

**LIMESTONE ADDITIONS TO AFFECT CHANGES  
IN LOADING TO REMEDIATE ACID MINE DRAINAGE<sup>1</sup>**

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**Abstract.** All things being equal, the acid potential of pyritiferous rock naturally outstrips the rate of alkaline production due to the differences in solubilities and rates of pyrite reaction and bicarbonate dissolution. Thus, mixtures of acid and alkaline waters produced by the two chemical systems usually result in net acid conditions when the blending of these two water types takes place. The study area watershed was indirectly impacted by mineral mining when pyrite-rich tailings were transported downstream and deposited. The acidity produced by the tailings deposits varied from 50 to 200 mg/l and, based on detailed field traverses, the area of the deposits was approximately 1672 m<sup>2</sup>. The strategy was to generate at least four times more flow through alkaline material than the acid horizons, thereby, adjusting alkaline loads to neutralize the acid drainage. A blanket application of imported limestone, 8 cm thick and covering approximately 6690 m<sup>2</sup>, was placed during June and July, 1995, near the headwaters and removed from the acid producing areas. To date we have seen the acidity levels reduced to about 45 mg/l. As designed, the critical placement of the limestone blanket is intended to affect the quality of 1) run-off, 2) near surface interflow and 3) groundwater. The effects of acid rain, coupled with the time necessary for impacts to take place on the groundwater and vadose zones, suggests that at this time, only the run-off component is reporting to the stream and that more time is needed for the flow path to become sufficiently alkaline and effect the drainage quality.

Additional key words: acid mine drainage

**Introduction**

From a geochemical standpoint, the acid potential of pyritiferous rock strata is not

constrained as the rate of alkaline production due to differences in their solubilities. The acid potential is related to several factors and

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may vary from 100-5000 mg/l acidity as  $\text{CaCO}_3$ , while the maximum solubility of limestone, under ideal conditions, is limited to about 400 mg/l alkalinity as  $\text{CaCO}_3$  under maximum  $\text{pCO}_2$  ( $\text{pCO}_2=10^{-1}$ ). Thus, because of the disparity, mixtures of acid and alkaline waters, all things being equal, often results in net acid conditions. In order to provide a suitable balance, acid and alkaline loads rather than concentrations should be used in determining the net acid potential.

In previous studies in two coal mines in Ohio and West Virginia, limestone was applied as a surface veneer to attempt to remediate the acid ground/spoil waters. In Ohio, coarse limestone was applied at a rate of 16 to 26 metric tons/hectare with minor effects. At this site, the backfill consisted of porous, acidic sandstone rubble and seeps had acidities varying from 75 to 5000 mg/l. As a result, with the exception of one sub-basin with low levels of acidity in which the sub-basin substantially decreased its acid load, the levels of alkalinity generated were too low to have a direct effect on the more highly acidic sub-basins of the study. While an overall decrease in the acidity of the system occurred with time, the decrease, with the exception of the sub-basin noted above, was similar to that of the control basins indicating that a natural decrease in acid loads was occurring. (Geidel and Caruccio, 1982).

Similarly at the Mercer site in West Virginia, the backfill was comprised of a porous shale/coal sequence and the

application of limestone was applied at a rate of 3 to 15 cm thick (up to approximately 110 metric tons/ha) and produced no significant improvement in seep discharge quality (Caruccio, Geidel, and Williams, 1985). Our studies to date have shown that surface veneers of limestone applied on the surface of acid producing materials, do not generate significant amounts of alkalinity (as bicarbonate) and cannot be used to remediate moderate to high acid groundwater. Though it was shown that the amount of alkalinity generated under atmospheric conditions (60 mg/l) was not sufficient to impact the acidity in these high acid areas, there was merit, however, in using this technique at sites where acid loads were low. This study was designed to test this possibility and determine if this treatment technique had any merit.

### Background

Within the watershed containing the current study area, less than 25 percent of the watershed was impacted by mining. On occasion, breaks in the tailings conveyance pipes caused pyritiferous tailings to spill downstream and through the action of the meandering stream, were deposited as point bar, pyrite-rich tailings. At this mine site the acid producing zones have been identified as discrete deposits within the stream and their inaccessibility by heavy equipment to remove the deposits, precluded the removal of the pyrite-rich tailings. The acidity produced by the tailings, varied from 50 to 200 mg/l.

The area has been mined intermittently during the last 40

years and the last operation was completed approximately ten years ago. In the processing of the ore, fine grained tailings were generated and transported, via pipe, to tailings ponds. However, during the course of the years of operation, some tailings were deposited, presumably as the result of a spill, in the headwaters of an intermittently flowing stream. The tailings deposited are comprised of fine grained quartz, clay and minor amounts of pyrite (on the order of about 2%).

The quality of the stream flowing through the study area is mildly acidic (around 200 mg/l) which most likely results from the oxidation and leaching of the tailings from within the stream bed and, in some cases, from the stream banks. The distance from the headwaters to the sampling point (Sampling Station 1) is approximately 215 meters. As the stream flows through the area, the flow occurs intermittently at the surface, with segments of the stream showing signs of overland flow and irregular acid loads only during high run-off precipitation events. That high flows have taken place is evidenced by the surface expressions.

The primary sampling point is located approximately 215 m downstream from where the stream first appears as a defined channel. This location was selected for a sampling point because continuous flow has been noted at this site and for approximately 55 meters above this point, the stream flow is sub-surface. During the few times when the stream was sampled, the flow varied from a low of approximately 0.3

liters/sec to a very high flow during summer high intensity, short duration rainfall events. This sampling point (SS1) had a continuous flow and, therefore, was selected as our sampling point.

### Methodology

In March 1995, a field survey determined the extent and occurrence of the tailings within the stream bed. Over the 215 m of stream, tailings were visible in about 96 m of stream bed and, while the remainder of the stream appeared to flow beneath the surface, it also contained tailings.

The surface area occupied by the zone of tailings or the potentially acidic material was determined to be 1672 m<sup>2</sup> based on field mapping of the site. Five samples were collected from various locations within the zone. The samples were analyzed for paste pH and the specific conductance of the resultant decanted leachate was measured. The results of these analyses showed paste pH values ranging from 3.85 to 2.55 and specific conductance values between 85 and 1030  $\mu$ S with the lowest pH and highest specific conductance samples from mid-stream sample points, as opposed to stream overflow or dry stream bed samples.

The stream, at Sampling Station 1 (SS1), has been sampled since November 1993 and provides some background data. The background acidity values vary between 45 and 205 mg/l acidity and the pH values vary between 3.75 and 3.8. The specific conductivity data show a variation between 187 to 300  $\mu$ S

with the lower value corresponding to the lower acidity value. The stream characteristics reflect the overall nature of the drainage basin and, as expected, average the variation in quality seen in individual soil samples. Using stream data, in conjunction with the rock sample analyses, the average acidity was established to be 200 mg/l over the area of influence.

Using the 200 mg/l acidity value, 200 mg/l of alkalinity which must be generated to neutralize the acidity. Limestone, by its nature and chemistry, can only produce approximately 60 mg/l alkalinity under normal atmospheric conditions of  $pCO_2 = 10^{-3.5}$ . Therefore, using a mass balance approach, there must be approximately three and one half times more alkalinity than acidity made available to the system. To neutralize each liter of acid water with an equivalent amount of alkalinity, and given that the maximum amount of alkalinity from limestone is 60 mg/l, increased "loads" of alkalinity are required such that the flow of the total system is at least 3.5 times greater in the alkaline zones than from the acid prone zones.

In a drainage basin where the zone of influence by the acidic material is 1672 m<sup>2</sup>, acid rain contacting this material will produce 200 mg/l acidity for the 1672 m<sup>2</sup>. To offset this acidity, rainwater must contact approximately 3.5 times more limestone and achieve equilibrium conditions so as to offset the acidity during a given rainfall event. Therefore, as a conservative measure, four times

the area of the acid zone was determined to be necessary; 6688 m<sup>2</sup>. In addition to the area of impact, the limestone must reach equilibrium conditions. Based on previous studies by Geidel, 1980 and Neuhaus, 1986, it was shown that a layer of coarse limestone (1 inch down to #30) which was 8 cm thick could provide the appropriate amount of alkalinity and at the same time not wash away during normal rainfall events.

The area scheduled for the limestone application was below the previously disturbed and reclaimed area of the mining operation and was within a southern hardwood forest. In consideration of minimizing land disturbance, the limestone was placed on the hillslopes with a minimum disturbance to the trees and shrubs. These areas with the alkaline addition will provide the alkalinity component and would take part in a balance against the acid production potential. Thus, the limestone (being removed from the acid producing material) would not become coated and should sustain an alkaline discharge. The areas for limestone application were staked out accordingly. During the first phase of the application, 2415 m<sup>2</sup> were delineated and limestone was stockpiled outside the area and brought to the various sites by a small front-end loader. The limestone was then manually spread in a layer 3 inches thick. Based on the ease of the first application, the second phase boundaries were established and the limestone application continued until the 6690 m<sup>2</sup> were covered with limestone. The total amount of limestone applied during June and July, 1995, was

972 metric tons.

### Results to Date and Future Plans

The results of the monitoring of SS1 (Figure 1) indicate that while the acidity levels have been consistently low since August 1995, the acidity and specific conductance were also low in November 1993, suggesting that the impact, at this time, has not been significant. Monitoring, however, will continue on a monthly basis for at least the next year and we anticipate that a continued improvement in water quality will occur.

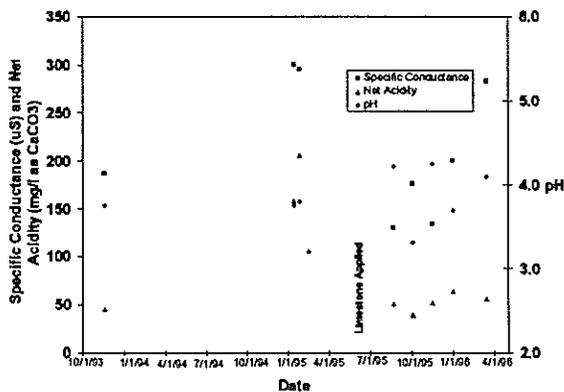


Figure 1. Net Acidity, pH and Specific Conductance for SS1.

There are several possible explanations for the short term (four month) lack of identifiable changes in the water quality. First, the rainfall in the area has been monitored during the past two years. The precipitation is acidic with pH values ranging between 3.3 and 4.2, specific conductance between 5 and 40 µS and net acidities between 7 and 16 mg/l as CaCO<sub>3</sub>. The limestone, therefore, utilizes between 10 and 20 percent of its available

alkalinity to neutralize the acidity of the rainfall. In addition, the clay rich soil over which the limestone was placed constitutes an acid reservoir which must be neutralized by the alkalinity generated by the limestone. Until the reservoir has been neutralized, the induced potential excess alkalinity generated by the limestone will not be available for neutralization of the acidity being generated by the tailings.

Secondly, during low intensity rainfall events, it has been observed that most of the rainfall infiltrates into the limestone and that there is little surface flow. Some surface flow is evident from the minor amounts of limestone that have washed or been transported from the application site. However, the wash has been minimal and in most areas, there appears to have been no movement of limestone. The significance of the infiltration is that the alkaline front is moving into the vadose zone via the rainfall and chemically interacting with the stream as a ground water discharge rather than as a surface water discharge. Long term, this is the preferred scenario because as the alkalinity increases in the groundwater, the alkalinity will become a portion of the base flow. This is important during low flow conditions because the acid components will continue to be affected even without a precipitation event.

The third reason for the lack of significant improvement in the water quality relates to the amount of alkalinity generated by the three inch layer of limestone. We are in the

process of installing a shallow monitoring network to evaluate the alkalinity immediately below the limestone layer and to evaluate the acid and alkaline potentials at shallow depths within the soil horizon. Although the studies by Neuhaus (1986) indicated that the limestone quality was not a significant factor related to equilibrium conditions, the field monitoring will indicate whether the flow-through time of the rainfall under field, rather than laboratory, conditions generates maximum alkalinity. The network will also provide information on any increases in alkalinity which may result from the increasing  $pCO_2$  as a result of surficial leaf decay.

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