

# ALKALINE ADDITION AND IN SITU SULFATE REDUCTION FOR CONTROL OF ACID MINE DRAINAGE

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## ABSTRACT

Experiments in the laboratory, in 400-ton test cells and in a 27-acre mine indicate that alkaline addition at conventional levels does not completely stop generation of acid mine drainage. Some acid continues to be generated, apparently in microenvironments around some pyrite grains. If enough alkaline material is added and well distributed in the spoil, the acid generated in the micro-environments is neutralized within the spoil and the drainage is acceptable, but for low-pyrite spoil, an excess of alkaline material appears to be necessary.

Lab experiments indicate that degraded sawdust and milk waste products are potentially applicable as organic sources for sulfate reduction by sulfate reducing bacteria. Under the right field conditions AMD can be remediated within coal mine spoil by this procedure. A field test is underway.

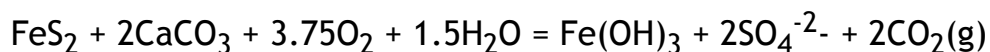
## INTRODUCTION

Many coal resources with sulfur-rich overburden cannot be permitted for mining under current regulations because of the potential generation of acid mine drainage (AMD), and many past surface mines are producing severe AMD. The purpose of this paper is to discuss experiments on the effectiveness of alkaline addition for preventing AMD, and on an in situ method for bio-remediating AMD with minimal surface disturbance.

## ALKALINE ADDITION

The addition of alkaline material to strip mine spoils in order to prevent and neutralize AMD is an obvious extension of the fact that spoil containing natural carbonate material does not generally produce acid (Hornberger, 1985). However, as pointed out by Brady et al. (1990) and Rose et al. (1994), alkaline addition has not been uniformly effective, and the amounts of alkaline material required are in dispute.

The neutralization of AMD produced by pyrite oxidation is conventionally taken to require 31.25 tons of  $\text{CaCO}_3$  for 1000 tons of spoil containing 1% pyritic sulfur, based on the following reaction:



However, if  $\text{HCO}_3^-$  is the product rather than  $\text{CO}_2(\text{g})$ , then the factor is 62.5 (Cravotta et al., 1990). If lime ( $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ) is the alkaline material, then the factor 31.25 is correct, using conventional methods of determining neutralization potential (NP, Sobek et al., 1978). Some trials have used markedly less alkaline material than the 31.25 factor and others have used this factor, with mixed success. Few trials have been well documented.

For the Kauffman Mine project, we have conducted tests at 3 scales: lab bench, 400 ton test cells, and on a 27 acre portion of the Kauffman Mine. The intent of these tests has been to investigate the processes and key variables in alkaline addition, and to demonstrate whether alkaline addition can be successful in preventing AMD.

## Laboratory Experiments

The laboratory experiments were directed at comparing the effects of limestone and lime kiln flue dust in preventing AMD (Rose and Daub, 1994). About 1 kg of pyritic material with 7% S was crushed to pass 1 cm and mixed with either limestone or lime kiln flue dust at a rate calculated from the 31.25 factor. The mixture was placed in a leaching vessel of the type designed by Hornberger (1985). Duplicate untreated vessels were also prepared. Distilled water (200 ml) was added weekly after draining the effluent from the previous week. The experiment was continued for 16 weeks.

The untreated samples produced extremely bad AMD (pH 1.5, acidity 20,000 mg/L  $\text{CaCO}_3$ , Fe 600 mg/L,  $\text{SO}_4$  15,000 mg/L). The limestone-amended sample was much better (pH 3.8, acidity 50 mg/L, Fe <1 mg/L and  $\text{SO}_4$  1600 mg/L). However, the effluent became progressively more acid with time, and particles of limestone near the top of the leaching vessel became visibly coated with Fe-oxide. Effluent from the lime-amended sample was highly alkaline and no acid was produced (pH 12, alkalinity 1500, Fe <1 and  $\text{SO}_4$  <5 mg/L). The lime kiln flue dust was determined to be a mixture of mainly  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  with lesser amounts of inert material. The complete inhibition of acid generation by the lime material, as well as its availability as a low-cost waste product, encouraged us to use it as the alkaline amendment at the Kauffman Mine.

## Test Cells

In October 1993, five test cells were constructed at the northern edge of the then active Kauffman Mine to investigate on a larger scale the effectiveness of different amounts of alkaline addition, and the thermal effects of alkaline addition. Details are reported by Evans and Rose (1995). The cells were placed in holes dozed into the side of the hill. Each cell has a floor area of about 40 x 20 ft filled with pyritic spoil to a depth of about 12 ft., and amounting to about 400 tons (Figure 1). The pyritic material was derived from the binder between the two Lower Kittanning seam in the adjacent mine and contained about 2% S. Two cells were untreated; the other three had additions of lime kiln flue dust of 85, 114 and 175% of the MPA calculated using a 31.25 factor, and the measured NP of 800 for the lime. The spoil was added with a front end loader to a depths of about 1.5 ft., after which the requisite amount of lime was added and mixed into the spoil by dragging the loader teeth across the mixture several times. The mixtures rest on a sandy zone, underlain by a plastic liner that conducts effluent to a collecting pipe and then to barrels for sampling. In July 1994, suction

lysimeters were emplaced at three levels in the untreated cells and in the 114 and 175% cells, to collect moisture above the cell floor.

The results were unexpected. All cells produced extremely acid effluent, though samples from the limed cells are considerably less acid (Figure 2). Effluent from the untreated cells has a pH of 2 or less, up to 70,000 mg/L acidity, and Fe about 15,000 mg/L. In contrast, the cell with 175% of the required alkaline addition produced effluent with pH 2.5 to 2.8, acidity about 4000 mg/L and Fe 600 to 1500 mg/L. Lysimeter data shows net alkalinity at depths of 2 to 4 ft in the 175% cell, but increasing acidity downward to values more acid than the effluent in the lysimeters just above the floor. Similarly, in the untreated cells, water from lysimeters about 1 ft. above the base has pH of 1.3 to 1.6 compared to outflow from the cells of 1.9 to 2.1 (Whitmire, 1995). After about 1 year, effluent flow from the base of the two most limed cells ceased.

Several interpretations can be made of the results. The pyritic spoil sat in a pile for about 5 weeks before it was mixed with lime, and the pyrite had visibly begun to oxidize. The stopping of ongoing oxidation may be more difficult than prevention of oxidation by unoxidized pyrite. However, a more fundamental problem is that the chemical environment within limed spoil is not uniform, as indicated by more acid values for the deep lysimeters compared with total effluent. Water films covering some pyrite grains may be highly alkaline, whereas others are not along flow paths of alkaline water and begin to generate acid, which may or may not later encounter alkaline material and be neutralized. The spoil in this view consists of a set of micro-environments, some alkaline and some acidic (Figure 3). The flow is characterized by channeling and differing flow rates and chemistry in micropores vs. macropores. The acidic environments are able to maintain themselves acid because of relatively rapid pyrite oxidation.

Another factor is cementation of the lime-bearing spoil by reaction of AMD with lime to form gypsum. A mixture of gypsum and Fe-oxide was observed in the spoil when it was excavated to install the collecting pipes (Evans, 1994). The gypsum cement may tend to fill pores and prevent further circulation of water through the lime-rich zones. This process is inferred to have caused the lack of flow out of the cells: water *infiltrating the* surface of the cell encounters a cemented zone and flows laterally out of the cell.

## Phase I of Kauffman Mine

The Kauffman Mine is located in Boggs Township, Clearfield County, Pennsylvania, about 6.4 miles southeast of Clearfield on Highway PA 153. The main coal seam mined on the property is the Lower Kittanning coal (LK coal), occurring as two seams about 20 and 10 inches thick, separated by a carbonaceous shale about 8 inches thick (Figure 4). A thin L. Kittanning Rider coal locally overlies the LK coal. The LK coal is overlain by 10 to 25 ft. of shale and then by up to 50 ft. of Worthington Sandstone, which underlies most of the hilltop at the mine. Beneath the coal is several feet of underclay. The sedimentary units dip at a few degrees WNW toward Clearfield Creek.

The area southeast of a gas pipeline is designated Phase I and is the site of the mine-scale alkaline addition project (Figure 5), which is described in more detail by Rose et al. (1995). Mining started in June 1993 at the SW end of Phase I, and was completed in late 1994 at the

NW end. An overburden hole near the SW end of Phase I (OB-4) indicated appreciable pyrite in and adjacent to the LK coal, and in and below the LK Rider coal (Fig. 4). -In contrast, overburden data for holes OB-3 and C-1 showed much less sulfur except in the LK coal. Neutralization Potential was negligible in all three holes. Acid-base accounting by the procedures of Smith and Brady (1990) using a threshold of 0.5% S showed an alkaline deficiency of 1094 tons/acre for the area of influence of OB-4, and 43 and 169 tons per acre for C-1 and OB-3, respectively. The alkaline material used was baghouse lime from Centre Lime and Stone, Inc., Pleasant Gap, PA. The NP of the lime was about 800 tons  $\text{CaCO}_3$ /1000 tons of lime. Compared to the requirement for 11,930 tons of  $\text{CaCO}_3$ -equivalent, 14,250 tons was actually added.

The more pyritic zones were special handled into pods. In the SW section around OB-4, the zones with significant pyrite (LK Rider and about 6 ft. underlying it, the binder in the LK coal, and pit cleanings) were placed into layers 2 ft thick, compacted by driving on them, and covered with about 30% of the alkaline addition. About half the alkaline material was spread on the mining area after blasting and was mixed with the rock during handling. The remaining lime was placed on the pit floor and on the surface prior to topsoiling, at a rate of 100 tons per acre.

In the NE area around C-1 and OB-3, about 50% of the required lime was placed above the special handling pods, with the remainder equally divided between the pit floor, blasted area and beneath topsoil. However, the requirement here was only about 100 tons/acre.

The success of the alkaline addition has been monitored by backfill wells drilled in the spoil. Well BF-1 was drilled in December 1993, hole BF-2 in June 1994, and hole BF-3 in May 1995. Each was sited in a low spot in the pit floor, based on surveys while the cuts were open, and collects water from an updip zone of the mined area. In addition, two monitoring wells in the pipeline right of way just downdip from the mined zone are sampled at the level of the LK coal.

The results for holes BF-1 and BF-2 are generally acceptable (Table 1). Both consistently have hundreds of mg/L of net alkalinity. Water from BF-1 generally has <0.5 mg/L Fe and <1.5 mg/L Mn; BF-2 samples show an early period of moderate Fe and Mn, but values since 5/95 have been <5 mg/L Fe and <6 mg/L Mn, with a declining trend. However, note that water from both wells typically has 400-600 mg/L  $\text{SO}_4$ . The high  $\text{SO}_4$  indicates that pyrite is oxidizing but the resulting acid solution is being neutralized by reaction with lime. The behavior is consistent with the existence of micro-environments of acidity and alkalinity described above. Apparently the lime is widely enough distributed to neutralize essentially all the acid that is formed in the acidic micro-environments.

Hole BF-3 *consistently shows* acidity exceeding alkalinity, with appreciable Fe, Mn and  $\text{SO}_4$ . Well W-1A in the pipeline right of way also shows acidic waters. These data are interpreted to mean that in the northern section of the mine, where less lime was added because of a much lower maximum potential acidity, appreciable acid is being produced and not neutralized. This behavior is *consistent with* the concept of micro-environments. The low amount of alkaline material is not able to neutralize the acid produced in local pyritic *environments*, *because* it is not widely enough distributed in adequate amounts.

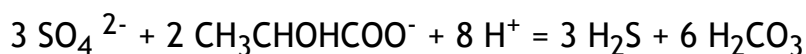
Based on the above data, the adjacent phase across the pipeline has been permitted on the *condition that* alkaline material be added in the entire phase at the rate required by the more pyritic OB-4 drillhole. *Mining will* start in this section in spring 1996, with appropriate monitoring.

## IN SITU SULFATE REDUCTION USING WASTE ORGANIC MATTER

Several promising passive methods of treating flows of AMD from coal mines have recently been developed and applied. These include aerobic and compost wetlands, anoxic limestone drains (ALD) and successive alkalinity producing systems (SAPS). we are evaluating these methods for a set of seeps along upper Paint Creek, Cambria County, PA, but are also investigating in situ sulfate reduction at this site. The flows are so large that wetlands are inadequate, and the acidity is too high for complete treatment by an ALD.

Both compost wetlands and SAPS utilize organic matter to create a reducing *environment*, *with* some accompanying sulfate reduction as one means of remediating the AMD. The process of sulfate reduction is an attractive one, because it leads to precipitation of Fe as Fe-sulfide, and also produces alkalinity. The *intent of* our experiments is to evaluate the possibility of promoting sulfate reduction within the surface mine spoil rather than after water has emerged at the surface. It is also attractive to use some form of waste organic matter, so that this material is disposed of in the process of *cleaning the* AMD.

Sulfate reduction is accomplished by a number of species of sulfate reducing bacteria (SRB) that react dissolved  $\text{SO}_4$  with organic matter to obtain energy for their metabolism. A typical reaction accomplished by these bacteria is:



where  $\text{CH}_3\text{CHOCOO}^-$  is lactate, a form of organic matter metabolized by SRB. The  $\text{H}_2\text{S}$  then reacts with  $\text{Fe}^{2+}$  to precipitate  $\text{FeS}$ . If the organic matter is not a simple species like lactate, the SRB are dependent on *fermenting bacteria* to break down the complex compounds to simple ones.

The major questions and problems in the use of in situ sulfate reduction are as follows:

1. SRB prefer to live in *near-neutral environments* and may not be viable in acid solution.
2. The rate of sulfate reduction may be too slow to be practical; also, the rate may slow with time.
3. A wide variety of waste organic materials is available (paper, sawdust, milk waste, etc.); these may have very different reactivity and properties, including different decrease in reaction rate with time.
4. A practical method of emplacing the waste materials in the spoil is needed.
5. Toxic organic waste or reaction products might be present in the effluent from the in situ reaction.
6. The  $\text{FeS}$  produced in the reaction must be kept under anoxic conditions in order that it not re-oxidize and produce AMD.
7. The acid groundwater must flow through or thoroughly mix with the organic matter along a flow path of significant length.

Stalker (1996) conducted lab experiments with milk waste (whey), lactate, fresh sawdust, degraded sawdust, newspaper, paper mill wastes and mushroom compost. The milk waste and lactate showed the highest reaction rates, presumably because the SRB used these materials directly, rather than depending on fermenting bacteria to degrade them. Among the other products, all cellulose based, the best results were obtained with degraded sawdust; similar rates were obtained with compost, but the other materials were unsatisfactory for various reasons. The sawdust and compost required completely oxygen-free environments, and sulfate reduction was most satisfactory at pH 5 and higher. However, by adding small amounts of alkaline material (dolomite or calcite), the reaction would start at pH as low as 3.

A field experiment was initiated in late July 1995 at the Pot Ridge mine of Cooney Brothers Coal Co. An area of about 100 acres was mined to the Mercer coal at a depth of 70 to 100 ft. At the downdip end of this mined area, a barrier was left, and only the Brookville and Clarion coals were mined in the area further downdip. The barrier thus furnishes a subsurface "dam" behind which AMD saturates the spoil to thicknesses of 30 to 40 ft. (Figure 6). This zone of ponded subsurface AMD, which is interpreted to be slowly leaking out through the barrier to form some of the seeps at the property, is the target for the in-situ remediation project. The lower part of this zone appears to be permanently saturated, so if it is kept reducing, the precipitated FeS will remain stable.

A mixture of degraded sawdust from a old sawmill at Portage, plus 5% fine dolomite and 5% sewage sludge was mixed with water to make a suspension with 13% suspended solids, kept mixed in a 3000 gal. hydroseeder truck. A 6 in. diameter air rotary drill was used to drill to about 75 ft. depths in the spoil. After some experimentation, it was found that the sawdust suspension could be pumped at rates up to 70 gal/min. through the drill rods into the hole, using the hydroseeder pump. The suspension flowed with little resistance into the spoil, which contained appreciable proportions of blocky sandstone that probably left large pores between fragments. A total of about 10 tons of sawdust was injected into 4 drillholes (MW15, -16, -17 and -18) spanning a distance of 100 ft. along the inferred flow path of the AMD. Well MW-20 located 100 ft. upflow from the injection holes was drilled to sample the AMD before it reached the injection zone, and another (MW-12) about 50 ft. downflow was intended to sample the result of the experiment.

The success of the field experiment is not clear at the time of writing. Unfortunately, wells 12, 15, 16, 17 and 18 caved just below the water level before they could be completed to their full depth, so water samples are available only from the upper levels of the saturated zone at the time of drilling. None of these wells penetrates into the zone where most of the sawdust was injected. During early fall 1995, the wells actually became dry, but recovered to contain about 20 ft. of water by January 1996. In contrast, MW-20, the updip well, was completed 5 to 15 ft. below the summer water table.

Based on the data currently available, water in MW-17, in the center of the injected zone, contains 440 mg/L or less acidity compared with 700 to 1500 mg/L acidity in the untreated water of MW-20. Similarly,  $\text{SO}_4$  is 600 to 1500 vs. 3000 to 4000 mg/L untreated, and Fe is 90 to 240 vs. 250 to 480 mg/L. On this basis, the in situ treatment has removed more than half the acidity,  $\text{SO}_4$  and Fe. However, the molar ratios of Fe-loss to  $\text{SO}_4$ -loss are much less than the expected value of 1 or greater. It seems possible that the AMD is stratified, and that MW-20 samples deeper, more acid water than is sampled by the other wells. A deeper well will be

drilled in the near future to obtain samples from the zone in which most of the sawdust was injected.

The rate of reduction using sawdust and other cellulose materials is relatively slow. If it turns out that it is too slow for satisfactory remediation, then milk waste products, the disposal of which is a considerable problem for milk processors, are an alternative. These materials are liquids, so they would have to be added relatively continuously, but if added in appropriate quantities should work well.

In summary, in situ sulfate reduction appears to be potentially viable, and deserves further experimentation to perfect its use.

## ACKNOWLEDGEMENTS

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Table 1. Analyses of water from monitoring wells  
(Fe, Mn and SO<sub>4</sub> in mg/L, Alkalinity and  
acidity in mg/L CaCO<sub>3</sub>)

Date	pH	Alk.	Acid.	Fe	Mn	SO <sub>4</sub>
<u>Well BF-1</u>						
12/10/93	6.90	37	2	.81	.10	79
3/23/94	5.6	15	12	.31	.98	41
4/28/94	6.0	103	2	.19	.80	341
6/16/94	6.7	87	13	.19	1.72	268
9/16/94	6.3	195	58	.06	1.10	97
12/21/94	5.95	202	8	.18	.75	529
3/22/95	6.3	199	37	.24	.45	561
6/22/95	6.1	206	37	.03	.54	628
<u>Well BF-2</u>						
7/27/94	6.6	132	24	5.	2.3	422
9/16/94	6.4	195	24	.1	.4	458
12/21/94	6.15	350	17	9.7	5.7	592
3/22/95	6.5	468	38	20.6	6.34	750
6/22/95	6.4	360	37	.05	4.59	580
7/20/95	7.0	450	0	.29	4.12	451
<u>Well BF-3</u>						
5/4/95	5.5	24	52	6.51	15.1	297
5/19/95	5.95	23	27	5.45	11.8	230
6/22/95	4.45	3	200	13.6	81.7	1197
7/19/95	4.5	6	174			525





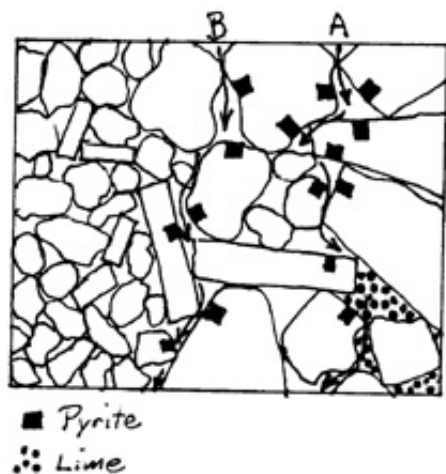


Figure 3. Schematic diagram of flow paths through micro-environments. Flow path A: acidity is neutralized; path B is not neutralized.

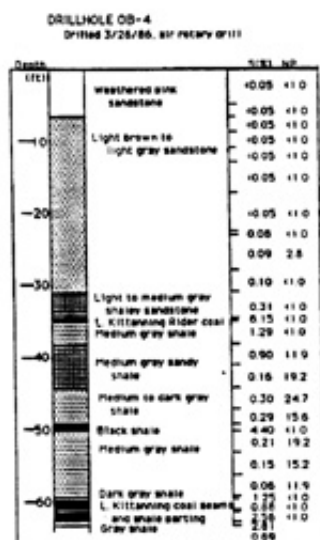


Figure 4. Drill log and overburden analyses of S and neutralization potential (NP) for air rotary hole OB-4.

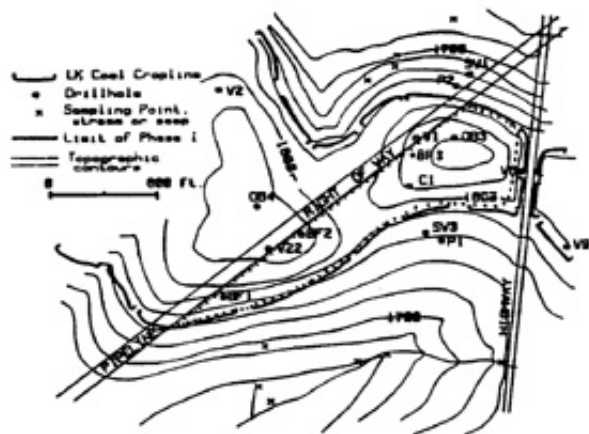


Figure 5. Map of Phase I at the Kauffman Mine, showing coal outcrop, drillholes, seeps, and other features.

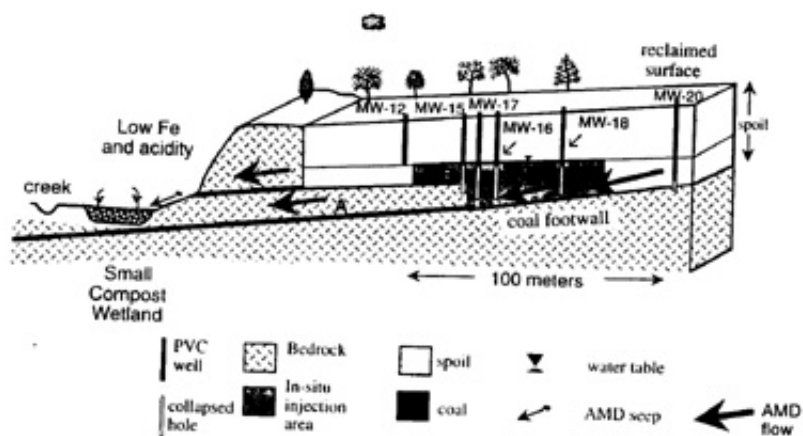


Figure 6. Schematic diagram of in-situ field experiment (after Stalker, 1996)