

PREDICTION OF ACID MINE DRAINAGE POTENTIAL FROM COAL MINES

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Acid mine drainage has been and continues to be a major problem generated by mining of coal in Pennsylvania and elsewhere in the world. Although some of the basic chemistry is understood as a result of research over the past 20 years, the process is complex enough that we are not yet able to make accurate predictions of future acid generation at proposed mine sites or to prevent or ameliorate acid drainage at an economically acceptable cost. As a result, many eastern and middlewestern coals are at an economic disadvantage to western coals and to the small proportion of low sulfur coals in the east and midwest. Coal operators are faced with uncertainty in whether they can mine a particular area in an environmentally acceptable manner, and the industry is unsettled by disputes over reclamation procedures.

Our lack of understanding is exemplified by mines that have superficially similar characteristics but produce highly variable amounts of acid. A wide variety of properties have been proposed to explain these wide ranges in acid generation. Because oxidation of pyrite and other iron sulfides is the source of the acid, the abundance of pyrite in the mine is obviously a likely factor in determining acid generation. Fine-grained pyrite, especially "framboidal" pyrite of complex shape, has been implicated in terms of increasing the surface area for oxidation. The crystallinity and impurity content of the pyrite may affect oxidation rate. The oxidation reaction requires that oxygen in air gain access to the vicinity of the pyrite, either by diffusion into the pile of coal or spoil by circulation of air through air-filled pore spaces. A plastic, highly compacted spoil might, therefore, tend to oxidize slowly or release only acid generated by oxidation during the mining step. Ground waters with alkalinity capable of neutralizing acid may consume acid or slow the acid-producing reaction. Alkalinity is furnished mainly by dissolution of limestone and other carbonate-bearing materials. Bacteria catalyze the acid-generating reaction by rapidly oxidizing ferrous iron to ferric iron, which then attacks the pyrite directly. The "health" of the bacteria may be important in the rate of oxidation.

Increased temperature up to 60-70% tends to increase the oxidation rate. Timing of wetting and drying episodes may be important because of high oxidation rates during periods when pH is less than about 3.

All the above factors, as well as others, interact to make prediction of acid relatively complex. At least four methods are currently used in predictions of acid drainage. The simplest, and perhaps the most successful to date, is to evaluate on the basis of mines on the same coal seam in nearby areas. As noted above, these predictions are semiquantitative at best, and occasional large errors are made. Areas lacking recent mines cannot be evaluated.

A second procedure that avoids this problem is to predict acid based on the regional

distribution of pyrite and carbonates, which is related to the regional geologic conditions at the time the coal and its overburden were forming. The relation between sulfur and paleoenvironments are presented in Table 1. In general, pyrite contents average high but are highly variable in shales deposited along ancient shorelines (brackish sediments); moderate pyrite is accompanied by appreciable carbonate in sediments deposited in ancient oceans (marine sediments), and consistently low pyrite is accompanied by moderate carbonate in sediments deposited in ancient lakes, swamps, and some rivers (fresh water sediments); however, sandy sediments of ancient rivers may locally contain moderate pyrite. The type of sediment, or sedimentary "facies", can be evaluated from rapid examination of rock exposures by specialists in sedimentary geology.

A third method is to analyze samples for pyrite and for carbonates and calculate from this the total acid that might be generated after neutralization by carbonates. This procedure is deficient in not allowing for the size, form, and interrelations of pyrite and carbonate.

A fourth method, using lab tests on the rate of acid generation from samples of coal and overburden was initially attempted by Carrucio¹ and has been developed further by Hornberger et al.² and the writers³. In the method currently used, a sample is placed in a beaker-like container and water poured over it to wet all surface. After an hour, the water is drained off, and the wetted sample left to oxidize for a week. Another portion of water is then added, drained off, and analyzed for pH, acidity, sulfate, iron, and other constituents to evaluate the acid-generating potential of the sample. This process is continued for 4-8 weeks. A representative set of samples can be used to evaluate a proposed mine. This method standardizes many of the acid-controlling variables, such as alkalinity of water and timing of wetting, and thereby allows meaningful comparison of rock properties. However, an accurate prediction of acid production still requires consideration of spoil placement, air permeability and interactions with varying types of ground water.

In order to evaluate the factors controlling acid drainage, we have carried out laboratory and field studies using the fourth type of tests to evaluate the various possible factors.

Laboratory Studies of Oxidation Rate

Figure 1A illustrates the results of leaching tests for several coal and overburden samples using the fourth method. The samples show a variety of patterns, some producing the highest amount of acid in the first week, and others after several weeks. For most samples, the rate peaks in the first few weeks. By extrapolation, one can expect the worst drainage from mines to occur relatively early after rocks are disturbed, followed by a long slow decay to lower levels. Rapid oxidation of pyrite exposed on rock surfaces, followed by slower oxidation of pyrite within fragments, probably controls the peak and decay. Slow buildup of bacterial populations is a possible cause of the variable peak time of different samples. We did not seed the samples with iron-oxidizing bacteria, state. This aspect deserves more attention.

The effect of calcite (CaCO_3) on acid production was tested by adding calcite to several samples. Results for a pyritic shale sample are illustrated on Figure 1B. The acidity in a sample mixed with 5% calcite was only 1% of the value for the original sample. Tests with calcite as a layer above the rock sample show a greater reduction in both acidity and sulfate than tests in which the calcite was mixed with the sample, suggesting that the relatively

alkaline water produced by passage through the calcite inhibits the acid-producing reaction, rather than merely neutralizing the acid after it is produced.

The severity of acid production from different samples has been compared using the highest 1-week acidity value per 100 g of each sample. Figure 2 illustrates the pattern of this data when plotted against the % of total sulfur in the rock, taken as a measure of pyrite content. The acidity is strongly related to sulfur content, at least above the 1% S. Below 1% S, the in order to test samples in a relatively natural amount of acidity generated is negligible, and there is no clear correlation of acidity with pyrite. Some sulfur in the low-sulfur samples may occur in an organic or sulfate form, which is not reactive to form acid, but many samples contain small amounts of visible pyrite, and the reason for negligible acidity is not clear. Most of these samples producing little acidity contain a small amount of siderite (FeCO_3), and it is possible that this has inhibited acid production. However, similar amounts of siderite in high-sulfur samples have no apparent effect on acid production. A complete explanation of this non-linear relation of acidity and sulfur will require further work, but it is clear that prediction of acid based on analyses for sulfur in overburden will require a non-linear formula, rather than the linear assumptions inherent in the third method mentioned previously.

Five samples with 1.5 to 5% S produce considerably less acid than the main group of samples, as do several samples to which calcite was added. Four of these anomalously low-acidity samples are shales deposited in a marine environment. One of the four samples contain 12% calcite, which appears to have inhibited and neutralized acid production. Calcite is observed in hand specimens from the other 3 localities, and the leachates contain high sulfate and moderate calcium, indicating neutralization of acid by calcite. In addition, microscopic examination suggests that these marine shales contain less of the very fine-grained "framboidal" pyrite that is common in shales deposited in brackish, shoreline environments.

The actual coals deposited in freshwater environments and enclosed in freshwater shales and clays contain relatively high sulfur contents (1.5 - 4% S) and produce relatively high acidity in laboratory tests (Figure 2), yet field sampling shows that drainage from strip mines in this type of sediment is rarely acid. In contrast, most freshwater shale lying above these coals contains little sulfur and produced little acid in laboratory tests. This evidence shows that in surface coal mines, it is the large volume of overburden, especially brackish and marine shales, that produces the acid drainage, not the coal. Note that in underground mines, where flow of water is channels along the workings in the coal seam, freshwater coals may produce considerable acidity in the outflow, although the common alkalinity of ground water flowing from the sediments into the mine may inhibit acid production at many underground mines in freshwater coals.

Field Studies in Western Pennsylvania

To test some of the ideas discussed above, we sampled drainages from two series of mines with varied types of overlying sediment. Sediments overlying coal in some areas of the Kittanning-Clarion Formation were deposited in marine and brackish environments and contain relatively abundant pyrite (>2% S), whereas in other areas, the coals are overlain by freshwater shales with less than 1% S. Limestone (calcite), which could neutralize or inhibit acid, occurs in the overburden in some areas and is lacking in others. A few areas in

northwestern Pennsylvania contain a layer of calcite-bearing glacial till over the coal-bearing sediments. Local areas also contain sandstones deposited along relatively narrow channels by ancient rivers. These porous sandstones tend to contain moderate to high amounts of pyrite that can oxidize relatively easily. The types of sedimentary sections sampled are summarized by Figure 3.

Water samples from mines in highly pyritic marine and brackish shales (Figure 4, Section 2) contained high acidities (average 400 mg/L CaCO₃ equivalent) and high sulfate (average 950 mg/L). In areas with limestone or glacial till accompanying highly pyritic shale (Section 3), acidities were less than 30 mg/L and sulfate was somewhat lower, indicating neutralization and some inhibition of acid production. Areas of porous pyritic sandstone (Section 4) produced acidities similar to pyritic marine shale (though with a large range), but similar areas with limestone (Section 1) average less than 10 mg/L acidity. Non-marine shales with low pyrite accompanied by limestone and sandstone also have low acid drainage (Section 5 and 6). A second study of coals and overburden in the non-marine Freeport Formation gave analogous results.

These field tests show that abundance of pyrite is probably the most important control of acid, and that calcite content can be extremely important in inhibiting and neutralizing acid. A regional approach can be used to classify the likely acid production into low, moderate, and high groups, based on the regional distribution of marine, brackish, and freshwater sediments and their associated pyrite and calcite contents. In freshwater sediments, sandstones can locally produce high acidity. Figure 5 illustrates the regional predictions for Lower Kittanning coals, using this facies approach. Similar maps have been prepared for all marine and brackish shales overlying the major coal rocks of the Pottsville and Allegheny Groups in Western Pennsylvania³. Maps of facies allowing classification into low, moderate, and high acidity groups are available for many coal basins in eastern and central U.S.

To test this method, about 20 strip mines in Western Pennsylvania were checked in the field. The observed acidity of outflows was compared with predictions from the sedimentary facies. Mines could be consistently classified into the three groups. For the "low" group, predictions seem to be very reliable. However, the range of acidity in the "high" group is large, and more quantitative predictions for this group are desirable.

Summary

The processes generating acid mine drainage are many, and the quantitative relations between factors are only partly understood. Pyrite and carbonate content of overburden at strip mines are probably the most important factors, but others, including access of air to spoil and grain size and shape of pyrite, may be important. Lab tests in which the many factors can be isolated have helped to elucidate the importance of some factors and deserve further experimentation. A thorough calibration of the lab tests and evaluation of factors probably require collection of complete data on critical properties of overburden and drainage at many mines. Regional predictions based on paleogeology can be successfully used in resource evaluation and to aid planning and permitting of mines.

Table 1. Total sulfur values of shale samples.

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	N	\bar{x}	s	range
All shales - Total	70	0.98	1.86	0.10-14.3
Marine	11	2.13	1.28	0.83- 4.31
Brackish	10	3.06	3.99	0.98-14.3
Freshwater	49	0.31	0.18	0.10- 0.95
Freeport Shales - Total (Freshwater only)	37	0.30	0.19	0.10- 0.95
Kittanning Shales - Total	30	1.86	2.61	0.14-14.3
Marine	11	2.13	1.28	0.83- 4.31
Brackish	9	3.18	4.21	0.98-14.3
Freshwater	10	0.35	0.16	0.14- 0.57
Clarion Shales - Total	3	0.78	1.05	0.13- 1.99
Brackish	1	1.99	--	--
Freshwater	2	0.18	0.07	0.13- 0.23

N - number of samples

\bar{x} - mean

s - standard deviation

Total Sulfur Values: error ± 0.06

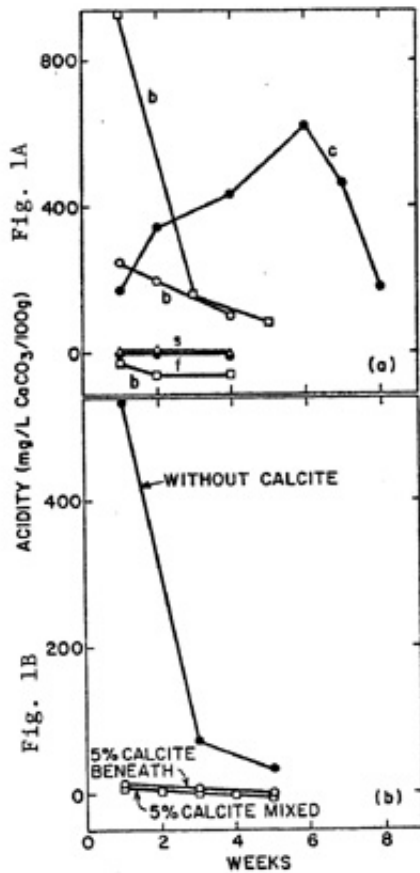


Figure 1. Acidity produced in leaching tests with time.

A. Typical patterns for coal (c), brackish shales (b), sandstone (s), and freshwater shale (f).

B. Comparison of acidity produced by pyritic shale, same shale with 5% calcite mixed in, and shale with 5% calcite in layer beneath shale.

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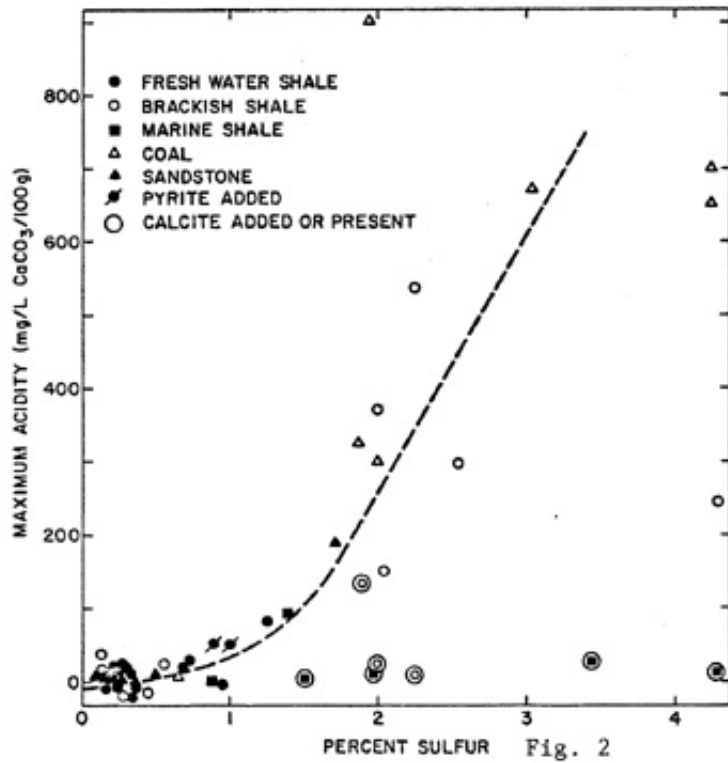


Figure 2. Maximum 1-week acidity in leaching tests vs. sulfur content of rocks. Dashed curve is the inferred pattern for coals and freshwater and brackish shales. Most samples markedly below and to the right of curve contain calcite and/or are marine.

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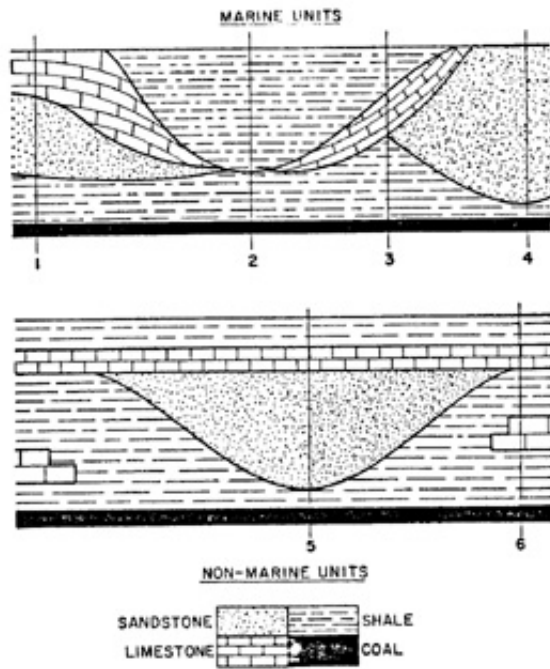


Figure 3. Schematic diagram showing the 6 types of sedimentary sequences in the Kittanning-Clarion model. See text for explanation.

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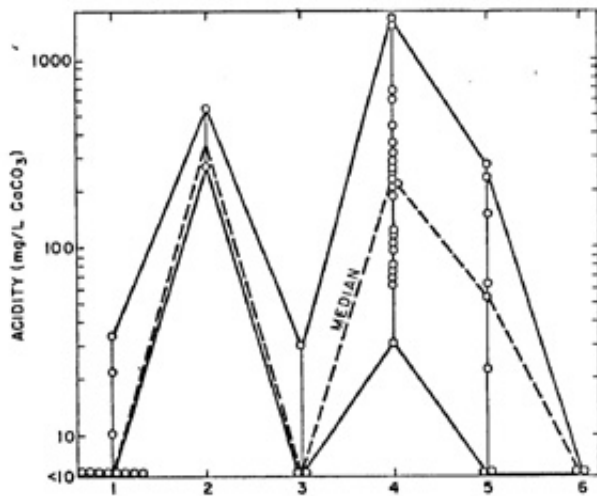


Figure 4. Acidity of drainage from mines in the 6 types of sedimentary sequences of Figure 3.

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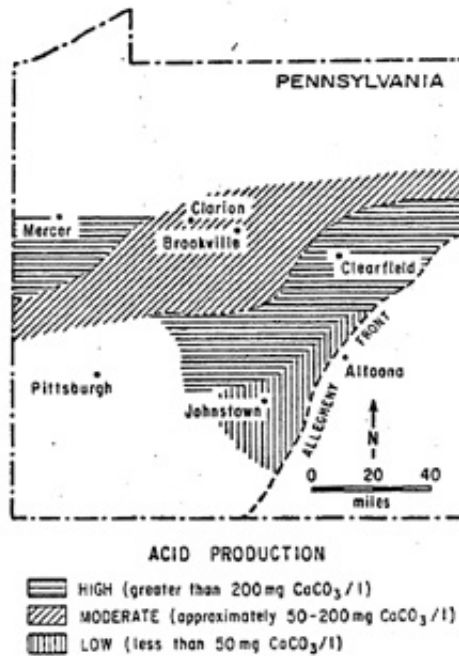


Figure 5. Acid production map based on sedimentary facies for the Lower Kittanning Fm. Brackish shales predicted to furnish high acid, marine shales moderate acid, and freshwater shales low acid.

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