Virginia Polytechnic Institute
And State University

The Charles E. Via, Jr.
Department of Civil Engineering

CENTER FOR
GEOTECHNICAL PRACTICE AND RESEARCH

Geotechnical Problems with Pyritic Soil and Rock

by

Lee Bryant
Matthew Mauldon
and
James K. Mitchell

Report of a study performed by the Virginia Tech Center for Geotechnical Practice and Research

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200 Patton Hall
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PREFACE

This engineering report is a compilation of information about geotechnical problems and engineering behavior of pyritic rock and soil, the underlying physicochemical processes, site investigation strategies, and known problematic formations. Several case histories documenting heave and other geotechnical consequences of pyrite oxidation are provided. Appendices include mitigation options, results of a practitioner survey, chemical test procedures, a glossary and a visual identification key for sulfidic geomaterials.

INTRODUCTION

Oxidation of pyrite can significantly affect properties and the behavior of soil and rock in civil construction. Case histories of heave due to oxidation of pyritic shale have been reported and continue to be reported worldwide. Examples include widespread structural damage in Pittsburgh, Pennsylvania (Dougherty and Barsotti 1972), and Ottawa, Canada (Morgenstern 1970; Penner et al. 1970); embankment fill problems at Carsington Dam in Derbyshire, United Kingdom; and differential movement of floors and walls of a multi-million dollar school built in Kentucky during the late 1990s, occurring three years after construction was complete (Partridge 2000). It is sometimes claimed in such cases that pyrite-induced heave was an unknown phenomenon and could not have been anticipated, or the damage is attributed to other causes.

Problems with pyritic soil and rock extend globally and across many disciplines. In addition to heave, consequences of pyrite oxidation include concrete degradation, steel corrosion, environmental damage, acid mine drainage (AMD), and accelerated weathering of rock with concomitant effects on strength and stability. Affected disciplines include soil science, mining, engineering geology, geochemistry, environmental engineering (especially water quality), and geotechnical engineering. While pyrite problems may be well known in their respective disciplines, there has been to date relatively little cross-disciplinary communication regarding problems with pyritic soil and rock. Researchers in geology and soil science, for example, have made major contributions to our understanding of acid mine drainage (Caruccio 1988; Skousen and Ziemkiewicz 1996; Evangelou et al. 1998; Barnhisel et al. 2000). It is not commonly realized, however, that extreme geotechnical consequences (e.g., heave) result from the very same chemical processes. Thus, there is a significant need to establish an inter-disciplinary and inter-regional awareness regarding the effects of pyrite oxidation and their prevention or mitigation.

The combined average annual losses resulting from natural disasters such as floods, earthquakes, tornadoes, and hurricanes constitute less than half of the damages incurred by expansive soils, such as those containing pyrite or expansive clay minerals (Dubbe et al. 1984). While extreme amounts of attention and money have been directed toward the control and mitigation of floods, earthquakes, etc., the efforts directed toward the damage to structures caused by expansive soil and rock are much more varied. In some regions, these problems are well known and considerable money and effort are being spent on mitigation. However, in other regions, damage from expansive material is either not recognized or attributed to some other causes, such as differential settlement, poor construction, or frost heave (Dubbe et al. 1984).

The need for an inter-disciplinary awareness regarding pyrite problems relates well to a poem, *The Blind Men and the Elephant*, by John Godfrey Saxe (1816-1887). This poem tells the story of "six men to learning much inclined, who went to see the Elephant (though all of them were blind), that each by observation might satisfy his mind" (Saxe). However, since each of them touched a different part of the elephant, the elephant was described as a wall (corresponding to the elephant's side), a spear (his tusk), a snake (his trunk), a tree (his knee), a fan (his ear), and a rope (his tail). Thus, each man was left with an extremely different interpretation of the exact same thing. Correspondingly, many people in different disciplines may be familiar with extremely different interpretations and effects of the pyrite oxidation process.

The study of pyrite and related environmental issues date back several thousand years. The degradation of pyrite to acid and salts was mentioned by Theophrastus (ca. 315 B.C.), and Pliny (23-79 A.D.) studied the leaching of pyritic rock to produce "oil of vitriol (sulfuric acid), vitriol (ferrous sulfate), and alum (aluminum sulfates)" (Nordstrom and Alpers 1999). While acid mine drainage (AMD) effects of pyrite oxidation have been issues of concern in the United States since before 1900 (Nordstrom and Alpers 1999; Barnhisel et al. 2000), the geotechnical effects are a much more recent concern. One of the first recorded incidences of pyrite-induced heave occurred in Pennsylvania in 1950 (Penner et al. 1972). However, geotechnical problems with sulfidic materials remained relatively undocumented until the early 1970s when now-classic formative studies on this subject were performed (Morgenstern 1970; Penner et al. 1970; Quigley and Vogan 1970; Dougherty and Barsotti 1972; Grattan-Bellew and Eden 1975). Current studies on these problems can be found in a wide range of more recent publications (Hawkins and Pinches 1992a; Cripps et al. 1993; Mesri et al. 1994; Belgeri and Siegel 1998; Chigira and Oyama 1999; Yamanaka et al. 2002).

Scope of Report

The purpose of this report is to combine information from various sources, disciplines and regions in an attempt to identify and describe geotechnical problems with pyritic rock and soil. The basic physicochemical processes involved with the pyrite oxidation process and the resulting consequences for geotechnical systems are summarized (Section 1). Case histories involving several of these consequences are included to establish evidence of the broad range of affected areas and problem types (Section 2). Guidelines for anticipating problems are outlined to help with the identification of problem formations and their associating visual clues (Section 3, Appendix E). Guidelines for practitioners summarize recommended procedures for site evaluations, estimated magnitudes and rates of the effects of pyrite oxidation, and possible mitigation options (Section 4, Appendices A & C). A survey was conducted to solicit input on the specific types of geotechnical problems encountered that are associated with pyritic materials and to determine which types of mitigation options and specific references are used in various regions (Appendix B). This survey was sent to representatives of each state Department of Transportation and Geological Survey office and to several geotechnical engineers and geologists from various regions in the U.S. and Canada. Five appendices are attached, regarding mitigation options, results of the survey of practitioners, chemical test procedures, a glossary, and visual identification of sulfidic geomaterials.

1 PHYSICOCHEMICAL PROCESSES AND CONSEQUENCES FOR GEOTECHNICAL SYSTEMS

1.1 Chemical reactions and attendant biological and physical processes

The alteration and stability of sulfur-bearing materials are major issues in the fields of geotechnical engineering and civil construction. These materials are problematic in both soil and rock. A basic understanding of the chemical processes involved in the alteration of sulfur-bearing materials is necessary to understand, anticipate, and mitigate problems. The degree of future oxidation and resultant weathering possible in a sulfur-bearing material may be used to define the potential for many geotechnical problems, including swell/heave problems, acid production, and failure of stabilization methods.

Sulfur-bearing materials can be found in bedrock and rock fill of a wide variety of lithologies, in sediments derived from such rock, and in the overlying soils. Over two hundred sulfur-bearing minerals have been recognized (Burkart et al. 1999). Based on the valence (oxidation state) of the sulfur, these minerals are grouped into three main chemical classes: (1) native/elemental sulfur (S^0, with a 0 valence condition), (2) the sulfides and sulfosalts group (with valence states of –1 and –2), and (3) sulfates (of valence state +6) (Burkart et al. 1999).

Although native sulfur will oxidize to sulfate, it is normally quite unstable near the earth's surface and is uncommon in surface rocks. However, it can be found in bituminous sedimentary deposits and hydrothermal metal-sulfide veins (Burkart et al. 1999). Sulfides (e.g., pyrite) are the primary chemical sulfur group found in surface rock and soils. Sulfates are produced as secondary minerals during the oxidation of pyrite and may be found in oxidized zones of pyrite and other ore deposits (Burkart et al. 1999).

It is important to distinguish between "sulfide-induced" and "sulfate-induced" problems when describing geotechnical, structural, or environmental impacts of the oxidation of pyrite and similar minerals. While both of these phrases are commonly used (Little and Petry 1992; Hawkins and Pinches 1997; Burkart et al. 1999), emphasis should be placed on the fact that they are not directly interchangeable. In this report, we primarily focus on "sulfide-induced" problems, which are defined as those problems resulting directly from the oxidation of sulfidic materials (e.g., pyrite) to form sulfates (e.g., gypsum, sulfuric acid). "Sulfate-induced" problems are defined as those resulting from the chemical reaction of sulfates (e.g., gypsum) to produce other forms of problematic sulfates (e.g., expansive sulfate minerals). Figure 1 defines (a) "sulfide-induced" heave problems and (b) "sulfate-induced" heave problems in accordance with terminology in this report.

Another important clarification in regard to terminology used in this report involves "sulfidic" materials. In this report, the term "sulfidic materials" applies to any geomaterials that contain sulfide minerals such as pyrite, and is used frequently to describe pyritic rock and soil. However, it is important to note that the USDA-NRCS

Soil Survey has a more stringent definition of "sulfidic materials", as discussed in Section 3.1.3. Materials classified as "sulfidic materials" in this report do not necessarily meet these soil science standards.

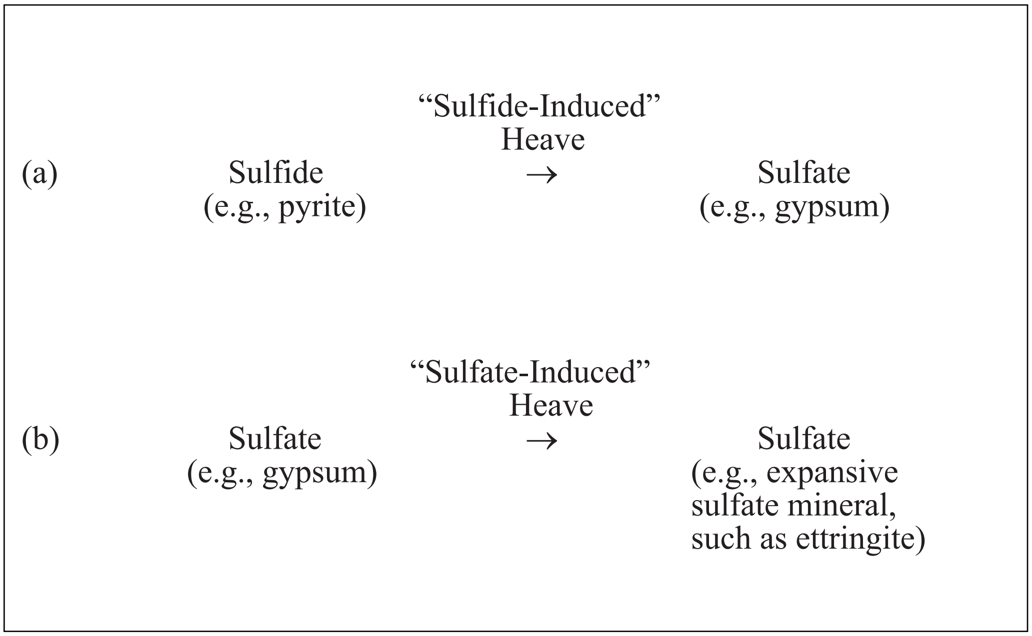
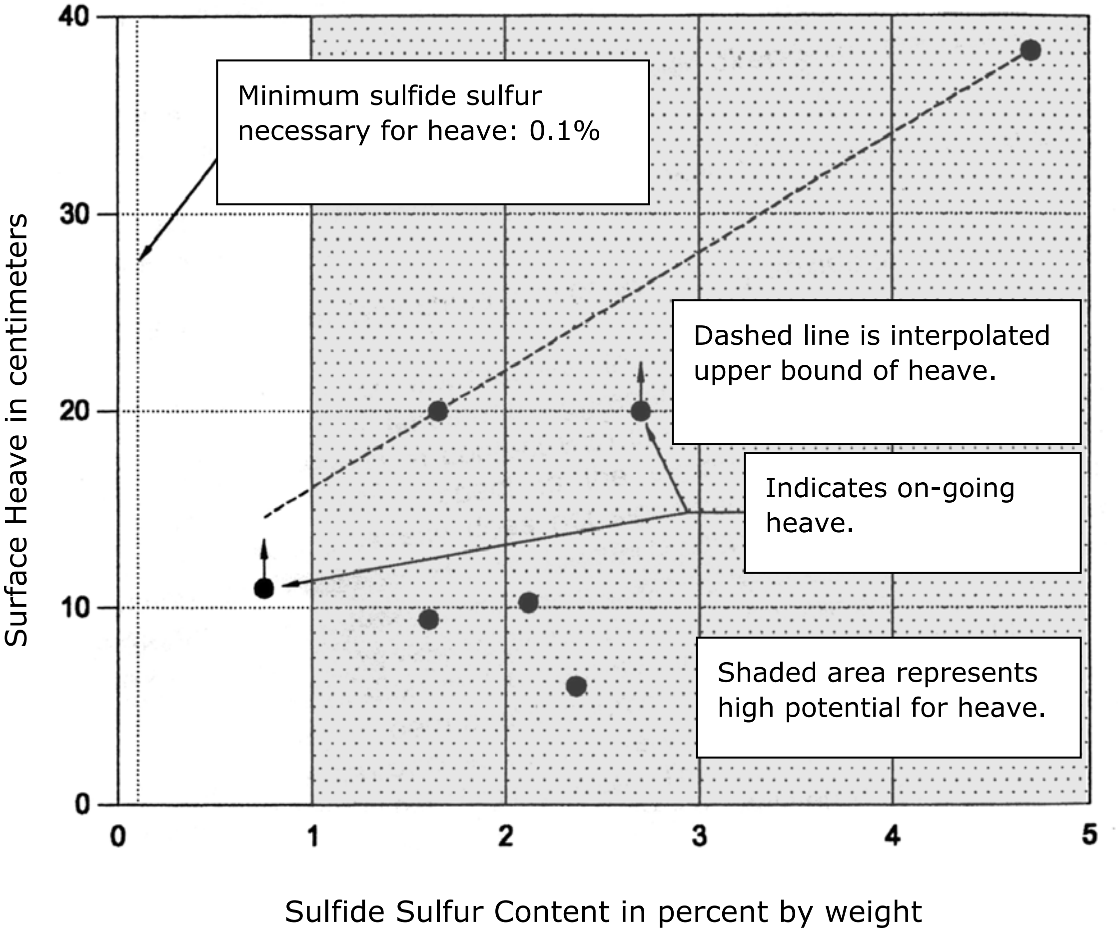


Figure 1 – Schematic of (a) "sulfide-induced" and (b) "sulfate-induced" heave.

1.1.1 Sulfide Minerals

Sulfides are mineral compounds linking sulfur with a metal. Sulfosalts are sulfides which contain both a metal and a semi-metal, creating a double sulfide such as enargite (Cu_3AsS_4) (Bates and Jackson 1984). The primary focus of this report is placed on sulfides. The amount of sulfide sulfur (also known as pyritic sulfur) present in a material may be used to define the potential for weathering and producing harmful oxidation products such as sulfates in the form of sulfuric acid (H_2SO_4). Sulfide-induced heave has occurred in materials containing as little as 0.1% sulfide sulfur (Figure 2) (Penner et al. 1972; Belgeri and Siegel 1998). Thus, sulfide minerals are generally the forms of greatest concern in regard to engineering systems. Pyrite, often found in sedimentary rocks such as shales and in most ore deposits, is one of the most common, widespread, and easily oxidized sulfide minerals (Berry et al. 1983; Burkart et al. 1999). Products of pyrite oxidation, in addition to sulfuric acid (H_2SO_4), include sulfate minerals and several iron oxides such as goethite (FeOOH) and hematite (Fe_2O_3). The sulfuric acid causes the dissolution of other metal sulfides present in the oxidation zone, thus allowing the effects of oxidation to increase as the process builds upon itself. Additional metal sulfides include marcasite (FeS_2), pyrrhotite ($Fe_{(1-x)}S$, (x = 0-0.2)), chalcosite (Cu_2S), covellite (CuS), chalcopyrite ($CuFeS_2$), molybdenite (MoS_2), millerite (NiS), galena (PbS), and sphalerite (ZnS) (Skousen and Ziemkiewicz 1996).



Minimum sulfide sulfur necessary for heave: 0.1%

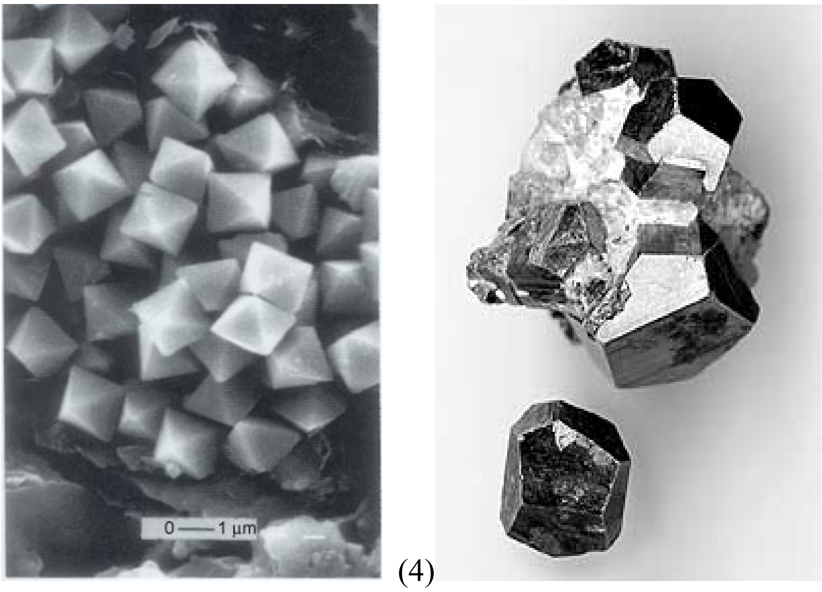
Dashed line is interpolated upper bound of heave.

Indicates on-going heave.

Shaded area represents high potential for heave.

Figure 2 – Plot of sulfide sulfur content vs. amount of heave, modified from (Belgeri and Siegel 1998).

The structure of pyritic sulfides consists of hexagonal sheets of sulfide ions with iron ions interspersed between the sulfide layers (Fasiska et al. 1974). Pyrite (FeS_2) can occur with smooth crystal surfaces (including octahedral (Figure 3), cubic, and pyritohedral), as conglomerates of irregular cemented particles or as a smooth sphere created by cemented crystals known as framboidal pyrite (Evangelou and Zhang 1995). Many of these forms can occur as crystals visible to the naked eye. The most common and recognizable form of pyrite is commonly known as "fool's gold," a relatively large and visible cubical form (Figure 4). Other forms, such as framboidal pyrite, occur in the microcrystalline form and may be visible only with a microscope. Pyrite microcrystals are typically 2 - 40 μm in diameter (Hawkins and Pinches 1997). Microcrystalline framboidal (raspberry-like) pyrite (Figure 5) is the most problematic form in terms of the effects of pyrite oxidation. The oxidation of pyrite is primarily surface controlled; the reactivity of pyrite increases as the grain size decreases and the relative surface area increases (Cripps et al. 1993). The reactivity of framboidal pyrite is also increased by a high porosity, which allows more access to air and water (Evangelou and Zhang 1995). Unfortunately, while these microcrystalline sulfide materials are the most problematic, they are also the most difficult to identify visually due to their small grain size. As a result, pyrite has been called the "invisible menace" since pyrite is most dangerous to engineering systems when it is too fine-grained to be visible (Cripps et al. 1993).


(3) (4)

Figures 3 and 4 - (3) Pyrite octahedral crystals in organic marine shale, from (O'Brien and Slatt 1980). The scale bar is 1 micrometer in length. (4) Cubical "fool's gold" form of pyrite. Photo from www.ugs.state.ut.us.

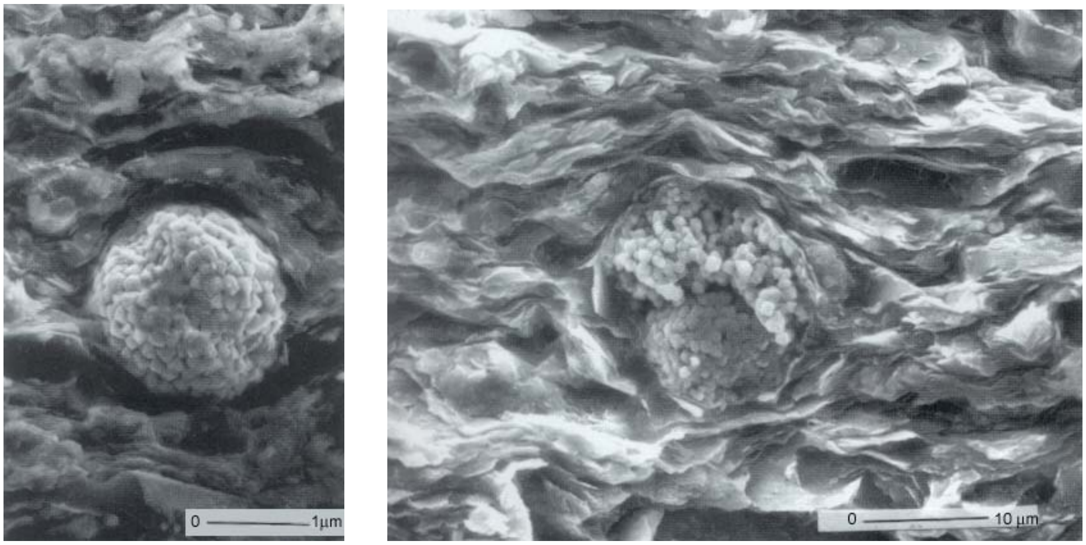


Figure 5 – Pyrite framboids (O'Brien and Slatt 1980). Scale bar in figure on left is 1 micrometer in length; scale bar in figure on right is 10 micrometers in length.

Other problematic sulfides closely related to pyrite include marcasite and pyrrhotite. Marcasite (FeS_2) has the same chemical formula as pyrite but with a different crystal form. Marcasite, which is relatively rare, is less acidic than pyrite but is also less stable and reacts much faster. Pyrrhotite ($Fe_{(1-x)}S$, ($x = 0\text{-}0.2$)) normally occurs as disseminated, anhedral grains (Figure 6) and interstitial masses in igneous and metamorphic rocks (Orndorff 2001). Pyrrhotite is extremely unstable and has been known to explode when coming into contact with air, resulting in surface cracking of fresh shales within minutes of exposure. In one case study, a freshly exposed slope in Montana exhibited crackling and popping as oxidation occurred in the pyrrhotite (Kennard et al. 1967).

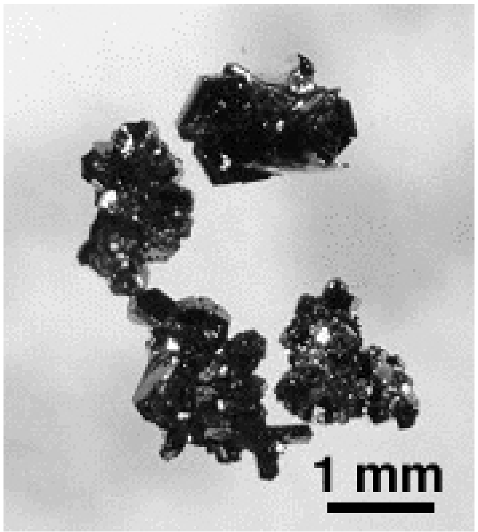


Figure 6 – Anhedral pyrrhotite grains. Photo from www.soest.hawaii.edu.

1.1.2 Sulfate Minerals

Sulfates are mineral compounds distinguished by the sulfate radical, SO_4 (Bates and Jackson 1984). Common sulfates include gypsum ($CaSO_4 \cdot 2H_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), anhydrite ($CaSO_4$), alunite ($KAl_3(SO_4)_2(OH)_6$), melanterite ($FeSO_4 \cdot 7H_2O$), and rozenite ($FeSO_4 \cdot 4H_2O$). The relative proportion of the sulfate form of sulfur to the amount of total sulfur present is indicative of the degree of weathering or oxidation that has occurred. The production of sulfates by pyrite oxidation results in an increase in volume and acidity as well as increased potential for further deleterious reactions, such as the formation of gypsum and expansive sulfate minerals in clays.

Sulfates have tetrahedral coordination created by four oxygen atoms surrounding a sulfur atom. The geometrical arrangement of sulfate ions causes a volume increase of approximately 350% per unit when compared with the original sulfide sheets (Fasiska et al. 1974). Sulfidic materials are relatively dense which partially explains how heave commonly results from their degradation. The products of pyrite oxidation reactions are significantly less dense and thus have a greater volume than the initial sulfide product (pyrite). For example, pyrite of specific gravity (G_s) 4.8-5.1 reacts with calcite ($G_s = 2.7$) to create gypsum ($G_s = 2.3$) (Hawkins and Pinches 1997).

Volume increases associated with the production of sulfates from several mineral transformations are given in Table 1. For comparative purposes, these percentages are based on the assumption that the altered rock was initially composed of 100% of the original mineral (Shamburger et al. 1975).

Table 1 – Volume Increases of the Crystalline Solid Phases of Selected Mineral Transformations [from (Fasiska et al. 1974; Shamburger et al. 1975; Taylor 1988)]

Mineral Transformation		Volume Increase of Crystalline Solids (%)
Original Mineral	New Sulfate Mineral	
Illite	Alunite	8
Illite	Jarosite	10
Calcite	Gypsum	103
Pyrite	Jarosite	115
Pyrite	Anhydrous ferrous sulfate	350
Pyrite	Melanterite	536

Sulfate crystals resulting from pyrite oxidation develop in the capillary zone and tend to localize along discontinuities due to a reduction in stress (Figure 7). This is a dominant factor in the vertical heave problems that occur in shales and other materials that have relatively horizontal laminated bedding fissility (Kie 1983; Hawkins and Pinches 1997). These effects occur to a lesser degree in materials that have more random fissuring, such as mudrocks and clays. The fissility of shales is typically associated with preferred parallel arrangement of clay particles. This fissility, which is extremely conducive to expansive mineral growth, is the product of weathering of a compacted fabric of parallel-aligned organic matter and clay particles which accumulate below anoxic bottom waters (Wignall 1994).

Figure 7 – Effects of pyrite oxidation in New Albany Shale, east of Elizabethton, Kentucky. Photo by Brandon Nuttall, Kentucky Geological Survey.

The formation of gypsum ($CaSO_4 \cdot 2H_2O$) is considered to be a primary cause of heave resulting from pyrite oxidation. Gypsum can be visually identified as a microcrystalline coating or as white or clear fibrous crystalline blades (Figure 8), although it is sometimes stained by iron oxides (Quigley et al. 1973a). Gypsum may be regarded as the primary and possibly "only calcium sulfate mineral in soils" (Nettleton et al. 1982) and the most common sulfate mineral in sedimentary rocks. Most case studies regarding failures of engineering systems resulting from pyritic heave have identified the presence of gypsum (Hawkins and Pinches 1997). Gypsum is the sole sulfate mineral present in all documented cases of problematic soil in north Texas (Burkart et al. 1999). Although pyrite is the initial cause of many of these problems, gypsum may contribute significantly to problematic heave conditions in calcareous soil and rock environments where calcium (from calcite ($CaCO_3$), limestone, lime (CaO), etc.) is present to react with the sulfates produced by pyrite oxidation. While these calcium-bearing materials are often used in mitigation work for stabilization and acid neutralization purposes, additional heave-related problems may be created by the formation of gypsum.

Acid drainage problems are sometimes associated with the presence of gypsum. Gypsum and sulfuric acid may both result from pyrite oxidation if calcium minerals are present; thus, gypsum is commonly found in acid drainage problem areas. However, gypsum is a neutral salt that does not contribute directly to the production of sulfuric acid (Sobek et al. 1987).

Figure 8 –Fibrous gypsum crystal (penny used for scale).

The growth of gypsum tends to occur in areas of decreased stress, such as weathered, fissured material or the cavities between fracture walls (Figure 9). This process is analogous to ice lensing in soils (Penner et al. 1972). The presence of gypsum is also controlled by its solubility. Gypsum is sparingly soluble, with a relatively high solubility product ($pK_{sp} = 4.59$). While gypsum is several orders of magnitude less soluble than highly soluble melanterite ($pK_{sp} = 2.21$), the solubility of gypsum is several orders of magnitude greater than that of low solubility minerals like barite ($pK_{sp} = 10$) or anglesite ($pK_{sp} = 7.8$) (Snoeyink 1980). The concentration of Ca^{+2} and SO_4^{-2} ions in equilibrium with gypsum ($CaSO_4{\cdot}2H_2O$), representing the solubility, is approximately several hundred ppm. In comparison, the solubility of melanterite ($FeSO_4{\cdot}7H_2O$), one of the few water soluble sulfate minerals, is in the range of tens of thousands ppm and the solubility of anglesite ($PbSO_4$) is only in the low ppb range. Due to gypsum's solubility, its occurrence is in some instances governed by groundwater and surface water movements. If a significant amount of water is present, gypsum ions remain in solution and are washed away. However, if limited water is present, then most of the ions will form crystalline gypsum.

The formation and solubility of gypsum are not directly controlled by the pH of a sulfate environment. The chemical processes governing these relationships are defined in greater detail in Section 1.1.3.2. However, low pH values and high levels of humidity do tend to increase the solubility of gypsum. At pH values < 2.5, gypsum solubility increases as a result of some of the SO_4^{-2} ions converting to bisulfate (HSO_4^{-1}). Seasonal variations in the amount of gypsum present in soil may occur in areas of high humidity (Burkart et al. 1999). Soils rich in clay and various types of shales and mudrock may retain gypsum as a result of low permeability. Once gypsum recrystallizes in these materials, it is frequently very difficult to dissolve or remove (Hawkins and Pinches 1997). Figure 10 shows a cross-section of the origin and migration of gypsum in soil overlying pyritic bedrock. Gypsum is transported downward by infiltration (solid arrows) and upward by capillarity (dashed arrows).

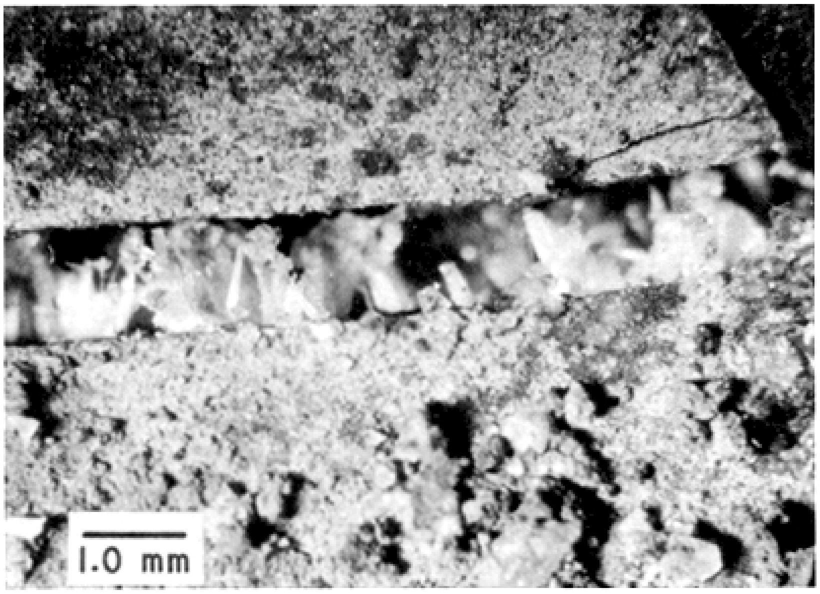


Figure 9 – Shale platelets forced apart by gypsum growth, from (Penner et al. 1972).

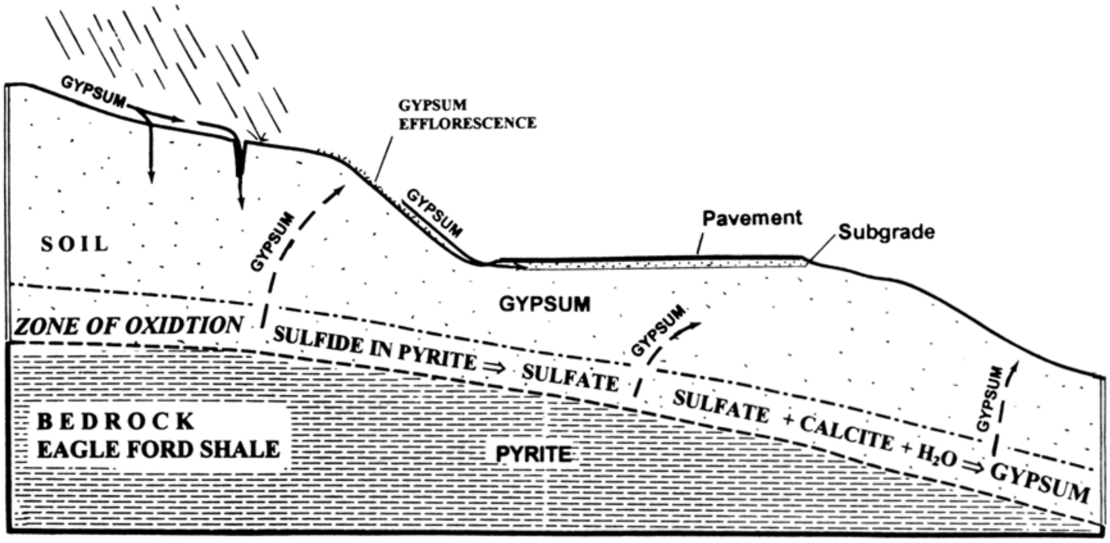


Figure 10 – Geologic cross-section showing origin and migration of gypsum in soil overlying pyritic bedrock, from (Burkart et al. 1999).

1.1.3 Physical, chemical, and biological weathering

The mechanical and hydraulic properties of geomaterials are directly affected by the degree and type of weathering that has occurred. Weathering of sulfidic materials results from both physical and chemical processes. The degree of weathering will depend on the severity and type of the weathering agents, the permeability of the rock, and the resistance to weathering of the various lithologies involved under previous and existing ground water conditions (Hawkins 1986).

1.1.3.1 Physical processes

Physical weathering can be considered a control on chemical weathering since physical disintegration of a rock leads to rapid increases in the reactive surface area and accessibility to oxygen (Steward and Cripps 1983). Weathering affects the granular structure and grain-size distribution of pyritic material. Physical and/or chemical weathering breaks down rock fragments into smaller sizes, creating increased amounts of fines and variations in permeability and void space. Decreased density due to erosion, channeling, and cracking may occur. Increased permeability and loss of cohesion may lead to self-compaction.

1.1.3.2 Chemical processes

Chemical weathering has varied effects on rock and soil quality. The principal chemical weathering process that affects pyritic rock and soil is pyrite oxidation. Volume changes will occur due to mineral dissolution and precipitation. Bulk density will be decreased as diagenic pyrite is removed by oxidation. As the sulfuric acid produced by the oxidation process is consumed by the dissolution of clays and other rock material (limestones, dolostones, etc.), the bulk density will be further decreased. Where pyritic rock is used as concrete aggregate, mineral dissolution can cause reductions in aggregate size with corresponding increases in void ratio and porosity.

The pyrite oxidation process is defined by the following equations. It should be noted that several alternate forms of these equations have been defined for the pyrite oxidation process (Nordstrom 1982; Evangelou and Zhang 1995; Hawkins and Pinches 1997). Equations 1-3 below show the steps involved during pyrite oxidation that produce both sulfates and acidity (H^+) as well as iron hydroxide precipitates ($Fe(OH)_3$), known as "yellowboy" (Skousen and Ziemkiewicz 1996).

Pyrite (FeS_2, iron disulfide) is oxidized in Equation 1, producing ferrous iron (Fe^{+2}, reduced iron), sulfate (SO_4^{-2}), and acidity (H^+) (Skousen and Ziemkiewicz 1996). Actual acidity is predominantly in the form of sulfuric acid (H_2SO_4).

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+ \qquad (1)$$

Ferric iron (Fe^{+3}) is created in Equation 2 by oxidation of the ferrous iron.

$$Fe^{+2} + \frac{1}{4}\ O_2 + H^+ \rightarrow Fe^{+3} + \frac{1}{2}\ H_2O \qquad (2)$$

Ferric iron can then be hydrolyzed to produce ferric hydroxide ($Fe(OH)_3$) and acidity, as shown in Equation 3.

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

Alternatively, ferric iron can act as a catalyst with pyrite in producing considerably greater amounts of ferrous iron, sulfate, and acidity, as shown in Equation 4 (Skousen and Ziemkiewicz 1996),

$$FeS_2 + 14Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+, \qquad (4)$$

which produces significant acidity from the resulting 16 moles of hydrogen ions per mole of FeS_2.

The rate of pyrite degradation is accelerated by several factors, including elevated temperatures, humid conditions, a low pH environment, and the presence of bacteria (Hawkins and Pinches 1997; Jerz and Rimstidt 2000). The above equations do not define reaction rates (Evangelou and Zhang 1995); however, Figure 11 shows a comparison of reaction rate constants (k) which define the rate of chemical reaction as a function of pH for Equations 1, 2, and 4 (above) (Nordstrom 1982). If Reaction 1 (Eq. 1) occurs in undrained conditions, the resulting contained acidity will inhibit further oxidation, as Fe^{2+} is stable in acidic conditions. However, acid loss due to drainage and the resulting neutralization are typical of natural environments. Thus, most oxidation processes commonly continue (Hawkins and Pinches 1997), as shown in Figure 11, as the rates of Reactions 1 & 2 (Eqs. 1 & 2) increase with an increase in pH. At neutral to alkaline pH values, rapid increases in the rate of Fe^{2+} oxidation occur, shown by the drastic rise of Reaction 2 (Figure 11) above a pH of 4.0. Reaction 2 (Eq. 2) is generally the rate-limiting step in abiotic environments (totally chemical with no bacterial catalyzation) because conversion from ferrous iron to ferric iron is relatively slow under abiotic conditions (Evangelou and Zhang 1995; Hawkins and Pinches 1997). However, when iron-oxidizing bacteria are present, the rate of ferrous iron oxidation (Eq. 2) can be significantly accelerated. Reaction 3 (Eq. 3) can take place in acidic environments (pH as low as 3) and serves as a significant contributor to releasing acid to the environment (Evangelou and Zhang 1995). Reaction 4 (Eq. 4), which produces the greatest amount of acidity (H^+), occurs only under very acidic conditions, as Fe^{3+} only behaves as an oxidizing agent in an environment with $pH < 3$ (Figure 11) (Hawkins and Pinches 1997).

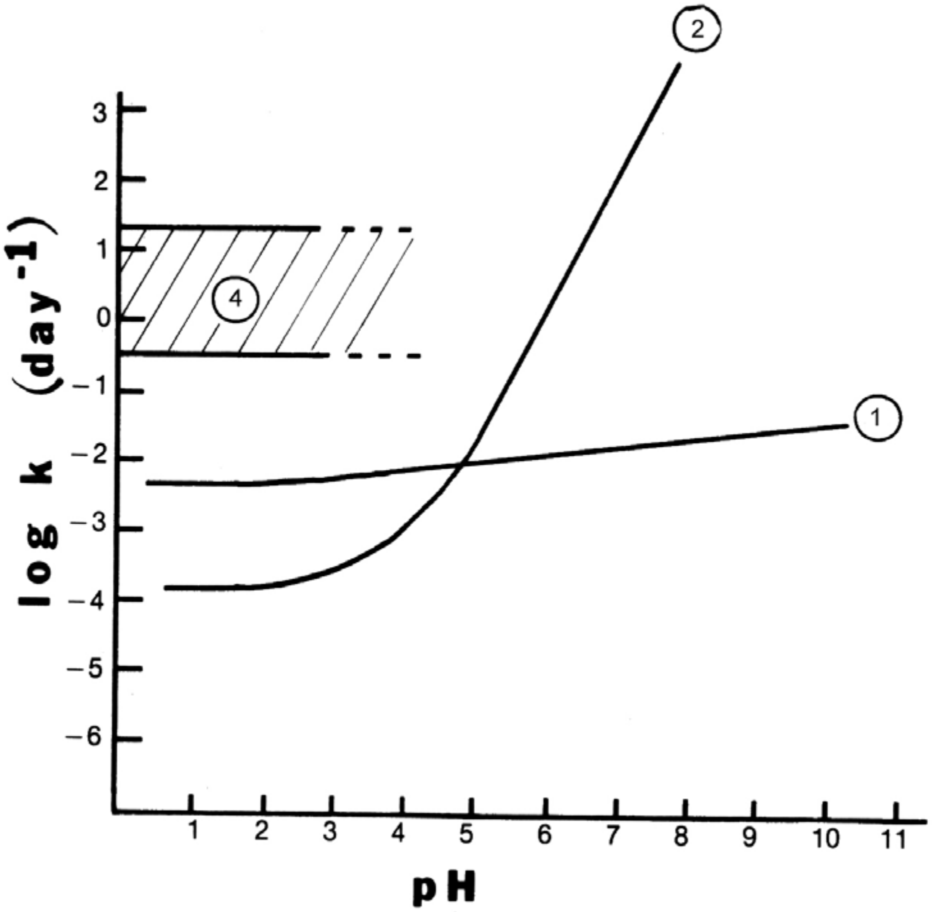


Figure 11 – Comparison of rate constants (k) in relation to pH for Equations 1, 2, and 4 (as defined in Section 1.1.3.2). Circled numbers in figure correlate with Equation numbers. Modified from (Nordstrom 1982).

Gypsum is formed when sulfate ions react with calcium in the presence of water. The formation of gypsum is defined by Equation 5.

$$Ca^{+2} + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (5)$$

As previously mentioned in Section 1.1.2, the chemical processes governing the formation and dissolution of gypsum are not directly controlled by pH (calculated by $pH = -\log [H^+]$), as shown by the absence of H^+ ions in Equation 5. While the solubility of gypsum does increase at $pH < 2.5$, the pH of formative environments for gypsum is generally much higher than this due to the presence of alkaline calcium-bearing materials like calcite or lime. Calcite ($CaCO_3$) is one of the most favored reactants for the chemical reaction that produces gypsum (Hawkins and Pinches 1992b). The chemical equation process associated with gypsum forming in the presence of calcite is depicted in Figure 12 (Diaz 1987).

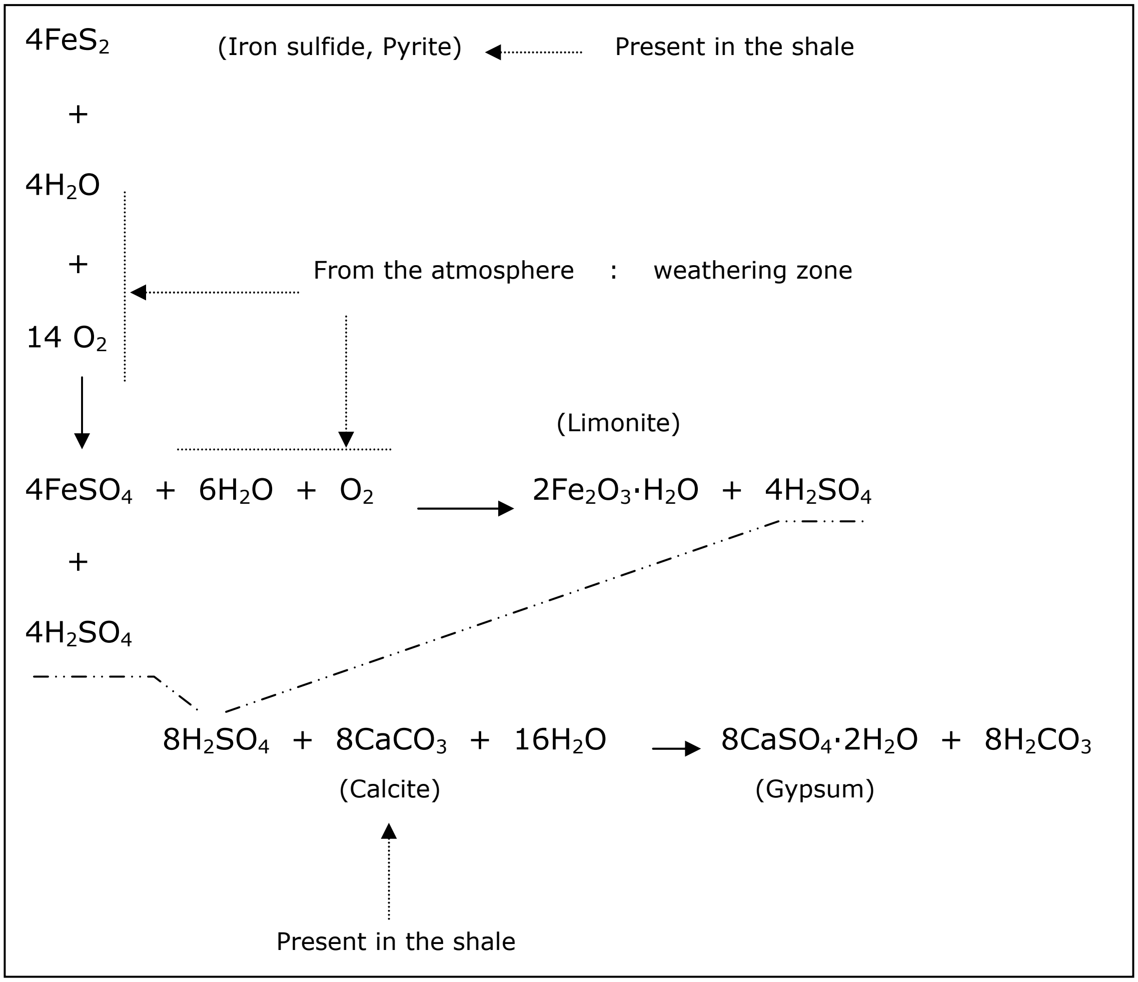


Figure 12 – The chemical alteration of pyrite and calcite into gypsum, recreated from (Diaz 1987).

Instead of gypsum, most of the sulfates in very low pH environments occur in the form of jarosite ($KFe_3(SO_4)_2(OH)_6$). Jarosite is another sulfate mineral that may be produced by pyrite oxidation and is commonly associated with sulfuric acid production. Jarosite is a distinctive bright yellow mineral that is created by the reaction of potassium (K^+), commonly coming from illite, with ferric iron (Fe^{+3}) and sulfate (SO_4^{-2}), two of the products of pyrite oxidation, as shown in Equation 6 (Driessen and Deckers 2001).

$$Fe^{+3} + 2/3\ SO_4^{-2} + 1/3\ K^+ + \frac{1}{4}\ O_2 + 3/2\ H_2O \rightarrow 1/3\ KFe_3(SO_4)_2(OH)_6 + H^+ \qquad (6)$$

However, due to its limited range of solubility, jarosite is rarely found in soils with a pH above 4 (Hawkins and Pinches 1997). When carbonates are not present, the acidity produced by pyrite oxidation is not neutralized and the pH decreases, creating an environment conducive to jarosite formation.

Jarosite may slowly break down to goethite (FeOOH) (Equations 7-8) and is replaced by gypsum in environments that become buffered and less acidic (Burkart et al. 1999). The brown coloration of goethite may be used as an indicator that pyrite oxidation has occurred.

$$1/3\ KFe_3(SO_4)_2(OH)_6 + H^+ \rightarrow 1/3\ K^+ + Fe(OH)_3 + 2/3\ SO_4^{-2} + H^+ \qquad (7)$$

$$Fe(OH)_3 \rightarrow FeOOH + H_2O \qquad (8)$$

Jarosite, while indicative of sulfidic material and frequently found in locations where heave has occurred, is sometimes debated as a cause of heave. Several researchers credit jarosite as being a significant factor in heave associated with the pyrite oxidation process (Penner et al. 1972; Hawkins and Pinches 1997); however, others state that the growth patterns of jarosite crystals indicate that it is predominantly a coating or void-filling mineral that does not grow against pressure (Quigley et al. 1973a).

1.1.3.3 Biological processes

Microbial activity strongly controls the rate of pyrite oxidation processes. Iron-oxidizing bacteria such as Thiobacillus ferrooxidans and Thiobacillus thiooxidans (Figure 13) can increase the rate of ferrous iron (Fe^{2+}) oxidation by a factor of up to 10^6 (Singer and Stumm 1970; Evangelou and Zhang 1995). These Thiobacilli microorganisms are autotrophic as they use carbon from carbon dioxide (CO_2) for cell growth, and aerobic as they obtain energy from the oxidation of reduced sulfur compounds (Hawkins and Pinches 1986). The Thiobacilli bacteria can exist in both rock and soil under acidic conditions, and T. ferrooxidans are extremely common in geologic areas containing pyrite. The first step of pyrite oxidation (Eq. 1) produces acidity that lowers the pH, thus preventing further chemical oxidation from occurring. However, if bacteria are present, the oxidation process can continue biologically (biotically) (Hawkins and Pinches 1986). The aerobic bacteria oxidize ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron (Eq. 2) which then regenerates the Fe^{3+} needed for further pyrite oxidation (Evangelou and Zhang 1995).

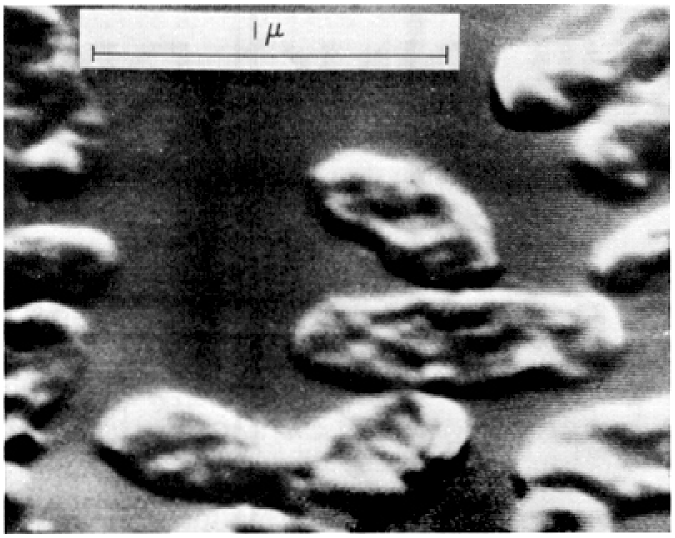


Figure 13 – Ferrobacillus-Thiobacillus bacteria isolated from weathered shale below a heaved floor, from (Penner et al. 1972).

According to Hawkins (1997(a)), optimal microbial conditions for activity of T. ferrooxidans occur with a temperature of 30°- 40°C (86°- 104°F). High temperatures are extremely conducive to microbial degradation of pyrite. Research has shown that an area of a basement kept artificially cool experienced much less heave than the warmer areas of the basement (Penner et al. 1972). These microorganisms also thrive in low pH environments, with optimal conditions of 2.5–5.8. Microbial colonies have been shown to establish within several days in neutral environments previously absent of bacterial growth (Temple and Delchamps 1953). As these microorganisms proliferate rapidly in low pH environments, the progression of pyrite oxidation and the subsequent increasingly acidic conditions create a self-perpetuating cycle that is extremely conducive for microbial growth and accelerated pyrite oxidation.

1.2 Consequences for geotechnical projects and systems

Oxidation of pyrite can have significant impact on a wide variety of geotechnical engineering projects and systems (Table 2). Heave due to uplift pressures, the expansion/deterioration of concrete, steel corrosion, environmental damage, and changes in strength and stability of the sulfidic rock or soil may all result from pyrite oxidation. It is quite remarkable that the same basic chemical and physical processes resulting from pyrite oxidation can cause such diverse and detrimental effects to so many types of geotechnical engineering projects. Case history examples illustrating such consequences are included in Section 2.

Table 2 – Pyrite Oxidation Effects on Various Geotechnical Projects and Systems

Geotechnical Project/System	**Physical/Chemical Processes**				
	Heave	**Swell Pressure**	**Concrete Deterioration**	**Steel Corrosion**	**Acid Drainage**
Shallow foundations	X	X	X		
Floor slabs	X	X	X	X	
Road sub-grades	X				X
Other lightly loaded structures	X	X	X		
Structural walls	X	X	X	X	
Concrete culverts	X		X		X
Concrete piles/drilled shafts	X		X		
Drilled shafts	X			X	X
Steel culverts	X			X	X
Steel structural components (piles, bolts, etc.)	X			X	X
Slope stabilization methods (tiebacks, rockbolts, anchors, soilnails, vegetation)	X			X	X
Rock piles	X				X
Tunnels	X	X			X
Rock Excavation					X
Roadcuts	X				X
Embankments	X				X

1.2.1 Heave and uplift pressures

Significant uplift pressures and heave can result from mineral expansion during oxidation of pyrite. As a direct consequence of the oxidation process, sulfides are altered to sulfate compounds that may occupy up to eight times the volume of the original sulfide mineral (Dougherty and Barsotti 1972). Sulfidic minerals such as pyrite are relatively dense. The products of pyrite oxidation reactions are much less dense and therefore occupy more volume than the initial sulfide product, which partially explains how heave commonly results from their degradation. The forces associated with this volume expansion can result in substantial uplift pressures that have significant effects on shallow foundations, floor slabs, road subgrades, or other lightly loaded structures overlying these areas. A summary of estimated pressures and amounts of resulting heave are given in Table 11 (Section 4.2.1).

Substantial remediation costs may be associated with occurrences of heave. Millions of dollars of structural damage has occurred in Pittsburgh, Pennsylvania, and Ottawa, Canada. The province of Quebec has promised to contribute 35 million Canadian dollars during the next decade to help approximately 5000 homeowners remediate damage caused by sulfide-induced heave (Gazette Quebec Bureau 2001). In 2000, the public library in Johnson City, Tennessee, built in 1979, was finally demolished due to structural damage from heave of pyritic shale. Legal action was being considered by a $10 million Kentucky school to obtain remediation costs from insurance to cover damage caused by pyritic shale (Partridge 2000). As stated by Lutenegger (1979), “expansive becomes expensive.”

1.2.2 Concrete expansion/degradation

“Sulfate attack” is unfortunately a relatively common problem where sulfuric acid produced from pyrite oxidation (Eqs. 1, 3, and 4 from Section 1.1.3.2) degrades concrete and results in significant loss of strength properties. Sulfates infiltrate the concrete and dissolve the cementicious matrix that holds the concrete together. Once concrete degradation begins, the process accelerates rapidly and is irreversible, with concrete eventually turning to debris. Concrete degradation occurs as a result of close proximity to acid-producing sulfidic geomaterial or acidic groundwater. Degradation can also occur from the presence of sulfide minerals in the aggregate (Chinchon et al. 1995).

Effects of “sulfate attack” include the formation of white, powdery stains (efflorescence) from resulting salt deposits, spalling, pop-outs, hairline cracks (etching), and concrete expansion/heave (Skalny 2000). Impacted structures include structural walls, floor slabs, shallow foundations, concrete culverts, and piles/drilled shafts. According to the National Association of Home Builders, “sulfate attack” can decrease the expected useful life of concrete from approximately 150 years to 15 years or less (Kasdan Simonds & Epstein 2002). Concrete culverts in Virginia have been known to degrade within two years (Rader 2002). A concrete underground bomb shelter in Norway was “transformed into mush” within 9 months of construction due to oxidation of pyrrhotite ($FeS_{1.14}$) in the Alum Shale on which it was constructed (Moum and Rosenqvist 1959).

Concrete degradation may be a concern even during the curing process or immediately following construction. Curing temperatures typically reach approximately 55°C (131°F) which are significantly higher than typical ground temperatures of 15° - 20°C (59° - 68°F). These elevated temperatures will accelerate oxidation processes if sulfides are present in the curing environment (Hawkins and Higgins 1997).

1.2.3 Steel corrosion

The sulfuric acid produced by pyrite oxidation can react with steel to cause corrosion of steel components. Steel corrosion is one of the more common and easily recognized clues for pyrite oxidation due to the resulting orange-colored rust stains. In addition to being aesthetically unpleasing, corrosion can cause significant decreases in strength as a result of loss of steel volume. Impacted structures of importance in geotechnical engineering include corrugated metal pipe (CMP), H-piles used with pyritic backfill, drilled shafts, culverts, structural components (beams, bolts), and slope stabilization techniques (tiebacks, rock bolts, anchors, soil nail tendons).

1.2.4 Acid production

Environmental problems related to pyrite oxidation result primarily from acid production and the subsequent effects on surface and subsurface water quality. Acid production and drainage, however, also impact many geotechnical projects and systems, either directly by altering rock or soil material properties (as discussed in Section 1.2.5) or indirectly through environmentally-driven guidelines or restrictions on the handling of pyritic construction materials. Tunnels, highway cuts, embankments, and other major construction projects exposing pyrite-bearing material are examples of projects that may be impacted by acid drainage. Attempts to establish vegetation on embankments and roadcuts often fail due to high levels of acidity when pyritic material is involved (Rader 2002). The durability of aggregates produced from pyrite-bearing rocks and rock pile stability may also be adversely affected as a result of acid attack. Agencies such as the Federal Highway Administration (FHWA), the Environmental Protection Agency (EPA), state agencies, and several international organizations are now very conscious of the potentially disastrous environmental consequences of careless handling of pyritic materials. Their site evaluation and excavation protocols include guidelines for prior detection and careful handling of such “hot rocks” (Table 3). The mining industry has similarly been influenced by the need to deal responsibly with acid drainage.

Table 3 – Published Guidelines for Handling Pyritic Materials	
Agency / Author	**Guideline / Report**
Federal Highway Administration (FHWA)	FHWA-FL-90-007 – Guidelines for Handling Excavated Acid-Producing Materials (Byerly 1990)
TN Department of Transportation (TDOT)	Standard Operating Procedure for Acid Producing Rock (TDOT and Moore)
TN Department of Transportation (TDOT)	The Use of Geomembranes for Mitigation of Pyritic Rock (Moore 1992)
TN Department of Transportation (TDOT)	Mitigation Measures for Acid Producing Rock (Moore and Trolinger 1997)
California Geological Survey (CGS)	Note 48 Checklist for the Review of Engineering Geology and Seismology Reports for California Public Schools, Hospitals, and Essential Services Buildings (Sydnor 2002)
Environmental Protection Agency (EPA)	EPA-600/2-78-054 – Field and Laboratory Methods Applicable to Overburdens and Minesoils (Sobek et al. 1978)
Quebec Association for Consumers Regarding Quality in Construction (ACQC : *Association des consommateurs pour la qualité la construction*)	Pyrite and Your House: What Home-Owners Should Know About Swelling Backfills (ACQC 1999)
Queensland Acid Sulfate Soils Investigation Team (QASSIT)	Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998 (Ahern et al. 1998)
D. W. Byerly, Dept. of Geological Sciences, Univ. of Tennessee	Handling Acid-Producing Material During Construction (Byerly 1996)

1.2.5 Strength and stability effects

Pyritic materials are very susceptible to the effects of both chemical and physical weathering. The original state of induration and the resulting diagenic grade of pyrite govern the extent to which a material ultimately weathers or degrades in terms of a reduction in strength (Anderson and Cripps 1993). Material behavior typically changes from rock-like to soil-like as weathering progresses, resulting in decreased shear strength. A weathering classification system (Table 4) suggested by Hawkins (1986) relates geological weathering descriptions and their engineering significance.

Table 4 - Simplified Weathering Classification System Relating Geological Description and Engineering Significance [from (Hawkins 1986)]

Term	Abbreviation	Description
Fresh	F	Rock shows no discoloration and is at approximately its maximum strength for that material in that situation.
Slightly Weathered	SW	Rock is discolored along discontinuities but there is little or no reduction in strength from the fresh rock.
Moderately Weathered	MW	Rock mass away from the discontinuities may be discolored and/or material adjacent to the discontinuities is reduced in strength.
Highly Weathered	HW	Rock mass may be more than 50% discolored and/or over 50% of the mass is reduced in strength. At this grade some rocks, such as claystones, behave more as an engineering soil than as a rock, hence may more appropriately be described as firm/stiff clay with claystone lithorelicts.
Completely Weathered	CW	Mass mostly discolored and/or reduced in strength such that it behaves and should be described as an engineering soil.

Acid generation directly influences weathering processes and the stability of pyritic material. Engineering properties of pyritic shales may be affected by fresh acid within days or weeks of initial exposure (Steward and Cripps 1983). Mineral dissolution by sulfuric acid and the precipitation of new minerals such as gypsum and jarosite or oxides and hydroxides such as hematite and goethite will lead to alterations in the bulk density value (Steward and Cripps 1983). The precipitation of oxides also creates a cementing effect. However, this effect is often temporary because these oxides are soluble. Similarly, calcite-based cements are commonly depleted when calcite reacts with sulfates to form gypsum. A quantitative evaluation of these effects would be dependent on the parent rock minerals, the permeability of the rock, and the amount of sulfuric acid produced from pyrite oxidation.

Oxidation of fresh exposures of pyritic rock or soil may alter even seemingly stable conditions. Using a fresh slope failure as an example, pyritic material newly exposed on a slip surface may react with acidic leachate as it infiltrates the slope. As a result, seemingly stable post-failure conditions may be altered, possibly leading to a progressive failure by decreasing the overall strength. A landslide underlain by pyritic Namurian Edale shale in Mam Tor, Derbyshire, United Kingdom was stated to have periodic instability, with relatively frequent small movements (Steward and Cripps 1983).

In this study, the permanent factor of safety against failure is assumed to be close to unity. Research performed by Vear and Curtis (1981) indicated that weathering reactions were occurring at depth inside the slide, including mineral dissolution by sulfuric acid and the formation of gypsum, jarosite, and goethite. The factor of safety was predicted to reach a critical failure condition within a few years if these processes resulted in decomposition of the fresh shale along the slip surface (Steward and Cripps 1983).

Pyritic materials such as shales that have clay constituents are also influenced by clay mineral interactions. Soluble products of the more rapid pyrite oxidation reactions will alter the porewater composition, which will result in further reactions with the pyritic shale. Clay layers and other shale constituents may become destabilized and dissolve, while other minerals may be precipitated from the altered pore/groundwater conditions (Steward and Cripps 1983). Sulfuric acid produced by pyrite oxidation can alter the cation compositions of clays, especially smectites. These alterations will drastically affect the bonding energies and swelling behavior of the clays, which in turn will affect the residual strength of the soil or rock material. Although acidic environments typically create a more flocculated clay structure, with subsequent increases in shear strength, extremely acidic environments may lead to decreased shear strength due to acid attack on the clay. In very low pH environments, breakdown and dissolution of the silicate clay surfaces can occur as cations in the clay (e.g., Ca^{2+}, Al^{3+}) lattice are pulled out of the octahedral units. Some of these cations are then adsorbed onto the clay cation exchange sites and OH^- ions are released to neutralize the excess H^+ ions in the acidic environment (Sposito 1989; Mitchell 1993). Other cations that are released from the clay lattice during acid attack may form non-crystalline (amorphous) clay-like material.

The coal mining industry has recognized shale deterioration upon cyclic exposures to temperature/humidity. According to a four-year study by Stateham (1987), the frequency of mine-roof falls follows a yearly absolute humidity cycle, with the roof failures typically lagging two weeks behind peak humidity. Over 50% of coal-mine fatalities in the United States are attributed to roof falls resulting from the deterioration of shales (Harper et al. 1979). While such roof falls result largely from the effects of humidity on shale slaking and physical degradation, these humid conditions are also extremely favorable for accelerated pyrite oxidation. Chemical degradation resulting from pyrite oxidation in the shales may often be an additional contributor to shale problems in the mining industry.

2 CASE HISTORIES

Numerous case histories have been reported in the literature. The following case histories have been selected to illustrate the wide range of consequences and locations of geotechnical problems with pyritic rock and soil.

2.1 Sulfide-induced heave study, Johnson City Public Library, Johnson City, Tennessee

The Johnson City Public Library, located in Johnson City, Tennessee, was constructed in 1979 (Belgeri and Siegel 1998). The library structure experienced significant levels of cracking of floor slabs and buckling of floors and partition walls by 1982 (Figure 14). Damage was particularly significant in areas constructed over fill. Following a geotechnical investigation, it was revealed that the subgrade beneath the building was composed of undisturbed shale and shale fill, both of the Sevier Shale formation. A photograph of the extremely black Sevier Shale from this site is included as Figure E.7 in Appendix E. Chemical testing established sulfide sulfur contents in the unweathered shale to range from 0.59-0.71%. Significant heave levels were measured. The floor slab was vertically displaced 2-3 cm at construction joints and differential vertical displacements were as much as 11 cm within a given room (Belgeri and Siegel 1998). Damage resulting from shale heave occurred much more quickly in areas constructed over the shale fill as opposed to over the undisturbed shale. Heave in the fill sections occurred within three years, while the undisturbed shale sections took eight years for heave damage to occur. This time difference is due to several factors. The shale fill has a greater exposed surface area than the undisturbed material. Thus, more material is available for pyrite oxidation and gypsum formation reactions. The greater permeability of the fill would also give it greater access to air and water, which would accelerate the rates of reactions producing swelling materials. The extent of damage to the library was so significant that the building was finally demolished in 2000. The very short life of this structure is a powerful example of how important a thorough understanding of site conditions and the use of appropriate mitigation options in the design phase are to the success of an engineering structure.

Figure 14 – Sulfide-induced heave of library floor and bookshelves at Johnson City Public Library, Johnson City, Tennessee.

2.2 Microbially-induced sulfidic heave study, Residential homes, Japan

Approximately 1000 homes in Japan were damaged by microbially-induced sulfidic heaving of the foundations (Yamanaka et al. 2002). The maximum height of heave that occurred was 48 cm. The homes were constructed on unweathered pyritic mudstone fill which was initially deposited during the Neogene.

Three types of bacteria are credited with catalyzing the pyrite oxidation process. Sulfate-reducing, sulfur-oxidizing, and iron-oxidizing bacteria (e.g., T. ferrooxidans and T. thiooxidans) were all present in the mudstone (Yamanaka et al. 2002). The hypothesized bacterial process initiates with the temperature of the freshly-exposed mudstone elevating above 25ºC, which stimulated the sulfate-reducing bacteria to actively reduce sulfate in the mudstone to hydrogen sulfide (H_2S). As the sediments beneath the houses gradually dried and became more permeable to air, the sulfur-oxidizing bacteria oxidized the H_2S to sulfuric acid. The sulfuric acid caused a decrease in the environmental pH to approximately 3 (Yamanaka et al. 2002). More acid was created as the acidophilic (acid-loving) iron-oxidizing bacteria then actively oxidized the iron in the pyrite. The resulting sulfuric acid reacted with (1) calcium carbonate ($CaCO_3$) to create gypsum and (2) ferric iron and potassium ions to create jarosite. Carbon dioxide gas (CO_2) was also created as a by-product of these reactions, causing an increase in soil voids. Widespread heaving occurred from the combined volume increases from the production of CO_2 and the formation of gypsum and jarosite crystals (Yamanaka et al. 2002).

2.3 Embankment fill study, Carsington Dam, United Kingdom

Carsington Dam, an embankment dam located in Derbyshire, United Kingdom, experienced structural problems as a result of being constructed from mudstone containing pyrite and expansive clay minerals (Cripps et al. 1993). Carsington is a zoned embankment dam composed of moderately weathered mudstone in the shoulders (5% pyrite and 7% calcite) and totally weathered mudstone in the core (0.8% pyrite and 0.25% calcite). The original dam, which experienced stability failure in 1984, had drainage blankets of Carboniferous Limestone. The pyritic mudrock fill oxidized to create sulfuric acid which then caused mineral dissolution within the limestone. Gypsum and iron hydroxide precipitates then formed and proceeded to block drains. Carbon dioxide gas was also generated and accumulated in drains, manholes, and excavations (Cripps et al. 1993). The accumulation of this gas tragically resulted in death by asphyxiation of four men in the inspection chamber. These severely detrimental effects of pyrite oxidation were addressed in the second design of the dam. Shear strength parameters were selected to allow for degradation of the material due to weathering. All drainage blankets were constructed of non-calcareous fill and gravel was placed on the downstream shoulder to sustain the growth of vegetation to prevent erosion. Gas accumulation in confined spaces was addressed by strict safety precautions. Protective coatings of bitumen were placed on all concrete structures to prevent sulfate attack. Lagoons were constructed downstream to provide long-term treatment of the drainage water (Cripps et al. 1993).

2.4 Subgrade study, Cedar Hill State Park, Texas

Twenty-seven percent of the Cedar Hill State Park road system in Dallas County, Texas, was affected by heave due to treatment of the subgrade with lime. The road subgrade overlies gypsum-bearing soils derived from calcareous shales of the Eagle Ford Group (Burkart et al. 1999). While pyrite was not found in the Eagle Ford study, the soils were found to contain iron oxide concretions, some with box-shaped cavities typical of oxidation and dissolution structures of pyrite (Burkart et al. 1999). Two miles of roadway were affected by up to one foot of localized heave in the form of transverse and longitudinal humps. A study on this site was formative in leading to the development of future standards regarding methods to determine the soluble sulfate content in soils (Petry 1994).

Sulfate-induced heave of the treated clay soils was indicated by several factors (Petry 1994). There were relatively high levels of soluble sulfates present. There was a noticeable lack of cementing pozzolan growth in the treated subgrade. Affected materials were confirmed by x-ray analysis and scanning electron microscopy to contain ettringite ($Ca_6[Al(OH)_6]_2\ (SO_4)_3\ 26H_2O$), an expansive sulfate mineral produced by the reaction of lime with gypsum (see more complete discussion on ettringite in Section 3.1.3). The problematic materials were noted to have reduced pH values which are atypical for lime-treated soil. Areas of poor drainage were also noted to lead to early full hydration of ettringite in many situations (Petry 1994). The Corps of Engineers eventually replaced all of the lime-treated subgrade with crushed stone for $1.6 million dollars (Burkart et al. 1999).

2.5 Stability study, Questa mine, New Mexico

Stability of large mine waste piles containing pyritic rock at the Questa mine in New Mexico has been the subject of recent studies. One of the main issues is whether or not acid production from pyritic-rock weathering within the mine waste is occurring at rates and levels sufficient to affect the stability of the rock piles. The Questa mine is located in the Sangre de Cristo Mountains, north of the Red River and near the town of Questa in Taos County, New Mexico. Between 1965 and 1983, 74 million tons of low-grade molybdenum ore was mined, producing 320 million tons of waste rock. This waste rock was deposited on the existing ground surface in nine mine waste piles which reach up to 1500 feet in height and span 677 acres, forming some of the highest mine rock piles in North America (Figures 15-16) (Shaw et al. 2002). Catastrophic failure involving static liquefaction or progressive, local failure involving more isolated slope failures could potentially lead to disasters on many levels, including loss of life, property damage, and environmental concerns. There is obviously much at stake in regard to the stability analyses of these massive piles. Site-wide characterization programs are currently being performed, including comprehensive drilling programs. Drilling programs have been implemented in phases to gain information regarding physical and geochemical properties of the mine waste at depth and to monitor temperature and oxygen variations at depth in the piles (Shaw et al. 2002). By attempting to evaluate the potential impact of weathering and other physicochemical processes (including oxidation of pyrite) that are on-going in the mine rock, the stability of the Questa mine waste piles may be further defined.

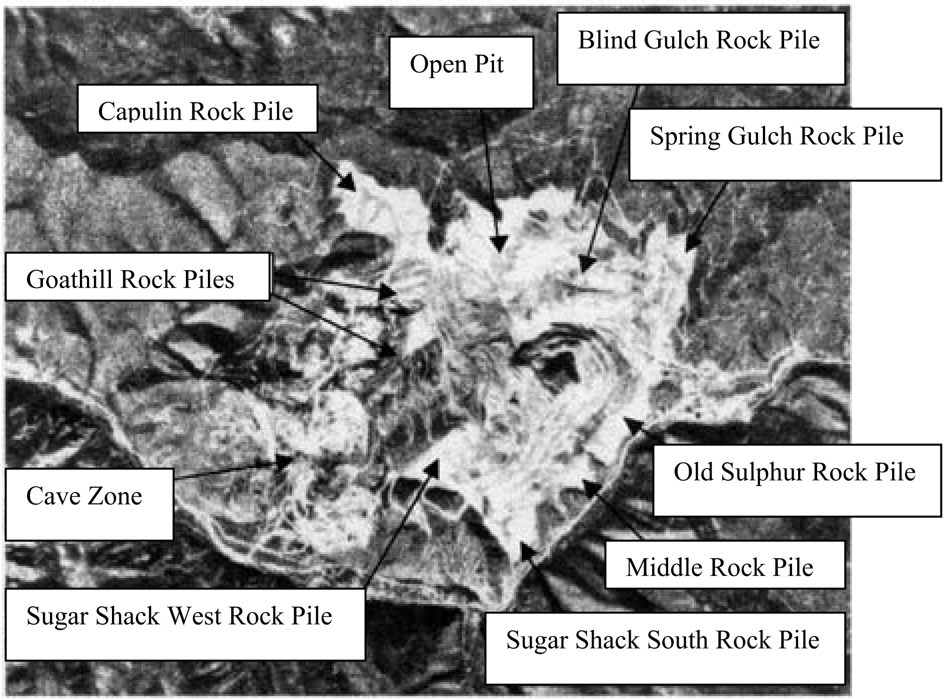


Figure 15 – Aerial photo of nine Questa mine waste rock piles, which span 677 acres, in Questa, New Mexico, from (URS Corporation 2001).

Figure 16 – One of the mine waste rock piles at the Questa molybdenum mine, Questa, New Mexico. Photo from Dr. James K. Mitchell.

2.6 Acid drainage study, North Carolina

Significant acid drainage problems have occurred from fresh exposures of acid-producing rocks during construction. Serious damage to aquatic life resulted from reconstruction efforts on U.S. Highway 441, near Newfound Gap, North Carolina, Great Smoky Mountains National Park, in 1963 (Mathews and Morgan 1982). Sulfuric acid leachate from the pyrite-bearing Anakeesta rock fill eliminated fish for approximately 8 km downstream from roadfill areas. A fishery study performed 9 years following reconstruction showed that the brook trout populations had not been re-established (Mathews and Morgan 1982).

During the construction of a transmission line corridor through the Blue Ridge Province in North Carolina, the effects of acid drainage were minimized by incorporating guidelines established by Byerly (1996) into a successful mitigation strategy. The potential for acid production of sulfidic rock units along the proposed transmission line corridor (graphite schists of the Anakeesta Formation, graphitic metasiltstones of the Nantahala Formation, and layers of sulfidic rock of the Ammons Formation-Horse Branch Member) was evaluated using geologic maps, petrographic studies, and Acid-Base Accounting testing (Schaeffer and Clawson 1996). During construction, successful mitigation efforts included drainage systems to divert water from fills and transmission line tower foundation excavations, mixing agricultural lime into the excavated sulfidic material, and then encapsulating the excavation with at least two feet of stock-piled topsoil. For problems with sulfidic material in existing roadbeds in this region, a limestone aggregate base was placed on the existing roadbed followed by a layer of lime-treated, compacted material with additional lime added between every lift. Compacted topsoil was then used to encapsulate the layers of treated material and limestone base. Additional limestone aggregate was used as the final road surface. An on-going monitoring program, established before construction began, has shown that these methods are minimizing environmental impacts of the pyrite oxidation process (Schaeffer and Clawson 1996; Orndorff 2001).

3 GUIDELINES FOR ANTICIPATING PROBLEMS

3.1 Problematic formations and associated identifying clues

Recognizing problematic rock formations is key to anticipating and addressing geotechnical concerns. Pyrite may be found in soft soils and sedimentary rocks created in anoxic environments with a constant supply of sulfur and may also be present in igneous and metamorphic rocks, ores, and veins as a result of sulfide mineral crystallization (Hawkins and Pinches 1997; Henika 2002).

Problem formations can be grouped according to four nonexclusive types: (1) shales created in marine or estuarine (near-ocean) depositional environments; (2) fine-grained rock and soil with significant pyrite content; (3) formations with recognized potential for acid production; and (4) formations in which heave from pyrite oxidation has been known to occur. Prior knowledge of the identifying characteristics of problem formations and of the degree of shale weathering that has occurred on site can help establish a comprehensive understanding of a site's potential for heave and other problems related to pyrite oxidation.

It is important to note that a problematic pyritic material may belong to more than one of the above groups. While certain methods of identifying pyritic material are applicable to specific types of problem formations, there are several methods that generally apply to all sites and rock/soil types. For example, a Devonian shale may be detected by clues listed for a marine formative environment as well as visual identification clues for a fine-grained rock with significant pyrite content.

Examples of each category of problem formation are included in summary tables in each of the following sections (Tables 5, 6, 8, 9). These tables are not complete lists in and of themselves but are intended to show the inter-regional and cross-disciplinary effects of pyrite oxidation in sulfidic materials.

3.1.1 Shale formations created in a marine or estuarine environment

Sulfidic materials are frequently found near marine or estuarine areas or in locations where these conditions existed in the formative environment of the parent rock or soil. Conditions most favorable for the formation of pyrite in marine environments include an anoxic environment, a constant supply of sulfates, an initial supply of iron and organic material, the presence of iron- and sulfate-reducing bacteria, and/or continuous tidal action (Figure 17). The rate of sedimentation is also an important factor in the formation of pyrite.

Anoxic, reducing conditions conducive to pyrite formation are typically found below the surface of marine sediments where all of the available oxygen supply has been depleted by the decay of organic material. Burial of sediments will eventually establish an anoxic environment; thus the formation of pyrite may occur at any time during the burial history of a marine mudrock (Hawkins and Pinches 1997; Brett and Allison 1998).

The saltwater in estuarine or marine environments provides an abundant source of sulfates necessary for the formation of pyrite. Sulfates in freshwater environments, however, are not continuously replenished. For this reason, the restricted sulfate supply limits the pyrite concentration in freshwater formative environments (Schieber 1995).

Pyrite production is partly controlled by the availability of organic matter. Organic matter is needed to supply energy to the iron- and sulfate-reducing bacteria. These bacteria are an integral part of the pyrite formation process and are present in all coastal sediments. Pyrite forms by the reaction of iron with elemental sulfur created by the oxidation of hydrogen sulfide, H_2S. Sulfur present in pyrite may come from either the decomposition of organic material or bacterial reduction of sulfates dissolved in seawater (Blatt 1980). The amount of H_2S which can be created by the bacterial reduction of sulfates in an anoxic environment is usually unlimited in a marine environment due to the constant supply of sulfates.

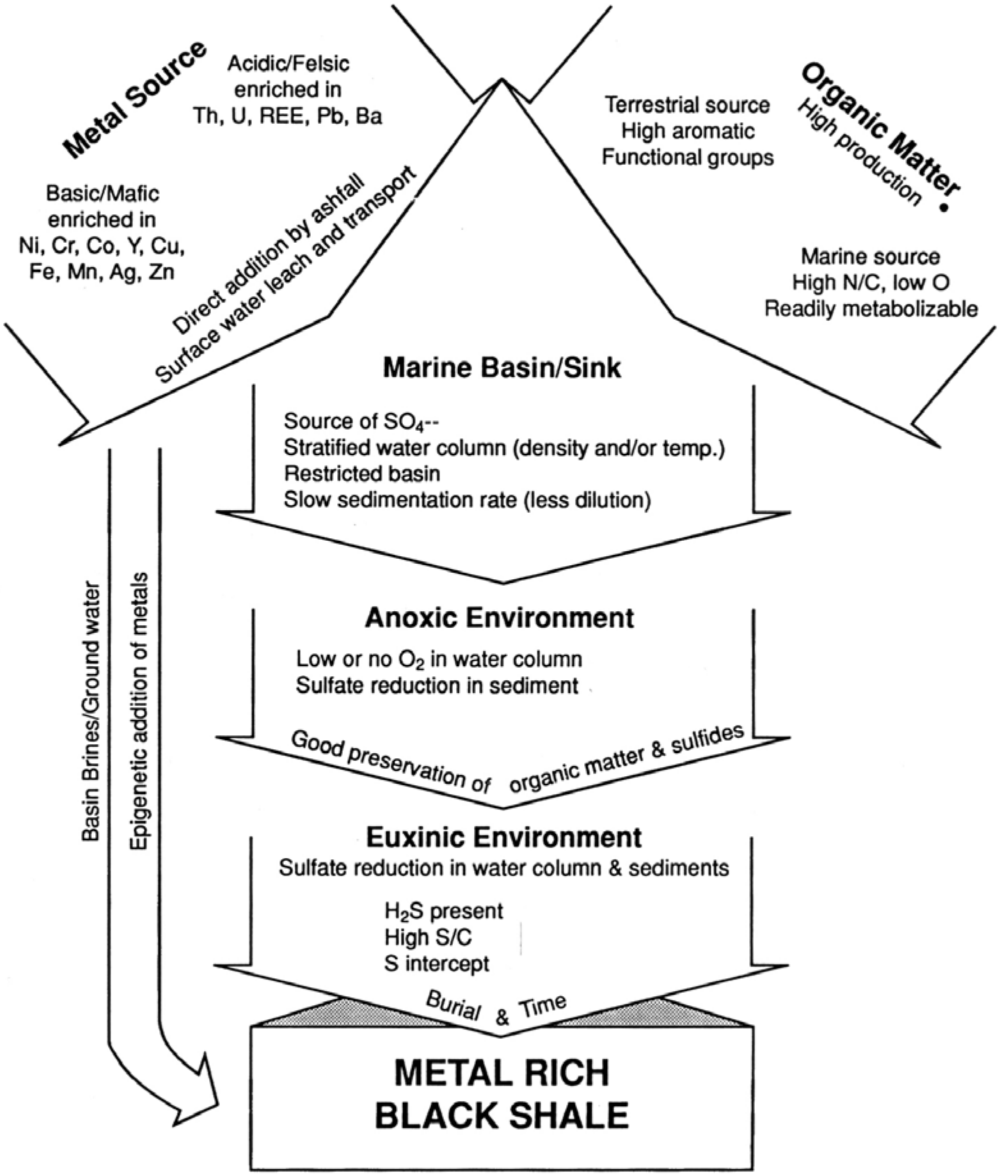


Figure 17 – Schematic diagram defining the conditions needed for the formation of metalliferous black shales, from (Leventhal 1998).

The highest accumulations of pyrite occur where tidal flushing is strong. Thick deposits of highly pyritic materials are associated with rapid rises in relative sea level (Pons et al. 1982). Tidal flushing removes dissolved sulfide and bicarbonate from the formative environment, lowering the pH and kinetically favoring the formation of pyrite. The tidal action also supplies dissolved oxygen needed for pyritization (sulfide accumulation) of reduced sulfates (Pons et al. 1982).

Sedimentation rates need to be slow enough to allow the combination of conditions required for pyrite formation to remain established long enough for pyrite to form (Driessen and Deckers 2001). Slow sedimentation, or deposition, rates allow for crystallization and agglomeration of colloidal size pyrite microcrystals, creating the more problematic framboidal pyrite form (Byerly 1990). However, if a large amount of organic material is present, higher rates of sedimentation are more conducive to pyrite formation in marine environments. When low rates of sedimentation occur in highly organic marine bottom waters, most of the pyrite may be removed before burial by the reworking of organic material (Wignall 1994). Typically only nonreactive material remains, which generates very little sulfide and establishes conditions similar to freshwater environments.

Pyrite formation can be summarized by the following equation (Fanning and Fanning 1989):

$$\begin{aligned}&Fe_2O_3 \text{ (ferric iron compound)} + 4SO_4^{-2} \text{ (sulfate)} + 8CH_2O \text{ (organic matter)} + \tfrac{1}{2}\,O_2 \rightarrow \\ &2FeS_2 \text{ (pyrite)} + 8HCO_3^{-1} \text{ (bicarbonate)} + 4H_2O \qquad (9)\end{aligned}$$

Bacteria reduce ferric iron (Fe^{+3}) to ferrous iron (Fe^{+2}) and sulfate (SO_4^{-2}) to sulfide (S^{-2}) in anoxic conditions. The bacteria decompose organic material during this process, producing neutralizing bicarbonates (HCO_3^{-1}). Thus, an initially neutral environment produces potential acidity (pyrite, FeS_2) and alkalinity (HCO_3^{-1}). Tidal flushing removes the bicarbonate while the pyrite remains.

Many shale areas are found along coasts as a result of tidal action along gently sloping shelves. Marine conditions occurring on the interior regions of continents throughout geologic history are responsible for pyrite deposition in these areas. The locations of problem shale formations may be connected to geologic time periods when marine conditions with high tidal action occurred. For example, in North America, extensive pyritic shale formations (Figure 18) were created 410 to 360 million years ago during the Devonian time period (Kentucky Geological Survey 2000b). Chattanooga Shale and other Devonian shales were created in relatively shallow formative marine environments when significant regions of the country were covered in ocean water only several tens of meters deep (Scheiber 1994). A diagram of the geologic time scale is shown in Figure 19.

Figure 18 – Locations of typically pyritic Devonian Shales in North America. Modified from (Ettensohn 1998).

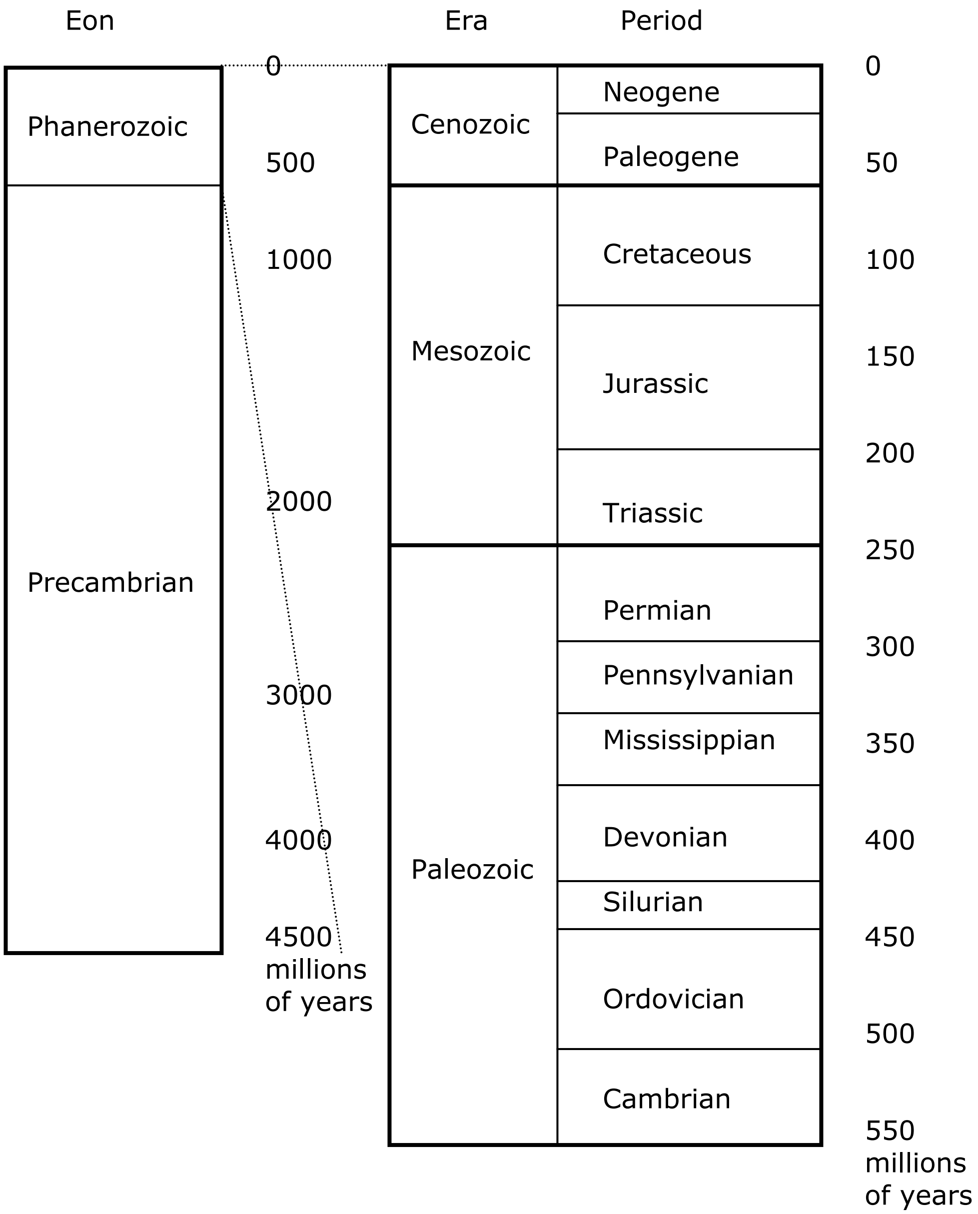


Figure 19 – Geologic time scale, recreated from www.uky.edu/KGS/.

Certain types of shale have characteristic mineralogy resulting from their formative environments. Shales formed in a marine environment generally contain chlorite. Kaolinite is consistently found in shales created in nonmarine environments. Siderite may also be indicative of a nonmarine formative environment (Shamburger et al. 1975).

Table 5 gives examples of shales created in marine or estuarine environments that are known to have significant pyrite content.

Table 5 – Examples of Pyritic Shales Created in a Marine or Estuarine Environment	**Reference**
Newland Formation – beds of shale up to 60m thick contain approximately 10^8 tons of pyrite; Mid-Proterozoic Age; Eastern Belt basin in Montana	(Schieber 1995)
Sevier, Chattanooga, Athens, and Rome Formations; Devonian Age; Eastern USA (Tennessee, Virginia, Kentucky)	(Belgeri and Siegel 1998; Schieber 2000)
Millboro Shale; Devonian Age; Virginia, USA	(Woodard 1998)
Crab Orchard Formation; Devonian Age; Kentucky, USA	(Diaz 1987)
Ohio, or New Albany, Formation; Upper Devonain Age; Ohio, Kentucky, and Tennessee, USA	(Shamburger et al. 1975)
Pierre shale; present under a large part of the Great Plains of the USA and in Canada	(Fanning and Burch 2000)
Calcareous, blue-grey marine Taylor shales; Cretaceous age; Texas, USA	(Mesri et al. 1994)
Shale beds associated with the Pennsylvanian and Mississippian coal beds; Eastern USA	(Rader 2002)

3.1.2 Visual indications of shales created in a marine or estuarine environment

Several visual clues can help with the recognition of shales created in a marine or estuarine environment. Such shales are commonly dark gray to black in color as a result of microcrystalline pyrite mineralogy in these materials. Dark colors may also result from organic material trapped in the rock during formation (Leventhal 1998). The tidal action of waves reworking the seabed is characteristic of the depositional history of Devonian shales. Erosion surfaces, evident for example in Chattanooga Shale, are characterized by lag deposits containing quartz sand, bone fragments, and pyrite (Schieber 2001). Reworked pyrite occurs in these locations in the form of framboids, diagenically pyritized fecal pellets, and pyritic fills of Tasmanite cysts (Schieber 1998). Pyrite on these erosional surfaces can be 20-30 times more concentrated than in regular black shales.

Marine fossils may be evident in shales formed in marine or estuarine environments (Figure 20), although they are frequently replaced by pyrite nodules (Pellant and Phillips 1990; Grimes et al. 2002). Common marine fossils include sponges (Porifera), corals (Cnidaria), lamp shells (Brachiopods) (Figures 21 and 22), snails (Gastropods), clams (Pelecypods), squid-like animals (Cephalopods), crinoids (Echinoderms), and microscopic animals (Kentucky Geological Survey 2000a). Palynomorphs are microscopic, resistant-walled organic bodies, such as pollen and spores (O'Brien). These may occur in marine shales and are frequently visible in SEM photographs. Tasmanites are a type of spore-like planktonic algae commonly found in Devonian-Mississippian dark shales. In SEM photographs of shale surfaces perpendicular to bedding, the spores have a distinctive "worm-like" appearance, as shown in Figure 23 (O'Brien and Slatt 1980).

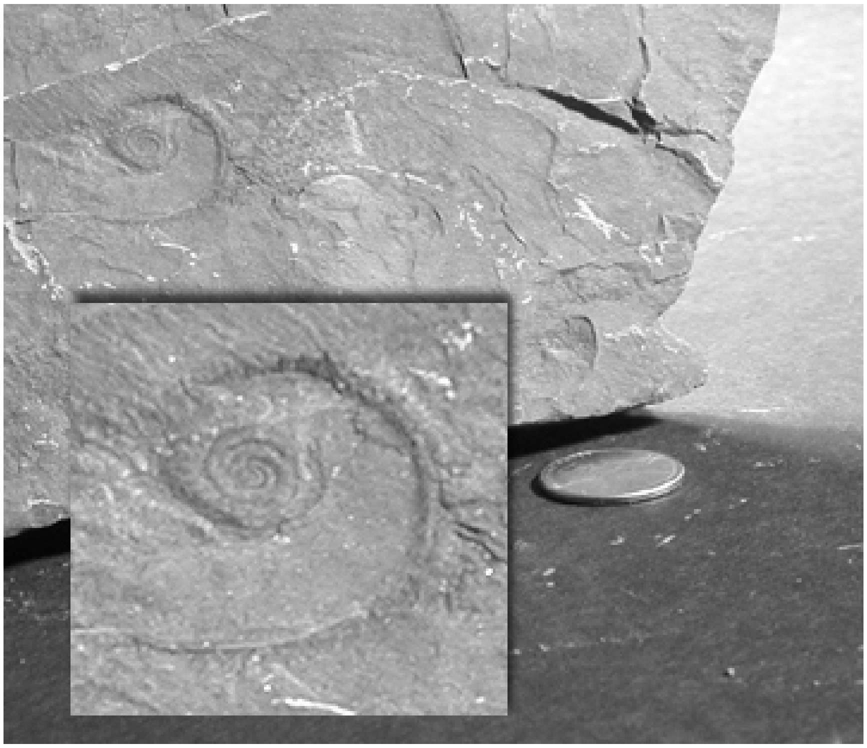
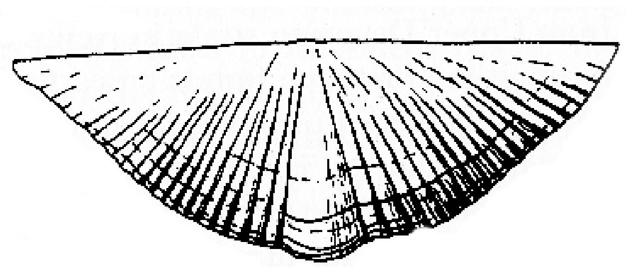
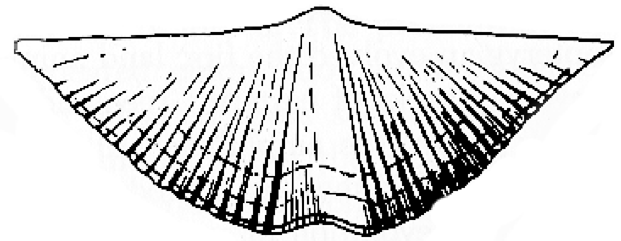


Figure 20 – Marine fossil found in Millboro Shale formation (Devonian age), along Rte. 100, Virginia. Note penny for scale.

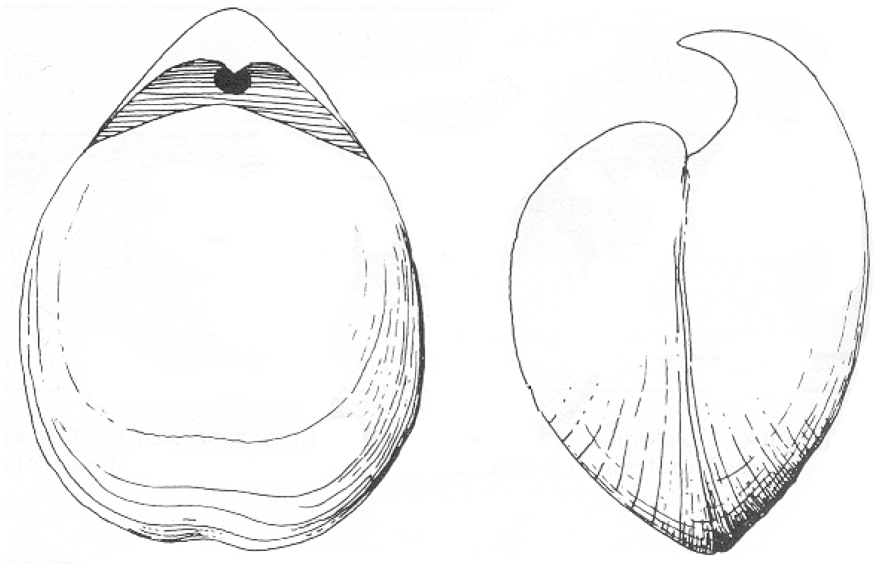


Mucrospirifer
dorsal view



Mucrospirifer
ventral view

Figure 21 – Devonian spiriferid (“winged” brachiopod), common in Devonian strata (Peterson et al.).



Stringocephalus

Figure 22 – Stringocephalus brachiopod commonly used to identify Middle Devonian strata (Peterson et al.).

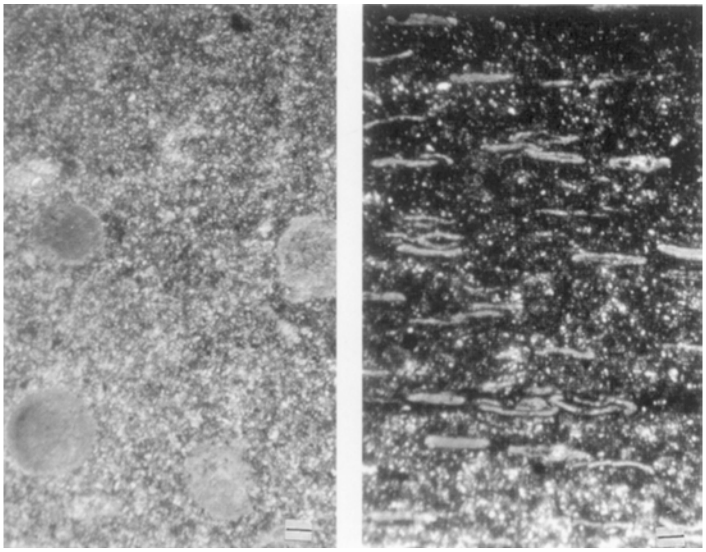


Figure 23 – SEM photographs of Marcellus shale formation, Devonian age, from Mason County, Virginia. The left photo is looking down at the bedding plane surface and shows circular Tasmanite spore-like bodies. The right photo is a cross-sectional view showing the worm-like appearance of these spores, from (O'Brien and Slatt 1980). Scale = 0.1 mm.

3.1.3 Fine-grained rock and soil with significant pyrite content

Soils with significant pyrite content have been extensively recognized and studied in coastal, estuarine environments. These soils, rich in pyrite due to their marine formative environment, are frequently referred to as “acid sulfate” soils. Acid sulfate soils are defined by the capability of producing sulfuric acid and are responsible for substantial acid drainage problems. They are associated with coastal, marsh and brackish lake sediments, valleys with poor drainage of sulfate-rich ground and surface water, dredged materials, mine spoils, and construction sites (Fanning and Burch 2000). The chemical composition of a young residual soil is predominantly a result of the chemical constituents of the underlying bedrock. Thus, pyritic soil may also be created from the weathering of pyritic rock. The transition from fine-grained rocks such as shales and mudrocks to soils is often difficult to define; however, problems from pyrite oxidation occur with all of these materials, regardless of their degree of induration.

Sulfidic materials and the various stages of sulfide accumulation and oxidation associated with acid sulfate soils have been clearly defined within the soil science discipline. Sulfidic materials, as defined by USDA-NRCS (1998), are mineral or organic soil materials with a pH ≥ 3.5, that contain oxidizable sulfur compounds and that, if incubated as a 1 cm thick layer under moist, aerobic conditions (field capacity) at room temperature, show a drop in pH of ≥ 0.5 units to a pH ≤ 4.0 (1:1 by weight in water) within 8 weeks. As stated in Section 1.1, geomaterials referred to as "sulfidic" in this report do not necessarily meet this more stringent USDA-NRCS definition.

The accumulation of sulfides in soil materials is known as sulfidization (also referred to as sulfidation or pyritization). Sulfuricization is the process during which sulfide-bearing materials are oxidized to produce sulfuric acid, with subsequent mineral weathering and new mineral phase formation from the dissolution products (Carson et al. 1982; Fanning and Fanning 1989). Sulfuricization may frequently result from geologic weathering.

Geomaterials experiencing sulfuricization are categorized into three idealized stages: presulfuricization, actively sulfuricizing, and postsulfuricization. These three processes may succeed one another within a period of a few years and may also occur in a single soil-geologic column (Fanning and Fanning 1989). The three stages of sulfuricization are defined by Fanning and Fanning (1989) as follows:

1. Presulfuricization: Sulfide-bearing materials existing in the presulfuricization stage contain essentially no sulfates, or only those sulfates associated with entrapped seawater, due to the prevention of oxidation. The pH may be ≥ 7. These materials may be sulfidic, as defined above, and are also referred to as potential acid sulfate soils.
2. Actively Sulfuricizing: Sulfide-bearing materials that are actively sulfuricizing are exposed and experiencing oxidation. These materials, also referred to as active sulfate soils, may have a pH < 3.5 and sulfuric acid is being produced. Active sulfate soils may be identified by a sulfuric soil horizon. A soil horizon is a parallel soil layer distinguished from adjacent soils by distinctive properties produced by the soil forming process. A sulfuric horizon is composed of mineral or organic soil material having a pH ≤ 3.5 with evidence that the low pH is a result of sulfuric acid. Such evidence is the presence of at least one of the following: (1) jarosite concentrations as indicated by color (Munsell hues of 2.5Y or yellower and chromas of 6 or higher), (2) directly underlying sulfidic materials, or (3) 0.05% or more of water soluble sulfate (USDA-NRCS 1998).

3. Postsulfuricization: Materials in this stage, also known as postactive or pseudo acid sulfate soils, have totally oxidized and the pH is typically ≥ 4. Evidence of postsulfuricization includes: (1) the presence of jarosite or other sulfates (e.g., gypsum, barite) with underlying materials showing evidence of presulfuricization and/or active sulfuricization, or (2) underlying materials showing evidence of presulfuricization and/or active sulfuricization and the column is lithologically continuous.

Coal and associated rocks like shale ore are common and more localized examples of fine-grained pyritic rocks. Coal is a sedimentary rock created in a reducing environment by the accumulation, alteration, and compaction of organic plant remnants (Skousen and Ziemkiewicz 1996). Shale ore deposits result from hydrothermal fluid deposition (Rader 2002). The main type of sulfur found in coal and associated rocks is sulfide sulfur, occurring primarily in the forms of pyrite and marcasite (Wilkes et al. 1992). Pyrite coatings are sometimes found on vertical fracture surfaces in coal seams, indicating the introduction of sulfur following the formation of coal. However, most pyrite in coal-bearing rocks occurs as crystalline grains intermixed with the organic coal constituents (Skousen and Ziemkiewicz 1996). Examples of pyritic soils, coal beds and fine-grained rocks are given in Table 6.

Table 6 – Examples of Fine-Grained Rock and Soil Types with Significant Pyrite Content	**Reference**
Coastal sediments of the Chesapeake and Tabb Formations and Lower Tertiary deposits, of the Virginia Coastal Plain Province	(Orndorff 2001; Rader 2002)
Quantico Slate and Arvonia Slate, Virginia	(Rader 2002)
Blackband or clayband ironstones	(Blatt et al. 1980)
Coastal soils in the Arabian Gulf coastal region, Saudi Arabia	(Azam and Abduljawad 2000)
London Clay	(Morgenstern 1970)
Lower Lias Clay	(Chandler 1972)
Coal beds and seams, such as those present in the Illinois Basin	(Skousen et al. 1987; Evangelou et al. 1998; Rader 2002)
Slate and phyllite in the Piedmont and Blue Ridge formations; Eastern U.S.	Orndorff 2001

Pyritic soils, as well as pyritic rock, can be subject to problems with heave. As previously defined, sulfide-induced heave results from the oxidation of sulfides (e.g., pyrite) to sulfates (e.g., gypsum) in soil, with an associated volume increase. However, sulfates produced by the oxidation of pyrite in soils can lead to additional problems. Heave problems associated with sulfate formation in pyritic soils can in some cases be exacerbated by the addition of calcium-based stabilizers (e.g., lime, Portland cement, type C fly ash) (National Lime Association 2000). Sulfate-induced heave problems, perhaps most commonly associated with lime stabilization projects, may result from the formation of expansive sulfate minerals such as ettringite or thaumasite when lime is combined with gypsum and a swelling clay such as montmorillonite (Mitchell 1986). In this way, adding lime to sulfate-bearing soils may cause serious geotechnical complications, a situation that could perhaps be avoided by improved cross-disciplinary communication about these complex relationships. Such sulfate-bearing soils are often residual soils; sites known for problems with sulfate-induced heaving of soils are commonly underlain by pyrite-bearing bedrock (Burkart et al. 1999).

Soils with high shrink-swell indices and high plasticity indices (PI) such as montmorillonite clay (frequently found overlying pyritic shale bedrock) are typically limed. A long-term increase in strength through the formation of pozzolan cement is the desired result of adding lime to these types of soils. Lime reduces the plasticity of clay (often resulting in a PI of zero), and therefore increases the shear strength (Petry 1994). Ideally, the addition of lime causes the dissolution of silica (Si) and aluminum (Al) from the clay. Pozzolanic cements, calcium silicate hydrate (CSH) and calcium aluminum hydrate (CAH), are then created as the silica and aluminum react with calcium and water. However, significant problems may occur when unstable soils with high sulfate contents are treated with lime. As a result of lime application, these soils may experience great levels of expansion and heave due to the growth of expansive sulfate minerals. Soils that have been affected by gypsum growth and sulfate-induced expansion are altered from the original compacted clay to loose, fluffy-textured, granular material. Significant strength loss in soils can be caused by as little as 1.5% gypsum (Nettleton et al. 1982). Gypsum growth causes an increase in the hydraulic conductivity. This exacerbates the expansion problem in sulfate-bearing soils as more water is allowed to infiltrate and support the growth of additional expansive minerals such as ettringite ($Ca_6[Al(OH)_6]_2$ $(SO_4)_3$ $26H_2O$) and thaumasite ($Ca_6[Si(OH)_6]_2$ $(SO_4)_2(CO_3)_2$ $24H_2O$). Both ettringite and thaumasite are extremely fine grained and very difficult to identify by visual inspection (Burkart et al. 1999).

Water is needed for the necessary hydration of ettringite and thaumasite and also transports dissolved sulfates that support further expansive mineral formation. Ettringite is formed when lime, water, gypsum, and montmorillonite clay react, as shown in the following reaction (Burkart et al. 1999):

$$3CaO\ (\text{lime}) + 3CaSO_4{\cdot}2H_2O\ (\text{gypsum}) + Al_{12}Si_4O_{10}(OH)_2^{-1}\ (\text{montmorillonite}) + 31H_2O \rightarrow Ca_6[Al(OH)_6]_2\ (SO_4)_3\ 26H_2O\ (\text{ettringite}) \qquad (10)$$

If gypsum and swelling clays are present in a soil, adding lime to increase strength is counterproductive unless the gypsum is taken into account. The desired strength effects from adding lime are not obtained in these soils if lime reacts to form ettringite or thaumasite and there is insufficient additional lime to achieve the required strength gain. Expansive mineral growth results in an increased PI (Plasticity Index), a decrease in pH, three-dimensional swell, a significant increase in moisture, and a significant decrease in the soil's dry unit weight (Petry 1994). Growth of the hydrous calcium aluminum sulfate ettringite has been reported to cause up to a 100% increase in volume and very high swell pressures (Hunter 1988).

Chemical analyses (e.g., the Soluble Sulfate test) used for determining the amount of sulfate present in soil, and the subsequent heave potential, are discussed in Section 4.1.5.6. Several methods of reducing the heave potential of sulfate-bearing soils have proven to be successful. If the total gypsum concentration of a soil is known, then an attempt to account for the formation of expansive minerals can be made by adding enough lime to completely react with the gypsum while still leaving enough lime to add the necessary strength to the unstable soil (Burkart et al. 1999). Providing adequate mellowing time immediately after the application of the lime can force the expansive sulfate minerals to form prior to compaction, thus preventing damage to the final stabilized soil system (National Lime Association 2000). Adding the necessary amount of lime in two separate increments (progressive, double application), rather than increasing the initial amount of lime to compensate for expansive mineral formation, also utilizes mellowing time to provide successful stabilization.

3.1.4 Visual indications of pyritic fine-grained rock and soil

Visual identification clues for pyritic rock and soil include the presence of cubical pyrite crystals (fool's gold) (Figure 24), gold flakes of iron oxide (yellowboy), clear gypsum crystals, and yellow jarositic alteration products (Belgeri and Siegel 1998). Gold flakes of yellowboy created by iron oxides [$Fe(OH)_{3(s)}$] have color variations that depend on the form and amount of iron present (Sobek et al. 1978). Pyrite may also appear black as a result of finer-grained particle size and weathering (Sobek et al. 1978). Appendix E contains color photographs of some of these pyritic materials to aid in visual identification. In addition to visual clues, pyritic materials also may often be identified by an odor of sulfur (Fanning et al. 1993).

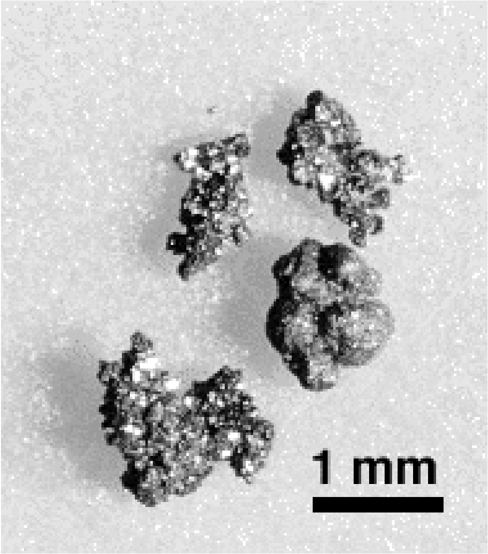


Figure 24 – "Fool's gold" pyrite crystals. Photo from www.soest.hawaii.edu/.

Micas, which are typically flaky and metallic in appearance, can be quite similar to flaky forms of pyrite visually but differ in several respects. Mica glistens on only one surface when tilted while pyrite glistens on all surfaces. Also, pyrite is opaque while mica is more translucent (Sobek et al. 1978).

In general, unweathered pyritic materials tend to be dark colored while materials in which pyrite has been oxidized tend to be lighter in color. Unweathered shale with sulfur still predominantly in the sulfide (pyritic) sulfur form may be almost black in color. Shales that have been weathered by pyrite oxidation (with sulfur predominantly in the sulfate form) will typically have more of a grey coloration. While the black color of shales may be attributed to other factors such as high levels of carbon, pyritic shales may frequently be dark, low-carbon rocks (Blatt et al. 1980).

Fine-grained pyrite is often difficult to detect visually. An aid to the identification of rock and soil with significant pyrite content is the Munsell Color Chart. These charts use hue, value (lightness), and chroma (color saturation) to establish a standard color system that provides uniformity in geologic descriptions. The Munsell system has defined numerical scales with visually uniform steps for each of these attributes. The Munsell Color Chart displays sets of colored chips arranged according to these scales (Figure 25) (www.munsell.com). Hue indicates the dominant spectral color (red, yellow, green, blue, and purple) and is related to the wavelength of light. Value measures the level of lightness or darkness and relates to the amount of total reflected light. Chroma defines the strength or purity of color or the departure from neutral with the same degree of light (Sobek et al. 1978).

The Munsell color notation is in the form *HAB v/c* where *H* is a numeral corresponding to the *AB* color hue (*H* may range from 0-100, extending throughout the color spectrum, as shown in Figure 26). Value is defined by number *v* (with a value of 0 representing pure black and 10 representing pure white). Chroma is defined by number *c* (with a chroma of 0 representing neutral colors and 30 representing fluorescent colors). A neutral (N) color designation, common for pyritic shales, has value but no chroma or hue. Examples of Munsell designations include 10GY 7/2 (Pale yellowish green; hue = 10GY, value = 7, chroma = 2) and 5G 7/2 (Pale green). The Geological Society of America (GSA) Rock-Color Chart (Goddard et al. 1970) shown in Figures 25 & 27 is the reference most appropriate for rock and is available for approximately $35 from several sources, including The Geological Society of America (granite.geosociety.org/). The Munsell Soil Color Chart is the reference most appropriate for soils and is also available from several sources, including Munsell Color Services by GretagMacbeth (www.munsell.com/) or ASC Scientific (www.ascscientific.com/) for approximately $100.

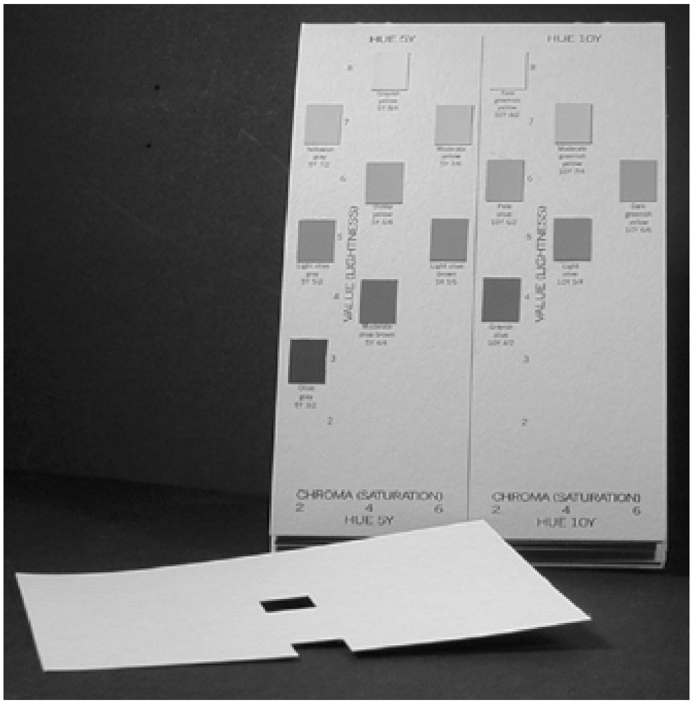


Figure 25 – Set of color chips from Munsell Color Chart. The card in the foreground is a mask used to isolate rock color.

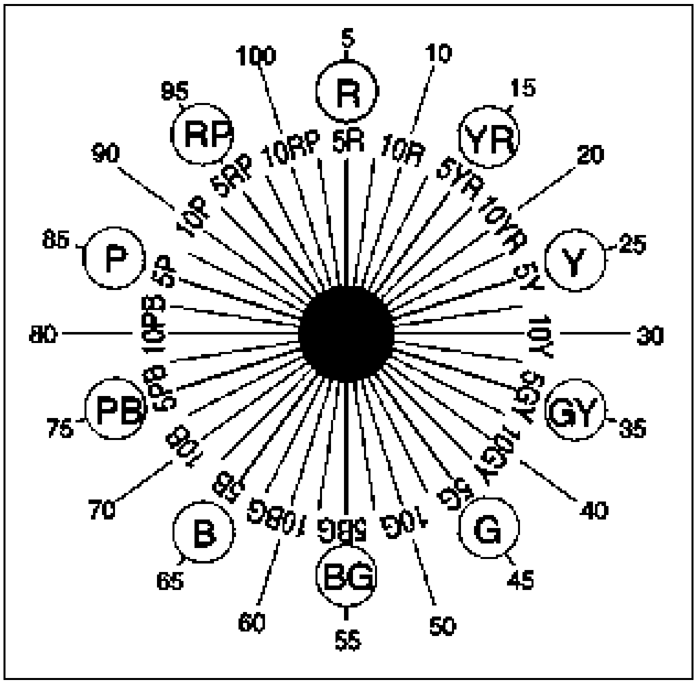


Figure 26 – Munsell hue designations. Figure from www.munsell.com.

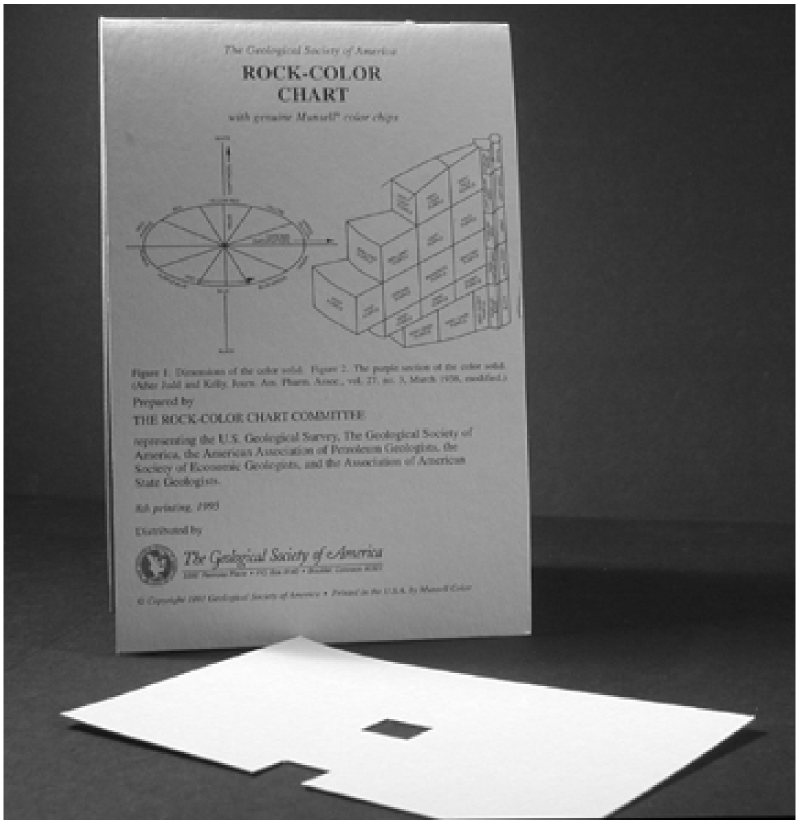


Figure 27 – Munsell Rock Color Chart.

The following Munsell color guidelines for pyritic geomaterials are defined by Sobek et al. (1978). Chroma is the easiest color attribute to recognize. Higher values of chroma (≥ 3) are typical of materials in weathered, oxidized zones. Zero or low chromas (corresponding to dark shades of gray) occur in rocks below the depth of pyrite oxidation. However, if leaching of iron oxides has occurred in weathered soils and rocks near the surface, low chromas may also result. Pyritic materials with a high sulfur content (> 1.0% sulfur) may have a low chroma (≤ 2) and a black streak or powder with a value ≤ 3. Dark colored clays or low carbon silty shales are indicated by a medium to light grey powder with a Munsell color value ≥ 4. Chromas ≤ 2 often indicate sufficient pyrite to cause a pH < 4.0 upon oxidation, while chromas ≥ 3 typically correspond with negligible percentages of pyritic sulfur. These Munsell color guidelines are summarized in Table 7.

Jarosite, a common sulfate alteration product of pyrite oxidation, is very easy to detect by its distinctive yellow coloration. Jarosite has hue ≥ 2.5Y or yellower and typically has chroma ≥ 6, though chromas of 3-4 can occur (USDA-NRCS 1998).

Table 7 – Munsell Color Guidelines for Pyritic Geomaterials [from (Sobek et al. 1978; USDA-NRCS 1998)]

Geomaterial Description	Munsell Color Designation
Weathered, oxidized material	Chroma ≥ 3
Unweathered material	Chroma < 3
Pyritic material > 1.0% sulfur	Chroma ≤ 2 Black streak or powder with value ≤ 3
Dark colored clay or low carbon silty shale	Powder with value ≥ 4
Pyritic material that can create a pH < 4.0 as a result of pyrite oxidation	Chroma ≤ 2
Material with negligible pyritic sulfur	Chroma ≥ 3
Jarosite	Hue ≥ 2.5Y Chroma ≥ 6

The amount of calcium in a pyritic earth material is a key factor in the formation of gypsum. Calcite impacts the color value of calcareous shales by affecting carbon absorption during formation (Hosterman and Whitlow 1980). Shales deposited in high-calcium environments tend to be darker (lower color value). In a study on Munsell color values of Devonian shales by Hosterman and Whitlow (1980), shales deposited in high-calcium environments range from 4.0 – 5.5 on the Munsell color value system and shales formed in low- or no-calcium environments typically range from 4.8 - 6.1.

Examples of recorded Munsell color designations for pyritic, calcareous shales include: 10 YR 4.4:0.5 for dark gray samples of the Sonyea Formation (averaging 5% pyrite and 5% calcite); N 6.0 (neutral) for samples of the Java Formation (averaging 5% pyrite); and N 3.4 for samples of Millboro Shale (averaging 5% pyrite and 25% calcite) (Hosterman and Whitlow 1983).

A color insert of examples based on these Munsell color designations is included in Appendix E.

3.1.5 Rocks with recognized potential for acid production from sulfide minerals

Acid mine drainage (AMD) and acid rock drainage (ARD) stemming from pyrite oxidation are significant problems in many areas of the world (Caruccio et al. 1977; Byerly 1996; Schaeffer and Clawson 1996; Skousen and Ziemkiewicz 1996; Evangelou et al. 1998). A brief list of examples of rocks with recognized potential for acid production is given in Table 8. The U.S. Bureau of Mines has estimated that over 19,000 kilometers of rivers and streams and over 73,000 hectares of lakes and reservoirs in the U.S. have been affected by AMD discharge (Evangelou et al. 1998).

Table 8 – Examples of Rocks with Recognized Potential for Acid Production from Sulfide Minerals	**Reference**
Coal beds throughout U.S. and Canada	(Evangelou et al. 1998)
Halifax Formation from the Meguma Group; Nova Scotia	(Fox et al. 1997)
Slates and phyllites in the Piedmont and Blue Ridge Provinces; Eastern U.S.	(Moore 1992; Orndorff 2001)
Cambrian and Ordovician shales and slates; Oslo, Norway	(Moum and Rosenqvist 1959)
Limestone and black shales from the Mont Palau quarry; Barcelona, Spain	(Chinchon et al. 1995)
Graphite schists of the Anakeesta formation, graphitic metasiltstones of the Murphy Belt, of the Nantahala formation, and thin layers of sulfidic rock within the Great Smoky Group, of the Ammons Formation – Horse Branch member; Eastern U.S.	(Byerly and Middleton 1981; Mathews and Morgan 1982; Morgon et al. 1982; Schaeffer and Clawson 1996)

3.1.6 Visual indications of sulfidic rocks with recognized acid potential

Damage resulting from AMD and ARD can produce distinctive orange iron precipitates along stream banks, culverts, etc., white calcium and aluminum precipitates, and black manganese oxide and hydroxide precipitates (Nordstrom 1982) as visual indicators of pyrite occurrence. The presence of gypsum, while not contributing to acid production, may indicate sulfidic geomaterials with acid producing potential. Additional clues include the corrosion of steel engineering structures, such as metal guardrails, metal culverts (Figure 28), or structural steel components (bolts, reinforcement bars). Failure to establish vegetation may be a noticeable effect of acid drainage. The effects of "sulfate attack" on concrete structures, including floor slabs, culverts, etc., are also strong visual indicators (Figure 29).

Figure 28 – Corrosion of corrugated steel buried culvert from pyrite oxidation. Photo from www.shef.ac.uk/civil/research/gge/.

Figure 29 – Concrete degradation resulting from "sulfate attack" and corrosion. Photo from corrosion.ksc.nasa.gov/.

3.1.7 Rock formations with recognized potential for heave from sulfide minerals

Many cases of sulfide-induced heave have been thoroughly documented in locations throughout the world. Selected formations with known sulfide-induced heave problems are listed in Table 9. Ranges of uplift pressures, recorded values of heave, and heave rates for various case studies are defined in Section 4.2.

Table 9 – Examples of Rock Formations with Recognized Potential for Heave from Sulfide Minerals	**Reference**
Billings Formation and Lorraine Formation mudrocks; Lower Paleozoic; Ottawa, Canada	(Penner et al. 1970; Quigley and Vogan 1970)
Westbury Formation of the Penarth Group; Triassic; Britain	(Hawkins and Pinches 1992a)
Hushpuckney shales; Kansas City	(Coveney and Parizek 1977)
Whitbian shales; Teesside, Britain	(Nixon 1978)
St. Mary's Well Bay Formation; Lower Jurassic; Glamorgan	(Wilson 1987)
Sevier Shale; Middle Ordovician; Tennessee and West Virginia	(Belgeri and Siegel 1998)
Eagle Ford Shales; Upper Cretaceous; Texas	(Burkart et al. 1999)
Conemaugh/Monongahlea Formation; Pennsylvanian and Permian; Pennsylvania	(Dougherty and Barsotti 1972)
Yunagaya Formation; Miocene; Japan	(Oyama et al. 1996)
Eastview Formation; Ottawa, Canada	(Grattan-Bellew and Eden 1975)
Sainte-Foy Formation; Quebec, Canada	(Berube et al. 1986)
Norwegian Alum shales; Late Cambrian; Oslo, Norway	(Jeng 1991)

3.1.8 Visual indications of sulfidic rocks with recognized heave potential

Formations with potential for sulfide-induced heave may be identified using visual indicators and knowledge of the proposed site. Prior heave problems in the vicinity of a site can help identify rock formations with sulfide-induced heave potential. Reviews of case histories and regional occurrences are likely the most informative sources. Physical evidence might include differential settlement or ground heave. Visual signs on established structures may include cracks, warped features, uneven joints or floors, etc., and other signs of differential movement (Figures 30 – 32).

Figure 30 – Floor heave resulting from pyrite oxidation, from (Carter 2002b).

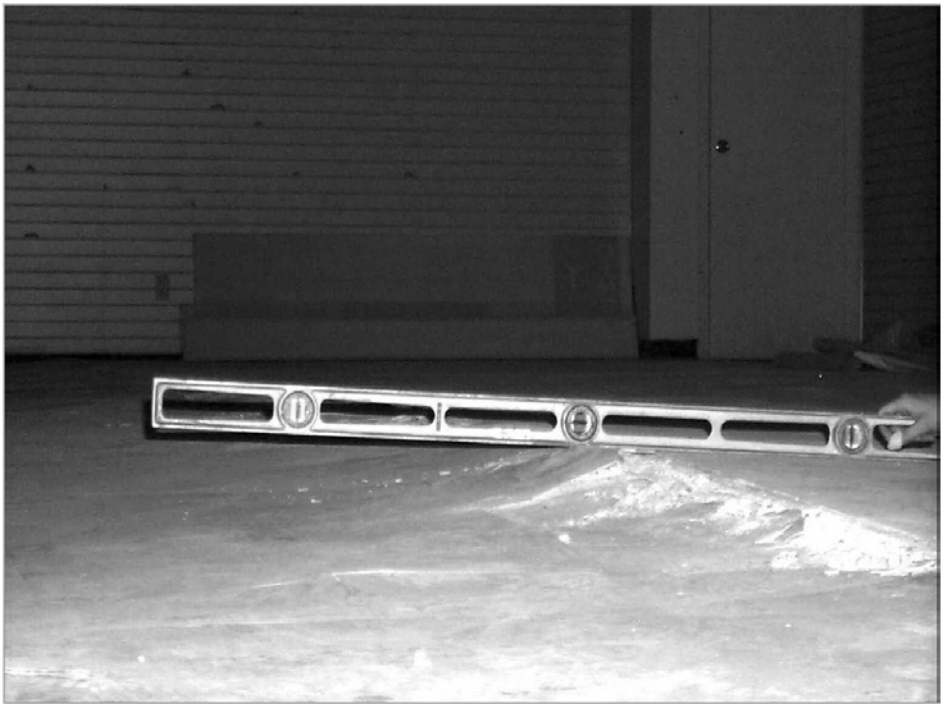


Figure 31 –Vertical displacement of floor from pyrite oxidation, from (Carter 2002b).

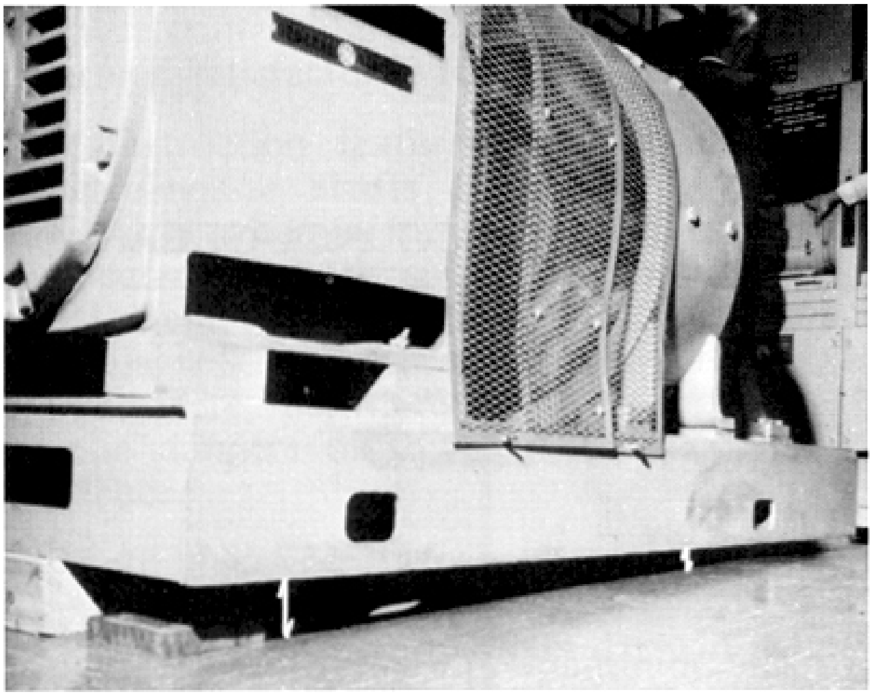


Figure 32 – Floor heave requires leveling of generators, from (Penner et al. 1972).

4 GUIDELINES FOR PRACTITIONERS

4.1 Recommended procedures for site evaluation

The need for a comprehensive site evaluation cannot be over-emphasized when dealing with pyritic geomaterials. The following guidelines define steps involved in the evaluation of the potential for geologic alteration due to pyrite oxidation. These guidelines should give a basic initial focus to the site evaluation. Additional steps and details should be added to characterize each specific site. Recommended procedures for a site evaluation include: a review of regional and site-specific geologic information, an early reconnaissance of the site, sampling of rock or soil for visual inspection, geophysical testing, and chemical testing. Documented procedures regarding site evaluations include ASTM D 420-98 Standard Guide to Site Characterization for Engineering Design and Construction Purposes (ASTM 1998a), ASTM D 3740-99c Standard Practice for Minimum Requirements for Agencies Engaged in the Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction (ASTM 1999a) and ASTM D 5522 Standard Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock, and Contained Fluid (ASTM 1999c).

4.1.1 Review of regional and site-specific geologic information

Information may be obtained from private, state, and federal sources. Modern standard soil surveys, county geologic reports, physical and mineralogical descriptions of rock formations, and 7.5-minute topographic maps may be good sources of information (Sobek et al. 1978). Sources of information include U.S. Geological Survey (USGS) or State Geological Survey geologic reports, aerial maps, U.S. Department of Agriculture - National Resources Conservation Service (USDA-NRCS) soil survey bulletins and the Soil Survey Geographic Database (SSURGO). The USDA-NRCS soil survey reports, available for every county in the U.S., are invaluable resources for various soil properties and other types of engineering information (e.g., sulfate content, pH, Atterberg Limits, approximate depths to bedrock, corrosion risk) specific to the given soil series on a site. If prior work has been done in the same area, it would be beneficial to review associated material. Air photo interpretation methods or remote sensing may be used to identify rock and soil conditions (Shamburger et al. 1975).

A form of remote sensing that can detect sulfidic geomaterials (and secondary minerals such as gypsum and jarosite) on a regional scale is Airborne Visible/Infrared Imaging Spectrometers (AVIRIS) (Swayze et al. 1996). Materials absorb and scatter sunlight at specific wavelengths. Each mineral has a unique spectral signature related to chemical composition, grain size, and other factors. Therefore, subtle differences in the reflectance spectra of minerals can indicate major differences in chemistry or some physical parameters (King et al. 1995). The secondary minerals (e.g., gypsum, jarosite) created by the pyrite weathering process produce spectrally detectable concentric zones around areas near the surface that contain significant amounts of pyrite. These mappable zones make imaging spectroscopy an effective tool for identifying these minerals (Swayze et al. 1996). The AVIRIS technology has been used by the USGS, NASA, and the EPA for remote mineral mapping, particularly in arid parts of the western United

States. In a USGS study of the area around Summitville, Colorado, the AVIRIS instrument was flown in an ER-2 aircraft (a modified U-2 spy plane) at 19,800 meters (65,000 feet). The swath width was approximately 11 kilometers. This study successfully mapped seven minerals, including goethite, hematite, K-jarosite and Na-jarosite (King et al. 1995).

Websites that may prove to be helpful references with respect to regional and site-specific geologic information include:

- USGS Homepage, www.usgs.gov
- USGS National Mapping Information, mapping.usgs.gov
- List of State Geological Survey Offices, http://web.umr.edu/~library/geol/geoloff.html
- USDA-NRCS Homepage, www.nrcs.usda.gov/
- USDA-NRCS National SSURGO Database, www.ftw.nrcs.usda.gov/ssur_data.html
- USGS Spectroscopy Lab, speclab.cr.usgs.gov

Knowledge about the location and behavior of the groundwater conditions of a site is an important part of defining the potential for pyrite oxidation. Although microbial action and the presence of dissolved oxygen in groundwater may allow oxidation to occur under saturated conditions, the most significant problems with heave and/or acid production resulting from pyrite oxidation are associated with the presence of both air and water. In nature, pyrite oxidation occurs predominantly in the partially saturated near-surface zone above the water table (Taylor 1988). Studies have shown that the diffusion of oxygen in unsaturated mine waste rock piles is the dominant rate-limiting step of the oxidation process (Nordstrom and Alpers 1999). Raising the local groundwater table to create permanently saturated, anaerobic conditions is a fairly common mitigation option used to halt the pyrite oxidation process. Groundwater fluctuations or undefined groundwater conditions may present significant problems in the stability of a structure as material thought to be stable becomes exposed to air and initiates oxidation processes.

4.1.2 Early reconnaissance of the site

One of the most important measures that can be taken to avoid sulfide-induced heave, acid production, and other problems related to pyrite oxidation is a comprehensive site reconnaissance for planned geotechnical projects. Knowledge of problem formations, identifying characteristics, and the degree of shale weathering that has occurred can establish a comprehensive understanding of a site's potential for pyrite oxidation. It should be recognized that ground chemistry can change significantly throughout a relatively small area (Cripps et al. 1993). The importance of site reconnaissance investigations and how they are performed is frequently emphasized. Investigations should be based on identifying potentially problematic materials, the chemical processes involved, and the visual indicators. Specific guidelines pertaining to a site reconnaissance are defined in Section 3.

4.1.3 Grab samples and drilled core samples for testing

Taking rock/soil drilled core samples and grab samples is an important part of a comprehensive site evaluation. Rock core samples should be taken in accordance with established coring methods such as ASTM D 2113 Standard Practice for Rock Core Drilling and Sampling of Rock for Site Investigation (ASTM 1999b). The cores may be examined visually for physical evidence of weathering, the presence of calcite streaks, and effects of pyrite oxidation (Belgeri and Siegel 1998). If further analysis is deemed necessary based on potential for pyrite oxidation, chemical testing may also be performed on rock core samples obtained during the site reconnaissance.

It is important to note when sampling that pyrite deposits often display significant variation horizontally, accumulating in clusters or random pockets rather than blanket deposits. Samples taken within centimeters of one another have displayed horizontal variations in pyrite content of up to 4% (Evangelou and Zhang 1995). Vertical variations within a particular pyrite deposit typically tend to be less abrupt.

4.1.4 Geophysical testing

Geophysical testing has proven to be a useful, non-invasive method of detecting problematic levels of pyrite concentrations. Induced Polarization (IP) and Self-Potential

(SP) are two geophysical methods commonly used for this purpose (Sato and Mooney 1960; Hovdan and Bolviken 1984; Khesin et al. 1993; Anderson et al. 1999; Campbell and Beanland 2001). The Induced Polarization method involves blocking induced ionic current that is applied to soil just below the ground surface. The apparent resistivity of the tested geomaterial, which is a function of soil/rock type, degree of saturation, and pore fluid, is measured as the frequency of the applied current is altered. Changes in apparent resistivity indicate the presence of metallic minerals (Byerly 1996; Moore and Trolinger 1997).

The Self-Potential method measures various (natural or spontaneous) potentials that are produced in soil and rock by mineralization differences, electro-chemical action, fluid flow, etc. Fixed-base electrodes are used during Self-Potential testing to measure the interaction between the natural oxidation-reduction potential gradient of the earth and electronically conductive minerals such as sulfides (Army Corps of Engineers 1995; Moore and Trolinger 1997).

4.1.5 Chemical testing

Chemical testing should be performed on materials to determine the weathering potential of a sulfidic material. As previously mentioned, the issue of concern is the amount of sulfide (pyritic) sulfur in a sample, which indicates the degree of potentially oxidizable material present. Many test procedures are used to obtain this information, with preference to method seemingly established by each discipline. General test methods include visual identification and x-ray diffraction analysis of the bulk sample of a material to identify mineral constituents (Shamburger et al. 1975) and pH testing to indicate the state of the natural environment. Tests specific to determination of acid production include Acid Base Accounting (ABA) (Sobek et al. 1978; Skousen et al. 1987; Sparks et al. 1996) and hydrogen peroxide (H_2O_2) oxidation methods (Sobek et al. 1978; Finkelman 1986; O'Shay et al. 1990; Jennings et al. 2000). The amount of gypsum present in a sample may be determined using soluble sulfate testing (Petry 1994) or a calcium analysis (Hawkins and Pinches 1992a). Total sulfur determination (Sobek et al. 1978; Sparks et al. 1996), which may be included as part of the ABA test procedure, and methods of sulfur fractionation are used by engineers to determine heave potential by defining the total sulfur, sulfide sulfur, sulfate sulfur, and organic sulfur contents (Belgeri and Siegel 1998). Other methods used to determine heave potential include the free swell test, the modified swell test, and induced gypsum crystal growth. Although swell tests are simple and inexpensive, they are very time-consuming as they are based on measuring the rate of pyrite expansion in laboratory samples, which occurs over long periods of time (Dubbe et al. 1984). Heave in shale resulting from induced gypsum crystal growth is measured using one-dimensional consolidometers; however, this test may not be a completely accurate representation of field conditions in which the oxidation of pyrite produces gypsum.

Important benchmarks relating problematic sulfidic material to testing procedures include:

1. Pyrite-related problems have resulted from materials containing as little as 0.1% sulfide sulfur (Penner et al. 1972; Belgeri and Siegel 1998).
2. Material containing 0.1% sulfide sulfur produces an amount of sulfuric acid that requires 3.125 tons of calcium carbonate to neutralize 1000 tons of the material (Sobek et al. 1978; Skousen and Ziemkiewicz 1996).
3. According to Nixon (1978), shales with potential for sulfide-induced heave will have a total sulfur content (recalculated as SO_3) greater than the acid soluble sulfate (sulfate sulfur) content. Also, in regard to the potential for gypsum formation, the acid soluble calcium content needs to be greater than 0.5%.
4. Potentially acidic material is defined as "any rock or earth material having a net potential deficiency of 5.0 tons of calcium carbonate equivalent or more per 1000 tons of material" (Sobek et al. 1978).
5. An indication of potential heaving in sulfate-bearing soils is established at 2000 mg soluble sulfate/kg tested material and 10,000 mg soluble sulfate/kg tested material indicates potential for serious damage (Petry 1994).

The chemical tests mentioned thus far are known as static tests; they measure the concentration of minerals in a sample. Kinetic laboratory tests are performed to simulate cyclic weathering of a sample and measure the resulting chemical products. Kinetic tests employing accelerated weathering and leaching processes may be used to measure the rate of oxidation of pyritic material. Accelerated weathering conditions are created by establishing humidity, temperature, microbial action, and air circulation at levels conducive to pyrite oxidation. Leaching in a lab environment is performed by placing rock fragments or scaled columns of rock or soil into water-tight containers, flushing the containers with water, and taking measurements on the resulting leachate. Total sulfate, acidity, alkalinity, iron, and pH values are typically measured (Skousen et al. 1987; Byerly 1990). Standard equipment for simulated weathering include humidity cells (Caruccio et al. 1977; ASTM 1996a) and Soxhlet extractors (Sullivan et al. 1986). Results from kinetic laboratory tests performed by Jeng (1991) to study acid generation from the weathering of Norwegian Alum shales are shown in Figure 33.

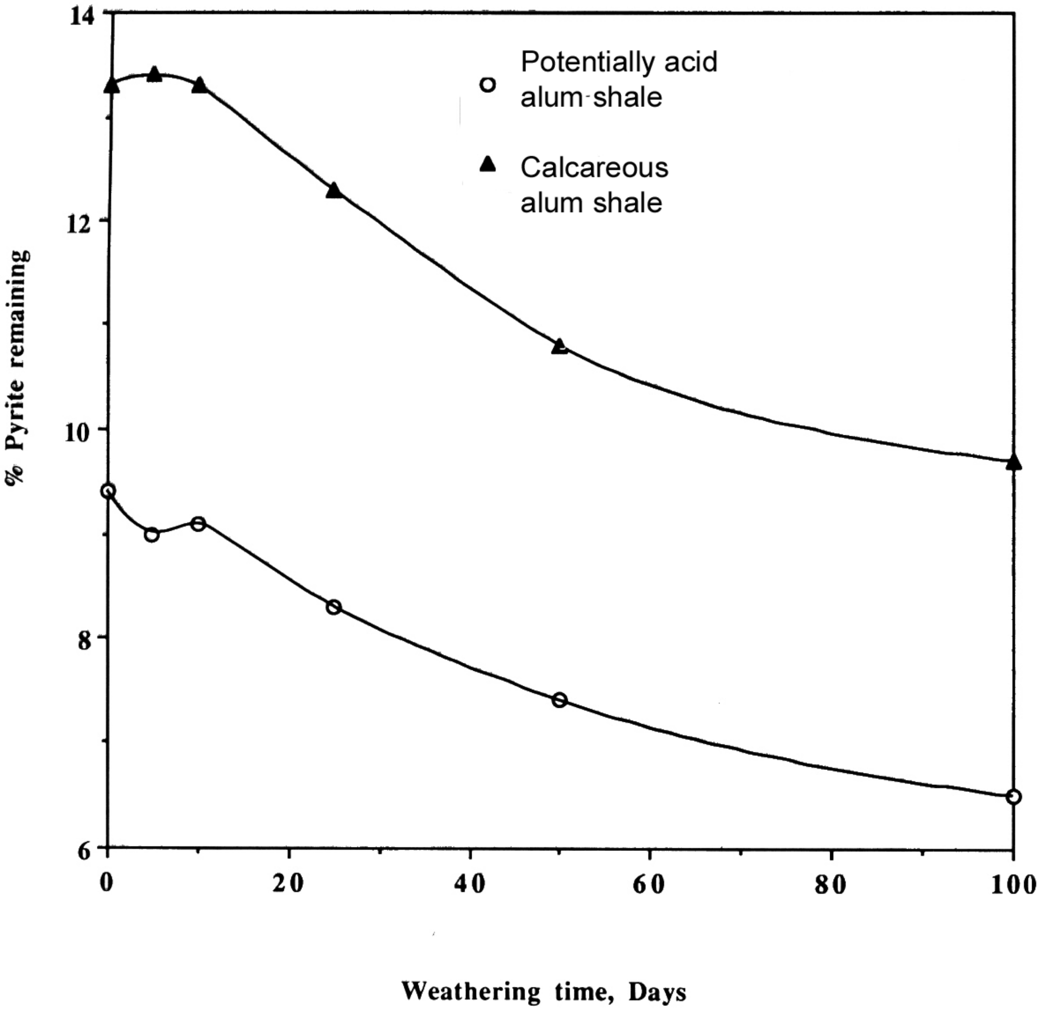


Figure 33 – Results of simulated weathering of Alum shales, from (Jeng 1991).

Emphasis should be placed on testing samples soon after extraction. The importance of testing samples soon after drilling is demonstrated by a study performed by Hawkins and Pinches (1986). Results of this study are shown in Table 10. Samples of black shale were taken from a freshly excavated face between a Carboniferous/Triassic unconformity and a limestone horizon of the Westbury Formation. These samples, stored in laboratory containers (stacks) for several weeks following recovery, demonstrated significant differences in sulfate contents (SO_3%) from the amounts found in fresh samples. The sulfate content in sample CSQ1 (a moderately weathered shale sample without significant alteration or discoloration) typically doubled within the span of one month (Hawkins and Pinches 1986). As oxidation progressed, increasing acidity was reflected in decreased pH values.

Table 10 – Iron and Sulfate Alterations in Shale Samples Over Time [modified from (Hawkins and Pinches 1986)]

Development of sulfate (%SO_3) in sample CSQ1 from an initial amount of 0.53% SO_3

Stack position	1 week	2 weeks	4 weeks
5 (top)	0.55%	0.93%	0.95%
4	0.69	0.88	1.09
3	0.65	0.78	1.18
2	0.78	0.86	1.14
1 (base)	0.53	0.54	0.80
Mean	0.64	0.80	1.03

Variable results of sulfate testing

Sample	Total Sulfur	Initial SO_3	Max. Potential SO_3
CSQ5	0.26%	0.21%	0.65%
CSQ4	0.23	0.30	0.57
CSQ3	1.19	0.70	2.97
CSQ2	2.48	0.28	6.19
CSQ1	1.45	0.53	3.62

pH measurements

Sample	Original pH	pH after one week (mean of 5 determinations)
CSQ5	7.8	7.5
CSQ4	7.6	7.4
CSQ3	6.3	5.7
CSQ2	6.6	4.5
CSQ1	6.5	3.8

As stated previously, several chemical tests are applicable for the testing of sulfuric material in soils and rocks. The tests most commonly used in geotechnical work include the Acid-Base Accounting (ABA) test, total sulfur testing, sulfur fractionation, and the soluble sulfate test. These tests are briefly described below. A simple field method for the detection of sulfide sulfur is defined. A basic procedure for the hydrogen peroxide (H_2O_2) oxidation method commonly used in mining and soil science work is also summarized. More detailed procedures for Acid-Base Accounting, total sulfur testing, sulfur fractionation, hydrogen peroxide oxidation testing, and pH determination are included in Appendix C.

4.1.5.1 Total sulfur test

Total sulfur testing determines the total amount of sulfur, occurring in the forms of sulfide (pyritic) sulfur, sulfate sulfur, and/or organic sulfur, present in a sample. The determination of total sulfur content has become a relatively precise and established process. Total sulfur high-temperature furnace combustion methods are simple, established, and accurate ways of determining total sulfur contents (Sobek et al. 2000). Several other methods of determining total sulfur contents exist, such as the Eschka method, leaching, and the modified Soxhlet method. However, these methods are typically less standardized or have been developed by the mining industry specifically for coal and are less applicable for geomaterials with mixed mineralogy (Sobek et al. 2000).

The total sulfur high-temperature combustion procedure is defined as follows (Sobek et al. 2000):

1. The sample is heated to approximately 1600ºC while a stream of O_2 is passed over the sample.
2. The sulfur dioxide (SO_2) released through combustion can be measured in several ways. Using a LECO Induction Furnace with Automatic Sulfur Titrator (LECO Corp., St. Joseph, MI), the SO_2 is collected in a 0.2M hydrochloric acid solution containing potassium, iodine, starch, and a small amount of potassium iodate.
3. The solution is then titrated with a standard potassium iodate solution to determine sulfur content.

4. Using infrared absorption, the resultant SO_2 gas is detected by infrared adsorption and compared to a standard calibration.

A more detailed procedure for the total sulfur combustion method (Procedure 3.2.4 by Sobek et al. (1978)) is included in Appendix C.

The total sulfur value is sometimes used as an accurate estimation of the sulfide sulfur content of a sample. In these cases, if the amount of total sulfur occurs in the sulfide sulfur form, the potential for sulfide-induced heave and the calculation of maximum potential acidity (for ABA testing) correspond to the actual potentials for heave and acid production. However, if a significant portion of the sulfur occurs in the sulfate or organic sulfur forms, these estimated sulfide sulfur values will be erroneously high. In cases where this may be an issue, testing to determine the actual fractions of the various sulfur forms present should be performed (Sobek et al. 1978).

4.1.5.2 Sulfur fractionation test

The most important aspect of sulfur fractionation testing in regard to sulfide-induced heave and other geotechnical problems relating to pyrite oxidation is the ability to define the types of sulfur involved. Total sulfur and sulfur (S) fractionation analyses are performed to define a material's total S, sulfide S, and sulfate S contents. The heave potential of a sulfidic material is directly correlated to the amount of sulfide (or pyritic) S present. Sulfide S represents the unweathered or unoxidized portion of sulfidic rock. The amount of alteration that has already occurred is represented by the sulfate S content. Sulfate S is a product of pyrite oxidation and gives a benchmark for the effects of weathering on a particular sample. When comparing the ratio of sulfate sulfur to total sulfur (sulfate S : total S), a ratio of approximately 100% represents an extremely oxidized or weathered sulfidic rock while a low ratio indicates an unweathered rock (Belgeri and Siegel 1998).

Sulfide S methods are less established and a wide range of methods are used by different testing laboratories (Brady and Smith 1990). Sulfate S is more easily measured and sulfide S is often determined by taking the difference between total S and sulfate S measurements. Methods commonly used to measure sulfide S contents by sulfur fractionation include a modified EPA method (Sobek et al. 1978; Sobek et al. 2000) and the Standard Test Method for Forms of Sulfur in Coal, ASTM D 2492 (ASTM 1998b). However, while ASTM D 2492 is commonly used for the determination of sulfide S, this procedure was developed for use on coal and is likely inappropriate for determinations on rock overburden, according to the ASTM Committee D-5 on Coal and Coke (Brady and Smith 1990). An ASTM/EPA combination method has been developed that attempts to minimize errors associated with each of these individual tests.

Another method of sulfide S determination is outlined in work done by Woodard (1998). During a study on pyritic Devonian Millboro Shales, sulfide S determination was performed using sodium carbonate digestion. For this procedure, a total sulfur analysis was performed using a carbon/sulfur analyzer. A weighed sample is then placed in a test tube and digested with sodium carbonate. The sample is heated, mixed, centrifuged, and dried. Following total S and sulfide S analyses, the sulfate S content may be obtained through calculations (Woodard 1998).

Although several alternative sulfur fractionation methods have been developed, the modified EPA method defined by Sobek et al. (1978) is one of the procedures most commonly used in the United States for identifying the different sulfur forms (Jennings et al. 2000). This method, also known as the HCl-Extractable, HNO_3-Extractable, and Non-Extractable Total Sulfur method, determines sulfide S by testing for the amount of nitric acid (HNO_3)-extractable sulfur. Sulfate S is determined by the amount of hydrochloric acid (HCl)-extractable sulfur present. The remaining non-extractable sulfur is mostly organic sulfur (Sobek et al. 1978). This modified EPA sulfur fractionation procedure is defined as follows (Sobek et al. 2000):

1. The sample is divided into three portions.
2. The total S content is determined by combusting one portion in a LECO S Furnace and then analyzing this portion without any pretreatment.
3. A second portion is leached with 4.8M hydrochloric acid (HCl) (to remove the sulfate S) and then combusted to determine the amounts of pyritic and organic S.
4. A third portion is leached with 4.8M hydrochloric acid and 2M nitric acid (HNO_3) (to remove the sulfate and pyritic S) and then combusted to determine the organic S.

5. The concentrations of each S form (pyritic, sulfate, and organic) are then calculated.

The HCl-Extractable, HNO_3-Extractable, and Non-Extractable Total Sulfur (Procedure 3.2.6) method for sulfur fractionation (Sobek et al. 1978) is cited and included in Appendix C of this report.

4.*1.5.3 Sulfide sulfur field method*

A simple field method procedure for the detection of sulfide sulfur in rocks, based on work by Fiegl (1958), is defined in McClellan et al. (1998). This field method uses an iodine-azide reaction (Eq. 11) to produce nitrogen when catalyzed by soluble and insoluble sulfides.

$$2NaN_3 \text{ (sodium azide)} + I_2 \text{ (iodine)} \rightarrow 2NaI + 3N_2 \text{ (nitrogen gas)} \qquad (11)$$

This test is based on the observation that sodium azide and iodine solutions do not react with one another under normal conditions. However, nitrogen gas bubbles are immediately produced when a source of sulfide S is present. While this reaction is catalyzed by sulfide S, no known effects occur from other sulfur forms, such as sulfate or organic S. This method was tested and found to indicate levels of sulfide S down to 0.3% (McClellan et al. 1998). While imprecise, this method may be used as an inexpensive, quick method of indicating the presence of sulfidic material.

4.1.5.4 Acid-Base Accounting (ABA) test

Acid-Base Accounting (ABA) is one of the most common methods for characterizing the acid potential of overburden rock and soil, especially in the environmental and coal mining industries (Skousen et al. 1987). ABA is a relatively simple, consistent, and inexpensive test. The analysis is based on the maximum potential acidity (MPA), neutralization potential (NP), pH, rock type, and depth below land surface of a material (Sobek et al. 1987). The main objectives of ABA include the identification of toxic or potentially acid-producing materials (defined by the amount of total or pyritic sulfur present) and the neutralization potential (defined by the amount of non-acid or calcareous materials present that may neutralize existing acid) (Skousen et al. 1987). ABA balances the MPA (represented as a negative value) to the NP (represented as a positive value). If the resulting balance is negative, then the geomaterial may be defined as acid-producing.

Several methods, as outlined by Sobek et al. (1987), are used to determine the acid potential (MPA) of a material including:

1. The determination of total sulfur content and calculation of acidity from a stoichiometric equation for pyrite oxidation.
2. The determination of Fe and calculation of acidity from a stoichiometric equation for pyrite oxidation.
3. Titration of acidity following oxidation of the sample by a strong chemical oxidant (e.g., hydrogen peroxide) or a simulated weathering procedure.

The NP is calculated from alkaline carbonates, exchangeable bases, silicates with weathering potential, or other rock sources with the ability to neutralize strong acids (as measured by their respective neutralization potentials) (Sobek et al. 1978). The NP is established by determining the amount of base required to neutralize an established amount of acid consumed by the pyritic geomaterial sample. NP values are typically expressed in terms of *tons* $CaCO_3$ *per 1000 tons of material* (ppt) (Kania 1998).

Methods for determining Maximum Potential Acidity by Total Sulfur Determination (Procedure 3.2.4) and the Neutralization Potential (Procedure 3.2.3), as defined by Sobek et al. (1978), are included in Appendix C.

The ABA test procedure has several limiting assumptions that should be considered when analyzing results. These assumptions include (Skousen et al. 1987):

1. The maximum potential acidity (MPA) and neutralization potential (NP) values represent maximum quantities from the entire rock analysis. It is unlikely that the chemical reactions involved (pyrite oxidation, etc.) will reach total completion in the field. Thus, the calculated maximum potential for acidity or neutralization will most likely be greater than the actual values occurring in the field.

2. ABA tests typically use total sulfur analyses to determine the MPA. Total sulfur analyses frequently overestimate the amount of sulfide (pyritic) sulfur in a sample because the other forms of sulfur may not be accurately accounted for.
3. Pyrite (acidity) and bases of a rock sample are assumed to weather at simultaneous rates. Reaction rates are most likely not equal, though ABA does not account for this difference.

4.1.5.5 Hydrogen peroxide oxidation test

Hydrogen peroxide (H_2O_2) oxidation testing is commonly used in the soil science and mining disciplines to determine the acid-producing potential of a geomaterial. This test method is based on the use of hydrogen pyroxide (30% H_2O_2 in deionized water) to rapidly oxidize pyrite, producing sulfuric acid (H_2SO_4) and iron hydroxide ($Fe(OH)_3$), as shown in Equation 12 (O'Shay et al. 1990).

$$FeS_2 + 15/2\ H_2O_2 \rightarrow Fe(OH)_3 + 2H_2SO_4 + 4H_2O \qquad (12)$$

The net amount of sulfuric acid produced by oxidation with hydrogen peroxide is then determined by titration with sodium hydroxide (NaOH).

The hydrogen peroxide oxidation method, also known as potential peroxide acidity (PPA) testing, determines the total potential acidity of a sample of geomaterial. The total potential acidity is the potential acidity plus the free acidity of the sample. The potential acidity is the acidity of the sample following pyrite oxidation and the free acidity is the acidity initially present in the sample (Barnhisel and Harrison 1976). The measured value of total potential acidity is directly related to the amount of total sulfur in the tested sample. While total sulfur (S) is defined as the combined amounts of sulfide (pyritic) S, sulfate S, and organic S, the acidity produced by peroxide acidity testing is predominantly from pyrite oxidation. The presence of certain sulfates (e.g., jarosite) may produce acidity, thus causing an overestimation of the calculated value of sulfide S. However, other sulfates (e.g., gypsum) do not produce acidity and will not affect the sulfide S value. Thus, the %S calculated from this test is considered to be an accurate estimate of the sulfide S content.

Leaching of the samples prior to peroxide acidity testing may be performed to remove any acid-producing sulfates and acid-neutralizing materials. The presence of acid-producing sulfates will cause an erroneously high estimate of the sulfide S content. Alkaline materials such as calcium carbonate ($CaCO_3$) or lime (CaO) neutralize the acidity produced by the sample, thus causing erroneously low values of potential acidity and sulfide S content.

Results of hydrogen peroxide oxidation tests, as done with ABA tests, are typically given in units of *tons* $CaCO_3$*/1000 tons material*, which represent the amount of calcium carbonate required to neutralize the acidity produced by 1000 tons of tested material. Values in these units (tons $CaCO_3$/1000 tons material) may be converted to %S using the established benchmark (previously defined in Section 4.1.5) which defines that a material containing 0.1% sulfide sulfur will produce an amount of sulfuric acid that requires 3.125 tons of calcium carbonate to neutralize 1000 tons of the material (Sobek et al. 1978; Skousen and Ziemkiewicz 1996).

Several procedures have been defined for the hydrogen peroxide oxidation method (Barnhisel and Harrison 1976; Sobek et al. 1978; Finkelman 1986; O'Shay et al. 1990; Jennings et al. 2000). Two of these procedures are included in Appendix C: (1) the Hydrogen Peroxide Method for Total Potential Acidity (Barnhisel and Harrison 1976) and (2) Procedure 3.2.11 Total Sulfur by Peroxide Oxidation (Sobek et al. 1978), which includes a method for leaching carbonates from the sample. An additional procedure for carbonate leaching, from O’Shay et al. (1990), is also included in Appendix C.

4.1.5.6 Soluble sulfate test

The potential for sulfate-induced heave/expansion of a certain soil sample may be determined by an accurate analysis of the sample’s soluble sulfate (e.g., gypsum) content. Soluble sulfate tests can be used to determine the potential of subgrade soils for sulfate-induced heave following the addition of chemical treatments such as lime. Water leaching through sulfate-bearing soils dissolves the sulfates in the soils and makes the sulfates more available for reaction with calcium to form ettringite or thaumasite. The soluble sulfate analysis is usually performed by quantitatively evaluating leachate from the problem soil (Puppala et al. 2002).

During a study of expansive clay soils in Texas, Petry observed the lack of existing standardized test procedures. This problem was addressed by defining test procedures for both the soluble sulfate analysis, which determines the amount of sulfates in a soil sample, and the three-dimensional swell test, which determines the amount of heave occurring in a clay sample (Petry 1994). This study placed an increased emphasis on identifying the potential for sulfate-induced heave of soils containing soluble sulfates. Following the investigation of both extraction fluids and ratios (fluid used : dry soil), a method was established using pure water (demineralized – deionized) and a fluid : soil ratio of 10:1. This method was deemed best for the extraction of soluble sulfates (Petry 1994). Benchmarks were established of 2000 mg soluble sulfate/kg tested material as an indication of potential heaving and 10,000 mg soluble sulfate/kg tested material indicating potential for serious damage (Petry 1994).

As noted by Petry, there are currently no ASTM standards established for sulfate measurements in soils. However, several other nonstandardized methods, including the method defined by Petry (1994), are used based on gravimetric analysis principles (Puppala et al. 2002). These methods include: EPA method #9038(18) (EPA 1986), Texas Department of Transportation Method (Tex-620-J Method) (National Lime Association 2000), U.S. Army and Air Force method (TM 5-822-14/AFJMAN 32-1019), the University of Texas at Arlington method (UTA) (Petry 1994), and a modified UTA method (Puppala et al. 2002).

4.2 Magnitudes, rates, and parameters governing the effects of pyrite oxidation

The damaging effects of pyrite oxidation including heave and acid production can develop rapidly. Even during the construction period, engineering properties may be altered, leachates produced, and minerals precipitated as a result of chemical changes (Cripps et al. 1993). Definitions of the anticipated timing, reaction rates, and potential uplift pressures are obviously key parameters for an engineering design involving sulfidic materials. The amount of time an engineering structure is expected to experience the additional, often extreme, increased stress induced by pyrite oxidation is also a very important design component.

4.2.1 Expected rates and magnitudes of swell pressures resulting from pyritic expansion

Various case studies (Dougherty and Barsotti 1972; Penner et al. 1972; Hawkins and Pinches 1992a; Belgeri and Siegel 1998) provide estimates for reaction times of material initially exposed by construction for specific sites and corresponding in-situ pyrite contents. However, an exact determination of swell pressures or time-rate of expansion is rarely possible for a specific formation or site due to natural variations in pyrite mineralization within a stratigraphic unit (Byerly 1990). Nonetheless, some understanding of expected magnitudes of uplift pressures resulting from pyrite oxidation and the expected time-rate of sulfide-induced heave is critical to developing appropriate and successful mitigation strategies and designs. Table 11 presents amounts and durations of heave from several reported case histories and lab tests.

Table 11 – Heave Parameters Resulting from Pyrite Oxidation [modified from (Belgeri and Siegel 1998)]

Geologic Formation/Process; Location (Reference)	**Heave (cm)**	**Duration of Heave (yr)**	**Heave Rate (cm/yr)**	**Uplift Pressure (kPa)**
Appalachian carbonaceous shale; eastern U.S. (Spanovich 1969)	37-50	----	----	475-575+
Billings & Lorraine Fms.; Ottawa, Canada (Penner et al. 1970)	9.5	≤ 40	0.6-2.2	----
Conemaugh / Monongahlea Fm.; Pennsylvania (Dougherty and Barsotti 1972; Dubbe et al. 1984)	38 (est.)	≤ 40	----	190-475
Eastview Fm.; Ottawa, Canada (Grattan-Bellew and Eden 1975)	6	----	----	----
Hushpuckney Shale; Kansas City (Coveney and Parizek 1977)	15-20	>30	----	----
Lorraine Fm.; Ottawa, Canada (Quigley and Vogan 1970)	10	----	0.25-2	72
Sainte-Foy Fm.; Quebec, Canada (Berube et al. 1986)	10-20+	----	>2	----
Sevier Shale; Tennessee /West Virginia (Long and Williams 1990)	11+	----	1.5	<75
Westbury Fm.; Britain (Hawkins and Pinches 1987)	6	5-30	----	----
St. Mary's Well Bay Fm.; Barry, Glamorgan (Wilson 1987)	2-5	----	----	----
Gypsum crystallization in Lorraine Fm. shale; Ottawa, Canada (Quigley et al. 1973b)	----	----	----	71.8
Gypsum crystallization in Hushpuckney shale; Kansas City (Lutenegger et al. 1979)	----	----	----	<2108

The amounts and durations of heave listed in Table 11 are based on actual values measured in the field or lab or on estimated values. Estimated values are typically calculated by relating heave that has occurred to the remaining unreacted sulfide sulfur content to predict future behavior. Methods for measuring uplift pressures from rock samples include using monitored rock bolts or lab instruments (such as one-dimensional consolidometers) that measure expansion and uplift pressures by using vertical restraints while allowing the specimen to have access to air and moisture (Dougherty and Barsotti 1972; Lutenegger et al. 1979; ASTM 1996b; ASTM 1996c). The Quebec Technical Committee on Pyrite is currently pursuing the development of established laboratory tests to determine the heave potential of pyrite-bearing fill (Carter 2002a).

Based on noted overburden pressures of black shale in Ottawa, Canada, expansion studies by Quigley (1970) suggest minimum heaving pressures from gypsum crystallization may exceed 71.8 kPa. Lutenegger et al. (1979) used a modified one-dimensional consolidometer to monitor shale heave resulting from artificially induced gypsum crystal growth and established a minimum heave pressure of 28.1 kPa resulting from gypsum crystallization. Further research by Lutenegger et al. was based on the observation of gypsum-induced heave being prevented by a floor-to-ceiling concrete block wall located inside of a mine. Using the strength of a hollow, nonload-bearing concrete block (standardized by ASTM C 129-64T Hollow Non-Loadbearing Concrete Masonry Units), an upper limit for the maximum uplift pressure resulting from gypsum formation was established to be approximately 2108.3 kPa (Lutenegger et al. 1979).

A standard rating system to classify the heave potential of a geomaterial has been developed by the Quebec Technical Committee on Pyrite. This rating system, referred to as the Petrographic Index of Heaving Potential (IPPG), is defined in Quebec BNQ Standards 2560-500 and 2560-510 (BNQ 2003a; BNQ 2003b). The IPPG rating system uses simple laboratory procedures to relate the potential for the presence of framboidal pyrite to heave potential (Carter 2002b). The IPPG is determined by oven-drying a sample and then passing it through a sieve to get the various grain size fractions separated. The fractions are then separated into different petrographic types (shale, shaly limestone, limestone with shaly seams, micrite (microcrystalline calcite), crystalling limestone, dolomite, igneous, etc.). This is either performed visually by a geologist or performed using stains and dyes. Each petrographic type is assigned a numerical value depending upon its potential to contain framboidal pyrite. The percentage of each petrographic type is then multiplied by the framboidal pyrite numerical value assigned to it in order to determine the IPPG number for that component. The sum of each individual IPPG gives an overall IPPG value that is then compared against the established IPPG rating table (Table 12). Based on this table, decisions are then made to perform further testing (chemical analyses, thin sections, etc.), make recommendations for remedial work, etc (Carter 2002b).

Table 12 – IPPG Rating Classification (Quebec Stds. BNQ 2560-500 and 2560-510)

Overall IPPG Rating	Heave Potential
0 -10	None
> 10 – 20	None to marginal
> 20 – 40	Marginal to medium
> 40 – 60	Medium to high
> 60 – 80	High
> 80 - 100	Very high

4.2.2 Time-rate of pyrite oxidation

While time-rate relationships help with engineering design and expected structure life, the weathering of sulfidic material is a continuing process that builds upon itself. The rate of expansion will likely increase as the rock becomes more fractured, allowing more air and aerated water to interact with unweathered pyritic material (Dubbe et al. 1984). The concept of continuous weathering is shown schematically by oxidation zone diagrams in Figure 34.

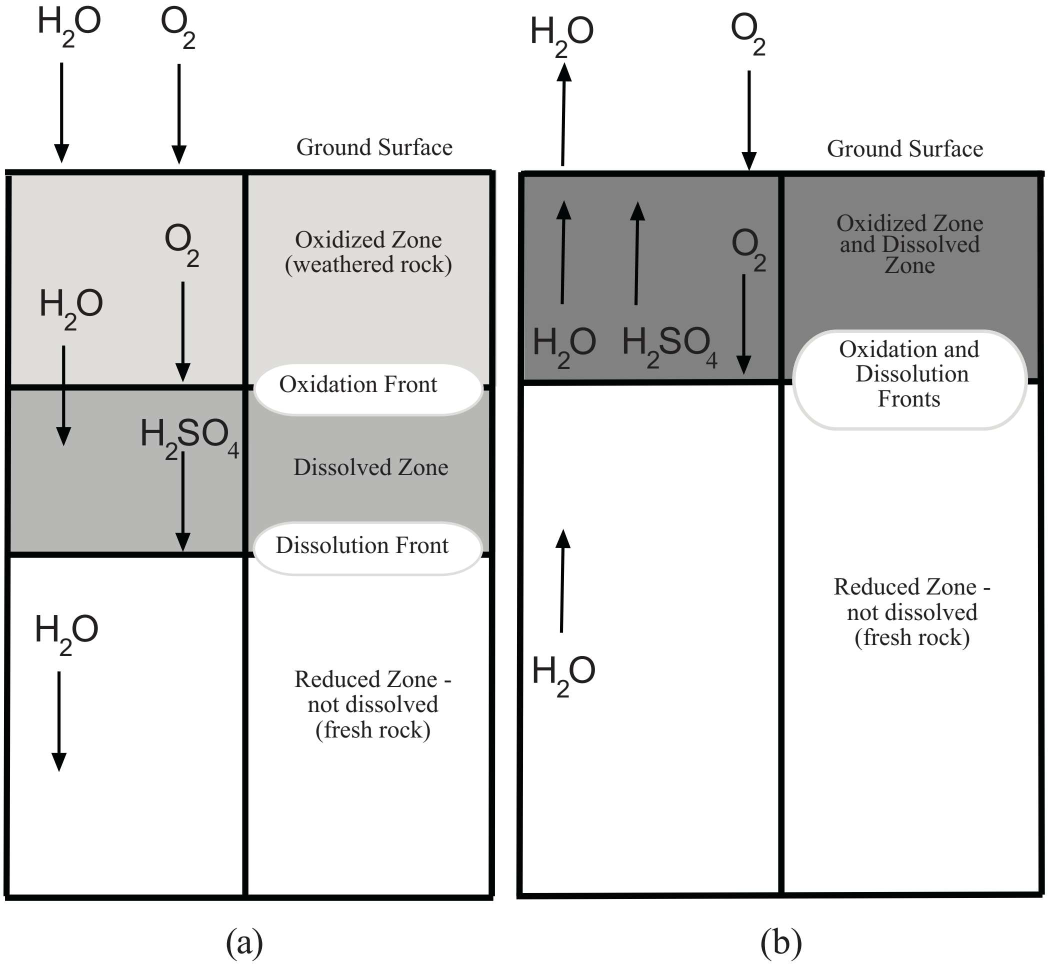


Figure 34 – Schematic diagrams of oxidation/dissolution zones and fluxes of oxygen and water (H_2O) transporting H_2SO_4. (a) Diagram for high elevations (e.g., mountaintops) where groundwater infiltrates downward, indicating fluxes of O_2 and H_2SO_4 in the same direction. (b) Diagram for lower elevations (e.g., valleys) where groundwater infiltrates upward, indicating fluxes of O_2 and H_2SO_4 in opposing directions. Recreated from (Chigira and Oyama 1999).

Significant work has been done by Oyama and Chigira on the effects of pyrite oxidation on rock weathering. One study establishes definitions of the weathering zones associated with the oxidation process (Chigira and Oyama 1999). The dissolution and oxidation zones are clearly defined by mineral alterations and subsequently altered rock properties. The oxidation of pyrite occurs at the oxidation front. Pyrite is depleted in the oxidized zone above the oxidation front. The dissolved zone occurs below the oxidation front as acid created during the oxidation process dissolves and leaches out rock-forming minerals. Decreased rock density and increased porosity define the dissolution front (Chigira and Oyama 1999). The area between the dissolution front and the reduced (fresh rock) zone is defined as the dissolution transition zone, where only slight chemical alterations are beginning to occur. A shallow region of the oxidized zone near the ground surface frequently has different properties from the deeper oxidation region due to the dissolution of cementing minerals, increased porosity, etc.; this region is referred to as the surface oxidized zone. Another study by Oyama and Chigira (1999) presents equations that define the rate of chemical weathering along a rock tunnel wall by relating the depth of the oxidation front to time.

Depending on the site, the on-going process of oxidation may or may not present stability problems. Weathering of the material directly affecting the integrity of the engineering system may reach completion and the zone of oxidation may develop further into regions that are no longer areas of concern. However, the drainage environment, the system components affected, and the exact nature of the sulfidic material involved all must be taken into account when considering the effects of continuing oxidation.

4.3 Mitigation options for geotechnical systems

This section focuses primarily on mitigation options to prevent or reduce sulfide-induced heave of geotechnical systems including shallow foundations, floor slabs, and road subgrades. A great deal of research has been done, however, in regard to water quality and other environmental problems stemming from sulfuric acid production. Thus, several mitigation options may bridge both geotechnical and environmental concerns. Mitigation options to prevent or reduce sulfide-induced heave are generally based on one of three approaches: (1) controlling the pyrite oxidation process, (2) use of counteractive forces or design measures that allow for movement, and (3) reducing the effects of acidity. Some techniques have proven to be successful on a broad scale while others are more site-specific. While a brief overview of several mitigation options is given below, a more thorough and detailed evaluation of methods used for mitigation is included in Appendix A.

Mitigation methods based on inhibiting chemical oxidation include encapsulation (Byerly 1990; Moore and Trolinger 1997) and site grading to remove pyritic material. Due to the increased rate of ferrous iron oxidation as a result of microbial activity, bactericides have been used to control the bacterial catalyzation of pyrite oxidation reactions (Hawkins and Pinches 1992a). Partially saturated conditions, which optimize the exposure of pyritic material to both oxygen and water, establish the most conducive environment for pyrite oxidation. Thus, several mitigation options are geared toward preventing these conditions. Access to air may be eliminated by raising the groundwater level to completely submerge the oxidizable material (Penner et al. 1972). Drains may be installed to intercept water that could initiate pyrite oxidation.

Some geotechnical practitioners working in localities where pyritic materials occur have developed approaches to geotechnical design that directly counteract the effects of sulfide-induced heave. These include using resin-bonded rock anchors to bolt footings down, the application of sustained dead-weight loads, and the use of suspended floors separated from pyritic bedrock by compressible (constructed with cardboard, etc.) structural units. These forms compress if heave occurs, thereby decreasing the potential for uplift and concrete cracking (Belgeri and Siegel 1998).

Acidity effects may be reduced by saturating shale near the ground surface with potassium hydroxide (KOH), which establishes a more neutral chemical environment (Dubbe et al. 1984; Byerly 1996). The pH may also be increased by the addition of alkaline amendments such as lime or limestone aggregate to pyritic soil or rock (Petry 1994; Burkart et al. 1999). However, caution should be taken in regard to possible gypsum formation when adding calcium-bearing amendments. Impermeable coatings on concrete and steel components to protect against "sulfate attack" and corrosion, the use of galvanized steel and fiberglass-reinforced concrete, and the incorporation of sacrificial areas of steel into designs may also alleviate the effects of acidity on geotechnical systems.

5 CONCLUSION

There is a need to establish an inter-disciplinary and inter-regional awareness regarding the adverse effects of pyrite oxidation on earth materials. Evidence shows that geotechnical problems related to pyrite oxidation are both widespread and costly and turn up in a variety of guises. Associated physicochemical processes, consequences to geotechnical systems, and inter-regional case histories have been described. Guidelines have been presented that provide basic initial focus on the identification of problem formations, recommended procedures for site evaluations, documented magnitudes and rates resulting from pyrite oxidation, and mitigation options. The Appendices contain: (A) possible mitigation options, (B) results of a survey conducted on the types of pyrite-related problems encountered in practice and mitigation options used, (C) applicable chemical tests, (D) a glossary, and (E) a visual identification key for sulfidic geomaterials.

All of these topics and guidelines address the wide range of deleterious effects of pyrite oxidation. However, solving the problem must be approached in much the same way as successfully describing an elephant – by taking all parts into consideration. The prevention and mitigation of pyrite oxidation problems are tied directly to establishing a collective awareness between the multiple disciplines involved. Total understanding of the related engineering geologic processes will require insights from geoscientists as well as geotechnical engineers.

6 POSSIBLE RELATED RESEARCH PATHS

Several very interesting directions for potential research stem from this study on the geotechnical effects of pyrite oxidation. Since the occurrence of pyrite is largely stratigraphically controlled, regional maps of geotechnical problem areas stemming from pyritic rock and soil could be created using a Global Information System (GIS). While the primary focus of this paper deals with geotechnical consequences of pyrite oxidation, extensive information exists on the diverse effects of pyrite oxidation. It would be very useful to examine predictive and diagnostic techniques used within other disciplines (e.g., soil science, mining, water quality) to see how these techniques might apply to a geotechnical context. In particular, it would be of great value to find ways to apply the vast knowledge base on acid generation, including studies on acid mine drainage (AMD) and acid rock drainage (ARD), to geotechnical work. Another promising development is remote sensing technology such as AVIRIS. Research needs to be done on the use of such methodology for gaining site-specific information about sulfidic geomaterials.

There is an obvious need for standardized testing of sulfidic materials to determine the potential for heave. The research for this report was primarily focused on a review of existing literature, case histories, and information obtained from various sources. However, laboratory testing that builds from the research presented in existing literature could be performed. Testing to define expected heave magnitudes and time-rates of a particular pyritic material would be extremely beneficial.

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*All website URLs included in this document are current as of December 2002.

Appendices

Pages

Appendix A – Mitigation Options

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Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
PREVENTION OF OXYGEN TO REACTIVE PYRITIC MATERIAL				
A structure should be designed above unweathered/ unoxidized shale only if fresh exposure of the shale (due to excavation, construction, etc.) is prevented or if mitigation efforts are included in the design to offset pyrite oxidation effects.	X	X	X	Structures are normally placed over the less-weathered rock on site for obvious stability purposes. However, this can be extremely dangerous for sulfidic rocks and could create a potential geologically volatile situation. If the amount of sulfidic material and environmental conditions are not thoroughly defined and tested, the degree and time frame of pyritic rock weathering remains unknown. This allows significant potential for the production of sulfates and the resulting acid production and heave to exist.
Use of non-pyritic material for backfill.	X	X	X	
Use of an impermeable coating (such as bitumen or gunite) on unweathered rock to create an anaerobic environment (encapsulation).	X	X	X	Encapsulation, or armoring, has been relatively successful and is used quite often, particularly when dealing with acid mine drainage material (AMD) (Vandivere and Evangelou 1998). This method controls oxygen access, water access, enhances alkalinity, and controls bacteria (Byerly 1996). Bitumen coatings are considered to be a good method of mitigation for sulfate attack because the capillary rise of water underlying the foundation is prevented from reacting with the concrete. Encapsulation is sometimes considered a less dependable solution since the problematic regions are sealed into the rock instead of treated and mitigated directly (Belgeri and Siegel 1998). Encapsulation may actually accelerate oxidation problems in areas of poor drainage. Weathering may be promoted if encapsulation prevents the oxidation products (acid, iron hydroxides, etc.) from dissipating. For example, under normal conditions, oxidized shale produces approximately 8”-10” of soil above 18”-24” of weathered rock. However, a natural armor (e.g. a river terrace) created above this same material produces 40’ of weathered material due to advanced zones of oxidation (Rader 2002).
Pyrite microencapsulation by mixing pyritic material with a phosphate or silica treatment (Vandivere and Evangelou 1998).	X	X	X	These microencapsulations, particularly the silica coatings, have proven to be very effective in lab tests on acid mine drainage (AMD) producing material (Vandivere and Evangelou 1998).

Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
Total encapsulation of pyritic rock with a synthetic high density polyethylene membrane (HDPE) geomembrane (Moore and Trolinger 1997) or a clay liner (Byerly and Middleton 1981).	X	X	X	
Site grading to remove or bury sulfidic material (Byerly 1990; Bruce and Belgeri 2000).	X	X	X	Methods of removal may depend partially on the degree of weathering that the sulfidic material has experienced. Shale rock material that has undergone moderate degrees of weathering can likely be excavated by conventional methods such as front loaders and scrapers. Unweathered shale may require more extreme measures such as ripping and/or blasting before excavation can occur (Bruce and Belgeri 2000).
Elimination of water access to swelling material by installing intercepting drains (Byerly 1996).	X	X	X	
Maintain use or disposal of pyritic material above level of water table (Byerly 1996).	X	X	X	
Diversion of drainage away from all sulfidic fill embankments and encapsulated areas (Byerly 1996).	X	X	X	
Decrease of pathways for oxygen diffusion (decrease porosity, increase tortuosity, etc.) by compacting surface material and embankments (Byerly 1996).	X	X	X	
Development of a logistics plan for transporting excavated pyritic material to eliminate on-site storage during construction (Byerly 1996).	X	X	X	
Use of bactericides to control bacterial catalyzation of pyrite oxidation reactions (Hawkins 1992).	X	X	X	
Temporary protection of exposed shale surfaces.	X	X	X	Use a concrete grout or asphalt coating if the rock material is to be exposed for more than 24 hours (Martna 1970; Penner et al. 1972). Soil may be used as temporary cover and should be placed on exposed material as quickly as possible (Rader 2002).
Complete fill of footing trenches with concrete (Penner et al. 1972).	X	X	X	

Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
Artificial adjustment of groundwater level in weathered zone to establish an anaerobic environment (Penner et al. 1972; Belgeri and Siegel 1998).	X	X	X	This can only be used at sites where there is reasonable control of groundwater conditions due to natural drainage. It may be difficult to control groundwater levels to a degree that prevents oxidation without flooding the structure of concern. Grout curtains may help. Observation wells will be needed to continually monitor the established groundwater conditions (Penner et al. 1972). By raising the groundwater level, the oxygen supply is cut off, eliminating a key component of the oxidation process. Projects that have a permanently shallow groundwater level such as a bridge abutment can maintain permanent anaerobic conditions for the unweathered shale, thus alleviating the bearing pressure requirements to ensure stability against heave (Belgeri and Siegel 1998). However, caution should be taken when depending on a groundwater source as a permanent part of an engineering design. Lowering of the water table could significantly alter the stress conditions if oxidation of the shales were to occur.
Accelerated weathering on-site.	X	X	X	This option forces the pyritic material to oxidize relatively quickly before construction occurs. However, the completion point of the reaction would be quite difficult to define (Dougherty and Barsotti 1972). Also, the increased porosity along bedding planes and joints created by pyrite oxidation may cause future subsidence problems. Thus, accelerated weathering on-site is not recommended unless additional preventative measures are taken during construction (Coveney and Parizek 1977).
Reduction of the effects of air ducts, which may accelerate oxidation with the escape of air (Hawkins 1992).	X			Creating an air gap around the ducts or using insulation may reduce the effects of air ducts. Pyritic weathering may be further accelerated by heated air in the ducts which will cause an increase in humidity and a subsequent increase in the rate of oxidation. Oxidation products would be transmitted upward into these weathered zones of decreased pressure, encouraging the growth of additional heave-inducing crystals (Hawkins and Pinches 1997).
Avoidance of stepped foundations (Hawkins 1987).	X			These create greater potential for differential heave by exposing larger surface areas at varying levels.
Extension of the foundation below the sulfidic material of concern or below the long-term water table level (Hawkins 1992).	X			

Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
Minimal exposure of pyritic material.	X	X	X	If roadway design does not allow for total avoidance of problematic sulfide material, these areas should be crossed as quickly as possible. By crossing at 90° angles, the shortest distance of exposure is established (Rader 2002).
APPLICATION OF COUNTERACTIVE FORCES OR DESIGN MEASURE TO ALLOW FOR MOVEMENT				
Using resin-bonded rock bolts to control swell/heave pressures (Belgeri and Siegel 1998).	X	X		Rock bolting has been used successfully for lightly loaded structures. Belgeri and Siegel recommend using rock bolts specifically for sites with contact pressures of less than 475 kPa, based on their work with the Sevier Shale Formation (Belgeri and Siegel 1998). The rock bolts are pre-stressed to a value at least equal to the contact pressure. Pre-stressing of the rock bolts is performed to both inhibit gypsum formation by keeping near-surface cracks closed and to prevent distress from tension during heave resulting from a non-prestressed anchor (Belgeri and Siegel 1998).
Removal of damaged floor slab and weathered shale and replacement with a structural floor that includes crawl space to allow for future movement (Penner et al. 1972).		X		By providing space between the expansive material and floor slab, the material is allowed to expand without causing structural damage. Footings can be designed to extend below the potentially expansive material (Dubbe et al. 1984). However, considerations must be taken to prevent future weathering of newly exposed shale.
Drilled shafts (deep foundations) (Belgeri and Siegel 1998).				Drilled shafts have small contact areas, limiting the exposure of potentially oxidizing pyritic material. Drilled shafts may also bear high loads. Also, since the drilled shaft extends deep into the rock and the water table typically remains within the first few feet of the rock, a majority of the drilled shaft remains in an anaerobic environment preventing pyrite oxidation (Belgeri and Siegel 1998).
Use of sustained loads to establish minimum required bearing pressures to counter the swell/heave pressures (Belgeri and Siegel 1998).	X	X		For light structures, these sustained loads may also need to be enhanced with rock anchors (Belgeri and Siegel 1998).
Reducing the size of the footing in order to increase the sustained contact pressure (Bruce and Belgeri 2000).	X	X		

Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
Use of collapsible structural units (Belgeri and Siegel 1998).		X		Suspended floors should be separated from pyritic bedrock with collapsible structural units constructed of cardboard, etc. (Belgeri and Siegel 1998). The collapsible forms will create a space separating the shale and floor slab. These forms will collapse if shale heaving occurs, decreasing the potential of uplift and concrete cracking.
REDUCTION OF ACID EFFECTS				
Incorporation of effects of lime interaction with sulfidic soil into design (Petry 1994; Burkart et al. 1999).	X	X	X	If the total gypsum concentration present in sulfidic material is known, then an attempt to account for the formation of expansive minerals can made by adding enough lime to completely react with the gypsum while still leaving enough lime to add the necessary strength to the unstable soil (See Section 3.1.3) (Burkart et al. 1999).
Reduction of acidity (increase of pH) by saturating shale near the ground surface with potassium hydroxide (Byerly 1996).	X	X	X	Submersion of the shale with potassium hydroxide (KOH) will create a more neutral chemical environment, thus reducing acidity effects and hindering the growth of autotrophic bacteria which catalyze the pyrite oxidation process (Dubbe et al. 1984). However, this mitigation option is often deemed problematic for several reasons. A permanent source of potassium hydroxide must be maintained to keep the upper portion of shale saturated. Total submersion of all rock discontinuities would also be difficult to ensure (Belgeri and Siegel 1998). Also, it has been determined that while 0.01 N and 0.1 N KOH solutions will stop the expansion process, 1 N KOH solutions actually accelerate the expansion rate by raising the pH beyond pyrite's stability field (Dubbe et al. 1984).
Reduction of acidity (increase of pH) by using alkaline amendments, such as limestone aggregate or a lime layer on unweathered shale (Belgeri and Siegel 1998).	X	X	X	It is particularly important to understand the chemical environment of the site when using this option. The addition of lime or limestone aggregate may reduce the acid attack on the structure itself by increasing the pH of the weathering environment. However, the presence of the added calcium carbonate may foster the growth of gypsum which would create additional heave problems. Another concern with increasing the alkalinity of a system to prevent acidity has been noted by Burt & Carrucio (Jeng 1991). Increased alkalinity may trigger increased oxidation of Fe^{2+}, which in turn produces more Fe^{3+} and accelerates the rate of pyrite oxidation.

Table A – Mitigation Options and Affected Systems

Mitigation Option	Systems Affected			Comments
	Shallow Foundations	Floor Slabs	Road Subgrades	
Use of an impermeable coating on concrete to protect against leachate infiltration and resulting “sulfate attack”.	X	X	X	
Use of an impermeable coating on steel components, such as bolts, H-piles, and beams.	X	X	X	Components affected include bolts, H-piles, beams, reinforcement bars, steel culverts, corrugated metal pipes (CMP), and slope stabilization techniques such as tiebacks, rock bolts, anchors, soil nails, etc.
Use of galvanized steel to reduce corrosion effects.	X	X	X	Components affected include bolts, H-piles, beams, reinforcement bars, steel culverts, corrugated metal pipes (CMP), and slope stabilization techniques such as tiebacks, rock bolts, anchors, soil nails, etc. Galvanized metal may work better than concrete in some cases such as road culverts (Rader 2002).
Incorporate sacrificial areas of steel into design.	X	X	X	Used to account for loss of steel area due to corrosion. In some cases, the amount of rebar needed has been doubled so that the required strength will be present at the end of 50 years (Priznar 2002).
Use of bottomless culverts.			X	Bottomless culverts are pre-cast with an open bottom. The stream/runoff acts as the base of the culvert, significantly reducing the amount of exposed material (steel or concrete) susceptible to degradation (Rader 2002).
Use of fiberglass-reinforced concrete or other types of protective concrete (Rader 2002).	X	X	X	

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Appendix B – Survey of Practitioners

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Background

A survey was sent to representatives of each state Department of Transportation and Geological Survey office and to several geotechnical engineers and geologists from various regions in the U.S. and Canada. This survey was created to gain information on a state and regional basis for several purposes: (1) to establish the specific types of geotechnical problems encountered that are associated with pyritic material, (2) to determine what types of mitigation measures are being employed, and (3) to identify specific references considered especially helpful to specific regional or state practitioners. A copy of the survey, which was sent out by email, is included on pages B-2 and B-3. Many informative and helpful responses were received from the survey. A summary of these responses, paraphrased and organized by state (U.S.) or country (Canada), is included in Table B. All of the responses received are greatly appreciated and proved to be excellent resources for this report. Out of respect for privacy, the names of these respondents are withheld.

Copy of Request for Information (sent out by email)

Subject: Geotechnical problems associated with pyritic rocks

To ________,

My name is Lee Bryant and I am a graduate student in the Geotechnical Engineering Program at Virginia Tech (www.ce.vt.edu/program_areas/geotechnical/). I am performing research on "geotechnical problems associated with pyritic rocks" for my master's thesis with Dr. Matthew Mauldon and Dr. James K. Mitchell, in association with the Center for Geotechnical Practice and Research (CGPR) at Virginia Tech.

I am building a base of contacts from which I can draw knowledge and insights and would be extremely grateful for any guidance you may be able to provide. The resulting report will help establish guidelines for recognizing (1) problematic rock formations and (2) design/construction scenarios that can mitigate problems with pyritic rocks. I have a few questions and would greatly appreciate your help. We will provide you with a copy of the final report, as well as the bibliography that I am compiling, to compensate you for your time and effort responding to this survey.

1. *I wish to establish contact with professionals experienced with this topic in each state, and have obtained your name from either personal referral, knowledge of your work in this area, your position with a State Division of Geology or DOT, or through the Association of Engineering Geologists. If you are not the person I should be communicating with about this, please suggest a more appropriate contact.*

2. *What geotechnical problems (interpreted broadly) are you aware of in your state associated with pyritic rocks? Examples might include:*
   - *Foundation heave or damage from swell pressures*
   - *Damage to concrete or steel (drilled shafts, culverts, etc) from acid production*
   - *Damage to erosion control or slope stabilization materials (vegetation, soil nails, tiebacks, etc) from acid production*
   - *Slope instability from rapid weathering of new construction cuts*
   - *Subgrade expansion due to pyrite-bearing materials*
   - *Water pollution from acid drainage*
   - *Durability issues of aggregates produced from pyrite-bearing rocks*
   - *Rock pile stability (e.g. mine waste rock piles)*

3. *What references (particularly specific to your region or state agency) could you recommend that provide details on such problems?*

I realize it will take some time and effort to respond and I would like to make this as easy as possible for you. So please feel free to respond in whichever manner most convenient –

by email, phone or fax, or if you provide me with a phone number and time I would be happy to call you at your convenience.

I would greatly appreciate hearing back from you by the end of July, or as soon as possible thereafter. Thank you very much for your assistance with this project.

Sincerely,
Lee Bryant

lebryan1@vt.edu Email
540-231-4417 - voice mail
540-231-7532 - Fax

Ms. Lee Bryant
Geotechnical Engineering Graduate Student
200 Patton Hall
Virginia Polytechnic Institute and State University
Blacksburg, VA 24060

Table B – Responses to Survey of Practitioners

State/Country	Summary of Survey Response
Alabama	A significant geotechnical problem related to pyritic rocks is oxidation and heating of deep underground coal mines. In some Alabama mines, this problem has presented a significant fire hazard.
Arizona	Arizona primarily has pyrite problems relating to acid mine drainage, encountering problematic material during construction, and expansive clays. AMD typically results from mine waste rock piles or disseminated copper deposits in Arizona. This drainage frequently causes problems with accelerated steel corrosion. Mitigation options used to control this problem include using higher galvanized steel or use a thicker, sacrificial amount of steel to compensate for the amount lost by corrosion. Problematic material encountered in construction is typically removed or attempts are made to control water infiltration with geomembranes. Guidelines by Harry Moore (TDOT) on impermeable geomembranes are often used. Expansive clays are typically stabilized with lime or over-excavated and replaced.
Arkansas	Water pollution from acid drainage is the most significant problem with pyritic material in Arkansas. Known examples include: 1. Acid mine drainage (AMD) from some of the underground and surface coal mines in the Arkansas Valley Region. Paleozoic shales of some of the coal-bearing formations contain pyrite. 2. AMD from certain bauxite-mined areas in the central Arkansas area of the Gulf Coastal Plain. Wilcox (Eocene) sedimentary units, in which the bauxite deposits occur, are rich in fine-grained organic matter and associated pyrite, cause this problem. 3. AMD from one area of clay production near Malvern, which is also in the Gulf Coastal Plain. Fine-grained pyrite and nodular pyrite/marcasite in the clay zone result in some problems. 4. AMD from tailings that are the result of mining of barite deposits located in the Ouachita Mountain Region of Arkansas. At one mine in Hot Springs County, finely divided pyrite in shale of the Stanley formation is altering, resulting in AMD. At a second mine in Montgomery County, pyrite/marcasite cements a highwall composed of the Arkansas Novaculite Formation. Alteration of this exposed pyritic material and subsequent washing by rains of dissolved alteration products result in a continuous source of acid renewal for a water containment pond.
California	Most of California is free of geologic formations that are rich in pyrite, resulting in pyritic problems that are localized but acute. Compared to other states, California generally lacks extensive coal deposits, lacks black shales that are commonly pyritic, and lacks significant iron-ore deposits. However, there are some notable exceptions that appear to have acute problems with pyrite-bearing soils. These exceptions include: 1. California has several EPA Superfund clean-up sites with acid mine drainage problems. The Iron Mountain Mine in Shasta County and the Leviathan Mine are among the most notorious. The lowest pH ever recorded is from Iron Mountain Mine. This was the subject of numerous papers and articles, including and article describing how acidic waters from this area could quickly dissolve a shovel blade. 2. California has many hot-spring areas with mineralization that includes pyrite.

California (cont.)	3. The Leona Rhyolite in the eastern San Francisco Bay area (Berkeley Hills, east of Oakland) reportedly has some problems with pyrite that result in corrosion of concrete. 4. Soluble sulfates in the soils of California are principally gypsum and jarosite. These two minerals are principally the cause of Type V Portland-cement being required for many construction projects, rather than Type II. 5. Pyrite in soils near Kestwick Dam, north of Redding, caused corroding and warping of steel railroad track.
Quebec, Canada	Most of the pyritic problems in Quebec are related to the expansion of pyrite-bearing crushed stone aggregate taken from local quarries. The framboidal form is very unstable and breaks down rapidly under certain conditions to form gypsum as a by-product. The expansion associated with this is responsible for upward heaving of floor slabs and lateral displacements of foundations. Sulfate attack (sulfatation) on concrete slabs/foundations is also very important due to the loss of mass, compressive strength, and floor slab thickness, particularly in warehouses where high loads are present. The loss of cross-sectional area usually results in cracking due to loading. There is also some expansion related to sulfate attack. Roadcuts and excavations are typically not as troublesome due to the fact that shale units in this region are quite thin and interbedded with limestone. Numerous methods of remediation affected buildings are utilized in the Quebec area. One of the most established methods is to demolish the affected floor slab, excavate all backfill materials, backfill with new materials, and pour a new slab. The method is expensive and can range in cost from \$10-\$40 / ft^2, depending on the depth of fill, and does not include civil works. Other methods include removing only the affected areas of slab, installing a vapor barrier, and pouring a new section of slab using Type 50 Portland Cement. An additional step is sometimes added to this method which involves removing the damaged sections of slab and the granular fill in the surrounding area, backfilling with new fill material, placing a vapor barrier, and then pouring the new slab with Type 50 PC. The method used typically depends on the client's budge and the risk he is willing to take. The amount of time required for problematic rock to totally react chemically and become stable is the "million dollar question." The reaction rates vary considerably, depending on the conditions present that are required to cause the reaction to take place. The reaction requires a humid environment, warm temperatures (not freezing), and the presence of the deleterious fill (a mix of pyritic shale and limestone). The reaction can be very quick, within a year if the material is very reactive, or it can take 10 to 15 years. The rate of heave is usually a few mm a year, generating humps in the floor and radial cracks. However, some material is so reactive that a newly renovated building was a disaster within a year. Ceramic floors cracked, doors were unable to close, and drywall joints sheared. All of this damage resulted from a 2 ft. thick layer of very organic-rich shale present in the crushed stone.

Quebec, Canada (cont.)	Expansion pressures are not measured in the field. The Quebec Technical Committee on Pyrite is currently pursuing the development of laboratory tests to determine the heaving potential of pyrite-bearing fill. An IPPG (Petrographic Index of Heaving Potential) rating system has been developed by the Quebec Technical Committee on Pyrite. Simply put, the IPPG is determined by acquiring a sample, returning it to the laboratory, drying it in the oven and passing it through a sieve to get the various fractions separated. The fractions are then separated into different petrographic types (shale, shaly limestone, limestone with shaly seams, micrite, crystalling limestone, dolomite, igneous, etc.). This is done visually by a geologist or by using stains and dyes. This nomenclature is particular to Quebec and documentation for this process is currently being established. Each petrographic type is assigned a numerical value depending upon its potential to contain framboidal pyrite. The percentage of each petrographic type is multiplied by the numerical value assigned to it in order to determine the IPPG number for that component. The sum of each individual IPPG gives a final IPPG value which is then compared against the established Rating table (Table 12 in Section 4.2.1), and decisions to do further testing (chemical analyses, thin sections, etc.), make recommendations for remedial work or note, are made accordingly.
Colorado	Many problems with foundation and slope stability and concrete corrosion are attributed to expansive soils and clay shales in Colorado. The bedrock is marine in origin and contains some amounts of pyrite. The weathered bedrock and soils contain pyritic weathering products, such as jarosite. Most of the uplift and heaving in these materials is attributed to smectite clays. The soils are mostly dry in Colorado, with the heaving occurring as a consequence of post-development wetting. Similarly, slope movements are also attributed to smectite clays, which have low shear strengths. There is no doubt that the weathering of pyrite contributes to these problems. However, the effects of pyrite appear to be very minor when compared to the contribution of expansive clay minerals. Pyrite weathering is a likely contributor to the concrete corrosion problems, which are variable problems around Colorado. There have been noted incidences of pyrite weathering in claystones which have resulted in the precipitation of gypsum and jarosite along bedding and fracture planes. However, clay minerals again seem to be the primary source of heave at these sites.
Delaware	The only significant problems regarding pyritic rocks in Delaware involve the Magothy formation. The Magothy formation contains some pyrite and marcasite and is difficult to vegetate when disturbed. The principal area of concern has been the banks of spoil excavated from the Chesapeake and Delaware Canal. Much of this area has been stabilized through time with vegetation encouraged by the use of sewage sludge as fertilizer.
Florida	Research is currently being performed by the Florida Geological Survey (FGS) on the mobilization of arsenic during aquifer storage and recovery acitivities. During this research, trace amounts of pyrite were found in the carbonate rocks in the study area. This pyrite may be the source of arsenic being released during the water-rock interaction.
Florida	Concrete popouts have occurred in sidewalks that reach up to 1 inch in diameter and ½ inch deep. Aesthetics problems include running stains.
Illinois	Illinois has very few pyrite-bearing strata that are both near the ground surface and located in areas of large populations with the associated need for deep excavations. Some pyrite is found in the coal-bearing strata located in the southern 2/3

Illinois (cont.)	of the state. Most of the coal-bearing strata in the state is covered with thick glacial sediments which relatively isolates this material from exposure due to human contact. AMD problems associated with the southern Illinois region have occurred in a few older mine waste piles. The Illinois Geological Survey and the Natural History Survey did some research in the 1980's on the characterization of the materials in these piles and the vegetation established on the piles.
Iowa	Poorly dolomitized aggregate containing finely dispersed pyrite is typically considered to be susceptible to deterioration, especially in the presence of deicing salts. Problems have occurred with the agglomeration of fine aggregates in stockpiles due to the oxidation of pyrite associated with lignite and coal particles. The agglomerates were formed following the dissolution of carbonate particles in the sand by low pH leachate in the stockpile. Gypsum forms at the particle-particle boundaries of the sand grains, leading to agglomeration.
Iowa	The majority of pyritic bedrocks in Iowa are dolomites and shales. Much of the coal in Iowa also contains pyrite.
Kansas	An article by Coveney and Parizek discusses limestone mine floor heave and sulfide alteration that occurred in Kansas (Coveney and Parizek 1977). However, it should be stressed that there are several mechanisms contributing to floor heave and the extent to which sulfide alteration contributes to the overall uplift is unclear. Acid mine drainage is also an established problem in southeastern Kansas.
Kentucky	Pyrite dissolution has led to several types of problems associated with pyritic shale in Kentucky. Sulfide and sulfate mineralization associated with pyrite dissolution has cracked school foundations, led to the collapse of retaining walls. Acid drainage is also an issue of concern. Significant pyrite expansion problems were encountered following the recent construction of a public school in Kentucky. The school's foundation was placed partly on in-place carbonaceous pyritic shale and partly on compacted fill derived from the same shale. Unexpected cracking of the floors and walls occurred soon after construction. This case emphasizes the importance of utilizing information, skills, and insight from both competent engineers and geologists during the planning and design phases of geotechnical projects.
Kentucky	There are two major problems with expansive shales containing pyrite in Kentucky. One of these is pyritic oxidation and the resulting expansion of minerals. This occurs when the sulfur in the pyrite oxidizes and combines with calcium to form a secondary sulfate such as gypsum, jarosite, melanterite, copiapite, or epsonite. This change in mineralogy creates a volume change in the rocks that results in heaving and subsequent foundation problems. The second major concern is the presence of any expansive clays in the shales. Expansive clays such as montmorillonite will expand and heave when in contact with moisture or water, resulting in foundation problems. It is very difficult to mitigate or correct geotechnical problems resulting from pyritic material. The main solution is to not build on these types of soils and perform preliminary geotechnical soil and chemical analyses. Remediation techniques include: 1. Prevent all sources of water from contacting the foundation, which is almost impossible to do, except by possibly using an expensive grout curtain around the structure. This may restrict or limit heaving.

Kentucky (cont.)	2. Foundation pilings driven deeper to more stable bedrock that can successfully support the structure. 3. Demolish and rebuild the impacted structure using a better foundation. In regard to the time-rate expansion of pyritic rock, since there is typically a constant source of pyrite, calcium, or expanding shale, there will be a perpetual problem. Material will not stabilize for foundations. Examples of sulfide-induced heave in Kentucky include: 1. Estill County Middle School – Serious foundation heaving and settling occurred, resulting in the eventual decision to rebuild another structure on more substantial footing. Extensive concrete wall, sidewalk, and gymnasium floor heaving occurred, doors will not open or shut, sliding bleacher seats will not retract from the gymnasium wall, and floors have cracked. Exterior drainage tiles have become plugged with growths of secondary sulfates. 2. Homes and private residences – Significant problems with wall cracking and floor buckling. If the home remains structurally intact, home modifications must typically be made.
Maryland	Acid run-off is the main problem resulting from pyritic materials in Maryland highway work.
Maryland	Geotechnical problems related to pyritic materials include damage to concrete or steel and water pollutin resulting from acid mine drainage. Acid mine drainage is a problem in Western Maryland's coal basins, which contain high sulfur coals with plenty of pyrite.
Michigan	Michigan does not have geotechnical problems with pyritic rock due to the fact that glacial drift, which on average has a very low concentration of pyritic material, covers a majority of the state. Even in areas where outcrops of bedrock exist, very little pyrite exists in the bedrock material.
Minnesota	MN/DOT has had very little trouble with pyritic rocks because there are very few of them in the state. The main problem with pyrite occurs in pavement applications where pyrite particles in the gravel aggregate sources cause pop-outs and streaking in the pavement surface. These pyrite particles also cause corrosion of steel in the pavements when they are located close to a dowel bar or other type of steel reinforcement. Specifications have been established that prohibit the use of gravel with > 1% pyrite (for concrete pavements) and > 2.5% (for bituminous pavements). Minnesota has very little pyrite in its bedrock sources, however there are some sulfide deposits in the arrowhead region (NE) that are buried at some depth. Mining of these deposits could be potentially feasible economically, which could result in the storage of above ground pyritic rocks.
Minnesota	Pyritic rocks in Minnesota are of concern when they are contained in materials stripped and stockpiled as a result of iron mining. Pyrrhotite, a mineral closely related to pyrite, is also a problem. Acid-drainage from waste rock resulting from the mining of these ores is a major issue. The Reclamation Unit of the Division of Natural Resources has been studying this for several years.
Missouri	Missouri rocks/formations include: Precambrian granites and rhyolites in the southeast part of the state in the St. Francois Mountains; Cambrian and Ordovician limestones, dolomites, sandstone and shale in the southern one-half of the state; localized outcrops of the Devonian and Silurian limestones, sandstones and shales; large areas of Mississippian

Missouri (cont.)	limesones with minor associated shales and large amounts of chert in some formations; Pennsylvanian limestones, sandstones, and shales in northern and western Missouri; Mesozoic formations; Permian rocks present only in one localized sandstone formation and should be disregarded for the purpose of this report; Triassic and Jurassic-age formations are mostly absent; Cretaceous formations consist of the McNairy formation at the surface and some subsurface formations in extreme southeast Missouri. The McNairy formation, named for its type locality in Tennessee, consists in Missouri of unconsolidated sediment and may be disregarded; Tertiary and Quaternary sedimentary deposits. Though the vast majority of the rocks are level or nearly so, there are structural features within Missouri that extend for quite some distance. A length of several hundred miles for some faults is not uncommon. Two anticlines exhibit surface expression, the House Springs Anticline and the Brown's Station Anticline. Two iron sulfide minerals are present in Missouri, pyrite and marcasite, which have identical chemical compositions. Pyrite crystallizes in an isometric crystalline form, while less stable marcasite crystallizes in an orthorhombic crystalline form. Due to identical chemical composition and geochemical reactivity, either or both minerals are commonly referred to as "pyrite". The main pyritic problems occurring in Missouri are associated with water pollution from acid mine drainage. Acid mind drainage problems occurred close to U.S. Highway 24 and were remediated by the Missouri Department of Natural Resources in 1990. The highway has not been affected by this acid drainage problem. An aggregate durability issue occurred related to pyrite-bearing limestone associated with the Mississippian-age Burlington and Pierson Limestones, at a quarry outside of Sedalia, Missouri. A comprehensive study, including chemical and physical testing, of the quarry stone was performed which led to the ultimate rejection of a particular ledge of limestone for concrete aggregate use. This study produced very interesting results. The Pierson Limestone is underlain by Northview shale, which behaved as an aquitard and prevented water from filtrating through the geologic column. Water saturated the Pierson Limestone, which contained approximately 2% pyrite in the quarry. A self-perpetuating oxidation reaction took place that produced sulfuric acid, which then dissolved the Pierson Limestone in some parts of the quarry. Some areas experienced such degrees of dissolution that limestone could be dug out bare-handed. These results were confirmed by chemical and petrographic testing, which led to the refusal of the ledge material.
New Mexico	There is an alignment in northeast NM, on SR38, between Questa and Red River where acidic conditions exist and are attributed to the presence of pyrite in the bedrock slopes of the canyon. There is virtually no vegetation on the slopes, excluding Ponderosa Pine. Additionally, the Red River, which flows through this canyon, does not sustain any fish within this reach. The Questa molybdenum mine (included as a case history in this report) is located within this reach of the canyon.

New Mexico (cont.)	The pH of soils in this area are measured between 3 and 4. The effects on geotechnical/construction structures include severe corrosion of corrugated metal pipes (CMP) and rebar in older concrete box culverts where concrete cracking or spalling has allowed water migration to the rebar. All of these culverts have been replaced with PVC pipe culverts. Also, a mechanically stabilized earth (MSE) wall, located in the town of Red River, required restricting the soil reinforcements to the use of HDPE goegrid in lieu of steel soil reinforcement elements.
North Carolina	Problems related to pyritic rocks in North Carolina are primarily related to road construction. These include: damage to concrete or steel (drilled shafts, culverts, etc.) from acid production, damage to erosion control or slope stabilization materials (vegetation, soil nails, tiebacks, etc.) from acid production, subgrade expansion due to pyrite-bearing materials, and water pollution from acid drainage. Pyritic rocks are considered to be a significant problem in North Carolina. The North Carolina Geological Survey (NCGS) planned to begin a 3-year mapping project along the N.C. segment of the Blue Ridge Parkway in the Fall of 2002. In addition to basic geologic mapping, geologic hazards including pyritic rocks and slope movements will also be inventoried.
Oklahoma	Water pollution associated with AMD from abandoned coal mines.
Oklahoma	Thick, black pyritic shales outcrop in eastern Oklahoma, namely the Fayetteville and the Chattanooga black shales. An active quarry located at Zeb, near Tahlequah, produces aggregate containing pyrite. There is some pyrite in the Miami chat (lead/zinc mine waste); however, since this is not commonly used in Portland Cement Concrete (PCC), this source is not a problem. Considerable acid mine drainage occurs as a result of coal mining and lead/zinc mine drainage. No significant problems have occurred from the drainage corroding metal pipe culverts or damaging PCC drainage structures. When pyritic aggregate is used in PCC, it produces cosmetic defects such as black stains that run down retaining walls, parapet walls, bridge piers, or across pavements, bridge decks, etc.
South Dakota	Acid-generating rock containing feldspars alter to clays as acid is generated. An interesting example of acid rock drainage (ARD) involved an ARD remediation project at a South Dakota mine in the mid-1990's. Feldspar alteration occurred in a large stockpile containing strongly acid-generating rock. The pile was initially constructed from very competent rock. However, when the pile was excavated approximately 2-3 years later, the rock had almost entirely altered to clay. This type of material would obviously make very poor construction materials.
South Dakota	Rock formations containing pyritic material in South Dakota are found mainly in the Black Hills, located in the western part of the state. The Black Hills area has abundant igneous intrusives and associated metamorphic rocks. This part of the state has problems with heaving, slope stability, and corrosion resulting from pyritic oxidation. However, geotechnical investigations typically focus on the types of soils or rock and their standard engineering properties rather than their chemical properties. Chemical analyses are performed on various rock types for use as construction materials such as backfill in retaining walls; however no materials of significant concern have been identified. Acid mine drainage is a concern within the Black Hills, particularly in the gold mining areas of the northern Black Hills.
Tennessee	Significant work has been done in Tennessee on the issue of pyritic rock problems associated with highway construction.

Tennessee (cont.)	A Standard Operating Procedure (Moore) dealing with pyritic rock has been developed for TDOT as well as technical papers on mitigation methods such as the use of geomembranes for encapsulating pyritic rock (Moore 1992; Moore and Trolinger 1997). Major research by Dr. Don Byerly, now retired from the University of Tennessee, has produced several publications regarding the handling of excavated acid-producing materials (Byerly and Middleton 1981; Byerly 1990). These documents were cited by sources as far away as Arizona as being standard sources of information for these types of problems (Priznar 2002). Most of the pyritic rock in TN is found in the Blue Ridge Province in the metamorphosed rocks like slate, phyllite, argillite, and some siltstone. In the Valley and Ridge Province, it is generally the Chattanooga Shale (a Devonian black shale with high concentrations of iron disulfides) which presents acid drainage problems. On the Cumberland Plateau, it is generally the Pennsylvanian Age shales and coal seams that contain the pyritc material and present problems. In Middle Tennessee (the Highland Rim and adjacent Central Basin), it is again the Chattanooga Shale that is the problematic rock unit. It is generally the dark gray to black shales and their metamorphic equivalents that pose the most problems in TN. Most of the problems in TN are related to acid drainage (and the associated metals that result from the acid drainage) from the fresh, broken pyritic rock that is used in embankment construction. There have been some problems with foundation have from pyritic shales in the Johnson City area of TN. A slab foundation was poured on top of an embankment composed of crushed Sevier formation material, primarily shale and siltstone containing large amounts of iron disulfides (pyrite). The library slab began heaving soon after the library construction was completed and resulted in drastic damage to the floors. The building has since been demolished. It seems that the heave problems become a more significant problem when the pyritic shales are also calcareous, such as the Sevier Shale present in eastern Tennessee. Sulfates that form from the breakdown of the sulfide minerals combine with any calcium carbonate present in these calcareous shales to form minerals like gypsum, which have associating volume increases that result in swelling/heave.
Virginia	Pyrite can come from marine, sedimentary environments or through volcanic deposition. The minerals crystallize during the volcanic process and create pyritic igneous and metamorphic rock. The rise and fall of the sea level is conducive to the formation of pyrite. The Devonian period was relatively calm. More rough formative processes occurred during the Mississippian age, followed by a very turbulent period during the Pennsylvanian age. During the Pennsylvanian age, a collision of continents created migrating bulges of coal and pyrite. These continent collisions created arc formations, which help identify "suspect terrains" of pyrite on maps worldwide by curved arcs.

Virginia (cont.)	Occurrences of sulfidic material in Virginia include: 1. Pyritic mica schists, created from shales initially created in marine environments. 2. Silurian sandstone up through the Cloyd conglomerate, present at Cloyd's Mtn., Dublin, on Rt. 100. 3. Stopes of pyrite and Pyrrhotite exist in the Great Gosson Lead area that are as large a multi-story building. 4. Acid drainage is an immense problem in the Big Stone Gap area. Piles of waste rock are treated with limestone trenches to neutralize the acid. One of the biggest problems in reclamation is related to dealing with mine waste piles. The collapse of waste piles in Wales and West Virginia have resulted in deaths as villages and towns are demolished. 5. In Altavista, VA, a cogeneration power plant for Lane Furniture was built on a saprolite bed. There was a loss of conductivity properties due to leaching of the saprolite. The plant drilled through 60' of the material to reach groundwater, but received no power with first attempts of putting the plant on-line. There was apparently a loss of conductivity properties as the pyritic oxidation zone progressed down through the saprolite. The formation was reduced to a dust-like material of quartz, muscovite, and sillimanite.
Virginia	The main pyritic rock bodies in Virginia and the surrounding regions include: 1. Devonian Shales 2. Quantico Slate, in Spotsylvania, Stafford County 3. Arvonia Slate, in Buckingham County The Valley and Blue Ridge Province has significant levels of pyrite predominantly in Devonian shales. Limestone in this region has some pyrite; however it is not very problematic due to buffering by acid. Shale ore occurrences, resulting from hydrothermal fluids, are more localized. Examples include a number of mines that dot the VA-Piedmont and Blueridge provinces and a mine in Grayson County, where pyrite is being extracted to make sulfuric acid. Virginia is fortunate, in terms of problematic pyrite, in that the coal here does not contain a great deal of pyrite. Coal from the Illinois Basin contains a significant amount of framboidal pyrite. Shale beds associated with the Pennsylvanian and Mississippian coal beds have lots of pyrite. This pyrite originates as marcasite (also FeS_2). The coastal plain contains pyritic clays and sulfate-bearing soils. Hard rock is not typically encountered until depths of 2500', which is obviously far out of range for excavations. Significant problems have resulted from the high levels of gypsum in the coastal region of Virginia. Gypsum breaks down quicker than pyrite, as it is somewhat soluble, thus making it more easily transportable. Gypsum creates significant acid drainage, resulting in vegetation and corrosion issues. Local examples and case histories include: 1. Problems with the establishment of vegetation behind the Richmond city jail due to acid drainage from gypsum-

Virginia (cont.)	bearing soils. 2. Visible pyritic problems have occurred on Highway 295, near the Richmond-Mechanicsville interchange. Effects include vegetation problems, evidence of culvert deterioration, and the visible conversion of clays to more expansive clay minerals. 3. Landslide on 460 West, in Narrows, VA In regard to the time-rate of expansion for pyritic materials, oxidation will continue as long as water can reach the rock. Oxidation will only cease by totally encapsulating the problem material, known as armoring. However, total encapsulation is almost impossible to accomplish. Oxidation typically continues under both natural (e.g. river terrace) or man-made (e.g. impermeable coatings, rip-rap) methods of armoring. Armoring often even promotes weathering by not allowing the oxidation products to dissipate.
Wisconsin	A major highway project currently being performed in the historic Upper Mississippi Valley lead-zinc district has experienced numerous problems related to mineralization in which pyrite and marcasite and their associative weathering products have caused unanticipated stability problems in road cuts. The Wisconsin DOT has had to redesign foundations for bridge abutments and redesign cut slopes to overcome problems caused by weathered mineral veins that reach the surface. Problems occur in flay-lying Ordovician carbonate rocks of the Platteville, Decorah, and Galena formations, and mineralization consists of galena, sphalerite, calcite and barite, in addition to iron sulfides (pyrite). Much of the material at the surface is highly weathered and only residual sulfides are present. Most sulfides are altered to iron oxides that are mixed with residual clay and clay residue from leaching by the ore solutions. This highway project was started recently, so long-term problems have not yet been evaluated. An additional problem related to pyrite includes the heaving of quarry floors due to the weathering of sulfide veins.

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Appendix C – Chemical Test Procedures

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-280 495

Field and Laboratory Methods Applicable to Overburdens and Minesoil

West Virginia Univ, Morgantown. Coll of Agriculture and Forestry

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio

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Andrew A. Sobek, William A. Schuller, John R. Freeman, and Richard M. Smith

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16. ABSTRACT

With the growing demand for environmental assessment of a mining site, it becomes apperent that a manual of field and laboratory procedures to study the overburden and the resulting minesoil is necessary.

Incorporated within this manual are step-by-step procedures on field identification of common rocks and minerals; field sampling techniques; processing of rock and soil samples; and chemical, mineralogical, microbiological, and physical analyses of the samples. The methods can be used by mining companies, consultant firms, and State and Federal agencies to insure mining efficiency, post-mining land and water quality, and long range land use.

Inherent to these methods is the definition of terms. Many common terms are used inconsistently even within small groups; and when multiple disciplines are involved, communication demands that many terms must be defined for that particular purpose. Thus, the definition of essential rock, soil, chemical, mineralogical, microbiological, and physical terms constitute an important part of this project.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Coal Mines, *Surface Mining, *Overburden, *Chemical Properties *Weathering	*Potential Toxicity, *Minesoils, *Neutralization Potentials, *Available Nutrients, *Physical Properties, *Acid-Base Account, *Preplanning, *Analytical Properties, *Mineralogical Properties, *Microbiological Properties	43F 48A 91A

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3.2.2 Paste pH

3.2.2.1 Principle--

Perhaps the most commonly measured soil characteristic is pH. Soil pH was defined by Sorensen (1909) as the negative logarithm of the hydrogen-ion concentration. However, in actuality, hydrogen-ion activity is measured instead of hydrogen-ion concentration.

Soil pH is measured by a glass electrode incorporated with a pH meter for this procedure. Water is added to the sample forming a paste. The electrode is placed in the paste with pH being read directly from the meter.

3.2.2.2 Comments--

Six factors affecting the measurement of pH are: (1) drying the soil sample during preparation; (2) soil:water ratio used; (3) soluble salts content;

(4) seasonally influenced carbon dioxide content; (5) amount of grinding given the soil; and (6) electrode junction potential (Jackson, 1958; Peech, 1965).

Care must be taken to insure electrode life and accurate pH measurements: (1) Electrode should not remain in the sample longer than necessary for a reading, especially if more alkaline than pH 9.0. (2) Electrode should be washed with a jet of distilled water from a wash bottle after every measurement (sample or buffer solution). (3) Electrode should be dipped in dilute (1 part acid to 3 parts water) hydrochloric acid for a few seconds and washed with distilled water to remove any calcium carbonate film which may form, especially from alkaline samples. (4) Drying out of the electrode should be avoided. Electrode is cleaned and suspended in distilled water (which is protected from evaporation) for storage. (6) Place pH meter in standby position when electrode is not in a solution (Jackson, 1958; Peech, 1965).

The pH meter and electrode should be standardized with buffers differing by 3 or 4 pH units, such as 4.0 and 7.0, before beginning a series of measurements. After every tenth measurement, recheck the standardization with both buffers. Care should be taken not to contaminate one buffer with the other buffer or with the test solution. Never return used standard buffers to their stock bottles. The procedure describes the technique for measuring pH with a glass electrode and meter. If pH is taken in the field using color paper strips or indicator solutions, modification will have to be made by qualified personnel to the procedure.

3.2.2.3 Chemicals—

1. Standard buffer solutions, pH 4.00 and pH 7.00.

2. Distilled water (H_2O).

3.2.2.4 Materials—

1. pH meter (Corning model 12 or equivalent) equipped with combination electrode.

2. Paper cups, 30 ml (1 oz) capacity.

3. Plastic cups.

4. Stirring rod.

5. Wash bottle containing distilled water.

6. Balance, can be read to 0.1 g.

3.2.2.5 Procedure—

1. Turn on, adjust temperature setting, and "zero" pH meter per instruction manual.

2. Place pH 4.0 and pH 7.0 standard buffers in two plastic cups (one buffer in each cup). NOTE: NEVER return used buffers to stock bottles.

3. Place electrode in the pH 7.0 buffer.

4. Adjust pH meter to read pH 7.0.

5. Remove electrode from buffer solution and wash with a jet of distilled water from a wash bottle.

6. Place electrode in the pH 4.0 buffer and check the pH reading. NOTE: If pH meter varies more than ± 0.1 pH units from 4.0, something is wrong with the pH meter, electrode, or buffers.

7. Weigh 10 g of less than 60 mesh material into a paper cup.

8. Add 5 ml of distilled water to sample. NOTE: Do not stir! Allow water to wet sample by capillary action without stirring. With most overburden and minesoils materials, the 2:1 (soil:water) ratio provides a satisfactory paste for pH measurements; however, for the very coarse textured and the very fine textured material, more material or water can be added to bring the soil near saturation. At near saturation conditions, water should not be puddled nor dry soil appear at the surface.

9. Stir sample with a spatula until a thin paste is formed adding more water or soil as required to keep soil at saturation point. NOTE: At saturation, the soil paste glistens as it reflects light and the mixture slides off the spatula easily. Wash the spatula with a jet of distilled water before stirring another sample.

10. Place electrode in paste and move carefully about to insure removal of water film around the electrode. CAUTION: Do not trap particles between electrode and inside surface of the sample container. Electrodes are easily scratched. Contact between paste and electrode should be gentle to avoid both impact and scratching damage, especially in sandy samples.

11. When reading remains constant, record pH and remove electrode from paste. Carefully wash electrode with distilled water to insure removal of all paste. If all pH measurements are completed, the electrode should be stored in a beaker of distilled water. NOTE: After every 10 samples, check meter calibration with standard buffers.

3.2.3 Neutralization Potential

3.2.3.1 Principles—

The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated to insure that the reaction between the acid and the neutralizers goes to completion.

The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide (Jackson, 1958).

3.2.3.2 Comments--

A fizz rating of the neutralization potential is made for each sample to insure the addition of sufficient acid to react all the calcium carbonate present.

During digestion, do not boil samples. If boiling occurs, discard sample and rerun. Before titrating with acid, fill buret with acid and drain completely. Before titrating with base, fill buret with base and drain completely to assure that free titrant is being added to the sample.

3.2.3.3 Chemicals--

1. Carbon dioxide-free water: Heat distilled water just to boiling in a beaker. Allow to cool slightly and pour into a container equipped with ascarite tube. Cool to room temperature before using.

2. Hydrochloric acid (HCl) solution, 0.1 N, certified grade (Fisher So-A-54 or equivalent).

3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 g of NaOH pellets in carbon dioxide-free water and dilute to 1 liter. Protect from CO_2 in the air with ascarite tube. Standardize solution by placing 50 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH using the following equation:

$$N_2 = (N_1V_1)/V_2, \text{ where:}$$

V_1 = Volume of HCl used.

N_1 = Normality of HCl used.

V_2 = Volume of NaOH used.

N_2 = Calculated Normality of NaOH.

4. Sodium hydroxide (NaOH) approximately 0.1 N: Dilute 200 ml of 0.5 N NaOH with carbon dioxide-free water to a volume of 1 liter. Protect from CO_2 in air with ascarite tube. Standardize solution by placing 20 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH using the equation in 3.2.3.3 No. 3.

5. Hydrochloric acid (HCl), approximately 0.5 N: Dilute 42 ml of concentrated HCl to a volume of 1 liter with distilled water. Standardize solution by placing 20 ml of the known Normality NaOH prepared in 3.2.3.3 No. 3 in a beaker and titrating with the prepared HCl until a pH of 7.00 is obtained.

Calculate the Normality of the HCl using the following equation:

$$N_1 = (N_2V_2)/V_1,$$ where:

V_2 = Volume of NaOH used.

N_2 = Normality of NaOH used.

V_1 = Volume of HCl used.

N_1 = Calculated Normality of HCl.

6. Hydrochloric acid (HCl), approximately 0.1 N: Dilute 200 ml of 0.5 N HCl to a volume of 1 liter with distilled water. Standardize solution as in 3.2.3.3.5, but use 20 ml of the known Normality NaOH prepared in 3.2.3.3 No. 4.

7. Hydrochloric acid (HCl), 1 part acid to 3 parts water: Dilute 250 ml of concentrated HCl with 750 ml of distilled water.

3.2.3.4 Materials—

1. Flasks, Erlenmeyer, 250 ml.
2. Buret, 100 ml (one required for each acid and one for each base).
3. Hotplate, steam bath can be substituted.
4. pH meter (Corning Model 12 or equivalent) equipped with combination electrode.
5. Balance, can be read to 0.01 g.

3.2.3.5 Procedure (revised and updated from Smith et al., 1974)—

1. Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.
2. Add one or two drops of 1:3 HCl to the sample. The presence of $CaCO_3$ is indicated by a bubbling or audible "fizz."
3. Rate the bubbling or "fizz" in step 2 as indicated in Table 1.
4. Weigh 2.00 g of sample (less than 60 mesh) into a 250 ml Erlenmeyer flask.
5. Carefully add HCl indicated by Table 1 into the flask containing sample.
6. Heat nearly to boiling, swirling flask every 5 minutes, until reaction is complete. NOTE: Reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

TABLE 1. VOLUME AND NORMALITY OF HYDROCHLORIC ACID USED FOR EACH FIZZ RATING

Fizz Rating	HCl (ml)	HCl (Normality)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

7. Add distilled water to make a total volume of 125 ml.

8. Boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling.

9. Titrate using 0.1 N NaOH or 0.5 N NaOH (concentration exactly known), to pH 7.0 using an electrometric pH meter and buret. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in step 5. NOTE: Titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.

10. If less than 3 ml of the NaOH is required to obtain a pH of 7.0, it is likely that the HCl added was not sufficient to neutralize all of the base present in the 2.00 g sample. A duplicate sample should be run using the next higher volume or concentration of acid as indicated in Table 1.

11. Run a blank for each volume or normality of acid using steps 5,7, 8, and 9.

3.2.3.6 Calculations--

1. Constant (C) = (ml acid in blank)/(ml base in blank).

2. ml acid consumed = (ml acid added) - (ml base added X C).

3. Tons $CaCO_3$ equivalent/thousand tons of material = (ml of acid consumed) X (25.0) X (N of acid).

3.2.4 Maximum Potential Acidity by Total Sulfur Determination

3.2.4.1 Principles--

This method measures the total sulfur in a sample. If all of the total sulfur occurs in pyritic forms, the calculation of maximum potential acidity from sulfur corresponds with actual potential acidity from sulfur. But if part of the sulfur occurs in other forms, the maximum as calculated will be too high. This is the reason that such calculations are referred to as maximums and in doubtful cases approximate determinations should be made which rule out other sulfur forms (see 3.2.6). These determinations are not necessary when the maximum acid from total sulfur is within safe limits.

A sample is heated to approximately 1600°C. A stream of oxygen is passed through the sample during the heating period. Sulfur dioxide is released from the sample and collected in a dilute hydrochloric acid solution containing potassium iodide, starch, and a small amount of potassium iodate. This solution is automatically titrated with a standard potassium iodate solution.

A trace amount of potassium iodate reacts with potassium iodide and dilute hydrochloric acid to yield free iodine, potassium chloride and water. The free iodine combines with the sulfur dioxide and water to yield sulfuric acid and hydroiodic acid. The amount of potassium iodate solution used during the titration is recorded. The calculation of the percent total sulfur is based on the potassium iodate measurement (Smith et al., 1974).

3.2.4.2 Comments--

Some samples, e.g. coal, when first placed in the furnace may change the color of the solution in the titration vessel to pink or purple (probably due to organic compounds). Some samples may contain halogens (iodine, chlorine, fluorine) which darken the solution in the titration vessel and will therefore produce results that are low. The halogen problem, if encountered, may be eliminated by the use of an antimony trap between the furnace and titration assembly. Interference may result with samples high in nitrogen; however, this does not appear to happen with rock samples. Additional information can be obtained by reading Leco Equipment Application 120 and Instructions for Analysis of Sulfur in Hydrocarbons by the Leco High Frequency Combustion Titration Procedure.

Materials with a low chroma (2 or less) may have a high (over 1.0%) sulfur content; therefore, use a 0.250 g sample when the chroma of the material is 1 or 2. If the chroma of the material is zero, a 0.100 g sample is used. If sulfur is not detectable or more accurate values are desired in this sample size, increase to next highest sample size and rerun.

Read entire manuals on both the Leco Induction Furnace and the Automatic Titrator.

Periodically clean titration chamber and associated glassware with acetone or concentrated hydrochloric acid and rinse thoroughly with distilled water.

The following procedure is for use with a LECO Induction Furnace, Model 521 with Automatic Sulfur Titrator, Model 532. Other similar or advanced models of this instrumentation may perform equally well; however, the following procedure will require detailed modifications by a qualified person for application to other instruments.

3.2.4.3 Chemicals--

1. Iron chip accelerator (Leco number 501-077).

2. Iron powder accelerator (Leco number 501-078).

3. Copper ring (Leco number 550-189).

4. Magnesium oxide (MgO).

5. Potassium iodate (KIO_3), 0.0052 N: Dissolve 1.110 g KIO_3 in distilled water and dilute to 1 liter.

6. Hydrochloric acid (HCl) solution: Dilute 15 ml of concentrated HCl to a volume of 1 liter with distilled water.

7. Arrowroot starch solution: Dissolve 4.0 g of arrowroot starch (Leco number 501-061) in 100 ml of distilled water in a 250 ml beaker. Stir on a mechanical stirrer with a stirring bar. While starch is stirring, boil 300 ml of distilled and deionized water in a 600 ml beaker. Remove from heat when boiling point is reached. Remove starch from stirrer. Place boiled water on mechanical stirrer with stirring bar. While water is continually stirring, add 5 ml of starch mixture in 20 second intervals until all starch solution has been added. Place a small amount of the solution in the 600 ml beaker back into the 250 ml beaker that contained the starch mixture. Wash beaker by hard swirling and then pour contents back into the 600 ml beaker. Continue stirring solution in the 600 ml beaker allowing solution to cool to 40°C. Add 12.0 g of potassium iodide (KI). Continue stirring for 15 to 20 minutes.

8. Potassium iodide (KI).

9. Sulfur standards (Leco number 501-502).

3.2.4.4 Materials--

1. Leco Automatic Sulfur Analyzer, package unit, number 634-700.

2. Scoops, 0.2 ml volume.

3. Ceramic crucibles with porous covers.

4. Carboys, 19 liters (5 gal).

5. Tongs.

6. Glass wool.

7. Oxygen regulators.

8. Mechanical stirrer.

9. Stirring bar.

10. Combustion tube, hydrocarbon (Leco number 519-004).

11. Hot plate.

12. Balance, can be read to 0.001 g.

3.2.4.5 Procedure (revised and updated from Smith et al., 1974)—

NOTE: Read entire manuals on Leco Furnace, Automatic Titrator and this entire procedure before starting.

1. Place one level scoop of iron chips in crucible.

2. Weigh 0.500 g of sample (less than 60 mesh) into the crucible.

NOTE: For samples that are suspected to contain over 1% sulfur or have a chroma of less than 2, see 3.2.4.2.

3. Add one scoop MgO.

4. Add one copper ring and then one scoop of iron powder.

5. Gently shake the crucible to evenly cover the bottom and place one porous cover on the crucible.

6. Turn on "Filament Voltage" grid tap to medium position.

7. Wait for one minute then turn "High Voltage" switch to ON.

8. Set "Titrate-Endpoint" switch to its middle position.

9. Turn on titrator (upper left switch above "Endpoint Adjust").

10. Drain "Titration Vessel" completely.

11. Set timer switch to ON, adjust timer to 10 minutes, or a time sufficient to satisfy steps 25, 26, and 27.

12. Slosh carboys containing HCl and KIO_3 to mix the condensate on the walls of the container.

13. Fill "Iodate Buret."

14. Fill "Titration Vessel" approximately one-third full with the HCl solution.

15. Turn on oxygen. Set the pressure to 15 psi, and the flow rate to 1.0 liter per minute. NOTE: Oxygen flow must be started before starch is added.

16. Raise the "Locking Mechanism Handle" WITHOUT a sample crucible on the pedestal, and lock in place. NOTE: Make sure there is an airtight contact between sample platform and combustion chamber by observing a vigorous bubbling in the "Titration Vessel" chamber.

17. Add one measure (5 ml) of starch solution. NOTE: If solution in "Titration Vessel" chamber turns turbid or yellow after starch solution is added, turn off the instrument following steps 33 through 39 and make NEW starch solution.

18. Set "Titrate-Endpoint" switch to "Endpoint."

19. After a few seconds when titrant level in "Iodate Buret" has stopped falling (Buret reading should be no more than 0.004) the solution in the "Titration Vessel" chamber should be a deep blue. NOTE: If the solution is a pale blue or almost black, turn off the instrument following steps 33 through 39 and make NEW starch solution.

20. Set "Titrate-Endpoint" switch to middle position and lower "Locking Mechanism Handle."

21. Refill "Iodate Buret."

22. Place sample crucible on pedestal, making sure it is centered, and carefully raise "Locking Mechanism Handle" and lock in place.

NOTE: Make sure there is an airtight contact between sample platform and combustion chamber by observing a vigorous bubbling in the "Titration Vessel" chamber.

23. Set "Titrate-Endpoint" switch to Titrate, or if it is known that sample will evolve SO_2 slowly, set switch at Endpoint. The Endpoint setting acts as a "Fine Control" allowing buret valve to discriminate smaller increments.

24. Push RED button on timer to start analysis.

25. Plate current must go to 400-450 ma for at least 2 minutes during the analysis; if not, reweigh and rerun sample.

26. Adjust rheostat to prevent plate current from exceeding 450 ma.

27. When buret reading does not change for 2 minutes, and Plate Current has achieved 400 to 450 ma, it can be assumed that all of the sulfur has been removed from the sample. If buret reading is still changing when timer shuts off instrument, set Timer Switch to OFF, which restarts furnace, leave furnace on until buret is stable for 2 minutes, then turn Timer Switch to ON.

28. Set "Titrate-Endpoint" to middle position. IMPORTANT: Record titration reading.

29. Lower sample platform, remove crucible using tongs, place fresh sample crucible in place, but do not close sample chamber.

NOTE: Slightly drain titrating chamber to maintain original level. Drain, flush, and refill titrating chamber every 3rd sample, or more often if a large quantity of titrant was used by the previous sample (steps 16-22).

30. Refill KIO_3 buret.

31. Close sample chamber, making sure it is tight. Check endpoint (steps 18, 19 and 21).

32. Go to step 23 and continue until all samples have been processed.

33. Turn "Titrate-Endpoint" switch to mid position.

34. Turn off main O_2 valve on top of tank.

35. Turn off "High Voltage."

36. Turn off Automatic Titrator.

37. Drain titration chamber; flush twice with a chamber full of HCl solution or water, cover and leave chamber full of HCl solution.

38. If O_2 has stopped bubbling in the purifying train, turn off small knurled valve on gauge outlet.

39. Turn off "Filament Voltage."

<u>3.2.4.6 Calculations</u>--

1. Percent sulfur. NOTE: Percent sulfur is dependent upon the concentration of potassium iodate titrant and sample size.

A. Using 1.110 g KIO_3/L and 0.500 g sample (0.005 - 1.00% sulfur range)
%S = Buret reading X 5.0.

B. Using 1.110 g KIO_3/L and 0.250 g sample (0.010 - 2.00% sulfur range)
%S = Buret reading X 10.0.

C. Using 1.110 g KIO_3/L and 0.100 g sample (0.025 - 5.00% sulfur range)
%S = Buret reading X 25.0.

2. To convert % sulfur to maximum $CaCO_3$ equivalents: Multiply % sulfur by 31.25 to get tons $CaCO_3$ equivalent/1000 tons of material.

3.2.6 HCl-Extractable, HNO_3-Extractable and Non-Extractable Total Sulfur

3.2.6.1 Principle—

In doubtful cases, as stated in 3.2.4.1, this method should be used to rule out HCl-extractable and non-extractable forms of sulfur which are not considered to be acid formers. The HNO_3-extractable sulfur is determined by calculations. This form of sulfur will react with oxygen to produce acid.

3.2.6.2 Comments—

It is necessary to remove chlorides and nitrates by water leachings after the hydrochloric and nitric acid (respectively) extractions before running total sulfur.

Care should be taken that no sample is lost by run over, splashing or breaking through the filter paper during all leachings.

3.2.6.3 Chemicals—

1. Hydrochloric acid (HCl), 2 parts acid to 3 parts water: Mix 400 ml of concentrated HCl with 600 ml of distilled water.

2. Nitric acid (HNO_3), 1 part acid to 7 parts water: Mix 125 ml of concentrated HNO_3 with 875 ml of distilled water.

3. Silver Nitrate ($AgNO_3$), 10%: Dissolve 10.0 g of $AgNO_3$ in 90 ml of distilled water. Store in amber bottle away from light.

4. Nessler's Solution (Fisher Scientific Co. No. So-N-24 or equivalent).

3.2.6.4 Materials—

1. Leco Induction Furnace and Automatic Sulfur Titrator as in 3.2.4.4.

2. Funnels, 28 mm I.D. polyethylene.

3. Filter paper, 5.5 cm glass fiber.

4. Flasks, Erlenmeyer, 250 ml.

5. Beakers, 100 ml.

6. Syringe.

7. Balance, can be read to 0.001 g.

3.2.6.5 Procedure (Revised and updated from Smith et al., 1974)—

1. Take three 0.500 g subsamples of less than 60 mesh material.

2. Take one subsample and analyze for total sulfur (see 3.2.4).

3. Taking care not to sharply crease the glass fibers, fold filter paper to fit a polyethylene funnel.

4. Place second subsample in filter. NOTE: Make sure all material is placed in the filter.

5. Place subsample and filter onto funnel holder in sink or other suitable pan which can receive outflow from funnel.

6. Using a syringe, pipette, or other graduated dispenser, add 2:3 HCl to almost the top of the filter paper. Caution: During this step and all other leaching steps, be careful not to lose any sample by runover, splashing, or breaking through the filter paper.

7. Repeat step 6 until a total of 50 ml of acid has been added.

8. Place funnel holder, containing funnel and subsample, over a 100 ml beaker.

9. Leach subsample with 50 ml of distilled and deionized water. Discard leachate. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Samples must be kept moist.

10. Leach subsample with another 50 ml of distilled and deionized water.

11. Test leachate for chlorides by adding 3 drops of 10% $AgNO_3$ with a dropper. NOTE: The presence of chlorides will be detected by a white precipitate.

12. Discard leachate and repeat steps 10 and 11 until no precipitate forms.

13. Discard leachate.

14. Air dry subsample and filter overnight.

15. Carefully fold glass fiber filter around the sample and transfer to a ceramic crucible for total sulfur analysis (see 3.2.4).

16. Place third subsample in a 250 ml Erlenmeyer flask. NOTE: Make sure all of the subsample is placed in the flask.

17. Add 50 ml of HNO_3 (1:7).

18. Let stand overnight at room temperature.

19. Taking care not to sharply crease the glass fibers, fold a filter to fit a polyethylene funnel.

20. Place a funnel holder over a sink or other suitable pan which can receive outflow from funnel.

21. Carefully pour subsample and acid from the Erlenmeyer flask into the funnel. NOTE: Do not get material above top of filter paper.

22. Repeat step 21 using distilled and deionized water to wash all materials remaining in the Erlenmeyer flask into the funnel.

23. Place funnel holder containing funnel and subsample over a 100 ml beaker. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Sample must be kept moist.

24. Leach subsample with 50 ml of distilled and deionized water. Discard leachate.

25. Leach subsample with another 50 ml of distilled and deionized water.

26. Test leachate for presence of nitrates by adding 3 drops of Nessler's Solution with a dropper. NOTE: If nitrates are present, the leachate will turn yellow within 30 seconds as seen against a white background.

27. Discard leachate and repeat steps 25 and 26 until no nitrates are detected.

28. Discard leachate.

29. Air dry subsample and filter overnight.

30. Carefully fold glass fiber filter around the sample and transfer to a ceramic crucible for total sulfur analysis (see 3.2.4).

3.2.6.6 Calculations--

1. HCl-extractable sulfur (mostly sulfates) = (Total sulfur of untreated sample) minus (Total sulfur after HCl treatment).

2. HNO_3-extractable sulfur (mostly pyritic sulfur) = (Total sulfur after HCl treatment) minus (Total sulfur after HNO_3 treatment).

3. Non-extractable sulfur (mostly organic sulfur) = Total sulfur after HNO_3 treatment.

3.2.11 Total Sulfur Estimation By Peroxide Oxidation

3.2.11.1 Principles--

Pyritic minerals begin to change into two new products when exposed to the atmosphere. The change may proceed slowly over a long period of time before the final products (yellowboy and sulfuric acid) are formed. The end product, "yellowboy," actually may form only when the sulfate is partially or completely neutralized by a basic substance. The chemical equation for this complete change in pyrite follows:

Pyrite + Oxygen + Water equals Yellowboy + Sufluric Acid

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 8H_2SO_4$$

Hydrogen peroxide greatly reduced the time needed for pyrite to oxidize to sulfuric acid and yellowboy.

3.2.11.2 Comments--

Alkaline materials interfere with the efficiency of hydrogen peroxide in oxidizing pyrite; therefore, overburden rock and minesoil samples containing carbonates need to be leached with acid and water as prescribed in steps 2 through 5 of the procedure.

When samples contain readily oxidizable organic matter, step 7 in the procedure may have to be repeated until the reaction stops.

The hydrogen peroxide used in this method must be 30% hydrogen peroxide. It must not contain stabilizers.

An important thing to remember is that this procedure works with fresh overburden and not with complex mixtures of minesoil material.

3.2.11.3 Chemicals--

1. Silver nitrate ($AgNO_3$), 10%: Dissolve 10.0 g of $AgNO_3$ with distilled water and make to a volume of 100 ml. Store in brown bottle away from light.

2. Hydrochloric acid (HCl), 2 parts acid to 3 parts water: Mix 400 ml of concentrated HCl with 600 ml of distilled water.

3. Hydrogen peroxide (H_2O_2), 30% (Fisher certified No. H-325 or equivalent).

4. Sodium hydroxide (NaOH), 1.0 N: Dissolve 40.0 g of NaOH pellets in carbon dioxide-free water (see 3.2.3.3. No. 1) and make to a volume of 1 liter. Protect from CO_2 in air with ascarite tube.

5. Sodium hydroxide (NaOH), 0.1 N: Dilute 10 ml of 1.0 N NaOH to a volume of 1 liter with carbon dioxide-free water (see 3.2.3.3. No. 1). Standardize solution (see 3.2.3.3. No. 4). Protect from CO_2 in air with ascarite tube.

3.2.11.4 Materials--

1. Sample, ground to pass a 60 mesh sieve.

2. Funnels.

3. Hotplate. NOTE: Bunsen burner may be substituted.

4. Thermometer, °C.

5. Beakers, 300 ml tall form.

6. Graduated cylinder, 25 ml.

7. Glass fiber filter (Reeve Angel 934AH or equivalent).

8. Burets, 50 ml capacity.

9. Balance, can be read to 0.01 g.

10. pH Meter (Corning Model 12 or equivalent) with combination electrode.

3.2.11.5 Procedure (modified and updated from Smith et al., 1974)—

1. Weigh 2.00 grams of less than 60 mesh sample.

NOTE: If the sample contains no carbonates and no sulfates, and the paste pH is less than 5.5, then steps 2 through 5 can be eliminated and procedure can be continued at step 6.

2. Place sample into a funnel fitted with filter paper and leach with 200 ml of 2:3 HCl in funnel-full increments.

3. Leach sample with distilled water (in funnel-full increments) until effluent is free from chloride as detected by 10% silver nitrate. Note: Add three drops of silver nitrate. If a white precipitate forms, chlorides are present.

4. Air dry filter and sample overnight, or place in 50°C forced air oven until dry.

5. Carefully scrape dried sample from filter surface and mix sample.

6. Place sample in a 300 ml tall form beaker.

7. Add 24 ml of 30% H_2O_2 and heat beaker on hotplate until solution is approximately 40°C. Remove beaker from hotplate and allow reaction to go to completion as shown when bubbling ceases. NOTE: Three blanks for each batch of samples should be handled in the same manner. CAUTION: Initial reaction may be quite turbulent when samples contain more than 0.1% sulfur.

8. Add an additional 12 ml of H_2O_2 (30%) to beaker and allow reaction to go to completion as shown when bubbling ceases.

9. Place beaker on hotplate and heat to approximately 90 to 95°C, solution temperature, until any unreacted H_2O_2 left in beaker is destroyed as shown when bubbling ceases. Do not allow to go to dryness.

10. Wash down the sides of the beaker with distilled water and make the volume of the solution to approximately 100 ml.

11. Place beaker on the hotplate and heat the solution to boiling to drive off any dissolved CO_2, then cool the solution to room temperature.

12. Titrate the solution with 0.0100 N NaOH, that is free to CO_2 and protected from the atmosphere, to pH 7.0 using a pH meter.

3.2.11.6 Calculations—

1. meq H^+/100 g = (ml of NaOH) X (N of NaOH) X (100g/weight of sample).

2. % S = 0.0185 (meq H^+/100g) - 0.0806. (Grube, et al., 1973).

3. To convert percent sulfur (% S) to maximum $CaCO_3$ equivalents: Multiply %S by 31.25 to get tons $CaCO_3$ equivalent/1000 tons of material.

HYDROGEN PEROXIDE METHOD FOR TOTAL POTENTIAL ACIDITY (PA)

SOIL TESTING LAB, DIVISION OF REGULATORY SERVICES, LEXINGTON, KY
Procedure re-typed from (Barnhisel and Harrison 1976)

1. Introduction

1.1. Development work on the Total Potential Acidity test was done to obtain reliable, reproductive and accurate values on a routine basis. The following meets these criteria except that if lime is present in the soil, an erroneously low Potential Acidity value will be obtained. An effervescence test for lime has been included in the procedure to aid in judgments made on potential acidity values. It is suggested that further work be done on the interferences encountered when lime is present.

1.2. The total Potential Acidity is the Potential Acidity plus the free acidity of the soil. The free acidity is the acidity of the soil as found and the Potential Acidity is the acidity of the soil after oxidation of sulfides has occurred. In this test, the sample is ground to 80-mesh, oxidized using reagent grade 30% H_2O_2 and titrated with 0.0200 to 0.0500 N NaOH to determine its total Potential Acidity. The total Potential Acidity is then reported as the amount of agricultural grade lime required to neutralize one acre of soil to plow depth (or 1000 tons of material).

1.3. One of the major sources of sulfides found around stripmine areas is from Pyrite (FeS_2). Its oxidation with H_2O_2 is shown as follows:

$$2FeS_2 + 15H_2O_2 \rightarrow Fe_2O_3 + 4SO_4 + H_2O + 8H^+$$

For every equivalent to FeS_2 present, 4 equivalents of hydrogen ion are produced.

1.4. Ten tons per acre of agricultural grade lime is the cut-off value determining whether or not a mine operator has to build holding ponds or not. This pertains only to highwall samples and not mine spoils. Highwall samples are core drillings or chippings of outfaces of rock before actual strip mining begins. Mine spoils are soil samples taken in an area which has been stripped and the area is being reclaimed. The material must be handled as toxic. From the equation, only 20 mg FeS_2 in a 5 g sample are needed to give a 10 tons per acre value. Because of the small quantities of Iron Pyrite involved, it is necessary to prepare the sample with care, especially in the grinding and mixing of the sample.

2. Sample Preparation

2.1. HIGHWALL: The sample is crushed through the jaw crusher to particles no larger than one-quarter inch. The whole sample is then ground in the pulverizer to pass through a 10-mesh screen. This sample is then placed into the sample container and stirred. Then several scoops of the sample are placed back through the pulverizer to pass through an 80-mesh screen. The 80-mesh sample is then placed in a 4-ounce plastic jar. A micro-mill may be used to finish grinding what the pulverizer did not grind. The mill is set to grind for 1 ½ to 2 minutes. At the end of the 2-minute cycle, turn the micro-mill completely over and run for 5 seconds. This allows the mill to clean itself to the top half for easier removal of the sample. Sieve this portion into the rest of the 80-mesh sample.

2.2. MINE SPOILS: The sample is given a lab number, then it is treated as a routine soil sample and ground to 10-mesh. For the total potential acidity test, the sample is split by riffling until one portion fits into a 4-ounce jar. Place all of the remaining sample in the pint box. The 4-ounce jar portion is then ground using the pulverizer until it all passes through to 80-mesh screen. A micro-mill may be used to finish grinding what the pulverizer did not grind fine enough. The mill is set to grind for 1 ½ to 2 minutes. At the end of the 2-minute cycle, turn the micro-mill completely over and run for 5 seconds. This allows the mill to clean itself to the top half for easier removal of the sample. Sieve this portion into the rest of the 80-mesh sample and place it back into the jar.

3. Apparatus

3.1. 500 ml beakers.

3.2. Watch glasses (ribbed).

3.3. pH meter and electrodes.

3.4. Balance – to weigh to nearest 0.01 gram.

3.5. Hotplate, adjustable to "simmer" and "boil".

3.6. Hot water bath.

3.7. Oxford pipettor, to dispense 10 ml portions of H_2O_2.

3.8. Magnetic stirrer, with stir magnets.

3.9. Rubber spatula.

3.10. Kimax Buret, 50 ml Class A, calibrated to 0.1 ml.

3.11. Thermometer, to measure to at least 50°C.

4. Reagents

4.1. Hydrogen Peroxide (H_2O_2), about 30%.

4.2. Sodium Hydroxide (NaOH), 0.02 to 0.05 N: Add 30 ml 1:1 NaOH to 18 liters deionized (DI) water. Titrate solution to find exact Normality. Store in Nalgene carbuoy.

5. Procedure

5.1. Weigh a 5.00 g sample into a 500 ml beaker and cover with ribbed watch glass. (Use top loading balance on 0.01 g sensitivity.)

5.2. Place sample beaker in hot water bath at 50°C.

5.3. By Oxford pipettor, add 10 ml H_2O_2 and wait until reaction stops. Continue adding 10 ml increments of H_2O_2 until a volume of 120 ml has been added. (Time process for 36 samples is 3 to 4 hours.) Keep at 50°C for the remainder of the day and the night, allowing the reaction to continue throughout the night.

5.4. Remove from bath and place on 95°C hot plate. Boil until all effervescence has stopped. Add DI water if volume gets low. DO NOT ALLOW TO BOIL DRY.

5.5. Allow samples to cool to room temperature and add DI water to make a total volume of 150 ml, cleaning insides of beakers with spatula and rinsing with DI water.

5.6. Titrate with (0.0200 to 0.0500) N NaOH while stirring, to a pH of 7.00.

5.7.

$$\text{Tons/Acre} = \begin{array}{c|c|c} \text{ml NaOH} & \text{N} & 15 \\ \hline & & \end{array}$$

5.8. If 5.7 is greater than 20 Tons/Acre, then repeat process using 1.0000 grams of sample. (Use analytical balance of 0.01 mg sensitivity.)

5.9. If 5.8 is greater than 100 Tons/Acre (Using 1.0000 gram sample), then repeat process using 0.2000 grams of sample.

6. Calculations

6.1.

$$\begin{array}{c|c|c} \text{ml NaOH} & \text{N} & 100\text{ g} \\ \hline & & 5\text{ g} \end{array} = \frac{\text{meq H}}{100\text{ g}}$$

6.2.

$$\begin{array}{c|c|c} \text{meq} & \text{H} & 0.01 \\ \hline 100\text{ g} & & \end{array} = \frac{\text{tons H}}{1000\text{ tons (material)}}$$

6.3. One ton of H requires 50 tons of pure $CaCO_3$ equivalent to neutralize it. Since agricultural lime is not pure $CaCO_3$ and it is also slow acting, it takes 1 ½ times the above amount or 75 tons for 1 ton H.

6.4. Complete Calculation:

$$\begin{array}{c|c|c|c|c} \text{ml NaOH} & \text{N} & 100\text{ g} & 0.01 & 75\text{ tons} \\ \hline & & & & \end{array} = \begin{array}{l} \text{tons of Ag. lime per 1000} \\ \text{tons material or 1 acre plow} \\ \text{layer of soil} \end{array}$$

6.5. Final Calculation:

$$\begin{array}{c|c|c} \text{ml NaOH} & \text{N} & 15 \\ \hline & & \end{array} = \text{tons Ag. lime / acre}$$

7. Remarks

7.1. Preliminary tests: Before doing the potential acidity test, two other tests may need to be made: pH and free carbonates.

8. Test for Free Carbonates

NOTE: For most soil samples, this test may not be necessary.

Scoop about 1 scoopful (4.5 cc) of dry 10-mesh soil sample into a 50 ml beaker, and add approximately 10 ml DI water and stir or swirl to remove bubbles. After the main portion of the soil has settled, pour off excess water. Add 4-6 ml of 1:1 HCl and stir with a small glass rod. Immediately observe the surface for bubbling (effervescence). Effervescence is rated a $^{+}$, $^{++}$, $^{+++}$, referring to carbonate particles as: few numerous to very numerous. An exceptionally vigorous effervescence is noted as $^{+++}$ "loaded" or excessive. Rating of effervescence is relative and proficiency in estimating it comes from experience.

Barnhisel, R. I. and J. Harrison (1976). Estimating Lime Requirement by a Modified Hydrogen Peroxide Potential Acidity Method. Lexington, KY, (Unpublished method for KY Agr. Ex. Sta., Soil Testing Laboratory).

PROCEDURE FOR LEACHING CARBONATES FROM SAMPLE OF PYRITE-BEARING GEOMATERIAL

Procedure from (O'Shay et al. 1990)

1. Soak a scoop (< 5 g) of sample ground to < 149 μm (< 100 mesh) for ≥ 2 hours in 100 mL of 6M hydrochloric acid (HCl) in a 250 mL Erlenmeyer flask. Continually agitate sample suspension in flask on a platform shaker at 180 excursions/minute during the soaking period.
2. Following soaking, transfer sample suspension to a vacuum filtration funnel fitted with Whatman 42 filter paper.
3. Remove the residual HCl from the sample by leaching with 300-400 mL of 1M calcium chloride ($CaCl_2$). Filter sample until it becomes dry.
4. Place sample in a forced-air oven at 40°C for several hours until totally dry.

O'Shay, T., L. R. Hossner, et al. (1990). "A modified hydrogen peroxide method for determination of potential acidity in pyritic overburden." Journal of Environmental Quality 19: 778-782.

Appendix D – Glossary

Appendix D – Glossary

All unmarked terms are from the AGI Dictionary of Geological Terms (Bates and Jackson 1984). Terms marked with an asterisk (*) are from Webster's Ninth New College Dictionary (Mish 1991). Terms marked with an (^{A}) are defined by the report authors. Although multiple definitions sometimes apply for a particular term, this glossary includes only those definitions applicable to this report.

ABA - see Acid Base Accounting

abiotic^A - occurring chemically with no bacterial catalyzation.

acid* - any of various typically water-soluble and sour compounds that are capable of reacting with a base to form a salt, that redden litmus, that are hydrogen-containing molecules or ions able to give up a proton to a base, or that are substances able to accept an unshared pair of electrons from a base.

Acid Base Accounting^A - Acid-Base Accounting (ABA) is one of the most common methods for characterizing the acid potential of overburden rock and soil, especially in the coal mining industry. The analysis is based on the identification of toxic or potentially acid-producing materials (defined by the amount of total or pyritic sulfur present) and the determination of the neutralization potential (defined by the amount of non-acid or calcareous materials present that may neutralize acid).

acid mine drainage (AMD) - drainage with a pH of 2.0 to 4.5 from mines and mine wastes. It results from the oxidation of sulfides exposed during mining, which produces sulfuric acid and sulfate salts. The acid dissolves minerals in the rocks, further degrading the quality of the drainage water.

acidic - when referring to hydrothermal, pegmatitic, or other aqueous fluids the term is used in its chemical sense of high hydrogen-ion concentration (low pH).

alkalinity - 1) the quantity and kinds of compounds present in a lake that collectively shift the pH to the alkaline side of neutrality. 2) the number of millequivalents of hydrogen ion that is neutralized by one liter of sea water at 20ºC.

AMD - see acid mine drainage.

anhedral - said of a mineral crystal showing no rational faces, or of a detrital grain that shows no crystal outline.

anoxic - having a deficiency of oxygen.

base* - any of various typically water-soluble and bitter tasting compounds capable of reacting with an acid to form a salt that are molecules or ions able to take up a proton from an acid or substances able to give up an unshared pair of electrons to form an acid.

basic^A - when referring to hydrothermal, pegmatitic, or other aqueous fluids the term is used in its chemical sense of low hydrogen-ion concentration (high pH).

biotic^{A} - of or relating to life; occurring with bacterial catalyzation.

bitumen* - any of various mixtures of hydrocarbons (as tar) often together with their nonmetallic derivatives that occur naturally or are obtained as residues after heat-refining naturally occurring substances (as petroleum).

bituminous* - of or containing bitumen.

calcareous - containing calcium carbonate. When applied to a rock name, it implies that as much as 50% of the rock is calcium carbonate.

carbonaceous - 1) said of a rock or sediment that is rich in carbon; coaly. 2) said of a sediment containing organic matter.

catalyst* - a substance that initiates a chemical reaction and enables it to proceed under different conditions (as at a lower temperature) than otherwise possible.

claystone - 1) an indurated clay having the texture and composition of shale but lacking its fine lamination or fissility. 2) a concretionary body of clay in alluvium or of calcareous material in clay.

deposition - 1) the laying-down of rock-forming material by any natural agent, e.g. the mechanical settling of sediment from suspension in water. 2) the precipitation of mineral matter from solution, e.g. of quartz in veins.

detrital - pertaining to or formed from detritus; esp. said of minerals occurring in sedimentary rocks, which were derived from pre-existing rocks either within or outside the basin of deposition.

Devonian - a period of the Paleozoic era (after the Silurian and before the Mississippian), though to have covered the span of time between 400 and 345 million years ago; also, the corresponding system of rocks. It is named after Devonshire, England, where rocks of this age were first studied. Informally known as the “age of fishes”.

diagenesis - 1) all the changes undergone by a sediment after its initial deposition, exclusive of weathering and metamorphism. It includes those processes (such as compaction, cementation, replacement) that occur under conditions of pressure and temperature that are normal in the outer part of the earth’s crust, and according to most U.S. geologists it includes changes occurring after lithification. There is no universally accepted definition of the term, or of its delimitation, e.g. with metamorphism. 2) the geochemical processes or transformations that affect clay minerals before burial in the marine environment.

disseminate* - to disperse throughout.

efflorescence - 1) a white powder, produced on the surface of a rock or soil in an arid region by evaporation of water, or by loss of water or crystallization on exposure to the air. It commonly consists of soluble salts such as gypsum, calcite, natron, or halite. 2) the process by which an efflorescent salt or crust is formed.

estuarine* - of, pertaining to, or formed in an estuary.

estuary* - a water passage where the tide meets a river current; an arm of the sea at the lower end of a river.

ettringite[A] - an expansive sulfate mineral, $Ca_6[Al(OH)_6]_2$ $(SO_4)_3$ $26H_2O$, produced when gypsum reacts with lime in swelling clay soils such as montmorillonite.

ferric* - 1) of, relating to, or containing iron. 2) ferric iron.

ferrous* - 1) of, relating to, or containing iron. 2) being or containing iron with a valence of two.

fissure - 1) an extensive crack, break, or fracture in the rocks. It may contain mineral-bearing material. 2) crevasse.

framboid - a microscopic aggregate of pyrite grains in shale, often in spheroidal clusters resembling raspberry seeds. It was considered to be the result of colloidal processes but is now linked with the presence of organic materials. Adj: framboidal. Etymol: French framboise, "raspberry."

geochemistry - the study of the distribution and amounts of the chemical elements in minerals, ores, rocks, soils, water, and the atmosphere, and their circulation in nature, on the basis of the properties of their atoms and ions; also, the study of the distribution and abundance of isotopes, including problems of nuclear frequency and stability in the universe. A major concern of geochemistry is the synoptic evaluation of the abundance of the elements in the earth's crust and in the major classes of rocks and minerals.

gypsum - a widely distributed mineral consisting of hydrous calcium sulfate: $CaSO_4 \cdot 2H_2O$. It is the commonest sulfate mineral, and is frequently associated with halite and anhydrite in evaporites, forming thick, extensive beds, esp. in rocks of Permian and Triassic age. Gypsum is used mainly as a retarder in portland cement, and in making plaster of Paris. Etymol: Greek gypsos, "chalk."

heave - an upward movement of a surface caused by expansion, as from swelling clay, removal of overburden, or frost action.

hydrothermal - of or pertaining to hot water, to the action of hot water, or to the products of this action, such as a mineral deposit precipitated from a hot aqueous solution; also, said of the solution itself. "Hydrothermal" is generally used for any hot water, but has been restricted by some to water of magmatic origin.

induration - the hardening of a rock or rock material by heat, pressure, or the introduction of cementing material; esp. the process by which relatively consolidated rock is made harder or more compact. See also: lithification.

iron - a heavy magnetic malleable and ductile chemically active mineral, the native metallic element Fe. Native iron is rare in terrestrial rocks but common in meteorites. In combination with other elements, iron occurs in a wide range of ores and in most igneous rocks. It is the most widely used of the metals.

leachate - a solution obtained by leaching; e.g. water that has percolated through soil containing soluble substances and that contain certain amounts of these substances in solution.

lithification - 1) the conversion of a newly deposited sediment into a solid rock, involving such processes as cementation, compaction, and crystallization. It may be concurrent with, soon after, or long after, deposition. 2) the lateral termination of a coal bed owing to an increase in impurities.

lithology - 1) the description of rocks, esp. in hand specimen and in outcrop, on the basis of such characteristics as color, mineralogic composition, and grain size. 2) the physical character of a rock.

microbe (microorganism)* - an organism of microscopic or ultramicroscopic size.

mitigate* - 1) to cause to become less harsh or hostile. 2) to make less severe or painful.

montmorillonite - 1) a dioctahedral clay mineral of the smectite group, $Na_{0.33}Al_{1.67}Mg_{0.33}Si_4O_{10}(OH)_2 \cdot nH_2O$. It represents a high-alumina end-member that has some slight replacement of Al^{+3} by Mg^{+2} and substantially no replacement of Si^{+4} by Al^{+3}. 2) a term formerly used for the group of minerals to which the mineral montmorillonite belongs. Confusion is avoided by using *smectite* for the group name.

mudrock - a synonym of *mudstone*.

mudstone - 1) an indurated mud having the texture and composition of shale, but lacking its fissility; a blocky fine-grained sedimentary rock in which the proportions of clay and silt are approximately equal; a nonfissile mud shale. 2) a general term that includes clay, silt, claystone, siltstone, shale, and argillite, and that should be used only when the amounts of clay and silt are not known or specified or cannot be precisely identified, or when it is desirable to characterize the whole family of finer-grained sedimentary rocks (as distinguished from sandstones and limestones). Syn: mud rock. 3) a mud-supported carbonate sedimentary rock containing less than 10% grains (particles with diameters greater than 20 microns); e.g. a calcilutite. Cf: wackestone; packstone; grainstone.

neutralize* - 1) to make chemically neutral. 2) to counteract the activity or effect of. 3) neither acid nor basic. 4) to make neutral by blending with the complementary color.

organic - (adj.) pertaining or relating to a compound containing carbon, especially as an essential component. Organic compounds usually have hydrogen bonded to the carbon atom. – (n.) a substance containing carbon, as in such expressions as “organic-rich shale”.

organic sulfur^A - this form of sulfur is typically bound in plant material or organically bound in coal. Organic sulfur is mainly found in coal beds and other carbonaceous rocks.

overburden - 1) loose or consolidated rock material that overlies a mineral deposit and must be removed prior to mining. 2) the upper part of a sedimentary deposit, compressing and consolidating the material below. 3) regolith.

oxidation (oxidizing)^A - the process of combining with oxygen, or losing hydrogen. Oxidation is the opposite of reduction.

oxidation number* - the degree of or potential for oxidation of an element or atom which is usually expressed as a positive or negative number representing the ionic or effective charge: valence.

oxide - a mineral compound characterized by the linkage of oxygen with one or more metallic elements, such as cuprite (Cu_2O), rutile (TiO_2), or spinel ($MgAl_2O_4$).

oxidized zone - an area of mineral deposits modified by surface water, e.g. sulfides altered to oxides and carbonates.

pH - the negative $\log_{10}$ of the hydrogen-ion activity in solution; a measure of the acidity or basicity of a solution.

physicochemical* - 1) being physical and chemical. 2) of or relating to chemistry that deals with the physicochemical properties of substances.

pozzolan - siliceous material such as diatomaceous earth, opaline chert, and certain tuffs, which can be finely ground and combined with Portland Cement Concrete (in a proportion of 15 to 40 percent by weight). The pozzolan reacts with calcium hydroxide that is liberated as concrete hardens, forming compounds with cementitious properties. Pozzolans also counteract the adverse effects of certain undesirable aggregates that may have to be used in concrete. Portland-pozzolan cements are highly resistant to penetration and corrosion by salt water. The name comes from the town of Pozzuoli, Italy, near which occurs a leucite tuff that was used in cement in Roman times.

pyrite - a common yellow isometric mineral, FeS_2. It is dimorphous with marcasite, and often contains small amounts of other metals. Pyrite has a brilliant metallic luster and an absence of cleavage, and has been mistaken for gold (which is softer and heavier). It commonly crystallizes in cubes, octahedrons, or pyritohedrons. Pyrite is the most widespread and abundant of the sulfide minerals and occurs in all kinds of rocks. It is an important ore of sulfur, less so of iron, and is burned in making sulfur dioxide and sulfuric acid; it is sometimes mined for the associated gold and copper. Syn: fool's gold.

pyrrhotite - a common red-brown to bronze pseudo-hexagonal mineral, $Fe_{1-x}S$. It has a defect structure in which some of the ferrous ions are lacking. Some pyrrhotite is magnetic. The mineral is darker and softer than pyrite; it is usually found massive and commonly associated with pentlandite, often containing as much as 5% nickel, in which case it is mined as an ore of nickel.

reduction (reducing)[A] - the removal of oxygen from a compound, or the addition of hydrogen. Reduction is the opposite of oxidation.

remediation* - the act or process of remedying (to provide or serve a remedy, relief).

saprolite - a soft, earthy, clay-rich thoroughly decomposed rock formed in place by chemical weathering of igneous or metamorphic rocks, esp. in humid or tropical or subtropical climates. The color is commonly red or brown. Saprolite is characterized by preservation of structures that were present in the unweathered rock.

SEM (Scanning Electron Microscope) - an electron microscope in which a finely focused beam of electrons is repeatedly moved across the specimen to be examined, and the reflected and emitted electron intensity is measured and displayed, sequentially building up an image. The ultimate magnification and resolution is less than for the conventional electron microscope, but opaque objects can be examined, and great depth of field is obtained.

shale - a fine-grained detrital sedimentary rock, formed by the compaction of clay, silt, or mud. It has a finely laminated structure, which gives it a fissility along which the rock splits readily, especially on weathered surfaces. Shale is well indurated, but not as hard as argillite or slate. It may be red, brown, black, or gray.

siltstone - an indurated silt having the texture and composition of shale but lacking its fine lamination or fissility; a massive mudstone in which silt predominates over clay. It tends to be flaggy, containing hard thin layers, and often showing primary current structures.

smectite - a group of expanding-lattice clay minerals of the general formula $R_{0.33}Al_2Si_4O_{10}(OH)_2 \cdot nH_2O$, where R includes one or more of the cations Na^+, K^+ Mg^{+2}, Ca^{+2}, and possibly others. The minerals are characterized by a three-layer crystal lattice (one sheet of aluminum and hydroxyl between two sheets of silicon and oxygen); by deficiencies in charge in the tetrahedral and octahedral positions balanced by the presence of cations (most commonly calcium and sodium) subject to base exchange; and by swelling on wetting, due to introduction of interlayer water in the c-axis direction. The smectite minerals are the chief constituents of bentonite and fuller's earth, and are common in soils, sedimentary rocks, and some mineral deposits. Montmorillonite, formerly used as a group name in the above sense, is now considered a member of the smectite group.

stope - an underground excavation formed by the extraction of ore.

stratigraphy - 1) the science of rock strata. It is concerned with all characters and attributes of rocks as strata; and their interpretation in terms of mode of origin and geologic history. All classes of rocks, consolidated or unconsolidated, fall within the general scope of statigraphy. 2) the arrangement of strata, esp. as to geographic position and chronologic order of sequence. 3) the sum of the characteristics studied in stratigraphy; the part of the geology of an area or district pertaining to the character of its stratified rocks.

sulfate (sulphates in the UK) - a mineral compound characterized by the sulfate radical SO_4.

sulfate sulfur[A] - the sulfate form of sulfur that represents the oxidized, weathered state of a sulfur-bearing material. Examples of sulfate sulfur include gypsum, jarosite, etc.

sulfate-induced heave[A] - heave induced by the chemical reaction of sulfates (e.g. gypsum). Sulfate-induced heave results from a volume increase associated with the products (e.g. ettringite, thaumasite) of this chemical reaction.

sulfide (sulphides in the UK) - a mineral compound characterized by the linkage of sulfur with a metal, such as galena, PbS, or pyrite, FeS_2.

sulfide (pyritic) sulfur[A] - the sulfide form of sulfur that represents the unoxidized, potentially damaging form of a sulfur-bearing material. Pyrite is a common form of sulfide sulfur.

sulfide-induced heave[A] - heave induced by the chemical oxidation of sulfides (typically pyrite). Sulfide-induced heave results from a volume increase associated with the products (e.g. gypsum) of this chemical oxidation process.

sulfidic[A] - containing pyrite. Materials classified as sulfidic materials in this report do not necessarily meet the more stringent USDA-NRCS Soil Survey Staff standards defined in Section 3.1.3.

sulfosalt -a type of sulfide in which both a metal and a semimetal are present, forming a double sulfide, e.g. enargite, Cu_3AsS_4.

sulfur bacteria - anaerobic bacteria that obtain the oxygen needed in metabolism by reducing sulfate ions to hydrogen sulfide or elemental sulfur. Accumulations of sulfur formed in this way are bacteriogenic ore deposits.

sulphate - see sulfate.

sulphide - see sulfide.

syntaxy - similar crystallographic orientation in a mineral grain and its overgrowth. Adj: syntaxial.

thaumasite[A] - an expansive sulfate mineral, $Ca_6[Si(OH)_6]_2\ (SO_4)_2(CO_3)_2\ 24H_2O$, produced when gypsum reacts with lime in swelling clay soils such as montmorillonite. Thaumasite is an end-member of ettringite that forms in the presence of carbonates.

total sulfur[A] - the total amount of sulfur present in a material, consisting of three sulfur forms: sulfide sulfur, sulfate sulfur, and organic sulfur.

Total Sulfur Test[A] - Total sulfur analyses are performed to define a material's total sulfur, sulfide sulfur, and sulfate sulfur content. This information is used to determine a material's potential for heave or the Maximum Potential Acidity (MPA) for the ABA test.

valence* - the degree of combining power of an element or chemical group as shown by the number of atomic weights of a univalent element (as hydrogen) with which the atomic weight of the element or the partial molecular weight of the group will combine or for which it can be substituted or with which it can be compared. Also, the unit of valence.

weathering - the destructive processes by which rocks are changed on exposure to atmospheric agents at or near the earth's surface, with little or no transport of the loosened or altered material; specif. the physical disintegration and chemical decomposition of rock that produce an in-situ mantle of waste and prepare sediments for transportation.

References

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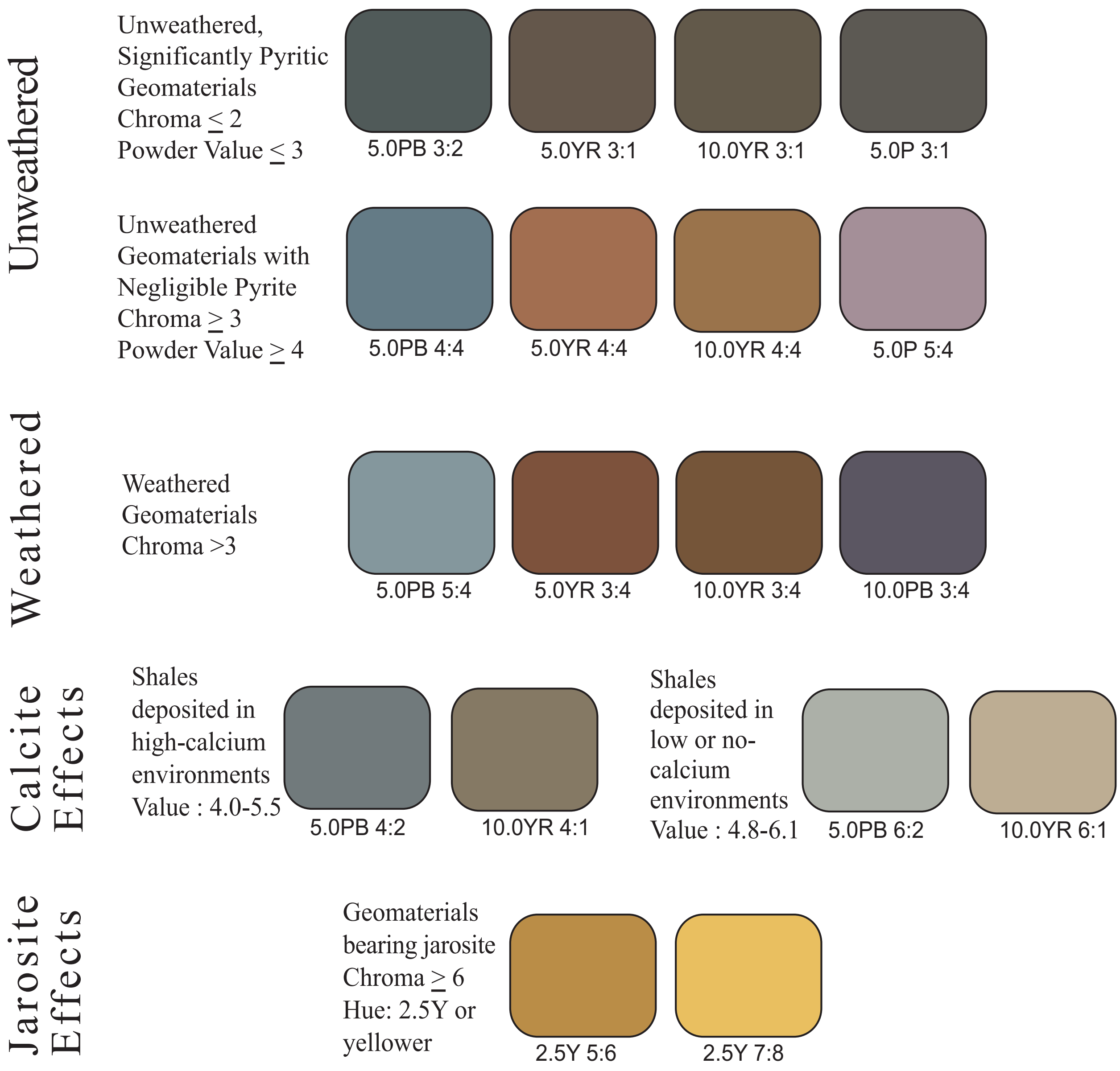
Mish, F. C., Ed. (1991). Webster's Ninth New Collegiate Dictionary. Springfield, Massachusetts, Merriam-Webster, Inc.

Appendix E – Visual Identification of Sulfidic Geomaterials

Appendix E - Visual Identification of Sulfidic Geomaterials

Figure E.1 - Reference Chart of Munsell® Colors* Associated with Sulfidic and Other Types of Geomaterials

Color Code: Hue Value:Chroma Example: Hue = 5.0PB, Value = 3, Chroma = 2



* Figure E.1 Reference Chart created using Macromedia Freehand 10® Munsell® Book of Color Library. Color guidelines from Sobek et al. (1978), USDA-NRCS (1998), and Hosterman and Whitlow (1980, 1983). These are true Munsell® colors in the Freehand® electronic file of this document. Pdf files and printing may render less accurate colors.

Figure E.2 - Flake of pyrite in Millboro Shale, Devonian age. Specimen found along Rte. 100, VA.

Figure E.6 - Effects of pyrite oxidation on New Albany Shale, east of Elizabethton, KY. Photo by Brandon Nuttall, Kentucky Geological Survey.

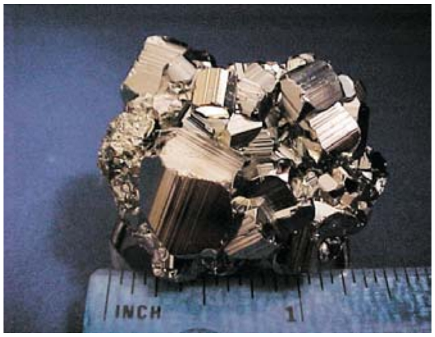


Figure E.3 - Cubical crystalline pyrite, "fool's gold." (www. crystalspecimens.com)

Figure E.7 - Outcrop of pyritic, calcareous Sevier Shale at the site of the Johnson City Public Library (TN), which had to be demolished due to sulfide-induced heave.

Figure E.4 - Fibrous gypsum crystal.

Figure E.5 - Marine fossil in Millboro Shale, Devonian age. Specimen found along Rte. 100, VA.

Figure E.8 - Visible evidence of weathering by pyrite oxidation of exposed face of Millboro Shale, along Rte. 100, VA.