Mine Water Environ (2018) 37:31–41
DOI 10.1007/s10230-017-0462-4

TECHNICAL ARTICLE

Assessing the Impact of Removing Select Materials from Coal Mine Overburden, Central Appalachia Region, USA

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Received: 25 August 2016 / Accepted: 31 May 2017 / Published online: 15 June 2017
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Abstract The exposure of readily soluble components of overburden materials from surface coal mining to air and water results in mineral oxidation and carbonate mineral dissolution, thus increasing coal mine water conductivity. A conductivity benchmark of 300 µS/cm for mine water discharges in the Appalachian region has been suggested to protect aquatic life and the environment. A USGS screening-level leach test was applied to individual strata from three cores collected from a surface mine site in the central Appalachian region to generate preliminary conductivity rankings, which were used to classify strata for two disposal scenarios: (1) unmodified scenario, which included all extracted strata and (2) modified scenario, which excluded 15% (by mass) of the overburden materials with the highest conductivities. We evaluated overburden leaching conductivity using EPA Method 1627 in 18 dry–wet cycles, generating conductivities of 1020–1150 µS/cm for the unmodified scenario and 624–979 µS/cm for the modified scenario. Hence, overburden segregation was successful in reducing the leachate conductivity, but did not reach the proposed benchmark. The leachate was dominated by sulfate in the first four cycles and by bicarbonates in cycles 5–18 in columns with higher sulfur content, while bicarbonates were dominant throughout experiments with overburden having lower sulfur content. The use of conductivity rankings, isolation of potentially problematic overburden strata, and appropriate materials management could reduce conductivity in central Appalachian streams and other surface mining areas.

Keywords Coal mine water · Total dissolved solids · Mine waste leaching · Conductivity · Materials management

Introduction

Surface coal mining, as practiced since the 1970s in the coalfields of the central Appalachian region in the US (Bernhardt et al. 2012; Craynon et al. 2013; Griffith et al. 2012), generates large volumes of overburden, which has typically been disposed of in valleys (Griffith et al. 2012). It is estimated that surface coal mining affects ≈4000 km of streams and 6.8% of the region's land by modifying the natural landscape, water, and air quality (Lindberg et al. 2011; Paybins et al. 2000; US EPA 2011a).

When overburden contains pyrite (FeS_2), exposure to ambient air and water promotes pyrite oxidation, with

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Electronic supplementary material The online version of this article (doi:10.1007/s10230-017-0462-4) contains supplementary material, which is available to authorized users.

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the subsequent release of H^+ and SO_4^{2-} (Descostes et al. 2002). According to Federal (40 CFR Part 434) and state regulations (Legislature 2016), acid-forming materials (e.g. pyrite) should be isolated in spoil disposal fills and co-disposed with alkaline materials to achieve neutral leachate and to avoid acid mine drainage (AMD). However, this handling does not reduce total dissolved solids (TDS). The main ions that comprise TDS and contribute to electrical conductivity (EC) in coal mine water (CMW) in this region of central Appalachia are Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- (Palmer et al. 2010).

While the background EC in undisturbed streams of the Appalachian region has been reported to range from 30 to 260 µS/cm, the EC in streams of mined sites has been reported to typically range from 159 to 2540 µS/cm, with peaks up to 6000 µS/cm (Griffith et al. 2012; Kennedy et al. 2005; Suter and Cormier 2013). The EPA recommended an in-stream limit of 300 µS/cm to protect 95% of the native aquatic macroinvertebrates in the central Appalachian region (Cormier et al. 2011; Pinto et al. 2016). High EC is largely due to the leaching of sulfate- and bicarbonate from sulfide and carbonate-containing minerals in the overburden. Thus, removing the fractions of the overburden that contain the highest concentrations of these minerals could reduce EC.

We propose the use of a leach test to generate conductivity rankings for overburden strata and the further segregation of potentially problematic materials in lined cells (lined with layers of compacted clay or other available natural materials that can reduce hydraulic conductivity and, hence, contaminants migration); while overburden with low conductivity potential could be used as fill material. The USGS field leach test, developed by the US Geological Survey (Hageman 2007), provides an indication of the readily reactable and soluble components present in solids (such as those generated by sulfide oxidation and carbonate dissolution), the consequent acid generation, and the dissolution of minerals reacting with the generated acid.

The objective of this study was to evaluate the leachate EC of overburden materials in a column test that was intended to simulate surface coal mining conditions and its correlation with cations, anions, pH, and alkalinity in two scenarios: 'Modified' and 'Unmodified'. For the unmodified scenario, all overburden strata were included in the leaching tests, while the modified scenario excluded the 15% of the overburden strata (by mass) with the highest conductivities, as measured in the screening-level assessment. The 15% criterion was based on the authors' professional judgment that this would be a reasonable overburden quantity to be selectively identified and isolated in a typical surface coal mining operation.

The correlations of the measured parameters were also evaluated to determine which of those could be used to predict high EC potential in the overburden leachate. Additionally, since overburden exposure to ambient air and water can produce acid, which can subsequently leach additional metals, acid–base accounting (ABA) tests were used to determine if the acid character predicted for the overburden matched the column test results.

Materials and Methods

Description of the Site and Sampling Locations

Three 3.8 cm-diameter core samples were obtained from an unmined site at the Middle Fork Development Corporation Mine (Middle Fork Mine) in Magoffin County, Kentucky, USA. The Middle Fork Mine is located on the White Oak USGS 1:24,000 quadrangle at the east of the Left Fork Licking River in the central Appalachian region. A rotary drilling rig equipped with a split spoon sampler was used to recover core samples with depths of 39.6 m for core 1 (N37°43′52.186″, W83°9′12.881″, altitude 371 m above sea level), 30.5 m for core 2 (N37°43′46.618″, W83°9′9.286″, altitude 359 m above sea level), and 30.5 m for core 3 (N37°43′44.017″, W83°9′3.823″, altitude 359 m above sea level) (Supplemental Fig. 1). The drill rig was located at the top of ridges to sample all of the strata that would be removed during coal extraction, but the top layers were too loose to be recovered by the split spoon.

Overburden Characterization

Geological characterization was performed according to Ferm and Weisenfluh (1981); rock type, grain size, and texture of the extracted strata were determined. The thickness of each stratum was measured and then the materials in the stratum were crushed, sieved, and weighed to obtain a mixture with a particle size distribution profile of: 4.75–9.5 mm (40%), 2–4.75 mm (25%), 1.2–2 mm (15%), 0.5–1.2 mm (10%), 0.251–0.5 mm (5%), and <0.251 mm (5%), as required by EPA Method 1627 (US EPA 2011b), and loaded into the experimental columns. Each mixture was homogenized and characterized for elemental composition, moisture, soil pH (EPA Method 9045D), and % sulfur. All marketable coal was excluded from the experiments.

Acid–Base Accounting

State regulatory agencies require the prediction of acid production to issue mining permits (Lapakko 2002; Skousen et al. 2002). ABA (ASTM 2013) of the strata mixtures for the experimental columns was performed by measuring neutralization potential (NP) using the method with H_2O_2 addition to oxidize dissolved Fe^{2+}, as described by Skousen et al. (1997), with the modification proposed by ADTI (2001), by determining maximum potential acidity (MPA) as 31.25 × %S and by net neutralization potential (NNP) as NP–MPA.

USGS Screening-level Leach Test

A USGS leach test (Hageman 2007) was used to obtain the EC for each strata of the three cores using a combined 0.5–2 mm particle size, except for a few strata in which a composite of 0.251–2 mm particle size was used due to a lack of spoil of the former size. Briefly, a 20 g subsample (smaller than the 50 g required by the method due to availability) was weighed in a 0.5 L HDPE bottle and 400 mL of DI water (liquid/solid, L/S ratio 20/1) was added. The bottle was vigorously shaken by hand for 5 min and allowed to settle for 10 min. The supernatant was analyzed for pH, conductivity, anions, and dissolved metals. The Tukey interquartile range method was used to detect outliers in the leachate data. A normality test of the EC data was run using the Shapiro–Wilk option in Origin 2016 (OriginLab Corporation, Northampton, MA).

Columns Test: EPA Method 1627 Kinetic Test Method for the Prediction of Mine Drainage Quality

EPA Method 1627 was designed to evaluate water quality in coal mines, and has been validated using samples from the Appalachian region, among others (Hornberger and Brady 2009). A total of 18 experimental columns were fabricated to test the three cores in the unmodified and modified scenarios in triplicate. For the unmodified scenario, the columns contained all sections of each core, proportional to the strata thickness, while for the modified scenario, the columns only contained sections not identified as the 15% high conductivity screening-level (HCSL) strata, based on mass. The %S was determined for each stratum % in the LECO furnace and those concentrations were used to calculate a %S weighted average for the columns' content.

The experimental plexiglas columns (5 cm in diameter, 76 cm in length) had 2 kg of overburden mixtures (occupying a length of 56–66 cm, with the masses included in Supplemental Table 1), with glass beads (5 cm) and filter pads at the bottom and top. The leaching test started with the 'initial flush', where each column was flushed using ≈250 mL each time (water volume that inundated the column), until leachate conductivity stabilized (<20% relative standard deviation, RSD). After that, the columns were run for 18 cycles, consisting of 6 'dry' days and 1 'wet' day. During the dry days, 1 L/min of a moisture saturated gas mixture (90% air, 10% CO_2) continuously circulated through the column; a higher than atmospheric CO_2 content is used to guarantee the complete dissolution of the carbonate rocks (Hornberger and Brady 2009). Enhanced pyrite oxidation and carbonate dissolution maximized conductivity in the columns leachate. During the wet day, ≈260 mL of DI water was used to inundate each column for 24 h. Then, the columns were drained and the aqueous phase was collected and analyzed for pH, conductivity, alkalinity, acidity, selected dissolved elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, and Zn), and anions. The temperature was maintained constant at 25 °C. The solid residues from the experimental columns were also characterized for elemental constituents. Statistical differences between the unmodified and modified scenarios for each core and differences between cores were calculated in Origin 2016 (OriginLab Corp., Northhampton MA, USA) using a one-way repeated measures ANOVA ($\alpha = 0.05$). The Bonferroni correction was used to correct the p values in the three cores comparison.

Analytical Methods

Soil pH was determined for each stratum using EPA Method 9045D and moisture content was determined using ASTM D2216-10. Sulfur content (%S) in the solid samples was measured using a LECO CS230 carbon/sulfur analyzer. Aqueous phase pH and conductivity were analyzed using a Fisher Accumet XL 600 (Fisher Scientific, Pittsburgh, PA) by EPA Methods 150.1 and 120.1, respectively. Alkalinity and acidity were measured following EPA Methods 310.1 and 305.1, respectively. Sulfate concentrations were determined using a Dionex ICS-5000 (Thermo Scientific, Sunnyvale, CA) by EPA Method 300.0. Aqueous phase samples were filtered using a 0.45 µm hydrophilic polypropylene membrane and then dissolved elements were measured in a Thermo IRIS Intrepid inductively coupled plasma-atomic emission spectrometer (ICP-AES; Thermo Scientific, Sunnyvale, CA) by EPA Method 6010B. The elemental composition of materials in each column was determined by acid digestion via EPA Method 3051 followed by ICP-AES analysis. The use of EPA Method 3051 was deemed appropriate because the focus of this study was to determine the quality of the leachate generated by the readily reactable and soluble components present in overburden, such as those generated by sulfide oxidation and carbonate dissolution.

Alkalinity and pH data were used to calculate the concentrations of CO_3^{2-}, HCO_3^-, and OH^- in each column leachate using the equations presented in Steele (2004).

Results and Discussion

Overburden Geological Characterization

According to Adkison (1957), the bedrock in the White Oak quadrangle, which includes the Middle Fork Mine, is mainly comprised of sandstone, siltstone, and shale, with small amounts of underclay, coal, limestone, calcareous siltstone, and shale. Most of these rock types were found in the collected cores (Supplemental Fig. 2). 39 unique strata were identified in core 1, 37 in core 2, and 44 in core 3. Sandstone and silt/shale were the dominant identified rock types in the three cores. Strata colors were primarily gray with a few were brownish or sand colored, while textures ranged from fine to coarse, as defined in Ferm and Weisenfluh (1981). Overall, the three cores contained similar rock types, as expected, since core spacing between the three cores ranged between 160 and 206 m. Six randomly selected strata analyzed by XRD showed that the crystallographic matrix of the overburden were comprised mainly of silicates, aluminosilicates, and sulfides (data not shown).

USGS Leach Test

The screening-level USGS leach test was used to generate preliminary conductivity ranking for each of the strata in the three cores, but was not performed on the column mixtures. It was not expected that USGS leach test results would resemble field conductivities because it does not mimic the chemical conditions, contact time, and L/S ratio of actual mine sites.

For the modified scenario, the strata for each core were ranked from the highest to lowest conductivity, and the top ranked strata were removed until the cumulative mass of the removed strata exceeded 15% of the core weight. The profiles for conductivity and other parameters with depth are shown in Supplemental Fig. 3.

- Modified core 1, 9 out of 39 strata were removed (the 10th ranked strata had conductivity of 42.0 µS/cm) (Table 1). These HCSL strata were identified as shale, siltstone, mudstone, and clay with pH values of 5.23–6.57, and sandstone with pH of 9.54.
- Modified core 2, 10 out of 37 strata were removed (the 11th ranked strata had a conductivity of 20.3 µS/cm). The HCSL strata ranged from pH of 5.23–6.00 (claystone, siltstone, shale) to alkaline pH of 7.91–8.59 (sandstone). unmodified core 2 had the highest reported conductivity measurement of 737 µS/cm for a single stratum (found below a coal seam at a depth of 9.39, 1.49 m thickness), which was identified as a claystone with a soil pH of 3.15 and 2.0%S.
- Modified core 3, 7 out of 34 strata were removed (the 8th ranked strata had a conductivity of 32.7 µS/cm). unmodified core 3 strata had the lowest maximum conductivity (88.5 µS/cm) among the three cores collected. Five of the HCSL strata were acidic: one silt/shale section with a pH of 4.61 and four sections (shale, siltstone, and claystone) of pH 6.34–6.58. Two HCSL strata (sandstone) had a pH of 8.4.

The alkaline pH for sandstone indicated the likely presence of carbonate-based minerals, while the other lithologies in the strata such as claystone, siltstone, and shale were likely dominated by silicate-based minerals. The dominance of certain types of minerals in the HCSL or in the modified cores influence characteristics of the leachate from the USGS leach test, such as pH, alkalinity, and neutralization potential, which could ultimately influence overburden segregation strategies.

Sulfate concentrations in the leachate had the strongest correlation with conductivity (R = 0.989, 0.992, and 0.902) for unmodified cores 1, 2, and 3, respectively, followed by Mg (R = 0.988, 0.988, and 0.874, respectively) (Table 2). Conductivity also had a strong correlation with Ca^{2+} for unmodified core 1 (R = 0.977), but moderate correlations for unmodified cores 2 and 3 (R = 0.658 and 0.659, respectively). Interestingly, Fe had a strong correlation with conductivity for unmodified core 2 only (R = 0.980), and poor correlations for unmodified cores 1 and 3 (R = −0.086 and −0.043, respectively), possibly because the high conductivity outliers in unmodified cores 1 and 3 did not have high Fe content (data not shown). All other measured parameters had poor correlations with conductivity ($R < 0.5$).

Higher sulfur content in overburden (expressed as MPA) is related to higher TDS release Odenheimer et al. (2013). The %S measured in the core strata correlated well with TDS in column leachate for unmodified cores 1 and 2 (R = 0.982 and 0.996, respectively) (Fig. 1a) but not as well (R = 0.770) in unmodified core 3; however, the correlation was lower (R = 0.504) when all outliers (%S > 0.2) were removed (Supplemental Table 2).

Table 1 Screening-level USGS leach test results summary: conductivity and pH

Sample	Cond. range (µS/cm)	Average cond. (µS/cm)	Number of high screening level strata	Highest accepted cond. for the modified scenario (µS/cm)	Average cond. in the strata for the modified scenario (µS/cm)	pH range
Core 1	6.40–315	47.4	9	42.0	22.1	4.3–9.6
Core 2	4.83–737	45.6	10	20.3	13.9	3.2–8.6
Core 3	4.47–88.5	19.5	7	32.7	14.8	4.6–6.4

Table 2 Neutralization potential (NP), sulfur content (% sulfur), maximum potential acidity (MPA), and net neutralization potential (NNP) in the overburden materials used in the columns study

Scenario	NP (g/kg $CaCO_3$)	% sulfur	MPA (g/kg)	NNP (g/kg $CaCO_3$)	NP/MPA
Core 1 unmodified	13.5	0.203	6.34	7.16	2.13
Core 1 modified	11.7	0.101	3.14	8.56	3.72
Core 2 unmodified	14.4	0.212	6.63	7.80	2.18
Core 2 modified	6.80	0.112	3.49	3.31	1.95
Core 3 unmodified	11.0	0.102	3.19	7.82	3.45
Core 3 modified	6.48	0.098	3.07	3.41	2.11

The correlation between %S and conductivity was high in the HCSL strata (R = 0.990, 0.998, and 0.927 for cores 1, 2, and 3, respectively) (Fig. 1b), although correlations were lower when the strata contained <0.2%S (R = 0.657, 0.554, and 0.580, respectively) (Fig. 1c). Hence, the outliers had a great influence on the correlation. Linear regression equations were not calculated because the data did not follow a normal distribution. We hypothesize that the lower correlation between conductivity and %S for core 3 was due to the lower average %S in Core 3 (%S 0.105) compared to core 1 (%S 0.194) and core 2 (%S 0.171, Supplemental Table 2). In cases of low sulfur content, the final conductivity was influenced by other reactions (carbonate dissolution, iron oxidation rates, etc.). Overall, %S could be an important indicator of potentially high conductivity strata in this geology.

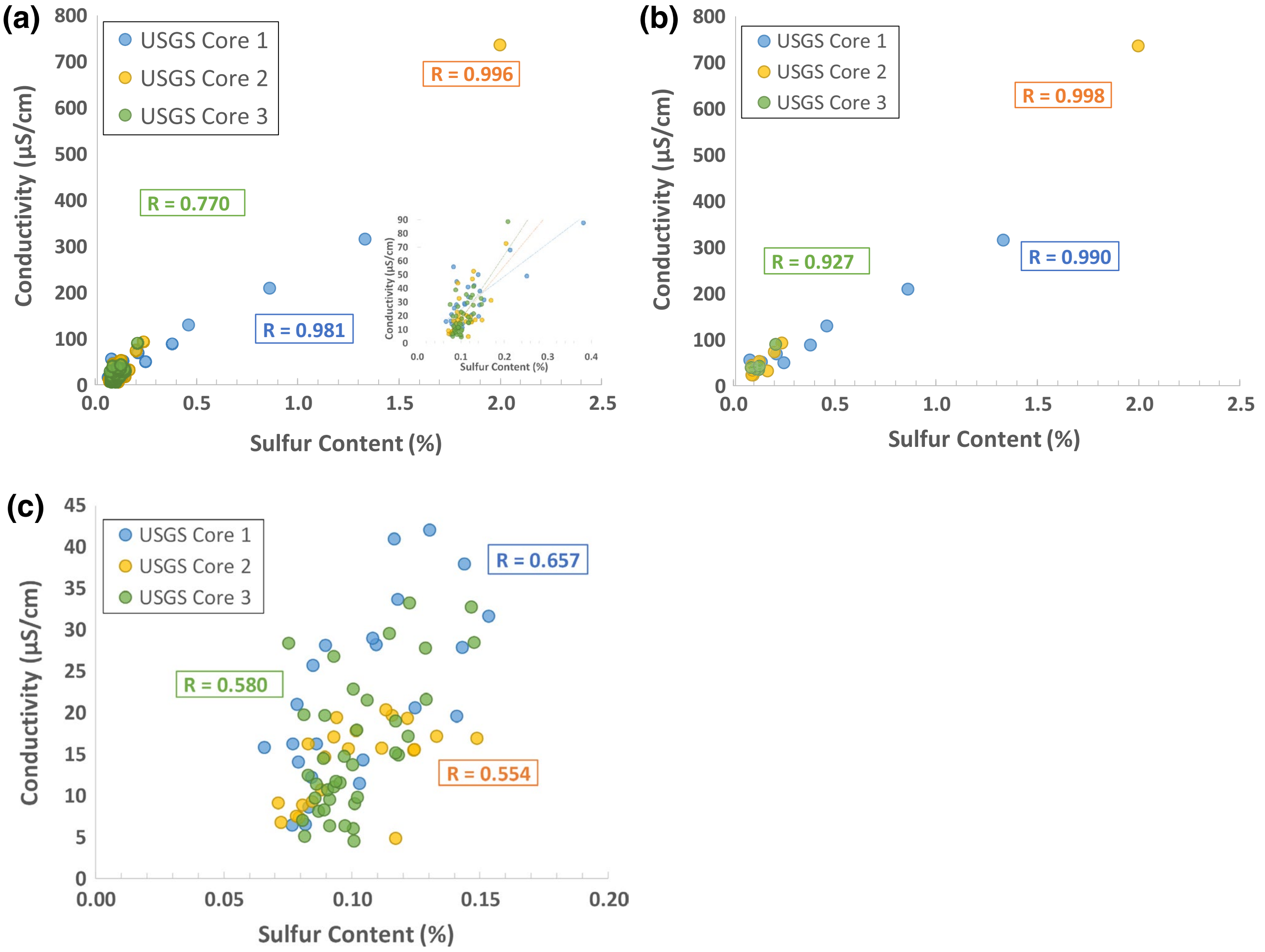

Fig. 1 Conductivity in the USGS leachate vs %S in the core strata with linear regression results for: **a** all strata included in the unmodified scenario; **b** 15% high conductivity strata, and **c** low conductivity strata included in the modified scenario

Kinetic Testing

Characterization of Mixtures Used in the Columns

The elemental composition obtained by acid digestion (EPA Method 3051) of the overburden mixtures loaded into the columns (Table 3) showed that Fe had the highest measured concentrations (14,300–21,000 mg/kg), followed by Al (3450–4670 mg/kg), Ca (1100–7830 mg/kg), Mg (2.270–2.920 mg/kg), K (526–738 mg/kg), and S (141–646 mg/kg).

Iron was one of the elements with the highest acid-extractable concentrations in all cores, with higher concentrations than aluminum, implying that much of the pyrite and iron oxides were extracted, compared to the aluminosilicates.

The sulfur content determined using EPA Method 3051 is the soluble portion of the total sulfur content shown on Table 4, which was determined using a carbon–sulfur analyzer. The sulfur content determined by EPA Method 3051 could also have been lowered due to potential formation and release of H_2S during the acid digestion process.

All elements reported higher concentration in the unmodified scenario than in the modified scenario. The ratio of Ca and S in the unmodified/modified scenario (higher in cores 1 and 2, lower in core 3) is especially high, suggesting that their contribution to conductivity was higher in the HCSL strata than in the other strata, although these ratios did not vary evenly across cores (Table 3).

The decrease in S, Ca, and NP in the modified core samples indicates: (1) a lower pyrite content, and consequently, a lower potential to release acid and sulfate, and (2) a reduction in the readily soluble minerals (e.g. carbonates), and consequently, less potential to release carbonate species and associated cations. These results could have been slightly different if a 3052 acid digestion was performed, because more aluminosilicates would have been released. However, since aluminosilicates are unlikely to be released by exposure of overburden to air and water, they are unlikely to affect leachate water quality parameters such as conductivity and NP.

Column Cycles

The initial column flush with 250 mL of DI water dissolved some salts and drew off a good portion of the columns' fine particles. The flush leachate started turbid and had high conductivities, before the leachate cleared and conductivity stabilized (<20% RSD between flushes) with subsequent flushes (turbidity not measured, Supplemental Table 3). After the initial flush, leachate conductivity reached steady state in the 5th cycle (Fig. 2a). In the first four cycles, the overburden minerals showed a rapid sulfate release, most likely because the reactions were dominated by sulfide oxidation. Later, in cycles 5–18, sulfates receded and the leachate was dominated by carbonate mineral dissolution, as is typical in alkaline drainage from coal mines.

Since the aim of this study was to determine the long term environmental consequences of TDS release, the EC trends and other parameters in the drainage from modified and unmodified scenarios were evaluated using data from cycles 5 to 18.

Table 3 Elemental composition of the overburden mixtures loaded into the experimental columns

Sample/scenario	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Zn
Core 1 unmodified	4670	4870	21,000	738	2920	470	49.3	295	616	164	61.5
Core 1 modified	4390	3950	20,200	705	2680	449	44.9	245	151	167	54.9
Core 2 unmodified	4180	7830	16,000	612	2710	303	43.7	193	595	133	51.6
Core 2 modified	3540	1210	14,300	526	2270	259	36.2	182	231	129	42.0
Core 3 unmodified	4420	3700	18,500	692	2780	416	41.7	235	184	154	52.6
Core 3 modified	4570	1100	16,900	649	2770	302	38.0	237	141	134	55.1
Average unmodified	4420	5470	18,500	681	2803	396	44.9	241	465	150	55.2
Average modified	4170	2090	17,100	627	2570	337	39.7	221	174	143	50.7

All elements concentrations are expressed in mg/kg

Table 4 Correlation coefficients (R) of the USGS leach test measured parameters with conductivity

Core	pH	Chloride	Sulfate	Al	Ca	Fe	K	Mg	Na	Si	% sulfur
Core 1	−0.357	−0.191	**0.989**	−0.236	0.977	−0.086	0.442	**0.988**	−0.083	0.144	**0.982**
Core 2	−0.374	−0.109	**0.992**	0.852	0.658	**0.980**	0.472	**0.988**	0.064	0.194	**0.996**
Core 3	0.041	0.112	**0.902**	−0.027	0.659	−0.043	0.167	**0.874**	0.213	0.146	**0.770**
All	−0.272	−0.059	**0.963**	0.240	0.688	0.841	0.195	**0.972**	0.032	0.027	**0.970**

Correlation coefficients R > 0.7 are bolded. Data did not follow normal distribution

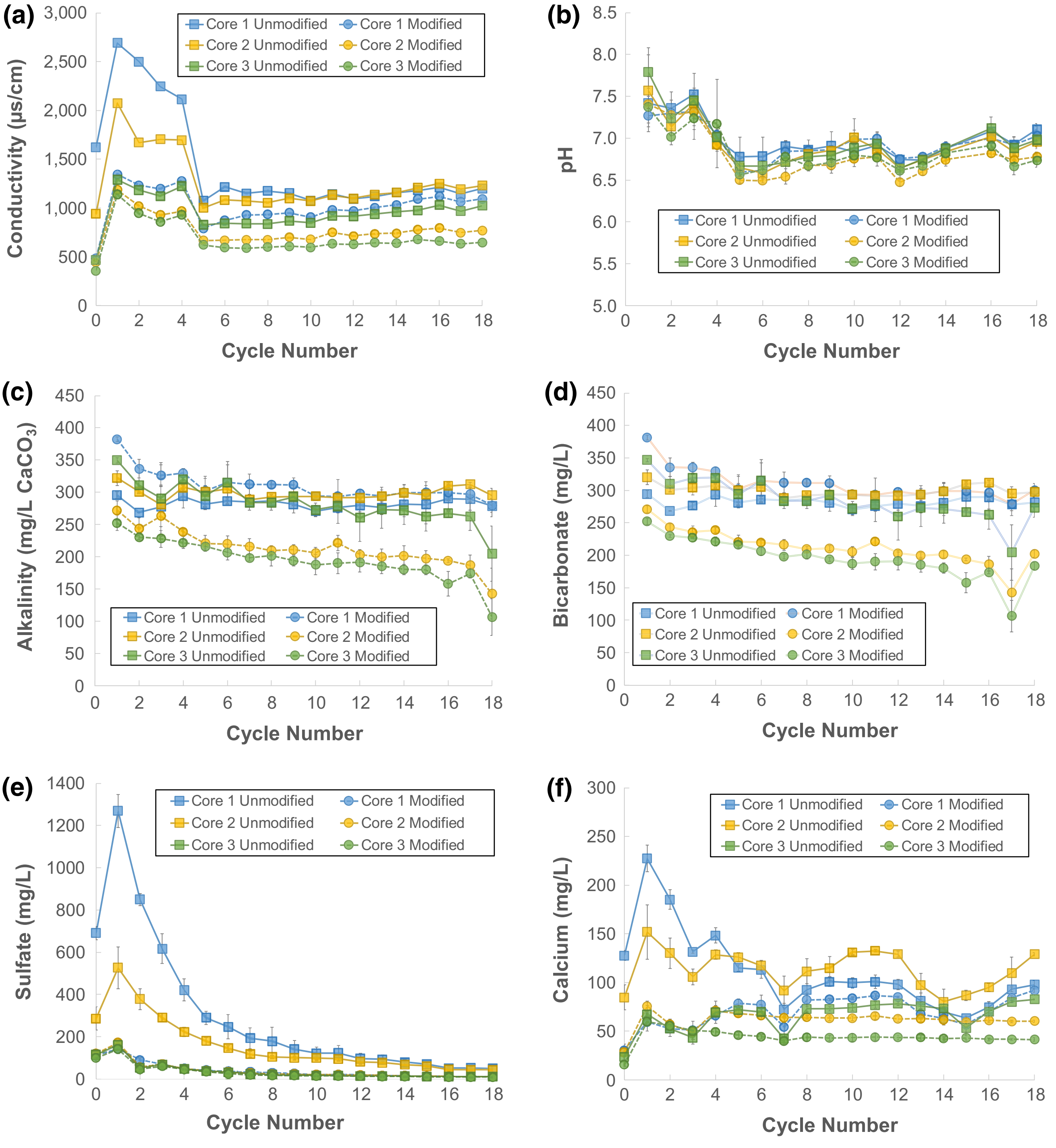

Fig. 2 **a** Conductivity, **b** pH, **c** alkalinity, **d** bicarbonate, **e** sulfate, **f** calcium vs cycle number in the EPA 1627 leaching test. The average conductivity of the columns flushes is reported for 'Cycle 0'

Acid–Base Accounting

ABA parameters have been used as an indirect measure of TDS and EC (Odenheimer 2013). Although NP was not designed to estimate leachate conductivity, EC and NP for the 18 column samples were moderately correlated (R = 0.80) (Supplemental Fig. 3a).

Since alkalinity had a similar correlation with NP (R = 0.795, Supplemental Fig. 3b), and silicates typically contribute little towards alkalinity in CMW, it was expected that most of the NP in the overburden samples was due to carbonates. Even though carbonate concentrations were ≈1%, they were not detected by XRD in the selected samples analyzed, and due to sample limitations, the amount of carbonates in the cores could not be determined using the LECO C/S analyzer. Although the leaching protocol used a moisture saturated gas mixture (90% air, 10% CO_2) that was continuously circulated through the column during each 6-day dry cycle, the high CO_2 content in the air mixture was not expected to increase the bicarbonate ion content or increase conductivity during each wet cycle.

Removal of the reactive fraction generally decreased S, Ca, and NP in the core samples. In all columns, the NP of the unmodified cores was similar (11–14 g/kg $CaCO_3$) and the NP of modified cores was less (Table 4). In cores 2 and 3, the NNP and NP/MPA were also lower in the modified cores; however, the NNP was higher in modified core 1 (8.6 g/kg $CaCO_3$) than in unmodified core 1 (7.2 g/kg $CaCO_3$) (Table 1). These results likely reflect ratios of pyrite and carbonates in the original unmodified and modified cores after 15% of the overburden had been removed.

Sulfur content (% sulfur, Table 1) was higher in unmodified cores 1 and 2 than in unmodified core 3, and MPA, calculated from %S, also followed that trend. The modified cores had lower %S.

Skousen et al. (2002) determined that values of $0 < NNP < 15$ gave mixed results for predicting the water quality of 56 mining sites in West Virginia and that the NP/MPA ratio was a better indicator: a $NP/MPA < 1$ would generate acidic water, values between 1 and 2 generated either acidic or alkaline water, while $NP/MPA > 2$ generated alkaline water.

In this study, all NNP data were in the range of 3.41–8.56 g/kg $CaCO_3$, and the NP/MPA ratio was 2.11–3.72, except for modified core 2 leachate, which was in the 'gray' zone ($NP/MPA = 1.95$). Bradham and Caruccio (1995) reported that at decreasing values of NP/MPA, the level of confidence to predict alkaline leachate decreased, with values of 50% confidence when NP/MPA was 2.3, which is about where the results of this study fell. Hence, while all other samples are more likely to produce an alkaline leachate, modified core 2 could generate acidic or alkaline leachate.

Conductivity Results

The average EC values for cycles 5–18 was 1150, 1090, and 1020 µS/cm for the unmodified scenario for cores 1, 2, and 3, respectively (Table 5). The corresponding average EC values for the modified scenarios for these cores were 979, 719, and 624 µS/cm. The EC values of all the cores were significantly higher in the unmodified scenario than in the modified scenario ($p < 0.05$), according to the one-way ANOVA.

Table 5 Average conductivity and percentage difference in the experimental columns by core

Sample/scenario	Conductivity (µS/cm)	Difference (µS/cm)	Difference (%)
Core 1 unmodified	1150 ± 45.7	168	14.6
Core 1 modified	979 ± 93.3		
Core 2 unmodified	1130 ± 72.8	407	36.2
Core 2 modified	719 ± 44.4		
Core 3 unmodified	911 ± 70.9	287	31.5
Core 3 modified	624 ± 26.4		
Average unmodified	1060 ± 131	287	27.4
Average modified	774 ± 184		

Conductivity can be driven by sulfate or bicarbonate. Calculated HCO_3^- had the highest concentrations in cycles 5–18 (Fig. 2d), while SO_4^{2-} had the highest concentrations in the initial four cycles (Fig. 2e). Leaching results and ABA results suggest that the removal of HCSL resulted in the removal of soluble calcium and carbonate-based minerals rather than other minerals. Despite this, alkalinity in the unmodified scenario was higher than in the modified scenario for cores 2 and 3, but not for core 1.

Carbonate and Bicarbonate

Carbonate mineral content was likely more uniform across all strata in core 1 than in cores 2 and 3, although the HCSL strata of cores 2 and 3 had a significantly higher proportion of carbonates than core 1. The difference in leachate conductivity between unmodified vs modified scenarios for cycles 5–18 was less for core 1 (14.6%) than for cores 2 and 3 (36.2 and 31.5%, respectively). These trends in leachate conductivity seemed to mimic the NP trends for the three cores, most likely due to the presence of carbonates in the overburden.

Bicarbonate leachate concentrations decreased over the first four cycles and then stabilized, except for cores 2 and 3 of the modified scenario, which continued to decrease throughout the study. This may reflect the more uniform distribution of carbonate across core 1.

Overall, HCO_3^- was the primary constituent of TDS (65.0–86.7% of all anions) in cycles 5–18, with higher concentrations in the unmodified than in the modified scenario in cores 2 and 3, while the opposite was observed in core 1 (Supplemental Table 4). Bicarbonate was not reduced, it was even slightly higher in the core 1 scenarios (see Fig. 2d; Supplemental Table 4). In contrast, bicarbonate decreased significantly in the other two cores, despite CO_2 circulating through the columns during the dry cycle. Core 2 bicarbonates decreased 32.0% from unmodified to modified and core 3 decreased 32.8% (Fig. 2d; Supplemental Table 4), mimicking the trends observed for NP.

% Sulfur and Sulfate

Sulfur content affected leachate conductivity. Core 3 had less sulfur content than cores 2 and 3 (Table 2). In a one-way ANOVA with 95% confidence Bonferroni test, the difference between the mean effluent EC of cores 1 and 2 was non-significant ($p = 0.058$), while the differences between mean effluent EC in cores 1–3 and between 2 and 3 were significant ($p < 0.01$), implying that core 3 had a different composition.

Sulfate was the dominant anion in leachate from unmodified cores 1 and 2 in the first four cycles (Fig. 2e), reflecting the higher %S content in these columns, while in all other columns and in cycles 5–18, bicarbonate was the dominant ion. Sulfate started with a lower concentration in the initial flush, then its highest concentration was reached in the first cycle, followed by a steady decline during the operational cycles.

Sulfate leaches primarily as a consequence of pyrite oxidation and dissolution, but could also have been released by any gypsum present. Pyrite oxidation releases acid that can attack other minerals, releasing cations such as calcium and magnesium (Orndorff et al. 2015). Unmodified scenarios had consistently higher SO_4^{2-} concentrations than modified scenarios. The sulfate drop from unmodified to the modified scenarios was 83, 77, and 18% for cores 1, 2, and 3 cycles 5–18, respectively, suggesting that the most reactive overburden contained more sulfur than the strata with less EC generation potential. Sulfur content in the overburden materials (≈0.20%) was high enough to generate high SO_4^{2-} concentrations of 1270 and 500 mg/L in the leachate in the first cycle in cores 1 and 2, respectively, but later stabilized to values of 120 and 90 mg/L (Supplemental Table 4). A mean %S of 0.1 generated less sulfate, with concentrations ranging from 140 to 170 mg/L SO_4^{2-} in the first cycle and then 15–22 mg/L in later cycles.

Surface waters in unmined areas of the Appalachian region have reported SO_4^{2-} concentrations of 4–58 mg/L, while mined affected areas reported a range of 231–1187 mg/L (Bernhardt et al. 2012; Orndorff et al. 2015). In our study, sulfate concentrations started in these ranges but fell to concentrations similar to the unmined areas at the end of the experiments; sulfate concentrations were always less in the modified scenario.

Alkalinity and pH

The pH remained in the neutral and slightly acid zone (range 6.47–7.12; Fig. 2b) in weeks 5–18. After the fifth cycle, the pH averaged 6.81–6.88 in the unmodified and 6.66–6.86 in the modified scenarios. Hence, removal of the HCSL strata did not significantly affect pH.

The reported pH of minimally disturbed streams in the Appalachian region is 6.9–7.2, while in mined areas, the pH usually increases to 7.5–7.9 (Bernhardt et al. 2012; Orndorff et al. 2015). Thus, the pH in both scenarios was within the range of undisturbed areas after the fifth cycle. However, during the first four cycles, the pH was higher, more similar to the 7.5–7.9 pH range reported for streams affected by valley fills.

Alkalinity also decreased during the first four cycles, but showed differing trends for cycles 5–18 (Fig. 2c): the unmodified scenarios reached a plateau, while the modified scenarios continued to decrease in alkalinity, except for core 1, which plateaued in both scenarios. This suggests that for cores 2 and 3, more carbonate was removed in the HCSL strata than remained in the modified cores. By comparison, the carbonate content in core 1 may have been more evenly distributed across all strata.

The ABA NP/MPA values, which predict alkalinity trends, were higher for the unmodified cores 2 and 3 than in the corresponding modified scenarios, while the opposite was true in core 1; the alkalinity results had the same general trends. The NP/MPA of the core 2 modified had the lowest NP/MPA value, which suggests a lower alkalinity; but in the columns, it was the core 3 modified sample that had the lowest average alkalinity (194 mg/L as $CaCO_3$), followed by core 2 modified (214 mg/L as $CaCO_3$).

Anions and Cations

Sulfate and bicarbonate were the anions with the higher concentrations, while all other anions were in minor concentrations (Supplemental Table 4). Sulfate had higher correlation coefficients (R) with Mg (0.95), Na (0.93), and K (0.88, data not shown) than bicarbonate [Mg (0.58), Na (0.54), and K (0.50)].

Ca^{2+} concentrations were the highest among cations in all cores and all scenarios except for modified scenario core 3, followed by Mg (Supplemental Table 5). After an initial increase during the first cycle, Ca^{2+} concentrations either plateaued (modified scenario for cores 2 and 3) or oscillated (all other scenarios) (Fig. 2f). In general, soluble minerals should behave similarly to sulfate; i.e. a high concentration after the flush that continuously decreases with more cycles. This does occur with Mg (Supplemental Fig. 5c). In the case of Ca^{2+}, the oscillatory patterns in the graph could be due to exposure of pockets of highly soluble

Ca-containing material (probably calcium carbonate) to the water flow.

Certain similar patterns in the release of sulfate, Ca^{2+}, and Mg^{2+}, suggest that there was some gypsum and epsomite present in the leached materials. The decreasing trend was also observed for Na^+ and K^+ (Supplemental Fig. 5d, e, respectively), but at lower concentrations. The sum of these four cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) comprised 93% of the total cations by mass in the leachate.

Conclusions

Orndorff et al. (2015) concluded that: (1) column studies would produce leachates with similar characteristics to actual water discharges in mined areas; (2) mine spoils noticeably change from site to site within the Appalachian region; (3) the practice of segregating small volumes of net-acid producing spoils into valley fills with larger volumes of alkaline spoils to obtain a positive ABA balance may accelerate EC generation, and that a better alternative would be the segregation of all potential acid-forming materials. Our study seems to corroborate the importance of mineralogy and the importance of segregating materials based on potential EC generation, and not solely on acid production. At the same time, our data suggested that the removal of HCSL results in the removal of soluble calcium and carbonate-based minerals; therefore, reducing conductivity could, in some cases, reduce the potential to neutralize acid.

One key finding was the effect of carbonate distribution. Core 1, which had a more homogenous carbonate mineral distribution than cores 2 and 3, had less of a decline in conductivity after reactive strata were removed, did not have as much of a difference in NP/MPA between the unmodified and modified scenarios, and alkalinity and bicarbonate plateaued in core 1 column experiments, while cores 2 and 3 continued to show declines.

The ABA method estimated a NP/MPA ratio >2 in the three collected cores, implying the generation of alkaline leachate, but did not provide information about potential conductivity release. Average conductivities of the unmodified scenario were within the lower half of the 159–2450 µS/cm range reported for mined sites in the Appalachian region (Griffith et al. 2012; Kennedy et al. 2005).

Despite an average decrease in conductivity of 27.4% from the unmodified (average 1062 µS/cm) to the modified scenario (average 774 µS/cm), the removal of the 15% HCSL strata did not achieve the recommended benchmark of 300 µS/cm. A greater percentage threshold of HCSL strata could decrease leachate conductivities further, but there is no guarantee that it would achieve that mark.

The USGS field test alone will not necessarily identify all strata in need of isolation and its use should be complemented with mineralogical characterization of the strata. Sulfate concentrations in the leachate and sulfur content (in overburden with sulfur content >0.2%) in the overburden were the parameters most highly correlated with conductivity and could be used to predict CMW conductivity, although low or moderate sulfur (%S < 0.2) content in the overburden reduced this predictability (similar trend to MPA).

Each mine would need to assess their overburden strata and implement spoil management to reduce mine water conductivity. The practice of placing high EC materials in tightly compacted layered cells could provide low hydraulic conductivity for the high EC potential overburden; while, low EC strata could be used as fill material.

Acknowledgements The research was funded and conducted through the US EPA's Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, Ohio. This paper has been subjected to the Agency's internal review and quality assurance approval. The views and conclusions presented herein are those of the authors and do not necessarily reflect the views of the Agency or its policy. Any mention of products or trade names does not constitute endorsement or recommendation for use by the US EPA. The authors want to thank Mr. Greg Higgins (Middle Fork Development Mining Co.) for his support in core acquisition. The authors also thank Mr. Eric Baumann, Ms. Andrea Burkes, and Ms. Elizabeth Kidd for laboratory work, Dr. Michael Desantis for the geological characterization of the core samples, and Dr. Raghuraman Venkatapathy for his help with the manuscript.

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