

LIMESTONE DRAINS TO INCREASE pH AND REMOVE DISSOLVED METALS FROM
AN ACIDIC COAL-MINE DISCHARGE IN PENNSYLVANIA¹

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Extended Abstract

Limestone drains are used to increase pH and remove dissolved metals from acidic mine drainage (Hedin et al. 1994). However, the chemistry of mine drainage is variable and geochemical processes within these treatment systems are poorly understood. To resolve uncertainties about some of the factors affecting chemical reactions within limestone drains, three identical drains were constructed in parallel to treat acidic drainage from an abandoned coal mine in east-central Pennsylvania (fig. 1). A static mixer was installed to enable aeration of the inflow to one or all three drains. Samples of water were collected at the inflow to the drains, at points within the drains, and at the outflow from the drains. The samples were analyzed to evaluate the rate of dissolution of limestone and the extent of hydrolysis and precipitation of iron, aluminum, manganese, and other dissolved metals. The inflow rate was varied to determine any effects on the rates of dissolution and precipitation reactions and the transport of reaction products through the drains.

As the water flowed through the drains, pH and concentrations of alkalinity and calcium increased, and concentrations of acidity and of dissolved and suspended iron and aluminum decreased, and concentrations of sulfate, magnesium, manganese, nickel, and zinc did not change (figs. 2-4). These water-quality trends and computed saturation indices (table 1) indicate that throughout the drains, limestone (CaCO_3) can dissolve and neither calcium nor sulfate can precipitate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), because the water is undersaturated with respect to these solids. However, as pH increases, first iron, and then aluminum, rapidly undergoes hydrolysis and precipitates as hydroxide compounds within the drains. At slow flow rates, iron and aluminum hydroxides tend to settle out of suspension and do not adhere strongly to (armor) limestone surfaces. Concentrations of dissolved manganese, nickel, zinc, and other trace metals are not limited directly by precipitation or sorption reactions. Only minor amounts of the trace metals are removed from solution by sorption onto iron and aluminum hydroxides at $\text{pH} < 5$ (Coston et al. 1995) because protons compete for sorption sites under the relatively low-pH conditions at which iron- and aluminum-hydroxide solids precipitate. Under "closed system" conditions in which hydrolysis products including protons and carbon dioxide can not escape the drains and are retained as reactants, limestone surfaces rapidly dissolve and hence armoring is avoided, despite oxygenated conditions. Water quality changed most near the inflow (fig. 3), because the rate of limestone dissolution slows with increasing pH and increasing concentrations of calcium and bicarbonate (Plummer et al. 1979). Although the concentration of calcium added to treated effluent was greatest at slower flow rates (fig. 5), or increased residence time, the overall average rate of dissolution of limestone, 4.4 kg/day, was independent of residence time. If the rate of dissolution remains constant, the 40,000 kg of limestone used to fill the drains theoretically will last 25 years.

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Table 1. Measured composition and calculated saturation indices for water samples¹

[Water-quality constituents in milligrams per liter, except for pH; saturation index and logPco₂, unitless; -- no data; < less than; > greater than]

Sample Measured Water-Quality Constituent Saturation Index²

| Distance | pH | SO ₄ | Alkalinity CaCO ₃ | Ca | Mg | Fe | Mn | Al | Calcite | Gypsum | Fe-(OH) ₃ | Al-(OH) ₃ | log P _{CO2} |
|----------|------|-----------------|---------------------------------|----|----|------|-----|------|---------|--------|----------------------|----------------------|----------------------|
| 0 ft | 3.50 | 210 | 0 | 28 | 26 | 1.70 | 3.0 | 0.79 | -- | -1.6 | -0.8 | -6.1 | -- |
| 5 ft | 4.30 | 210 | 0 | 36 | 26 | .680 | 2.9 | .64 | -- | -1.5 | -2 | -3.8 | -- |
| 10 ft | 4.85 | 210 | 3 | 39 | 27 | .240 | 3.0 | .63 | -4.7 | -1.5 | -3 | -2.2 | -1.4 |
| 20 ft | 5.95 | 210 | 24 | 49 | 26 | .020 | 2.9 | .27 | -2.6 | -1.4 | -1 | -4 | -1.6 |
| 40 ft | 6.40 | 200 | 70 | 70 | 26 | .007 | 3.0 | .08 | -1.5 | -1.3 | -1 | -4 | -1.6 |
| 60 ft | 6.70 | 200 | 110 | 81 | 26 | .011 | 2.9 | .05 | -1.0 | -1.2 | .4 | -3 | -1.7 |
| 80 ft | 6.65 | 200 | 118 | 88 | 26 | .007 | 2.9 | .05 | -1.0 | -1.2 | .1 | -3 | -1.6 |

¹Water-quality data for samples collected on April 25, 1995, from points at increasing distances downflow in drain 2; influent is at 0 ft and effluent is at 80 ft.

²Saturation index [SI = log (IAP/Ksp)] calculated with WATEQF (Plummer et al. 1976) and reported measured data (above), other constituents (silica, chloride, sodium, potassium, strontium, and zinc), temperature, and Eh. A value of zero (-0.5 < SI < +0.5) indicates the solution is in equilibrium with the solid; values that are negative (SI < -0.5) and positive (SI > 0.5) indicate the solution potentially can dissolve or precipitate the solid, respectively.

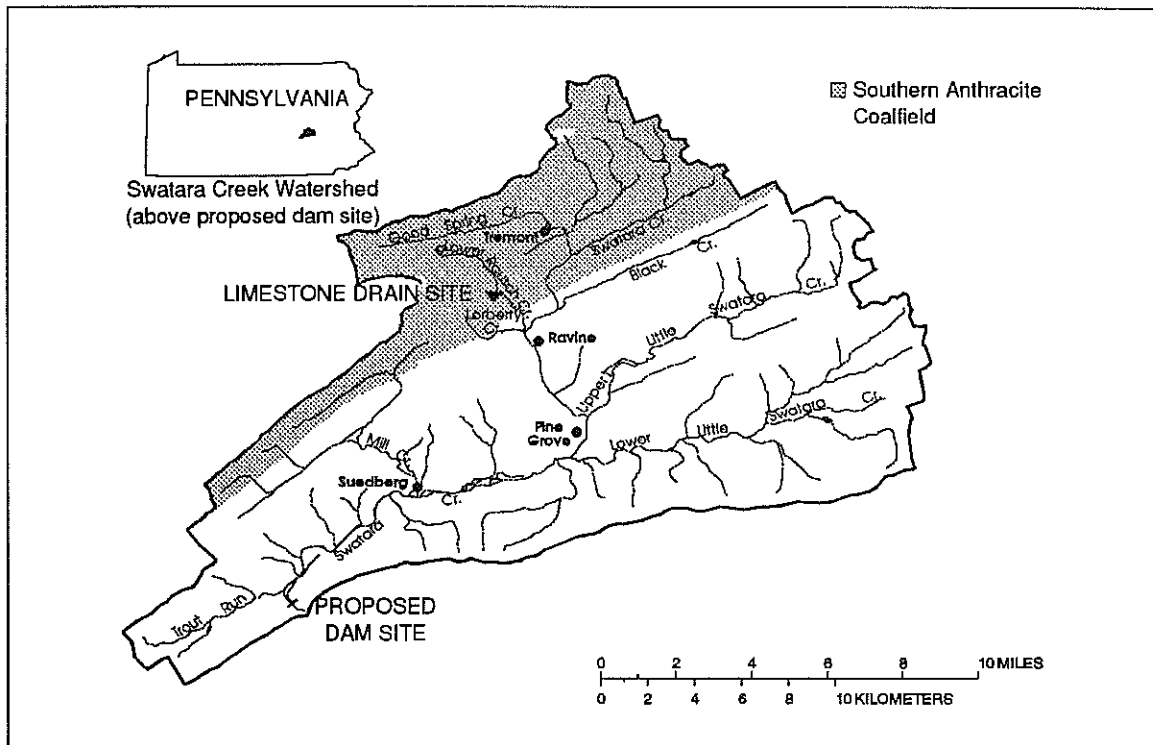


Figure 1. Location of limestone drain study site in the upper part of the Swatara Creek watershed, east-central Pennsylvania.

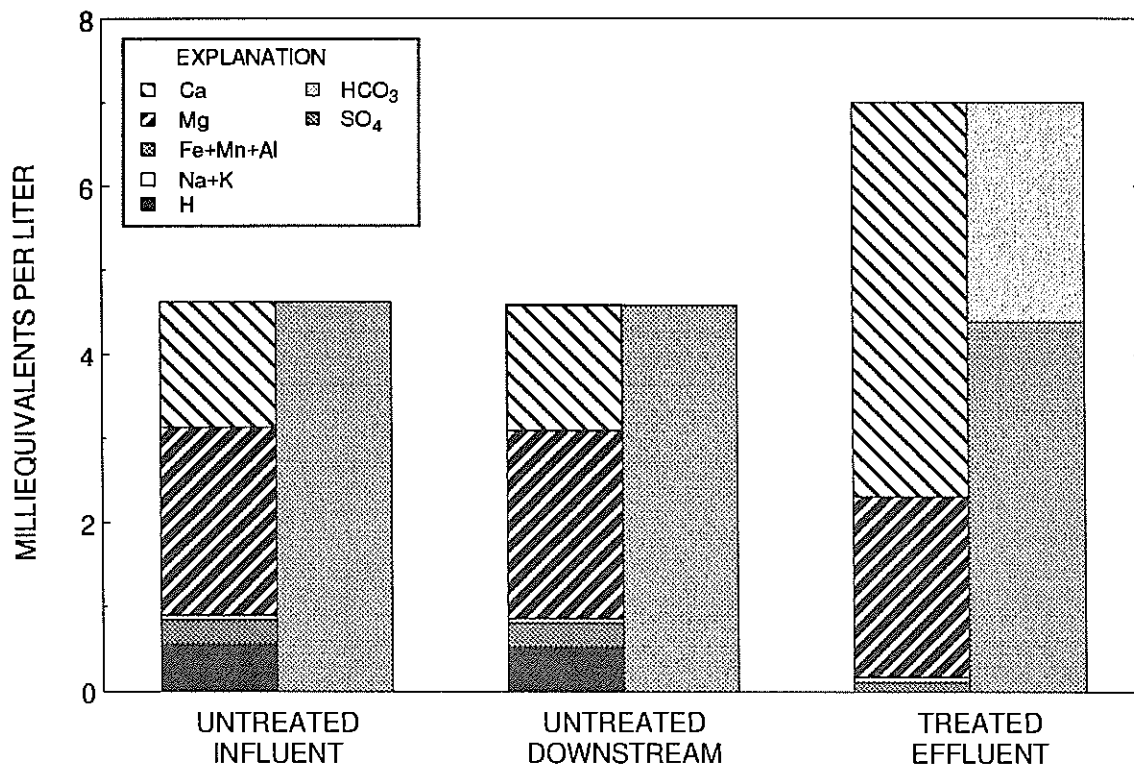


Figure 2. Major-ion composition of discharge before and after treatment by limestone drain 2. Data for samples collected March 23, 1995.

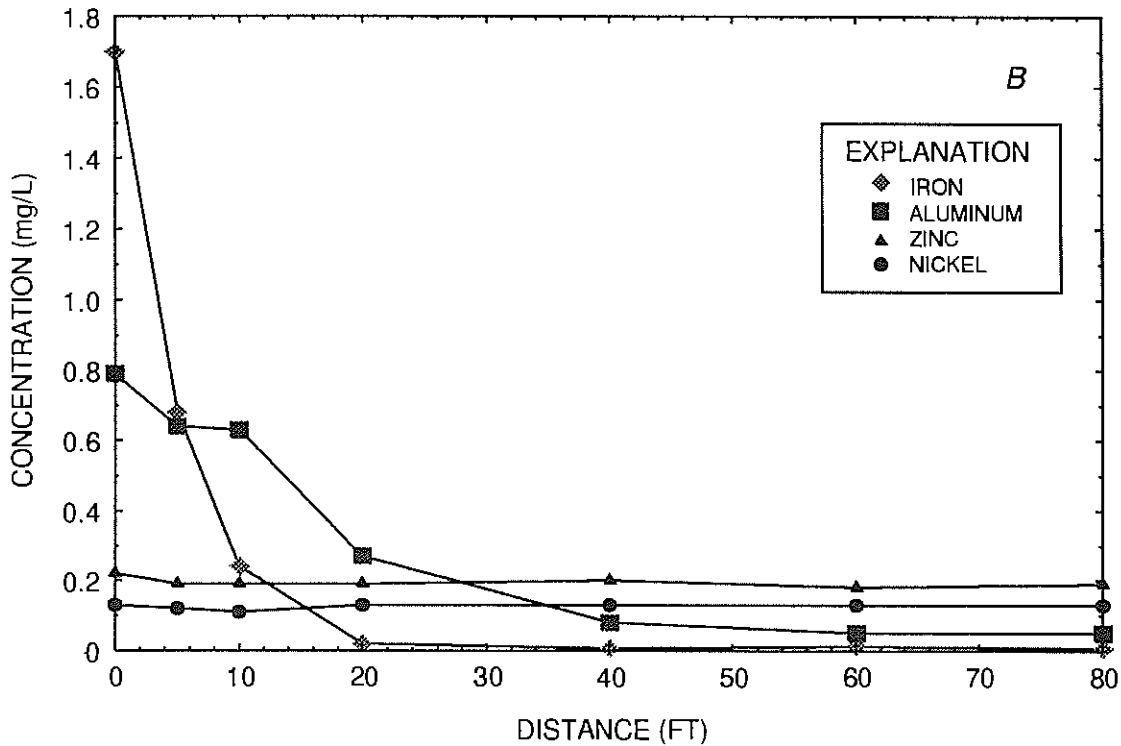
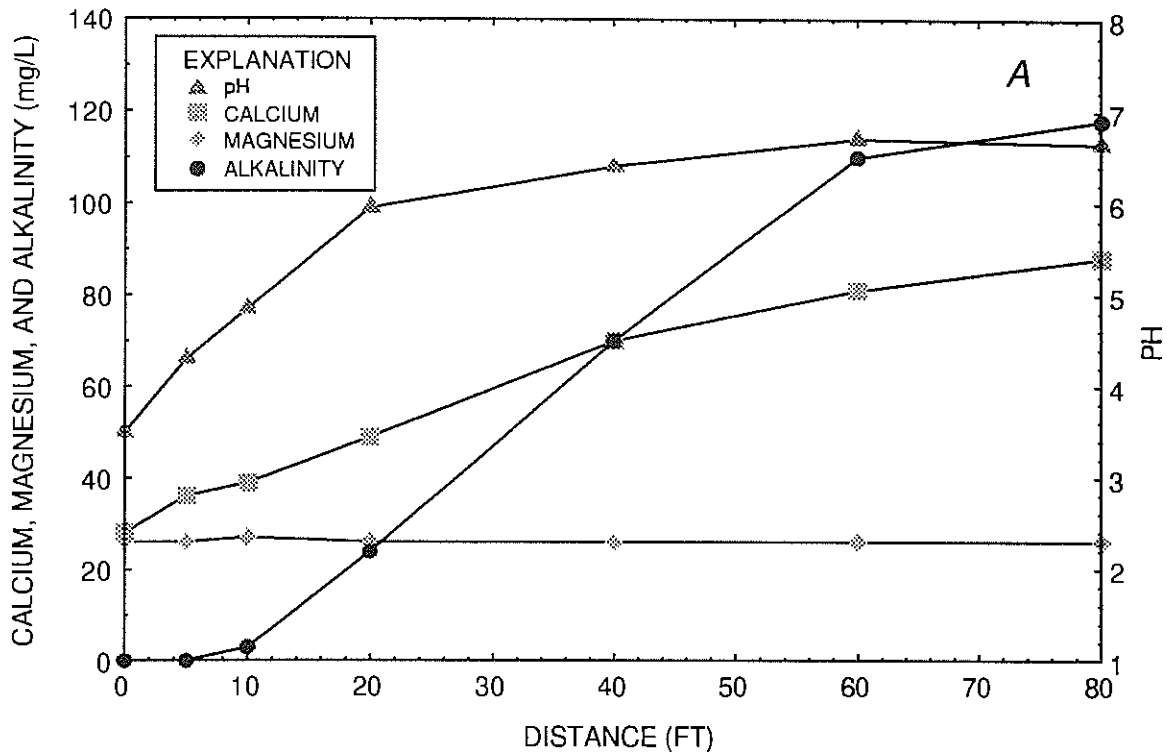


Figure 3. Sequential changes in water quality within a limestone drain: A, pH, and concentrations of alkalinity and dissolved calcium and magnesium; B, concentrations of dissolved iron, aluminum, zinc, and nickel. Data for samples collected April 25, 1995 from drain 2.

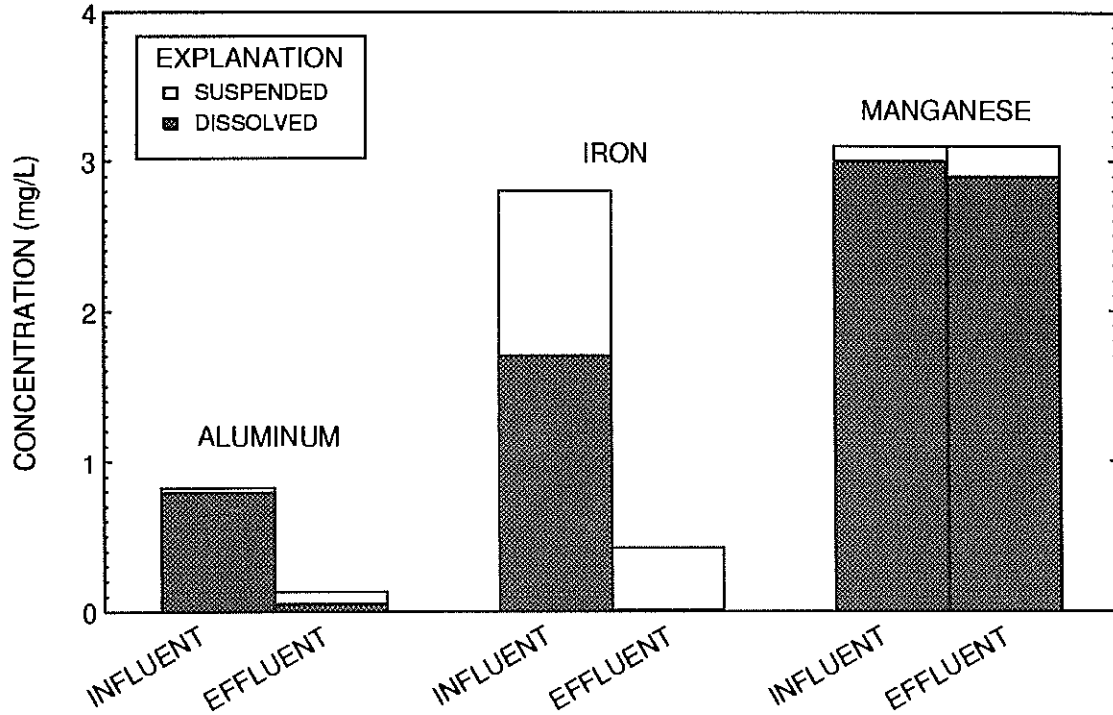


Figure 4. Concentrations of suspended and dissolved manganese, iron, and aluminum in discharge before (influent) and after (effluent) treatment by limestone drain. Data for samples collected April 25, 1995 from drain 2.

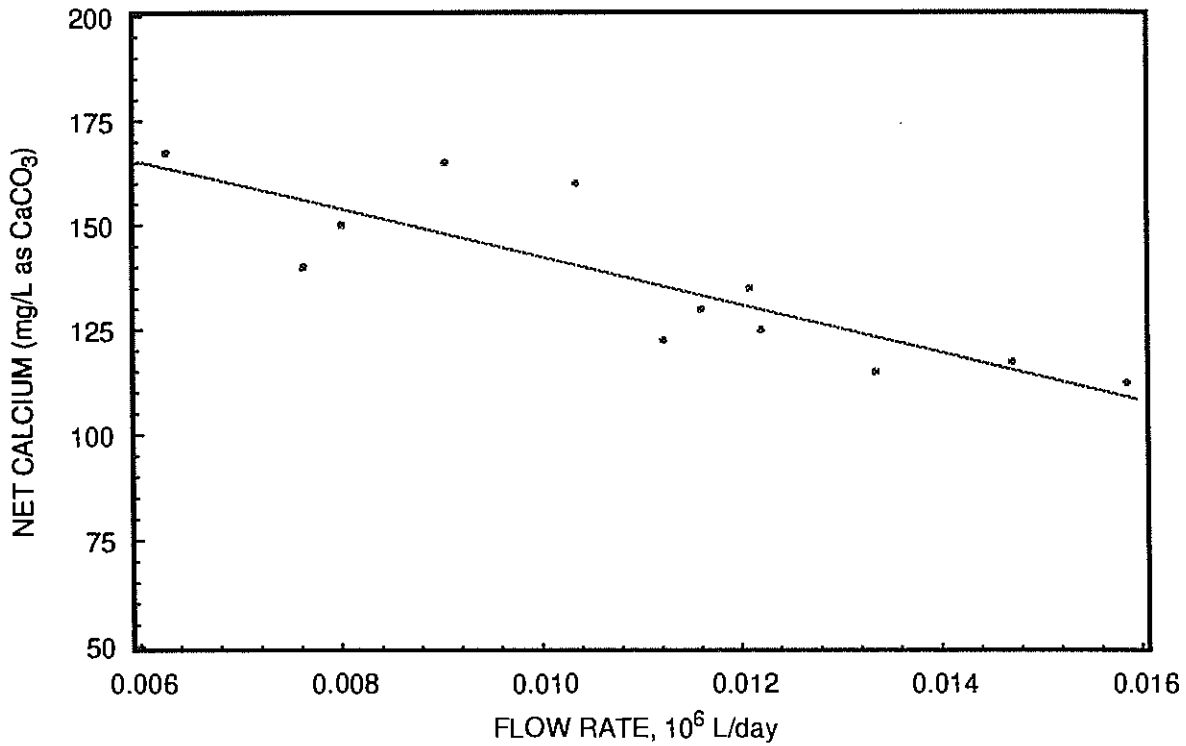


Figure 5. Concentrations of calcium added to effluent from limestone dissolution as a function of discharge rate. Data for samples collected March - August, 1995 from drains 1, 2, and 3.