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effects are the cause of limited growth under acid conditions above pH 3.

Many authors list pH 4, and others pH 4.5, as a lower limit for reclamation plantings. They are right only if the spoils have an ionic composition which results in one or, more likely, a number of toxic conditions. Under the right geochemical conditions plants grow very well at pH levels typically measured on barren spoils. For example, spoil banks in Saline County, Illinois, which averaged pH 3.4, much lower than the pH of many "toxic" banks, were planted to 17 tree species in 1947. After 30 years those plots had a vigorous young forest with strong invasion of oaks and other species. Sweet gum trees averaged 9.3 inches in diameter and were larger than the trees on the other 12 plots of this study in Illinois, all of which were at higher pH (Ashby et al. 1978).

Chemical tests are widely used guides for revegetation management, and pH is the best test we now have. Unfortunately our understanding of the role of acidity in reclamation practice is much like that of alcohol in society. Alcohol is generally believed not to be harmful of itself, but it leaves a legacy of derelict individuals, broken homes, health problems, shortened life spans and deaths on the highway. Acidity is widely regarded as undesirable. At present we may be in a prohibition

era, banning acidity by liming or other means because we do not have enough understanding to work out which of its numerous indirect effects limit plant growth and could be corrected in other ways.

Direct Effects of Pyrite Oxidation — There are four direct effects of pyrite oxidation. First, the oxidation reactions liberate quantities of hydronium ion in proportion to the amount of pyrite undergoing oxidation (reactions 1-4). If there are insufficient quantities of neutralizing materials in contact with the pyrite to counteract it, the obvious effect of the hydronium ion is to lower the pH of the area in which the pyrite is undergoing oxidation. In such a situation, the liberated acid may spread the products of the oxidizing pyrite beyond the spoil through surface and ground water and may be felt many miles downstream.

The second effect is the liberation of ferrous ion. If the oxidation potential and/or the pH of the environment is low, the oxidation of ferrous to ferric ion is slow and large quantities of iron may be mobilized. Seeps emerging from pyritic spoil materials frequently contain hundreds to thousands of mg/1 of iron. Since the seeps are simply ground water that flows onto the surface, similar concentrations of ion may be available in the rooting environment.

Continues on page 36

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Reclamation

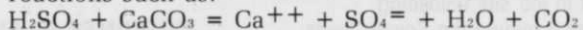
The third direct effect is the liberation of sulfate ion. Again, concentrations of thousands of mg/l of sulfate are reported in seeps from acidic spoil materials. Hundreds to a few thousand mg/l of sulfate can be found in seeps and streams draining non-acidic, but nevertheless pyritic, spoil material. Similar concentrations can be expected in the ground water and soil solutions. A recent study by Hood and Hood (in press) suggests that typical sulfate yields of minespoil in the southern Illinois area are on the order of 4.1 kg/hectare/day which would mean about one-half ton of sulfate per year is generated and leached from each acre of minespoil under the climatic conditions of that area. If most of the oxidation of pyrite takes place in the upper few inches of the minespoil, there should be an abundance of sulfate present in the near-surface environment. *The increasingly widespread recognition of sulphur deficiency under continuous intensive agriculture would not be a problem on soils created in mining.*

A fourth direct effect is the release of trace metals. Geologic materials are seldom completely pure, and pyrite is no exception. Many pyrite samples contain trace elements that are released as the pyrite oxidizes. Such elements include the micro-nutrients cobalt, copper, manganese and zinc as well as arsenic, antimony, cadmium, chromium, lead and nickel (Harper 1977, Blumthal 1977).

Although present in small quantities in the pyrite, in places where oxidizing pyrite is abundant the concentrations of these elements in solution may become appreciable. In southern Illinois, however, trace elements released directly by the oxidation of pyrite generally account for less than ten percent of such elements in water (Harper 1977). The remainder are leached from associated overburden rocks.

Indirect Effects of Pyrite Oxidation — The sulphuric acid generated by the oxidation of pyrite is a powerful agent of chemical attack on overburden materials. These reactions take place within spoil micro-environments. The general result of such attack is the reduction of the hydronium ion concentration (elevation of pH) coupled with release of various soluble cations to the soil solution and ultimately, to the drainage waters.

Attack on carbonate rocks. Carbonate rocks, such as limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), are susceptible to attack through reactions such as:



The reaction for dolomite is similar, albeit slower, and liberates magnesium as well as calcium. The effectiveness of this means of neutralization of acid is, of course, dependent on the availability of the carbonate minerals, whether as discrete rock



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Reclamation

units or as accessory minerals in other overburden rocks. The concentration of these ions in the soil solution can become large. They affect the calcium-to-magnesium and other ratios of calcium, magnesium and potassium which are of importance in plant growth.

Using southern Illinois as an example, it has been established that there is nearly a 1:1 relation between sulfate and hardness in stream water (Hood 1977). This relationship is little affected by pH. Hardness, reported as CaCO_3 , is a measure of $\text{Ca} + \text{Mg}$ and can be approximated as Ca. If sulfate is 1000 mg/l, hardness would also be about 1000 mg/l and Ca and Mg approximately 400 mg/l. Runoff waters from coal mines frequently contain on the order of 1000 ppm sulfate or more, so calcium and magnesium are abundant in soil water. These runoff waters supplied by irrigation to soils locally deficient in sulphur or magnesium can be expected to increase plant growth.

Attack on shale. Shale is one of the most common overburden materials. Acids generated through oxidative weathering of pyrite can attack shale in a variety of ways. In the simplest fashion, there can be an ion-for-ion exchange of hydronium ions from solution for exchangeable ions of the clay minerals. This can release nutrient ions which subsequently may enhance plant growth, or be lost in runoff or percolation waters. The clays then become hydrogen clays, which makes the removal of any remaining nutrient ions by plant rootlets very ineffective.

A high aluminum concentration is the most common cause of failure of agriculture crops on acid spoil.

It is well known that clays affected by acidity can convert to aluminum clays, with aluminum migrating out of the clay structure and onto cation exchange sites. In this situation, the hydronium ion is attacking the interior of clay, liberating aluminum which migrates to the clay surface and becomes fixed, reducing the effectiveness of the clay as an ion exchange substrate for supplying nutrients to plants. Aluminum in the soil renders phosphorus unavailable by forming aluminum phosphates. Russell (1973) states,

"A high aluminum ion concentration is the most common cause of failure of agricultural crops on acid spoil. It probably has two quite distinct effects. A high aluminum concentration in the free space of the root surface may prevent the root taking up phosphate, and aluminum inside the living cell may interfere with sugar phosphorylations."

Identification of aluminum toxicity is difficult because clear-cut visual symptoms are lacking. Plant yields can be depressed, leaves show a purplish coloration, and roots usually are stunted but there are exceptions. These relationships are most likely to be found on acidic mine spoils.



Problem spots like this are understandable and correctable with basic geochemical and soil knowledge.

Manganese oxides are common in shales, frequently making up a few tenths of a percent of the rock. In typical southern Illinois overburden rocks Hood and Stepusin (1975) found 0.05 percent manganese, of which about 60 percent is very readily dissolved in aqueous solutions of pH 2 and 3 formed in pyrite oxidation.

Although manganese toxicity is known for moderately well-drained agricultural soils below pH 5 (Manganese 1973) and is enhanced by acid soils with poor aeration, its occurrence on strip-mine spoils is difficult to determine. Changes in the ion balance of iron and manganese can lead to deficiencies or toxicities of either element. In view of the probable high levels of either iron or manganese on mined lands, attention to the balance of these ions is important. Foliar diagnoses of iron and manganese deficiencies or toxicities are confusing because of their similar appearances which include yellow or dead spots on leaves.

Coatings of iron and manganese oxides are rather common in earth materials. These coatings frequently act as sinks for various heavy metals. In association with oxidized pyrite these coatings can dissolve, releasing iron, manganese and the adsorbed trace elements such as cadmium, chromium, cobalt and nickel into solution.

Further relationships. Other minerals are locally abundant in overburden materials in the midwest. Sphalerite (ZnS) is one such mineral. It is

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