

Water, Friend or Foe in the Control of Acid Mine Drainage

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Introduction

Anyone concerned with the problem of acid mine drainage (AMD) is familiar with the role water plays in the formation and transport of this acid. Water has traditionally been considered an enemy in the battle to halt the formation and transport of AMD. Published research is sufficient to give a good understanding of most processes affecting the formation of AMD, and offers adequate proof that water can be used as a tool to prevent, or even reverse, the formation of AMD. There has been a reluctance among many researchers to advocate the use of water to prevent formation of AMD because of restraints placed by federal law and because of the strong opposition by many who could most benefit from a solution of the AMD problem. Federal restrictions against allowing water in pyritic spoils are easing and some of the control measures previously advocated are proving ineffective, so this seems a favorable time to explore, and perhaps advocate, the use of water to prevent formation of AMD.

Pyrite and related sulfide minerals were formed under water. The process by which this occurs has been known and understood at least since 1886, when van Bemmelen published some of his findings on acid sulfate soils in the Netherlands (Pons 1973). Pyrite and related minerals are typically formed under anaerobic conditions in swamps or peat bogs by sulfate-reducing bacteria that use energy from readily decomposable organic matter to transform sulfates dissolved in the water and iron contained in ferric oxide. Some of the iron and sulfur may also come from decomposing organic matter and other sources. Rickard (1973) and Bloomfield (1969) describe these processes in some detail. Hydrogen sulfide gas (H_2S) is the first product of sulfate reduction by bacteria. Some of this gas is released into the atmosphere, removing a certain amount of sulfur from the system. Hydrogen sulfide gas is responsible for the "rotten egg" smell commonly noticed in swamps or marls that contain decaying organic material. The hydrogen sulfide remaining in the reducing environment of the swamp reacts with iron compounds to form FeS and then, in turn, FeS_2 or pyrite, which is usually by far the most important sulfur compound in waterlogged soils. Bloomfield also states that in coastal areas these processes can produce large concentrations of sulfur compounds, with total sulfur contents of 4 to 5 percent being quite common. Ku and Mikkelsen (1981) stress the importance of straw incorporated into the soil of rice paddies in stimulating the reduction of sulfate; however, any other readily decomposable organic matter would serve just as well. The decomposing organic matter utilizes all dissolved oxygen from the water, making oxidation of immersed pyritic materials impossible.

Immersing Pyritic Materials to Reduce Formation of AMD

Since pyrite was formed under water we should anticipate that water might be useful in preventing its oxidation. This is indeed the case. Braley (1954a) demonstrated in the laboratory that flooding sulfuritic material reduced the production of acid to about 1/17th that in a moist but unsubmerged sample. Depth of flooding (4 1/2 to 34 1/4 inches) did not affect the quantity of acid produced. From about 7 to 14 mg/l oxygen are normally dissolved in water. This is adequate to permit some minor oxidation of pyrite, but not enough to present an acid mine drainage problem unless the water is agitated and kept well aerated. If water containing the maximum of 14.2 mg/l oxygen percolates through a bed of reactive pyrite then this oxygen has the potential of generating drainage water containing 7.1 mg/l ferrous iron, 12.2 mg/l sulfate ion, and enough hydrogen ion to lower the pH of pure unbuffered water from 7.0 to 6.6. The oxygen diffusivity in water is only 1/10,000 that in air (Coulson and Richardson 1964), which indicates that pyrite placed under water is almost inaccessible to oxygen. Had decomposing organic matter been present with Braley's submerged samples there should have been no oxidation of pyrite.

The Coal Industry Advisory Committee (1964, p. 1) states that complete submergence of acid producing materials under water will prevent their exposure to air and eliminate acid production. Braley (1954b), referring to underground mines, states that mine sealing is effective if the mine can be completely flooded by natural inflow of water so that its sulfurous materials are sealed against contact with air. When an underground mine is first flooded the outflow of acid mine drainage will not cease immediately. The pyritic oxidation products present when the mine is flooded must be flushed from the mine, and this can take a long time. Frost (1979) reported that in several flooded underground mines in the United States and England the oxidation product concentrations at the mine outlet had a half life of 334 to 350 days; that is, the oxidation product concentrations in the mine effluent should be cut in half in approximately 1 year. He also concluded that any pyrite submerged by groundwater or mine water would be effectively prevented from oxidizing further.

If the flooding of pyritic coal seams is effective in preventing the formation of AMD in underground coal mines, why can't flooding be used to prevent the formation of AMD in surface mines? It is possible that in many instances it could, but its use would not be without difficulties. First, surface mines are generally above the regional water table, frequently high up on mountainsides where containing and controlling water can present problems. Second, parts 816.48 and 816.103 of the Code of Federal Regulations relating to surface mining (Federal Register 1979a) seem to prohibit or discourage allowing water to contact acid-forming materials. Effective May 24, 1983, part 816.103 of the law was removed and on June 25, 1982, the removal of part 816.48 was proposed, so these rules may no longer be the obstacle they once were. Also, recent laws pertaining to the abandoned mine reclamation fund have provided for impoundments for fish and wildlife habitat (Federal Register 1980, 1982). Public law 95-87, Section 515(b)(8) relates to the creation of permanent impoundments of water on mining sites as part of reclamation activities and clearly indicates that it is not the intent of the act to prohibit permanent impoundments (Grandt 1983). Section 701.5 (Definitions) of the permanent rules and regulations (Federal Register 1979b) includes developed water resources as one of 10 recognized land uses. Even where Federal regulations still discourage or prohibit contact of water with toxic spoil, an experimental practice exemption (Federal Register 1983) should allow testing of some methods for using

water to control AMD.

There are good examples of the use of water to prevent the formation of AMD in surface mines and in tailings. Perhaps the best example was reported by Hamilton and Fraser (1978) from the Mandy Mine in Manitoba, Canada. The tailings were extremely high in sulfide sulfur (15.4 percent), yet after 32 years storage in a shallow lake they still did not produce acid. The pH of inlet water was 7.6 and that of outlet water was 7.7. With no expenditures on rehabilitation or site maintenance, water quality was good and aquatic animal and insect life moved into the tailings area. Vegetation colonized the area and produced a mat of organic matter covering the entire surface of the tailings. Whether this sulfide is "reactive" or not is not known; however, even massive pyrite has been shown to produce soluble iron, hydrogen, and sulfate ions on exposure to air and water at a rate directly proportional to the surface area of the mineral (Paciorek and others 1981).

Nawrot and Yaich (1982a) investigated naturally vegetated impoundments of toxic coal mine slurry in southern Illinois. They found that the saturated substrate prevented pyrite oxidation and acid production. The moist soil zones provided by the saturated slurry substrate formed a favorable root growth medium similar to that found in natural wetlands. Submergence of acid producing materials to prevent formation of AMD has also been advocated by Pionke and Rogowski (1982), and Rosso (1980). The use of lakes, ponds, marshes, or wetlands in reclaiming mined land has been promoted by Klimstra and Nawrot (1982), Nawrot and Yaich (1982b), Parr and Scott (1983), Fulton and others (1983), Goering and Dollhopf (1982), Olson (1981), Rosso (1980), Grandt (1983), and Anonymous (1980).

The fact that AMD can be prevented by submerging unoxidized toxic spoils under water in the presence of oxidizable organic matter has been well established. There is even evidence that AMD will revert to pyrite or other reduced form if conditions similar to those under which the pyrite was initially formed, in ancient bogs, marshes, swamps, or lakes, are reestablished. Wieder and others (1982) presented data showing that some of the chemicals that cause acid mine drainage were extracted from a stream during its passage through Tub Run Bog in West Virginia. The pH of water increased from 3.4 to 4.5 and specific conductance decreased from 222 to 38 micromhos/cm. The odor of hydrogen sulfide gas in the bog made it evident that not all of the sulfur was being deposited as insoluble sulfides; some was being released into the atmosphere.

It may be practical, in some cases, to remove acid mine drainage and sulfates from water by passing it through swamps or lakes rich in readily oxidizable organic matter. Eutrophic ponds or lakes rich in algae and wetland vegetation seem ideally suited for this purpose. Some investigation will be required to find out how much of each component of acid mine drainage can be removed on a continuing basis by a pond of given size. We also need to know how temperature affects reclamation of the polluted water and what concentrations of toxic materials in the polluted water could be tolerated without overwhelming the aquatic life in the wetlands or lakes. Reclamation of water in this way may be less effective in the cold season than in the warm season.

Valleys that receive low or moderate concentrations of AMD may, under some conditions, be converted into a series of lakes, ponds, and marshes, allowing some or all of the AMD to be removed from solution and converted back to pyrite. Maintaining a series of dams to impound water in this way might not be economically feasible; however, beavers have been

successfully used in the western United States to build and maintain such impoundments at minimal expense where trees and shrubs edible by beavers were growing adjacent to the streams or were otherwise made available (Stipp 1983). Beavers are adaptable to almost any part of Appalachia, and are now common on several surface mines in Alabama, Ohio, and Pennsylvania.

Let's consider some additional ways in which water could be used on surface mines to combat formation of AMD. In area mining the toxic materials should be disposed of in the bottom of the pit, covered with spoil, and allowed to flood as soon as possible. One way to promote flooding of such spoils would be to mine from the lowest elevation of the coal seam toward the highest. Drains releasing water from the first cut should be closed or controlled so that water can back up over the mined spoils nearly to the area of active mining.

Throughout Appalachia, toxic coal washings are frequently stored under water in small lakes or tailings ponds. This appears to prevent formation of toxic quantities of AMD; however, lime equivalent to the oxidizable sulfur is generally added to the slurry. When it is time to abandon these tailings ponds, it should be a simple matter to maintain the water table just high enough to cover unneutralized toxic materials, then either allow marsh vegetation to grow or else add enough topsoil or non-toxic spoil on top of the submerged toxic material to support the species of vegetation desired. This same procedure could be used to dispose of highly toxic spoil materials from surface mines.

Mine sites in a mountainous state like West Virginia are much more difficult to flood than they would be in flat terrain, but even here it seems that manipulation of water and toxic spoils can at least cut down on the production of acid mine drainage. The Coal Industry Advisory Committee (1964) stated that the amount of acid contributed by a given material is related to the length of time that material is exposed to air and water. This should be self-evident. Toxic spoils that are submerged half the year should produce only about half as much acid mine drainage as those that are above the water table all year. That could cut treatment costs almost in half.

Let's consider a typical contour bench such as that illustrated in Figure 1. The toxic spoils could be placed exactly where the coal came from, perhaps a little thicker on the side next to the highwall. This is pretty much in accordance with recommendations frequently voiced 10 to 20 years ago. The outcrop barrier and blossom coal should be left in place as a natural dam behind which water can pond to flood the toxic spoils. If the outcrop barrier is weak in places it should be reinforced or sealed with nonpermeable materials. In this way the toxic spoils could be kept under water for much of the year, if not permanently. A recent study by Dickens and others (1983) in Tennessee indicates that water does saturate the lower level of spoils on contour benches much of the year -- sometimes all year. There is every reason to believe that water would tend to accumulate in the same way at the base of the highwall on contour benches that have been returned to the original contour, provided water is not diverted from slopes above the highwall. Gradual seepage of water from that impounded on contour benches or fills should also have the beneficial effect of increasing streamflow during critically dry seasons. This technique for developing a water table on mine benches or "back to original contour" spoils will not likely be effective if the underlying stratum is highly permeable or tilts steeply toward the outslope, or if the overburden weathers to rock and sand with little clay content.

Spoil is generally replaced to a considerable depth on the flat mountaintop exposed during mountaintop removal. A water table will develop with time in this spoil; and if its base is perfectly flat the mound of water should be thickest near the center and taper off toward the edges. Pyritic spoil buried in the thickest portion of this mound of water is likely to be immersed most or all of the time and so should produce little or no AMD. Several things can be done to encourage the development of a water table in this hydrologic setting, as shown in Figure 2. If the outcrop barrier and blossom coal are left in place on the perimeter of the mountaintop, they would restrict drainage from the mined area and increase the depth of water over the entire water table. Weak places or breaks in the outcrop barrier could be sealed with bentonite or other poorly permeable material to further impede drainage. Surface drainage on the mountaintop could be directed toward a central depression and/or pond, a procedure now practiced successfully on some mines in Kentucky. This would force the water to follow a longer flow path in its exit from the mine and would assure a higher water table and maximum submergence of spoil materials.

The Environmental Protection Agency (Deely 1977) has proposed draining the bench and diverting surface water flowing downhill toward it, or exactly the opposite of what is being advocated here. The procedures EPA has recommended have generally been counterproductive to its stated intention of reducing water pollution; however, as mentioned earlier, these recommendations have now been either removed from the law code or proposed for removal.

Some have tried submerging toxic spoils but still had an acid mine drainage problem. This is quite possible. If spoils were exposed for a month or longer, pyritic materials may have oxidized; then the oxidation products would pollute any water that may eventually inundate them. There are two ways to prevent large scale oxidation of temporarily exposed pyritic materials: One is to keep exposure time to no more than a few days; the other would be to treat the pyritic spoils with sodium lauryl sulfate, phosphate, or other oxidation inhibitors for as long as these spoils are exposed (Kleinmann 1982, Stiller 1983).

Watkin (1983) and earlier workers point out the uniqueness of each mine in location, topography, waste materials, and other factors that affect the type and dispersal of environmental contaminants. Because each mine is different in some respect, it will likely be necessary to manipulate the water and other physical resources available in somewhat different ways on different sites to achieve the greatest advantage -- or the least detriment.

A Word of Caution

The theory that immersing or flooding toxic spoils will reduce AMD is controversial and not fully proven. Therefore, before extensive field tests of these techniques are undertaken, it may be desirable to identify in the laboratory any circumstances under which flooding could not be expected to reduce the formation of AMD.

To explain some of their observations, Barnes and others (1964) proposed mechanisms by which, in theory, the mere presence of water, without oxygen, may induce production of AMD; however, the fact that pyrite has remained in place in the Appalachian Mountains for geological ages while soluble salts were leached away should be ample evidence that these mechanisms do not normally operate under natural conditions.

Several researchers questioned the contention that production of AMD will be reduced in proportion to the time toxic spoils are kept under water. It has been reported (details not presently available to the author) that under some conditions intermittent flooding of toxic spoils does not decrease the production of AMD and may, in fact, increase it.

The General Futility of Attempting to Keep Water from Toxic Spoils

Consider now the alternative to using water as an ally to prevent AMD. It is becoming increasingly clear that keeping water away from toxic spoil material does not permanently prevent formation of acid mine drainage or its entrance into streams. In some cases, release of the acid into streams may be slowed to the point that the need for treatment is lessened or even removed; however, any AMD formed on site is likely to reach the streams eventually unless it is neutralized on site or chemically reduced to its original pyritic state.

Water is a component of the air we breathe, its commonest measure being relative humidity. One can not keep this water away from spoils any more than one can keep the air and the oxygen it contains away from the spoil. Braley (1954a, p. 275) discusses the futility of sealing underground mines to keep fresh air and oxygen out, a task likely to be far easier than keeping them out of unsaturated surface mine spoil. The Coal Industry Advisory Committee (1964, P. 1) stated that if we could completely eliminate either air or water from coal mine operations there would be no acid mine drainage; they observed, however, that this had proven impossible by either physical or chemical means. This is essentially true today; however, chemical treatments tested by Kleinmann (1982) and Stiller (1983) have effectively reduced production of AMD for periods of several months. Shielding toxic spoils from water with plastic is now being tested on about 52 acres of surface mine (Nicholas and Foree 1982). A partial covering of this area has reduced AMD and may continue to be effective for many years; however, only long-term testing can prove the ultimate value of plastic covering.

Several researchers have described the processes by which moisture is condensed from air onto mine walls. Morth and others (1970, p. 135) describe the condensation that occurs when warm moist air from outside condenses on the cool walls of a mine and then drips to the floor. Further, the products of pyrite oxidation are hygroscopic and will absorb water from moist air at any season of the year. Smith and Shumate (1971, p. 49) describe the "weeping" of saturated solutions of reaction products that will drip from pyritic materials in mines. A pyrite sample lay on a desk for 2 years with little apparent change, then one humid August morning I found it sitting in a pool of extremely acid liquid composed of highly concentrated oxidation products dissolved in water hygroscopically extracted from the atmosphere. When the relative humidity dropped, salts replaced the liquid. Within 2 months, the pyrite disintegrated as it became enveloped in a mass of white salts. Morth and others (1972, p. 19-20) observed similar oxidation when pyritic coal was exposed to 100% humidity. This phenomenon was already well known more than 150 years ago when sulfuric acid was prepared from the leachate draining from pyrite heaps exposed to moist air (Lowson 1982, p. 475). The dark oily appearance of highly toxic spoils is also caused by water absorbed from the atmosphere and retained by the hygroscopic salt and acid products of pyrite oxidation (Haynes and Klimstra 1975, p. 8). It can even be observed under hot, arid conditions.

How much moisture is necessary for the formation of AMD? This is debatable, but Brock (1975) found that the lower limit at which iron could be oxidized from the ferrous state to the ferric

state was -23 bars, a little dryer than the -15 bars which is commonly accepted as the permanent wilting point for most plants. This would seem to indicate that the rapid oxidation of pyrite by ferric iron would be blocked at this moisture level, though the slower direct oxidation of pyrite by oxygen might continue. Morth and Smith (1966, p. 85,91) observed that the oxidation rate was a function of relative humidity in vapor phase oxidation and the rate at 100% relative humidity was the same as in liquid phase (aqueous) oxidation at the same partial pressure of oxygen. The relative humidity of a spoil atmosphere can be expected to be nearly 100 percent essentially all the time, so water is likely to be adequate for both the oxidation of pyritic materials and for at least limited transport of the resulting oxidation byproducts. This would be true even when deliberate attempts are made to protect toxic spoils from percolating rainfall and from inflowing groundwater.

There is evidence that water may not even be a necessary reactant in the oxidation of pyrite. Burke and Downs (1937, 1938) observed appreciable oxidation of pyrite by dry oxygen at 88' C and Renton (1983) found more oxidation of pyrite in a dry oven at 1050 than at 100% humidity at 45' C.

Once pyritic materials in mine spoils have oxidized, the oxidation products will almost certainly move, though admittedly this may be a very slow process. Smith and Shumate (1971, p. 49) and Shumate and others (1971, p. 14) describe how pyritic oxidation products may typically accumulate for a long period of time and then quickly be transported from the mine when a surge or trickle of water reaches them. Unless all water entry to and drainage from the system can be eliminated, the system drainage may ultimately reach a new equilibrium, lower in flow rate, but proportionately higher in acid products (Brant and Shumate 1971, p. 65-66). One may be able to slow their rate of movement and change the direction in which they move, but unless these oxidation products can be stored in a bottle we are not likely to halt their movement.

Conclusions

In summary, attempts to keep water from toxic spoils seem likely to prove no more than partially effective in preventing the formation and transport of acid mine drainage, whereas most evidence indicates that deliberately flooding these spoils may lead to a permanent solution to the problem. People should be encouraged to take another look at what is a largely neglected tool in the control of AMD; one that has the potential of being the ultimate solution to the AMD problem. Water can be either friend or foe in the control of AMD. The choice may be ours.

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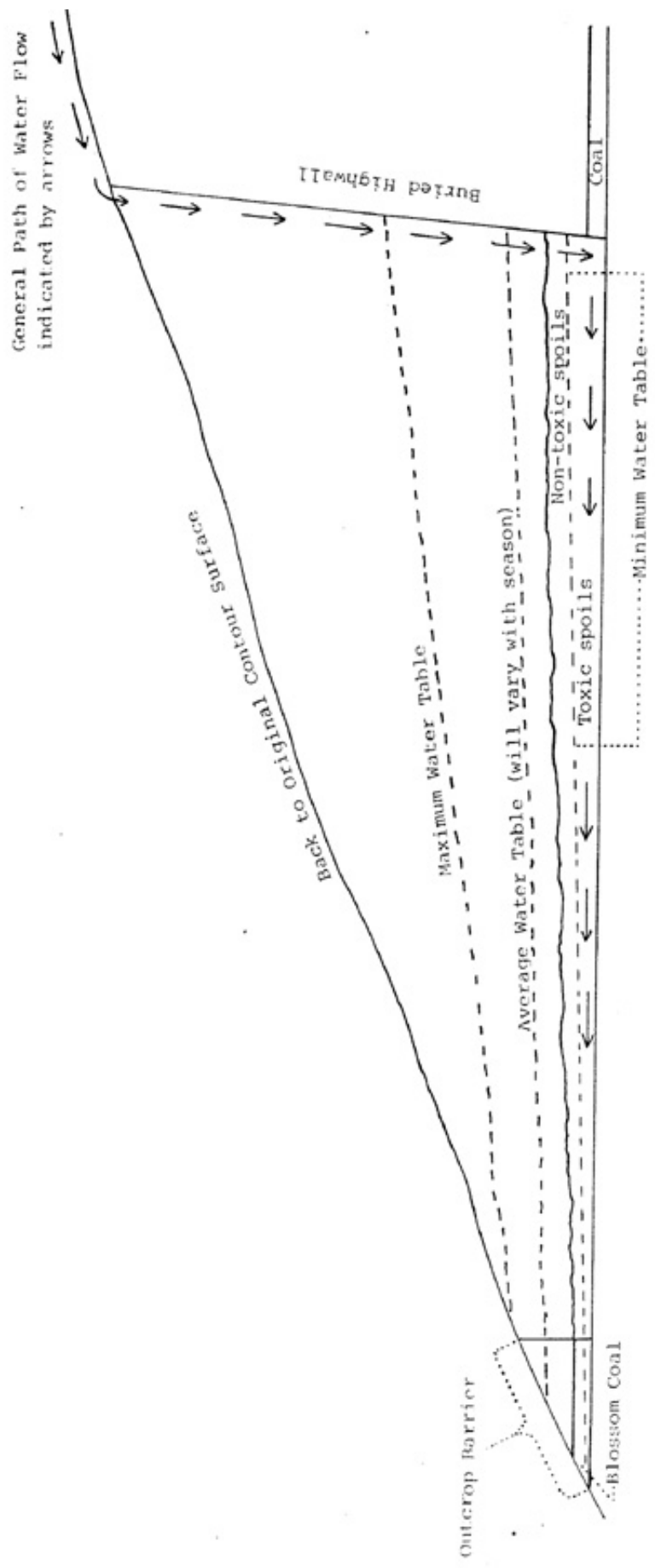


Figure 1.--Cross-section of a contour strip mine showing spoil placement to maximize contact of water with toxic spoil.

Note: The water table illustrated here is based on observations of mountaintop removal areas in Kentucky where water drains into ponds which have never overflowed, then moves underground toward the edges of the spoil area. At present the ponds function as a major source of recharge to the aquifer. Water levels observed in the ponds have always been higher than those observed in wells in the surrounding spoil, though in time this may change as the perched water table under the spoil continues to develop.

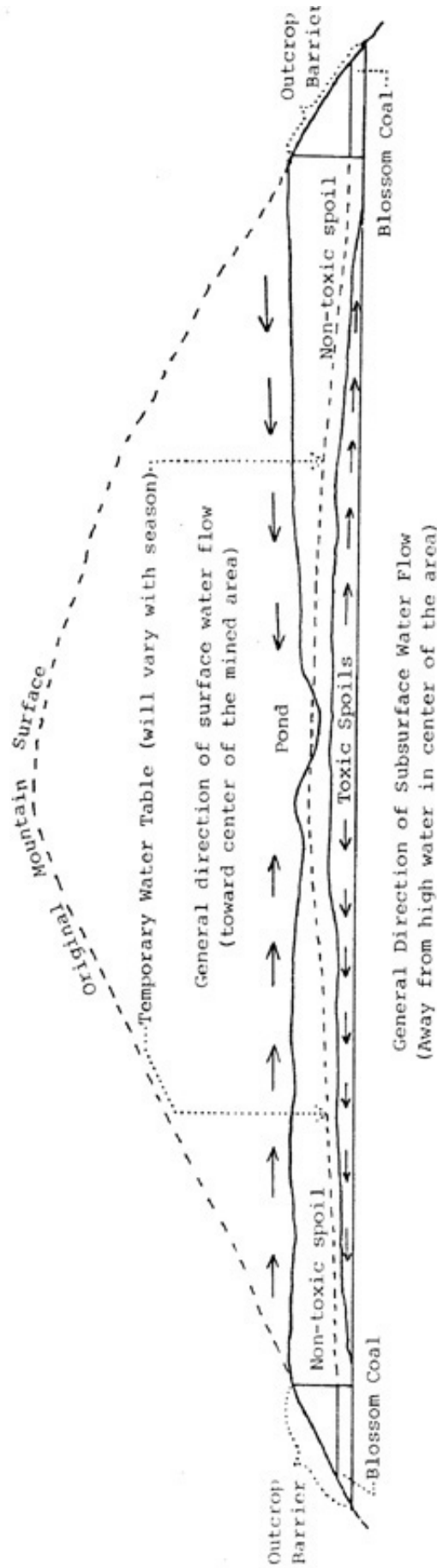


Figure 2.--Cross-section of mountaintop removal area showing spoil placement to maximize contact of water with toxic spoil.