometric titration using a microburette that dispensed 0.1 or 0.01 N HCl reagent until the pH was less than 4.5. Samples with initial pH values of <4.5 were not titrated because their carbonate alkalinity was likely near zero at

this pH. The second sample was filtered (0.45µm) and acidified to less than pH 2.0 with concentrated ultra pure nitric acid for ICP-MS analysis for 44 cations (dissolved metals; Lamothe *et al.* 2002). The third sample was filtered and unacidified for direct spectrophotometric determination of iron species (Fe(tot) and Fe^{2+} were analyzed; Fe^{3+} was by difference, i.e., Fe(tot) - Fe^{2+} = Fe^{3+}). Iron species were analyzed immediately after collection using a Hach spectrophotometer and iron reagent vials; dilutions of 10-100X were often needed, especially for samples from the earliest reaction times. The total volume of solution removed for samples was less than 15 percent of the initial volume and would not account for the large decreases in metals concentrations observed during an experiment.

Iron solids captured on the filters were dried and x-rayed to determine if the material was amorphous, crystalline, or a mixture of these two phases. If any crystalline material was present, this was considered evidence that some of the iron solid had time to form a more-ordered structure, and therefore was likely formed many years ago. If only amorphous material was present, this indicated that nearly all of the Fe-solids were of recent origin and formed after the waste rock had been deposited on the surface or even in the reaction vessel (Stanton *et al.* 2007). Water samples from the small vessels were obtained and treated in a similar manner to those from the large vessels, except that only one sample was taken for each of the three analyses listed above.

Results and Discussion

Changes in pH and alkalinity

Significant changes in pH were observed in the ANC and MW waters in large vessels within 1-2 days after addition of DI (Figure 2a). ANC pH increased by almost one pH unit whereas the MW pH increased by 0.5 units. After about two weeks, the ANC pH had risen almost two units, but the MW pH remained relatively constant (3.8-4.0). The pH values in both layers were 5.30 after 17 days of reaction (Figure 2a). Concentrations of dissolved metals and ions generally decreased after reaching a maximum at about seven days, as shown in Figure 2b.

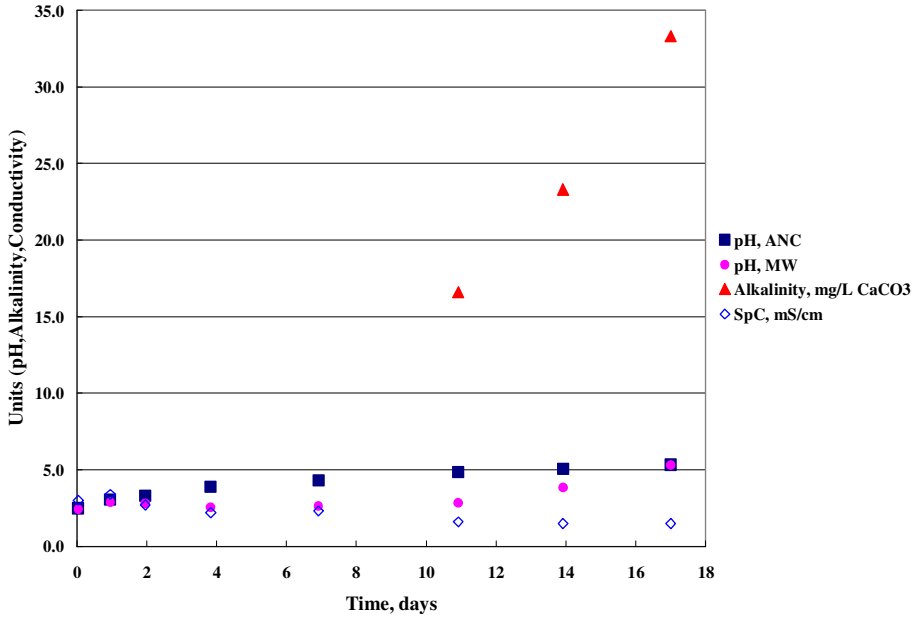

Figure 2a. Changes in selected reaction variables with time for large vessel tests.

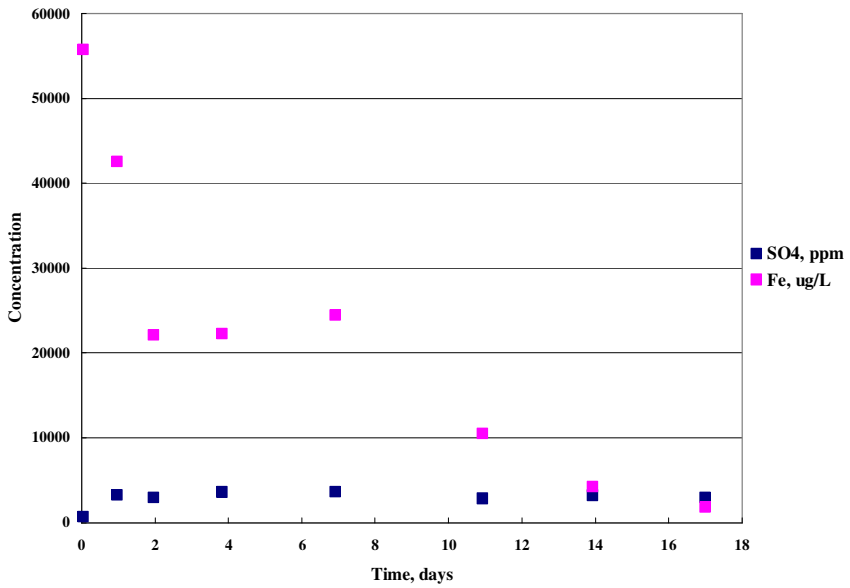

Figure 2b. Changes in dissolved iron and sulfate concentration with time for large vessel tests.

These results suggest that alkalinity was being produced at a rate capable of neutralizing acidity being generated by the dissolving/reacting MW. In fact, alkalinity reached 66 mg/L $CaCO_3$ as shown in Figure 2a (the reaction was allowed to continue for 6 additional days, but no other analyses were made). Results from the fine-grained tests (small vessels) showed even higher pH values (up to 6.9) after just 5 days of reaction (Figure 3). Thus, the small grain tests reached higher pH values more quickly. The highest pH of all tests (8.2) resulted from the reaction of MW with the limestone control (Figure 3).

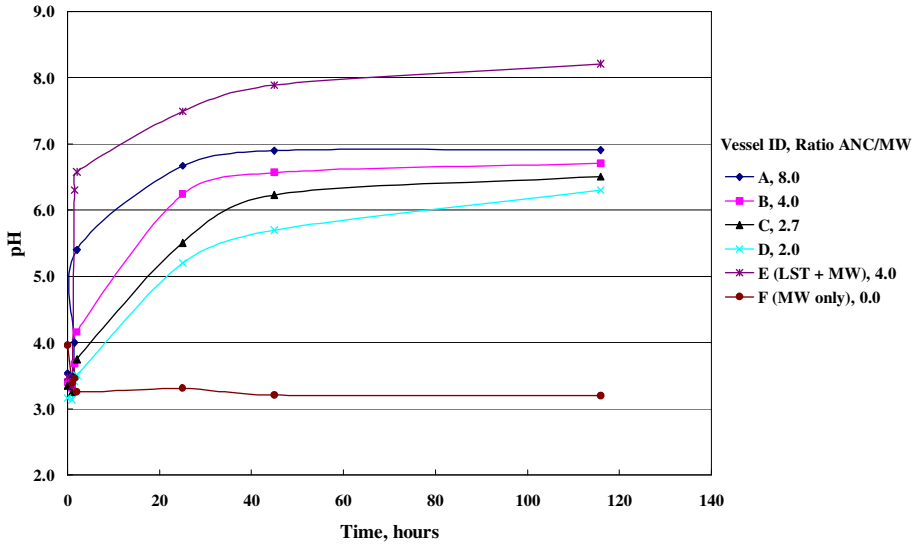

Figure 3. Results from small vessel tests (using the <2 mm fraction of ANC and MW solids) showing increase in pH with reaction time for different mass ratios of ANC to MW. Vessel ID letter corresponds to those shown in Table 1.

Formation of iron solids

Iron solids began to form in the large vessel when the pH had risen above approximately 4.0 (7 days of reaction). The iron solids became abundant, but appeared to be concentrated within the ANC rocks (Figure 4), likely as a result of higher pH values in close proximity to the ANC rock. Additionally, a trend of decreasing aqueous iron concentration with increasing pH indicated that more of the aqueous iron (as measured by ICP-MS) was being precipitated (Figure 2b). A probable scenario was that the iron was being dissolved from the MW then diffused downward to the ANC rock where the increasingly higher pH led to precipitation as an iron-bearing solid. Sulfate values (from ICP-MS analyses) remained relatively constant after 7 days, suggesting that pyrite oxidation, which would have resulted in additional iron release and an increase in sulfate, was either slowed or inhibited by the increasing pH. The decrease in specific conductivity (SpC) shown in Figure 2a is also an indicator of lower dissolved species within the water.

These results have important implications for the fate of trace metals in mine wastes in the study area. Most of the MW had simply been covered with limestone. Mine water (issuing from adits) or surface precipitation therefore has limited contact with the surficial limestone, and as water infiltrates through the waste pile and reaches the mine waste underneath, it again becomes acidic in the absence of any additional limestone. This leads to increased acid drainage that eventually "leaks" out of the bottom of the waste piles; leakage of this type was observed during field work in the study area.

Figure 4. Newly-formed iron solids on ANC rock surfaces.

Aqueous metal concentrations
Concentrations of metals associated with sulfides (e.g., Cu, Fe, Pb) tended to reach a maximum value, then decreased with longer reaction time. Iron as shown in Figure 2b is an example for most metals. The time of occurrence of the metal maxima varied but generally coincided with stabilization of pH at higher values (about four days to one week), suggesting that dissolved metals were being adsorbed onto mineral surfaces rather than remaining in solution. The decreasing concentration of many metals with increasing pH has been well documented and is thought to result from greater adsorption onto surfaces and/or coprecipitation with iron oxides (Stanton *et al.* 2007; Zanker *et al.* 2002).

Crystallinity of iron solids
XRD results indicated that the iron solids formed on ANC rock were amorphous and thus had formed recently within the vessel. This confirmed the visual observation of iron solids actively forming on the surface of the ANC rock during the reaction period (Figure 4). Only a minor fraction of the iron solids indicated crystalline phases.

Effect of ratios of ANC and MW
Differences in pH are reflected by the mass ratios of ANC rock to MW rock (Table 1). The greater the mass of ANC compared to MW, the greater the neutralization that occurred. When the ratio of ANC to MW was 2.0, the end pH was 6.3; when the ratio was 8.0, the end pH was as high as 6.9. Although this is only a difference of 0.6 pH units, it may be significant under field conditions where dilution conditions or excess MW are present. The limestone control (with an ANC/MW ratio of 4.0) showed a much higher end pH of 8.2. These data not only show that a higher ANC/MW mass ratio results in slightly higher pH values, but also that limestone is more effective than the volcanic ANC rock at buffering the system to a higher alkaline pH. Similarly, when the water/MW rock mass ratio was higher, more neutralization was observed; at lower ratios, neutralization decreased (i.e., lower pH values). Greater solubility of ANC minerals likely occurs as the volume of water, relative to the MW mass, increases.

Conclusions
1. Volcanic rock with low abundances of carbonate minerals was able to provide ANC to neutralize some of the acidity and raise pH close to circumneutral values. Increasing the ratio of ANC rock to MW would be a logical choice to enhance the effectiveness of the ANC. Conversely, with increasing mass of MW, the effectiveness of neutralization by a fixed mass of ANC was diminished.

2. An important result of the tests was that aqueous metal concentrations decreased with increasing reaction time. Considering that metals are, next to acidity, the most environmentally significant component of AMD, their removal would be considered a positive outcome of remediation using the ANC rock.

3. Volcanic ANC rock may be a lower-cost alternative at sites where it is present and limestone is not, although it is not as efficient as limestone. The volcanic rock could be used to reduce the acidity of AMD to a more-manageable, acceptable value ($\geq$6.0). Neutralization of MW acidity with pure limestone led to buffering at pH near 8.0, thus demonstrating the greater effectiveness of limestone as an ANC source. The volcanic ANC rocks contain much less calcite and so are not as effective as limestone.

4. Local rocks (crystalline or sedimentary) might also be examined for their ANC, and perhaps employed to provide neutralization similar to the volcanic rock in this study. These other sources of carbonate-bearing rocks should be looked at as alternate sources of ANC, especially when limestone is not readily-available and if the scale of the remediation project is small.

5. Current work involves examining the influence of the silicate minerals within the volcanic ANC rocks to determine their role in the total ANC. Early results indicate that chlorite may be the most effective

silicate in providing ANC, but further work needs to be done to identify how each individual mineral contributes to (or detracts from) the measured ANC. Similarly, the behavior of each mineral during long-term kinetic neutralization reactions needs to be examined, that is, do these rocks and minerals continue to provide ANC for long periods of time, for example, up to 100 years?

6. Engineering for MW treatment should include either thorough mixing of the ANC rock with the MW or placing layers of ANC rock (including a bottom layer) within the MW. Such engineering designs would probably be limited to smaller waste piles or wastes that can be readily moved from one location to another. For larger waste piles, mixing or layering would require significant usage of earth-moving equipment.

7. The reaction sequence is much faster in the <2 mm tests than in the large vessels with larger grain sizes. This is not unexpected because smaller grains are usually more reactive. However, it does point out that in a field situation, the presence of cobbles, pebbles, and even boulders will probably slow the rate of remediation as a result of slower reaction between ANC and MW rock. Usage of smaller grain sizes of ANC rock, as seen in this study, should enhance the rate of production of alkalinity and resultant increases in pH.

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Acronyms

ANC: Acid Neutralizing Capacity
MW: Mine Waste