

GEOCHEMICAL FACTORS AFFECTING PLANT GROWTH IN RECLAMATION

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Reclamation under the strict requirements of the federal Surface Mining Control and Reclamation Act of 1977 requires a high level of knowledge of plant growth requirements in relation to geochemical factors on each mine site. A desirable reclamation goal would be to consider all feasible alternatives for creating productive soils and attractive landscapes. The raw materials for achieving such a goal are the rocks and unconsolidated overburden that are commonly termed spoil after mining. Misdirected reclamation tasks can introduce unnecessary costs, lessen success of revegetation, and deny opportunities for building a land better than before mining.

In this paper we focus on the geochemical processes, to which the various minerals contribute on an uneven scale. Sulphur-containing rocks and minerals dominate the geochemical processes. We do not evaluate the highly important role of soil physical conditions in reclamation.

In many respects the soil-plant relationships on mine spoils can be understood as an extension of knowledge from traditional agricultural studies. Agricultural soils are, however, composed for the most part of materials which have been exposed to weathering processes for thousands of years. They typically are leached and ion-poor. Mine spoils contain large amounts of minerals freshly exposed to weathering; these minerals may release large quantities of ions. Spoils underlying topsoil are subject to these same oxidative weathering processes, although probably at slower rates. Spoil thus differs from other midwestern soils in that it involves an ion-rich environment.

The Geological — Overburden is the general term that is applied to all the materials that lie between the earth's surface and a coal bed. A very large variety of materials can exist as overburden. These range from solid rocks such as shale, limestone and sandstone through various unconsolidated surficial materials of diverse origin, such as sediments deposited by streams, lakes, glaciers and wind. Soils can be developed on any of these materials.

Certain minerals or groups of minerals are common in all of these assorted earth materials. The clay minerals make up most of the fine-grained rocks such as shale and mudstone and are common in limestones, siltstones and some sandstones.

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Geochemical knowledge is vital to solving complex reclamation problems.

They are equally abundant in fine-grained unconsolidated sediments and are important constituents of soils.

Quartz is the most important mineral in the coarser sediments and rocks, such as sand and sandstone, and is very common in nearly all other types of overburden rocks. The mineral calcite is the chief constituent of limestone and is common in shales and as a cementing agent in sandstones and surficial materials. Lesser amounts of the minerals feldspar, mica, dolomite and siderite are frequently found. Manganese and iron oxide coatings frequently act as cements to hold grains together.

Although generally minor in amount, sulfide minerals such as pyrite, marcasite and sphalerite are quite important in the geochemistry of weathering of overburden materials. Indeed iron sulfide, pyrite (or occasionally marcasite), is the main geochemically active mineral in overburden materials and any portion of the overburden that contains this mineral may give rise to conditions that affect plants. Because surficial materials have frequently been through one or more episodes of oxidative weathering, they are generally devoid of such minerals. On the other hand, the ancient sedimentary rocks may contain appreciable quantities of sulfide minerals and may cause major

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geochemical changes when weathered. Last, the salts that have been trapped within the pore spaces of sedimentary rocks may become mobile when the rocks are exposed by mining operations.

Sulphur in Overburden — Although sulphur in coal has attracted a lot of attention, sulphur in overburden rocks has only in the past few years begun to attract the attention it merits. Smith *et al.* (1976) have examined the sulphur contents of a large number of overburden materials and report sulphur contents ranging from 0.005 percent to 12.03 percent. Thin layers less than a foot thick occasionally show much higher sulphur contents; one such layer 0.3 foot thick had a sulphur content exceeding 22 percent. Smith *et al.* point out that nearly all of the sulphur-bearing material in the upper six meters (about 20 feet) of most overburdens has been oxidized and neutralized, and is incapable of producing acids. In the Midwest, total sulphur contents of such weathered zones are almost never more than 0.1 percent and frequently are 0.01 percent or less. On the other hand, sulphur contents of unweathered sedimentary rocks are frequently in the range of a few tenths of a percent total sulphur. Much of this sulphur is pyritic, that is, the reduced sulfide form of sulphur present in such minerals as pyrite and marcasite.

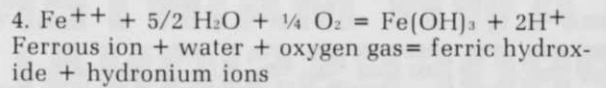
At present, we may be in a prohibition era banning acidity by liming or other means because we do not have enough understanding of other indirect factors limiting plant growth.

It is well known that the oxidation of pyrite and related minerals generates acid mine drainage. Some of the oxidation reactions that have been proposed are:

1. $\text{FeS}_2 + 7/2 \text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{++} + 2\text{SO}_4^{=} + 2\text{H}^+$
Pyrite + oxygen gas + water = iron + sulfate + hydronium ions
2. $\text{Fe}^{++} + 1/4 \text{O}_2 + \text{H}^+ = \text{Fe}^{+++} + 1/2 \text{H}_2\text{O}$
Ferrous ion + oxygen gas + hydronium ions = ferric ion + water
3. $\text{Fe}^{+++} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+$
Ferric ion + water = ferric hydroxide + hydronium ions

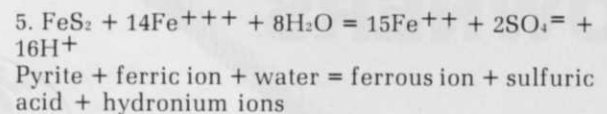
Equation 1 shows how one mole of pyrite can be oxidized in the presence of water and oxygen to liberate ferrous ions, sulfate and two moles of hydronium ion. Equation 2 illustrates the further oxidation of ferrous to ferric iron, and equation 3 shows how ferric ions hydrolyze to give a precipitate of ferric hydroxide with the liberation

of still more hydronium ion. Equation 2, in which hydrogen is consumed, can be combined with the hydronium-liberating equation 3 to give the overall reaction:



It should be noted that the original oxidation of the sulfide ion to sulfate generates two moles of hydronium ion and the oxidation of ferrous ion to the ferric state, coupled with the precipitation of ferric hydroxide, generates an additional two moles. Thus, the complete oxidation of pyrite will generate four moles of hydronium ion, or two moles of sulfuric acid.

The ferric ion, although not usually present in solution in large amounts, can act as a strong oxidizing agent on pyrite. The equation is:



At first glance, this equation would appear to release much more acidity than the earlier equations. However, it must be realized that the generation of each mole of Fe^{+++} requires one mole of H^+ ; there is a net gain of two moles of hydronium in the oxidation of pyrite to ferrous and sulfate ions, the same number as were liberated in equation 1.

The fact that pyritic sulphur is present in overburden rocks is not in itself bad nor does it in itself mean the overburden will become acidic or toxic to plant life. The form of the pyrite is an important determinant in the rate at which the pyrite oxidizes and the rate at which acid is generated (Caruccio 1970, 1975). Smith et al. (1976) carefully point out that the balance between the acidity potential and the neutralization potential is an important factor in determining whether minespoil becomes acidic when weathered. Present regulations require the burial of rock which contains highly reactive forms of pyritic material in quantities exceeding the ability of the minespoil to neutralize the acid. Not quite so obvious is the situation where the upper portion of a minespoil contains reactive pyrite and an abundance of neutralization materials. This situation can create environments especially rich in ions and salts, which may be stressful to plants as discussed in a later section.

Effects of Acidity on Plant Growth — *Neither the best methods for the determination of soil acidity nor its interpretation in terms of soil chemistry and the effects of acidity on plant growth are agreed upon and well understood. Most plants in the eastern United States probably grow best from pH 5.6 to 6.5, medium to slightly acid soils.*

Plant physiologists agree that only below pH 3 (greater than 0.001 molar hydronium ion) are plants harmed directly by acidity itself (Arnon and Johnson 1942). Indirect effects, such as the liberation and mobilization of toxic elements, also may severely limit growth below pH 3. These indirect

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 iron may be available in the rooting environment.

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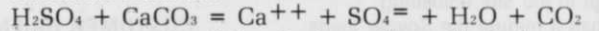
The third direct effect is the liberation of sulfate ion. Again, concentrations of thousands of mg/l of sulfate are reported in seeps from acidic spoil materials. Hundreds to a few thousand mg/l of sulfate can be found in seeps and streams draining non-acidic, but nevertheless pyritic, spoil material. 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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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

present in fractures in coal, in siderite nodules, and in other ways in the overburden. This mineral is soluble in acids, and can also be oxidized by ferric ions in reactions similar to the oxidation of pyrite by ferric ions. Sphalerite frequently contains appreciable quantities of cadmium; thus oxidation and acid leaching of the sphalerite can release appreciable quantities of zinc and cadmium to aqueous solutions.

Nutrients found in minute or trace quantities in plants in addition to iron and manganese include boron, zinc, copper, molybdenum, cobalt (required for symbiotic nitrogen-fixing plants), and chlorine. In the past deficiencies and toxic levels of these and other trace elements were found on mines; however, these are not likely to be found under the regulations promulgated by the new federal Office of Surface Mining.

Plant Growth on Mined Lands — Successful plant growth results from placing each species in a suitable environment. Pasture and forest species have been widely used in reclamation and have given excellent growth. Success with these plantings has resulted from the use of species which were not highly bred for a local environment. Success with a variety genetically tailored for a previous soil condition, such as hybrid corn, cannot be expected on a newly created mine soil, just as corn tailored for northern Illinois soils does not excel in southern Illinois.

Fertilization recommendations for reclaimed stripmines need to be tentative.

Fertilization recommendations for reclaimed stripmines need to be tentative, irrespective of whether the surface rooting medium consists of mixed overburden materials or of replaced soil. Recognition should be accorded and advantage taken of the mineral- and ion-rich environments which can be created from overburden materials underlying geologically impoverished soils on unmined land in many areas (Smith *et al.* 1976). Plant growth, or bioassay, will probably be a better means for assessing fertility relationships than chemical tests on selected nutrients.

Grandt and Lang (1958) analyzed 1,800 soil samples from 15 mining counties in Illinois. They found most of the samples to be very high in phosphorus and high in potassium. Test plots supported excellent growth of pasture.

Plots with 17 tree species each were established in 1947 by the USDA Forest Service on mined and unmined land in Randolph County, Illinois (Ashby *et al.* 1978). In 1976 the unmined plots were at pH 5.0 with extractable phosphorus (P) levels of 4 pounds and extractable potassium (K) of 144 pounds per acre. In contrast one set of mined plots with no previous management was at pH 7.2 with 9 pounds P and 354 pounds K and a



Grass grows in earthmover's tracks indicating the compacted earth was a better growing medium than the uncompacted on this site.

second set at pH 7.7 with 10 pounds P and 224 pounds K using the Bray acidified ammonium fluoride soil extraction method. Differences in P and K levels of the unmined and mined lands were even more marked using the Olsen sodium bicarbonate soil extraction method. Loblolly and short-leaf pine grew best on the unmined plots. These species are common on abandoned fields in the southeastern states. In contrast, black walnut grew much better on the mined plots. Soil which supports good black walnut growth is considered desirable for corn.

Until the properties of a newly-restored field are known, some nutritional requirements may go unrecognized. A good way to find out the nutritional status of reclaimed land is to grow a select group of indicator plants which differ in their nutritional requirements. An initial planting of mixed species for bioassay of the chemical environment on a mine site also serves to build organic matter, create root channels, and condition graded spoils for growth of later plantings.

Total Dissolved Solids — Stripmine soils and drainage waters commonly have high concentrations of total dissolved solids (TDS) resulting from direct and indirect effects of pyrite oxidation. Further TDS may be formed from neutralization of acidity with lime, fly ash, or other soil amendments.

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Although some of the soluble sulfate may then precipitate out as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), high levels of calcium and sulfate remain in solution. Much of the iron may precipitate out as iron hydroxide.

Soils workers commonly measure salt levels, which can be equated to TDS, as electrical conductivity (EC) and plant physiologists interpret salt effects in terms of osmotic pressure (Salinity Handbook 1954). A large osmotic disparity between the soil solution and plant cells can lead to unfavorable water relations and consequent impaired growth and photosynthesis, and even plant death.

Drought markedly increases the effects of dissolved ions.

Plants differ markedly in their tolerance to salt levels. As reported by Jackson (1958) EC may affect germination at 1 mho/cm, reduce growth of some "salt"-sensitive plants at 2, and result in severe injury to many species at 3 mho/cm. Some plants can grow at much higher salt levels. Plants adapted to high-salt soils have been found to increase their cell-sap concentration and maintain a favorable osmotic gradient and water supply (Ashby and Beadle 1957).

Salinity problems have been reported chiefly in relatively arid climates where pH, EC, and soluble sodium content are associated. Most natural soils of the humid, midwestern United States have low EC values irrespective of pH, and low sodium content. In contrast, midwestern mine spoils often have high TDS/EC values from sulfate, calcium, and iron.

Drought markedly increases the effects of dissolved ions. As soil moisture is depleted by evaporation and transpiration, the concentration of dissolved ions becomes progressively greater and some may even reach saturation. Roots thus may actually encounter concentrations of dissolved ions much more limiting than those measured using laboratory procedures.

Use of high-salt plants may be the most successful means of coping with TDS/EC levels. An established cover of adapted plant species will mitigate salt problems by reducing salt levels through ion uptake, and by furnishing a mulch on the soil surface and developing root channels which improve water movement down through a soil to hasten leaching losses of excess salts. Subsequent effects on stream quality must be considered.

Halophytes, or plants adapted to salts in soils, are characteristic of western areas with low precipitation. Some western species such as kochia which have flourished as weeds on midwestern stripmines may scarcely be present on adjacent farmlands. Their vigor may be related to an ability to compete favorably with typical midwestern species on mined soils with high TDS. The value of hardy pioneer plants in re-establishing vegetation should be recognized. Use of suitably adapted plants, within the constraints of management, is a key to successful reclamation.

Conclusions — Many stripmines differ from surrounding agricultural lands. The degree of difference is a variable related to type of overburden, climate, and other factors. Agricultural lands are typically ion-poor, and stripmines ion-rich. These ions are released from sedimentary rocks and minerals brought to or near the surface where oxidation and other weathering processes can take place. Iron sulfide (pyrite) is the dominant geochemically active mineral in overburden materials. It may be present in small but important amounts.

Pyrite oxidation liberates hydronium, ferrous, sulfate and other ions directly and calcium, magnesium, manganese, iron, aluminum, and other ions indirectly. Under present regulations acidity from pyrite oxidation which is not neutralized by basic materials in the overburden is controlled by applications of lime and other soil amendments. Some ions such as iron precipitate out at higher pH. Many ions such as sulfate or calcium remain in solution and are measured as high levels of total dissolved solids typical of mined areas. As soils are leached these ions move from sites of production to drainage waters. The loss of ions may be slow compared to the production.

Plant growth depends on a supply of ions from the soil and may be enhanced by the increased availability of minerals on mined lands. Acidity is not necessarily harmful to plant growth. An imbalance of ions, an excess of one ion, or a very high level of total dissolved solids can be deleterious to growth of some species. The plants to be used in reclamation should be carefully chosen for the site, particularly if the site cannot readily be changed to suit a certain species. Both native and introduced species or varieties may have suitable ranges of ecological tolerance for use in revegetation.

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