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Identification of Source Materials for Acid Leachates in Maryland Coastal Plain

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Acid leachates are produced in the oxidation of naturally occurring, sulfide-bearing sediments distributed throughout much of the Maryland Coastal Plain. Geologic ages for the sediments span from Lower Cretaceous through Tertiary. When these sediments are exposed to the atmosphere, sulfuric acid is produced in quantities sufficient to prohibit plant growth, dissolve concrete, and corrode metal. Initial pH values of near neutral or above may drop to as low as 2 after the sulfidic sediments undergo oxidation. In addition to pH, characteristics useful in identifying sulfide-bearing Coastal Plain sediments include sulfur content, sediment morphology, presence of sulfide or sulfate minerals, and morphology of surface soils formed from the sediments. Unoxidized sulfidic sediments are mostly dark colored. Typical colors include black (5Y 2.5/1), gray (10YR 5/1), or dark gray (5Y 4/1). Pyrite has been identified as the principal sulfide mineral present in the sediments. Pyrite morphology ranges from large megascopic crystals associated with Lower Cretaceous lignitic deposits to microscopic framboids common in Upper Cretaceous and Tertiary formations. Sulfate minerals formed from pyrite oxidation are useful field indicators of acid-generating sediments. Sulfate minerals that have been identified in acidic sediments include rozenite, szomolnokite, ferroxahydrate, copiapite, gypsum, and jarosite. Jarosite is a highly persistent mineral and has often been observed in naturally weathered soil profiles formed from sulfide-bearing sediments. The identification of jarosite in near-surface soil horizons thus may serve as an indication of underlying sediments with acid-generating potential.

The generation of excessive amounts of sulfuric acid often becomes a severe problem when excavation activities cause the exposure of sulfide-bearing rocks and sediments to the oxidizing environment of the earth's surface. One of the most common examples of this phenomenon is the well-known problem of acid mine drainage associated with coal mining excavations. Interception of sulfide-bearing strata by earth-moving operations is, however, not a hazard unique only to coal or other mining activities. Numerous reports (1-8) have described the occurrences of sulfidic strata across a wide spectrum of geologic settings.

Soil materials that have undergone sulfide oxidation and have excessively low pH values are commonly referred to as acid sulfate soils or cat clays. In the past, these terms have been used principally for identifying acid-generating soils in tidal areas of the world. Recently, investigators have also found it appropriate to apply these terms to upland Coastal Plain soils that display features derived from sulfide oxidation processes. With studies of acid sulfate features in upland Coastal Plain soils (9-11) has come the recognition of the widespread nature of sulfides in many subsurface Coastal Plain strata. Because of the hazards these sediments pose to building materials and ecosystems when exposed to the atmosphere by excavation, identification of sulfidic strata is an important first step in the

course of construction activities to avoid or control acid sulfate problems.

MATERIALS AND METHODS

Study sites were selected on the basis of morphological properties observed in the field. Sites were located by reconnaissance of areas where outcropping geologic formations were suspected of containing sulfides. Soil and sediment samples were retrieved from road cuts, hand-dug pits, and hand borings.

Samples were air-dried and passed through a 10-mesh (2-mm) sieve. Soil pH was measured by using a 1:1 ratio of soil to water. Identification of sulfur minerals was accomplished by either scanning electron microscopy with energy-dispersive X-ray microanalysis or X-ray diffraction. X-ray diffraction analyses were performed by using a Phillips diffractometer with a 2-theta compensating slit and graphite crystal monochromator. Concentrations of sulfur and free iron were determined by the X-ray spectroscopic procedures of Snow (12) and Fanning and others (13), respectively.

RESULTS AND DISCUSSION

Properties of Sulfidic Strata

At least seven geologic formations in the Maryland Coastal Plain were found to contain subsurface sulfide-bearing strata that, when exposed to the atmosphere, were capable of producing high amounts of sulfuric acid. These sediments were found throughout much of the western and central portions of the Maryland Coastal Plain. The general properties of the sulfidic strata are given in Table 1.

As is apparent from Table 1, a common property shared by each of the sediment types was dark coloration. Dark colors for these materials probably result from the presence of organic compounds associated with reduced sulfidic strata as well as darkness of metallic sulfides (mostly pyrite) themselves. In applying Munsell soil color notation for describing chroma and value, sulfide-rich materials generally have chromas of 1 or less and values of 4 or less.

Beyond color, however, few other similarities existed for the sulfide-rich strata. Textures ranged from loamy sand to clay, and geologic ages for the materials span from Lower Cretaceous through Miocene. In addition, it must be emphasized that the formations listed in Table 1 are generally not

Table 1. General characteristics of sulfidic strata in Maryland Coastal Plain formations.

Formation	Geologic Age	Typical Color (moist)		Textural Class ^a	Other Feature
		Munsell	Common Name		
Potomac Group	Lower Cretaceous	10YR 2.5/1 10YR 5/1	Black Gray	Silty clay loam to clay	Lignitic
Magothy	Upper Cretaceous	5Y 2.5/1	Black	Sandy loam	Glauconitic
Matawan	Upper Cretaceous	5Y 2.5/1	Black	Sandy loam to loam	Glauconitic
Monmouth	Upper Cretaceous	5Y 2.5/1	Black	Fine sandy loam to sandy clay loam	Glauconitic
Aquia	Paleocene	5Y 4/1	Dark gray	Fine sandy loam to loamy sand	Glauconitic
Nanjemoy	Eocene	5Y 4/1 5Y 3/1	Dark gray Very dark gray	Fine sandy loam	Glauconitic
Calvert	Miocene	5GY 4/1	Dark greenish gray	Silt loam	

^aU.S. Department of Agriculture classification.

Table 2. Chemical properties and color with depth in an oxidizing sulfidic sediment.

Depth (cm)	pH	Percentage of		Color	
		S	Fe _D ^a	Munsell	Common Name
Oxidized					
0-6	2.7	0.22	1.72	10YR 4/4	Dark yellowish brown
6-20	2.7	0.58	1.11	5Y 3/2	Dark olive gray
20-30	3.2	0.60	0.92	5Y 3/2	Dark olive gray
Mostly Unoxidized					
30-35	4.1	1.60	0.91	5Y 2.5/1	Black
35-46	7.7	1.59	0.87	5Y 2.5/1	Black
46-56	8.1	1.47	0.55	5Y 2.5/1	Black
56-66	8.3	1.54	0.58	5Y 2.5/1	Black
66-82	8.3	1.58	0.45	5Y 2.5/1	Black
82-97	8.4	1.63	0.27	5Y 2.5/1	Black

^aDithionite extractable Fe.

characterized by high concentrations of sulfides throughout. In many instances, sulfide-bearing strata may be thin and laterally discontinuous. Such characteristics are particularly true for sulfide-rich beds within the Potomac Group of sediments. Glauconitic sediments were found to be the most uniformly sulfidic in unoxidized zones.

Measurement of pH of fresh sulfidic samples is of little use in identifying materials with harmful acid-generating potentials. Freshly obtained, unoxidized samples of sulfidic sediments were found to have pH values that ranged from 5 to more than 8. When oxidized, the same sediments had pH values of less than 3.

Similarly, routine chemical analyses for soil fertility performed by most soil testing laboratories would fail to demonstrate the potentially harmful nature of unoxidized sediments. Concentrations of extractable nutrients are often high in these materials. Thus, without measurement of the sulfide content, sulfidic sediments may be incorrectly assessed as fertile media for plant growth.

Pyrite (FeS₂) was identified as the principal sulfide mineral occurring in the sediments. Sulfidic Potomac Group deposits of Lower Cretaceous age typically contained large secondary pyrite crystals that are easily discernable to the unaided eye. The pyrite was usually associated with fragments of lignite in these sediments. In sulfidic deposits of Upper Cretaceous and Tertiary ages, pyrite crystals were not discernable without extreme magnification. The dominant form of pyrite in these sediments is likely that of microscopic (less than 25µm) clus-

ters of pyrite crystals known as framboids. Pyrite framboids were identified by scanning electron microscopy in a sample of the Monmouth Formation of Upper Cretaceous age. Framboidal pyrite, perhaps because of its smaller size and greater surface area, is considered to be more reactive than megascopic pyrite (14).

Properties of Oxidized Strata

Properties so far discussed have been for unoxidized strata only, and sulfidic strata exposed to oxidizing conditions undergo considerable morphological and chemical alterations. This is true for both naturally weathered sediments as well as those that have undergone artificially induced oxidation due to excavation or drainage.

In terms of general appearance, oxidized sediments are distinguished from originally sulfidic materials by usually more reddish hues, lighter color values, higher chromas, and mottling or staining by iron oxides and sulfates. Chemically, differences are dependent on the original chemical composition of the sulfide-rich sediment, especially sulfur content, and on the degree to which oxidation has progressed. Although other factors such as sulfide form or natural acid neutralizing capacity of the sediment can be important, it is generally true that the higher the original concentration of sulfides in the sediment, the greater will be the amount of free acid generated. As long as conditions are sufficiently aerobic, sulfuric acid generation will continue until the supply of oxidizable sulfides is exhausted.

Table 2 gives the characteristics of a soil profile in which both oxidized and unoxidized materials are present. The soil profile is formed from sulfidic sediments of the Monmouth Formation and is situated within a highway cloverleaf. At the time of highway construction, the site appears to have been scalped to a depth of approximately 2-3 m, which exposed unoxidized sediments. The conditions shown in Table 2 have formed within 15 years of the construction work.

As indicated by very low pH values, the most oxidized portion of the profile extends to a depth of about 30 cm. In this zone, pyrite oxidation has resulted in both chemical and morphological changes. In addition to the low pH values typical of acid sulfate soils, the upper oxidized horizons have lower concentrations of sulfur, higher concentrations of free iron oxides, and slightly higher color values than the underlying sulfidic horizon. Lower sulfur values in the most acidic part of the profile have probably resulted from sulfur losses due to leaching of soluble sulfates. Sulfur losses

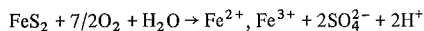
Table 3. Sulfate minerals identified in oxidized, originally sulfidic Coastal Plain sediments.

Mineral	Approximate Formula	Appearance	ASTM Card File No.
Rozenite	FeSO ₄ · 4H ₂ O	White; powdery	16-699
Szomolnokite	FeSO ₄ · H ₂ O	White; powdery	21-925
Ferrohexahydrate	FeSO ₄ · 6H ₂ O	White; powdery	15-393
Copiapite	(Mg,Al)(Fe,Al) ₄ (SO ₄) ₆ (OH) ₂ · 2OH ₂ O	Lemon yellow; powdery	20-659
Gypsum	CaSO ₄ · 2H ₂ O	White to colorless; small needle-like clusters	6-46
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	Straw yellow; mottles and pore fillings	22-827

by volatilization during oxidation may also be a factor.

In contrast to the near-surface oxidized zone, the mostly unoxidized sulfidic sediment below 30 cm has been little altered from its original state. Sediment color is black, and concentration of total sulfur is uniformly high with depth. Values for soil pH are also high and appear to be regulated by calcium carbonate from fossil shell fragments present in the sediment. Concentrations of free iron oxides decrease progressively with depth; however, higher values in the upper portion of the dark-colored zone may indicate an initial stage of pyrite oxidation in which iron sulfates are released. Thus, while sharp differences exist between the oxidized and mostly unoxidized zones, downward migration of the acid-sulfate zone appears to be an ongoing process. It should also be noted that some of the free iron extracted from lower increments of the profile may have formed as a result of pyrite oxidation during air drying of the samples in the laboratory.

The conversion of pyritic sulfur to sulfate sulfur is fundamental in the transformation of reduced sulfidic sediment to oxidized acid sulfate soils. Simplistically, the overall reaction that shows oxidative decomposition of pyrite may be expressed as follows (15):



In nature, the reactions that produce sulfates, ferric iron, and acid are rarely so direct or as complete, and numerous reactions that produce an assortment of sulfate and iron compounds are usually involved. Detailed discussions of many of these reactions have been given by van Breemen (16,17), and an effort to recount them will not be expanded here.

Basically, the kinds of sulfates present on a site are dependent on the chemical composition of the original sulfidic sediment and on the nature of the environment to which the sediments have been exposed. Sulfates can begin to form within weeks or even days of the exposure of sulfidic sediments to an oxidizing environment. For this reason, identification of sulfate minerals in the absence of prior investigations for sulfide occurrence can be important in the early recognition of acid-producing materials. Table 3 lists sulfate minerals that have been identified by X-ray diffraction of samples from Coastal Plain sediments and soils.

The most soluble sulfate minerals in Table 3 are the first four given. These soluble sulfates are also among the first to form in freshly excavated sulfide-rich sediments. They appear as white or yellow powdery efflorescences on the soil surface and often are bitter or astringent to taste. Gypsum is a slightly less-soluble mineral and forms in oxidizing sulfidic sediments that have a high calcium content, such as those containing fossil shells. This mineral has been observed as small (1- to 2-mm) clusters of needlelike crystals in recently dis-

turbed sulfidic sediments. Jarosite is the least soluble of the sulfate minerals identified, and it is one of the most commonly encountered. This conspicuous straw-yellow (5Y 7/6) mineral has been identified in mottles or pore fillings in materials ranging from freshly exposed sulfidic sediments to naturally weathered soil profiles of great age (10).

The identification of jarosite in naturally weathered soil-geologic columns has utility in predicting potential occurrences of sulfide-bearing strata. Because of its low solubility, jarosite may persist well after the processes of sulfide oxidation that formed it have ceased. Thus, jarosite can be found in soils and geologic strata in which sulfides have long since been oxidized and natural buffering systems have restored pH levels to more than 4. In such weathering columns, jarosite was observed in the upper oxidized zone, marking strata that have in the past gone through extremely acid conditions. Given the relative uniformity of the original geologic material with depth, zones that are below the level of natural oxidation may still be sulfidic. As an indication of the former presence of sulfides, jarosite frequently serves as a warning of more deeply lying sulfidic strata. In the weathering profiles studied, the natural depth to sulfides was found to be in the range of about 2-10 m, whereas jarosite was usually present within 1-2 m of the land surface.

CONCLUSIONS

Many of the geologic formations comprising the Maryland Coastal Plain contain sulfide-rich strata. These strata are all darkly colored but have other properties that vary with the geologic formation. Several of the formations that contain sulfides are also glauconitic. Pyrite is the main sulfide mineral in the sediments studied.

Sulfidic sediments undergo considerable morphological and chemical changes when oxidized. Color becomes lighter, and mottles of iron oxides and jarosite form. The conversion from a sulfide-rich material to a sulfate-rich material is marked by extreme lowering of pH, loss of sulfur, increase in iron oxide content, and the formation of sulfate minerals. One of the most common sulfate minerals that forms under the extremely acid conditions produced by the oxidation of pyrite is jarosite. Jarosite is a highly persistent mineral and often occurs in the upper, naturally oxidized zones of soil-geologic columns. As a remnant of extremely acid conditions in the past, jarosite mottling near the surface may indicate the presence of more deeply lying sulfidic strata. Natural weathering depths to sulfidic strata range from approximately 2 to 10 m according to the sites examined in the Coastal Plain in Maryland.

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Leachates from Excavations and Fills: Summation

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There are extensive data available on leachate quality and quantity, but the environmental effects and leachate control methods have not been investigated as thoroughly as might be expected. Test methods are primarily centered in the laboratory; there is a need to establish field evaluation methods.

The purpose of this paper is to summarize the five papers presented at the Symposium on Leachates from Highway Fills and Cuts organized by the Committee on Physicochemical Phenomena in Soils (A2L03). It describes the state of the art by identifying areas where information on the role of leachates is available as well as topics that require study or further investigation.

Among the various environmental concerns that have surfaced during the past decade or so, the problem of leachates from fills and excavations has been rather sporadically studied. On the one hand,

pollutants and their sources have been rather well identified; on the other hand, field and laboratory testing, which enable the determination of leachate quality and quantity, has not reached the point of established meaningful criteria. It appears, then, that the problem has not been approached with a well-designed overall research plan and balanced emphasis.

GROUPING OF REPORTS

The five papers reviewed herein, as given in Table 1, differ in scope and methodology. Another possible way to categorize these papers is to group them according to the following dimensions of leachates:

1. Source characterization,