EVALUATION OF SULFIDIC MATERIALS IN VIRGINIA HIGHWAY CORRIDORS[1]

Zenah W. Orndorff[2], W. Lee Daniels, and Luiz E. Dias

Abstract. Road construction through sulfidic materials in Virginia has resulted in localized acid rock drainage (ARD) that threatens water quality, fill stability, integrity of building materials, and vegetation management. Two objectives of this study were: i) to develop a statewide sulfide hazard rating map based on characterization of the geologic formations associated with acid road cuts, and ii) to evaluate potential acidity testing procedures on geologically diverse materials. Characterization of geologic materials included potential peroxide acidity (PPA), expressed as calcium carbonate equivalence (CCE), and total content S. Formations identified at acid road cuts were grouped into four categories based on potential acid-producing severity: i) the Tabb Formation in the Coastal Plain (PPA < 6 Mg CCE/1000 Mg; S < 0.2%), ii) the Lynchburg Group of the Ashe Formation in the Blue Ridge (PPA < 18; S < 2.0%), iii) Chesapeake Group and Lower Tertiary deposits in the Coastal Plain, and Millboro shale, Marcellus shale, and the Needmore Formation in the Valley and Ridge (PPA < 60; S < 2.6%), and iv) Chattanooga shale in the Valley and Ridge and Quantico slate in the Piedmont (PPA < 99; S < 3.9%). Comparison of PPA and conventional Acid-Base Accounting (ABA) for 14 diverse samples indicated that PPA and ABA were highly correlated, with PPA consistently predicting less acidity than ABA. Potential acidity by Soxhlet extraction and PPA were equivalent for 3 of 4 diverse samples. Sulfide hazard analysis should be an essential step in the pre-design phase of highway construction and other earth-disturbing activities.

Introduction

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 Plain, certain slate and phyllite bearing formations in the Piedmont and Blue Ridge, coalfields of

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some of the black shales in the Valley and Ridge, and sulfide-rich coal seams in the Coastal southwest Virginia. In many of these settings, exposure of sulfidic materials during road construction has resulted in localized acid rock drainage (ARD), which presents a number of technical, environmental, and social problems. Technical problems are primarily related to the degradation of construction materials from acid attack (Figures 1 and 2), 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 (Figure 2). Local surface water quality is threatened as high acidity and elevated levels of heavy metals are detrimental to aquatic life (Figure 3). From an aesthetic point of view, ARD diminishes the appearance of roads by killing roadside vegetation and by causing unsightly orange stains on curbs (Figure 4). The combination of visible pollution and adverse conditions for aquatic life limits recreational uses of impacted surface waters. With these problems in mind, this study was designed to assist the Virginia Department of Transportation (VDOT), and other groups involved with major earth-disturbing activities, identify and manage potentially acidic soil and geologic materials. Although the disturbance environment studied here (deep road cuts and fills) is not due to mining per se, the results are directly applicable to estimating potential acidity and developing prescriptions for a wide range of mid-Atlantic USA mining conditions. Two specific objectives of this study were:

1) the delineation of sulfide-bearing geologic formations and compilation of a statewide sulfide hazard rating map; and
2) the evaluation of existing potential acidity procedures to determine their applicability to diverse sulfidic materials.

Figure 1. Acid drainage from the Quantico slate Stafford, Virginia, (see also Fig. 4) has caused extensive iron staining and concrete etching along the curbs and sidewalks of the Hampton Oaks subdivision.

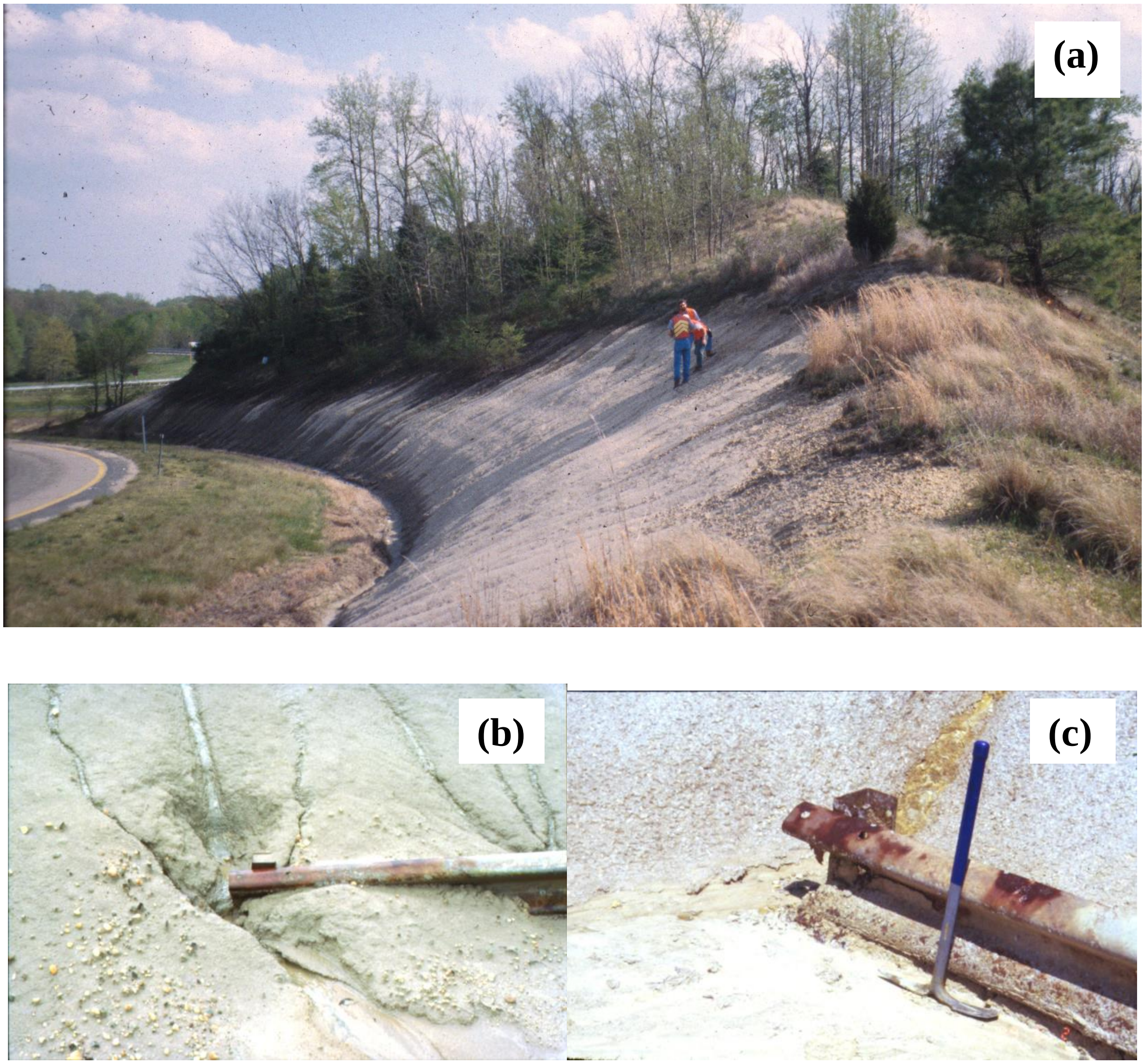

Figure 2. (a) This road cut along the cloverleaf of Rt-360W to I-295S, near Mechanicsville, Virginia, exposes the Eastover and Calvert formations of the Chesapeake Group. Sulfide oxidation has created extremely acid surface soil conditions (pH < 3.5).

(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.

Figure 3. Acid drainage from the Millboro shale, exposed along I-64 in Clifton Forge, has contaminated this stream. The pH of water samples from the downstream end of the culvert has ranged from 2.9 to 7.1. Iron and aluminum precipitates coat the streambed, and concrete joints within the culvert have been degraded.

Figure 4. Acid drainage from the Quantico slate in Stafford, Virginia (see also Fig. 1), 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.

Materials and Methods

State Map

In the fall of 1997, a questionnaire regarding occurrence of acid road cuts was distributed to all of the VDOT planning districts. Twenty completed forms were received from around the state by the spring of 1998. All reported sites were visited during the next year. Additional sites were reported later or discovered independently. The locations of all sampling sites are indicated in Figure 5. Detailed descriptions of all research procedures may be found in Orndorff, 2001, and are summarized below.

Geologic materials were collected from all sites. Both fresh and weathered representative samples of lithologies present at each site were obtained and immediately sealed in plastic bags. 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. 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 and surface samples from rock exposures that contained a sufficient amount of soil-sized particles (< 2mm in diameter) were tested for pH in H_2O and KCl using a combination electrode, and for particle size analysis (PSA) by the pipette method (Gee and Bauder, 1986).

Samples of road drainage, where present, were also collected. Grab water samples also were collected from a shallow well installed at the base of a road cut along the cloverleaf of Rt-360W to I-295S in Mechanicsville, Virginia. Water samples were tested in the field for pH. 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).

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

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, Greensville Co.
5. Near Fort Lee Mil. Res.: north of I-295/Rt-36 intersection, Prince George Co.
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.
16. I-95, milepost 134.4, Stafford County
17. I-95, milepost 140.2 Stafford County
18. Mine Rd: I-95 and Rt-610.
19. I- 95, milepost 148, Spotsylvania County
20. Rt-750 and Rt-735, Floyd Co.
21. Rt-8, between Rt-750 and Rt-705, Floyd Co.
22. I-77, mileposts 21 – 22, Carroll County
23. VDOT quarry, Rt-600 bw. Rt-50 and Rt-608, Frederick Co.
24. Rt-250 and Rt-614, Highland County
25. I-64, Clifton Forge, Alleghany Co.
26. Numerous sites along Rt-23 near Rt-610, Wise Co.

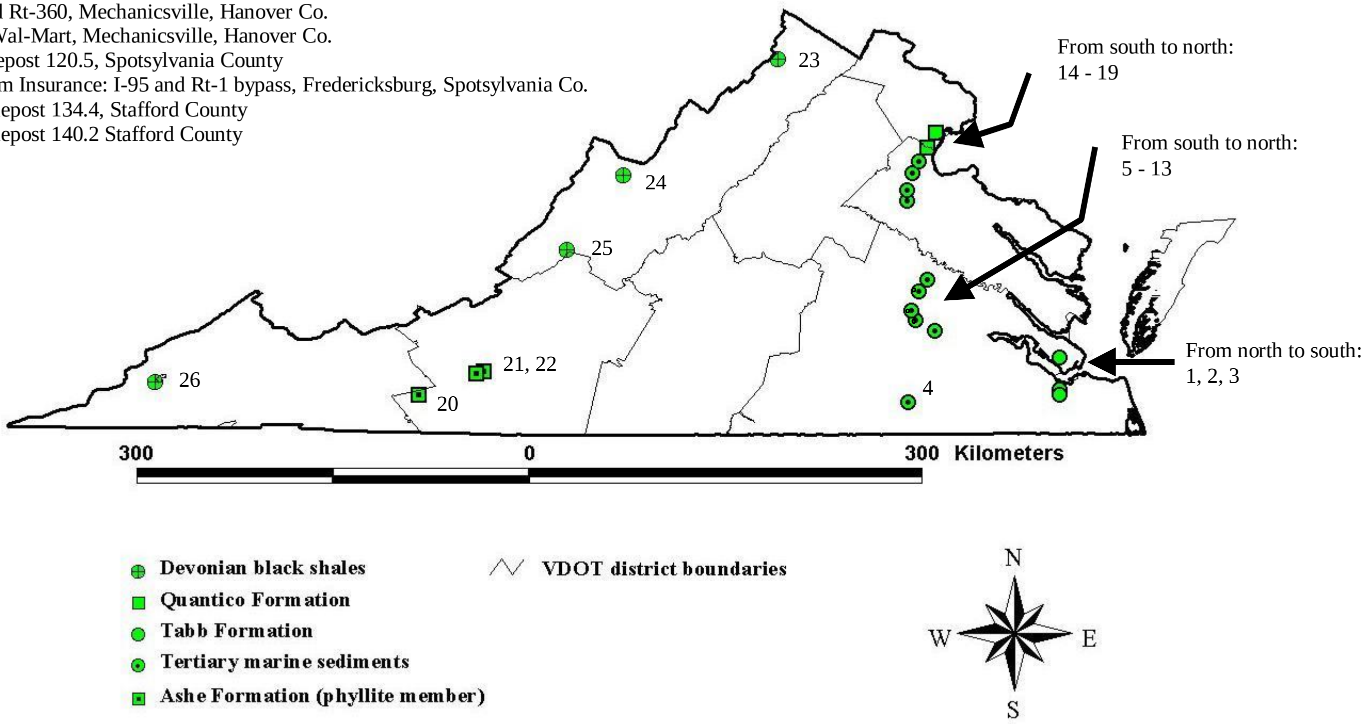

Figure 5. Sampling locations from statewide survey of documented acid-sulfate road cuts in Virginia with VDOT districts outlined.

with consideration of standard vegetation management practices, a sulfide hazard-rating scheme was developed with four levels of severity. This statewide 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.

Procedures Comparison

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) at Virginia Tech. To evaluate the applicability of this method to diverse sulfidic materials two hundred and ninety-six rock and sediment samples collected from acid road cuts in Virginia were analyzed 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 included eleven samples from Virginia and three samples from Brazil. 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 maximum potential acidity (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. To characterize the morphology of sulfide minerals, polished sections were prepared and observed using reflected light microscopy (Craig and Vaughan, 1994).

Soxhlet extraction analysis was used for four samples. The samples were selected to i) be the same or similar to materials from the subset of 14 samples, and ii) 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, 300 ml 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^{o} 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 concentrations.

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. For Floyd, Clifton Forge, and Mechanicsville water samples were collected from culverts that drain the road cuts. For Clifton Forge, additional samples were collected from a drainpipe that collects leachate directly from the backfill into the culvert. For Mechanicsville, additional samples were collected from a shallow well installed at the base of the outcrop. For Stafford, water samples were collected at two locations, a few hundred feet apart, from a drainage ditch at the base of the outcrop.

Results and Discussion

A summary of acid road cut locations, the geologic formations identified at these sites, and results from analyses of geologic materials and drainage are presented in Table 1. All sites exhibited lack of vegetation due to very low pH of surface materials, and numerous sites exhibited Fe staining on concrete, deterioration of concrete and metal construction materials (drainage ditches, culverts, and guardrails), Fe and Al precipitation on streambeds, and sulfate salt efflorescence on road cut surfaces.

Coastal Plain Occurrences

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). 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. Acid sulfate weathering problems were 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 revealed few, small, dispersed, subhedral grains of pyrite.
Weathered materials at the surface of road cuts 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 $CaCO_3$/1000 Mg material, and retain less than 1% S. Less oxidized, underlying gray sediments have higher pH values, ranging from 5.5 – 8.0, and much higher PPA values, ranging from 30-50 Mg $CaCO_3$/1000 Mg material. Sediment samples collected from road cuts and a construction site in the Tabb Formations had pH values ranging from 3.2 – 4.6, PPA values ranging up to 6.00 $MgCaCO_3$/1000 Mg material, and S values less than 0.2%. Previous sampling at nearby Sandy Bottom Nature Park indicated, with few exceptions, that these materials generally had PPA values under 10 Mg $CaCO_3$/1000 Mg material and contained less than 0.2% sulfur (Daniels et al., 1995).

Road drainage and shallow well samples collected at various locations throughout the northwest portion of the I-295/US-360 interchange (Chesapeake Group sediments) in Mechanicsville exhibited low pH (< 4.0) and relatively high metal concentrations. Samples from

Table 1. Summary of Potential Peroxide Acidity (PPA) and %S for geologic samples, and pH and metal content of a representative road drainage sample.

Geologic Formation	Sample Locations	Geologic samples			--------------- Road Drainage Sample---------------						
	County (or city)	Number of samples	PPA†	%S	pH	Fe	Al	Mn	Cu	Zn	S
						-------------------- mg/L --------------------					
Tabb	Cities of Suffolk and Hampton	49	20.9	0.79	3.09	13.9	49.5	2.1	<0.1	<0.03	298
Tertiary Marine Sediments	Greensville, Prince George, Chesterfield, Henrico, City of Richmond, Hanover, Spotsylvania.	10	3.2	0.1	3.05	12.4	15.2	2.4	<0.1	0.6	136
Quantico Slate	Stafford, Prince William.	13	32.7	1.09	2.61	114.2	66.9	17.4	0.4	3.5	639
Ashe	Floyd, Carroll	21	4.8	0.3	3.22	39.7	20.1	1.4	<0.1	0.6	182
Marcellus, Needmore, Millboro, Chatanooga (Devonian Black Shales)	Frederick, Highland, Allegheny, Wise	49	12.1	0.75	2.67	59	162.5	38.5	<0.1	8.3	1011

† Mg $CaCO_3$/1000 Mg material

the culvert outlet across the road indicated that the drainage was diluted as it flows towards a local stream, although pH was still low and Al and S values were relatively high. Water samples from Proctor's Creek at SR-288 and 145 (Chesapeake Group sediments) in Chesterfield County had moderate pH values, suggesting that ARD from the sediments was diluted by channel throughflow. Water samples from two small lakes at Hampton Roads Center (Tabb Formation) had low pH values and relatively low metal concentrations.

As a rule of thumb, materials with PPA values below 10 Mg $CaCO_3$/1000 Mg are readily reclaimed with proper management, while materials with PPA values between 10 - 60 require intense reclamation management (Daniels et al., 1995). 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 still require intense reclamation efforts.

Piedmont Occurrences

Acid road cuts along I-95 and Mine Road (SR-610) in Stafford occur in pyritic phyllite and slate of the Quantico Formation. Reflected light microscopy of polished sections from Mine Road 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 $CaCO_3$/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 $CaCO_3$/1000 Mg material, and contained $>$ 3.8% S. Previous analysis of six samples collected by VDOT at Mine Road revealed PPA values ranging from 1 - 85 Mg $CaCO_3$/1000 Mg material. Based on these values, sulfides appear to be unevenly distributed throughout the road cut; however, more detailed sampling would be necessary to characterize this spatial variability.

Drainage samples collected along the base of Mine Road had low pH values, and high EC and metal concentrations (Table 1). Extensive iron staining and concrete etching were evident along drainage ditches at the base of this road cut, 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 metal concentrations, indicating that acid 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 higher acidity and metal concentrations than any other evaluated road cut. Exposure of the Quantico Formation may be considered highly likely to produce severely problematic roadside management conditions, which require intense reclamation efforts. Road cut surfaces of the Quantico Formation may be quite steep due to the well consolidated nature of the material 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 Occurrences

Acid road cuts along SR-8 and SR-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 road cuts in both Floyd and Carroll County are dominantly a steel-gray, fine-grained phyllite with pods of amphibolite and calcsilicate gneiss. Efflorescent sulfate coatings are common on the Floyd County exposures, but minimal along the Carroll County road cuts. Reflected light microscopy of polished sections from Floyd County revealed 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 road cuts 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 indicated the presence of coarse grains and veinlets of pyrite, anhedral grains of chalcopyrite and sphalerite, and lathes of graphite. The PPA values for Floyd County ranged from 0.48 – 17.54 Mg $CaCO_3$/1000 Mg and S ranged from 0.05 to 1.93%. For Carroll County, PPA values ranged from 0.93 to 9.26 Mg $CaCO_3$/1000 Mg material and S values ranged from 0.06 – 0.36%.

Water drainage from the SR-750 road cut has significantly impacted a local stream, and decimated a fishpond on a neighboring property. Water sampling by VDOT during the past fourteen years, in addition to sampling for this study, indicated that water from the source spring upstream of the road cut has maintained pH values ranging from 5.8 to 7.1 (Paul Johnson, personal communication). Water samples from the downstream end of the culvert have consistently tested at pH values below 4.0 and have high metal concentrations. Iron and aluminum precipitates heavily coat the streambed for at least 30 m downstream of the culvert.

Along the SR-8 road cut in Floyd, iron staining, concrete etching, and deterioration of a metal culvert were evident along the base of the road cut. 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 SR-750 in Floyd. Road drainage from Floyd was comparable to drainage from the I-295/US-360 road cut; however, stream damage appeared 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, road cut 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 Occurrences

Acid road cuts 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 indicated 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 $CaCO_3$/1000 Mg material; however, numerous samples from the US-250 road cut in Highland County contained $CaCO_3$ as indicated by the fizz test. The S values ranged from 0.0 to 3.3%.

Water drainage from I-64 in Clifton Forge has significantly impacted a local stream (Orndorff, 2001). One water sample, upstream from the road cut, revealed near-neutral pH, low EC, and low metal concentrations. Water from a drain inside the culvert, representing the most concentrated drainage, had low pH, high acidity, high EC, and high metal concentrations. Water samples from the downstream end of the box culvert had variable pH values and correspondingly variable metal concentrations. Iron and aluminum precipitates heavily coat the bed of the stream, which appeared to be biologically dead for at least 0.5 km downstream of the road cut. Water drainage from a drainage ditch along US-250, and from a nearby sedimentation pond and stream, had moderate to near-neutral pH values, but high EC values. Overall, metal values were 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 road cut 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 US-23 road cut 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 road cut.

Sulfide levels in materials sampled from Devonian and Mississippian black shales were more variable than other evaluated sulfidic materials. Overall, for samples that do not contain carbonates, PPA and S values were 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 road cut at Clifton Forge had higher acidity and metal concentrations than any other studied road cut. 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 always 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. (1995).

Construction of a Statewide 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. The following scheme was developed to assess geologic materials with general ratings in terms of sulfide hazard. Materials were placed into four classes based on PPA and S values:

1) Materials for which 90% of samples tested less than 10 Mg $CaCO_3$/1000 Mg material and contained less than 0.5% S.
2) Materials for which 90% of samples tested less than 10 Mg $CaCO_3$/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 $CaCO_3$/1000 Mg material and less than 10% of samples tested greater than 60 Mg $CaCO_3$/1000 Mg material.
4) Materials for which more than 10% of the samples tested greater than 60 Mg $CaCO_3$/1000 Mg material.

The 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 Figure 6. 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.

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 due to their minimal surface area that limits oxidation reactions. Nonetheless, these formations should be noted and may require evaluation. The geographic extent and hazard rating of sulfide-bearing geologic materials is shown in Figure 6.

Potential Peroxide Acidity Procedure

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. Regression analysis of the remaining samples indicated %S was a highly significant predictor of PPA and explained a large amount of the variability ($R^2 = 0.81$, $p < 0.001$).

Results from the analyses reported above (Orndorff, 2001) and from evaluation of quartz sand and pyrite standards, indicated that accuracy of PPA depended on the use of appropriate sample sizes. As suggested by the procedure, samples from low S materials must be large enough to produce enough acidity that results will not be significantly affected by laboratory error, while samples from high S 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.

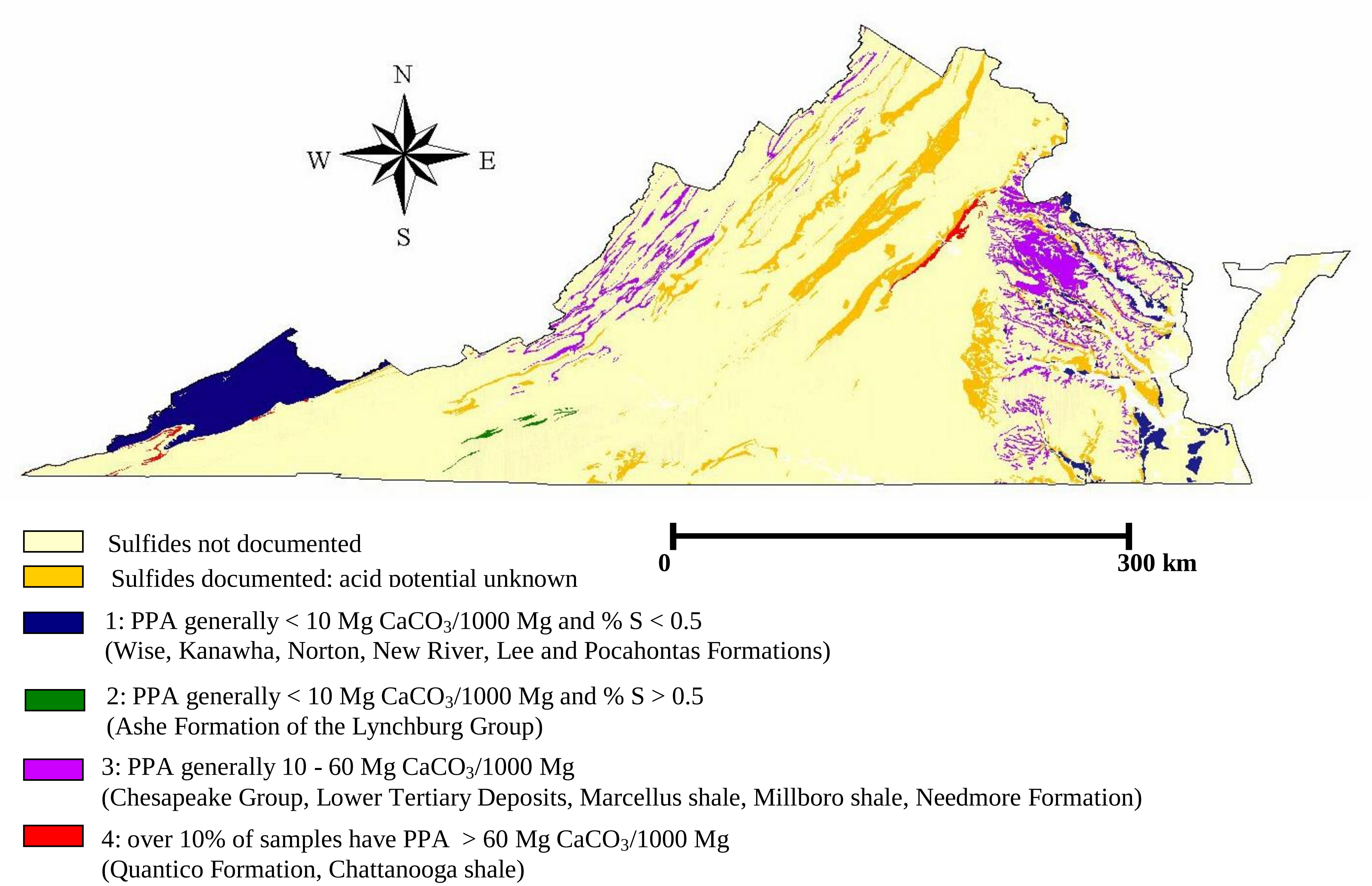

Figure 6. Geographic extent and hazard ratings for sulfide-bearing geologic materials in Virginia.

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. Overall, high correlations between S and PPA were found for slates, shales, and sediments (r = 0.99, 0.98, and 0.92 respectively), whereas phyllites had a poor correlation (r = 0.36). This may be explained by the presence of sulfate precipitates, which were significantly more prominent along SR-750 than any other sampled road cut. 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, and has been widely critiqued in the literature (Ammons and Shelton, 1988; O'Shay et al., 1990; Finkelman, 1986). With the current laboratory setup in the SS + MLR Laboratory, it takes a minimum of three days to process 15 samples at a cost of at least \$12/sample just for materials. In comparison, S can be determined 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, 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, S will over predict 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, S provides an adequate screening tool which could save considerable time and expense in the routine analysis of potentially acid materials.

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

In addition to PPA, a number of other methods 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 (Table 2) representing diverse sulfidic materials were analyzed by PPA and ABA. All potential acidity values are expressed as Mg $CaCO_3$/1000 Mg material.

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 (Figure 7). 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, as seen in Figure 7, 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 had high proportions of sulfate-S because they are 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 affected by the presence of carbonates, which will neutralize some or all of the acidity. Some authors (Grube et al., 1973; 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 14 samples were tested for PPA after removal of carbonates by leaching the samples with 0.5 N HCl, and by the standard PPA method. Results are presented in Figure 7. Two samples - 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. Although the ni sample also tested slightly positive for carbonates it did not show a noticeable increase in PPA after carbonate removal. For this sample, the carbonate level was trivial compared to its very high sulfide level. Four samples – stf4, wc4, bass, and fc4 - noticeably decreased in PPA after leaching with HCl, indicating

Table 2. Summarized description of 14 samples used to compare potential acidity procedures.

sample	Geologic formation	Major sulfide mineralogy and morphology	Accessory minerals	Other comments
fl19	Alum phyllite (Ashe Formation)	Few subhedral grains of pyrite about 0.1mm x 0.1 mm. Small pyrrhotite inclusions in sphalerite.	Sphalerite, trace amount of chalcopyrtie.	
gold	Tailing from Brazilian gold mine	Few pyrite grains ranging up to 1.5 mm x 1 mm. Subhedral grains of goethite pseudomorphs replacing pyrite with little pyrite remaining.	Trace amount of chalcopyrite.	
stf4	Quantico slate	Few, small, euhedral and subhedral grains of pyrite.	Chalcopyrite, covellite	
mcv5-4	Chesapeake Group sediments	Framboidal pyrite dispersed throughout sample. Framboids are larger than ‘bass’ sample.		Loam
mcv6-16	Chesapeake Group sediments	Framboidal pyrite dispersed through sample. Framboids are larger than ‘bass’ sample and less abundant than ‘gas’ samples. Few weathered subhedral pyrite grains.		Silt loam.
mcv6-28	Chesapeake Group sediments	Framboidal pyrite dispersed through sample. Framboids are larger than ‘bass’ sample.		Clay.
gas16	Chesapeake Group sediments	Framboidal pyrite dispersed through sample. Clusters of pyrite microcrystals with grains about 0.008mm in diameter. Clusters are about 0.16 mm x 0.25 mm, ranging up to 0.5 mm x 0.4 mm.		Clay loam.
fl9	Alum phyllite (Ashe Formation)	Polycrystalline lamellar aggregates of pyrrhotite, drawn out parallel to foliation of the rock	Few anhedral masses of chalcopyrite	Contains carbonates.
wc4	Chattanooga shale	Framboidal pyrite and clusters of pyrite microcrystals dispersed through sample.		

Table 2 (continued). Summarized description of 14 samples used to compare potential acidity procedures.

sample	Geologic formation	Major sulfide mineralogy and morphology	Accessory minerals	Other comments
fc4	Marcellus shale	Framboidal pyrite, clusters of microcrystals, euhedral and subhedral grains, and anhedral masses dispersed through sample.		
gas32	Chesapeake Group sediments	Framboidal pyrite and cluster of pyrite microcrystals are dispersed through the sample.		Sandy loam. Contains carbonates.
bass	Acid sulfate soil from Brazil	Framboidal pyrite heavily dispersed throughout sample. Framboids are mostly smaller than 0.004mm in diameter, but range up to about 0.012 mm in diameter. Numerous subhedral grains of pyrite about 0.004mm X 0.004 mm.		
stf1	Quantico slate	Pyrite occurring in corroded subhedral grains.	Chalcopyrite	
ni	Mine tailings from Brazilian nickel mine	Anhedral grains of pyrrhotite dispersed through sample. Grains are about 0.5 to less than 0.002mm in diameter.	Chalcopyrite, magnetitc, digenite	Contains carbonates.

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 moderate 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, we contend that PPA should be determined on samples that have not been leached with HCl.

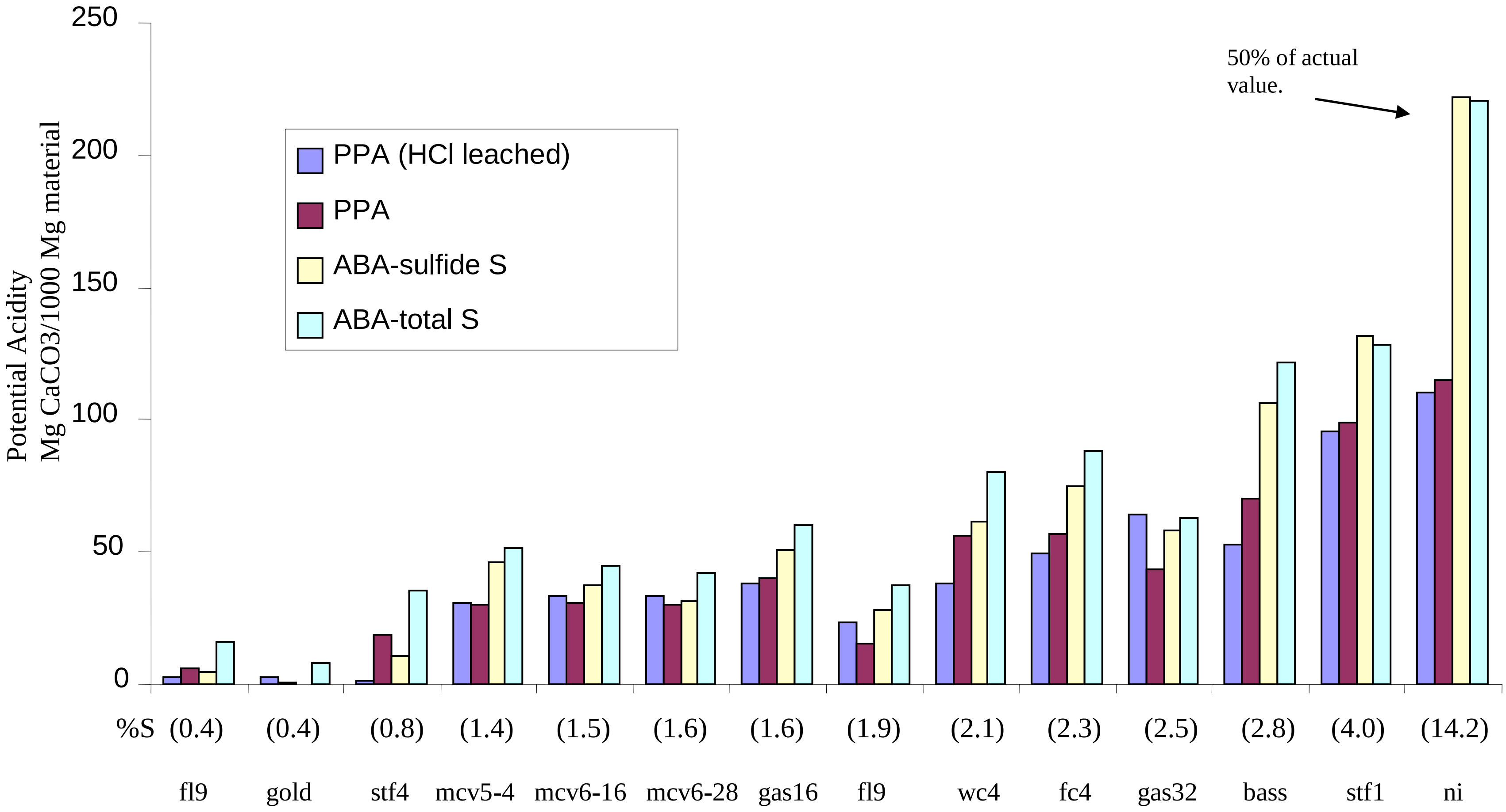

Figure 7. Results for potential acidity procedures on fourteen diverse samples arranged by increasing sulfur content, with %S indicated below each sample label.

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. Overall acid-base accounting results are illustrated in Figure 7. As expected, ABA using total-S (ABA-TS) was highly correlated with ABA using sulfide-S (ABA-SS; r = 0.98). 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 $CaCO_3$/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 $CaCO_3$/1000 Mg material, with a standard deviation of 12.8, and ABA-SS was 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 ABA-SS and 0.703 for ABA-TS).

The PPA and ABA results also may be compared by considering the ratio of PPA to ABA (Figure 8). The PPA/ABA-TS values ranged from 0.06 to 0.77 and were moderately correlated with %S (r = 0.67). Three samples (fl9, stf4, and gold) which contained high proportions of sulfate-S, and two samples (wc4 and bass) which had the highest absolute sulfate-S values account for the most of the low-end PPA/ABA-TS values. 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. Sample fl9, which contained carbonates, also had a low PPA/ABA-TS value. 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 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 $CaCO_3$/1000 Mg material when the sample weight was decreased from 1.0 g to 0.19 g. Reduction in sample size, or increased H_2O_2 additions may further increase the potential acidity results.

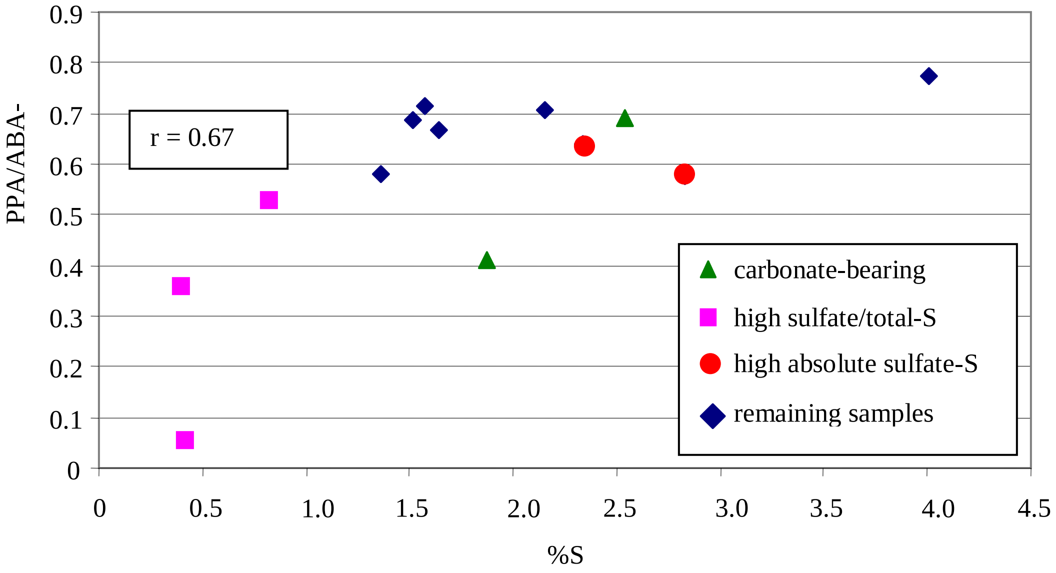

Figure 8. The ratio of potential peroxide acidity to acid-base accounting using total-S to calculate maximum potential acidity (PPA/ABA-TS) versus %S for 14 samples of diverse sulfidic materials.

Soxhlet Extractors

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. These results are illustrated in Figure 9.

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. By the final leaching, these three samples were producing low amounts of acidity, as indicated in Figure 10. 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 and the samples were was still producing high amounts of acidity at the time the experiment was terminated. Replicates for Stafford were similar, but more variable than the other three samples.

The difference in potential acidity predictions for the Stafford sample 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.

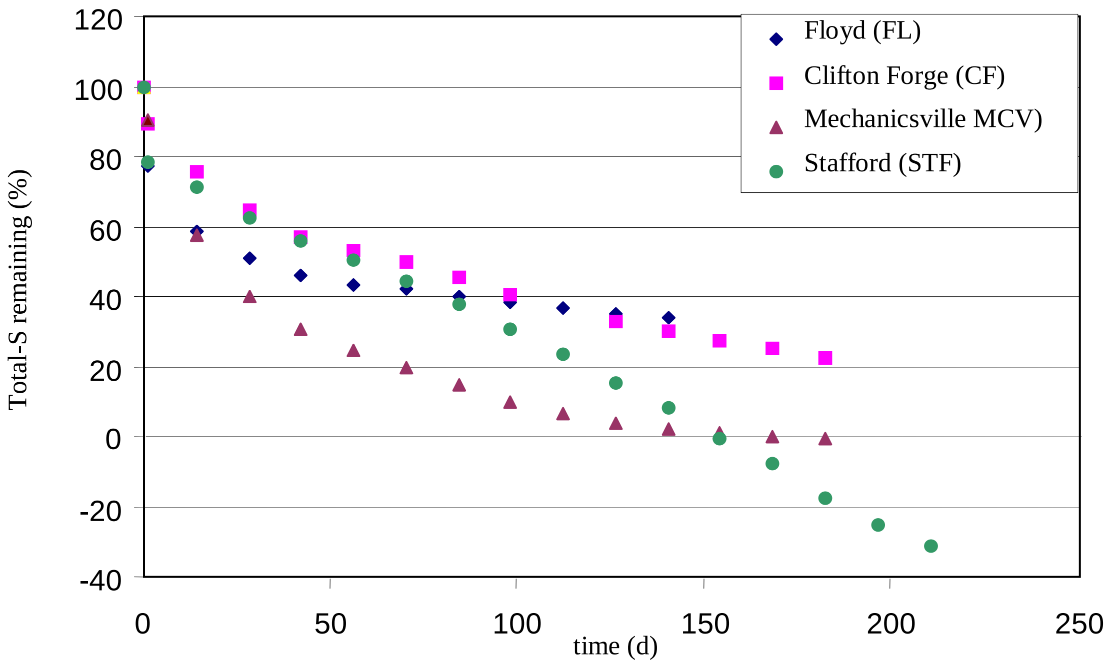

Figure 9. Percent S remaining in solid material after sequential Soxhlet runs as estimated by subtracting the amount of S (determined by ICP) in the leachates from the initial amount of total-S (determined using a CNS analyzer).

For the Stafford and Mechanicsville samples the %S values appeared to drop below zero, which was likely the result of error in the initial S 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 use 1 g samples was recommended for S determination on the CNS analyzer, it has since become apparent that at high S levels (i.e. above 3.5%) the CNS analyzer used may under-report S.

Evaluation of acidity and metal levels for a small number of samples suggested that strong relationships may exist between water quality from the Soxhlet extractors and from road drainage (Orndorff, 2001). 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.

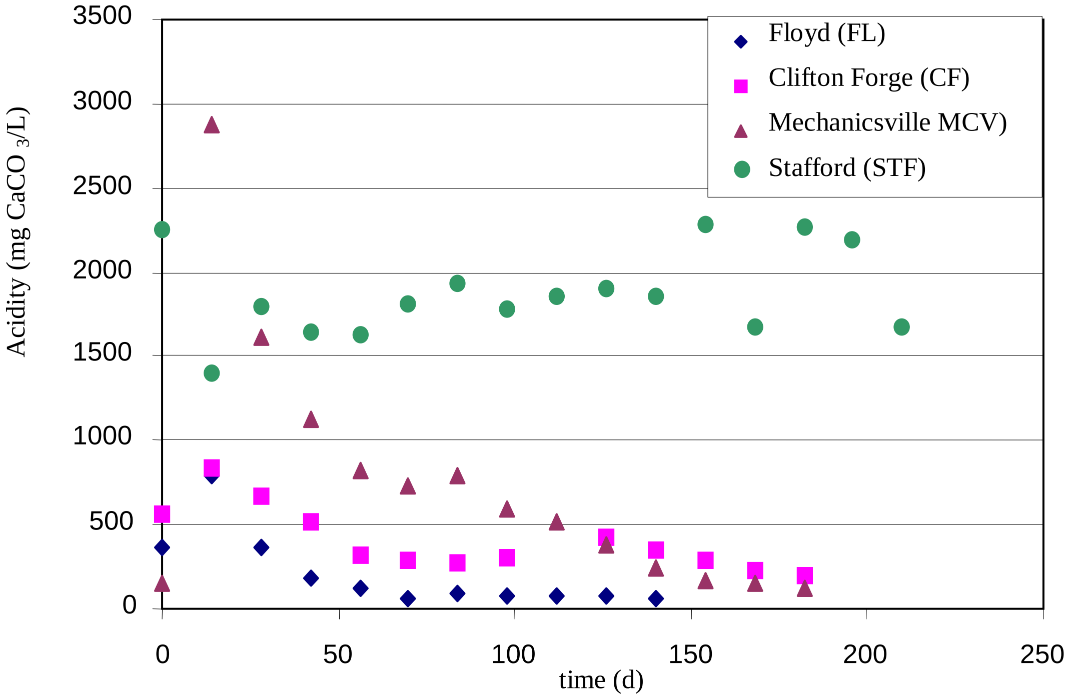

Figure 10. Acid production from Soxhlet extractors for sequential runs.

Conclusions

Sulfidic materials exist in various geologic and geomorphic settings across Virginia. Where sulfidic materials are likely to occur as indicated by the statewide sulfide hazard-rating map, detailed sampling and characterization of materials can minimize ARD-related problems. Sulfide hazard analysis, including the extent and nature of problematic formations, should be considered an essential step in the pre-design stage of highway construction and other earth-disturbing activities. The extent of ARD can be minimized by immediate application of remediation procedures, which require proper characterization of potential acidity. 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 sulfates, which may produce noticeable amounts of acidity upon dissolution. In comparison to other potential acidity tests, PPA yielded less acidity than ABA for 14 diverse samples, and equivalent amounts of acidity as Soxhlet extraction for 3 out of 4 samples. Comparison of average acidity, and metal contents, of leachate 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 is needed.

Acknowledgements

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