

FINAL CONTRACT REPORT

**DELINEATION AND MANAGEMENT OF SULFIDIC MATERIALS
IN VIRGINIA HIGHWAY CORRIDORS**

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ABSTRACT

Excavation through sulfidic geologic materials during road construction has resulted in acid drainage related problems at numerous discrete locations across Virginia. Barren acidic roadbanks, and acidic runoff and fill seepage clearly cause local environmental problems along Virginia road corridors. Degradation of construction materials may necessitate road repairs, which can be time-consuming, costly, and a nuisance to travelers. These problems can be minimized, and even prevented, by incorporating sulfide hazard analysis into the pre-design stage of highway construction. Evaluating the likelihood of encountering sulfidic materials can decrease exposure of problematic materials. When exposure cannot be avoided, proper characterization of the material allows for immediate application of appropriate remediation procedures.

Failure to rigorously identify and remediate acid-forming materials in the road planning and construction process will inevitably lead to the mix of engineering and environmental problems discussed and documented in this report. While the barren and erosive slopes resulting from acidification of cut roadbanks are the most obvious indicator of this problem, the long term emission of acidic drainage from fills is clearly the most serious environmental compliance problem that VDOT will face with sulfidic materials over time. Unfortunately, many of these problems (e.g. acid seepage from fills) do not become obvious for some period of time after the road construction contracts have been closed, leaving the full liability for environmental compliance resting upon VDOT maintenance budgets. Therefore, the true cost of identifying, handling and disposing of potentially acid-forming materials must be rigorously assessed and designed for in the road building process.

BACKGROUND & INTRODUCTION

Acid rock drainage (ARD) develops when sulfidic materials are excavated from below the Earth's surface and are subsequently exposed to water, dissolved oxygen, and atmospheric oxygen (Evangelou, 1995). The sulfides oxidize to form sulfuric acid, which dissolves surrounding materials and generates a highly acidic metalliferous leachate. This leachate pollutes local surface waters and corrodes construction materials. Visual indicators of ARD include orange iron precipitates in streambeds, black manganese oxide and hydroxide precipitates, white calcium and aluminum precipitates, and white sulfate salt precipitates along stream banks and rocks (Nordstrom, 1982). The degree to which these features occur varies significantly, depending on such factors as sulfide mineralogy and morphology, composition of the host rock and surrounding geologic formations, and availability of water and oxygen. Most commonly, ARD is associated with mining and mineral processing; however, it may result from other earth-disturbing activities such as road construction. In the case of road construction, sulfide oxidation and its associated problems of extreme soil acidification and ARD presents a number of technical, environmental, and aesthetic problems. Technical problems are primarily related to the degradation of construction materials from acid attack, weathering of sulfidic fill materials and precipitation of sulfates which compromise structural stability, and the depletion of roadside vegetation which increases erosion and acid runoff. Local surface water quality is threatened as high acidity and elevated levels of heavy metals are detrimental to aquatic life. From an aesthetic point of view, ARD diminishes the appearance of roads by killing roadside vegetation and by causing unsightly red stains on curbs. The combination of visible pollution and adverse conditions for aquatic life limits recreational uses of impacted surface waters.

Sulfidic deposits are found in various geologic and geomorphic settings across the state of Virginia. These settings include unconsolidated sulfide-rich sediments in formations of the Coastal Plain, certain slate and phyllite bearing formations in the Piedmont and Blue Ridge, some of the black shales in the Valley and Ridge, and sulfide-rich coal seams in the coalfields of southwest Virginia. In many of these settings, road construction has resulted in localized ARD problems. Increasing development over the past several years, along with wetland excavation and the ever-deepening nature of road cut designs, has resulted in numerous new problem sites throughout the state. While such problems historically had been considered isolated occurrences, over the past decade the Virginia Department of Transportation (VDOT) has come to recognize these sites as manifestations of the same underlying cause. It is also becoming obvious that a number of older poorly understood "problem areas" in statewide rights-of-ways owe their management difficulties and environmental complications to the presence of sulfidic materials. For example, a number of concrete box structures and metal guard-rails have been seriously degraded by contact with these materials. The first step in preventing ARD from future road construction is to identify potential acid-producing materials and delineate their boundaries. Geologic formations containing microcrystalline sulfide forms, such as pyrite framboids, are particularly problematic because as grain size decreases, the surface area available for acid-producing reactions from a given amount of sulfide increases. Only a small part of the state has been covered by large-scale mapping that includes the level of detailed petrographic analyses which is necessary to detect and describe the occurrence of fine-grained, disseminated pyrite (William S. Henika, Virginia Tech, personal communications). Consequently, the occurrence of fine-grained, disseminated iron sulfides has generally remained undocumented. Sulfide

occurrence is a function of geologic setting. If sulfides are identified in numerous rock samples from a specific geologic formation, then the entire formation may be considered as “at risk” for containing sulfides. Therefore, on a statewide scale, delineation of potentially acid materials is best accomplished by identifying the boundaries of sulfide-bearing formations based on the Geologic Map of Virginia.

Hundreds of millions of dollars have been spent on these combined problems in mining environments over the years, but the “magic bullet” to stop these problems once the soils are disturbed and oxidation has initiated has not yet been found. Before the initiation of this study, none of this body of available science and engineering design had been applied to VDOT’s road planning and engineering design process.

PURPOSE AND SCOPE

The purpose of this research effort was to develop methods by which VDOT could determine the location of highly sulfidic materials and properly manage these materials if encountered. With advance detection, highway corridors could be sited to avoid or minimize exposure of sulfidic materials. When sulfidic materials cannot be avoided, advance knowledge of the nature and extent of these materials will allow for adequate development of remediation procedures. Accurate prediction of acid drainage has been the topic of much research, particularly with respect to mining. While some techniques for predicting acid drainage are more commonly applied than others, there is no universal protocol for evaluating sulfidic materials. Understanding the utility and limitations of different commonly utilized procedures allows for appropriate application of methods and interpretation of results.

The overall objectives of this research program were:

1. Characterization of sulfide-bearing geologic formations in Virginia, and the compilation of a statewide sulfide hazard rating map.
2. Development of a GIS based procedure for evaluating the risk of encountering sulfidic materials within specific excavation depths within the Virginia Coastal Plain.
3. The evaluation of existing potential acidity procedures to determine their applicability to diverse sulfidic materials.
4. To assess various alternatives for chemically and physically stabilizing sulfidic materials when they are encountered by VDOT.

This report presents research results and interpretations related to the identification, characterization, and treatment of sulfidic materials in VDOT highway corridors. As a parallel component of this study, extensive research on the topic of revegetation strategies for acid-sulfate soil materials was conducted, and will be reported on separately. A detailed literature review on the relative economics and efficacy of various approaches to treating acid rock drainage is given by Skousen et al. (2000).

LITERATURE REVIEW

Engineering and Environmental Impacts of Sulfide Oxidation

Engineering impacts from sulfide oxidation, including structural damage to buildings, disintegration of construction materials, and degradation of local surface water quality have been documented at a number of locations around the world (Table 1). Sulfide oxidation may produce certain sulfate minerals that occupy several times the volume of the minerals from which they form. The forces exerted by this expansive crystal growth can cause heaving in overlying structures (Berube et al., 1986; Chinchon et al., 1995; Dougherty and Barsotti, 1972; Grattan-Bellew and Eden, 1975; Hawkins and Pinches, 1987; Moum and Rosenquist, 1959; Parizek, 1982; Penner et al., 1970; Quigley and Vogan, 1970). A few studies describe concrete degradation due to use of sulfidic aggregates (Ayora et al., 1998; Chinchon et al., 1995). In a somewhat different situation Burkart et al. (1999) identified sulfate-induced heaving under roads constructed on montmorillonitic soils containing gypsum. The soils were formed over pyritic shales. Addition of lime to stabilize the soils resulted in the formation of expansive sulfate minerals that destroyed the pavement subgrade. It should be noted that acid sulfate weathering already occurred naturally in these soils and was not due to exposure of sulfidic materials from construction. This indicates that in some situations acid-sulfate type problems may result without actual exposure of sulfidic materials. One study on an abandoned railroad suggests that heat generated from sulfide oxidation in the underlying fill resulted in thermal expansion and localized deformation of rails (Prokopovich, 1987). In addition to heave, structural damage may result from sulfate and acid attack on cement and concrete (Chinchon et al., 1995; Grattan-Bellew and Eden, 1975; Moum and Rosenquist, 1959; Oyama and Chigira 1999; van Holst and Westerveld, 1973). Studies on the impact of ARD from highway construction focus mainly on the generation of acid drainage and its effect on local surface waters (Adams et al., 1999; Fox et al., 1997; Igarishi and Oyama, 1999; Mathews and Morgan, 1982; Morgan et al., 1982). Less work has been completed on the deterioration of road materials and related structures upon exposure to acid sulfate weathering (Sahat and Sum, 1990; Vear and Curtis, 1981).

Exposure of sulfidic materials from road construction presents a number of technical, environmental, and social problems. Technical problems are primarily related to the degradation of construction materials, weathering of sulfides exposed along roadcuts or in fill material, and limitation of roadside vegetation, which promotes erosion and continual exposure of fresh sulfidic materials. First, construction materials such as metal pipe culverts, concrete box structures, and metal guardrails cannot withstand extended exposure to ARD. In some problem areas in Virginia galvanized steel guardrails have a life span of only two to five years. At one site near Covington, Virginia, deterioration of local water quality due to acidic fill leaching has necessitated the construction of a discharge treatment facility. Second, rapid weathering may severely disintegrate and decompose road banks resulting in landslides and road closures (Vear and Curtis, 1981). Similarly, difficulties occur when sulfidic materials that are excavated from roadcuts and borrow pits are used as fill materials in roadbeds. In addition to leaching acid, oxidation of these materials results in volumetric changes which compromise fill stability and may lead to subsidence and pavement buckling (Pye and Miller, 1990). Finally, failure to establish roadside vegetation due to extremely acid soil conditions increases sediments and acid runoff from bare road banks (Miller et al., 1976). These geotechnical problems are a nuisance to

Table 1. Engineering impacts of acid sulfate weathering.

Reference	Location	Materials*	Problems
Adams et al., 1999	Buchanan, Georgia	py bearing schist (Sandy Springs group)	decline in local water quality due to acid drainage
Ayora et al., 1998	Central Pyrenees, Spain	po and py bearing schist	concrete degradation due to formation of expansive sulfates in the aggregate
Berube et al., 1986	Sainte-Foy, Quebec, Canada	py bearing black shale (Sainte-Foy formation)	concrete floor slab heaved more than 10 cm.
Chinchon et al., 1995	Barcelona, Spain	po and py bearing shales and limestone	concrete degradation due to formation of expansive sulfates in the aggregate
Dougherty and Barsotti, 1972	southwest Pennsylvania	py bearing coals and shales (dominantly the Conemaugh and Monongahela formations)	structural damage due to heaving
Fox et al., 1997	Nova Scotia	po bearing slate	decline in local water quality due to acid drainage
Grattan-Bellew and Eden, 1975	Ottawa, Ontario, Canada	py bearing black shale (Eastview formation)	basement floor heaved up to 6.3 cm sulfate attack on concrete
Hawkins and Pinches, 1987	Cardiff, U.K.	py bearing black mudstone (Westbury formation)	heaving in the floor slab
Igarishi and Oyama, 1999	central Japan	py bearing rhyolite	acidification of reservoir water
Mathews and Morgan, 1982	North Carolina	py bearing black shales (Anakeesta formation)	metalliferous, acid leachate destroyed aquatic ecological systems
Miller et al., 1976	Texas	py bearing sediments (Weches and Queen City formations)	Vegetative failure, causing increased erosion, on road banks.
Morgan et al., 1982	North Carolina and Tennessee	py bearing black shales (Anakeesta formation)	metalliferous, acid leachate destroyed aquatic ecological systems
Moum and Rosenquist, 1959	Oslo, Norway	po in slightly metamorphosed shales (alum shales, alum slates)	concrete deterioration due to sulfate attack foundation upheaval
Parizek, 1982	Kansas City, Missouri	py bearing black shales (Upper Pennsylvanian beds)	building floor heave up to 10 inches mine floor heave up to 8 inches
Penner et al., 1970 Penner et al., 1973	Ottawa, Ontario, Canada	py bearing black shale (Billings formation)	basement floor slab cracked by 10.2 cm of differential heave

*py = pyrite; po = pyrrhotite

Table 1 (Continued)

Reference	Location	Materials*	Problems
Prokopovich, 1987	Redding, California	massive py ore	thermal expansion and deformation due to heat from oxidation reactions
Pye and Miller, 1990	Derbyshire, U.K.	py bearing black shale (Namurian shale)	collapse of a shale embankment from volumetric changes due to acid leaching
Quigley and Vogan, 1970 Quigley, et al., 1973	Ottawa, Ontario, Canada	py bearing black shale (Lorraine formation)	interior columns heaved up to 7.6 cm
Sahat and Sum, 1990	Malaysia	py bearing granite, hornfels	disintegration of road aggregates
Swaine, 1986	Liddell, New South Wales	framboidal py in siltstone	rapid weathering of excavated siltstone due to acidity and expansion effects
Van Holst and Westerveld, 1973	The Netherlands	Unspecified sulfides	Corrosion of concrete piles poured in situ (unsatisfactory hardening due to sulfates)
Vear and Curtis, 1981	Derbyshire, U.K	py bearing black shale (Namurian shale)	slope instability, landslides, and acid drainage along roadcut

* py = pyrite; po = pyrrhotite

highway engineers, as well as the general public, and costly to remediate. Acid rock drainage from road construction also poses environmental threats to water quality, aquatic life and vegetation. The high acidity and elevated levels of heavy metals are toxic to most plants and detrimental to aquatic life. Adverse community responses of stream organisms to conditions induced by ARD are well-documented (Huckabee et al., 1975; Klapper and Schultz, 1995; Morgan et al., 1982; Nathan and Katz, 1969). Furthermore, the combination of visible pollution and adverse conditions for aquatic life limits recreational uses, such as fishing and swimming in surface waters (Morgan et al., 1982). From an aesthetic point of view, ARD diminishes the appearance of roads by killing and preventing roadside vegetation, and by causing unsightly orange stains in culverts and on curbs

Most studies regarding the impact of road construction through sulfidic materials have focused on water quality issues. In 1963, reconstruction of U.S. Highway 441 near Great Smoky Mountains National Park involved cut and fill operations in the Anakeesta formation - a sulfidic shale. The demise of local aquatic life, in some areas reaching up to 8 km from the highway, was attributed to indiscriminate use of pyrite bearing rock as rip rap along the stream embankment (Huckabee et al., 1975; Mathews and Morgan, 1982). Construction beginning in 1965 of the Tellico-Robbinsville Highway between Tennessee and North Carolina, also through the Anakeesta shale, caused a similar decline in water quality. A variety of remediation techniques, including NaOH additions at the headwaters of affected streams, lime additions over selected road embankments, and installation of soil blankets were applied in the Tellico Wildlife Management Area in 1978, but all proved to be minimally effective (Morgan et al., 1982). Again, in 1978, disturbance of sulfidic shales during highway construction in southeast Tennessee caused deterioration of culverts, guardrails, and aquatic life. Rehabilitation, which included placement of a sealant barrier and topsoil, revegetation, and addition of alkaline solutions to affected streams, exceeded the original highway cost (Anderson et al., 1991).

Halifax International Airport in Nova Scotia provides another dramatic example of adverse ARD impacts. Construction of the airport between 1955 and 1960 exposed large volumes of sulfide-rich slate of the Halifax formation from the Meguma Group. Since that time, acid drainage has severely impacted surrounding watersheds. Remediation efforts beginning in the early 1980's have included capping of the waste rock pile with clay and topsoil, a water treatment facility, wetlands, and other experimental techniques. Initial remediation costs exceeded over two million dollars, with operation and maintenance costing about \$240,000 annually since 1982. Nonetheless, acid drainage from the airport and associated sites continues to be a problem (Zentilli and Fox, 1997; Fox et al., 1997).

Highway Planning for Sulfidic Materials

Over the past few decades, increased recognition of the problems associated with acid-sulfate weathering has led the United States and other countries, such as Australia and Canada, to develop guidelines for handling sulfidic materials. While specifics may vary, the following principles are universally applied. First, geologic and/or soils mapping is a basic tool for assessing ARD potential in proposed construction areas. Second, where necessary, samples from outcrops and drill cores should be evaluated for potential acidity. Third, measures should be taken to avoid or minimize excavation of acid-producing materials. Fourth, when sulfides cannot

be avoided, handling and treatment plans should be clearly defined prior to construction since immediate implementation of remediation plans is essential to minimizing environmental impacts. Incorporating these steps in the pre-design phase of a project is a worthwhile investment compared to the impact of environmental damage and the expense of mitigation after construction.

In the 1980's, the United States Federal Highway Administration initiated studies on handling acid-producing materials during construction. Guidelines were developed for detecting and evaluating potential ARD problems and for handling acid-producing materials (Byerly, 1990 and 1996). Byerly (1990) developed three sets of guidelines dealing with different stages of construction. The first set pertains to the pre-design stage, which is usually the time period of corridor selection. Figure 1, adapted from Byerly (1990), provides an outline of steps utilized in the pre-design phase. The second set of guidelines pertains to the design phase and deals mainly with procedures for handling and disposing acid-producing materials. Actual design plans are site specific, and are controlled by factors such as the nature and volume of acid-producing material, topography, climate, geology and hydrology. The third set of guidelines pertains to the construction phase and addresses the need for continual identification, segregation, handling, and storage of acid-producing materials during construction.

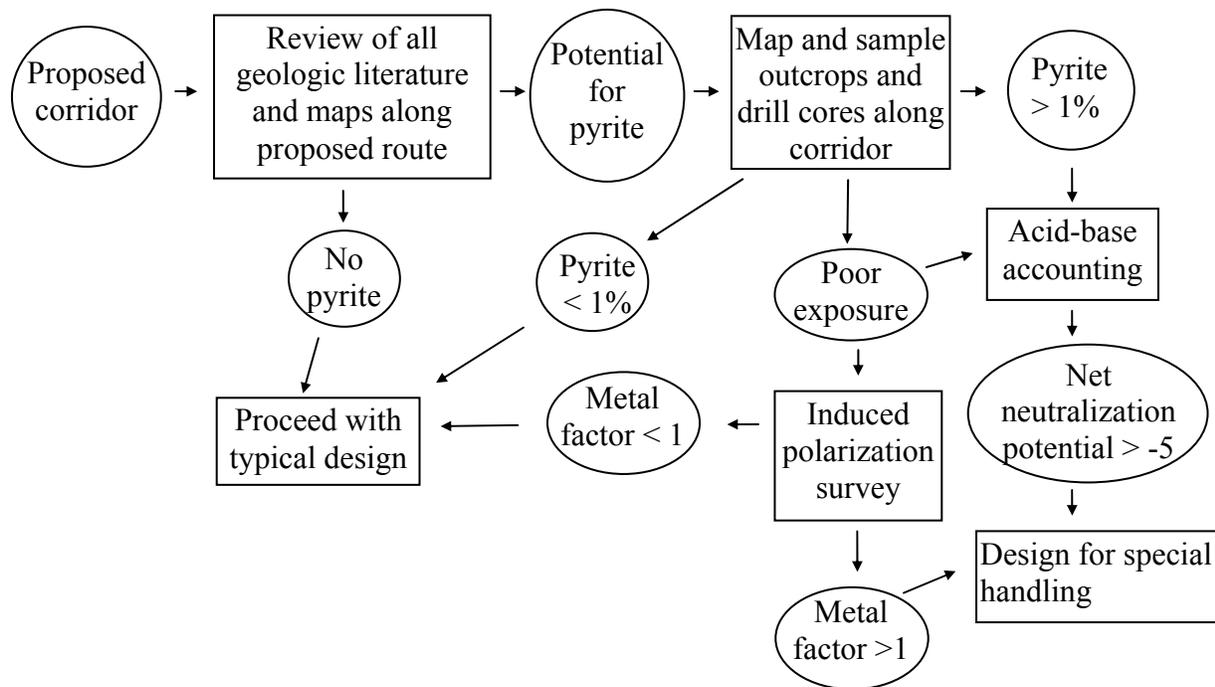


Figure 1. Flowchart for evaluating potentially sulfidic material in the pre-design phase of highway construction (adapted from Byerly, 1990). Metal Factor is based on resistivity and polarizability from an Induced Polarization survey.

A recent study by Schaeffer and Clawson (1996) indicates that incorporation of the guidelines proposed by Byerly (1996) successfully minimized the impact of acid-producing materials along a transmission line in the Blue Ridge Province of southwestern North Carolina. A three-year water-quality program, monitoring streams in the corridor before, during, and after construction, indicated that remediation efforts minimized environmental impact from construction. No problems related to ARD had been observed along the corridor as of seven years since completion of the study (M. F. Schaeffer, 2000, personal communication).

Additional research has been completed on assessment, management, and remediation of acid sulfate soils from coastal sediments. In 1994, New South Wales, Australia, established the Acid Sulfate Soils Management Advisory Committee (ASSMAC) to coordinate an overall government response to acid soil issues. ASSMAC produced an extensive manual with detailed guidelines addressing planning, assessment, management, laboratory methods, drainage, groundwater, and industry (Stone et al., 1998).

Similarly, environmental damage and the high cost of remediation measures led the Nova Scotia Department of the Environment to establish “Sulphide Bearing Materials Disposal Regulations” under the Nova Scotia Environment Act. These regulations outline procedures for notification, screening, sampling, analysis and disposal of acid generating materials. Anyone excavating a stated volume of sulfide-bearing slate must obtain approval, proving that their plans for excavation and disposal of the slate will be consistent with regulations (Environment Act, 1995).

Prediction of Sulfide Oxidation Rates and Acid Rock Drainage

Perhaps the most critical step in characterizing and managing sulfidic materials is the development and testing of accurate techniques for screening the acid-forming potential of geologic materials. Extensive research has been conducted on this topic over the past thirty years in various mining environments (Sobek et al., 2000; Geidel and Caruccio, 2000). A wide array of techniques has been developed by various research groups to predict *potential acidity* - the net amount of acidity that a given sulfidic material will liberate as it oxidizes over time. The most commonly used approach is known as “acid-base accounting”, or ABA (Sobek et al., 1978), and was developed and tested in coal mining environments in West Virginia before being applied to various mining environments worldwide. This approach assumes that all S in a sample will oxidize to sulfuric acid. This acid production potential is stoichiometrically balanced against the neutralization potential present in the sample. Every 1% sulfidic-S is assumed to produce acidity equivalent to 31 Mg of calcium carbonate lime per 1000 Mg of material. This reporting convention (parts per thousand of lime equivalence) equates directly to the English tons of lime required per acre per 6” or 15 cm depth of material treated. Alternative approaches to estimate potential acidity include the use of H₂O₂ as a bulk oxidizing agent, various humid incubation techniques, and Soxhlet reflux-type extractors (Renton et al., 1988). Each of these techniques is supported by an extensive literature base (see Orndorff, 2001). However, before this study, they had not been tested for effectiveness across the breadth of geologic materials found in Virginia.

Summary

Exposure of sulfidic materials during highway construction in various environments worldwide and in Virginia has resulted in severe geotechnical, environmental, and social problems at a number of discrete locations. As indicated by the studies discussed above, understanding the geographic distribution of these materials can help prevent their exposure during future highway construction. When sulfidic materials cannot be avoided, accurate characterization of their acid potential is necessary to establish optimal handling and remediation procedures.

METHODS AND MATERIALS

Compilation of a Statewide Sulfide Hazard Rating Map

In the fall of 1997, a questionnaire regarding occurrence and locations of acid roadcuts was distributed to all of the Virginia Department of Transportation (VDOT) districts (Appendix A). Twenty completed forms were received from around the state by the spring of 1998. All sites reported as a result of this questionnaire were visited over the following year. Additional sites were reported later or discovered independently. Sampling locations are shown in Figure 2.

1. Hampton Roads Center: I-64 and Big Bethel Rd., Hampton
2. I-664 and Rt-17, Suffolk
3. I-664 and Rt-337, Suffolk
4. Otterdam Swamp: north of I-95/Rt-58 intersection, Green
5. Near Fort Lee Mil. Res.: north of I-295/Rt-36 intersection
6. Proctor's Creek: Rt-288 and Rt-145, Chesterfield Co.
7. Walthall exit: I-95 and Rt-620, Chesterfield Co.
8. I-295 and Rt-156, Henrico Co.
9. Behind Richmond City Jail
10. E. Main St. and 14th St., Richmond
11. E. Richmond Rd. landfill, Richmond
12. I-295 and Rt-360, Mechanicsville, Hanover Co.
13. Behind Wal-Mart, Mechanicsville, Hanover Co.
14. I-95, milepost 120.5, Spotsylvania County
15. State Farm Insurance: I-95 and Rt-1 bypass, Fredericksburg, Spotsylvania Co.
20. I-77, mileposts 21 – 22, Carroll County
21. VDOT quarry, Rt-600 bw. Rt-50 and Rt-608, Frederick County
22. Rt-250 and Rt-614, Highland County
23. I-64, Clifton Forge, Alleghany County
24. Numerous sites along Rt-23 near Rt-610, Wise County

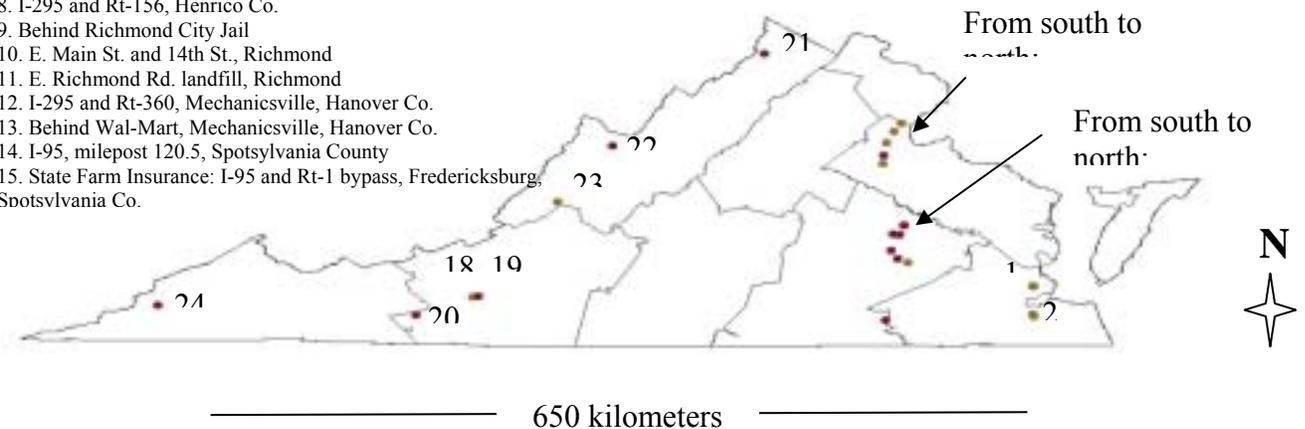


Figure 2. Sampling locations from state-wide survey of documented acid-sulfate roadcuts in Virginia with VDOT districts outlined.

Geologic materials and road drainage grab samples, where available, were collected from all sites. Both fresh and weathered representative samples of lithologies at each site were obtained using a shovel. Rock samples were stored in plastic bags or cardboard containers. Subsamples of rock material were crushed to pass through an 80-mesh sieve then stored in paper

envelopes. Reduced Coastal Plain sediment samples were stored on dry ice during transport, and placed in a freezer upon arrival at the laboratory to minimize oxidation prior to analysis. One week before analysis, sediment subsamples were spread out to air-dry. Approximately 50 g of the subsample were crushed to pass through an 80-mesh sieve then stored in paper envelopes. The remaining material was passed through a 10-mesh sieve then stored in cardboard boxes. All processed materials were stored at room temperature.

Samples of road drainage were collected in 250-ml Nalgene bottles. The bottles were rinsed three times with drainage from the collection site prior to obtaining a sample. Water samples also were collected from a shallow well installed at the base of a roadcut along the cloverleaf of Rt-360W to I-295S. The well consisted of three sections. The base, which served as a drainage reservoir, was 36 cm in height and built out of solid PVC pipe. The middle section, through which drainage entered the well, was 66 cm in length and built out of 10-slot PVC pipe. The top section, which prevented entry of surface water, was 38 cm in length and built out of solid PVC pipe. The well was installed so that the top of the middle section laid approximately 15 cm beneath the ground surface. The well was evacuated 24 h prior to sample collection and allowed to recharge overnight before sampling.

The geologic formations and specific rock types at all sites were determined through field observations, personal communications with state geologists, and geologic maps. All geologic samples were tested for potential peroxide acidity (PPA) using the H_2O_2 method of Barnhisel and Harrison (1976), for total-S using an Elementar Vario Max CNS analyzer, and rated for presence of carbonates by the HCl “fizz test” (Sobek et al., 1978). Coastal Plain sediments were tested for particle size analysis (PSA) by the pipette method (Gee and Bauder, 1986) and pH in H_2O and KCl using a combination electrode. Surface samples from rock exposures that contained a sufficient amount of soil-sized particles (< 2mm in diameter) also were tested for pH in H_2O and KCl. Water samples were tested for pH and for electrical conductivity (EC) using a Cole-Parmer conductivity meter. Water subsamples were filtered, preserved with HNO_3 , and analyzed for Fe, Al, Mn, Cu, Zn, and S concentrations by Inductively Coupled Plasma Emission Spectroscopy (ICPES).

Geologic materials were sampled in detail at two sites to evaluate the heterogeneity of the materials with regards to S levels and PPA. The first site was along the shoulder of the northwest cloverleaf at the interchange of I-295/360 near Mechanicsville in Hanover County. Samples of the Calvert and Eastover Formations of the Chesapeake Group were collected along a grid at horizontal intervals of 4.6 and 9.2 m for 102 m, and at vertical intervals of 1.9 m (starting at 1 m from the base of the roadcut) for 7.3 m. The grid was divided into three sections, one central densely sampled area, and two neighboring areas with larger sampling intervals. Surface maps were generated for each section using Excel, and then attached to illustrate the entire sampling area.

To approximate depth of weathering for the first few holes at the Mechanicsville roadcut, pH was tested at depth intervals of 30 cm using a Hanna conic point combination electrode, inserted directly into moist sediment samples, and a field pH meter. These measurements were used only to estimate pH during field sampling. All reported pH values in this report, unless otherwise indicated, refer to laboratory determined pH. The pH of unoxidized sediments

typically ranges between 5.5-8.0, whereas the pH of oxidized material is significantly lower. To ensure the material was minimally affected by oxidation, samples were collected below a depth where pH measured 5.5. Samples were collected by augering perpendicular into the exposure and collecting material at approximately 1.4 m. At two locations, samples were collected at 15, 50, 75, and 100 cm into the exposure to characterize depth of weathering. Samples were tested for PPA, total-S, pH in H₂O and KCl, and PSA.

The second detailed sampling site was along Rt-250 in Highland County. Samples of the Millboro shale and Needmore Formation were collected from two sections of the roadcut. Starting at the western extreme of the roadcut, on the shoulder of the westbound lane, samples were collected at a height of 1.5 m from the base of the cut at 6.2 m intervals for 142 m, ending just west of a blanket of riprap. Starting on the eastern edge of the riprap, samples were collected at 15.4 m intervals for 277 m. Samples were tested for PPA and total-S.

Based on laboratory results for the geologic formations evaluated in this study, and in conjunction with field observations of acid sulfate weathering damage at specific locations, and with consideration of standard vegetation management practices, a sulfide hazard rating scheme was developed with four levels of severity. Ratings are based on the proportion of samples for a given formation with PPA and S values within defined ranges. A state-wide hazard map was produced by i) assigning the appropriate rating to each studied formation, ii) identifying the respective map unit on the Geologic Map of Virginia for each formation, iii) color-coding the four ratings, and iv) applying the code for each formation to its respective map unit on a digital version of the Geologic Map of Virginia using ARCVIEW Geographic Information Systems (GIS) software. An unpublished version of the digital geology map was provided by the Virginia Division of Mines and Mineral Resources (VDMR, 2001). Documented sulfide-bearing formations, not evaluated in this study, are identified on the hazard map with a fifth color code.

Predicting Depth to Sulfidic Materials in the Coastal Plain

Field relationships between depth to sulfide-bearing sediments and landscape parameters were evaluated for a study area northeast of Richmond (Figure 3). Regional depth to reduced sulfide-bearing marine sediments (hereafter referred to as depth-rs) was determined from water well logs provided by the Hanover County Health Department. Depth-rs was determined based on distinct color changes between the overlying oxidized sands and gravels and the reduced sediments. Oxidized materials are typically described as red, yellow, or brown. Underlying reduced materials are typically described as gray, blue, or green. In some cases the boundary was identified at a specific depth, but often it was identified as occurring within a depth interval. For example, the data may be recorded as '14 – 34 ft: red sand to blue clay'. In such cases, the mean depth (i.e. 24 ft) was used as depth-rs. Well locations were determined from parcel plats provided with the well logs. Only well logs that clearly marked both the location of the well, and depth-rs, were used. This data set consisted of 408 well logs. The utility of basing a predictive model on existing groundwater well logs is that such data are readily available, and can be used in other areas to construct similar hazard rating maps at relatively low cost. Also, the economics of this study clearly would not have supported such an extensive drilling program.

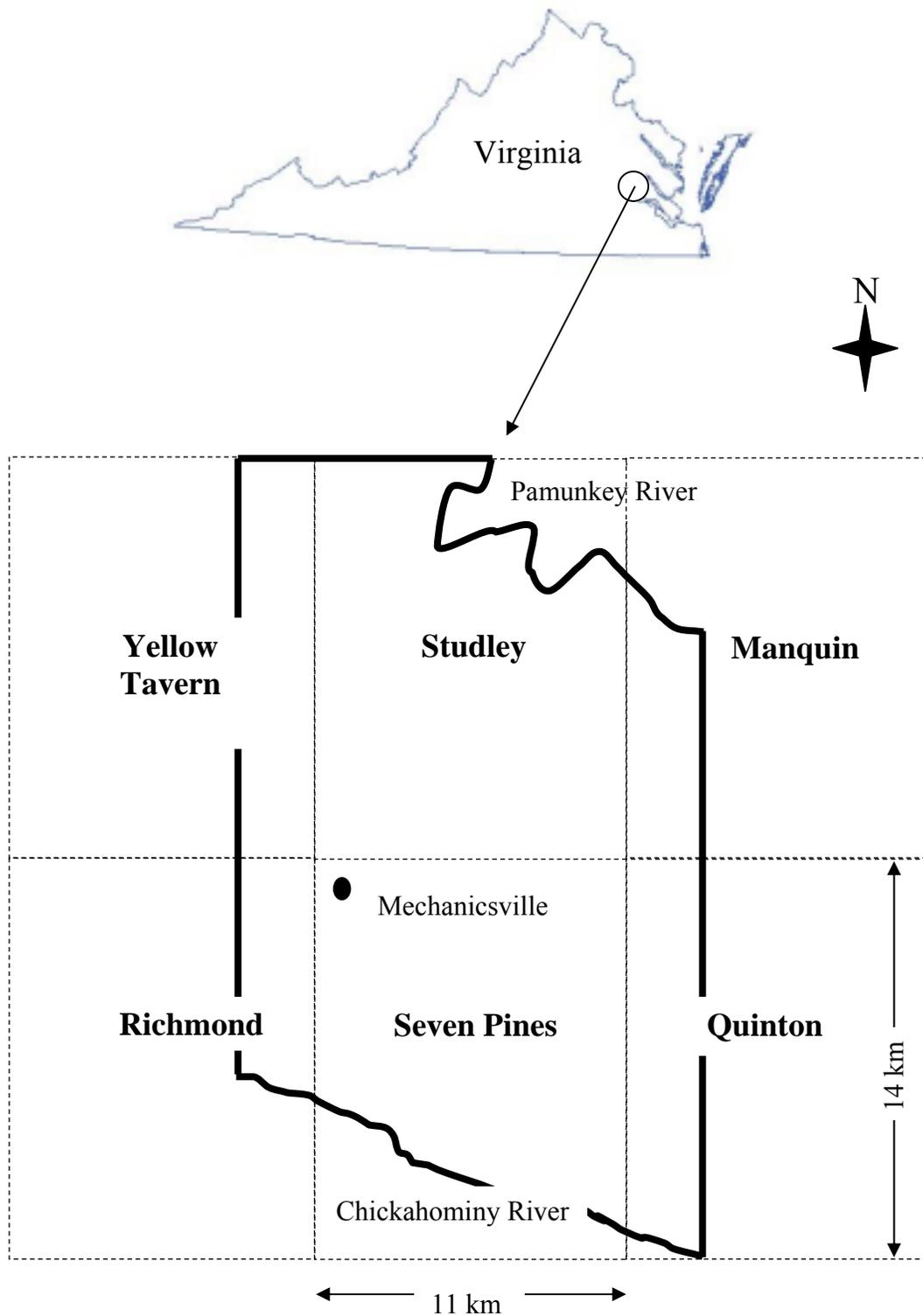


Figure 3. Location of study area outlined in bold with USGS 7.5 minute topographic quadrangles identified and outlined with dashed line.

Twenty-three detailed borings were drilled by personnel from the Department of Crop and Soil Environmental Sciences throughout the study area for use as validation points to test the accuracy of interpretations from the well logs and to assess the frequency of S occurrence. Samples from within the first 30 cm of reduced sediments were collected from these detailed borings, analyzed for %S using an Elementar Vario Max CNS analyzer, and rated for presence of calcium carbonate by the HCl fizz test (Sobek et al., 1978).

A digital map of Hanover County streams, and spatial data transfer standard digital elevation maps (SDTS DEM's) with 30 m horizontal resolution for the 7.5-minute quadrangles, were obtained from the USGS. A digital tax parcel map was provided by the Hanover County Planning Office, and a digital soils map for Hanover County was obtained from the United States Department of Agriculture. The USGS 7.5 minute geologic maps for this area were digitized in-house. Digital maps were analyzed using ARCVIEW geographic information systems (GIS) software to determine elevation, slope, distance to streams, surficial geology and soils for all data points.

Three approaches were used to predict depth-rs. The first approach used regression analysis to evaluate relationships between depth-rs and landscape variables, including elevation, slope, distance to streams, and surficial geology, to develop a predictive model. Secondly, interpolation was used to calculate a depth-rs surface based on depth-rs from the well logs. The data were randomly divided into two sets of points. The first set of points, which included approximately three-fourths of the total data set, was used to generate an interpolated surface in ARCVIEW using the default options of inverse distance weighting on the twelve nearest neighbor points. The remaining well points were used to evaluate the accuracy of the predicted values. This approach was repeated three times. Finally, a third procedure was developed which created probability maps to indicate the likelihood of encountering reduced sediments within a given depth for defined elevation groups. The procedure used two risk factors – one based on elevation and one based on soil type. The data were divided into seven elevation classes. For each class, the depth-rs data were summarized with descriptive statistics, including the relative proportion of data points with depth-rs less than 5, 9 and 13 m. Elevation risk factors were designated and quantified, as indicated in parenthesis, for each elevation class based on the proportion of wells with depth-rs below the specified depth. Risk factors were assigned in the following manner: i) > 50% is a very high risk (4), ii) 26 – 50% is a high risk (3), iii) 11 – 25% is a moderate risk (2), and iv) $\leq 10\%$ is a low risk (1). The data also were divided based on soil mapping units. For each map unit the depth-rs data were summarized with descriptive statistics. For soil map units containing at least 5 well data points, the relative proportion of wells with depth-rs less than 9 m was calculated and used to assign soil risk factors as follows: i) > 25% is a high risk (3), ii) 11 – 25% is a moderate risk (2), and iii) $\leq 10\%$ is a low risk (1). For soil map units with fewer than 5 data points, soil risk factors were designated based on mean depth-rs as follows: i) ≤ 9 m is a high risk (3), ii) 10 to 19 m is a moderate risk (2), and iii) ≥ 20 m is a low risk (1). A final compiled map was generated to indicate the two risk factors using DEM's and the digital soil map.

Evaluation of Acid Rock Drainage Prediction Procedures on Diverse Sulfidic Materials

Samples of sulfide-bearing shales, phyllites, slates, and coastal sediments were collected from acid roadcuts and excavation sites throughout the state of Virginia. The potential peroxide acidity (PPA) procedure of Barnhisel and Harrison (1976) is currently the standard potential acidity procedure used to evaluate materials in the Soil Survey and Mined Land Reclamation Laboratory (SS+MLR) of the Crop and Soil Environmental Sciences Department at Virginia Tech. To evaluate the applicability of this method to diverse sulfidic materials, 296 rock and sediment samples collected from acid roadcuts in Virginia were tested for PPA, total-S using an Elementar Vario Max CNS analyzer, and qualitative presence of carbonates by the HCl “fizz test” (Sobek et al., 1978).

Detailed characterization was completed on a subset of fourteen diverse samples, which are described in detail below. This subset included eleven samples from Virginia and three from Brazil which were used as external mining environment comparative samples. The samples were selected to represent different rock types, sediments of varying textures, and samples containing carbonate minerals. The samples were tested in duplicate for PPA by the standard method and in triplicate for PPA after leaching with 0.5 N HCl to remove carbonates. Total-S was determined using triplicate samples. To determine sulfidic-S, a subsample was leached with 0.5 N HCl to remove sulfates, and then S content was measured on the leached material. This method was modified from ASTM Method D2492, which uses 5N HCl. For ABA, two MPA values were calculated, one using total-S and one using sulfide-S. The NP was determined on duplicate samples by the method of Sobek et al., (1978). Correlation was used to compare PPA and ABA results. Whole sample mineralogy was determined using x-ray diffraction on powder mounts. To characterize the morphology of sulfide minerals, polished sections were prepared and observed using reflected light microscopy. For finer textured sediments and tailings, clay mineralogy was determined using x-ray diffraction on oriented clay mounts (Rich and Barnhisel, 1977).

Description of Subset Samples

stf1 – minimally weathered, underlying material collected at a depth of 15 – 30 cm from Mine Road in Stafford County. This roadcut was approximately five years old when the material was collected. Indications of intense acid sulfate weathering at this site included low soil pH values, lack of vegetation, highly acidic road drainage, and iron staining and deterioration of concrete along this cut and an adjacent neighborhood. This roadcut exposes dark gray, graphitic, pyritic phyllite and slate of the Quantico Formation. The mineralogy consists mainly of quartz, with minor amounts of mica, kaolinite and pyrite and trace amounts of chlorite. The pyrite occurs as few, subhedral grains, approximately 0.1 mm x 0.1 mm. Trace amounts of pyrrhotite and chalcopyrite also are present.

stf4 – partially weathered surface material from the same location as stf1. The mineralogy consists mainly of quartz and mica, with minor amounts of chlorite and pyrite. The pyrite occurs as corroded subhedral grains.

f19 – partially weathered material collected from the surface of Rt-750 in Floyd County. This roadcut was most recently disturbed approximately 13 years prior to the time of sampling.

Indications of acid sulfate weathering include prominent sulfate salt efflorescence along the roadcut surface, lack of vegetation, acidic drainage, and Fe- and Al-precipitates along a local streambed. This roadcut exposes the Ashe Formation of the Lynchburg Group. Locally the rock is mapped as Alum Phyllite, and consists of a steel-gray, fine-grained phyllite with pods of amphibolite and calcsilicate gneiss. This sample was collected from the amphibolite. The mineralogy consists mainly of quartz, chlorite and mica with trace amounts of feldspar, calcite, and pyrrhotite. The pyrrhotite occurs as polycrystalline lamellar aggregates.

fl19 – partially weathered material collected from the surface of Rt-8 in Floyd County. This roadcut consists of similar material described for fl9, and the sample is from the phyllite. The mineralogy consists mainly of quartz and mica with trace amounts of chlorite.

fc4 – minimally weathered sample of Marcellus Shale from a small VDOT quarry off Rt-600 in Frederick County. The mineralogy consists mainly of quartz, mica, and chlorite with trace amounts of feldspar and pyrite. The pyrite occurs as framboids, clusters of microcrystals, euhedral and subhedral grains, and anhedral masses dispersed throughout the sample.

wc4 – minimally weathered sample of Chattanooga shale from Rt-23 in Wise County. This roadcut was approximately 10 years old at the time of sampling. Indications of acid sulfate weathering include precipitation of sulfate salts on the roadcut surface, iron staining and concrete deterioration along the base of the cut, and guardrail corrosion. The mineralogy of this sample consists mainly of quartz, with minor amounts of mica and trace amounts of feldspar, chlorite and pyrite. The pyrite occurs as framboids, and cluster of microcrystals, dispersed through the sample.

gas32 – previously undisturbed, reduced, sandy loam sediments, collected at 9.7 m (32 ft) depth, from a deep boring behind the Citgo gas station at the intersection of Rts 156 and 630 in Hanover County. These sediments are believed to be from the Chesapeake Group, which are Tertiary marine sediments. The mineralogy consists mainly of quartz, with minor amounts of mica and pyrite, and trace amounts of kaolinite and calcite. Pyrite occurs as framboids and clusters of microcrystals dispersed throughout the sample. Clay mineralogy consists mainly of mica, montmorillonite, hydroxy-interlayered vermiculite (HIV)/intergrade, and hydroxy-interlayered smectite (HIS)/montmorillonite intergrade, with minor amounts of kaolinite, vermiculite, and quartz, and trace amounts of feldspar.

mcv5-4 – undisturbed, reduced, loam sediments, collected at 1.2 m (4 ft) depth from a deep boring between the cloverleaf and exit ramp in the northwest section of the I-295/360 interchange near Mechanicsville in Hanover County. These sediments are from the Calvert Formation of the Chesapeake Group. Indications of acid sulfate weathering include very low soil pH, lack of vegetations, yellow jarosite mottles, iron-staining and concrete deterioration along drainage ditches, and acid drainage. The mineralogy consists mainly of quartz, with minor amounts of mica and feldspar, and trace amounts of chlorite and pyrite. The pyrite occurs as framboids dispersed throughout the sample. Clay mineralogy consists mainly of HIS/montmorillonite intergrade, montmorillonite, and mica, with minor amounts of HIV/intergrade, kaolinite, vermiculite, chlorite, quartz and feldspar.

mcv6-16 – same location as mcv5-4, but inside the cloverleaf. Undisturbed, reduced, silt loam sediments from the Chesapeake Group were collected from a depth of 4.9 m (16 ft). The mineralogy consists mainly of quartz, with minor amounts of mica and feldspar, and trace amounts of kaolinite, pyrite and chlorite. The pyrite occurs as framboids and few weathered subhedral grains. The clay mineralogy consists mainly of montmorillonite, mica, and HIS/montmorillonite intergrade, and HIV/intergrade, with minor amounts of chlorite and kaolinite, quartz, vermiculite, and feldspar.

gas16 – same location as gas32. Undisturbed, reduced, clay loam sediments from the Chesapeake Group were collected at a depth of 4.9 m (16 ft). The mineralogy consists mainly of quartz, mica and pyrite, with minor amounts of kaolinite. The pyrite occurs as framboids and clusters of microcrystals. The clay mineralogy consists mainly of mica, montmorillonite, HIV/intergrade, HIS/montmorillonite intergrade, with minor amounts of kaolinite, vermiculite, quartz and feldspar.

mcv6-28 – same location as mcv6-16. Undisturbed, reduced, clay sediments from the Chesapeake Group were collected at a depth of 8.5 m (28 ft). The mineralogy consists of quartz, with minor amounts of mica, and trace amounts of kaolinite, pyrite and chlorite. The pyrite consists of framboids dispersed throughout the sample. The clay mineralogy consists mainly of HIS/montmorillonite intergrade, montmorillonite, and mica, with minor amounts of HIV/intergrade, kaolinite, vermiculite, quartz, feldspar, and chlorite.

ni – tailings from a nickel mine in Brazil. The mineralogy consists mainly of kaolinite, with minor amounts of amphibole and pyrrhotite, and trace amounts of quartz and chlorite. The pyrrhotite occurs as anhedral grains dispersed throughout the sample. The clay mineralogy consists mainly of kaolinite and mica, with minor amounts of HIV/intergrade, chlorite, quartz, feldspar, and gibbsite.

bass – acid sulfate soil from Brazil. The mineralogy consists mainly of quartz, with minor amounts of kaolinite and mica, and trace amounts of chlorite and pyrite. The pyrite occurs as framboids dispersed throughout the sample, and numerous subhedral grains. The clay mineralogy consists mainly of kaolinite and mica, with minor amounts of HIV/intergrade, and trace amounts of quartz, chlorite, and trace amounts of feldspar, and gibbsite.

gold – tailings from a gold mine in Brazil. The mineralogy consists mainly of quartz, with minor amounts of mica and feldspar, and trace amounts of kaolinite and pyrite. Pyrite occurs as few subhedral pyrite grains, small amounts of pyrite remaining in goethite pseudomorphs, and small amounts of chalcopyrite. Clay mineralogy consists mainly of mica, montmorillonite, kaolinite, with minor amounts of quartz, HIS/montmorillonite intergrade, and trace amounts of feldspar and gibbsite.

Soxhlet Extraction

Soxhlet extraction analysis was evaluated for four samples. The samples were selected to be i) the same or similar to materials from the subset of 14 samples that were characterized in detail, and ii) to represent roadcuts where acid drainage could be collected from the field for

comparison. The applied method was similar to that described by Renton et al. (1988). Prior to analysis, subsamples were analyzed for total-S and PPA. Standard 123 mm Soxhlet extractors were used in triplicate for each sample. For each triplicate, 100 g of sample, crushed to less than 1 cm diameter fragments, were weighed into cellulose thimbles. A wad of cotton was placed over the sample to minimize splashing and channeling of the percolating leachate within the material. The thimbles were placed in the extractors, 300ml of distilled, deionized water were placed in the reservoir, and 50 ml of distilled, deionized water were poured into the thimbles to “pre-wet” the samples. The samples were leached for 24 hours, after which time the leachate was collected for analysis. The thimbles were placed in a tall-form beaker and transferred to a 105° C oven for 14 days to reoxidize the sample. At the end of the reoxidation period, the thimbles were returned to the extractors and leached again. The oxidation/leaching cycle was repeated 10 to 15 times. Each time the leachate was analyzed for pH, acidity, and S. The initial weight of S for each sample was calculated based on the initial sample weight and percent total-S. After each leaching the cumulative amount of S in the leachates was subtracted from the initial amount of S, and the percent S that presumably remained unreacted in the sample was calculated. For the first six leachings the leachate was analyzed for Al, Fe, Mn, Cu, and Zn by ICPES.

Road drainage was collected from each of the sites represented by the Soxhlets on three occasions and analyzed for acidity, sulfate, Al, Fe, Mn, Cu, and Zn. At the Floyd, Clifton Forge, and Mechanicsville sites, water samples were collected from the outlet of culverts that drain the roadcuts. Additional samples were collected at Clifton Forge from a drainpipe that feeds leachate directly from the backfill into the culvert. At Mechanicsville, additional samples were collected from a shallow well installed at the base of the outcrop. At Stafford, water samples were collected at two locations, a few hundred feet apart, from a drainage ditch at the base of the outcrop.

Regression, correlation, and paired t-tests, were used to evaluate potential acidity procedures, and to model relationships. All statistical analyses were completed using MINITAB 13. Graphs were generated using MINITAB 13 and Microsoft Excel 2000.

RESULTS AND DISCUSSION

Compilation of a Statewide Sulfide Hazard Rating Map

Locations of documented acid roadcuts, and the geologic formations identified at these sites, are described in Table 2 and illustrated in Figure 2. A summary of results from analyses of geologic materials and road drainage is presented in Table 3. All sites exhibited lack of vegetation due to very low pH of surface materials, and numerous sites exhibited iron staining on concrete, deterioration of concrete and metal construction materials (drainage ditches, culverts, and guardrails), iron and aluminum precipitation in streambeds, and sulfate salt efflorescence on roadcut surfaces (Figures 4-7).

Table 2. Locations and geologic formations of documented acid roadcuts and excavation sites in Virginia.

City/County	Roadcut location	Codes	Geologic formation
Coastal Plain			
Hampton	Hampton Roads Center: I-64 and Big Bethel Rd.	HRC	Tabb, Sedgefield member
Suffolk	I-664 and Rt-17	SUF 1, 2	Tabb, Sedgefield member
Suffolk	I-664 and Rt-337	SUF 3, 4	Tabb, Sedgefield member
Greensville Co.	Otterdam Swamp: north of I-95/Rt 58	ODS	Chesapeake Group
Prince George Co.	Near Fort Lee Mil. Res.: north of I-295/Rt-36 intersection.	FTL	Tertiary marine sediments
Chesterfield Co.	Proctor's Creek: Rt-288 and Rt-145	CHF	Lower Tertiary Deposits
Chesterfield Co.	Walthall exit: I-95 and Rt 620	WHE	Lower Tertiary Deposits
Henrico Co.	I-295 and Rt-156	HEN	Chesapeake Group
Richmond	Behind Richmond City Jail	JAIL	Chesapeake Group (Calvert)
Richmond	Broad St. and 14 th St.	WALL	Chesapeake Group
Richmond	East Richmond Rd. landfill	LF	Chesapeake Group/Lower Tertiary Deposits (Eastover, Calvert, Aquia)
Hanover Co.	I-295 and Rt-360	MCV	Chesapeake Group (Calvert, Eastover)
Hanover Co.	Behind Mechanicsville Wal-Mart	WM	Chesapeake Group
Spotsylvania Co.	I-95, milepost 120.5	SPT	Chesapeake Group/Lower Tertiary Deposits
Spotsylvania Co.	State Farm Insurance: near I-95 and Rt-1 bypass	SFI	Chesapeake Group/Lower Tertiary Deposits
Piedmont			
Stafford Co.	I-95, milepost 148	STF 7	Quantico Formation
Stafford Co.	Mine Rd: I-95 and Rt-610	STF 1-6	Quantico Formation
Blue Ridge			
Floyd Co.	Rt-750 and Rt-735	FL 1-13	Ashe Formation of the Lynchburg Group (Alum phyllite)
Floyd Co.	Rt-8: two roadcuts between Rt-750 and Rt-705	FL 14-22	Ashe Formation of the Lynchburg Group (Alum phyllite)
Carroll Co.	I-77: mileposts 21 - 22	CC	Lynchburg Group of the Ashe Formation
Valley And Ridge			
Frederick Co.	VDOT quarry: Rt 600, bw. Rt-50 and 608	FC	Marcellus shale
Highland Co.	Rt-250 and Rt-614	HC	Millboro, Needmore shales
Clifton Forge	I-64	CF	Millboro shale
Wise Co.	Numerous sites along Rt-23 near Rt-610	WC	Chattanooga shale

Table 3. Summary of Potential Peroxide Acidity (PPA) and % total-S for geologic samples, and pH and metal content of a representative road drainage sample from each site.

Geologic Formation	Geologic samples			Road Drainage Sample						
	Number of samples	PPA*	%S	pH	Fe	Al	Mn	Cu	Zn	S
					mg/L					
Tabb Formation	49	20.9	0.79	3.09	13.9	49.5	2.1	<0.1	<0.025	298
Tertiary Marine Sediments	10	3.2	0.1	3.05	12.4	15.2	2.4	<0.1	0.6	136
Quantico Slate	13	32.7	1.09	2.61	114.2	66.9	17.4	0.4	3.5	639
Ashe Formation	21	4.8	0.3	3.22	39.7	20.1	1.4	<0.1	0.6	182
Devonian Black Shales	49	12.1	0.75	2.67	59	162.5	38.5	<0.1	8.3	1011

*Mg CaCO₃/1000 Mg material.



Figure 4. Sulfide-bearing sediments of the Chesapeake Group are exposed along this stretch of I-95 in Spotsylvania County. The stability of this signpost is compromised due to concrete degradation from acid attack. Furthermore, acid conditions (soil pH ~ 2.5) limit vegetative growth, which makes these sites particularly prone to erosion.



Figure 5. Acid drainage from the Quantico slate in Stafford, Virginia, has caused extensive iron-staining along curbs and sidewalks through the Hampton Oaks subdivision. Also, concrete etching occurs when acid drainage “dissolves” out the cement, deteriorating the concrete. Homeowners in this neighborhood apply the equivalent of 2 Mg agricultural lime per hectare per month to maintain soil pH above 5.5.



Figure 6. Proctor's Creek was redirected due to road construction near the intersection of Rts-288 and 156 in Chesterfield County. The creek was routed into an excavated channel through Lower Tertiary deposits. Extremely acid soil conditions ($\text{pH} < 2.5$), which developed upon oxidation of the sediments, have inhibited vegetation along the stream bank.



Figure 7 (a) This roadcut along the cloverleaf of Rt-360W to I-295S, near Mechanicsville, Virginia, exposes the Eastover and Calvert formations of the Chesapeake Group. Sulfide oxidation has created extremely acid surface soil conditions ($\text{pH} < 3.5$). **(b)** A few years after construction, erosion began to expose the end of this metal guardrail further, and corrosion is evident. **(c)** Within 5 years, erosion has removed over 30 cm of sediment and the metal is severely corroded.

Coastal Plain

Acid sulfate weathering problems in the Coastal Plain primarily result from exposure of unconsolidated Tertiary marine sediments, particularly those mapped as the Chesapeake Group and Lower Tertiary deposits. These sediments occur in drab shades of green, blue and gray, and consist of fine- to coarse-grained, quartzose sand, silt, and clay that is variably shelly, diatomaceous, and glauconitic (Rader and Evans, 1993). Formations of the Chesapeake Group include Chowan River, Yorktown, Eastover, St. Mary's, Choptank, and Calvert. Formations of the Lower Tertiary deposits include Brightseat, Aquia, Marlboro, Nanjemoy, Piney Point, and Chickahominy. Of these formations, the Eastover and Calvert specifically have been identified as being acid-forming at the I-295/360 interchange, behind the Richmond City Jail, and along Proctor's Creek at Rts-288/145. The Eastover, Calvert, and Aquia formations have been identified at the East Richmond Road Landfill (R. Berquist and G. Johnson, VDMR, personal communication). Reflected light microscopy of polished sections from numerous samples of Tertiary marine sediments indicated that sulfides occur as abundant dispersed framboids, clusters of microcrystals, and small, weathered, subhedral grains of pyrite. All forms were present in all samples, and no major differences in morphology or grain size were noted among the samples.

Analysis of samples from twenty-three deep borings throughout an area of approximately 55 square miles northeast of Richmond indicated that completely reduced sediments have pH values ranging from approximately 5.5 – 8.0, PPA values ranging from approximately 30-50 Mg CaCO₃/1000 Mg material, and total-S values ranging from approximately 1.0 – 2.5%. Relatively high S values (> 0.2%) were found at all locations indicating that S occurrence may be ubiquitous in the Chesapeake Group. Sediments containing carbonates have lower PPA values, generally ranging from 0 – 20 Mg CaCO₃/1000 Mg material, and were found in only few samples from deep borings and not in acid road banks. This suggests one of the following: i) carbonate-bearing layers in the Tertiary marine sediments tend to occur at greater depths, ii) excavation through carbonate-bearing sediments does not result in severe ARD, or iii) carbonates have been leached out of existing roadcuts by acid drainage.

Upon exposure, sulfide oxidation causes pH to decrease rapidly. Weathered materials at the surface of roadcuts through the Chesapeake Group and Lower Tertiary deposits typically appear yellowish-brown, have pH values between 2.5 – 3.5, have PPA values between 10-20 Mg CaCO₃/1000 Mg material, and retain less than 1% S. Less oxidized, underlying gray sediments have slightly higher pH values and much higher PPA values, ranging from about 30-50 Mg CaCO₃/1000 Mg material. Samples from the I-295/360 interchange which was constructed approximately 20 years ago, indicate that within 50 to 75 cm from the surface the sediments are yellowish-brown in color, have pH values below 3.5, and PPA values below 15 Mg CaCO₃/1000 Mg material. Below this upper weathering surface, a transition zone exists for about 75 to 100 cm where the material is grayer with a few yellow jarosite mottles and/or red redoximorphic features evident. Moving down through this zone, pH steadily increases and PPA values are high (> 30 Mg CaCO₃/1000 Mg material). Below the transition zone, at depths greater than 120 cm, the material is uniformly dark gray, has relatively high pH values (> 5.5), and high PPA values indicating that the material has been minimally affected by oxidation. Qualitative observations

during detailed sampling of the roadcut indicated that this sequence was uniform over the entire roadcut.

Sediments from the Calvert and Eastover Formations of the Chesapeake Group, along the shoulder of the cloverleaf from Rt-360E to I-295S, also were sampled in detail (Figure 8). Sulfide levels across the roadcut are relatively homogenous laterally, but somewhat variable vertically. The S values increase from 0.5-1.0% at the base of the outcrop to 1.0-1.5 for the upper half of the acid portion of the roadcut (non-acid Quaternary sediments overlie parts of the roadcut). A discontinuous band of higher-S material (1.5-2.0%) runs laterally along the middle of the sampling area, approximately 5m up from the base of the roadcut. Similarly, the PPA values increase from 10 –20 Mg CaCO₃/1000 Mg material at the base of the roadcut to 30-40 Mg CaCO₃/1000 Mg material for the upper half. A few locations, corresponding to the pockets of high-S material, had values ranging between 40-50 Mg CaCO₃/1000 Mg material.

Road drainage, collected at various locations throughout the northwest quadrant of the I-295/360 interchange, exhibited very low pH (< 4.0). Samples collected from a shallow well installed at the base of the outcrop represent the most concentrated road drainage. These samples exhibited high levels of Fe, Al, Mn, and S. In comparison to EPA effluent limitations for coal-mine drainage (Table 4), Fe significantly exceeded the daily maximum load and Mn exceeded the 30-day average load. Samples from the outlet of a culvert on the other side of the road indicate that the drainage is diluted as it flows towards a local stream, although pH is still very low and Al and S values are relatively high. Water samples from Proctor’s Creek at Rts-288 and 145 in Chesterfield County have moderate pH values and low EC values, suggesting that ARD from the sediments is sufficiently diluted by channel throughflow, which limits adverse effects on water quality.

Table 4. EPA Best Available Technology for Coal Mine Drainage. (40 CFR 434)

Parameter	One Day Maximum	30 Day Average
Total Iron (mg/L)	7	3.5
Total Manganese (mg/L)	4	2
pH	6-9	6-9

Acid sulfate weathering problems are less severe at a few sites that are surficially mapped as the Sedgefield member of the Tabb formation. The Sedgefield member consists of fossiliferous brackish-bay sand, beach and near-shore marine clayey sand, and lagoonal and marsh clay and clayey sand. Reflected light microscopy of a polished section from material collected at Hampton Roads Center (HRC3) revealed few, small, dispersed, subhedral grains of pyrite. The presence of sulfides in this formation is not identified in detailed local geologic mapping of the area (Johnson, 1976) or in the expanded explanation for the Geologic Map of Virginia (Rader and Evans, 1993). Based on this work, and one previous study (Daniels et al., 1995), sulfides appear to occur in discontinuous pockets throughout the Sedgefield member of the Tabb formation. Alternatively, depending on the thickness of the Tabb at a given location, sulfides may be exposed from the underlying Shirley Formation.

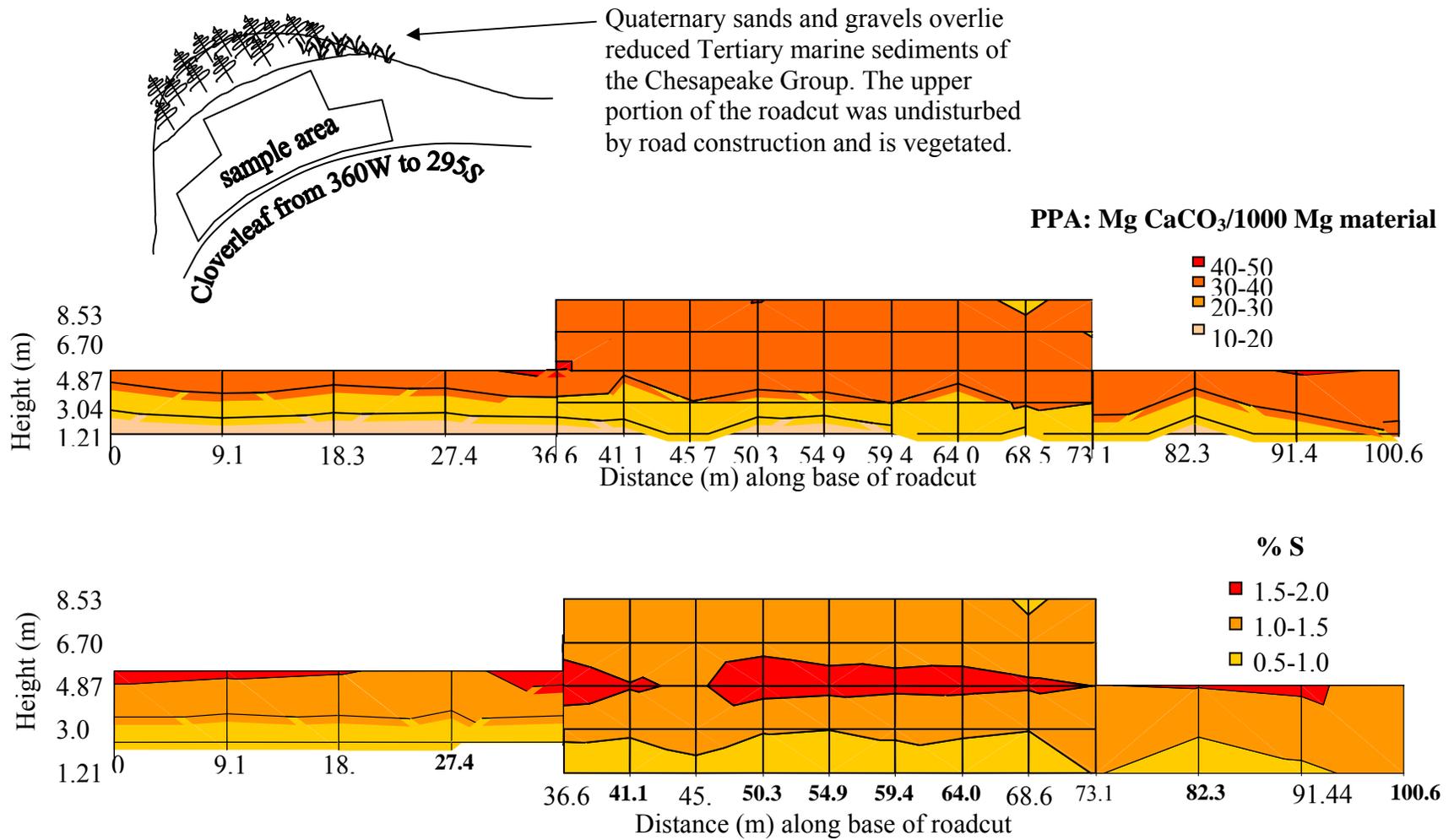


Figure 8. Potential peroxide acidity (PPA) values and % total-S from detailed sampling along the shoulder of the cloverleaf from Rt 360W to I-295S.

Sediment samples, believed to be from the Sedgefield member, collected from two roadcuts in Suffolk, and a construction site in Hampton, had pH values ranging from 3.2 – 4.6, PPA values ranging up to 6.00 MgCaCO₃/1000 Mg material, and sulfur values less than 0.2%. Previous sampling at Sandy Bottom Nature Park (also known as Chisman Lakes) indicated, with few exceptions, that materials generally had PPA values under 10 Mg CaCO₃/1000 Mg material and contained less than 0.2% S (Daniels et al., 1995). Qualitative field observations at the two Suffolk roadcuts indicate that severe soil compaction also may limit vegetation growth. Samples could not be collected from deeper than 0.2 m because the material was too compact to penetrate with a shovel. Water samples from two small lakes at Hampton Roads Center (adjacent to Sandy Bottom Nature Park) had low pH values around 3 – 4, moderate EC values, and relatively low metal concentrations. Water drainage from a stockpile of excavated material at the same site had a very low pH, high EC, and high levels of Fe, Al, Mn and S. In comparison, water samples from two small lakes had slightly higher pH values, and lower EC and metal concentrations.

As a rule of thumb, materials with PPA values below 10 Mg CaCO₃/1000 Mg are readily reclaimed with proper management, while materials with PPA values between 10 - 60 require intense reclamation management (Daniels et al., 2000). Considering these guidelines, and the widespread occurrence of S through the Chesapeake Group and Lower Tertiary deposits, exposure of Tertiary marine sediments may be considered highly likely to produce problematic roadside management conditions which require intense reclamation efforts. Exposure of the Sedgefield member of the Tabb formation may be considered likely to produce moderately problematic roadside vegetation management conditions, which could require special reclamation efforts.

Piedmont

Acid roadcuts along I-95 and Mine Road (Rt 610) in Stafford occur in pyritic phyllite and slate of the Quantico Formation. Reflected light microscopy of polished sections from Mine Road (STF1:15-30cm and STF4:1-5cm) revealed the presence of pyrite as corroded subhedral and euhedral grains, along with chalcopyrite and covellite. Microcrystalline forms, such as those described for Coastal Plain sediments, were not observed. The PPA values for surface samples ranged from 6 – 22 Mg CaCO₃/1000 Mg material, and S values ranged from 0.24 – 1.00%. One sample from relatively unweathered underlying material had a significantly higher PPA value, 99 Mg CaCO₃/1000 Mg material, and contained over 3.8% S. Previous analysis of six samples collected by VDOT at Mine Road revealed PPA values ranging from 1 - 85 Mg CaCO₃/1000 Mg material. These values indicate sulfides are unevenly distributed throughout the roadcut; however, more detailed sampling would be necessary to characterize this spatial variability.

Drainage samples collected along the base of Mine Road very low pH values, and high EC and metal concentrations. Extensive iron-staining and concrete etching are evident along drainage ditches at the base of this roadcut, and throughout an adjacent neighborhood. Nonetheless, one water sample from the vicinity of where road drainage enters a local stream had neutral pH and low EC and metal concentrations, indicating that acid road drainage may be sufficiently diluted so as to limit adverse effects on surface water quality. Neutralization reactions between acid drainage and concrete may also decrease acidity.

Compared to sulfidic sediments of the Coastal Plain, sulfide levels in the Quantico Formation appear to be more variable and occur over a much larger range of S values. With one exception, drainage from this site had lower EC, and higher acidity and metal concentrations, than any other evaluated roadcut. Exposure of the Quantico Formation may be considered highly likely to produce severely problematic roadside management conditions, which require intense reclamation efforts. Roadcut surfaces of the Quantico Formation may be quite steep and generally consist of shallow, rocky, weathered material over bedrock, and rock outcrops, which are less suited for standard soil remediation methods than the unconsolidated sediments of the Coastal Plain.

Blue Ridge

Acid roadcuts along Rt-8 and Rt-750 in Floyd County, and along I-77 in Carroll County, occur in the Ashe Formation of the Lynchburg Group. The rock exposed in Floyd County is mapped locally as the Alum Phyllite (Dietrich, 1959). The Ashe Formation consists of amphibolite, gneiss, schist, and phyllite. The roadcuts in both Floyd and Carroll County are dominantly a steel-gray, fine-grained phyllite with pods of amphibolite and calcisilicate gneiss. Efflorescent sulfate coatings are common on the Floyd County exposures, but minimal along the Carroll County roadcuts. Reflected light microscopy of polished sections from Floyd (FL9, FL19) indicates the presence of polycrystalline, lamellar aggregates of pyrrhotite, small pyrrhotite inclusions within sphalerite, small, subhedral grains of pyrite, and few, scattered, anhedral masses of chalcopyrite. Of the sampled roadcuts in Virginia, this was the only occurrence of pyrrhotite, which reacts more rapidly than pyrite but produces less acidity on a molar basis. Polished sections from Carroll County indicate the presence of coarse grains and veinlets of pyrite, anhedral grains of chalcopyrite and sphalerite, and lathes of graphite. The PPA values for Carroll County ranged from 0.93 to 9.26 Mg CaCO₃/1000 Mg material and S values ranged from 0.06 – 0.36%. For Floyd County, PPA values ranged from 0.48 – 17.54 Mg CaCO₃/1000 Mg and S ranged from 0.05 to 1.93%.

Water drainage from the Rt-750 roadcut has significantly impacted a local stream, and a fishpond on a neighboring property. Shortly after the roadwork was completed, a neighboring landowner reported the death of fish in his pond downstream from the road drainage culvert. Water sampling by VDOT over the past fourteen years, in addition to sampling for this study, indicated that water from the source spring upstream of the roadcut has maintained pH values ranging from 5.8 to 7.1 (Paul Johnson, VDOT, personal communication). Water grab samples from the upstream end of the culvert draining to the fishpond have consistently tested at pH values below 4.0. Three water samples (FL4-1(1) – (3)) from the downstream end of the culvert indicate high levels of Fe, Al, and Mn. Iron and aluminum precipitates heavily coat the streambed for at least 30 m downstream of the culvert.

Along the Rt-8 roadcut in Floyd, iron staining, concrete etching, and deterioration of a metal culvert were evident along the base of the roadcut. Drainage samples from ditches along I-77 in Carroll County had near-neutral pH values and low EC and metal concentrations. An interview with a VDOT environmental manager for the Bristol district revealed that natural drainage “up the mountain” from this site regularly has pH values around 10 (George McCloud,

VDOT, personal communication). Local bedrock apparently provides enough alkalinity to neutralize acid drainage.

Compared to materials from the Coastal Plain and the Piedmont, PPA values are much lower for materials from the Ashe Formation. Nonetheless, drainage from this material may have significant adverse effects on local surface water as was seen at Rt-750 in Floyd. Road drainage from Floyd is comparable to drainage from the I-295/360 roadcut; however, stream damage appears more significant at Floyd where concentrated drainage flows directly into a smaller stream. Exposures of phyllitic material from the Ashe Formation may be considered somewhat likely to produce moderate to severe problematic roadside management conditions. As with the Quantico Formation in the Piedmont, roadcut surfaces through the Ashe Formation tend to be quite steep and consist of shallow, rocky, weathered material over bedrock, and rock outcrops, which may not be suited for standard soil remediation methods.

Valley and Ridge

Acid roadcuts in the Valley and Ridge result from the exposure of Devonian and Mississippian black shales, including the Marcellus shale (northeast of Shenandoah County), the Millboro shale (southwest of Shenandoah County except in extreme southwestern Virginia), the Needmore Formation (occurs with Marcellus and Millboro), and the Chattanooga shale (southwestern Virginia). Reflected light microscopy of polished sections (FC4, CF1-2, HC43, WC4) indicates the presence of pyrite as framboids, clusters of microcrystals, and weathered, anhedral and subhedral grains at all locations. The PPA values ranged from 0 to 61 Mg CaCO₃/1000 Mg material; however, numerous samples contained CaCO₃ as indicated by the fizz test. All of the carbonate-bearing samples, except one, came from the Rt-250 roadcut in Highland County. One carbonate-bearing sample was collected from Frederick County. The S values ranged from 0.0 to 3.3%. Analysis from detailed sampling along 500 meters of the Rt-250 roadcut in Highland County indicated that sulfide occurrence is not laterally homogenous. Differences of up to 2% S were noted for samples within 15 m of each other, and variation did not seem to appear to be systematic. Locally occurring pyritic seams and septarian concretions, evident along this roadcut, account for discrete high-S occurrences. Similarly, calcium carbonate appeared sporadically as secondary vein fillings and as a fine-grained cementing agent, at varying concentrations, throughout the exposure.

Water drainage from I-64 in Clifton Forge has significantly impacted a local stream. One water sample, upstream from the roadcut, revealed near-neutral pH, low EC, and low metal concentrations. Water from a drain inside the culvert, representing the most concentrated drainage, had very low pH, high acidity, high EC, and very high metal concentrations. Water samples from the downstream end of the box culvert have variable pH values and correspondingly variable metal concentrations. Iron and aluminum precipitates heavily coat the bed of the stream, which appears to be biologically dead for at least 0.5 km downstream of the roadcut. Water drainage from a drainage ditch along Rt-250, and from a nearby sedimentation pond and stream, have moderate to near-neutral pH values, but high EC values. Overall, metal values are low except for high Mn values at the sedimentation pond and the stream. Drainage from this site is partially neutralized by calcium carbonate, which occurs throughout the roadcut both in veins and fine-grained particles as indicated by the fizz test. Nonetheless, iron-staining

and concrete etching was evident along a drainage ditch at the base of the road, and Fe-flocculation was significant in the sedimentation pond. Although drainage was not present at the Rt-23 roadcut in Wise County at the time of sampling, iron-staining, concrete etching, and deterioration of a metal guardrail were evident in a drainage ditch along the base of the roadcut.

Sulfide levels in materials sampled from Devonian and Mississippian black shales appear to be more variable than other evaluated sulfidic materials. Overall, for samples that do not contain carbonates, PPA and S values tend to be slightly higher than those for reduced Tertiary marine sediments, but lower than those for the Quantico Formation. Carbonates may appear sporadically and at various concentrations, causing PPA values to drop significantly despite high S values. Although the Chattanooga and Marcellus shales tested higher than the Millboro shale and Needmore Formation, more exposures would need to be evaluated to make definitive statements regarding their relative differences. Drainage from the I-64 roadcut at Clifton Forge had higher acidity and metal concentrations than any other studied roadcut. This drainage has significantly affected local surface water quality. Exposures of the Marcellus, Millboro, and Chattanooga shales, and the Needmore Formation, may be considered somewhat likely to produce severely problematic roadside management conditions.

Appalachian Plateau

The Appalachian Plateau geologic region of Virginia was not sampled in this study due to the relatively large research base associated with potential acidity in Appalachian coal mining environments (Sobek et al., 2000). In Virginia, the vast majority of strata within the Pennsylvanian system exposed to potential road-building excavation are fluvial-deltaic facies that are generally low in pyritic-S. Many of the massive sandstones that dominate the Lee, Norton and Wise formations contain secondary carbonate cementing agents (Howard et al., 1988) which offset the relatively minor amounts of sulfides found in most geologic sections. Significant accumulations of sulfides do occur in coal seams throughout the region; however, these seams are relatively thin (< 3 m) and are usually completely removed and marketed during road corridor development. Several relatively thin sections of overburden in Virginia (e.g. the Standiford seam interburden of the middle Wise formation) do generate rock spoils with significant (> 10 Mg/1000 Mg) levels of potential acidity, but these intervals represent less than 10% of the entire geologic section. Detailed reviews of procedures for evaluating southwest Virginia mine spoils and coal-like materials for potential acidity and revegetation potential are given by Daniels and Zipper (1997) and Daniels et al. (2000).

Final Compilation of a State-wide Sulfide Hazard Rating Map

The impact of acid drainage resulting from the exposure of sulfidic materials during road construction depends on many variables, including the relative volume of ARD moving to surface stream flow, the flow rate of local surface waters, and the neutralizing capacity of surrounding geologic materials. Although materials may be rated based on characteristics related to S content, PPA, and rock drainage quality, the true risk of environmental impact will depend on site-specific conditions. For example, the materials at acid roadcuts in Floyd County and Carroll County are relatively similar; however, environmental impact is significantly greater in Floyd County due to specific site conditions such as lack of abundant neutralizing materials and

direct drainage of ARD into a small stream. Similar comparisons may be made between the Rt-250 cut in Highland County and the I-64 cut in Clifton Forge. With this in mind, the following scheme was developed to assess geologic materials with general ratings in terms of sulfide hazard. Materials are rated into four classes based on PPA and S values:

- 1) Materials for which 90% of samples tested less than 10 Mg CaCO₃/1000 Mg material and contained less than 0.5% S.
- 2) Materials for which 90% of samples tested less than 10 Mg CaCO₃/1000 Mg material and more than 10% of the samples tested greater than 0.5% S.
- 3) Materials for which more than 10% of samples tested greater than 10 Mg CaCO₃/1000 Mg material and less than 10% of samples tested greater than 60 Mg CaCO₃/1000 Mg material.
- 4) Materials for which more than 10% of the samples tested greater than 60 Mg CaCO₃/1000 Mg material.

These class boundaries were determined with consideration of standard remediation methods and the observed properties of a wide range of sulfidic materials. Application of these ratings to the geologic materials evaluated in this study is shown in Table 5. Again it should be emphasized that these ratings are based strictly on the acid-producing potential of a particular material, whereas actual acid production and severity of impact will depend on site conditions.

Table 5. Sulfide Hazard Rating for Evaluated Geologic Materials.

Geologic Map Unit	Sulfide Hazard Rating*
Tabb Formation – Sedgfield Member	1
Wise, Kanawha, Norton, New River, Lee and Pocahontas Formations	1
Ashe Formation of the Lynchburg Group	2
Chesapeake Group	3
Lower Tertiary deposits	3
Marcellus shale and Needmore Formation	3
Millboro shale and Needmore Formation	3
Quantico Formation	4
Chattanooga Shale	4

*1 = least severe, 4 = most severe.

In addition to the materials evaluated for this study, sulfides have been documented in numerous other geologic formations in Virginia (Rader and Evans, 1993; Penick, 1987; J. Peper – personal communication). In many cases the sulfides occur as large crystals, which generally are considered non-hazardous to road construction due to their minimal surface area that limits oxidation reactions. Nonetheless, these formations should be noted and may require evaluation. This is not intended to be an exhaustive list of pyrite-bearing formations. As previously discussed, the most problematic forms of pyrite such as framboids are rarely noted in general rock descriptions since they are not evident in hand specimens. In the Appalachian Plateau and Valley and Ridge, additional pyrite-bearing map units include igneous rocks (p), Bluefield Formation (Mbf), and Price Formation (Mpr), and Edinburg Formation (Oeln). In the Blue Ridge and Piedmont, additional pyrite-bearing map units include the Everona Limestone (Eev), assorted formations of the Lynchburg group including Charlottesville Formation (Zch), Monumental Mills Formation (Zmm), graphitic phyllite and metasilstone (Zlg), metgawacke (Zlm), and banded marble (Ezac), metabasalt of the Catoclin Formation (EZc), felsic volcanic

and volcanoclastic rocks (Zav), border gneiss (Ybr), Accotink Schist (Eza), Rich Acres Formation (Cra), Diana Mills Complex (PzZdm), diorite and hornblendite of the Green Springs Pluton (PzZgs), Shelton Formation (Ost), members of the Arvonian Formation including slate and porphyroblastic schist (Oa), kyanite quartzite and schist (Obq), Buffards Formation (Obf), and Columbia pluton (Ocg), Chopawamsic Formation (Ecv), kyanite schist of the central Piedmont (ks), Petersburg granite (Mpg). In the Coastal Plain, an additional pyrite-bearing map unit is the Shirley Formation (Qsh). The geographic extent of sulfide-bearing geologic materials is shown in Figure 9.

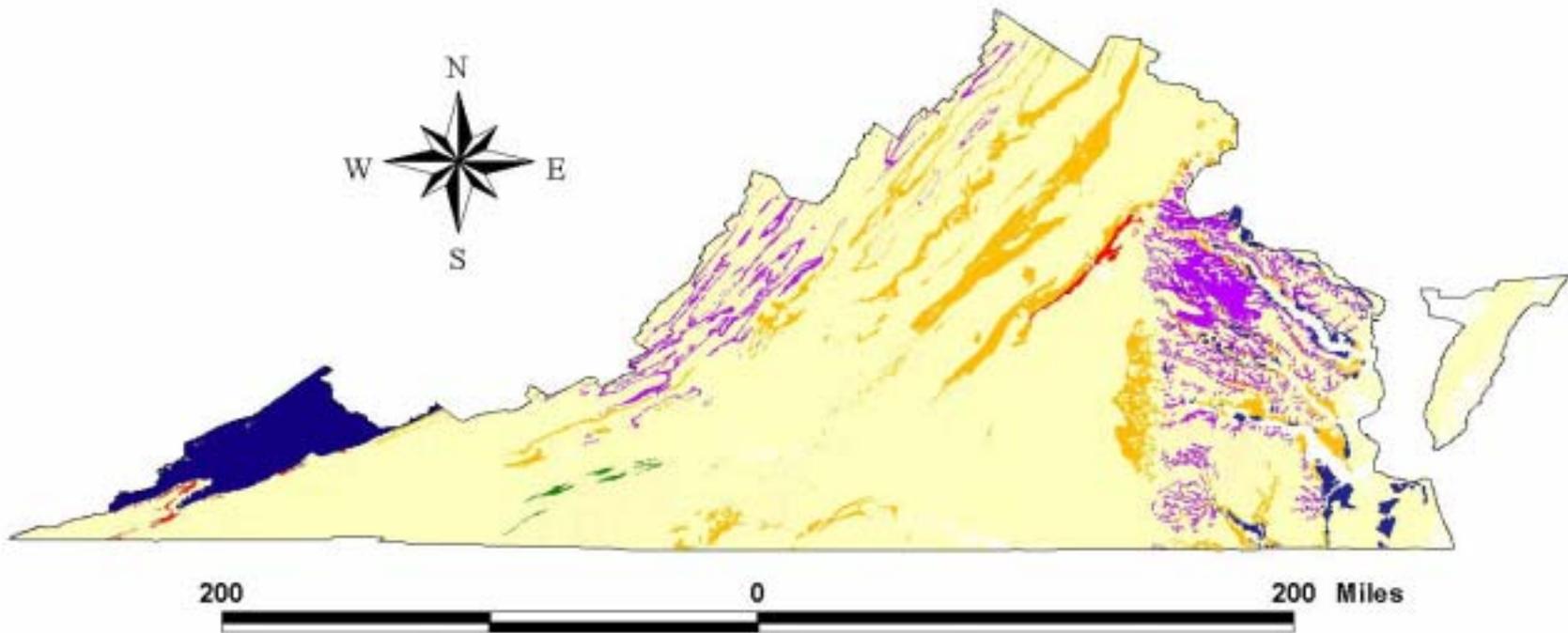
Predicting Depth to Sulfidic Materials in the Coastal Plain

Cross-sections developed from well logs in the study area indicate that the surface of reduced Tertiary sediments tends to parallel surface topography. However, despite this apparent relationship, a plot of depth-rs versus elevation for all data points indicated that variability increased significantly with increasing elevation and shallow depth-rs values (< 4 m) consistently occurred at all elevations. Regression analysis of depth-rs versus elevation was not significant ($r^2 = 0.22$). Regression using various combinations of elevation, slope, distance to streams, and geology did not improve results. Despite repeated efforts, a model could not be developed by regression analysis to adequately predict depth-rs using landscape variables.

A number of factors may help explain these poor results. Depth-rs is mainly controlled by two variables: depth of sediments overlying the sulfidic strata and depth of weathering within that strata. Where Tertiary marine sediments are surficially exposed, depth-rs is a function of weathering, and is largely affected by hydrology. Surface features such as elevation, slope, and distance to streams should be related to depth-rs. However, as indicated in Table 6, these factors alone could not be used to predict depth-rs. Underlying factors, such as textural changes between layers, may affect hydrology in locations that otherwise seem similar. Furthermore, local topographic features, such as intermittent streams or depressions, which are not apparent at the available map scale, may help explain discrepancies between seemingly similar locations.

Table 6. Coefficients of determination (R^2) from simple and multiple regression analyses of depth to reduced sediments against selected landscape variables.

Variable	Data set	R^2
Elevation	all wells	0.22
Slope	all wells	0.02
Distance to nearest stream	all wells	0.02
Elevation/slope/distance to nearest stream	all wells	0.23
Elevation	Wells from areas surficially mapped as Tertiary sediments	0.03
Elevation/slope/distance to nearest stream	Wells from areas surficially mapped as Tertiary sediments	0.23
Elevation	Wells from areas surficially mapped as Cretaceous sand and gravel	0.13
Elevation	Wells from areas surficially mapped as alluvium	0.15



- Sulfides not documented
- Sulfides documented: acid potential unknown
- 1: PPA generally $< 10 \text{ Mg CaCO}_3/1000 \text{ Mg}$ and $\% \text{ S} < 0.5$
- 2: PPA generally $< 10 \text{ Mg CaCO}_3/1000 \text{ Mg}$ and $\% \text{ S} > 0.5$
- 3: PPA generally $10 - 60 \text{ Mg CaCO}_3/1000 \text{ Mg}$
- 4: over 10% of samples have PPA $> 60 \text{ Mg CaCO}_3/1000 \text{ Mg}$

Figure 9. Geographic extent and hazard ratings for sulfide-bearing geologic materials in Virginia.

Where Tertiary marine sediments occur in the subsurface, depth-rs is determined more by depth of sediments overlying the sulfidic strata than by hydrology. This depth is a function of the depositional, structural, and erosional features that control the thickness of overlying Quaternary sediments, and may be further complicated by geologic factors such as lateral variation in sedimentary facies during deposition, the shallow dip of Coastal Plain sediments to the southeast, and the occurrence of normal faults. Consequently, the variables that control depth-rs over the entire study area may be too complex for regression analysis to allow approximations, let alone precise predictions, of depth-rs.

To avoid excavation of sulfidic materials it is most important to be able to identify locations where depth-rs is most likely to be shallow. Figure 10 indicates that sites with shallow depth-rs are dispersed throughout the study area and occur over the full range of elevations. Shallow depth-rs is expected at lower elevations because overlying Quaternary sediments have been removed and the water table occurs at shallower depths; however, shallow depth-rs is more difficult to explain for higher elevations. Sorting the data identified 12 high-elevation wells with depth-rs less than 7 m. These wells were not geographically clustered, and they occurred at various elevations (45 m – 61 m), stream proximities (175 – 720 m) and slopes (1 – 15%). While these data do not explain the shallow depth-rs values, site visits could reveal local conditions that help account for these occurrences. Further, features such as soil types, which are controlled by the same factors that influence depth-rs, may provide useful indicators for estimating depth-rs.

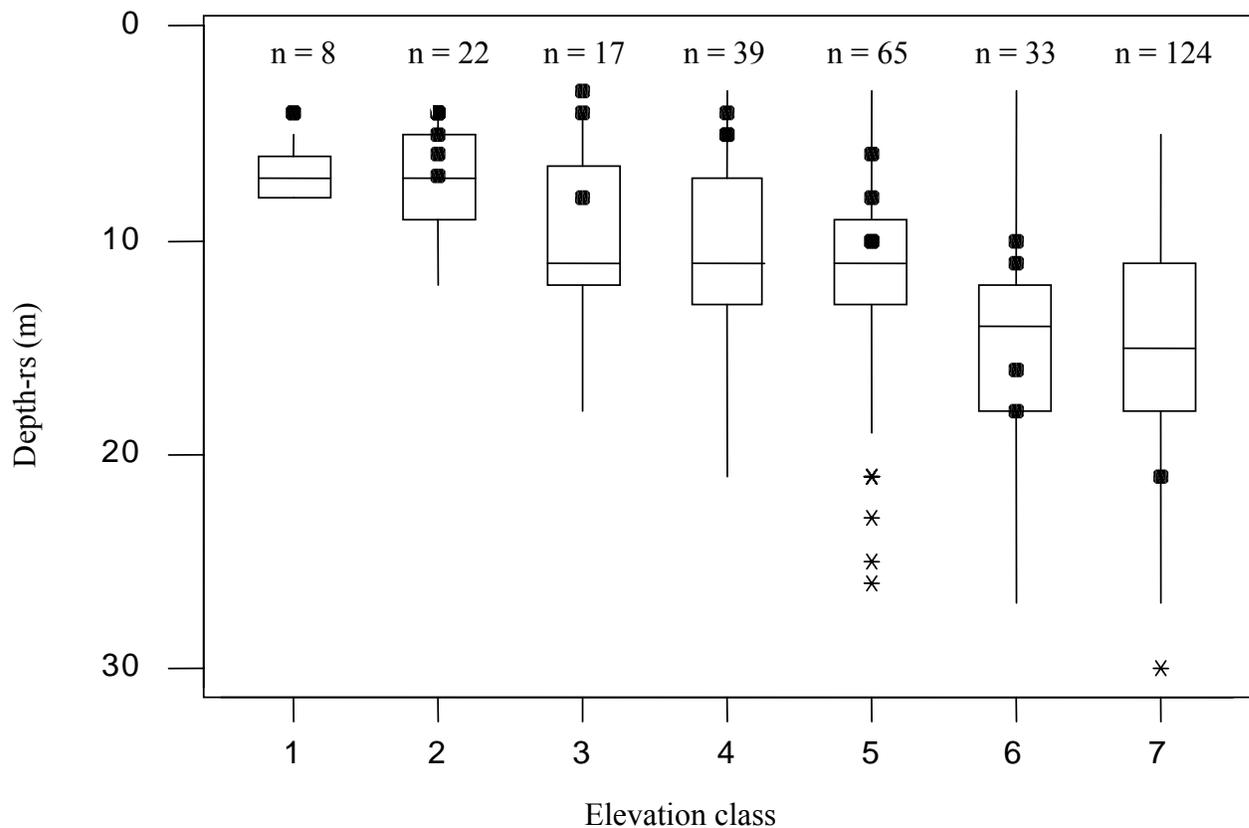


Figure 10. Boxplot of depth to reduced sediments for elevation classes. Asterisks indicate outliers from the well log data. Bullet markers indicate validation drill holes.

Finally, while it is impossible to assess the true extent of data error, a number of possible sources may contribute to the poor regression results. For example, three issues must be considered with the use of DEMs. First, most of these maps have a vertical accuracy of 7.5 m root-mean-square error. Given the relatively low elevations through the study area, such error could significantly impact elevation determinations. Furthermore, the SDTS DEMs, released prior to January 1, 2001, have positional errors resulting from the use of incorrect origins used to calculate the coordinate grid for each 7.5-minute quadrangle. The positional error does not exceed the spatial resolution of the DEM, in this case 30 m, and would likely have a trivial impact for the majority of data points in this study. Nonetheless, in some cases a slight positional shift could result in a relatively large elevation difference that could affect results. Finally, at the time this study was completed, DEMs for the study area were available only at 30 m resolution. Use of finer resolution DEMs, which are currently being created, may improve results by providing for more accurate elevation data. While use of digital maps and GIS allows for rapid data analyses, the data available at the time of this study may not be suitable for the level of precision required to accurately evaluate depth-rs as a function of landscape variables.

Other sources of data error may arise from the precision and accuracy of the well logs. The boundary between reduced sediments and overlying materials is quite distinct, so it is unlikely that the well logs were misinterpreted. However, while some logs identified the boundary at a specific depth, others identified the boundary as occurring within a depth interval, usually around 6 m. When the boundary was identified within an interval, depth-rs was assigned the mean depth value for that interval. This could result in an error of a few meters from the true value. Furthermore, the accuracy with which these logs are recorded is unknown, and may vary among well drillers. Nonetheless, it seems likely that errors would be more significant with increasing depth. Consequently, error in the well logs does not account for the unexpected shallow depth-rs occurrences at higher elevations. For most of the logs, the well location was clearly indicated on a parcel plat. In most cases, elevation changes were minimal in the vicinity of the well location, so precise location of the well was not critical. However, in some cases, even a slight positional change resulted in a significant elevation difference. Therefore, mislocation of some wells may have resulted in inaccurate elevation determinations.

Interpolation of Depth to Reduced Sediments

For a second approach to predicting depth to reduced sediments, depth-rs values were interpolated to generate a depth-rs surface. The interpolation procedure was repeated three times using randomly selected subsets of the well data. Regression analysis of the interpolated depth-rs values and the known depth-rs values for the remaining well points indicated poor results for all three trials ($r^2 = 0.19, 0.19, \text{ and } 0.24$). In each case, the root-mean-square error was approximately 5 m with a standard deviation of 4 m. Interpolation cannot adequately predict depth-rs because the surface of the sulfide-bearing strata is too variable and some areas are not adequately represented with well data. While some regions of the study area have dense clusters of data points, such as where new housing developments have been constructed, other regions yield few data points. In particular, because these are drinking water wells, they are generally located at a distance from creeks and rivers and so those areas are poorly represented. Furthermore, well log data have been kept on file at the Health Department only for the past few decades. The existence of numerous old farms throughout the study area results in relatively

large regions without data. Considering the significant landscape changes that may exist between data points depth-rs is too variable to be accurately interpolated with the density and distribution of available sample points for this study area.

Probability Mapping of Depth to Reduced Sediments Based on General Elevation Classes

Although regression analyses and interpolation could not provide accurate means for predicting depth-rs, evaluation of the data did reveal a few generalizations. Most importantly, depth-rs values increase with increasing elevation, and shallow depth-rs values are found over the entire elevation range, although they are less frequent at higher elevations. To provide general estimates of depth-rs, the data were grouped into seven elevation classes and depth-rs values were summarized by descriptive statistics. These results are provided in Table 7 and illustrated in Figure 10. Overall, the data may be divided into three groups based on mean values. Mean depth-rs was 7 m, at elevations below 26 m, 10 - 12 m at elevations between 27 - 47 m, and 15 m at elevations greater than 48 m. Standard deviation increased noticeably above 26 m, indicating that depth-rs is much more variable at moderate to high elevations.

Table 7. Descriptive statistics summarizing depth to reduced sediments (depth-rs) from well log data for seven elevation classes in the study area.

elevation (m)	n*	mean depth-rs(m)	median depth-rs (m)	standard deviation (m)	min depth-rs(m)	max depth-rs (m)
< 20	8	7	7	1	5	8
20 - 26	22	7	7	2	4	12
27 - 33	17	10	11	4	4	18
34 - 40	39	11	11	4	3	21
41 - 47	65	12	11	5	3	26
48 - 54	133	15	14	5	3	27
> 55	124	15	15	5	5	30

*Number of wells.

The three groups discussed above coincide with the three main landforms present in the study area. Elevations below 27 m are found primarily in floodplains, and to a lesser extent in drainages. Depth-rs is consistently shallow at lower elevations for two reasons. First, the floodplain landforms, which dominantly occur at low elevations in the study area, have naturally exposed Tertiary marine sediments at the surface, although a thin layer of alluvium covers some areas. Second, floodplains have high water tables that prevent oxidation of these sediments. Therefore, sulfidic sediments are maintained in a reducing environment at relatively shallow depth. Elevations between 27 – 46 m typically occur within the incised valleys surrounding drainages. Within this setting, Tertiary marine sediments may be naturally exposed at the surface, or they may be covered by a thin layer of alluvium or a variably thick layer of Quaternary sands and gravels. These geological differences, in combination with variable water table depths, result in a higher range of depth-rs values than for the floodplain landscapes. For a large extent of the study area, the 150 ft (46 m) contour line marks a distinct break between upland topography and incised drainage slopes. Elevations greater than 47 m typically occur in the broad, gently rolling uplands. In this landscape, a variably thick layer of Quaternary sands and gravel overlies the Tertiary marine sediments. This blanket of material, in combination with

various possible structural and micro-relief features previously discussed, result in the highest mean and range of depth-rs values.

Summarizing the data in the manner described above provides predictive ranges for depth-rs using elevation to represent related landforms. To evaluate the accuracy of these ranges, 23 deep borings were made at ten sites dispersed throughout the study area. Data from these borings are illustrated in Figure 10. For one high-elevation point, reduced sediments were not encountered before reaching the maximum drill depth of 20 m. Depth-rs for this hole was assigned a value of 21 m to represent the minimum value at which reduced materials would be likely to occur. For each of the validation points, depth-rs fell within the depth-rs ranges defined for each elevation class, as indicated in Figure 10. However, at lower elevations the validation points tended to lie within the shallow end of the depth-rs range, while at higher elevations the validation points were mostly within or beyond the deep end of the range. The apparent overprediction of depth-rs by the well log data for lower elevations may be due in part to inadequate distribution of the validation points. The twelve lowest elevation validation points, which represent the three lowest elevation classes and part of class 4, were located in areas where Tertiary marine sediments were exposed at the surface, or overlain by only a thin layer of alluvium or terrace deposits. Most of the well log data for elevation classes 1 and 2 were from similar geological settings. Class 1 had only 1 validation point, which lay at the extreme shallow end of the depth-rs values. For class 2, the validation points span over half of the depth-rs range defined by the well log data. As elevation increases, the well logs are increasingly located in areas overlain by Quaternary deposits. Therefore, for elevation classes 3 and 4, overlying Quaternary sediments will result in greater depth-rs values for the well logs than for the validation points. More uniform distribution of validation data over the different geologies may have resulted in closer agreement between the well log data and the validation data. For the remaining elevation classes, well log data and validation data were from areas where reduced sediments are generally overlain by Quaternary deposits. Validation points for elevation classes 5 and 6 were mostly within the average range of depth-rs values. Class 7 had only 1 validation point, which lay within the deep end of depth-rs values. Overall, agreement of the validation points with the defined depth-rs ranges supports the use of the summarized well log data for providing general estimates of depth-rs based on elevation.

In the study area, and surrounding regions, most highway construction tends to involve excavation to depths of less than 9 m. For each elevation class, the relative proportion of data with depth-rs less than 9 m indicates the likelihood of encountering sulfidic materials within common excavation depths. This process may be repeated with the data set for any depth of interest. For example, for each elevation class the data was evaluated to determine the proportion of wells with depth-rs less than 5, 9, and 13 m. The results are presented in Table 8. Elevation risk factors were designated based on the proportion of wells with depth-rs below the specified depth for each elevation class as follows: i) greater than 50% is a very high risk (4), ii) 26-50% is a high risk (3), iii) 11-25% is a moderate risk (2), and iv) less than 11% is a low risk (1). As shown in Table 8, elevations below 26 m have a very high probability of encountering reduced sediments within 9 m. The probability is high between elevations of 27 – 40 m, moderate for elevations between 41 – 47 m, and low for elevations above 47 m.

Table 8. Proportion of well logs for each elevation class with depth to reduced sediments (depth-rs) less than 5, 9, and 13 m, and associated risk factor designations.

Elev. class	Elev. (m)	depth-rs < 5 m				depth-rs < 9 m			depth-rs < 13 m		
		n	n5*	n5/n	risk**	n9*	n9/n	risk	n13*	n13/n	risk
1	< 20	8	0	0.00	1 (1)	8	1.00	vh (4)	8	1.00	vh (4)
2	20 - 26	22	2	0.09	1 (1)	15	0.68	vh (4)	22	1.00	vh (4)
3	27 - 33	17	1	0.06	1 (1)	7	0.41	h (3)	14	0.82	vh (4)
4	34 - 40	39	1	0.03	1 (1)	14	0.36	h (3)	29	0.74	vh (4)
5	41 - 47	65	1	0.02	1 (1)	15	0.23	m (2)	48	0.74	vh (4)
6	48 - 54	133	1	0.01	1 (1)	9	0.07	l (1)	45	0.34	h (3)
7	> 55	124	0	0	1 (1)	10	0.08	l (1)	45	0.36	h (3)

*n5, n9, and n13 = number of wells with depth-rs less than 5 m, 9 m, and 13 m, respectively.

**risk assessment: l = low probability of encountering sulfidic sediments, m= moderate probability, h = high probability, vh = very high probability. Value in parenthesis indicates quantification of risk.

Probability Mapping of Depth to Reduced Sediments – Application of Soil Type Data Base Information to Improve Predictions.

Soils data may provide additional information for predicting general depth-rs values. Soil development results from the interaction of five factors – parent material, time, climate, organisms, and relief. Locally, areas that are mapped with similar soil series likely have experienced the same relative influence of these factors. Furthermore, to some extent, the factors that control soil formation may affect depth-rs. For example, depth-rs values should be shallowest where Tertiary marine sediments are naturally exposed at the ground surface, and depth-rs is primarily a function of the weathering profile. Specific soil types that form over Tertiary marine sediments may be associated with shallow depth-rs, and therefore can be used as a useful indicator. Similarly, certain soils that form over Quaternary sands and gravels may indicate deeper depth-rs values by reflecting the presence of this material overlying sulfidic sediments.

To evaluate the relationship between soil map units and depth-rs in the study area, the well log data were summarized to indicate the number of wells in each represented soil map unit, along with the minimum, maximum, and average depth-rs for those wells. The proportion of wells with depth-rs less than 9 m was calculated for map units represented by at least 5 data points. Thirty-seven map units were represented by the well log data. For map units with 5 or more data points, soil risk was designated in a manner similar to elevation risk based on the proportion of wells with depth-rs less than or equal to 9 m. A number of map units contained few data points and additional data would be necessary to accurately assess these units. Nonetheless, soil risk factors based on mean depth-rs were assigned to help illustrate the interpretive process. Map units with a high risk factor included 46, 8, 30, 43, 70B, 70F, 54B, 69C, 70C, 70D, and 70E. Hanover County Soil Survey map units with a moderate risk included 65B, 2, 12D2, 63A, and 13B2, 13C2, 25A, 39B, 40B, 47A, 47B, 50A, and 63B. Map units with a low risk included 10B, 40A, 63C, 25B, 34B, 39C, 41, 49B, 50B, and 69C.

Finally, two sets of data points were used to evaluate risk assessments based on elevation and soil type. The first set consisted of the previously described validation points. The second set consisted of 35 well logs provided in Daniels and Onuschak (1974). These well logs included

engineering test borings, public water wells, and Virginia Department of Mineral Resources test borings. In the following discussion these two sets of data are referred to collectively as the test points. As described above each test point was assigned an elevation risk factor and a soils risk factor for encountering depth-rs at less than or equal to 9 m. Three test points occurred in soil map units which were not previously represented by the well log data. These points, were assigned soil risk factors based on comparison of the map unit descriptions. An overall risk was assigned by multiplying the elevation and soil risk factors. Overall risk values of 1 or 2 indicate that the most severe risk is moderate for only one factor, and therefore suggest a relatively low probability of encountering depth-rs within 9 m. Overall risk factors of 3 or higher indicate that at minimum either one factor has a high risk, or both factors have moderate risks, and therefore suggest a relatively high probability of encountering depth-rs within 9 m.

Of the 58 test points, 20 had depth-rs less than 9 m. Of these 20 points, 18 (90%) were accurately assigned high overall risk factors of at least 3. The 2 points with low overall risk values had borderline depth-rs values of 7 and 8 m. Of the 38 points with depth-rs greater than or equal to 9 m, 34 (89%) were accurately assigned low overall risk factors of 1 or 2. Of the 4 points with high overall risk values, 3 had borderline values of 9 or 10 m. These results demonstrate that use of the elevation risk factor, in conjunction with the soil risk factor, can successfully predict if depth-rs is less than 9 m. These interpretations were applied to DEMs and soils maps using ARCVIEW to generate a risk map (Figure 11) that may be used to evaluate the likelihood of encountering reduced sediments within 9 m for specific locations. By evaluating the well log data with respect to a specified depth-rs, and appropriately re-assigning risk factors, this process could be repeated for other depth-rs values. These elevation and soil risk factors are specific to the study area, and should not be extrapolated beyond its boundaries. However, this method of risk assessment could be applied to other areas in the Coastal Plain, where the data are available.

Exposure of reduced Tertiary sediments is problematic only if the material contains high levels of S (> 0.2%). Therefore, the deep borings were used to evaluate the large-scale lateral distribution of S in reduced Tertiary sediments. From each boring, a sample was collected from the upper 30 cm of reduced sediments and evaluated for %S and presence of calcium carbonate. Previous work indicated that %S is highly correlated with potential peroxide acidity for samples that do not contain calcium carbonate. All samples had relatively high S values and none of the samples contained CaCO₃, indicating that exposure of reduced Tertiary sediments would always present a high risk of acid production.

Evaluation of Acid Rock Drainage Prediction Procedures on Diverse Sulfidic Materials

Potential Peroxide Acidity Procedure

The PPA procedure was developed as a tool for overburden analysis in coal mining. However, sulfidic materials occur in numerous other geologic settings across the state of Virginia. As discussed earlier, theoretical predictions suggest that 1% S has an MPA of 31 Mg CaO₃ /1000 Mg if all of the pyrite in a sample is completely oxidized. In the absence of interfering factors, such as carbonates that neutralize acidity, %S and PPA should have a direct

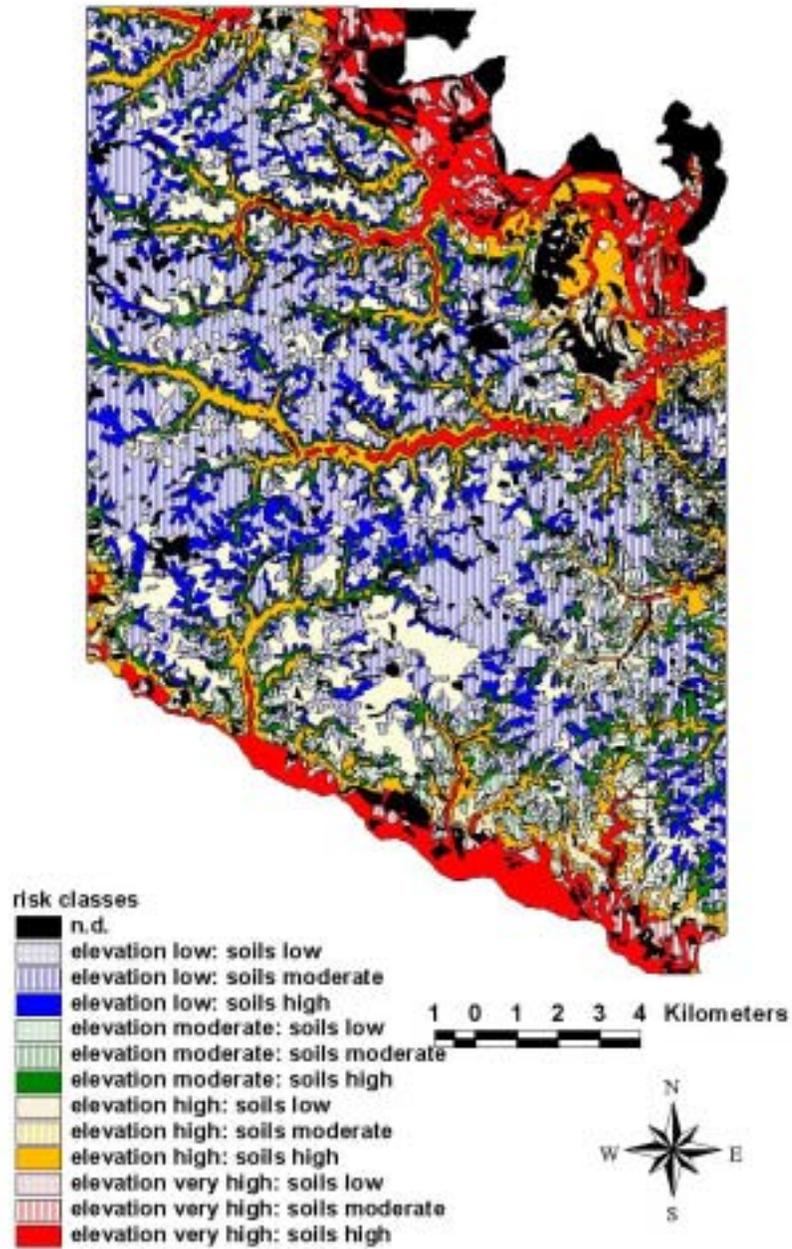


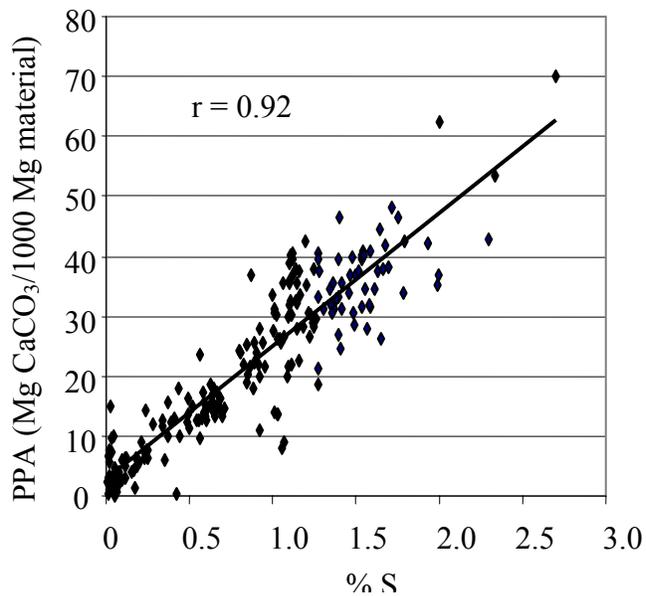
Figure 11. Risk map, based on elevation and mapped soil type, for encountering reduced sediments within a depth of 9 m for study area near Mechanicsville, VA (see Figure 3).

linear relationship. To investigate the relationship between %S and PPA for diverse sulfidic materials, 296 samples, run as single samples, were analyzed for total S, PPA, and presence of carbonates. Twenty-seven samples were eliminated after testing positive for carbonates. As expected, the remaining 269 samples showed strong correlation between PPA and %S ($r = 0.94$). Regression analysis on these samples resulted in residual values (predicted values – measured values) that are not normally distributed, rendering the regression invalid. Irregular distribution of residuals occurred dominantly with low S values. Removing samples that contain less than 0.25% S resulted in normal distribution of the residuals, supporting the use of regression analysis. Removal of these samples was justified since samples with less than 0.2% S would have little acid-producing potential. Regression analysis of the remaining samples indicated %S was a highly significant predictor of PPA and explained a large amount of the variability ($R^2 = 0.806$, $p < 0.001$).

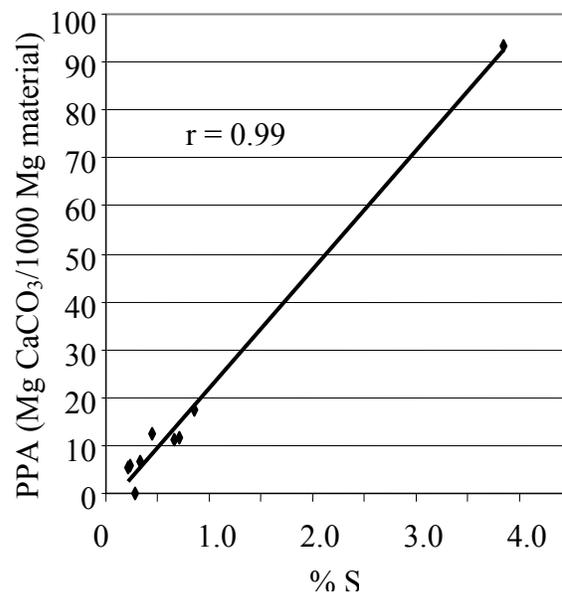
Results from the combined analyses reported above, and from evaluation of pyrite standards, indicated that accuracy of PPA depended on the use of appropriate sample sizes. As suggested by the procedure, samples from low sulfur materials must be large enough to produce enough acidity that results will not be significantly affected by laboratory error, while samples from high sulfur materials must be small enough to allow complete reaction of the sulfides. Due to the large number of samples analyzed in this study, 1 g samples were routinely used for all samples. Results would likely improve if low- and high-S samples were re-tested with larger and smaller sample sizes, respectively.

To further investigate the relationship between S and PPA for different materials, the samples were divided into four groups based on general geologic classification: Coastal Plain sediments, slates, phyllites and shales. Samples containing carbonates were removed from analysis. Scatterplots of PPA and S for each group are shown in Figure 12. Overall, high correlations between S and PPA were found for slates, shales, and sediments ($r = 0.99$, 0.98 , and 0.92 respectively). Phyllites had a poor correlation ($r = 0.36$). A closer look at the phyllite data revealed a high correlation ($r = 0.88$) between S and PPA for the 10 samples from the I-77 roadcut in Carroll County, but a poor, negative correlation ($r = -0.14$) for the samples collected at Rt-750 and Rt-8 in Floyd County. Again, although there were only a few samples, dividing the data by roadcut revealed that the 4 samples collected from Rt-8 had a poor, positive correlation ($r = 0.45$) whereas the 6 samples from the Rt-750 roadcut had a poor, negative, correlation ($r = -0.34$). This may be explained by the presence of sulfate precipitates, which were significantly more prominent at the Rt-750 roadcut than any other sampled roadcut. Compared to sulfides, sulfate precipitates produce less or no acidity, as would be expected. Although mineralogy was not completed on these samples, the presence of gypsum, which does not produce acidity, was confirmed for this location by x-ray analysis of a powder mount prepared from precipitate material that was scraped off of the roadcut surface. Furthermore, carbonates have been documented at this location. Some samples may contain low levels of carbonates which were not readily apparent by the “fizz test”, but which could have noticeably affected PPA results since these were relatively low-acid producing materials.

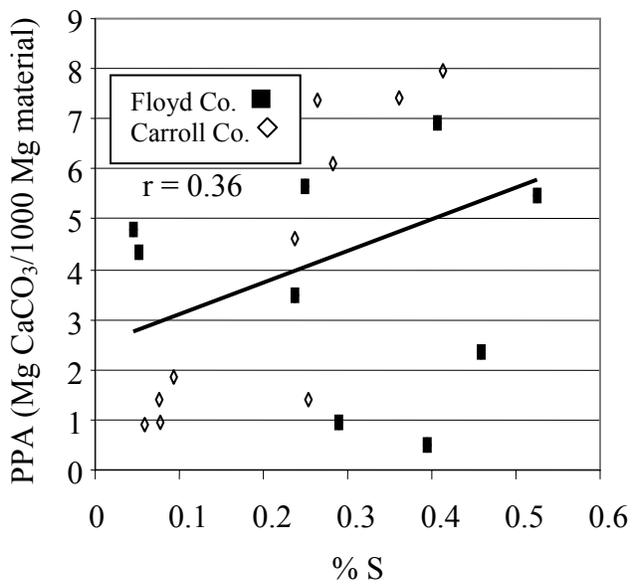
Overall, the PPA procedure has proven to be a robust test, which may be applied to a wide variety of sulfide bearing geologic materials. Nonetheless, this procedure is somewhat time-consuming and expensive. With the current laboratory setup in the SS + MLR Laboratory,



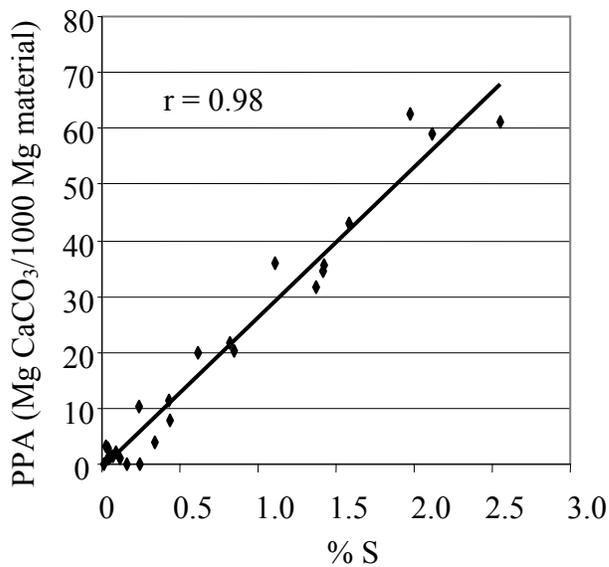
(a) Coastal Plain sediments



(b) Slates



(c) Phyllite



(d) Shale

Figure 12. Simple correlation plots of potential peroxide acidity (PPA) versus % S for (a) Coastal Plain sediments, (b) slate, (c) phyllite, (d) shale.

it takes a minimum of three days to process 15 samples at a cost of at least \$12/sample just for materials. In comparison, total-S can be determined by furnace techniques for over 60 samples in one day at about one-fourth of the cost. As indicated by regression analysis, in the absence of carbonates and certain sulfate minerals, total-S is a highly significant indicator of PPA and therefore may be used for initial evaluation of materials. Samples with high S (> 0.2%) may be further analyzed by other tests as necessary. When carbonates or sulfate minerals are present in a sample, total-S will overpredict PPA. This is an acceptable error since samples with high S will be re-assessed by further analysis. No causes are evident, other than laboratory error, which would result in an underestimation of PPA based on S. Therefore, total-S provides an adequate screening tool which could save considerable time and expense in the routine determination of potentially acid materials.

Potential Peroxide Acidity and Acid-Base Accounting on Diverse Sulfidic Materials

In addition to PPA, a number of other tests may be used to evaluate the potential acidity of sulfidic materials. The most commonly applied static test is acid-base accounting (ABA), which, like PPA, was developed for overburden analysis in coal mining. To evaluate the application of these methods to different materials, a set of 14 samples representing diverse sulfidic materials were analyzed by PPA and ABA. All potential acidity values are expressed as Mg CaCO₃/1000 Mg material. The samples were also characterized by mineralogy, pH, and texture.

Tests that predict net potential acidity are primarily controlled by two factors – the amount of sulfides in a sample, which can produce acidity upon oxidation, and the amount of carbonates in a sample, which can neutralize all or some of the acidity. Results are affected to a lesser extent by the presence of sulfates, which may release some acidity upon dissolution. Therefore, in order to evaluate and compare the results of potential acidity tests on diverse sulfidic materials it is important to be familiar with the sulfide-S, sulfate-S, and carbonate characteristics of the samples. Total-S for the sample set ranged from 0.40 - 14.3% S, although all but two of the samples were below 3.0%. As a percentage of total-S, sulfate-S values ranged from 1 – 95%. However, only three samples (stf4, fl19, and gold) contained a significant proportion of sulfate (63 – 95% of total-S). These three samples also had the lowest total-S values (0.40 – 0.82%). Samples STF4 and fl19 contained high proportions of sulfate-S because they were highly weathered compared to the other samples. For samples with S ranging from 1.36 – 2.83%, the sulfate-S proportions varied non-systematically from 12 – 28%. For the two samples with the highest total-S, the sulfate-S proportion was less than 1%. Only three samples, fl9, gas32, and ni tested positive for carbonates, showing weak effervescence by the “fizz test.”

Potential peroxide acidity results are also affected by the presence of carbonates, which will neutralize some or all of the acidity. Some authors (Grube et al., 1971; O'Shay et al., 1990) suggest that carbonates may unpredictably influence the amount of acidity being generated and therefore should be removed prior to peroxide analysis. Others (Barnhisel and Harrison, 1976) argue that since carbonates neutralize acidity in the field they should remain in the sample. To compare the difference between results with and without carbonate removal, the fourteen samples were tested for PPA after removal of carbonates by leaching the samples with 0.5 N HCl, and by the standard PPA method. These results are illustrated in Figure 13. Two samples -

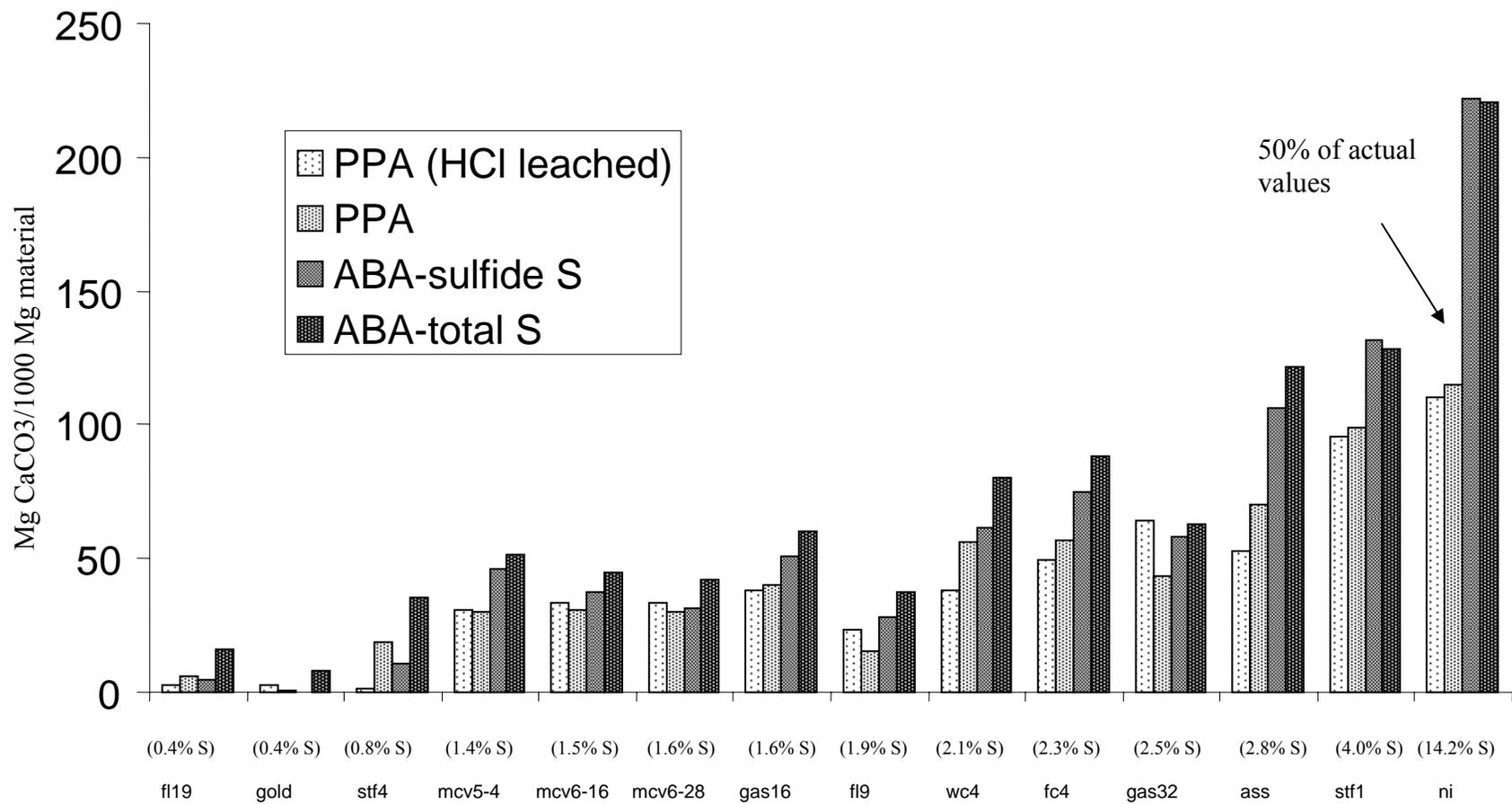


Figure 13. Results for potential acidity procedures on fourteen diverse samples arranged by increasing sulfur content, with % total-S indicated below each sample label. (Note: x-axis not to scale)

gas32 and fl9 – showed noticeable increases in PPA after carbonate removal. This was expected since these were two of the three samples that tested positive for carbonates. The ni sample also tested slightly positive for carbonates, but it did not show a noticeable increase in PPA after carbonate removal. The low carbonate levels had little impact compared to the very high sulfide level. Four samples – stf4, wc4, bass, and fc4 - noticeably decreased in PPA after leaching with HCl, indicating that an acid-producing component was removed. This was likely due to the removal of sulfate weathering products, such as jarosite, that release acidity upon dissolution. The four samples that showed decreased PPA after leaching had the highest absolute values of sulfate-S. For the eleven non-carbonate containing samples a moderately strong correlation existed between percent sulfate-S and difference between PPA values before and after leaching with HCl ($r = 0.71$). Analysis of samples that have been leached to remove carbonates may underestimate PPA by removing acid-producing sulfate minerals. Furthermore, the presence of carbonates is easy to assess, and, if necessary, neutralization potential may be determined separately for carbonate-bearing samples. Therefore, PPA should be determined on samples that have not been leached with HCl.

In the following discussions on ABA and PPA (standard method) results, the ni sample is described separately because it is extremely different from the other samples. Acid-base accounting results are illustrated in Figure 13. Acid-base accounting using total-S (ABA-TS) was highly correlated with ABA using sulfide-S (ABA-SS; $r = 0.98$). This result was expected since the only samples with significant proportions of sulfate-S have relatively low total-S values, while most of the remaining samples had sulfate-S proportions that varied within a relatively narrow range of values, and the two samples with the highest total S had very low proportions of sulfate-S. The PPA values were highly correlated with ABA-TS ($r = 0.98$) and ABA-SS ($r = 0.98$). The average difference between ABA-TS and PPA was 21.5 Mg $\text{CaCO}_3/1000$ Mg material, with a standard deviation of 11.5, and ABA-TS was higher for all samples. The average difference between ABA-SS and PPA was 11.2 Mg $\text{CaCO}_3/1000$ Mg material, with a standard deviation of 12.8, and ABA-SS is higher or almost equivalent to PPA for all samples. The differences between PPA values and ABA values were highly correlated with total sulfur ($r = 0.850$ for ABAss and 0.703 for ABAts).

The PPA and ABA results also may be compared by considering the ratio of PPA to ABA. The PPA/ABA-TS values ranged from 0.06 to 0.77 and were moderately correlated with %S ($r = 0.67$). The three samples (fl9, stf4, and gold) which contained high proportions of sulfate-S account for three of the four lowest PPA/ABA-TS values (0.06 – 0.53). Two of the next lowest PPA/ABA-TS values had the highest absolute sulfate-S values (wc4 and bass). These results were expected because sulfates produce much less acidity than sulfide for a given %S, but ABA-TS calculates MPA as if all S was sulfidic. Therefore, MPA will be higher than PPA when noticeable amounts of acid-producing sulfate minerals are present in the sample. Furthermore, these sulfates will generate acidity during NP analysis and so they are accounted for twice in the ABA-TS calculation. Although the samples with the four lowest NP values also had the highest sulfate-S levels, overall a poor negative correlation ($r = -0.42$) was found between NP and sulfate-S for samples that did not contain carbonates.

The fourth sample with a low PPA/ABA-TS value, fl9, contained carbonates. Although carbonates may reduce the oxidation efficiency of H_2O_2 at pH values > 5.8 , which will reduce

PPA results, this was unlikely a factor for this sample as the final suspension pH was 3.1. Alternatively, the NP procedure for ABA may have underestimated the actual NP for this sample. The NP procedure proved to be difficult to complete without previous experience. For example, the procedure calls for heating the samples on a hot plate to near boiling, yet, it was difficult to determine if the samples were effervescing or beginning to boil. Thermometers kept in a few samples indicated that temperatures remained below 95° C. Furthermore, the hot plates did not heat uniformly over the entire surface, making it difficult to maintain all samples at a temperature near boiling without having some of them start to boil. Therefore, underestimation of NP may have resulted from laboratory error.

The remaining samples had PPA/ABA-TS ratio values ranging from 0.57 to 0.77. In comparison, PPA/ABA-SS values ranged from -2.9 to 1.7. As expected, the largest differences between PPA/ABA-SS and PPA/ABA-TS are for the high-sulfate samples. After removing the high-sulfate and carbonate-bearing samples, PPA/ABA-SS values ranged from 0.65 to 0.95. For the sample from the nickel mine tailings, ABA-TS was almost double PPA. The PPA values likely underestimate the potential acidity of this sample. Potential acidity increased by 80 Mg CaCO₃/1000 Mg material when the sample weight was decreased from 1.0 g to 0.19 g. Reduction in sample size, or increased H₂O₂ additions may further increase the potential acidity results.

Soxhlet Extractors

In comparison to static tests, simulated weathering procedures more closely approximate field conditions and allow analysis of change in materials and leachates over time. To evaluate the use of a kinetic test on diverse sulfidic materials, four samples were analyzed using Soxhlet extractors. After each leaching, S remaining in the solid material was calculated by subtracting the amount of S in the leachate from the amount of S in the initial solid sample. Following the initial leaching, three samples – Floyd, Clifton Forge, and Mechanicsville - exhibited exponential decline in remaining sulfur and acid production. The Stafford sample exhibited a linear decline in remaining sulfur, which corresponded to its relatively constant rate of acid production.

Soxhlet potential acidity values were calculated using the total amount of acidity generated by each sample. For Floyd, Clifton Forge, and Mechanicsville these values were equivalent to PPA values (Table 9). For Floyd and Mechanicsville, the values were noticeably lower than ABA-TS and slightly lower than ABA-SS. Acid-base accounting data were not available for Clifton Forge. By the final leaching, these three samples were producing low amounts of acidity; therefore, additional leachings would be unlikely to raise the potential acidity values by a significant amount. Replicate Soxhlet values were similar for these three samples. For Stafford, potential acidity based on Soxhlet acid generation exceeded the PPA value, but were lower than ABA values. Furthermore, this sample was still producing high amounts of acidity, which will noticeably increase the potential acidity value. Replicates for Stafford were similar, but more variable than the other three samples. The difference in potential acidity predictions may be due to underestimation by the PPA method. This sample was just within the appropriate potential acidity range to justify the use of a 1 g sample; however, it is now apparent that a smaller sample may have yielded higher, more accurate, results.

Table 9. Potential acidity and half-life for samples analyzed with Soxhlet extractors.

Sample	Total acidity* (3 replicates)			Soxhlet potential acidity** (3 replicates)			PPA**	ABA- TS**	ABA- SS**	t _{1/2} [†]
	1	2	3	1	2	3				
Floyd	2247	2262	2190	7.9	7.9	7.7	7.8	24.6	13.9	3
C. Forge	4428	5532	5865	15.5	19.3	20.5	19.3	NA	NA	5-6
Mechanic.	10611	10473	9660	37.1	36.6	33.8	36.8	46	38.42	2-3
Stafford	34342	24603	31476	120	86	110	89.7	128.25	131.74	6-7

*mg CaCO₃/L.

**Mg CaCO₃/1000 Mg material.

†t_{1/2} indicates approximate leaching cycle for which 50% of initial S remains in the solid phase.

Half-life values, the point at which 50% of the initial sulfur remains in the solid material, in terms of leaching cycle are also reported in Table 9. The samples from Mechanicsville and Floyd appeared to react more rapidly than Clifton Forge and Stafford. These results may be explained by sulfide mineralogy, morphology, and grain size. The Floyd sample was crushed phyllite containing sulfide primarily in the form of pyrrhotite, which reacts more rapidly than pyrite. The Mechanicsville sample consists of unconsolidated sediments with sulfide primarily in the form of framboidal pyrite, which reacts more rapidly than larger grains. The Clifton Forge sample was crushed shale with sulfide occurring as pyrite in framboids, clusters of microcrystals, and subhedral grains. Although the sulfide grain size was only slightly larger than the Mechanicsville sample, this material should react slower because the overall sample texture is significantly larger which limits exposure of sulfide surfaces to weathering. The Stafford sample consisted of crushed slate with sulfide occurring primarily as subhedral grains, which reacted more slowly than the finer grained sulfides found in the other three samples. Again, since this material consisted of crushed rock, sulfide weathering should be slower than for unconsolidated sediments.

For the Stafford and Mechanicsville samples the %S values appeared to drop below zero, which was likely the result of error in the initial sulfur determinations. The error appeared to be small for Mechanicsville, but significant for Stafford. Two factors account for error in the Stafford sample. First, sulfide distribution in the Stafford sample was highly variable and therefore it was difficult to accurately represent the large samples used in the Soxhlets with the small samples used in S determination. Second, although the technician in charge of the CNS analyzer (housed in the Forestry Department) advised the use of 1 g samples, it has become apparent that at high S levels (i.e. above 3.5%) the CNS analyzer may under-report S for that volume of sample. This is a new instrument and optimal procedures are still being established for the most efficient use of the machine. In future studies, the use of numerous smaller samples obtained from a well-mixed material may improve the accuracy of S estimation.

Comparison of Road Drainage with Soxhlet Leachate

Geologic material at a given road cut may be variable and difficult to accurately represent with laboratory scale samples. Furthermore, many factors aside from rock type affect water quality at a specific location. Therefore, comparisons between leachate from the Soxhlet extractors and road drainage (Table 10) from the vicinity of the collection sites are semi-

quantitative and intended to represent initial findings rather than definitive conclusions. For Floyd and Clifton Forge, road drainage values were based on three samples collected at the outlet of culverts draining the roadcuts. Samples collected from inside the Clifton Forge culvert were “pure” roadcut drainage and contained exceedingly high values for acidity and metals. To maintain consistency, these samples were eliminated from the analysis because none of the other sites had “pure” leachate collection areas. For Mechanicsville and Stafford, road drainage values were based on five samples.

Table 10. Road drainage data, used for comparison with leachate from Soxhlet extractors, for four acid roadcuts.

sample	pH	acidity (mg CaCO ₃ /L)	total metal (mg/L)*
FL4-1(1)	3.73	178	17
FL4-1(2)	2.48	232	34
FL4 1(3)	3.24	184	30
CF2-1	5.28	257	5
CFs1	2.74	318	62
CFs2	7.10	20	0.9
MCV1.1	3.16	226	3
MCV1.2	2.71	350	32
MCV1.3	2.62	336	1
MCV2.1	3.09	416	66
MCV2.2	3.91	258	39
STFn1	2.27	2070	597
STFn2	2.61	990	296
STFn3	2.47	1465	317
STFf1	2.36	1238	139
STFf2	2.70	935	238

*total metal value is sum of Al, Fe, Mn, Cu, and Zn.

The highest and lowest acidity values for road drainage samples, along with the average acidity values from the Soxhlet extractors, are illustrated in Figure 14. For Clifton Forge, Mechanicsville, and Stafford, average acidity for the Soxhlet extractors was calculated based on acidity values from all leachings. For Floyd, average acidity was based on the first seven leachings, as acidity values were constant for subsequent leachings. Average acidity for road drainage and average acidity from the Soxhlet extractors were highly correlated (0.98).

Metal content was compared in a similar manner. For each sample, levels of Fe, Al, Mn, Cu, and Zn were summed to determine total metals (TM) values for each of the first 6 leachings. Since metal values were not available after the first 6 leachings, average TM values could not be calculated in the same manner as average acidity. However, regression analyses indicated significant relationships between TM and acidity for all samples. Average TM values were predicted using these formulae with the average acidity values for the Soxhlet leachates. Figure 15 reports site the highest and lowest TM values for each sample for road drainage, along with average TM values from the Soxhlet extractors. Average TM for the road drainage and average TM from the Soxhlet extractors were highly correlated ($r = 0.98$). These results indicate that strong relationships do appear to exist between water quality from the Soxhlet extractors and from road drainage; however, a more detailed controlled study would need to be conducted to quantify the relationships.

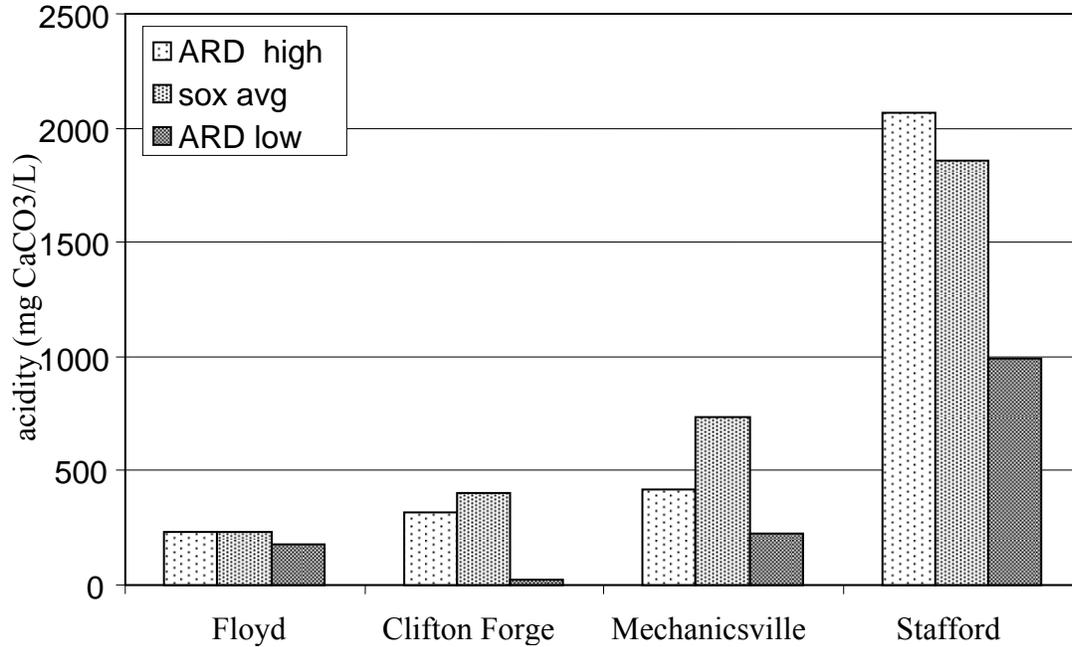


Figure 14. Comparison of average acidity from Soxhlet leachate (sox avg) with high and low acidity values from road drainage (ARD high and ARD low).

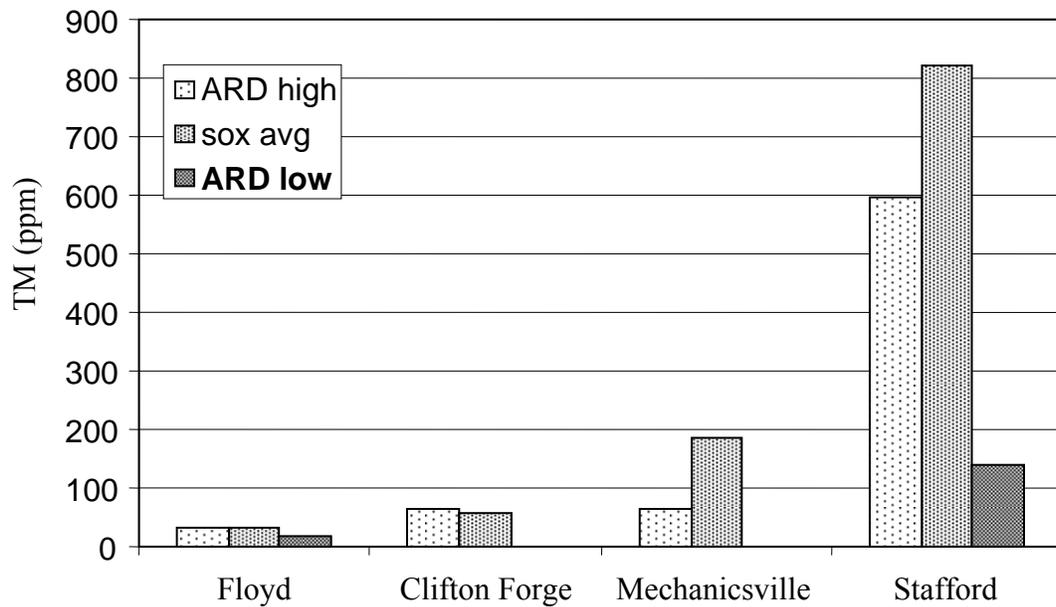


Figure 15. Comparison of average total metals (TM) from Soxhlet extractor leachate (sox avg) and high and low total metals values from acid road drainage (ARD high and ARD low).

SUMMARY AND CONCLUSIONS

Excavation through sulfidic geologic materials during road construction has resulted in ARD-related problems at numerous discrete locations across Virginia. Barren acidic roadbanks, and acidic runoff and fill seepage clearly cause local environmental problems along Virginia road corridors. Degradation of construction materials may necessitate road repairs, which can be time-consuming, costly, and a nuisance to travelers. These problems can be minimized, and even prevented, by incorporating sulfide hazard analysis into the pre-design stage of highway construction. Evaluating the likelihood of encountering sulfidic materials can decrease exposure of problematic materials. When exposure cannot be avoided, proper characterization of the material allows for immediate application of appropriate remediation procedures.

Two studies were conducted to develop approaches for VDOT to evaluate the likelihood of encountering sulfidic materials. First, geologic materials from existing acid roadcuts across the state were identified and characterized to develop a statewide sulfide hazard rating map. Sulfide occurrence is a function of geologic setting. If sulfides are identified in numerous rock samples from a specific geologic formation, then the entire formation may be considered as “at risk” for containing sulfides. On a statewide scale, delineation of potentially acid forming materials is best accomplished by identifying the boundaries of sulfide-bearing formations using the Geologic Map of Virginia. Geologic formations associated with acid roadcuts were characterized by PPA and total-S, and grouped into four categories based on potential acid-producing severity: i) the Tabb Formation in the Coastal Plain (PPA \leq 6 Mg CaCO₃/1000 Mg; S \leq 0.2%), ii) the Lynchburg Group of the Ashe Formation in the Blue Ridge (PPA \leq 18; S \leq 2.0%), iii) Chesapeake Group and Lower Tertiary deposits in the Coastal Plain, and Millboro, Marcellus, and Chattanooga shales, and the Needmore Formation in the Valley and Ridge (PPA \leq 60; S \leq 2.6%), and iv) Quantico slate in the Piedmont (PPA \leq 99; S \leq 3.9%). Additional sulfide-bearing formations were identified through a geologic literature review, and were indicated on the map, although the acid-producing severity of these materials has not been evaluated. Where planned highway corridors intersect the specified formations, detailed geologic sampling is essential to identify the presence, extent, and nature of sulfidic materials. Unfortunately, the most troublesome sulfide forms are fine-grained, and as such, they are not readily apparent in hand specimens and they often remain undocumented. Therefore, the statewide sulfide hazard rating map presented in this report may be considered to be the first approximation of a dynamic database that can be amended by future studies. VDOT would benefit tremendously from testing for total-S with depth and for PPA on high S samples ($>$ 0.2%) in all future road corridors passing through known risk zones.

The second sub-study reported here was conducted to develop a procedure for evaluating depth to sulfidic sediments in the Coastal Plain. Sulfides appear to be ubiquitous in formations of the Chesapeake Group and Lower Tertiary deposits, which occur at variable depths throughout the Coastal Plain. A study area near Richmond, Virginia was evaluated using landscape parameters, including elevation, slope, distance to streams, and mapped soil type, and data from well logs to estimate depth to sulfidic sediments. Within the study area a number of variables control depth to reduced sediments, including factors that control the thickness of overlying Quaternary sediments, and weathering processes that control the reducing environment in which sulfides are stable. Due to the complexity of these interacting factors, a model could not be

developed for precisely predicting depth to sulfidic sediments based on landscape parameters. However, it was determined that the likelihood of encountering sulfidic sediments within a given depth for a specific location was strongly related to geomorphic surface, which can be represented by elevation, and mapped soil type.

Since excavation in the sulfide depth risk study area is generally within 9 m from the ground surface, the data were evaluated with respect to this depth. To assign risk factors based on elevation, the data were divided into seven elevation classes. Risk factors were designated based on the proportion of wells with depth-rs < 9 m as follows: i) greater than 50% is a very high risk, ii) 25 - 49% is a high risk, iii) 11 – 24% is a moderate risk, and iv) less than 11% is a low risk. Similarly, to assign soil risk factors, the data sets were divided by soil map unit. For soil map units with at least five data points, risk factors were assigned based on the proportion of wells with depth-rs < 9 m as follows: i) greater than 25% is a high risk, ii) 11 – 25% is a moderate risk, and iii) less than 11% is a low risk. For soil map units with fewer than five data points, risk factors were assigned based on mean depth-rs as follows: i) ≤ 9 m is a high risk, ii) 10 to 19 m is a moderate risk, and iii) > 19 m is a low risk. Evaluating the elevation risk factor in conjunction with the soils risk factor successfully predicted whether or not sulfidic sediments would be encountered for 90% of 58 test points. By re-evaluating the well log data, and appropriately re-assigning the elevation and soil risk factors, this process could be repeated for other excavation depths. Furthermore, this method could be applied to evaluate other areas in the Coastal Plain.

Sulfide oxidation reactions occur rapidly to generate acidity within weeks of exposure. The extent of ARD can be minimized by immediate application of remediation procedures, which require proper characterization of potential acidity. The current standard procedure of the Virginia Tech Soil Survey and Mined Land Reclamation Research Laboratory is PPA. This procedure was developed for overburden analysis for coal mine operations, and it's applicability to other diverse sulfidic materials remained in question. Extensive application of the PPA procedure, in comparison with other potential acidity procedures, indicated that PPA is a robust test for assessing the potential acidity of diverse sulfidic materials. For samples that did not contain carbonates, PPA results were highly correlated to S, indicating that S can be used as a quick, inexpensive screening tool to identify samples requiring further analysis. Samples may be screened for carbonates using the "fizz test." The practice of removing carbonates prior to PPA analysis is not recommended as this procedure also removes jarosite and other sulfates, which may produce noticeable amounts of acidity upon dissolution. In comparison to other potential acidity tests, PPA yielded 0.6 to 0.95 the amount of acidity as ABA for 14 diverse samples, and equivalent amounts of acidity as Soxhlet extraction for 3 out of 4 samples. Differences were greatest for high-S samples ($> 3\%$) and were likely due to the use of a sample size (1 g) that was larger than the recommended amount (0.2 g). Although the procedure recommends beginning with a 5g sample and sequentially using smaller samples as necessary, the 1g sample size was appropriate for the majority of samples. Use of a 1g sample is justified when sulfides are suspected; however, subsequent analysis of a larger or smaller sample may be necessary. Average acidity and metal contents of leachates from the Soxhlet extractors were highly correlated with average acidity and metal contents of road drainage, indicating that Soxhlet extractors may be a useful tool for evaluating long-term road drainage. However, these results

were based on a very small number of samples and further research in this area would be worthwhile.

Once potentially acidic materials are exposed in road-cuts and disposed of in oxidized fill environments (unsaturated), the thermodynamics of pyrite oxidation will inevitably lead to acid generation. In surface mining environments, any geologic materials with a net potential acidity of 5 parts per thousand or higher are considered potentially toxic materials and must be handled in such a way as to isolate them from drainage and the surface rooting zone. Unfortunately, the only known proven technique for permanently remediating this situation is to bulk-blend lime or other alkaline materials with the cut surface or the bulk of the disposal fill based upon appropriate ABA procedures (Daniels et al., 2000). Where feasible, placement of the sulfidic materials below the (1) water table or (2) beneath an impermeable engineered cap will also drastically limit or prevent acid generation. Obviously, avoidance of sulfidic materials in the road planning process is clearly the preferred mitigation alternative. However, it is obvious that in many instances (1) road corridors cannot be relocated sufficiently to miss sulfide-bearing strata, and (2) the increasing depth of cut in modern road designs in rolling topography will lead to increased probability of intercepting sulfidic materials. While the barren and erosive slopes resulting from acidification of cut roadbanks are the most obvious indicator of this problem, the long term emission of acidic drainage from fills is clearly the most serious environmental compliance problem that VDOT will face with sulfidic materials over time. It is clear that acid seepage from fills is causing local damage to Virginia's streams at various locations. While the extent of this damage is very localized and not extensive to date, the costs of capturing and treating these discharges could represent significant long-term costs if and when they are identified as point source discharges.

Failure to rigorously identify and remediate acid-forming materials in the road planning and construction process will inevitably lead to the mix of engineering and environmental problems discussed and documented in this report. Unfortunately, many of these problems (e.g. acid seepage from fills) do not become obvious for some period of time after the road construction contracts have been closed, leaving the full liability for environmental compliance resting upon VDOT maintenance budgets. Therefore, the true cost of identifying, handling and disposing of potentially acid-forming materials must be rigorously assessed and designed for in the road building process.

RECOMMENDATIONS

1. ***Evaluate all proposed road corridors for the occurrence and extent of sulfidic materials.*** The state-wide sulfide hazard map provided with this report documents geologic formations in Virginia that are likely to contain sulfidic materials. This map may be used as general planning tool. If available, more detailed geologic maps and literature for specific areas should be reviewed for further information. Local geomorphic models of depth to probable sulfide occurrence should be developed by VDOT for high probability areas.
2. ***Evaluate the total-S and potential acidity of suspected materials.*** Geologic materials that are suspected of containing sulfides should be sampled and analyzed for total-S. Materials

containing over 0.2% total-S should be evaluated for potential acidity using the peroxide potential acidity procedure or standard acid-base accounting.

3. ***Re-evaluate corridor alignment and grade when highly sulfidic materials are present.*** Highway corridors should be sited to avoid or minimize exposure of sulfidic materials, especially those with potential peroxide acidity values exceeding 60 Mg CaCO₃/1000 Mg material. If sulfidic materials are present, evaluate the possibility of shifting or re-grading the route to avoid or minimize exposure of sulfides.
4. ***Establish standard acid material remediation procedures.*** Overall material handling, treatment and revegetation procedures should be defined, based on potential acidity results, prior to excavation. Remediation of road banks will be most effective if sulfidic materials are treated immediately upon exposure. Procedures for handling of sulfidic materials that will be excavated and removed should be defined prior to excavation. This includes identification of disposal sites, and adequate remediation plans such as bulk liming, disposal below the water table, or capping.
5. ***Integrate the full cost of identifying, handling, and treating acid-forming materials into the road planning and construction contracting process.*** Assuming all corridors are properly evaluated for the occurrence and extent of sulfidic materials, as stated in recommendation #1, accurate cost estimates for the proper management of these materials should be developed and then incorporated into overall construction cost estimates.

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APPENDIX A

Survey form distributed to VDOT district environmental managers to identify possible acid sulfate roadcuts.

Acid Sulfate Materials Inventory Form

Please fill this form out as completely as possible for each potential occurrence of acid sulfate geologic/soil conditions on your District. Partially completed forms are “ok” as long as items one through four are fully documented! Thanks for your help.

1a. District: _____ 1b. Person making report: _____

2. Contact’s phone number and best time to call: _____

3. Location of possible acid sulfate materials: _____

(Please attach a map of the site which would allow us to find it without you!)

4. Symptoms or evidence that led you to submit this report _____

5. Have you ever specially treated this area? If so, how? Examples would be heavy liming, rip-rap, revegetation mats, replaced guardrails, etc...

6. Geologic formation estimated or mapped (circle one) at this location:

7. What is the date of original and last disturbance or treatment of this area?

Original disturbance: _____ Most recent disturb. or treatment: _____

Please fill out a copy of this form for each site that you identify and return it to:

W. Lee Daniels, Dept. of Crop and Soil Env. Sci., Va Tech, Blacksburg, VA, 24061-0404