A REVIEW OF IRON SULFIDES AND OXIDES
IN COAL MINE WASTE, HUFF RUN WATERSHED, OHIO

A thesis submitted to the
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by

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I. INTRODUCTION

*Coal Mining in the U.S.*

In the United States, coal is a major energy resource accounting for nearly 15% of national energy consumption, and 62% of the coal mines are surface mining operations concentrated primarily in the Powder River Basin and Appalachia as reported by the U.S. Energy Information Administration (“Annual Coal Report”, 2016). In Ohio alone, 3.6 billion tons of coal have been mined since 1800 through surface and underground mining, and much of this was done before the enactment of stringent reclamation requirements after a site is mined for coal resulting in over 450,000 acres of land impacted by surface mining and 1,300 miles of streams polluted by acid mine drainage before remediation laws were put in place in 1972 as reported by the Ohio Department of Natural Resources’ Division of Mining Resources (“Abandoned Mine Land Reclamation Programs”). Surface mining of coal often results in the disposal of mine waste in the form of spoil and waste rock that are dumped near or over the previously mined locations. Even in the restoration of mined land, only the uppermost layers of coal mine waste are replaced and packed. Permeability of the material is then reduced, and the bulk of the waste is left on site as near surface material in an oxidizing environment. When the coal mine waste is subsequently oxidized it leads to acid mine drainage (AMD). In AMD, the oxidation of the associated iron sulfides, pyrite (FeS₂), marcasite (FeS₂), and mackinawite (FeS), in the coal mine waste both acidify and contaminate the water flowing through the coal mine waste (Johnson and Hallberg 2005, Nordstrom 1982).

*Iron Sulfides*
The primary iron sulfide associated with coal deposits is pyrite existing mostly as spherical clusters of smaller pyrite crystals called framboids or larger euhedral crystals potentially crystallized from the framboids (Wignall et al. 2004, Soliman and Goresy 2012). It can also be present in fracture filling, cell replacement, and dendritic forms in coal deposits although it is less common outside of secondary precipitation by hydrothermal fluids (Diehl et al. 2012). Secondary minerals such as marcasite and mackinawite can also be present but are not as thermodynamically stable as pyrite outside of extremely reducing conditions (Schoonen 2004). The precipitation of the iron sulfide mineral greigite (Fe$_3$S$_4$) is also speculated to be a necessary step in the formation of framboidal pyrite, but this has not been directly proven and mechanisms have been shown to form framboidal pyrite without greigite (Sawlowicz 1992, Wignall et al. 2004, Butler and Rickard 2000).

Pyrite is known to incorporate trace metals and metalloids such as As, Se, Co, Cd, Ni, Pb, and Zn (Diehl et al. 2012, Houben et al. 2016). Since pyrite consists of the reduced forms of Fe and S, it can oxidize as it is exposed to atmospheric oxygen and water releasing the associated trace metals and metalloids into the mine drainage. The mobility of these species within a watershed is dependent upon their speciation under surface conditions and the degree to which they adsorb to mineral surfaces and organic matter (Campbell and Nordstrom 2014).

*Acid Mine Drainage Chemistry*
Both the acidity and the abundance of trace elements in AMD can be attributed to the oxidation of pyrite within the mine spoil. Pyrite oxidizes following the four equations below:

(1) \(2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+\)

(2) \(4 \text{Fe}^{2+} + 10 \text{H}_2\text{O} + \text{O}_2 \rightarrow 4 \text{Fe(OH)}_3 + 8 \text{H}^+\)

(3) \(2 \text{Fe}^{2+} + \text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{Fe}^{3+} + \text{H}_2\text{O}\)

(4) \(\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+\)

(Singer and Stumm 1970, Salomons 1995)

Reaction (1) occurs in oxidized environments in pH conditions >4.5 both abiotically and through bacterial mediation. This accounts for the initial release of sulfate into solution as well as an decrease in pH essential to reaction (2) which occurs at a lower pH range between 2.5 and 4.5. In reaction (2) the ferrous iron is oxidized and directly precipitated as insoluble ferric hydroxides. This step is, however, mostly determined by the bacterial activity of \(T. \text{ferrooxidans}\) in the system. Reaction (3) operates primarily due to oxidation by iron-oxidizing bacteria although it can occur abiotically. It serves as the rate determining step for the overall reaction series of pyrite oxidation in determining the concentration of \(\text{Fe}^{3+}\) in solution (Salomons 1994). Reaction (3) also serves as the rate determining reaction for reaction (4), which under low pH conditions leads to the increased dissolution of pyrite and release of sulfate as well as a further decrease in pH (Rimstidt and Vaughan 2002).

Important, his reaction series shows that the oxidation of pyrite does not only ultimately oxidize the iron but also oxidizes sulfur. The pH conditions for reactions (3)
and (4) are also relatively low, so raising the pH of the system should theoretically lead to the oxidation and precipitation of the iron in solution without the occurrence of reaction (4) (Salomons 1994). The ferric iron would then readily precipitate out at higher pH values as it is relatively insoluble (Nordstrom 1982).

*Iron Oxides*

As the ferric iron oxidizes to form insoluble ferric hydroxides, minerals such as ferrihydrite (Fe(OH)$_3$) or iron sulfates such as jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$) in more acidic and sulfate rich systems precipitate out of solution (Nordstrom 1982, Choppala et al. 2017). Jarosite over time will naturally transforms to ferrihydrite. Ferrihydrite is a poorly crystalline iron (oxy)hydroxide that is not stable over extended periods of time as it undergoes dehydration reactions to form goethite (FeOOH) and hematite (Fe$_2$O$_3$) respectively (Nordstrom 1982, Zboril 2001). Defined by its x-ray diffraction (XRD) peaks, ferrihydrite precipitates initially as the more amorphous 2-line ferrihydrite and recrystallizes to 6-line ferrihydrite as it becomes more ordered (Waychunas et al. 2005). Metalloids such as As and Se can adsorb strongly to ferrihydrite as oxyanions under natural conditions which presents a form of sequestration for the toxic elements that is formed as a result of AMD (Biswas et al. 2016). Recrystallization of the ferrihydrite to more crystalline phases, competitive sorption with molecules such as phosphate, and speciation of the As and Se oxyanions can all serve, however, to reduce the percent which adsorbs to the surface of the ferrihydrite (Campbell and Nordstrom 2014, Houben et al 2017). As ferrihydrite recrystallizes to the more stable forms, the relative surface
area to volume ratio decreases lowering the amount of surface sites to which these oxyanions can bind (Fischer and Schwertmann 1974, Waychunas et al. 2005).

**Research Objectives**

The mine waste covering abandoned coal mines dominates surface material through which runoff will flow into local waterways and soil will continue to develop. The presence of iron sulfides in large abundance, primarily pyrite, within the soil or waste rock may lead to an increased concentration in these trace metals and metalloids within natural water catchments and the overlying vegetation. Using one such site in the Huff Run watershed near Mineral City, Ohio, we attempted to analyze the potential for contamination per the abundance and nature of pyrite within the mine waste. In order to quantify the percent mineral abundance of pyrite in the soil, quantitative x-ray diffraction (XRD) analysis using the reference intensity ratio (RIR) was used on multiple soil samples and the coal waste rock found within the soil collected from the site. Different grain size fractions were analyzed by XRD and scanning electron microscopy (SEM) to determine particle morphology, texture, and composition. This allowed an establishment of the relationship between grain size and mineral assemblages, and it helped indicate the potential of trace metal and metalloid release. Smaller grain sizes would have higher reactive surface areas and be more susceptible to oxidation and dissolution. If the associated minerals in which the pyrite crystallizes are also susceptible to dissolution in the more acidic conditions of AMD, a higher potential for pyrite oxidation would be expected. Lastly, we determined mineralogical transformations in the iron
(oxy)hydroxides caused by heat to determine the possible natural progression of iron oxide formation over time on coal mine spoil.

II. METHODS

*Field Site Description*

The soil, coal shale, and ferrihydrite samples for this study were collected from the Huff Run watersheds 25 (HR25) and 4 (HR4). These sites are two of multiple catchments in the watershed where the acid mine drainage is being remediated before it discharges into a nearby tributaries flowing into the Huff Run. The Huff Run watershed covers approximately 36 square kilometers with the stream itself running roughly 16 kilometers through Tuscarawas and Carrol counties, Ohio as reported by Ohio Watershed Data (“Huff Run Watershed Restoration Partnership”). HR4 and HR25 were host to both underground and surface mining of coal, and as a result, they serve as modern point and

*Figure 1: AMD at Huff Run*. Images showing the iron oxides precipitated from AMD in the Huff Run Watershed. Picture courtesy of David Singer, November 11, 2016.
nonpoint sources for contamination of the local watershed with trace metals and metallocoids associated with the oxidation of iron sulfides. HR25 currently has a treatment system for remediation of discharge from the intersecting underground coal mine, while the coal mine waste that overlies much of the area is untreated. The first soil core, located near a beaver pond (BP), was collected at the base of a slope alongside the tributary, and the second soil core (BY) was collected at a slightly higher elevation.

Sample Preparation

The two soil cores, BP and BY, were collected by auger, sorted by every 10 cm of depth, and stored in sample bags at room temperature in dry conditions. The BP soil core was collected from 0-80 cm in depth while the BY soil core was collected from 0-50 cm in depth. For particle sizes under 2 mm, the soils were dry sieved into three size classes: <63 μm, 63-250 μm, and 250-2000 μm. Following grain size separation, each sample was powdered using a ball mill in preparation for XRD and SEM analysis. The coal shale was stored at room temperature in dry conditions near the soil samples. Multiple coal shale samples were ground down by mortar and pestle and underwent the same sieving procedure as the soil samples.

The ferrihydrite samples were collected from HR4 from a layer of bright, orange sediment coating the area around an inadequate treatment system and from HR25 along the sides of a limestone channel in the AMD treatment system. They were stored in plastic sample containers and refrigerated at 4°C. Each sample was then sieved using a 1900 μm sieve to remove large organic material mixed in with the iron oxides. The
samples were then heated in an oven to an initial temp of 50ºC for three days to dry the samples and were newly stored in glass vials at room temperature. Separate samples were heated to temperatures of 110ºC, 210ºC, 260ºC, and 290ºC for one week each. They were again stored at room temperature after being heated.

**XRD and SEM Analysis**

Each soil and coal shale sample were analyzed using a Rigaku Miniflex 600 X-Ray Diffractometer while the XRD patterns of the iron oxides were collected on a Rigaku Geigerflex Powder X-ray Diffractometer. The soil and coal shale samples were run at 45 kV and 15 mA at 3º per minute from 3º to 90º 2θ. All the iron oxides outside of the sample heated to only 50ºC were run at 45 kV and 25 mA at 2º per minute from 3º to 80º 2θ. Each sample was then analyzed using PDXL-2 for the soil and coal shale samples and JADE for the iron oxide samples to determine peak identification and relative percent composition of the dominant mineral phases. For the samples analyzed with PDXL-2, relative ratio intensity analysis (RIR) was used to quantify percent mineral composition and whole powder pattern fitting (WPPF) was used for pattern refinement. Following these results, representative samples were selected for analysis by scanning electron microscopy on a Hitachi TM3030 Scanning Electron Microscope for visual and elemental analysis. Energy dispersive x-ray spectroscopy (EDS) was used for elemental analysis of the selected samples.

**III. RESULTS**
**Coal Shale**

*XRD Mineral Identification and Percent Composition*

The XRD patterns for the two samples of the coal shale, each separated by grain size, depicted three patterns with dominant amorphous peaks accompanied by peaks for quartz, kaolinite, pyrite, and marcasite. The amorphous peak for all three grain sizes centered around 21° and varied slightly in intensity between the three grain sizes and extended from 0 to approximately 36°. Intensities in the three XRD patterns have maximums of under 700 counts as opposed to the soil samples which range from 2000 to 7000 counts under the same measurement parameters.

For the largest particle size fraction (250-2000 μm), a crystallinity of 25% and 19% between the two coal shale samples, coal shale 1 and 2, were determined with the amorphous constituent composing the remainder of the sample aside from the minerals quantified in Table 1. Kaolinite and quartz were shown to be the most dominant of the crystalline phases. Relative intensity ratio (RIR) analysis determined the proportion of pyrite in the crystalline fraction to be 18.1% and 11% of the crystalline fraction for samples 1 and 2 respectively. The average iron sulfide content for the bulk of the two samples was 3.5%.

The intermediate particle size fraction (63-250 μm) was the most amorphous of the three fractions with the crystalline fraction only comprising 10.9 and 12.3% of the total composition. The percent composition of quartz for this size range was the lowest of the three samples at an average of 15% of the crystalline fraction. This was relatively low in comparison to the percent quartz in the crystalline fraction for the smallest and largest
grain sizes. Iron sulfides comprise 22.7% and 21.4% of the crystalline fraction for samples 1 and 2 respectively in the intermediate particle size. This means that iron sulfides account for an average of 2.6% percent of the bulk composition of the intermediate grain size fraction.

The smallest particle size fraction (<63 μm) shows an intermediate crystallinity and the highest average percent quartz (42.5%) and iron sulfides (22.4%) of the three grain sizes in the crystalline fraction. With an average crystallinity of 25.6%, it is more similar to the largest particle size fraction than the intermediate, and the amount of kaolinite is lower in both samples than the previous intermediate sample. The average iron sulfide content between the two samples accounted for 5.8% of the bulk composition.

### Coal Shale Sample 1

<table>
<thead>
<tr>
<th>Grain Size (μm)</th>
<th>% Mineral Content (Crystalline Fraction)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartz</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>250-2000</td>
<td>29.0%</td>
<td>53.0%</td>
</tr>
<tr>
<td>63-250</td>
<td>17.5%</td>
<td>60.0%</td>
</tr>
<tr>
<td>&lt;63</td>
<td>45.0%</td>
<td>33.0%</td>
</tr>
</tbody>
</table>

### Coal Shale Sample 2

<table>
<thead>
<tr>
<th>Grain Size (μm)</th>
<th>% Mineral Content (Crystalline Fraction)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartz</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>250-2000</td>
<td>69.0%</td>
<td>19.0%</td>
</tr>
<tr>
<td>63-250</td>
<td>12.5%</td>
<td>66.0%</td>
</tr>
<tr>
<td>&lt;63</td>
<td>40.0%</td>
<td>37.0%</td>
</tr>
</tbody>
</table>

**Table 1: Coal Shale Mineral Content and Crystallinity.** Percent mineral composition for the crystalline fraction of the coal shale samples for coal shale sample 1 (upper) and sample 2 (lower) along with values for crystallinity are shown in this table.
**SEM Imaging and Elemental Analysis**

SEM images coupled with EDS analysis of the two smaller grain size fractions of the coal shale demonstrated the form, location, and nature of pyrite crystallization within the coal shale. The overall SEM images for the smallest and intermediate grain sizes consisted of a mix of amorphous carbon grains, silicates, and iron sulfides. The amorphous carbon grains show the least amount of contrast with the also carbon rich background and appear a much darker shade than the both the silicates and iron sulfides. Between the iron sulfides and the silicates, the iron sulfides show the highest contrast appearing much brighter than the light grey color of the silicate minerals in the samples as seen in figure 2.

The iron sulfides show two main crystal forms: pyritohedral and octahedral. The octahedral crystals of pyrite constitute most of the pyrite frambooids throughout the sample, and rounding was common at the corners of the iron sulfide octahedrons. The octahedrons ranged in size from <1 to 10 μm with the larger crystals more commonly located in frambooids. The octahedrons along veins or independent in the amorphous carbon grains were generally under 2 μm with some exceptions. The pyritohedral crystals were not commonly associated with the framboidal clusters and existed as independent crystal both separate from and embedded in the amorphous carbon grains. The size of these crystals was larger exceeding 63 μm with the most notable being the grain exceeding 100 μm in figure 2B. These can also be seen in crystal sizes around 10 μm in figures 14.1 and 14.3 in the appendix.
The pyrite crystals in these samples are primarily associated with the amorphous carbon grains in the samples as opposed to the inorganic mineral constituents. SEM images in figure 2 show that the iron sulfide in the framboids, aggregated in veins, and individually formed are commonly embedded within the carbon constituent of the samples.

Figure 2: Representative Iron Sulfide SEM Images. SEM images of pyrite crystal forms throughout the samples. A) Iron sulfides associated with clay mineral on the surface of an organic carbon. B) An image of a fractured pyrite crystal exceeding 100 μm with a pentagonal shape and iron sulfide overgrowths. C) A fractured pyrite grain exceeding 63 μm with solid organics along the base of the grain. D) Microcrystalline framboids of pyrite can be seen in the lower half of this image with dodecahedrons crystals along the rim of the grain in the upper half. Clay interlayers are visible in the roughly textured locations in the left half of the image.
**BP Soil Core**

The samples from the BP soil core show a similar representative mineralogical composition across depth of quartz, muscovite, kaolinite, and albite (Fig. 3). Across soil depth, the relative mineral composition showed no definite trend. Quartz and muscovite

### BP Grain Size: 63-250μm

![Bar Chart: BP Soil Core - 63-250μm](chart1.png)

### BP Grain Size: <63μm

![Bar Chart: BP Soil Core - <63μm](chart2.png)

### BP Grain Size: 250-2000μm

![Bar Chart: BP Soil Core - 250-2000μm](chart3.png)

**Figure 3: BP Soil Core: Mineral Content Results.** Percent mineral composition for the crystalline fraction of the BP soil core samples by depth for the smallest (<63 μm), intermediate (63-250 μm), and the largest (250-2000 μm) grain size fractions.
were the dominant minerals for most samples and grain sizes. Kaolinite usually ranged between 10 and 25% of mineral composition, and albite ranged from roughly 0 to 20%.

Unlike the coal shale samples, the soil samples showed no clear evidence of an amorphous peak or pyrite. The XRD analysis revealed that the samples were for the most part near 100% crystalline with no amorphous constituent detected. Pyrite was not detected in the soil samples collected. BP 60-70 and 70-80 did have coal fragments upon as seen in the hand sample that were not detected by bulk XRD analysis.

Differences in quartz, feldspar, and albite concentrations were also apparent between grain sizes in the BP soil core. The percent composition of feldspar was highest for all cases, in the largest particle size fraction, with little to no feldspar appearing in the intermediate grain size fractions. The relative percent mineral content of quartz was highest in the intermediate size fraction while muscovite and kaolinite showed variable difference between the three grain size fractions.

**BY Soil Core**

The BY soil core, like for the BP soil core, showed primarily the same four minerals: quartz, muscovite, kaolinite, and albite (figure 4). Also similar to the BP soil core, BY had no clear mineralogical trends shown with depth as the changes in percent composition was seemingly erratic. Muscovite and kaolinite were more dominant in the BY core with greater average values than that of BP accompanied by a smaller percent values for quartz across all grain sizes. One unknown peak was found in multiple XRD patterns for this soil core at roughly 6°. This likely corresponds to montmorillonite or a
similar clay mineral with a major XRD peak at this angle, but a clear match with data for determining mineral percent composition could not be found. This could have led to a difference in muscovite and kaolinite, which share similar secondary peaks, being higher than they were.

Coal fragments could be seen in the BY 40-50 sample although there was no significant amorphous component in the XRD pattern. The samples for the BY soil core were nearly 100% crystalline, and pyrite was not detected for the soil samples.

The BY soil column also showed differences across grain sizes like in the BP soil samples as illustrated in figure 4. The percent of quartz was highest in the intermediate grain size fraction similar to the BP soil core, and the largest grain size fraction had the highest percent muscovite for all soil depths. Albite was variable across grain sizes with the smallest grain size fraction having the highest albite content for the two depths at which mineral composition was obtained.

**BY Grain Size: 63-250μm**

![Bar chart for BY Grain Size: 63-250μm]

**BY Grain Size: 250-2000μm**

![Bar chart for BY Grain Size: 250-2000μm]

*Figure 4: BY Soil Core: Mineral Content Results* Percent mineral composition for the crystalline fraction of the BY soil core samples by depth for the intermediate (63-250 μm), and the largest (250-2000 μm) grain size fractions.
Iron Oxides

Mineral Identification and Percent Composition

The iron oxides, heated to increasing temperatures, produced low intensity XRD patterns with high levels of background between the representative peaks. Through the background, however, iron oxide peaks could be identified representing ferrihydrite, goethite, hematite, and quartz. As temperature was increased, the original ferrihydrite sample generally transitioned to goethite and then hematite as expected (Figure 5). The transition was not complete in that ferrihydrite still showed up throughout increasing temperatures with varying intensities. The original sample was reanalyzed on a Rigaku Miniflex for percent composition, and the analysis showed that the sample was 90% ferrihydrite and 10% goethite. The drying process possibly led to the recrystallization of a

Figure 5: The Thermodynamic Mineral Transition for Iron Oxides. This figure shows the XRD patterns for select iron oxides patterns after being separately heated to 75°, 210°, and 290°C from left to right for a week. Q-quartz. F-ferrihydrite. G-goethite. H-hematite.
small fraction of the ferrihydrite to goethite suggesting the original sample was more purely ferrihydrite than shown by XRD analysis.

At the lower temperatures ranging from 70 to 160°C, the sample showed a range of crystallization for goethite. The goethite peak had the highest intensity at 110° with a 6-line ferrihydrite still present and showing a higher intensity peak in the sample than the goethite. As the goethite peak intensity began to wane at 160°C, hematite began to precipitate. From 160 to 290°C, hematite crystallization was shown in the XRD patterns where the intensity and prominence of the peaks increased with increasing temperature. The 6-line ferrihydrite peaks remained relatively prominent at the higher temperature samples.

**SEM Imaging and Elemental Analysis**

The iron oxides produced in dry heating the relatively pure ferrihydrite samples from HR4 were shown to be mostly amorphous to poorly crystalline for each sample over increasing temperature. Few distinct ordered or clear crystal structures indicating more crystalline minerals such as goethite or hematite were present compared to the poorly crystalline ferrihydrite. The iron oxide crystals, lacking a definite structure as shown by the SEM images in figure 21.1, showed no clear aggregation or arrangement until higher temperatures. In the 260°C sample, aggregation of the iron oxides was present (fig. 21.3) as they formed spherical clusters giving higher energy readings for iron and oxygen.

The crystals were commonly elongated throughout all the samples, but higher temperatures showed more of the elongated mineral and an unraveling sheet structure seen in figure 21.2. Examples of twinning were seen for the 160°C sample between the
elongated crystals, but this was not significant. Higher temperature samples also showed the formation of a few more crystalline iron oxide crystals seen in one example in the 260°C SEM image in figure 21.3. The samples were overall amorphous to poorly crystalline over the full range of temperatures with the exception of the previously mentioned crystals.

IV. DISCUSSION

Soil Mineralogy and Source Characteristics

The coal shale samples gave XRD patterns with four main mineral constituents, quartz, kaolinite, pyrite, and to a lesser degree marcasite. Low crystallinity values indicate that the samples are primarily coal as defined by the prominent and broad amorphous peak and low crystallinity values (Manoj and Kunjomana 2012). The amorphous constituent could also include amorphous silica within the shale portion of the source rock (Williams et al. 1984). The percent composition of iron sulfides was slightly variable across grain size. The bulk totals were highest in the smallest grain size fraction as expected and lowest in the intermediate grain size fraction. This difference most likely corresponds to pyrite crystals from the framboids detaching during fracturing rather than an association with another mineral constituent. Even though fragments of coal could be seen in select soil samples, the XRD patterns provided no evidence of an amorphous peak in the associated soils. Looking at the SEM images in figure A14.1, the framboidal pyrite occurred primarily in association with the organic grains as opposed to the clay minerals. Since the pyrite framboids are located on the organic grains primarily, pyrite oxidation in
this case may have strong ties to the degradation of the organic grains. Any process that may increase the breakdown of these grains would increase the potential exposure of pyrite to weathering.

The high abundance of quartz and presence of feldspars in the soil indicates that in addition to a source material of shale and coal examined by XRD, the coal mine waste was also derived from interbedded sandstone layers around the coal seams of interest (Hosterman and Whitlow 1983). The quartz in the soils were predominantly in the larger grain size fraction, while the coal shale had more quartz below silt size, <63μm. The coal shale also did not show any percent feldspar in its mineral composition, but feldspars were present within the soil as shown by XRD. This also means that since the coal shale cannot be treated as the lone parent material to the soil, the percent of pyrite likely to be present should be lower than directly anticipated from weathering of the coal shale. The soil also shows no defining trend in mineralogy over depth suggesting a more heterogeneous soil with little time to develop clear mineralogical differences.

The overall mineralogy of the soil samples analyzed from HR 25 show that quartz, muscovite, kaolinite and albite are the primary mineral constituents. In the BY soil samples a peak in the XRD patterns at <10° was also indicative of the expandable clay mineral montmorillonite, but the database lacked a pattern with appropriate values for RIR analysis leading to its exclusion from mineralogical analysis. Illite, which is also a common clay mineral in soils, overlaps with muscovite at major peak positions but showed a relatively poor fit to the rest of the pattern. It is possible, however, that illite was present in the samples as indicated by the same major peak as muscovite but not at a
significant proportion, and it was therefore excluded from quantitative peak fitting analysis. These two considerations could result in an overestimation of some of the minerals, primarily muscovite, in the soil samples, but they do not affect the overall goal of the research in identifying the abundance of iron sulfides or iron oxides within the soil. Aggregation of the clay minerals in the soil samples as well as incorporation in the larger coal fragments could have led to a higher percent composition in the larger grain size fractions (Ashman et al. 2002).

Since the XRD results of the soils overlying the coal mine waste showed no evidence of pyrite at any grain size and depth within the soil column, it can be assumed that the pyrite has either completely oxidized and leached from the system or is in at an abundance below the detection rate of XRD analysis (~2%). The quantitative peak fitting and crystallinity analysis from the XRD patterns of the coal shale showed a maximum bulk pyrite content of 6.7% and a minimum of 2% which in accounting for partial dissolution as the waste rock weathers to form soil, could reasonably put it below detection limits. This means that the percent of pyrite or other iron sulfides within the overlying mine waste, excluding the solid waste rock, is not present in the bulk phase but could still be present in low abundance below detection limits for XRD. A larger potential for contamination more may stem from the direct weathering of the larger chunks of coal shale mixed throughout and below the heterogeneous mine waste soil more so than the low abundance of pyrite present in the soil. This can still be problematic in upper layers of the soil in these sites as the waste rock can be intermixed at various soil depths as this was observed while collecting the soil samples.
Iron Sulfide Crystal Size and Form

Dissolution is strongly related to the reactive surface area of a particle. As grain sizes decrease, reactive surface areas increase due to a decrease in the surface area to volume ratio (Navrotsky et al. 2008). SEM imaging revealed three primary crystal sizes of the most common iron sulfide, pyrite, in the samples: <1μm, 1-10 μm, and >63 μm. The <1 μm fraction of pyrite exists mostly in the pyrite framboids, and it was often organized within the spherical framboids, and the individual crystals were octahedral in shape. As the smallest grain size of pyrite with the highest specific area in the coal shale, these are likely to have the highest rate of oxidation (Heidel et al. 2009). The pyrite crystals with sizes between 1 and 10 μm were the most common throughout the sample. They were often in framboids and were present as individual grains as well. Some individual grains are likely from framboids but were separated during the fracturing. The crystal forms in this case varies between octahedra which are truncated on the edges and more complex pyritohedral shapes such as the dodecahedrons in figure 2D. The largest crystal size of pyrite being greater than 63 μm was not present in the smallest grain size fraction but instead was found occasionally throughout the other two grain size fractions. It was not as common as the framboidal pyrite in the sample and has the smallest reactive surface area which would give it the slowest rate of oxidation out of the pyrite crystal forms (Heidel et al. 2009).

The more poorly crystalline iron sulfides that were too small for SEM analysis occurred on a grain from the largest grain size fraction along with clay minerals on a
fracture. This is more likely the marcasite seen in the XRD analysis than pyrite due to the smaller crystal size and its proximity to the clay minerals. In sedimentary environments, pyrite is more likely to form in framboids on the lignite as opposed to the clay minerals, and this was seen in the coal shale samples collected (Schoonen 2004, Sawlowicz 1992, Soliman and Goresy 2012). Marcasite, however, forms in more clay rich fractures with a lower pH than pyrite making it the more likely iron sulfide shown in figure A18.2. Marcasite is less thermodynamically stable making it more prone to oxidation within the coal mine waste than the pyrite (Schoonen 2004).

Iron Oxide Mineralogy

In dry heating the ferrihydrite samples from HR25, an expected trend of increasing mineral content of goethite and hematite for increased temperature ranges was observed in the XRD patterns. Within the temperature range of 70°C to roughly 160°C goethite was shown to form from the recrystallization of ferrihydrite, and for temperatures above 160°C, goethite was no longer present as hematite began to form. At 160°C both hematite and goethite were present in the sample. This implies that temperatures beyond 160°C cause the dehydration of goethite to hematite. The existence of goethite and hematite with prolonged heating at equal temperature ranges in this experiment was potentially due, in part, to differences in grain size instead of incomplete dehydration to hematite. Goethite is more stable than hematite over a larger range of temperatures for smaller grain sizes allowing it to exist in a finer grained structure alongside hematite (Navrotsky et al. 2008).
Unexpectedly, a persistence of 6-line ferrihydrite was evident in the samples heated to a higher temperature indicating an inhibitor in the dehydration reaction of ferrihydrite for the dry heating approach. In the SEM images, the poorly crystalline ferrihydrite grains present at lower temperatures of 50°C and 75°C also were continuously present to 290°C despite the formation of the more crystalline phases of goethite and hematite. The 6-line ferrihydrite peaks in the XRD pattern for 290°C (Figure 5) were greater than the hematite peaks. This suggests that this method for inducing mineralogical transformation in iron oxides is relatively ineffective in completely recrystallizing the ferrihydrite.

V. CONCLUSION

Without restoration or remediation of the coal mine waste produced, abandoned coal mines across Appalachia and other regions of the U.S. pose a threat to the health of local ecosystems and drinking water sources (Houben et al. 2016, Tiwary 2000). Understanding the form, rate of oxidation, and perhaps more importantly, the abundance of iron sulfides in these areas filled by coal mine waste helps in the prospective treatment and long-term remediation of these sites. Iron sulfides are primarily associated with both acidity and heavy metal and metalloid contamination of AMD. This means the grain size, crystal form, and mineral association of iron sulfides in the coal mine waste are important to understanding the contamination of the areas around the abandoned coal mine sites (Tiwari 2000).
Iron sulfides can serve as a sink for multiple trace elements in anoxic sedimentary environments as Co, Ni, and As are commonly sequestered in pyrite as well as Se, Cd, Zn, and to a lesser degree Pb (Houben et al. 2016, Campbell and Nordtrom 2014, Strawn et al. 2002). Drinking water and local streams may become if these elements become concentrated within them (Houben et al. 2016). Arsenic is one of the most common toxic elements associated with pyrite and can often form an As-rich form of pyrite known as arsenopyrite (FeAsS) (Biswas et al. 2017, Lowers et al. 2007). The oxidation of pyrite in coal mine wastes threatens the release of As, which is fairly mobile in natural systems, and therefore, it threatens drinking water (Diehl et al. 2014). For the coal shale samples in this study, arsenopyrite was not detected in the bulk composition, but As could still be present as a minor constituent of the pyrite.

The pyrite in the samples collected were predominantly framboidal and larger euhedral grains. The framboids had a high reactive surface area due to the relatively small grain size of the individual crystals making the framboids more susceptible to oxidation and trace metal release (Heid el et al. 2009). Framboids, however, typically have lower concentrations of As and other toxic trace elements than the larger euhedral grains of pyrite (Diehl et al. 2012). The larger euhedral grains would oxidize at a slower rate due to the lower relative surface area to volume ratio of larger grains (Heidel et al. 2009). The mobility of the toxic elements after release is a factor of oxidation, pH, and fluid dynamics of the mine waste discharge (Tiwary et al. 2000).

Under natural conditions, the oxidation of pyrite leads to the subsequent precipitation of iron hydroxides, and the iron hydroxides can serve as sorbents for the
trace metals and metalloids released (Nordstrom 1982). The formation of iron hydroxides creates a potential method of sequestration for the trace elements that would otherwise be mobilized in pyrite oxidation. Ferrihydrite, the initial iron oxide to precipitate, readily adsorbs As, Se, and other toxic trace elements (Strawn et al. 2002). Since ferrihydrite is poorly crystalline and has a relatively small crystal size, it has more bonding sites for the trace metals and metalloids (Waychunas et al. 2005). The phase transformations observed in the dry heating experiment, however, can serve to reduce the number of surface sites to which trace metals and metalloids can bind causing a delayed release after the recrystallization of ferrihydrite to the more crystalline phases, goethite and hematite (Waychunas et al. 2005, Campbell and Nordstrom 2014). Understanding more about the transition of iron oxide phases after precipitation of ferrihydrite may provide valuable insights into the release of these associated contaminants. These insights may assist with the development of long-term remediation plans for abandoned surface coal mine waste.
VI. REFERENCES


thermodynamic properties of goethite (alpha-FeOOH) up to 500 K. European Journal of Mineralogy, 6(6), 967-983.


Fig. 6: BP XRD Patterns 0-30cm. XRD patterns and database patterns for BP soil samples at depths of 0-10cm, 10-20cm, and 20-30cm from top to bottom respectively for grain sizes 63-250μm (Left) and 250-2000μm (Right). In descending order the database mineral patterns are quartz, muscovite, kaolinite, and albite.
Fig. 7: BP XRD Patterns 30-50cm. XRD patterns and database patterns of BP soil samples from depths 30-40cm (Left) and 40-50cm (Right) for grain sizes <63μm, 63-250μm, and 250-2000μm from top to bottom respectively. Quartz-black, Muscovite-orange, Kaolinite-blue, Albite-grey.
Fig. 8: BP XRD Patterns 50-70cm. XRD patterns and database patterns of BP soil samples from depths 50-60cm (Left) and 60-70cm (Right) for grain sizes <63μm, 63-250μm, and 250-2000μm from top to bottom respectively. Quartz-black, Muscovite-orange, Kaolinite-blue (or lighter grey), Albite-grey.
Fig. 9: BP XRD Patterns 70-80cm. XRD patterns and database patterns of the BP soil sample from 70-80cm depth for grain sizes <63μm, 63-250μm, and 250-2000μm from top to bottom respectively. Quartz-black, Muscovite-orange, Kaolinite-blue (or lighter grey), Albite-grey.
Fig. 10: BY XRD Patterns 0-20cm. XRD patterns and database patterns of BY soil samples from depths 0-10cm (Top) and 10-20cm (Bottom) for grain sizes 63-250μm (Left) and 250-2000μm (Right) from top to bottom respectively. Quartz-black, Muscovite-orange, Kaolinite-blue (or lighter grey), Albite-grey.
Fig. 11: XRD patterns and database patterns of BY soil samples from depths 0-10cm (Left) and 10-20cm (Right) for grain sizes <63μm, 63-250μm, and 250-2000μm from top to bottom respectively. Quartz-black, Muscovite-orange, Kaolinite-blue (or lighter grey), Albite-grey.
### BP Grain Size: 163μm

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<tr>
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<tr>
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<td>60-70</td>
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<tr>
<td>70-80</td>
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### BP Grain Size: 63-250μm

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### BP Grain Size: 250-2000μm

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Tables 2-4: BP % Mineral Content for <63μm, 63-250μm, and 250-2000μm. Table 2 (Top) shows percent mineral composition for the smallest grain size fraction (<63μm) of the BP soil core across depth. Table 3 (Middle) shows percent mineral composition for the intermediate grain size fraction (63-250μm) of the BP soil core across depth. Table 4 (Bottom) shows percent mineral composition for the largest grain size fraction (250-2000μm) of the BP soil core across depth.
### BY Grain Size: 63-250μm

<table>
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### BY Grain Size: 250-2000μm

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**Tables 5 and 6: BY % Mineral Content for 63-250μm and 250-2000μm.** Table 5 (Top) shows percent mineral composition for the intermediate grain size fraction (63-250μm) of the BY soil core across depth. Table 6 (Bottom) shows percent mineral composition for the largest grain size fraction (250-2000μm) of the BY soil core across depth.
Fig. 12: Coal Shale XRD Patterns for 1 and 2. XRD patterns and database patterns for coal shale samples 1 (Left) and 2 (Right) for grain sizes <63μm, 63-250μm, and 250-2000μm from top to bottom respectively. For the left column, the database minerals in descending order are quartz, kaolinite, muscovite, pyrite, amorphous. For the right column, the database minerals in descending order quartz, kaolinite, pyrite, muscovite.
Figure 13: Coal Shale <63μm Composite SEM Image. An SEM image depicting a broad scale view of the coal shale sample 1 for the <63μm grain size depicting the three SEM images of figure 14. The image shows a collection of quartz (light grey), clay (light grey), organic (dark grey), and iron sulfide (very light grey to white) grains throughout the sample.
Figure 14: Coal Shale <63μm Characteristic SEM Images. Three SEM images of the coal shale sample 1 for the <63μm grain sizes depicting iron sulfide crystal form and habit. 1) This image showed a rare case of three roughly 5μm, pyritohedral crystals of pyrite embedded in an organic grain and surrounded by clay minerals depicted by the O element map. 2) A poorly ordered pyrite frambooid is shown with average crystal size of roughly 3μm embedded within an organic grain. 3) this image shows a uniquely euhedral silicate grain with two pyritohedral grains of pyrite in the size range of 1-10μm. Pyrite crystals <1μm can be seen throughout the image as the brighter white crystals in points of both higher S and Fe intensities in the elemental map.
Figure 15: Coal Shale 63-250μm Composite SEM Image. An SEM image depicting a broad scale view of the coal shale sample 1 for the 63-250μm grain size depicting the three SEM images of figure 16. The image shows a collection of interlayered clay (light grey), organic (dark grey), and iron sulfide (very light grey to white) grains throughout the sample.
Figure 16: Coal Shale 63-250μm Characteristic SEM Images. Three SEM images of the coal shale sample 1 for the 63-250μm grain sizes depicting iron sulfide crystal form and habit. 1) This image shows the largest seen pyrite grain among the samples at more than 100 μm across. The roughly pentagonal surface delineates fractures and has possibly iron sulfide overgrowths on the upper and lower right-hand side of the grain. It is embedded in a larger organic grain. 2) Pyrite crystals ranging from <1 to 5 μm long can be seen filling fractures in the organic grain. Other iron sulfide minerals may be present in the finer grained crystals. 3) Poorly crystalline iron oxides fill a fracture in an organic grain with more crystalline pyrite crystals surrounding it.
Figure 17: Coal Shale 250-2000μm Composite SEM Image. An SEM image depicting a broad scale view of the coal shale sample 1 for a crushed portion of the 250-2000μm grain size depicting the three SEM images of figure 18. The image shows a collection of quartz, interlayered and scattered clay (light grey), organic (dark grey), and iron sulfide (very light grey to white) grains throughout the sample.
Figure 18: Coal Shale 250-2000μm Characteristic SEM Images. Three SEM images of crushed portion of the coal shale sample 1 for the 250-2000μm grain sizes depicting iron sulfide crystal form and habit. 1) This image shows one of the larger pyrite grains >63μm that is heavily fractures with organic material on the base of the grain. 2) Very finely crystalline iron sulfides <1μm are depicted in this image amongst clay minerals lining the surface of an organic grain. 3) Within the organic part of an interlayered grain of organic and clay constituents are two framboïds of pyrite with individual crystals <1μm in size. A more disordered cluster of pyrite dodecahedrons can be seen in the upper middle of the image.
**Figure 19: Original Ferrihydrite Oxide Sample Results.** This figure depicts the XRD pattern produced from the original iron oxide sample collected at HR25 along the limestone channel after drying at 50°C and the percent mineral content of the sample. The sample may have undergone slight crystallization to goethite during the drying period resulting in a higher goethite percent than was in the wet sample.
Figure 20: Iron Oxide XRD Results. These six graphs show the XRD patterns of the iron oxides dried at 75°, 110°, 160°, 210°, 260°, and 290°C reading across from top to bottom. The database patterns underneath depict the major peaks of 2-line and 6-line ferrihydrite, goethite, hematite, and for a couple of the patterns quartz.
Figure 21: Iron Oxide SEM Results. These three SEM images depict the overall crystallinity and crystal form of the iron oxides dried at 75°, 160°, and 260°C with associated element maps of Fe, O, and S.