# Predicting Total Dissolved Solids Release from Overburden in Appalachian Coal Fields

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## ABSTRACT

The Appalachian coal industry has been successful in developing technologies to identify, handle, treat and isolate potentially acid-forming overburden materials during coal mining to reduce or eliminate water quality problems. However, the techniques used to predict acid mine drainage potential have not been tested for total dissolved solids (TDS) prediction; therefore, new techniques may need to be devised. With a goal to develop methods to predict TDS release from overburden materials, our objective for this paper was to determine the effect of a dilute nitric acid ($HNO_3$) solution on weathering of overburden materials. Fifteen overburden samples (five strata from three locations) were collected from surface mines in West Virginia and three of these samples were used in this study. Ground samples were mixed with a dilute $HNO_3$ solution and shaken for two weeks to simulate weathering. Supernatants were extracted and analyzed every other day for pH, EC, and other selected ions. Acid-Base Accounting (ABA) parameters, which measure sulfur and neutralization potential (NP), were compared to results from our weathering tests. Results showed that predictions of TDS release by ABA were similar to the actual release of constituents in our weathering study. Sample WV 2 released the highest concentrations of elements, including high Fe, Al, Mn, and Ca, which are primary elements of concern in acid mine drainage. These results were consistent with this sample's moderate pyrite and NP contents. WV 3 and WV 4 produced lower levels of TDS release, which was consistent with lower pyrite and NP contents in these samples. An additional test using EDTA as a chelator will be performed.

## INTRODUCTION

Coal is the primary source of fuel for electricity production in the United States, contributing more than 50% of the electricity generated nationwide. Due to land disturbance activity and environmental impacts that can occur during surface mining, the coal industry has been at the forefront of controversy surrounding human and environmental health and safety. Deforestation, leveling of mountains, acid mine drainage, erosion, subsidence, acid rain, and air pollution are just a few environmental impacts caused by the extraction and burning of coal.

Proper reclamation can lessen and in some cases eliminate the effect of many of these impacts through proper planning and identification of materials being disturbed. Overburden material, which covers the coal seam, is blasted apart and moved in order to reach the coal. It is this mining process (overburden blasting, removal and placement) that allows exposure of the rock materials to physical and chemical weathering, which can release soluble constituents into surrounding water sources. All of the blasted overburden cannot be put exactly back into place because the volume of rock increases due to blasting (Merricks et al. 2007). This excess material is commonly placed in valley fills or other constructed fills (Robins 1979; White and Barata 1995; Peng 2000; Messinger and Paybins 2003; Pond et al. 2008). Depending on the chemical composition of the rocks, weathering can promote acid mine drainage, alkaline mine drainage (Berhhardt et al. 2012), as well as release of total dissolved solids and heavy metals in runoff.

The application of innovative procedures during mining and reclamation has helped alleviate negative impacts of coal mining activities. The Acid-Base Accounting (ABA) procedure is an analytical method that determines the total amount of acidity and alkalinity that may be produced from the weathering of overburden materials (Skousen et al. 1997). ABA is the most common method for predicting post-mining water quality (Perry 1985). Unfortunately, no such method currently exists for the prediction of TDS release from overburden material. ABA does, however, provide information on how reactive the overburden is. Pyritic materials and carbonates are the two most common reactive components of overburden material, and if present in high quantities a large quantity of total dissolved solids is a probable outcome. TDS are defined as the total sum of cations and anions in solution, in units of mg/L. Common ions are $SO_4^{2-}$, $HCO_3^-$, $Cl^-$, $Ca^{2+}$, $K^+$, $Na^+$, and $Mg^{2+}$, but any dissolved ion that is present in solution will contribute to TDS. Since ion concentrations control electrical conductivity (EC) in water, EC can be used to estimate TDS with a conversion factor of 0.64. This conversion factor is generally used in waters dominated by chloride; however, this conversion factor underestimates TDS in sulfate-rich solutions (Evangelou 1998).

### TDS and Influences on Human and Aquatic Health

Congress passed the Safe Drinking Water Act in 1974, which requires the United States Environmental Protection Agency (USEPA) to determine safe levels of chemicals in drinking water. TDS is considered a secondary pollutant with a maximum criteria limit of 500 ppm. TDS is not expected to harm human health at this level, but may be toxic to aquatic life and can damage water treatment equipment (USEPA 2012). Appalachian streams not influenced by coal mining commonly have TDS concentrations less than 75 mg/L and TDS is primarily comprised of bicarbonate, calcium, and chloride. In streams that are impacted by coal mining, TDS levels can range from 400 to 2,000 mg/L and TDS is primarily made up of sulfate, bicarbonate, calcium and magnesium (Timpano et al. 2010; Pond et al. 2008).

Aquatic organisms are commonly used in lab toxicity tests to evaluate the levels at which TDS becomes harmful. Common indicator species are benthic macroinvertebrates. Pond et al. (2008) found that mining activity impacted benthic macroinvertebrate communities with a strong correlation to a gradient of ionic strength. Pond et al. (2008) showed that EC in streams in unmined areas of the Appalachian region is generally less than 75 µS/cm, compared to up to 30 times unmined levels downstream of mountain top mining sites. Aquatic insects make up a large portion of benthic macroinvertebrates. Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies) are orders of aquatic insects that are collectively termed EPT. These three orders in particular are commonly analyzed because of their sensitivity to pollution. The EPT Index is not a standard method of water quality assessment used within the Natural Resourses Conservation Service, but is useful in monitoring the species richness of a particular stream (USDA EPT Index). These organisms are the foundation for many food chains and are critical for the processing and cycling of nutrients (WVDEP 2012).

TDS is not the only water quality parameter that creates stress on organisms in aquatic ecosystems and therefore is not independent of other stressors in central Appalachian streams, which makes it difficult to monitor its direct effects (Timpano et al. 2010). A quick laboratory or field technique for estimating constituent release potentials from coal overburden material would be helpful for mine planning, placement and abatement procedures for coal operators, which also could help to minimize impacts to mined streams.

Our objective was to create a simple laboratory weathering technique to accurately predict the amount of TDS released from overburden materials. To do this, we compared a weathering/shaking procedure using dilute $HNO_3$ to predictions from ABA parameters.



## MATERIALS AND METHODS

### Field Overburden Collection

Fifteen overburden samples from each of three West Virginia surface coal mines were collected. These 15 samples represented a specific type of rock with an expected high, medium, or low TDS potential based on our experience with ABA or other methods of inference (e.g., local water quality data). From these 15 samples, three were chosen for this weathering study. In selecting our three overburdens, a preference was placed upon sampling rock units with variation in sulfur and alkalinity contents, and that would most likely be disposed of in valley fills or backfills instead of those strata that will be isolated as toxic strata and presumably hydrologically isolated.

### Sample Processing

For each sample, all material was crushed and passed through a 1.25 cm (0.5-in.) sieve. All samples were further ground using a BICO pulverizing mill, until roughly half of the sample could pass through a 250 µm (0.0098-in.) sieve.

### Laboratory Analysis of Mine Spoils

Three grams (3.00 g) of each of the three overburden samples were mixed with 2,000 mL of a dilute nitric acid ($HNO_3$) (0.0159 M) solution (prepared as a 1/1000 dilution of 15.9 M trace metal grade $HNO_3$). The dilute $HNO_3$ had a blank EC of 5.93 mS/cm and a pH of 2.0. The overburden samples were collected from the top of a 250 µm (0.0098-in.) sieve to control for particle size. Containers with 3-g samples in $HNO_3$ solution were replicated three times and placed on a reciprocating shaker for 14 days. After 24 hours, a 15-mL aliquot of solution was extracted and analyzed. Additional aliquots were taken and analyzed approximately every other day for two weeks. Electrical conductivity and pH were determined using standard methods. Ca, Mg, Na, K, P, Fe, Al, Mn, B, Sr, Pb, Cu, and Ni were determined by ICP-OES (Optima DV-2100, Perkin-Elmer, Norwalk, CT), but only data for Fe, Al, Mn, and Ca are displayed here.

## RESULTS AND DISCUSSION

Under current thinking, rocks with high TDS potential may be shales or sandstones with high sulfur contents or high carbonate (neutralization potential, NP) contents or those containing both. Rock units with medium potential may be shales or other rocks with low to moderate sulfur and/or carbonate content. Rock units with low potential may be hard sandstones or oxidized/weathered sandstones or soil-like materials. In standard ABA, the relative amount of acid-producing rock is compared to the amount of acid-neutralizing rock to predict the water quality of a site (Skousen et al. 2002). We predicted, using the mining operation's overburden ABA analysis, that sample WV 2 would have the highest TDS release because of the moderate sulfur concentration (0.15%) and high NP (30 g/kg) (Table 1). WV 3 would be expected to release intermediate TDS because of the low sulfur concentration (0.001%), but high NP (60 g/kg). Sample WV 4 had moderate sulfur (0.10%) but very low NP (3 g/kg), which we expected to release less TDS than the other two samples.

Predicted TDS release using ABA parameters was proportional to final cumulative concentrations of elements released after two weeks of shaking in dilute $HNO_3$. Sample WV 2 had the highest concentrations released during weathering, WV 3 was intermediate and WV 4 produced the lowest concentration of constituents released (Figure 1). However, ABA only provides relative TDS release predictions (high, medium or low) without describing or identifying actual levels or concentrations, nor does it provide a rate of release. Therefore, additional analyses were needed through the use of weathering studies.

**Table 1. Acid-base account parameters for three overburden samples from West Virginia surface coal mining sites**

| Sample | Color | Rock Type | pH | S % | MPA g/kg | NP g/kg | NET NP g/kg | Predicted TDS Release |
|---|---|---|---|---|---|---|---|---|
| WV 2 | 2.5Y 6/1 | Black shale | 6.0 | 0.15 | 30.0 | 30.0 | 0 | High |
| WV 3 | 5Y 7/1 | Gray shale | 8.1 | 0.001 | 0.25 | 60.0 | 60.0 | Medium |
| WV 4 | 2.5Y 3/1 | Sandstone | 5.0 | 0.10 | 4.0 | 3.0 | −1.0 | Low |

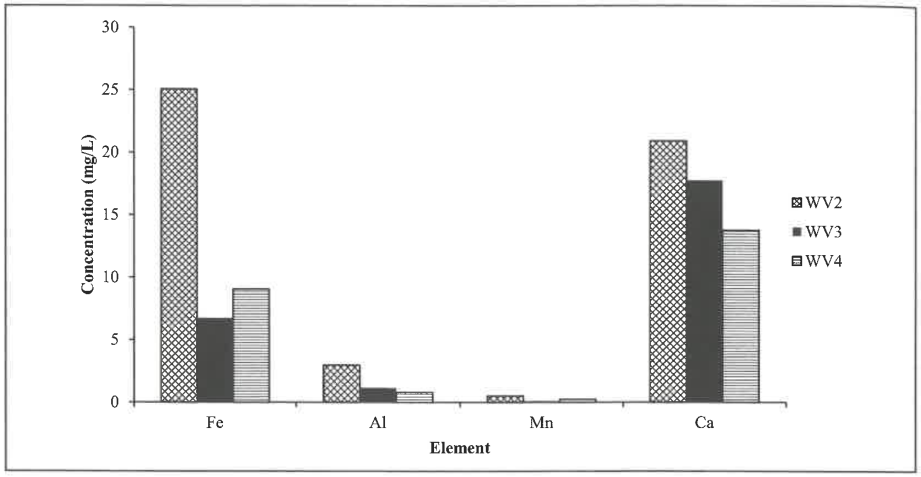


**Figure 1. Concentrations of Fe, Al, Mn, and Ca from three West Virginia surface coal mine overburden samples at the end of the two-week shaking period with dilute $HNO_3$ extracting solution**

## Ions

The pH of the extracted solution stayed strongly acidic over the two weeks (Figure 2), which provided us with the ability to assume that once the ions went into solution, they would remain in solution.

The oxidation of pyrite ($FeS_2$) is a significant factor in the formation of acid mine drainage (AMD). AMD is produced when sulfide minerals associated with coal seams react with oxygen and water to form low pH, sulfate rich, and high iron solutions (Mack et al. 2010). As expected, the largest Fe concentrations in solutions from our weathering studies were observed after 24 hours (Figure 3) and followed the expected pattern of rapid pyrite oxidation with samples containing sulfur (Table 1). WV 2, with the highest sulfur concentrations, had much higher Fe concentrations during the first shaking period compared to the other two samples.

The largest Al concentrations were observed after shaking for 192 hours for all three samples. Al concentrations dropped rapidly after 192 hours and increased again after 240 hours (Figure 4). Low pH conditions accelerate the release of aluminum and other toxic elements from minerals (Bigham et al. 1996; Kittrick et al. 1982) and the pH of our solutions stayed at about 2.0 during the course of the two-week period. These time periods corresponded to the length of time required for the dilute $HNO_3$ solution to promote the breakdown of aluminum- containing minerals in the samples and no alkalinity was present to neutralize the acidity (Seidel et al. 1998). Additional time was required for more Al to be dissolved during the 240- to 288-hr time period.



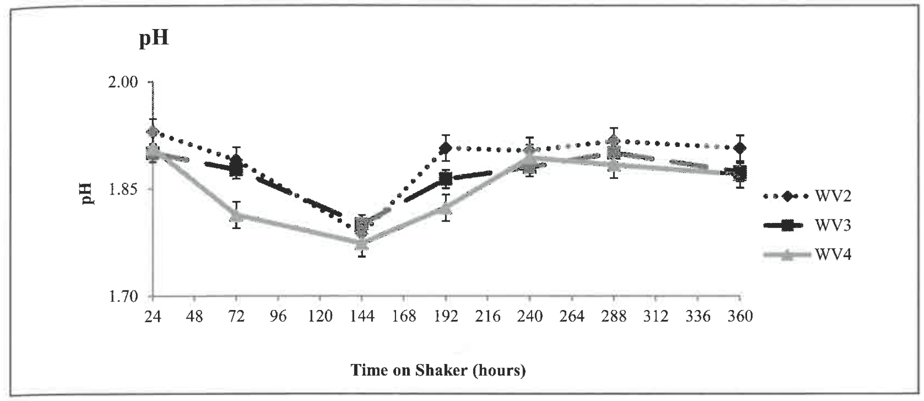


**Figure 2. pH of solution over two weeks for the three overburden samples**

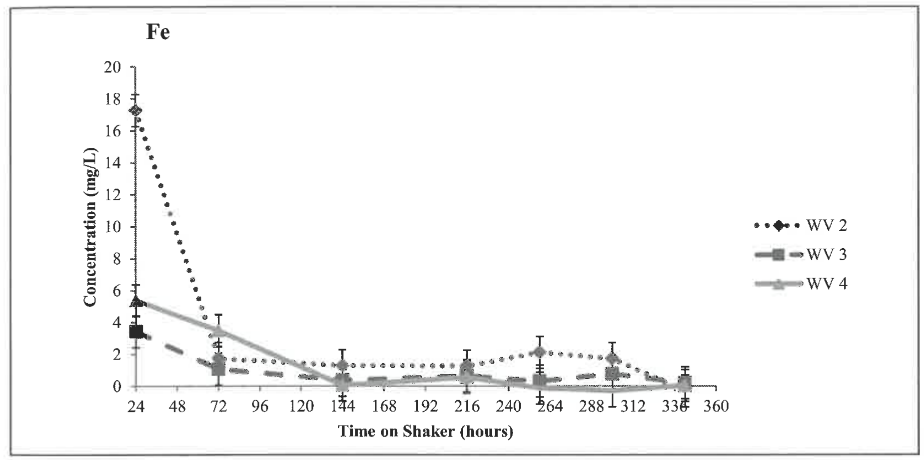


**Figure 3. Iron concentrations released over time from three overburden samples with a dilute $HNO_3$ extracting solution from a West Virginia surface coal mine**

Very little Mn was released from these samples with dilute $HNO_3$ (Figure 1), but sample WV 2 showed higher amounts of Mn release than the other two samples, even though the total amount was small (Figure 5). Manganese has been found to be directly related to carbonate carbon and NP (Morrison et al. 1990). The trends in Mn release are consistent with the ABA results from these samples (Table 1).

Most alkaline material is in the form of calcareous minerals containing primarily calcium carbonate ($CaCO_3$) (Johnson 2005). Limestone is composed of $CaCO_3$ and is commonly found in the Appalachian region. From the NP listed in Table 1, we predicted that WV 2 and WV 3 could potentially release more Ca compared to WV 4, which had little NP. Both WV 2 and WV 3 released high levels of Ca, with higher amounts of Ca from WV 2, which we presumed to be because of rapid weathering of $CaCO_3$ due to the acidity generated by pyrite oxidation and the acidity from the dilute $HNO_3$ solution.

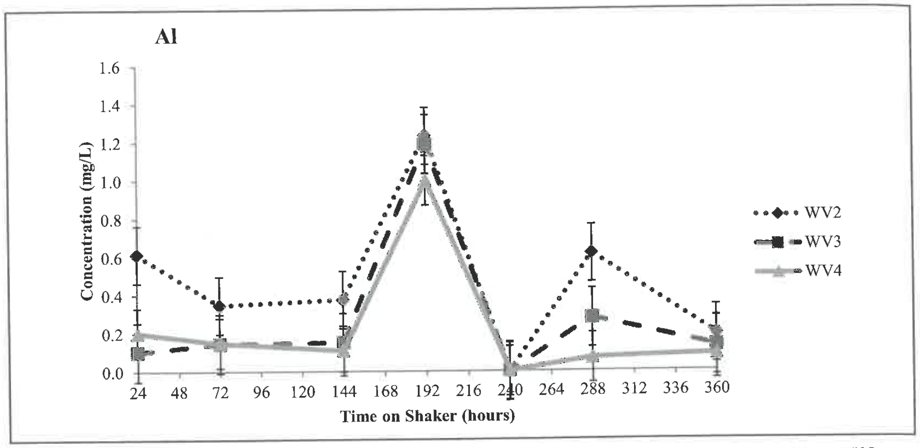


**Figure 4. Aluminum concentrations released over time from three overburden samples with a dilute $HNO_3$ extracting solution from a West Virginia surface coal mine**

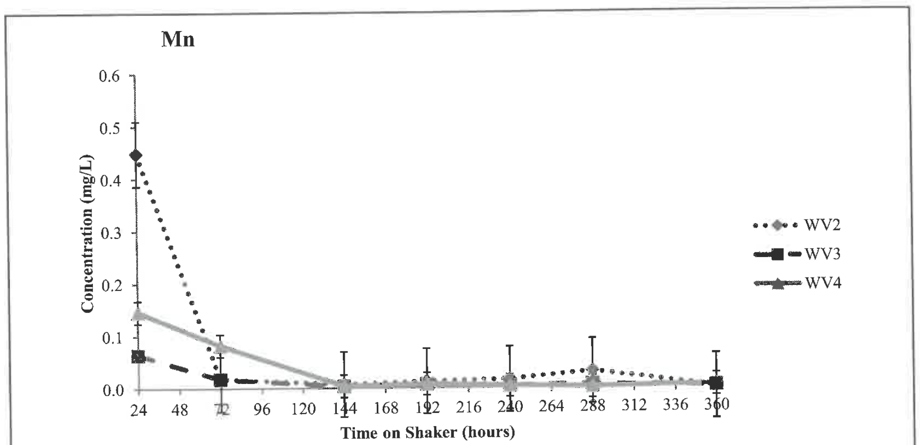


**Figure 5. Manganese concentrations released over time from three overburden samples with a dilute $HNO_3$ extracting solution from a West Virginia surface coal mine**

Although there was no pyrite in sample WV 3, high levels of Ca were released due to the low pH of the dilute $HNO_3$ solution. Most of the Ca was released after shaking for 144 hours (Figure 6). Ca must be mostly dissolved prior to the onset of any significant leaching of Al (Seidel et al. 1998). Al began dissolving after 144 hours, which is the same time in which Ca dissolution was complete (Figure 4).

## EC and TDS

Soluble salt content as measured by EC from overburden material is important for the planning and placement of overburden material because of its relationship to TDS. Accurate determination of TDS is a slow and tedious procedure, but TDS can be estimated by a common function provided by the U.S. Salinity Laboratory Staff (1954) using



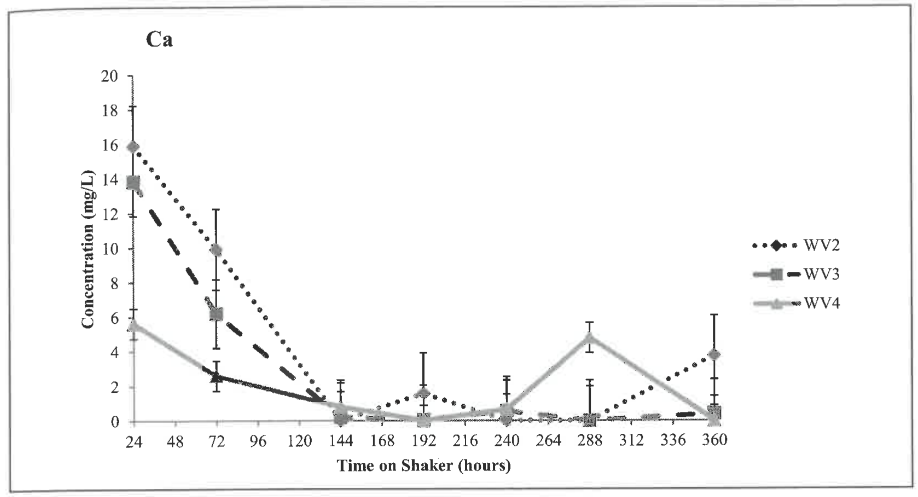


**Figure 6. Calcium concentrations released over time from three overburden samples with a dilute $HNO_3$ extracting solution from a West Virginia surface coal mine**

a conversion factor between TDS and EC. This conversion factor is 0.64 if the EC is less than 1 mmho/cm (Evangelou 1998). Equation 2 is utilized when EC is greater than 1 mmho/cm (Evangelou 1998). These conversion factors are generally used in waters dominated by chloride; however this may underestimate TDS in sulfate-rich solutions (Evangelou 1998). The highest EC we encountered was about 0.85 mmho/cm (850 µS/cm), implying that the conversion factor in Equation 1 is suitable for these samples.

$$TDS = 0.64 * EC\ (\mu S/cm) \quad (1)$$

$$TDS = 0.64\ [EC\ (\mu S/cm)]^{1.087} \quad (2)$$

Figure 7 displays the trend in net EC (the measured EC of the solutions minus the initial blank EC) from our three overburden samples over our two- week weathering procedure. All three overburden samples showed a rapid release of soluble salts and high EC (800 to 875 µS/cm) after 24 hours, then a decrease to less than 100 µS/cm after shaking for 144 hours. Small increases were found between 240 and 288 hours. Since all three overburden samples showed similar trends, the average net EC treadline was plotted in Figure 8 against the treadline for predicted TDS using Equation 1. The average net EC and estimated TDS fell below the TDS maximum criteria limit (MCL) of 500 mg/L within the first 24 hours.

## CONCLUSIONS

Depending on the physical and chemical composition of overburden from surface coal mining sites, weathering can promote the release of TDS into the environment. Some studies have indicated that high TDS has detrimental effects on aquatic life. Therefore, TDS release from disturbed overburden must be better understood, and techniques to predict TDS levels after disturbance need to be developed.

Three samples from strata at West Virginia coal mining sites were collected and compared to ABA parameters. Based on the amount of sulfur and neutralization potential from the ABA, we predicted that sample WV 2 should generate the highest TDS release of the three, while WV 4 should generate the least TDS. The predictions of TDS release from ABA were proportional to the total amounts of elements released during a two-week weathering study with a dilute $HNO_3$ extracting solution. WV 2, having moderate

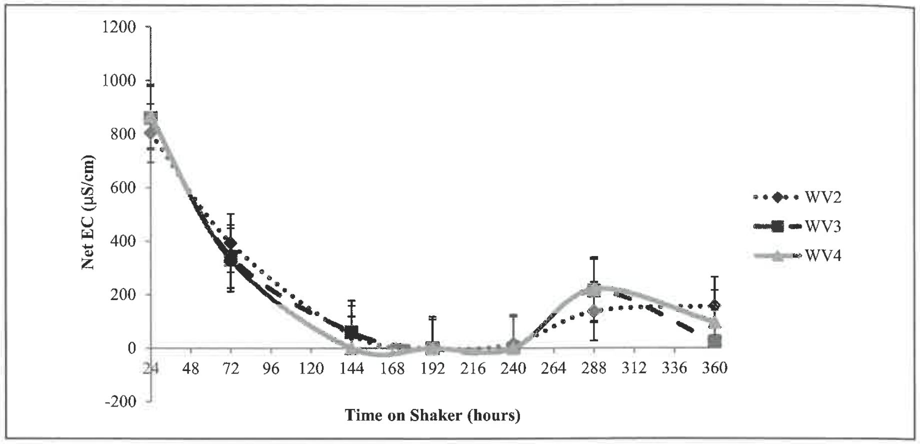


**Figure 7. Net electrical conductivity of three overburden samples after shaking and weathering in a dilute $HNO_3$ extracting solution from a West Virginia surface coal mine over time**

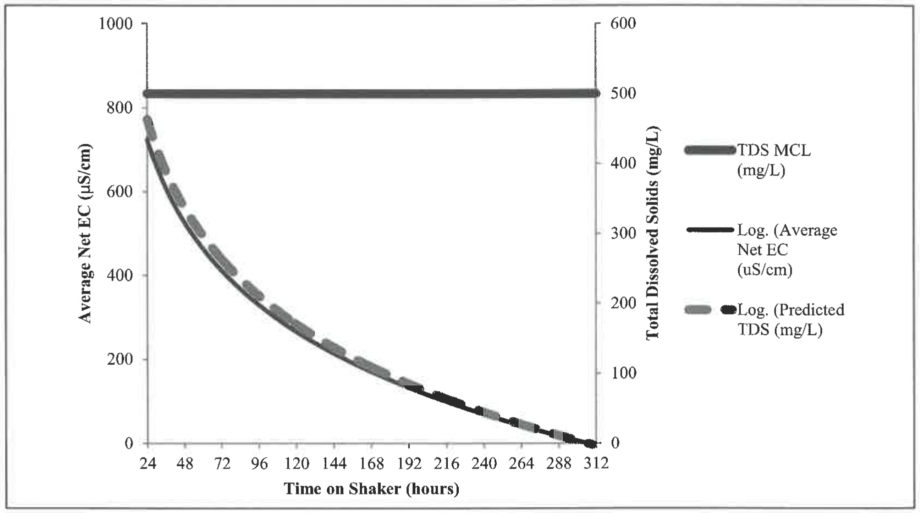


**Figure 8. A comparison between the average net EC and estimated TDS from three overburden samples from a West Virginia surface coal mine over time**

levels of sulfur and NP, displayed the highest concentrations of elements released during shaking and extraction, including high Fe, Al, and Mn, and Ca. WV 3 and WV 4 released lower levels of TDS due to lower amounts of sulfur and NP. EC was converted to a predicted TDS concentration using equations in the literature. We found that within the first 24 hours, TDS release from these three rock samples decreased to levels below the TDS MCL of 500 mg/L. Release rates from our weathering study show that TDS concentrations decline rapidly during weathering.

The next step of our research will be to repeat this shaking experiment using EDTA as the extracting solution on a greater number and variety of overburden samples. Although the solid: solution used in this experiment is very different from field leaching, we are hoping to develop an index that can be correlated to column leaching and field leaching experiments for future prediction of TDS release from overburden material in Appalachian coal fields.



## ACKOWLEDGMENT

This study was sponsored by the Appalachian Research Initiative for Environmental Science (ARIES). The views, opinions and recommendations expressed herein are solely those of the authors and do not imply any endorsement by ARIES employees, other ARIES-affiliated researchers or industrial members. Information about ARIES can be found at http://www.energy.vt.edu/ARIES.

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