2013/2014 Powell River Project Annual Report

Locating and Identifying Low TDS Strata in Appalachian Soil-Overburden Sequences

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Executive Summary

Release of total dissolved solids (TDS) from Appalachian coal mine spoils to headwater streams has emerged as a significant concern for the coal mining industry, its regulatory agencies, and non-governmental organizations. The overall objective of this project is to develop a new set of techniques to reliably predict the amount, ionic composition, and temporal pattern of TDS release from a range of spoil and overlying soil materials from regional coal surface mines. This project was initiated in 2010 with sole support from Powell River Project. Between 2011 and 2013, we received significant parallel funding for this program from the Appalachian Research Initiative for Environmental Science (ARIES) to support our collaboration with the University of Kentucky and West Virginia University to broaden the scope to the central Appalachian region while continuing to focus on SW Virginia in more detail. Therefore, we are utilizing Powell River Project (PRP) funds to focus specifically on the determination of TDS release potentials of soil-saprolite-hard rock sequences in SW Virginia and adjacent counties in eastern Kentucky and southern West Virginia. This information will better allow operators to determine the thickness and availability of low TDS forming strata for use in new and innovative mining and reclamation plans designed to limit TDS release to local streams.

For the PRP portion of this study, we are sampling 20-30 different locations in representative SW Virginia strata where we can clearly sample a relatively intact section of weathered surficial soils, underlying oxidized and partially weathered (brown) rock strata, continuing down into unweathered gray strata with depth. Samples are being analyzed for size consist, approximate mineralogy, acid-base accounting parameters, Fe-oxide content, abrasion pH/hydrolysis and total elemental analysis. We are also investigating net TDS release from ground/crushed spoil fractions equilibrated with varying soil:water and soil:H_2O_2 ratios to develop TDS release indices. The amount and temporal pattern of TDS release for each material will then be related to the chemical and mineralogical analyses described above to determine which field vs. laboratory determined spoil properties are the best predictor(s) of TDS release potentials.

To date, we have sampled seven locations (with 24 complete weathering sequences) from surface soils down to underlying spoils and preliminary results are presented here. In last year's report, we focused on our findings related to interface between weathered and oxidized surficial materials, specifically that deeper unweathered strata could be clearly delineated by changes in pH and electrical conductance (EC), but not always clearly separable by color. The break between soft/saprolitic bedrock and hard competent rock is also commonly associated with significant increases in EC and presumably TDS leaching potentials. Finally, we noted that the separation between oxidized/brown strata above vs. harder reduced/gray strata below was often marked (or controlled) by thin shale/mudrock strata or coal seams. In this report, we discuss additional findings based on further detailed laboratory analyses of our field weathering sequences along with further refinements of our working model for the location of varying TDS potentials among strata.

Background

This report is a continuation of our research over the past decade focusing on TDS release from surface coal mining overburden in central Appalachia (Orndorff et al., 2010). TDS release from surface coal mining overburden continues to be a major topic of public and regulatory concern (Merricks et al., 2007; Pond et al., 2008) giving rise to the need for further research in the area. Over the past three years we have collaborated with the Virginia Center for Coal and Energy Research and major regional coal producers (Alpha, Arch, Patriot, TECO and others) in the development of a large multi-state research consortium, as the Appalachian Research Initiative for Environmental Science (ARIES; http://www.energy.vt.edu/ARIES). The overall program and detailed scope of work continue to evolve, but our TDS prediction research program was expanded greatly (with ARIES funding) to include significant cooperation with the University of Kentucky (UK - Richard Warner and Chris Barton) and West Virginia University (WVU - Jeff Skousen and Louis McDonald). The expanded program involves a much larger sample set and more detailed analyses than we were capable of addressing with PRP funding. However, the ARIES monies allocated to Virginia Tech are budgeted to support column leaching testing on a much larger (e.g. 40 to 50 spoils) regional sample set, to develop scaling factors for field application of the column data, and to develop a regional GIS + spoil testing data base for future statistical analyses and modeling efforts (Daniels et al., 2013).

For the past three years, we have utilized the funds provided by PRP to continue our focused and detailed efforts on sampling combined weathered:unweathered soil:spoil sequences in SW Virginia along with analytical testing of those materials and improved TDS prediction methods specific to our strata. Meanwhile, the ARIES funded collaborations with UK and WVU have enabled us to "farm out" our Virginia spoil samples (> 20) for much more comprehensive lab testing procedures than would have been possible under our original PRP proposal and will also allow us to correlate results with a much wider range of strata from the adjoining region. Thus, the methods and results detailed below remain specific to the work that we are conducting with PRP funds and do not reflect the larger ARIES project per se.

2011 to 2014 Specific Objectives

1. Measure the net TDS elution potential of a range of materials originating from the Pottsville Group in SW Virginia and analyze the difference between (a) fresh relatively unweathered materials at depth; and (b) well-weathered surficial materials.

2. Determine which indicator has a stronger correlation with TDS elution potential in select mine spoils: (a) Previous long-term exposure to the earth's surface, leading to reduction in soluble salts from the long-term leaching effects of percolating water; or (b) variations in the elemental composition of varying geologic strata.

3. Investigate the nature of the boundary between high and low TDS strata in order to determine if: (a) An abrupt boundary exists at some confining layer, such as a shale; or (b) the boundary is more diffuse, being more related to distance from the earth's surface; or (c) no discernible boundary exists; variations occur with variations in parent material.

4. Determine if a relationship exists between TDS elution potentials and field description traits such as: HCl "fizz" reaction, H_2O_2 reaction and/or Munsell color (e.g. gray vs. brown colors).

Methods and Procedures

A range of weathering x depth samples is being collected from the dominant coal bearing formations of the Pottsville Group throughout SW Virginia. Several samples may also be taken from adjoining areas of Kentucky and West Virginia. Sampling locations are chosen where a clear association between the surface weathered soil horizons and underlying partially weathered rock horizons can be confirmed and the materials are accessible. It is assumed that many of the surficial soils sampled are comprised of colluvium (gravity slope deposits), but that it is locally derived. Ideally, we will sample 3 to 4 replicate sequences from some of the 20-30 primary locations to offer some level of replication and to allow for study of variance within local strata. For the purpose of this study, a "location" is comprised of similar soil to overburden weathering sequences within several hundred meters of one another. First of all, detailed soil and saprolite to rock morphological descriptions are made including textures, structure/rock fabric, weathering features, nature of layer contacts, etc. Samples are being collected from each distinct soil horizon or rock layer/zone (see Fig. 1) beginning from the soil surface and extending to some depth (15 to >50 m) below the surface where visual evidence of weathering and oxidation are not present. Samples are handled as either "soil" horizons or "rock" layers, each being treated differently. Soil samples are passed through a 2mm sieve for subsequent physical and chemical analysis. Rock samples are crushed and sieved until all material also passes through a 2mm sieve. Samples will be further ground as called for by specific tests. After preparation, samples are being analyzed for a range of physical and chemical parameters that we assume may assist in prediction of TDS loadings.

Our overall results will be used to help determine which spoil materials will be relatively low with respect to TDS production for use in final reclamation of backfills and valley fill areas where significant contact with groundwater is anticipated. We also will generate field guidance for depth of cut or removal of these materials vs. easily measureable or observable field criteria.

All samples are being analyzed for the following parameters:

Complete USDA-NRCS morphological description for soil horizons

Saturated paste electrical conductance (EC) and pH

Saturated paste EC and pH following hydrogen peroxide oxidation

Exchangeable cations

Dilute acid extractable nutrients and metals

Extractable Fe and Mn oxides

Total-S and S-forms if $S \geq 0.2\%$

Calcium carbonate equivalence (CCE)

% Rock fragments

Particle size analysis

These parameters will be compared to field description traits such as color, depth, cementation, etc., to determine if any relationship exists between quickly identifiable field characteristics and long term TDS elution potential.

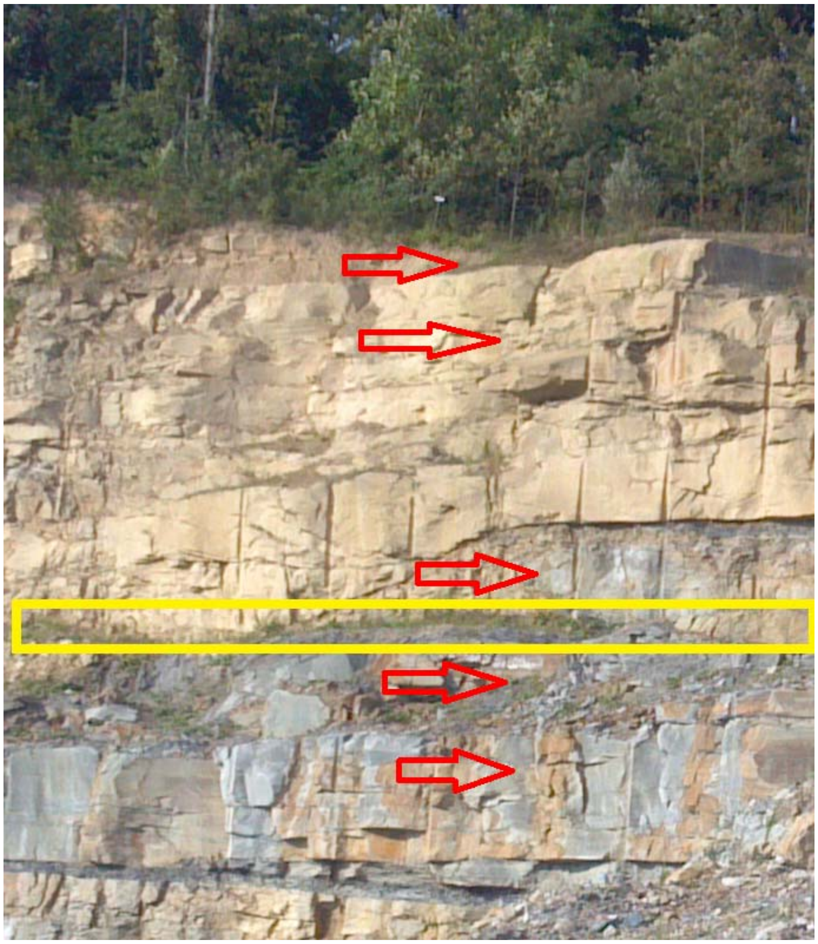

Figure 1 – An example profile illustrating the field sampling scheme employed. Each distinct layer (red arrows) is collected and described. Special notice of the boundary between brown and gray materials (yellow box) is also taken, in an effort to better characterize the transition between these materials. Of the 24 samples to date, this boundary is often a tight shale layer or thin coal seam.

Results to Date (August 2014)

Objective 1. *Measure the net TDS elution potential of a range of materials originating from the Pottsville Group in SW Virginia and analyze the difference between (a) fresh relatively unweathered materials at depth; and (b) well-weathered surficial materials.*

Twenty four weathering sequences at seven different locations have been sampled to date, with a total of 160 individual samples collected. Each weathering sequence represents several samples of both (a) and (b) per Objective 1 above. Replications have been collected at three locations.

Most samples have been processed and analyzed for saturated paste EC and pH, 1:1 water EC and pH, 1:1 hydrogen peroxide pH, total S, and CCE. Lab analysis is still in process include analysis for extractable Fe and Mn. All samples have been described using field methods (e.g. Munsell color, texture, coarse fragments, rock type, HCl fizz test, peroxide fizz test). The approximate mineralogy of select samples has also been determined from thin sections.

Objective 2. *Determine which indicator has a stronger correlation with TDS elution potential in select mine spoils: (a) Previous long-term exposure to the earth's surface, leading to reduction in soluble salts from the long-term leaching effects of percolating water; or (b) variations in the elemental composition of varying geologic strata.*

Currently, we are using saturated paste EC as a preliminary indicator for initial TDS potential and EC generally increases with depth below the surface. Typically, materials within four meters of the surface produce low EC values. Low EC materials extended deeper than four meters at several of the sampled locations, which is influenced largely by the local geology, site landscape position and other factors. At most sample locations, EC values increase strongly below the first cemented, unweathered shale seam encountered (see Fig. 2). Initial data shows this exposure to near-surface weathering and leaching seems to have a stronger influence on TDS elution potential than the variation of geologic strata (e.g. sandstone vs. shale).

Rock type does have some correlation with TDS potential though. In general, shales were found to have higher EC than sandstones and soil layers, but some sandstones also produced high EC values. Unweathered coal and the associated materials (e.g. black shales, underclays, fireclays) were found to have the highest conductivity values. Soil B horizons (subsoil layers) were found to have the lowest EC on average, while R layers (hard bedrock) had the highest.

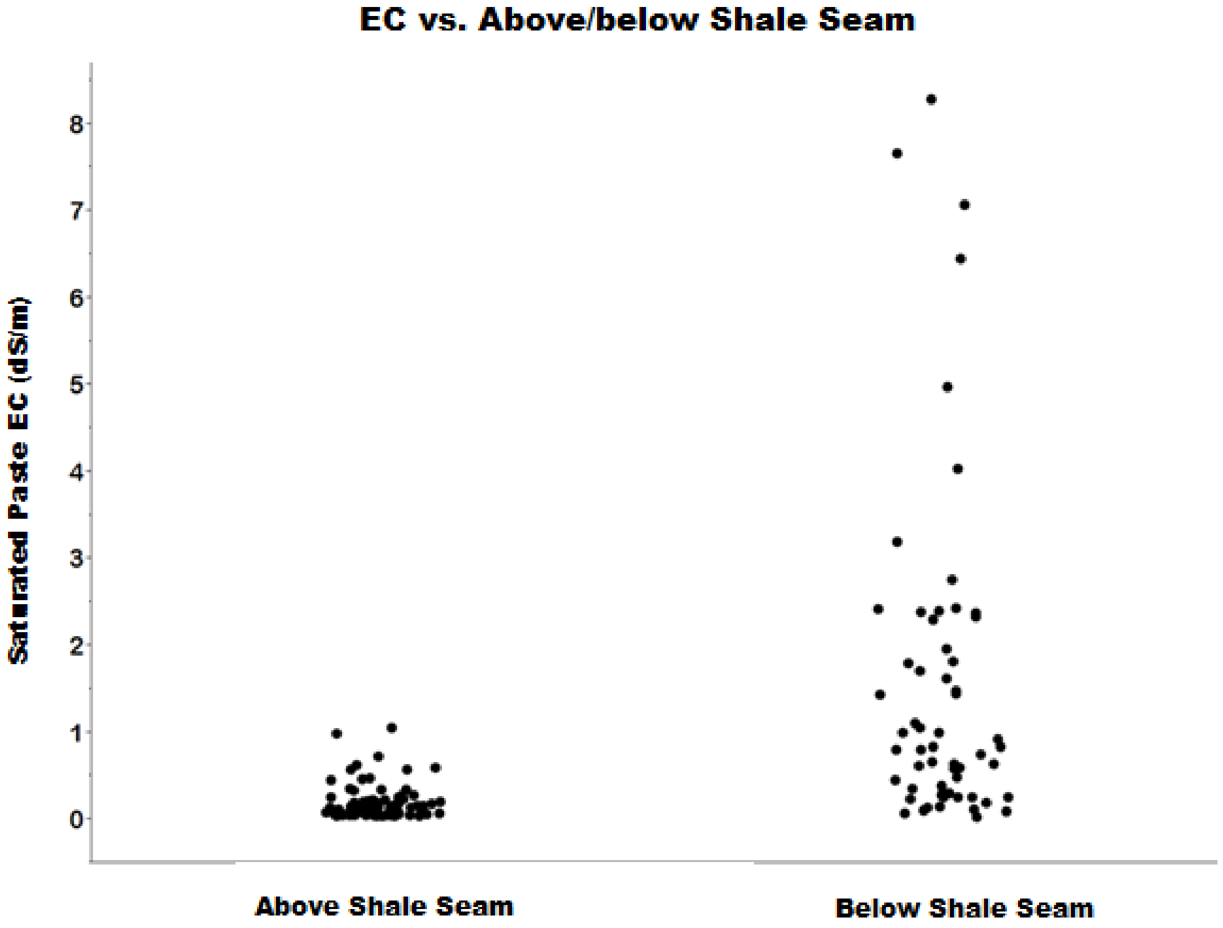

Figure 2 – Saturated paste EC values for 160 samples. Samples are separated based on whether they were collected above or below the first intact shale seam encountered below the earth's surface. The first intact shale seam commonly occurs around a depth of four meters below the surface, but this depth varies widely from area to area.

Interestingly, A horizons (topsoil layers) produced higher EC than subsoils, presumably due to their increased organic matter and associated soluble element concentrations via biocycling. Increased cation concentrations in topsoil versus subsoil horizons seem to explain some of this difference. However, most A horizons in the area are generally less than 10 cm thick, which is not a substantial volume considering most surface mines remove tens of meters of material or more. Initial analyses for the partial data set indicate that differences in total-S account for 61% of the overall variation in EC (see Fig. 3). Sulfur was determined on a Leco$^{©}$ S analyzer and has ranged from 0% up to 1.1%. Sulfur contents, like EC, generally increase significantly below the first intact shale seam. Other variables such as bulk spoil mineralogy in addition to S likely control the rest of the variation in EC (in addition to natural variability). Our research is currently looking into what other factors may be controlling the variation in EC between materials in addition to S concentrations.

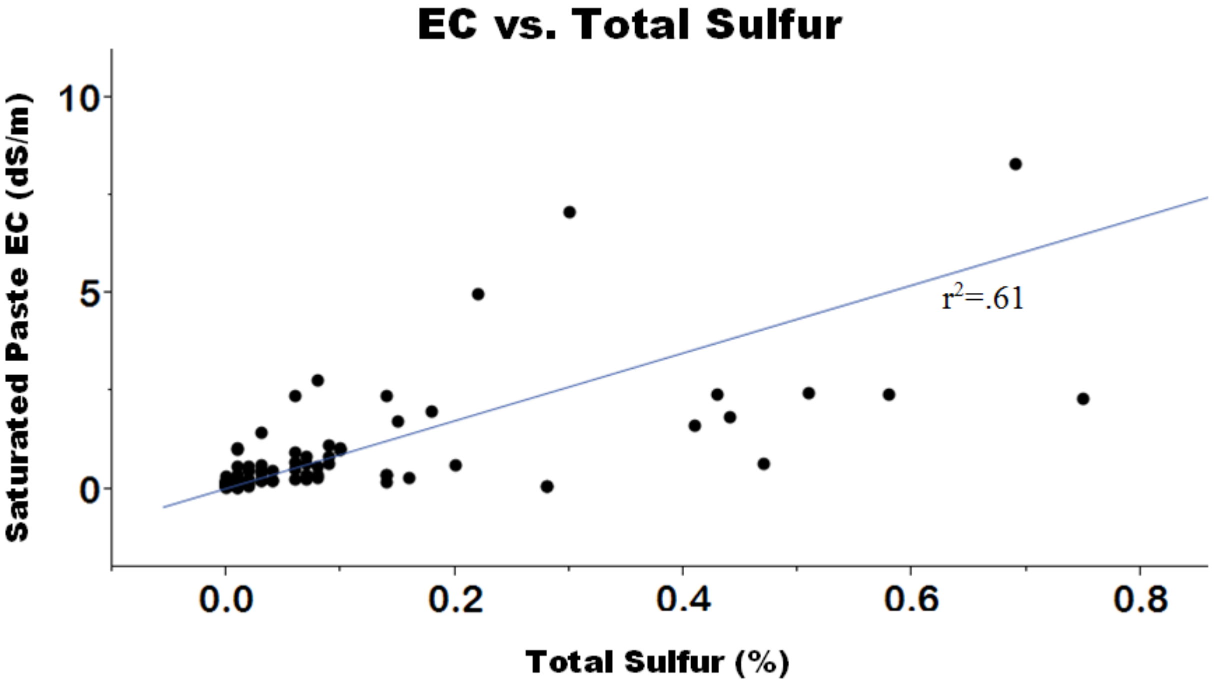

Figure 3 – Saturated paste EC values vs. total Sulfur for 117 samples. Total Sulfur was analyzed using a Leco© Sulfur analyzer.

Objective 3. *Investigate the nature of the boundary between high and low TDS strata in order to determine if: (a) An abrupt boundary exists at some confining layer, such as a shale; or (b) the boundary is more diffuse, being more related to distance from the earth's surface; or (c) no discernible boundary exists; variations occur with variations in parent material.*

The boundary between weathered and unweathered materials is very complex and is influenced by a large number of factors. The study location is in a humid climate with high rainfall, which drives most of the weathering reactions. It makes sense that at some depth, materials would begin to be unaffected by the surficial weathering reactions taking place, but this depth has proven to be highly variable from site-to-site. At a number of sites (see last year's report), we have noted a significant increase in EC between the lowermost saprolitic material and hard rock contact (R layers). The occurrence of a shallow, intact, cemented shale layer at many sites largely appears to control the depth of weathering by preventing further downward movement of water and oxygen into the weathering soil:rock profile. Most sites were observed to abruptly change from brownish to grayish colors directly below shallow occurring shale layers. Lab analysis revealed that this change is coupled with a sharp increase in EC (and often pH). Shale layers which have undergone significant weathering (e.g. fractured, lost cementation) lose this restrictive effect on water and oxygen and allow weathering to penetrate through the layer and more deeply into underlying strata. Sites lacking a near-surface shale layer tend to have more diffuse transitions from the weathered zones into unweathered materials and deeper overall weathering. Figure 4 shows a theoretical example of the relative location and of materials with varying TDS potential in a typical ridge system on an Appalachian surface coal mine.

The overall relationships shown in Figure 4 is generalized, however, and influenced by a number of local factors. First of all, the overall depth of groundwater penetration and associated long-term weathering and oxidation (e.g. "brown spoils") in the region is strongly affected by the local depth of stress relief fracturing (Borchers & Wyrick, 1981; Kipp & Dinger, 1987) due to long-term geologic unloading. Thus, the depth of pre-mine oxidation generally increases with elevation above local drainage and is best expressed on high local ridges and decreases as one approaches the valley floor and local base level. This phenomenon also leads to the common observation of brown oxidized zones exposed in overburden that extend down through largely gray reduced surrounding strata. Thus, in many instances, deeper rocks that might appear to be

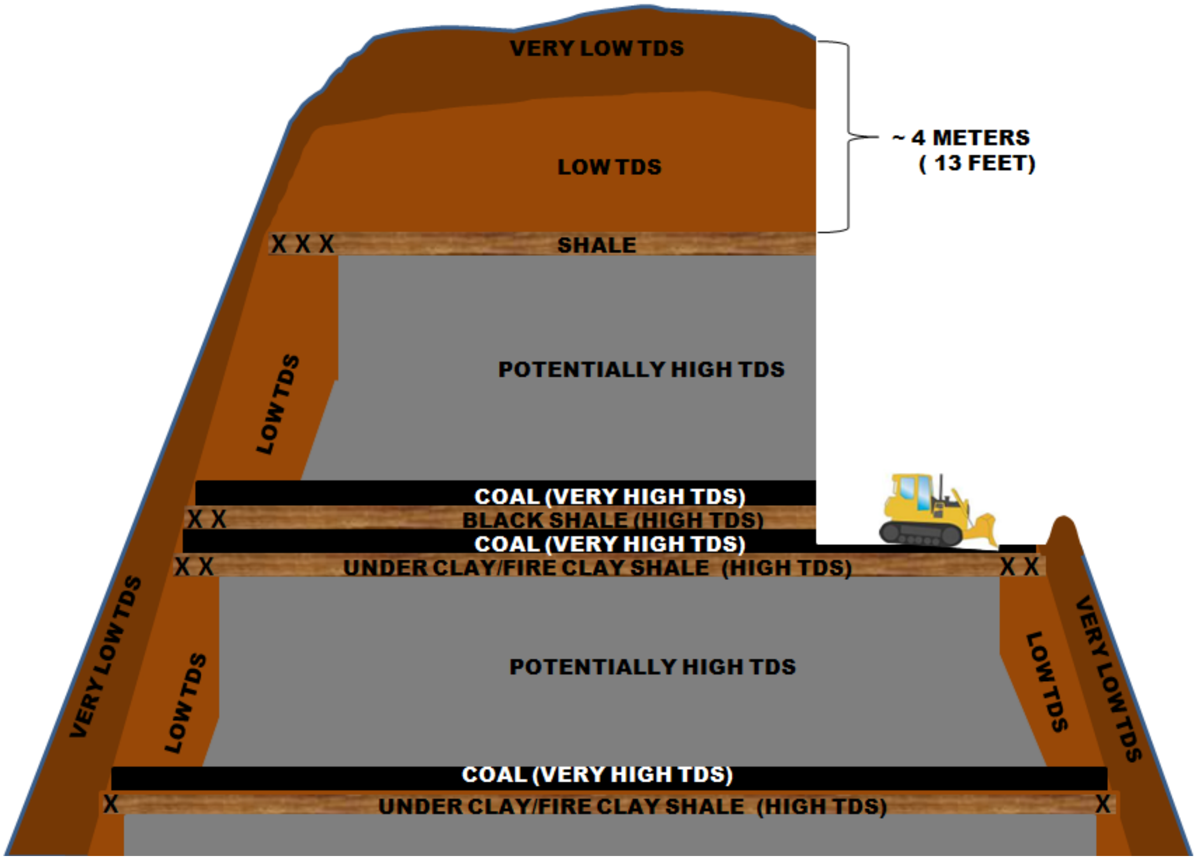

Figure 4 – Layering of materials in an Appalachian coal surface mine. Relative TDS elution potentials are indicated as very low, low, high, or very high. However, related work (Daniels et al., 2013) indicates a wide range in actual TDS leaching potentials among the deeper reduced rocks shown as "potentially high TDS" here. In general, intact non-weathered shale layers prevent the downward movement of water and oxygen, limiting the long-term weathering of TDS producing sulfides, carbonates and feldspars in deeper rocks. The capping of low TDS surficial soil + weathered rock has generally been about 4 meters thick, but has been much deeper in some areas, especially those lacking a near surface shale layer.

well-oxidized in highwalls or the outside of large spoil boulders may only reflect the exposed fracture trace and not the bulk of the overburden behind that surface. Secondly, even though deeper rock strata that are protected by shale layers are typically gray in color and reduced, they can still have a very wide range of TDS production potentials due to variations in sulfide content, reactive mineralogy and rock type (Daniels et al., 2013). Thirdly, as discussed above, the EC of the weathered surface soil profiles (the A, B and C horizons) is generally lower than the more partially weathered and soft saprolitic rock material that underlie the soil profile.

The combined thickness of the weathered soil and rocks observed in our sampling to date has generally been at least 4 m thick, but extends deeper in many areas. Other studies have noted the extent of this weathered zone throughout the Appalachian Plateau and found similar result. Kleinmann (2000) described the weathered zone as extending to 5 to 20 m below the surface, but typically being on the order of 6 to 12 m thick. Another study (Smith et al., 1974) found the weathered zone to vary in thickness, but generally to be about 6m thick.

Objective 4. *Determine if a relationship exists between TDS elution potentials and field description traits such as: HCl "fizz" reaction, H_2O_2 reaction and/or Munsell$^{©}$ color (e.g. gray vs. brown colors).*

Color can be an accurate field predictor of EC, but must be used with caution. Generally, grayish (chroma 1) materials produced higher EC values than brownish materials (chroma >1). Figure 5 shows the saturated paste EC values versus the colors noted in the field. Some samples with mixed matrix colors in ratios as low as 10% gray to 90% brown returned high EC values more typical of a gray material than a brown material. Colors presented in Figure 5 represent the grayest (or lowest chroma) color present in each sample based on Munsell$^{©}$ color charts. A few outlying brown materials also returned quite high EC values. Further investigation is needed to determine the cause of this phenomenon. We hope that some of our more specialized lab analyses (e.g., thin section mineralogy) will reveal what is different about these few samples.

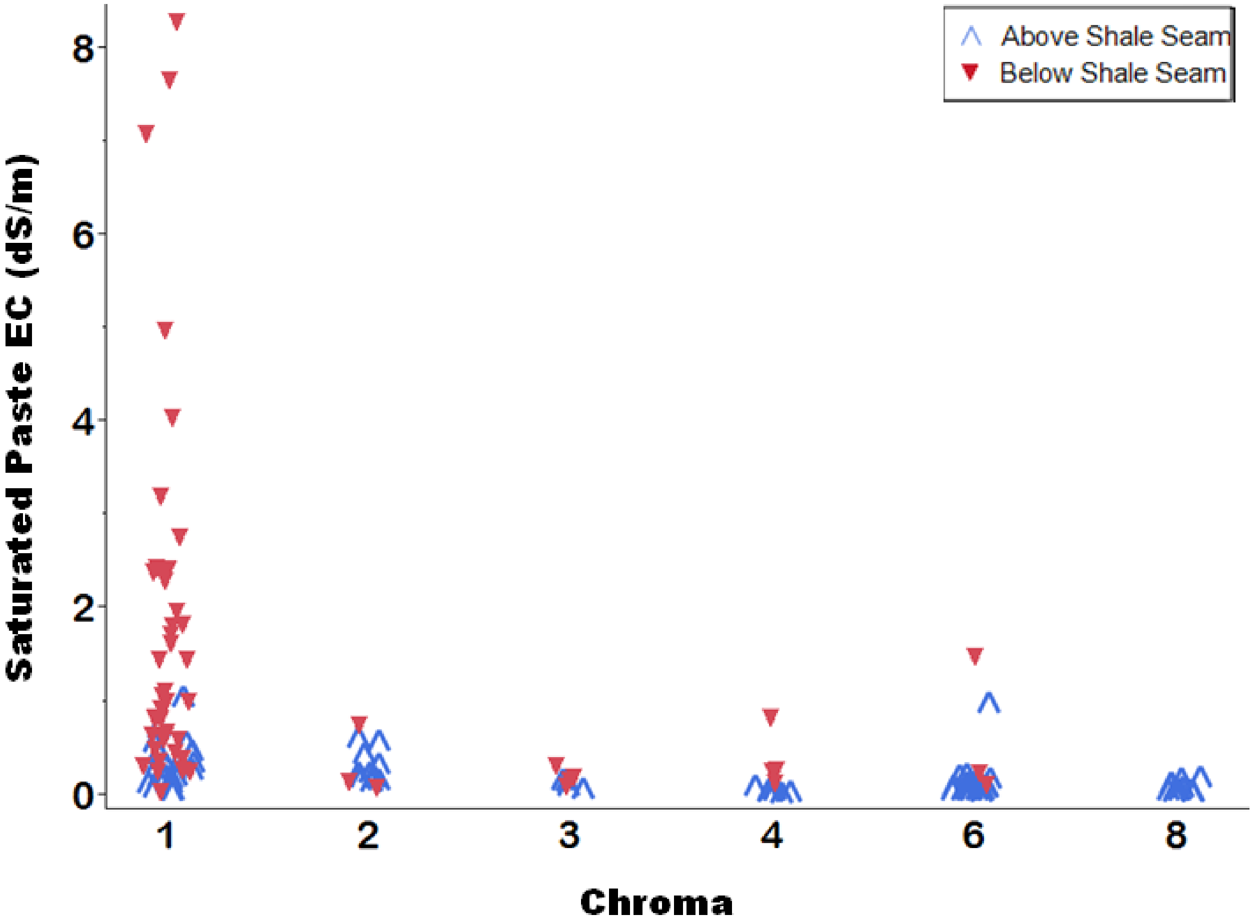

Figure 5- Saturated paste EC versus Munsell© color chart "chroma" recorded for moist samples. Lower chromas represent darker, grayer samples. The colors represent the lowest chroma present in the case of mixed matrix colors.

Originally, we had hoped that use of a simple 3% commercially available hydrogen peroxide or a weak HCl acid rinse on a sample would provide a quick field indicator of TDS/EC potential. However, as shown in Figure 6, using 3% hydrogen peroxide as a field indicator for EC seems to be limited in its usefulness based on the initial data. Although samples with extremely high EC tended react more vigorously, some samples with relatively high EC only reacted slightly or not at all (see Fig. 6). While samples with violent effervescence in the 3% hydrogen peroxide had a significantly higher ($P=.005$) EC value on average than samples with no effervescence, some samples in both categories were low EC and some samples in both categories were relatively high EC. The reaction with 3% hydrogen peroxide alone does not seem to be a reliable predictor of EC, but further study may still show it to be useful.

The 1M HCl acid "fizz test", similar to the peroxide test, is also of limited usefulness. Of the 139 initial samples tested, only several samples have reacted at all (see Fig. 7). Noneffervescent samples ranged from low to very high EC. Curiously, the three samples

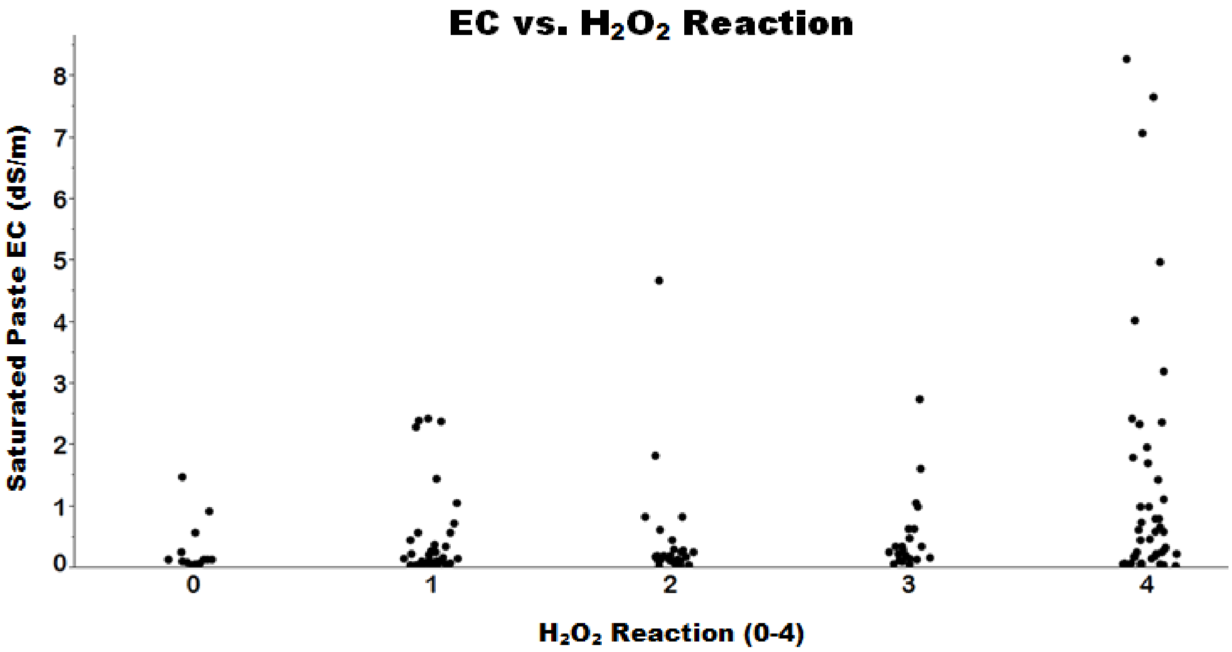

Figure 6 – Saturated paste EC values versus 3% hydrogen peroxide (H_2O_2) reaction for 148 samples. 0=noneffervescent, 1=very slightly effervescent, 2=slightly effervescent, 3= strongly effervescent, 4=violently effervescent.

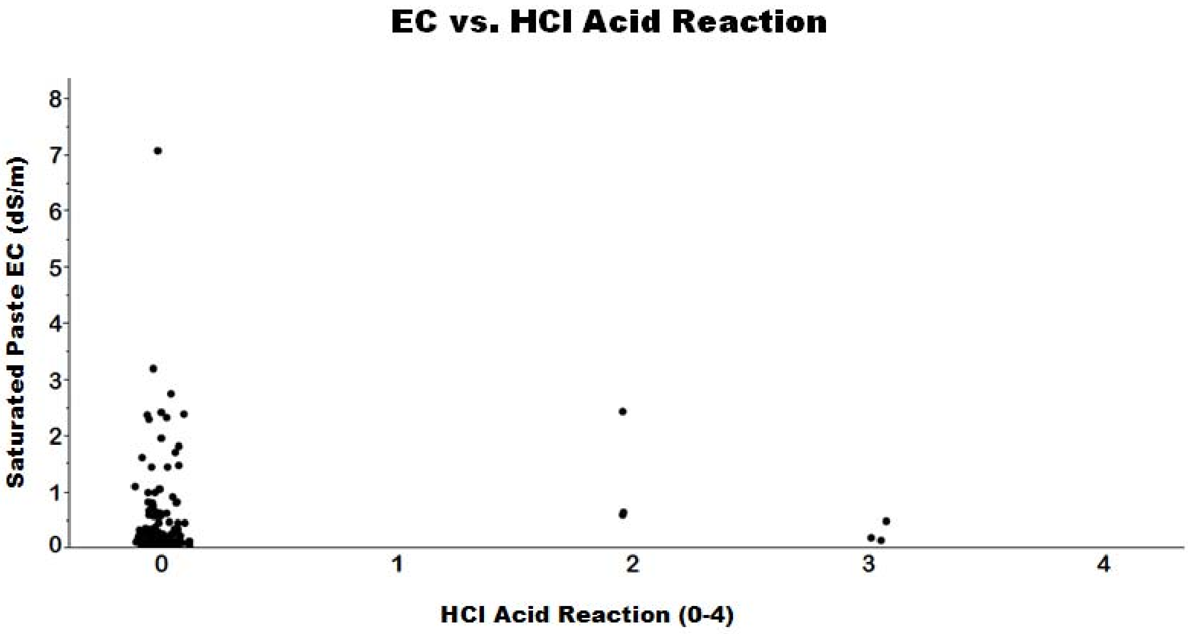

Figure 7 – Saturated paste EC values versus 1M hydrochloric acid (HCl) reaction for 139 samples. 0=noneffervescent, 1=very slightly effervescent, 2=slightly effervescent, 3= strongly effervescent, 4=violently effervescent.

shale seam, or rock type may be coupled with the acid and peroxide fizz tests to produce more reliable results. We are currently looking into this with statistical analyses.

Fossils are an important feature to note when trying to separate high/low TDS materials. Layers noted as containing visible fossils produced drastically higher conductivity values than similar layers without fossils. Fossils have dominantly been found in shales or mudstones. Various fossil types have been noted, including shells, roots, leaves, stems, bark, and even tree trunks; these have all had the same effect of increasing EC value. Layers containing prominent and abundant fossils should be handled separately and isolated, where feasible.

Future Plans and Deliverables

We are collecting the last few samples for this overall research program in the upcoming months, hopefully rounding out the total number of sites to near 30. Lab analyses will be completed as the final samples come in and should be completed by the end of 2014. Final data analysis and reporting for the project will be completed by the late summer 2015.

Preliminary results from this research were presented at the June, 2013, American Society of Mining and Reclamation conference in Laramie, WY, and are available online at: http://www.asmr.us/Meetings/2013/Wednesday%20S-12/12-1%20Johnson.mp4. A wide array of publications is expected, including additional conference presentations and journal articles along with Daniel Johnson's underlying PhD dissertation.

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