

SIMULATED WEATHERING OF PYRITIC SHALE WITH ADDED LIMESTONE AND LIME¹

Arthur W. Rose and Gary A. Daub²

Abstract: The addition of alkaline material to pyritic coal mine spoil in order to inhibit or neutralize acid mine drainage (AMD) has shown mixed success. We have conducted simulated weathering experiments with a pyritic shale containing 7% S amended by limestone and limekiln flue dust to evaluate the method. The alkaline material was added in a molar ratio of 2 CaCO₃:1 FeS₂ (31.25 st per 1,000 st of 1% S spoil), reacted in a container designed by Hornberger (1985).

Unamended samples produced severe AMD, leveling off after about 4 weeks at about pH 1.5, 17,000 mg/L SO₄, 19,000 mg/L CaCO₃ acidity, 7,000 mg/L Fe and 15 mg/L Mn. The limestone-amended samples were less acid at pH 3.4 to 4.2, 1,600 mg/L SO₄, 30 to 40 mg/L acidity, usually <1 mg/L Fe and 5 mg/L Mn. Limestone particles near the surface were coated by Fe-oxides by the fifth week; this feature extended deeper as the experiment continued. The lime-amended samples were not acid, having pH of 11.3 to 12.3, 1,500 to 2,000 mg/L alkalinity, <5 mg/L SO₄, and nondetectable Fe and Mn.

The significant levels of AMD in the limestone-amended sample probably resulted because the pore solution was not alkaline enough to prevent acidic microenvironments in which bacteria can catalyze the acid-forming reaction; the coarser grain size of 2 to 5 mm for the limestone may also be a factor. In contrast, the lime treatment appears to have completely prevented AMD, even preventing Mn mobility, which is evident in the calcite-amended experiments.

Additional Key Words: acid mine drainage, coal spoil, coal mine wastes, neutralization potential.

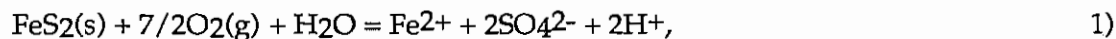
Introduction

The addition of supplemental limestone and other alkaline material from offsite is increasingly being used in an attempt to prevent or ameliorate the production of acid mine drainage from pyritic spoils of surface coal mining. In general, limestone or lime is added to the spoil in amounts calculated to neutralize the amount of acidity that might be generated by complete oxidation of pyritic sulfur in the overburden. Most workers in the past had considered that a ratio of 2 mols of CaCO₃ to 1 mol of FeS₂ (31.25 st CaCO₃ per 1,000 st of 1% pyritic S) was adequate to prevent or neutralize AMD (Brady et al. 1990). The success of alkaline additions was evaluated by Brady et al. (1990), who found mixed results. At most of the sites studied by Brady et al. (1990), the alkaline addition did not result in alkaline drainage, though at some sites the addition was at a ratio considerably less than 2:1. They suggested, based on the concurrent work of Cravotta et al. (1990), that the 2:1 ratio was inadequate and needed to be doubled to 4:1 (62.5 st CaCO₃ per 1,000 st of 1% S).

The purpose of this paper is to examine the effectiveness of two types of material for alkaline addition, limestone and limekiln flue dust, in controlled laboratory experiments. The investigation is described in more detail by Daub (1992).

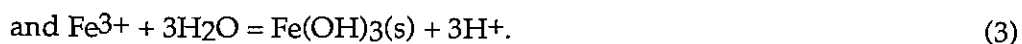
Chemical Theory

It is generally accepted that pyrite oxidation by oxygen to produce AMD can be expressed as a series of reactions (Singer and Stumm 1970):

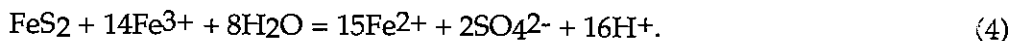


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In addition, once Fe^{3+} is present, it acts as a direct oxidant of FeS_2 :



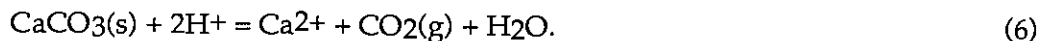
Reaction 2 is catalyzed by bacteria of the species *Thiobacillus ferrooxidans*, which are most active between about pH 1.5 and 5.0. These bacteria markedly accelerate Fe^{2+} oxidation compared with inorganic rates (Singer and Stumm 1970), and since reaction 2 is commonly the rate-controlling step, they accelerate AMD production accordingly. In severe AMD, it appears that reactions 2 and 4 are the important reactions, with reaction 3 occurring where acid is neutralized.

The overall reaction for oxidation of pyrite to its products is the sum of reactions 1, 2, and 3:



As indicated by this series of reactions, the SO_4 is released in an early step (reaction 1 or 4) and is an indication of the amount of pyrite that has been decomposed; the amounts of H^+ and Fe^{2+} in solution depend on the extent to which reactions 2, 3, and 4 have proceeded.

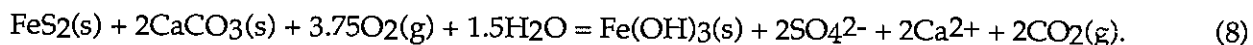
In the presence of acid, calcite initially neutralizes acid by the reaction



However, if pH is increased above about 6.5, the carbonate product will be HCO_3^- rather than CO_2 :



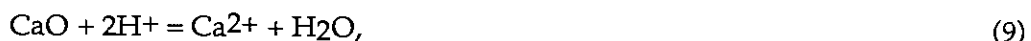
In effect, twice as much CaCO_3 would then be required to neutralize a given amount of acidity because the CO_2 (or H_2CO_3) requires additional neutralization to convert it to HCO_3^- . If reaction 6 is representative, the overall reaction with pyrite is



However, this solution might still be acid, as pointed out by Cravotta et al. (1990).

If CO_2 does not escape from solution during neutralization (eq. 7), twice as much CaCO_3 is necessary to neutralize the AMD ($4\text{CaCO}_3:1\text{FeS}_2$). It appears likely that some CO_2 loss occurs during early stages of neutralization in natural environments, but in order to complete neutralization, HCO_3^- must be a product for at least some of the carbonate. A molar ratio of $\text{CaCO}_3:\text{FeS}_2$ between 2 and 4 seems likely for complete neutralization by calcite (or dolomite) in nature.

In the case of lime as a neutralizing material, the active ingredients may be CaO or $\text{Ca}(\text{OH})_2$. These compounds undergo similar reactions:



If the neutralizing compound is $\text{Ca}(\text{OH})_2$, the reaction is



The difference in reaction stoichiometry for CaCO_3 versus lime, in combination with the method commonly used to determine neutralizing potential (NP) of alkaline materials, leads to some ambiguities in current methods for alkaline addition. The NP method (Sobek et al. 1978) measures NP by reaction 6, in which all carbonate is released as $\text{CO}_2(\text{g})$, yet reaction 7 implies that a need for twice as much CaCO_3 may be appropriate. In contrast, the NP technique measures CaO and $\text{Ca}(\text{OH})_2$ by reactions 9 or 10, but commonly expresses the results in terms of CaCO_3 determined by reaction 6; i.e., an impure lime sample

may produce a result of 800 st CaCO₃ per 1,000 st of sample. In actuality, most lime materials are mixtures of CaO, Ca(OH)₂, CaCO₃, and probably other materials, and conversion from CaO to Ca(OH)₂ to CaCO₃ with exposure to water and air is likely.

Methods

The sample of pyritic shale used in the experiments was collected at the Emigh-1 Mine approximately 3 km north of Phillipsburg, PA, in a group of strip mines operated by Al Hamilton Contracting Co. and known as the Penn South group. Approximately 25 kg of pyritic shale from a 20 cm-thick zone immediately overlying the Middle Kittanning Coalbed (C coal) was collected from an active part of the mine. The sample was crushed to pass 1 cm, and a 0.5-kg split was pulverized and analyzed to contain 7.0% S and 0.17% carbonate carbon. Other materials used were the Valentine Limestone from Centre Lime and Stone, Pleasant Gap, PA, and limekiln flue dust from the same source. Chemical analyses of these materials are listed in table 1.

The simulated weathering procedure of this study is modified from the method of Hornberger (1985), as also used by Williams et al. (1982) and Morrison et al. (1990). In this method, 1 kg of the crushed sample is placed in a 2-L plastic leaching vessel above a layer of 6-mm-diameter glass beads. A measured amount of de-ionized water is then poured into the vessel, wetting the sample and draining gradually into the beads in the bottom of the container. This configuration allows the wet sample to oxidize in the presence of air. After a specified period of time, the water is drained from a plug at the bottom of the vessel, and an additional aliquot of water is added to the top, flushing residual AMD from the sample. The volume of effluent is measured and analyzed chemically. The columns were placed in an air-tight enclosure through which water-saturated air was circulated to minimize evaporation during the experiment; however, 5% to 10% of the water was still lost in some form.

The sample of Valentine Limestone was crushed and sieved. The 2- to 5-mm sieve fraction was used in the experiments. Duplicate columns were prepared with 220 g of limestone thoroughly mixed with 1 kg of shale. This ratio was calculated from the 2:1 molar ratio of CaCO₃ to FeS₂. In a similar

Table 1. Analyses of materials.
(Data in weight percent unless otherwise indicated)

	Valentine Limestone ¹	Limekiln flue dust ²	Shale
SiO ₂	0.64%	7.80%	NA
Al ₂ O ₃	0.22	3.88	NA
Fe ₂ O ₃	0.96	3.79	NA
CaO.....	54.5	56.0	NA
MgO.....	0.36	0.75	NA
MnO.....	0.005	0.75	NA
K ₂ O.....	NA	0.44	NA
LOI ³	43.7	18.6	NA
S.....	0.01	NA	7.0
Carbonate C...	NA	NA	0.17
CO ₂	NA	17.2	NA
Neutralization Potential ⁴ ..	NA	957.	NA
Insoluble Residue.....	NA	22.	NA

1 Valentine Limestone from Centre Lime and Stone Co. Pleasant Gap, PA, analyzed by the company.

2 Baghouse lime, Centre Lime and Stone Co., Pleasant Gap, PA, analyzed by Scott Atkinson, Materials Research Laboratory, PA State Univ., plus CO₂ and neutralization potential by Joel Morrison, PA State Univ. For the limekiln flue dust, an x-ray diffraction pattern indicates calcite and unidentified poorly crystalline mineral(s). Calculated to contain 39% calcite, 22% insoluble residue, and remainder soluble and mostly "lime."

3 Loss on ignition.

4 st CaCO₃-equivalent per 1,000 st

manner, 231 g of limekiln flue dust were mixed with a 1-kg sample. The flue dust was in particles from dust to 1 mm in size, and was used without sieving, again at a 2:1 ratio of CaCO₃ neutralizing equivalent based on a neutralization potential of 950 st CaCO₃ per 1000 st. A pair of vessels were also prepared with no alkaline addition, as a control. The three pairs of vessels were tested on a flushing interval of 1 week and a water volume of 200 mL, which have been standard conditions for most previous studies using the method.

Immediately after the effluent was drained from the vessels, the water was tested for pH, Eh, specific conductance, temperature, and alkalinity. The effluent was then filtered through Whatman #41 filter paper, and hot acidity and sulfate were determined. The remaining filtered effluent was acidified with 2 mL of concentrated HNO₃ and later analyzed by plasma spectrometry for Fe, Mn, and Ca. Methods are summarized in table 2. Effluent temperatures, which represent laboratory temperature, ranged from 20.50 to 280 C during the experiments. The weekly draining, refilling and analysis were continued regularly for 12 weeks, after which some effluents were discarded while others were analyzed up to the 20th week, when the experiment was discontinued.

Table 2. Analytical methods

Method	Procedure
pH	Combination electrode with pH 4, 7 and 10 buffers
Specific conductance	Method 120.1 of E.P.A. (1979) using Beckman Model RC-16C conductivity bridge.
Alkalinity	Bausch and Lomb alkalinity test kit.
Acidity	Method 305.1 of E.P.A (1979), using heated solution with added H ₂ O ₂ to oxidize Fe.
Sulfate	Turbidimetric, using method 375.4 of E.P.A. (1979).
Fe, Mn, Ca	Plasma spectrometry (ICP), with dilution for samples >800 mg/l.

Results

In general, the duplicate columns reproduced within about 20% of their mean. Although this difference is appreciable, it does not significantly affect any of the conclusions, so the duplicate columns have been averaged.

The results are illustrated in figure 1. Compared to the pH values of 1.5 in the untreated vessels, the limestone-amended vessel started at pH 7.6 for week 1 and leveled off at pH values of 3.4 to 4.2. Thus, the limestone treatment clearly produced a higher pH, but the solutions were nevertheless distinctly acid. Sulfate values averaged about 1,600 mg/L compared to 17,000 mg/L in the untreated samples, and acidity was about 30 to 40 mg/L CaCO₃, compared with 19,000 mg/L in the controls. Iron was generally undetectable (<0.2 mg/L) in the calcite-amended samples compared with about 7,000 mg/L in the controls. However, Mn averaged about 5 mg/L compared with 10 to 20 mg/L in the controls.

The lime-amended samples had pH values of 11.3 to 12.3 and consistently contained large amounts of alkalinity (approximately 1,500 mg/L CaCO₃). Sulfate was mostly less than 5 mg/L, and both Fe and Mn were undetectable.

Examination of the limestone-amended sample showed that after about 5 weeks, limestone fragments near the surface of the column were coated with reddish-brown iron oxide. By the end of the experiment, the limestone in the top centimeter was 90% to 100% coated, and in the zone 2 to 5 cm below the surface, 40% to 60% of the limestone was coated. Coating was generally lacking at the bottom of the vessel. Iron oxide also stained the walls of the container above the water level. The iron oxides seemed to form in areas of increased aeration and lower moisture. Crystals of gypsum were also noted on the surface of the column, indicating that measured sulfate in the effluent does not represent all the sulfate that was formed.

Iron oxide and gypsum were not observed on the lime-amended column, but the material did

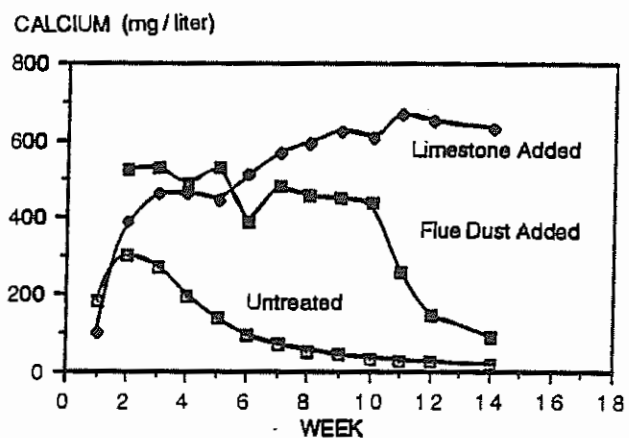
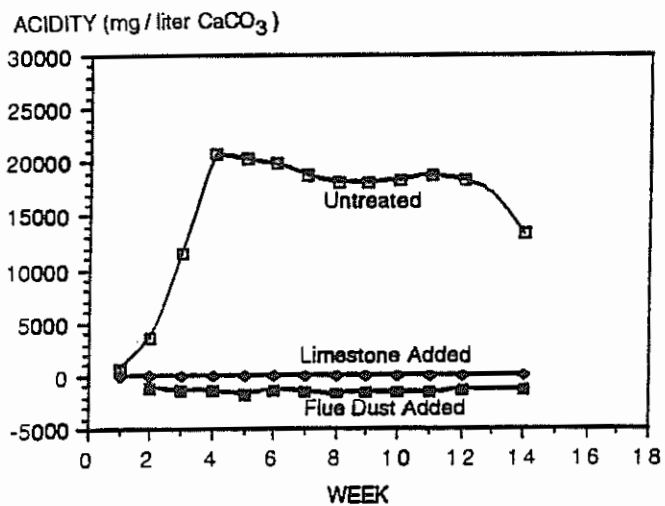
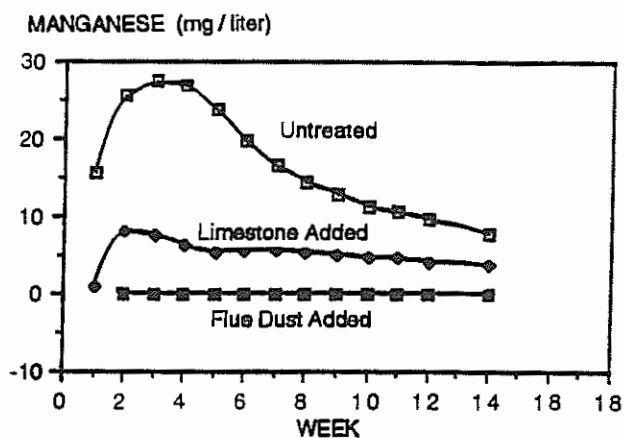
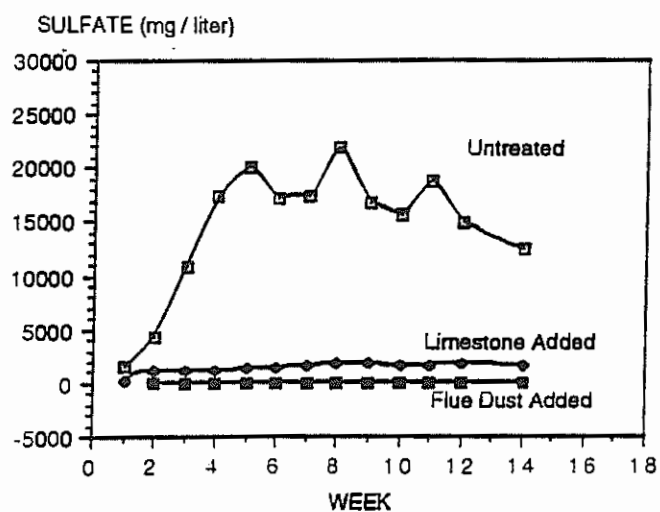
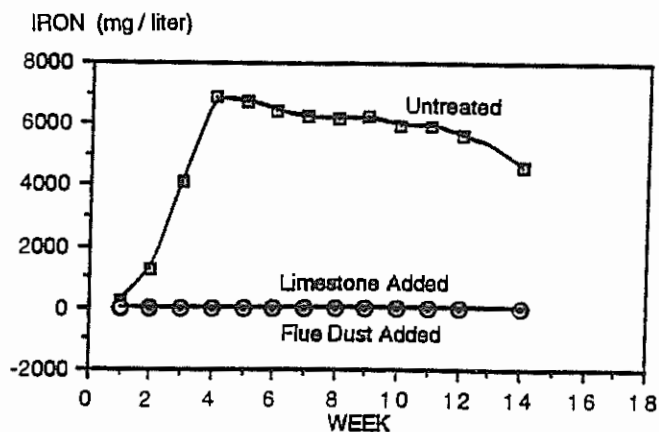
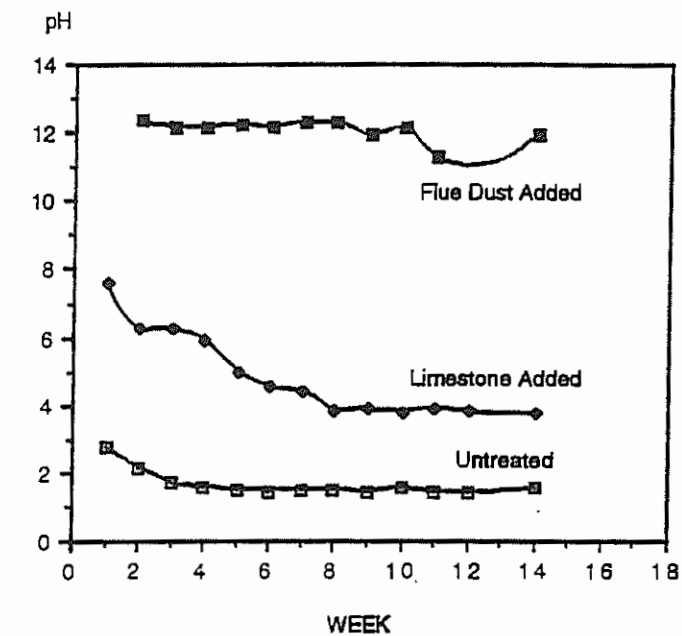


Figure 1. Concentration of solutes in weekly effluent samples from the experiments.

consolidate to a hard but porous block within a few weeks, indicating some sort of cementation. One column of the pair was broken up at week 7 by inserting a glass stirring rod through the material, allowing better infiltration of water but not significantly affecting the effluent.

Discussion

The limestone treatment markedly decreased the amount of acid produced and improved the leachate quality, but did not prevent formation of AMD. The pH values for one column were about 3.5 for weeks 8 to 14, and low but appreciable values of acidity were generated. The presence of 1,500 to 2,000 mg/L SO_4 indicates that acid was being formed in these columns but was in part being neutralized. Concentrations of Mn exceeded the allowable limit for effluents.

In contrast, the lime-amended samples produced essentially no SO_4 and no detectable Fe or Mn. The effluents contained considerable alkalinity and had a high pH, actually higher than that allowed for mine discharges. In view of the fact that gypsum was undersaturated by a factor of about 10^{-2} , the lack of SO_4 in the effluent indicates that essentially no pyrite was being oxidized in these samples; the acid-forming reaction was prevented.

Two possible reasons are suggested for the difference between the effects of limestone and lime. The limestone was coarser than the lime (2 to 5 mm vs. powdery to 1 mm), leading to higher reactivity for the lime particles. Secondly, the lime produces a more strongly alkaline environment. As a result of these differences, we suggest that some small volumes (micro-environments) in the limestone-amended sample lacked significant alkalinity, and bacteria were able to metabolize to create acidity and dissolved SO_4^{2-} , Fe^{2+} , and Mn^{2+} . This acidity was later largely neutralized, but if the neutralization occurred where this packet of solution encountered a limestone particle, the resulting precipitation of Fe oxides coated the limestone. After a few weeks, increasing proportions of the near-surface limestone particles were coated, drastically reducing their effectiveness in maintaining a neutral environment.

In contrast, the lime treatments appear to have completely prevented acid formation. It is hypothesized that the pore water in the lime-amended vessel was everywhere so alkaline that no micro-environments favorable for pyrite oxidation were present. The pH is so alkaline that normal Fe-oxidizing bacteria cannot metabolize, and inorganic oxidation is evidently slow.

Based on these data, the use of lime for alkaline addition appears to be preferable to use of limestone. In addition to its efficacy in preventing AMD, the limekiln flue dust used in this study is a waste product available at little cost except haulage. The addition of lime at a 2:1 ratio of NP (CaCO_3 equiv.) to FeS_2 is more effective than a 2:1 ratio of CaCO_3 .

A complication to the above statements is that a CO_2 analysis of our sample of limekiln flue dust indicated about 40% CaCO_3 , either as unreacted limestone or from CO_2 absorption from the air. Although this calcite "impurity" is less desirable because of the stoichiometric considerations previously discussed, it may also be an advantage. The $\text{Ca}(\text{OH})_2$ and similar compounds are relatively soluble, so that they may be significantly leached from the spoil in a few years. However, CaCO_3 has relatively low solubility at near-neutral conditions, so a mixture of the two may preserve a near-neutral environment over a longer term than pure lime.

Conclusions

Laboratory experiments on a highly pyritic shale from a surface coal mine show that amendment with limekiln flue dust at a 2:1 molar ratio of NP ($\text{CaCO}_3\text{:FeS}_2$) is completely effective in preventing formation of acid effluent. In contrast, addition of limestone at the same ratio allows the formation of a slightly acid effluent, though it is markedly less concentrated than the untreated sample. In the limestone-amended sample, particles of limestone in the aerated zone are coated with Fe oxides and thereby inhibited from acting as effective sources of alkalinity. This process may explain some of the poor results from alkaline addition in the past. Fine grain size and thorough mixing may improve the results of limestone addition. Lime products probably prevent formation of acid because of their much more extreme pH effects as well as their fine grain size, and deserve careful trial as alkaline amendments. A mine-scale trial and several large test cells with varying amounts of lime are currently being evaluated at the Kauffman Mine of Al Hamilton Contracting in Boggs Township, Clearfield County, PA, with support by the Pennsylvania Energy Development Authority.

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