# LEACHING POTENTIALS OF COAL SPOIL AND REFUSE: ACID-BASE INTERACTIONS AND ELECTRICAL CONDUCTIVITY[1]

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**Abstract:** Unweathered overburden and coal processing wastes in southwestern Virginia contain varying amounts of carbonates and pyrite which affect water quality as spoil and refuse materials weather and leach. In addition to pH effects, these materials can input significant total dissolved solids (TDS) loads to drainage waters under both low and circumneutral pH conditions. The objective of this study was to evaluate acid-base interactions and overall TDS elution (as measured by electrical conductivity/EC) in leachates from a variety of spoil and refuse materials. Ten spoils and three pairs of coarse/fine refuse samples were characterized and subjected to leaching in columns for five months (2 leaching events per week) under saturated and unsaturated conditions. Leachates were analyzed for pH, EC, and cations and oxyanions of concern. The pH of the bulk samples (prior to leaching) were typically near-neutral to alkaline. Bulk EC produced by fresh spoils was relatively low (< 1.0 dS $m^{-1}$), although a few values ranged up to 3.5 dS $m^{-1}$. Relatively low total S (< 0.25%) in conjunction with calcium carbonate equivalence (CCE) levels of 1.3 – 6% resulted in low (3.6 Mg $CaCO_3$ per 1000 Mg material or less net acid) peroxide potential acidity (PPA) levels. For refuse samples, total S was slightly higher (0.27 – 1.25%), CCE ranged from 5.0 to 6.9%, and PPA ranged up to 31.2 Mg $CaCO_3$ per 1000 Mg material of net acidity. Leachate pH increased noticeably for most materials over the first few leachings, but after approximately one month, the majority of samples showed no major changes. Electrical conductivity decreased over the first several leachings and most samples achieved a relatively steady state with relatively low levels (< 1.0 dS $m^{-1}$) within two months. Leachate pH, EC, bicarbonate, Ca, Fe, Mn and sulfate elution were directly related to internal acid-base reactions and water saturation regime. Surprisingly, no major significant or consistent differences were apparent between coarse and fine refuse materials for any parameter of long term leaching concern.

**Additional Key Words:** acid-base reactions, leachate, overburden, total dissolved solids.

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[1] Paper was presented at the 2010 National Meeting of the American Society of Mining and Reclamation, Pittsburgh, PA ***Bridging Reclamation, Science and the Community*** June 5 - 11, 2010. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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# Introduction

The Surface Mine Control and Reclamation Act (SMCRA) of 1977 contained a number of contentious provisions including the allowance for use of pre-selected overburden materials as topsoil substitutes when (A) the native A+E horizon materials are less than 15 cm (6”) thick, and (B) the physical and chemical properties of the proposed substitute spoil materials are deemed suitable for such use. Since native topsoil layers throughout the Appalachian coalfields are usually less than 15 cm thick, and removing them from steep slopes is difficult and expensive, the vast majority of coal mined lands in the region have employed topsoil substitutes.

Over the past decade, the concept of topsoil substitution has been criticized from a number of perspectives including potential effects on water quality. Regulation and monitoring of coal mine discharges to surface and ground-waters in the central Appalachian coalfields (WV-VA-TN) have traditionally focused on pH, Fe, and Mn. However, the leaching of both mine spoils and refuse materials is also a primary source of total dissolved solids (TDS) discharges which may affect surface water quality in mined areas. Common ions comprising TDS include, but are not limited to, $HCO_3^-$, $SO_4^{2-}$, $Cl^-$, $Ca^{2+}$, $K^+$, $Mg^{2+}$, and $Na^+$. Since ion concentrations control electrical conductivity (EC) in water, EC can be used to estimate TDS. Several recent studies (Chapman, 2000; Goodfellow, 2000) have addressed the issue of TDS as a major stressor upon receiving streams in mine waters. The release of TDS has been implicated as a component of mining related surface water degradation under both low and moderate pH conditions. In fact, it now appears that mining discharges will be directly regulated for TDS over time and reducing bulk TDS may be a much more difficult water treatment proposition for the coal industry than limiting more conventional parameters such as pH and total Fe and Mn.

The primary focus of the work presented in this paper was to characterize the potential leaching behavior of selected mine spoil, coarse coal refuse, and fine coal refuse slurries in terms of pH, EC, and cations and anions related to acid-base reactions (Ca, Fe, $HCO_3^-$, and $SO_4^{2-}$). Characterization of the mine spoils and coal refuse materials for total elemental composition and relative solubility of As, Cr, Mo, Se and other elements of interest, and for the net leaching potential of these elements, is presented in Daniels et al. (2009).

# Materials and Methods

## Mineralogy and Geologic Associations

Fifteen mine spoils and ten coal refuse samples (including both coarse and fine refuse materials) associated with major surface mining activity and valley fills in southwest Virginia and eastern Kentucky were collected from six mine sites. A subset of ten spoil samples, 3 coarse refuse samples, and 3 fine refuse samples were selected for use in a column leaching study. These samples were selected based on 1) results from static testing, 2) representation of diverse spoil types including sandstones, siltstones and mudstones, as well as different degrees of weathering, and 3) pairing of coarse and fine refuse material. Geologic descriptions and associated information for these 16 samples are presented in Table 1. Note: All samples are labeled as "OSM #" due to the sponsorship of the study and the need to keep exact sample locations relatively anonymous.

## Spoil and Refuse Characterization Methods

All analyses were conducted in triplicate unless specifically noted otherwise. Electrical conductance (EC) (Rhoades, 1982) and pH were determined on saturated paste extracts from the materials. Each spoil or refuse sample was mixed with deionized (DI) water until it formed a glistening paste, equilibrated for $\geq$ 2 hours, then filtered and analyzed. As opposed to using a defined quantity of water, this method allows comparison of materials under similar levels of saturation (i.e. coarser materials will require less water than fine materials to achieve saturation). For comparison, pH was also determined on a 2:1 water:sample solution. Peroxide potential acidity (PPA) was determined by a modified $H_2O_2$ oxidation technique as described by Orndorff et al. (2008). The method oxidizes all sulfides with 30% $H_20_2$ and assumes net internal reaction of acids formed with carbonates and other neutralizers. Total net acidity is determined by whole sample titration following full reaction. Total S was run via combustion on an Elementar CNS analyzer. The calcium carbonate equivalence (CCE) was determined via AOAC method 955.01 (AOAC International, 2002).

Table 1. Geologic description and associated information for 10 mine spoil and 6 coal refuse samples used in column leaching study.

| **Lab-ID** | **Material** | **Geologic Description** | **Geologic formation** | **Coal Seam** | **Particle size %** | |
|---|---|---|---|---|---|---|
| | | | | | **< 1 cm** | **> 1 cm** |
| OSM 1 | Mine spoil Unweathered | 98% unweathered, gray and orange, medium to coarse grained, feldspathic sandstone; 2% unweathered gray silty mudstone. (No coal apparent.) | Norton | Raven1 | 23 | 77 |
| OSM 2 | Mine spoil Unweathered | 93% dark gray carbonaceous silty mudstone; 6% unweathered, gray, fine-grained sandstone/siltstone; 1% coal. | Four Corners Formation; Breathitt Group | Hazard #7 and Hazard #8 | 60 | 40 |
| OSM 3 | Mine spoil Partially-weathered | 50% highly weathered, gray and orange, fine grained and medium to coarse grained, feldspathic sandstone; 30% unweathered gray silty mudstone ; 10% unweathered feldspathic sandstone; 8% unweathered gray silty mudstone; 2% coal. | Middle Wise | Kelly/Imboden | 87 | 13 |
| OSM 4 | Mine spoil Weathered | 98% weathered, reddish-brown silty mudstone; 1% weathered sandstone; 1% coal. | Lower Wise | Clintwood/Blair | 85 | 15 |
| OSM 6 | Mine spoil Unweathered | 90% minimally weathered gray clayey siltstone; 10% brown silty mudstone; trace coal. | Lower Wise | Clintwood/Blair | 79 | 21 |
| OSM 7 | Mine spoil Weathered | 85% weathered brown-gray silty mudstone; 13% unweathered gray silty mudstone; 2% weathered sandstone. (No coal apparent.) | Middle Wise | Kelly/Imboden | 62 | 38 |
| OSM 10 | Mine spoil Unweathered | 97% unweathered gray silty mudstone; 2% coal; <1% unweathered sandstone; <1% brown shale. | Upper-middle Wise | Phillips | 72 | 28 |
| OSM 11 | Mine spoil Weathered | 99% weathered sandstone; 1% silty mudstone; trace coal. | Upper-middle Wise | Taggart | 68 | 32 |
| OSM 12 | Mine spoil Unweathered | 98% unweathered, gray, medium grained sandstone; 1% weathered sandstone; 1% silty mudstone. | Upper-middle Wise | Taggart | 45 | 55 |
| OSM 14 | Mine spoil Weathered | 80% weathered, gray and orange, feldspathic sandstone; 20% gray silty mudstone. (No coal apparent.) | Lower Wise | Clintwood/Blair | 65 | 35 |

(Table 1 continued)

| Lab-ID | Material | Geologic Description | Geologic formation | Coal Seam | Particle size % | |
|---|---|---|---|---|---|---|
| | | | | | < 1 cm | > 1 cm |
| OSM 16* | Coarse refuse | Carbonaceous shales, mudstones and coal. | Norton | Lower Banner, Jawbone, and Splashdam | 45 | 55 |
| OSM 22* | Fine refuse | Carbonaceous shales, mudstones and coal | | | 100 | 0 |
| OSM 18* | Coarse refuse | Shales, mudstones and coal mixture | Upper-middle Wise | Taggart, Taggart Marker, Phillips and Standiford | 46 | 54 |
| OSM 19* | Fine refuse | Shales, mudstones and coal mixture | | | 100 | 0 |
| OSM 21* | Coarse refuse | Shales, mudstones and coal mixture | Norton | Norton, Lower Banner | 57 | 43 |
| OSM 25* | Fine refuse | Shales, mudstones and coal mixture | | | 100 | 0 |

*Samples OSM16-25 are out of order to more readily indicate the "pairing" of fine and coarse refuse samples according to common sources (preparation plant).

## Experimental Procedures for Column Leaching Trial

All samples were air-dried prior to processing. To eliminate preferential flow within the column, coarse and large fragments of mine spoil and coal refuse were crushed to pass a 1 cm sieve and then carefully back-blended. Particulates in the slurry of fine coal refuse were allowed to settle for one month after which time the clear waste water was decanted. The "paste-like" fine refuse was spread out to air dry and subsequently sieved to pass a 2 mm sieve.

The leaching columns were built from 7.6 cm PVC pipe with an inside diameter of 7.4 cm, length of 40 cm, and a concave PVC endcap. The column was drained through a 1 cm PVC pipe nipple fitted and glued with two-component adhesive into the center of the endcap. An attached Tygon tube drained the leachate and provided the flexibility to create anaerobic conditions in the saturated columns by preventing drainage and gas exchange via a saturated loop at the bottom of the column. To prevent leaching losses of particulate matter and blockage of the drainage hole by particulates, a 0.1 mm nylon mesh circle was glued into the endcap and covered with a 7.6 cm diameter Whatman #1 filter paper. The filter paper was covered with a 2.5 cm layer of acid washed coarse sand to promote uniform drainage. The sand layer also served as a leachate reservoir to ensure that the bottom section of the sample material remained unsaturated in those treatment columns. The column was then filled with a sample volume of 1200 $cm^3$, and capped with a 2.5 cm sand layer to facilitate uniform distribution of the applied leaching solution. Each sample was run in triplicate under saturated and unsaturated conditions (6 columns per sample).

Simulated rainfall (pH 4.8; prepared according to Halvorson and Gentry, 1990) was applied twice per week to provide approximately 2.5 cm of rainfall per event (100 ml per leaching event). The water was dispensed into a perforated cup placed on top of the sand to uniformly apply the solution to the sample material. During the first week of the experiment the dosing cycle was accelerated to satisfy the hydration demand to a point where leachates were generated in essentially a "piston flow" response over 48 to 72 hours in response to the surface dosing regime. Our intent was to keep the bulk of the unsaturated columns at approximately field capacity so that after a precipitation event an equal volume (~100 ml) of leachate would drain freely into the collection bottles. However, we do acknowledge that a thin portion of the sand pack and possibly the lowermost portion of the treatment zone were probably saturated for some period of each cycle due to "perching" at the atmospheric interface. The saturated columns were kept saturated to the surface. After the addition of simulated precipitation the Tygon tubing at the bottom of the column was opened long enough to collect 100 ml of leachate. As needed, small amounts of simulated rainfall water were added to the columns to compensate for evaporative losses and to assure that the top of the columns remained saturated.

The leachate samples were analyzed and/or preserved after an 18 hour leaching/collection period. This precipitation/sampling procedure was repeated every three/four days; simulated acid precipitation was applied Mondays and Thursdays, samples were collected and analyzed on Tuesdays and Fridays. The samples were analyzed for pH and EC, and subsamples were analyzed by ICPES for several elements including Ca, Fe, and S. Dissolved inorganic carbon (IC) and total carbon (TC) were run on the Sievers 900 Laboratory TOC.

## Results and Discussion

### Characterization of Chemical Properties

Selected chemical properties of the sample set are presented in Table 2. The pH of the samples was generally in the neutral to alkaline range which is typical of fresh, relatively unweathered materials from this region due to hydrolysis reactions involving broken primary mineral grains and carbonate dissolution. Only a few of the mine spoils were slightly acidic with no sample pH below 6.2. The soluble salt content, as indicated by EC, produced by fresh spoils was relatively low ($< 1.0$ dS $m^{-1}$), although a few values ranged up to 3.5 dS $m^{-1}$. Further discussion of the relationship between soluble salt content and EC is provided with the leaching column results. Samples with elevated EC values appeared well-related to either their potential acidity (as estimated by PPA) and/or CCE. It is interesting that some samples (e.g. OSM 21) that were high in potential acidity (by PPA) would have been predicted to be non-acid forming using a conventional acid-base accounting approach where all the total S (e.g. 1.27 % or 40 T/1000 T maximum acidity for OSM 21) would be assumed to be sulfidic and balanced against the CCE (5.6% or 56 T/1000 T net neutralizers). Only three out of the 16 samples had a total sulfur content of > 0.70%, which is not unusual for the region sampled. Somewhat surprisingly, paired coarse and fine refuse samples showed no consistent differences in %S, CCE or PPA. We had assumed that finely divided reactive pyrites would have been selectively concentrated into the fine refuse, but this appears not to be the case for these facilities and their associated coal cleaning technologies.

A comparison of the pH values determined by saturated paste ($pH_{sp}$) versus in a 2:1 water:sample mix ($pH_{2:1}$; Table 2) indicated lower pH values by the 2:1 method for the samples at $pH_{2:1} < 7.0$. This may be due to the difference in equilibration time (much longer for the saturated paste method) allowing some of the alkaline mineral surfaces to react with acidic components. Direct comparison of properties from weathered mine spoils versus unweathered mine spoils showed that weathered mine spoils tended towards lower pH (Table 2) as expected. Only one weathered sample (OSM 7) had a neutral $pH_{2:1}$, 7.03, the other weathered samples all had $pH_{2:1}$ values between 5.22 and 5.74. The pH among the partially weathered/unweathered mine spoils followed the trend that those with higher percentages of weathered material generated lower pH.

Table 2. Selected chemical properties of the 16 column leaching study samples.

|  |  | 2:1 | Saturated paste |  | PPA[1] | CCE[2] | Total S |
|---|---|---|---|---|---|---|---|
| **Lab-ID** | **Material** | **pH** | **pH** | **EC dS m$^{-1}$** | **- Tons CCE / 1000 Tons** | **%** | % |
| OSM 1 | MS[3] unweathered | 7.98 | 6.88 | 1.27 | 0 | 2.7 | 0.06 |
| OSM 2 | MS unweathered | 7.14 | 7.04 | 3.48 | 0 | 4.6 | 0.23 |
| OSM 3 | MS partly weath. | 5.24 | 6.93 | 0.94 | 3.58 | 1.3 | 0.07 |
| OSM 4 | MS weathered | 5.22 | 6.46 | 0.29 | 0.22 | 1.6 | 0.03 |
| OSM 6 | MS unweathered | 7.02 | 7.26 | 1.40 | 0 | 2.1 | 0.14 |
| OSM 7 | MS weathered | 7.03 | 7.66 | 0.20 | 0.12 | 4.7 | 0.03 |
| OSM 10 | MS unweathered | 8.14 | 7.85 | 0.66 | 0 | 6.0 | 0.11 |
| OSM 11 | MS weathered | 5.24 | 6.28 | 0.56 | 0.28 | 3.7 | 0.03 |
| OSM 12 | MS unweathered | 8.64 | 7.84 | 0.40 | 0 | 5.3 | 0.12 |
| OSM 14 | MS weathered | 5.74 | 7.49 | 0.36 | 0.12 | 3.4 | 0.03 |
| OSM 16[4] | Coarse refuse | 9.40 | 9.13 | 0.99 | 0.06 | 6.2 | 0.26 |
| OSM 22[4] | Fine refuse | 8.98 | 8.43 | 0.83 | 0 | 6.0 | 0.74 |
| OSM 18[4] | Coarse refuse | 9.35 | 9.03 | 0.96 | 2.20 | 5.0 | 0.41 |
| OSM 19[4] | Fine refuse | 6.60 | 7.58 | 2.79 | 10.45 | 6.0 | 0.62 |
| OSM 21[4] | Coarse refuse | 9.12 | 8.75 | 0.90 | 31.16 | 5.6 | 1.27 |
| OSM 25[4] | Fine refuse | 9.02 | 8.10 | 1.16 | 0.61 | 6.6 | 0.76 |

[1] Potential Peroxide Acidity (PPA). Values shown represent net acidity/lime demand.
[2] Calcium Carbonate Equivalent (CCE)
[3] MS = Mine spoil
[4] Coarse/fine refuse from same source material at prep-plant: OSM16/22, OSM18/19, OSM21/25

### Leaching Column Trial

The data presented in Fig. 1-15 report results from 45 leaching events over a 22 week period. The data are presented in groupings of the source materials - mine spoil, coarse refuse, and fine refuse - and to contrast the results from weathered versus unweathered materials and saturated versus unsaturated conditions. We highlight pH, EC, sulfate, bicarbonate and other elements particularly relevant to acid-base reactions. All data presented below represent the mean observations from three replicate columns. Detail on column replicability (which was outstanding) can be found in Daniels et al. (2009).

pH. Unweathered overburden in southwestern Virginia can contain significant amounts (0.5 to > 3.0%) of carbonates (Howard, 1979) and to a more limited extent, reactive pyrite (Sobek et al., 2000). Depending on the distribution and quantity of these minerals, the pH of unoxidized overburden is between 6.5 and 8.0 (Roberts et al., 1988) while that of weathered/partially weathered overburden is generally between 4.5 and 6.0. The pH of coal refuse materials as they leach and weather also depends primarily upon pyrite content vs. neutralizers and their relative rates of reaction. When exposed to an oxidizing environment, the pH of highly sulfidic, reactive leached refuse can quickly drop to < 2.5 (Daniels et al., 2006).

For most materials used in this study, leachate pH (Fig. 1-3) from the first leaching events was substantially lower than the initial saturated paste pH data on the fresh bulk materials ($pH_b$). This difference was more readily observed in weathered than in unweathered materials, and was least apparent for the unweathered sandstone and the fine refuse. With few exceptions, leachate pH increased over the first few leaching events, and achieved a relatively stable equilibrium within 10 to 20 leaching events. Only one sample (OSM 21) experienced a major change in pH, dropping from 8.0 to 5.1, over the 22 week leaching period. The unsaturated columns were usually higher in pH than for the same material under saturated conditions. For the unsaturated columns, most materials achieved pH values comparable to or surpassing $pH_b$ within a few leaching events. The main exception to this was the coarse refuse for which all three samples equilibrated well below $pH_b$. Under saturated conditions, only 4 samples (OSM 1, OSM 2, OSM 11, and OSM 25) equilibrated to pH values near $pH_b$, while the remaining 12 samples (saturated) maintained pH values that were approximately 0.3 to 1.0 pH unit less than $pH_b$.

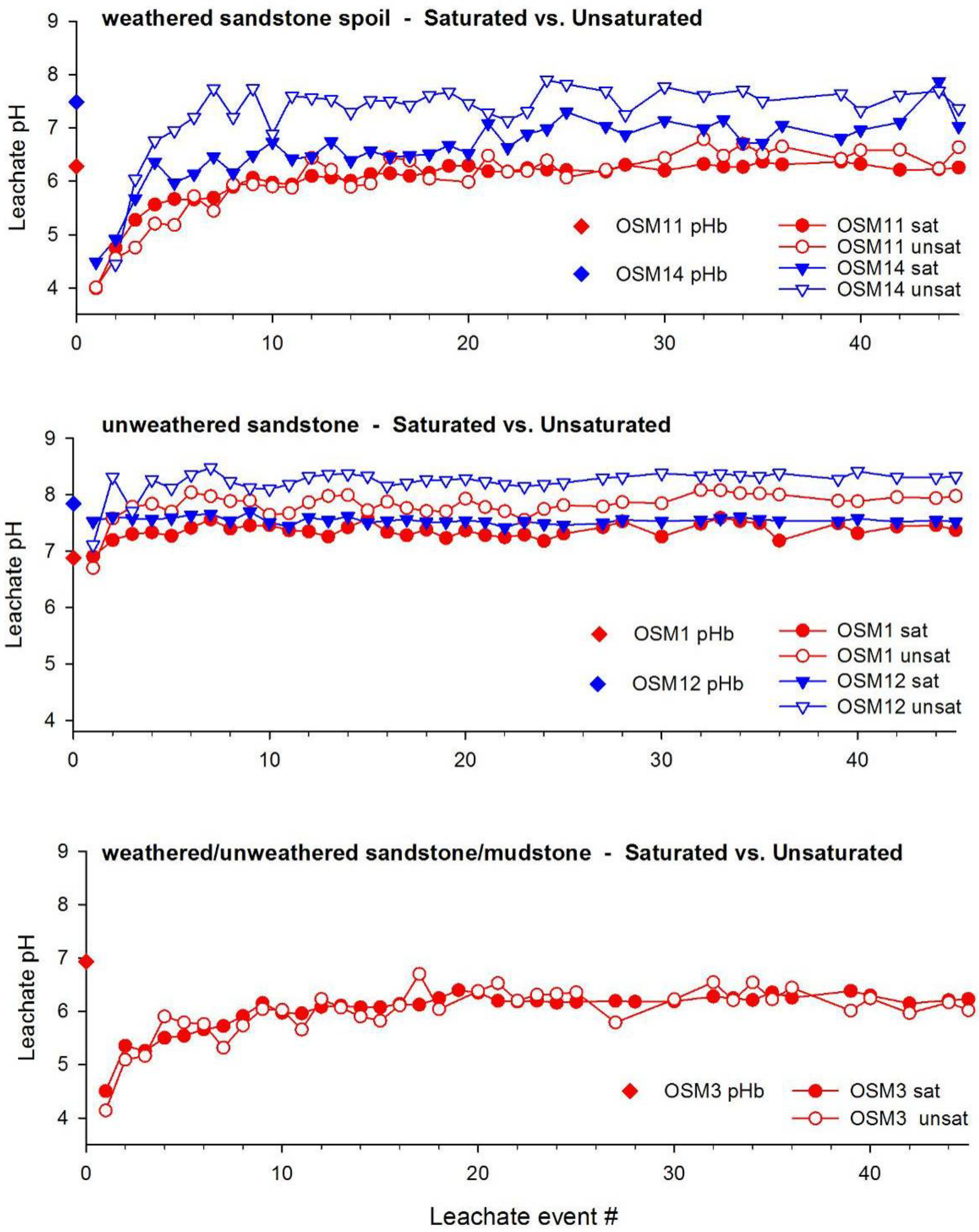

Figure 1. Leachate pH from weathered and unweathered sandstone spoil and mixed spoil material under saturated and unsaturated conditions. Saturated paste pH of the initial bulk material ($pH_b$) is indicated on the Y axis. The 45 leachate events occurred over 22 weeks.

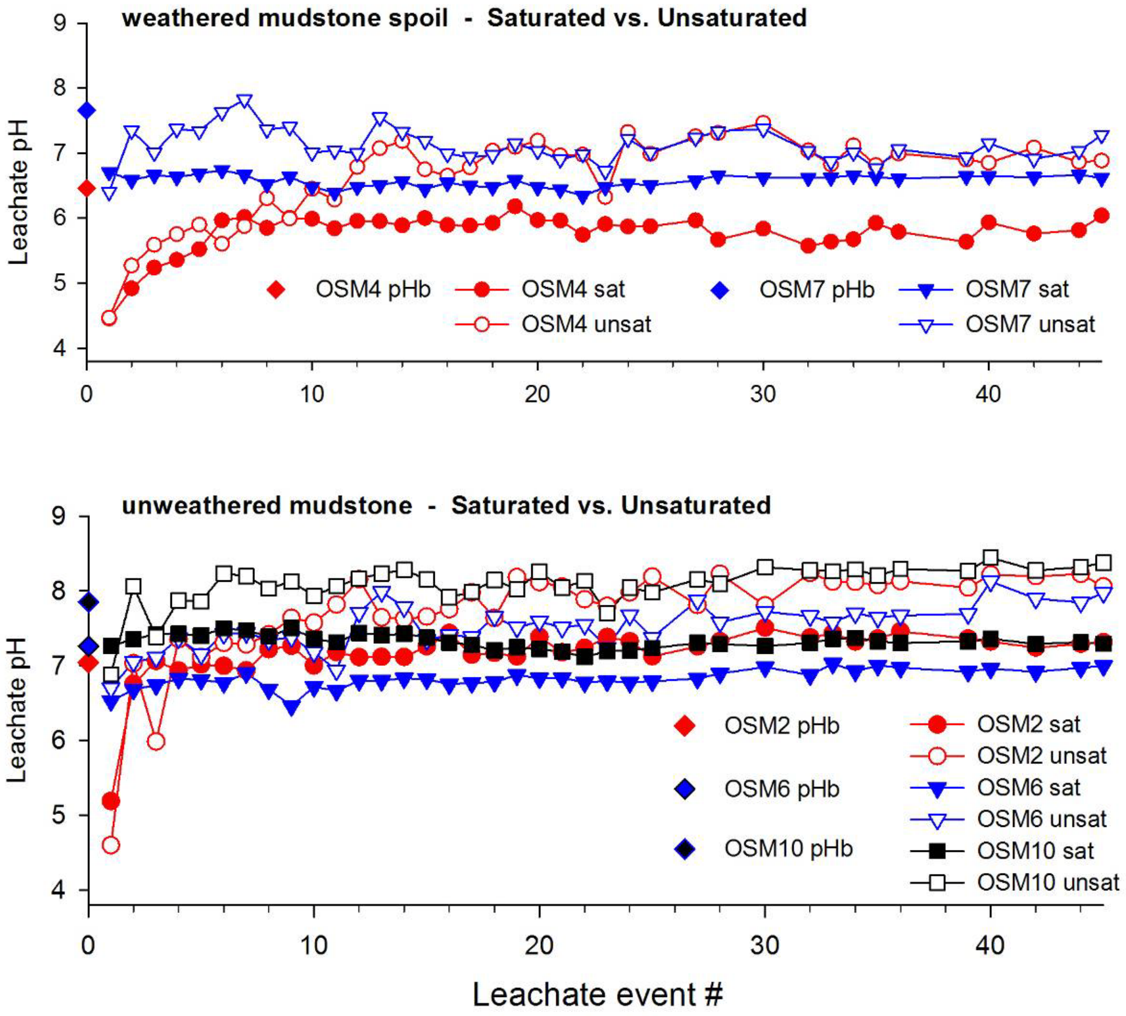

Figure 2. Leachate pH from weathered and unweathered mudstone spoil under saturated and unsaturated conditions. Saturated paste pH of the initial bulk material ($pH_b$) is indicated on the Y axis. The 45 leachate events occurred over 22 weeks.

The higher pH levels from unsaturated conditions could be due to the effects of $CO_2$ partial pressures on carbonate dissolution in the unsaturated columns or perhaps siderite ($FeCO_3$) formation in the saturated columns. Based on PPA values for some of the refuse samples, we anticipated that pH values would drop as the sulfidic materials oxidized. However, only OSM 21 which had the highest PPA value exhibited a significant drop (from pH 8.0 to 5.1). We continued to leach the columns beyond the data sets reported here, and by leaching #65, the pH for this sample dropped to 4.0. These observations contrast with previous trials (Daniels et al. 2006) where rapid drops in pH to 2.0 occurred. A major difference between the two studies is that the majority of samples used in this trial had substantial liming capacities (4.0 to 6.2% CCE) while the refuse used in the 2006 study was much lower in CCE. Thus, acidity produced by sulfide oxidation was directly neutralized via dissolution of carbonates, with the exception of the later leachates produced by OSM 21. The effects of these complex S oxidation and carbonate dissolution reactions are also indicated by changes in leachate EC, Ca and $SO_4^{-2}$ as discussed below. We have no reasonable explanation for the erratic pH pattern in unsaturated fine refuse sample OSM 19 other than redox cycling appeared to be active in the unsaturated columns of this treatment, perhaps due to plugging by fines and/or limited gas exchange with the column surface.

Electrical Conductance (EC). Parallel studies completed in conjunction with the results presented here (Daniels et al. 2009) indicated a high correlation coefficient (r = 0.98) between EC and TDS, as expected, indicating that EC can be used as an effective proxy for TDS. Leachate EC from unweathered mine spoil (Fig. 4-5) was consistently higher than from partially oxidized and weathered samples of similar geology. The difference in results between weathered and unweathered samples was more pronounced for mudstone than for sandstone. For most spoil samples, initial EC values dropped quickly, and typically achieved a steady state within 10 to 20 leaching events, maintaining relatively low levels for the remainder of the leaching trial. Most notable among the spoil materials were OSM 2 and 6, both unweathered mudstones, which maintained values greater >1.0 dS $m^{-1}$ through the first 10 leachings.

Fine refuse samples generated very high EC values in initial leachates, particularly for samples OSM 22 and 25; however, these two samples dropped to EC < 1.0 dS $m^{-1}$ by the third leaching. In contrast, leachate from the third fine refuse sample (OSM 19) produced an initial EC of 3.8 dS $m^{-1}$, and declined slowly maintaining values >2.0 dS $m^{-1}$ over the 45 leaching events (5 months) for the unsaturated columns. The saturated columns for OSM 19 experienced a noticeable drop over the last 6 leaching events dropping from 1.9 to 0.7 dS $m^{-1}$.

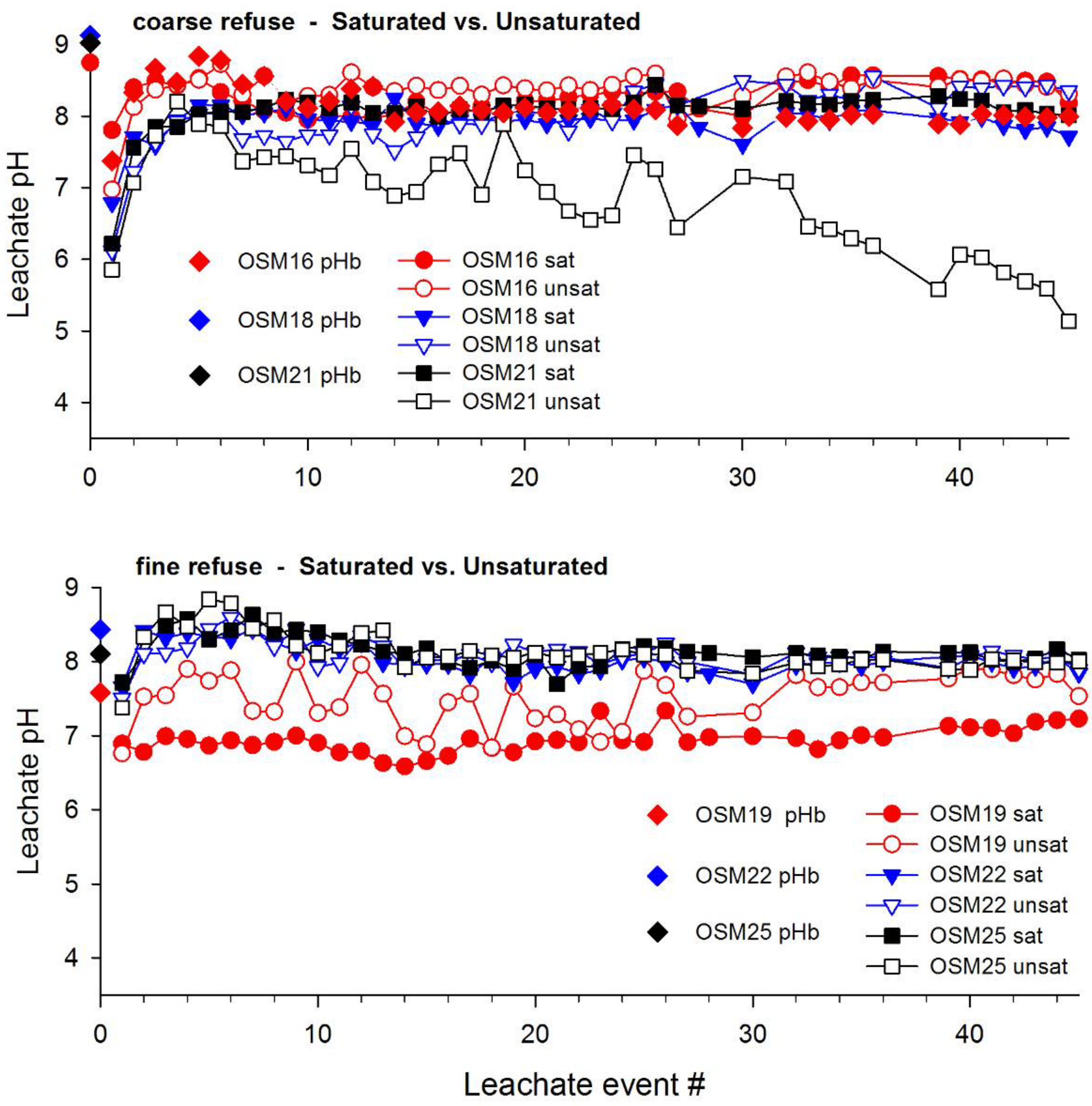

Figure 3. Leachate pH from selected coarse and fine refuse under saturated and unsaturated conditions. Saturated paste pH of the initial bulk material ($pH_b$) is indicated on the Y-axis. The 45 leachate events occurred over 22 weeks.

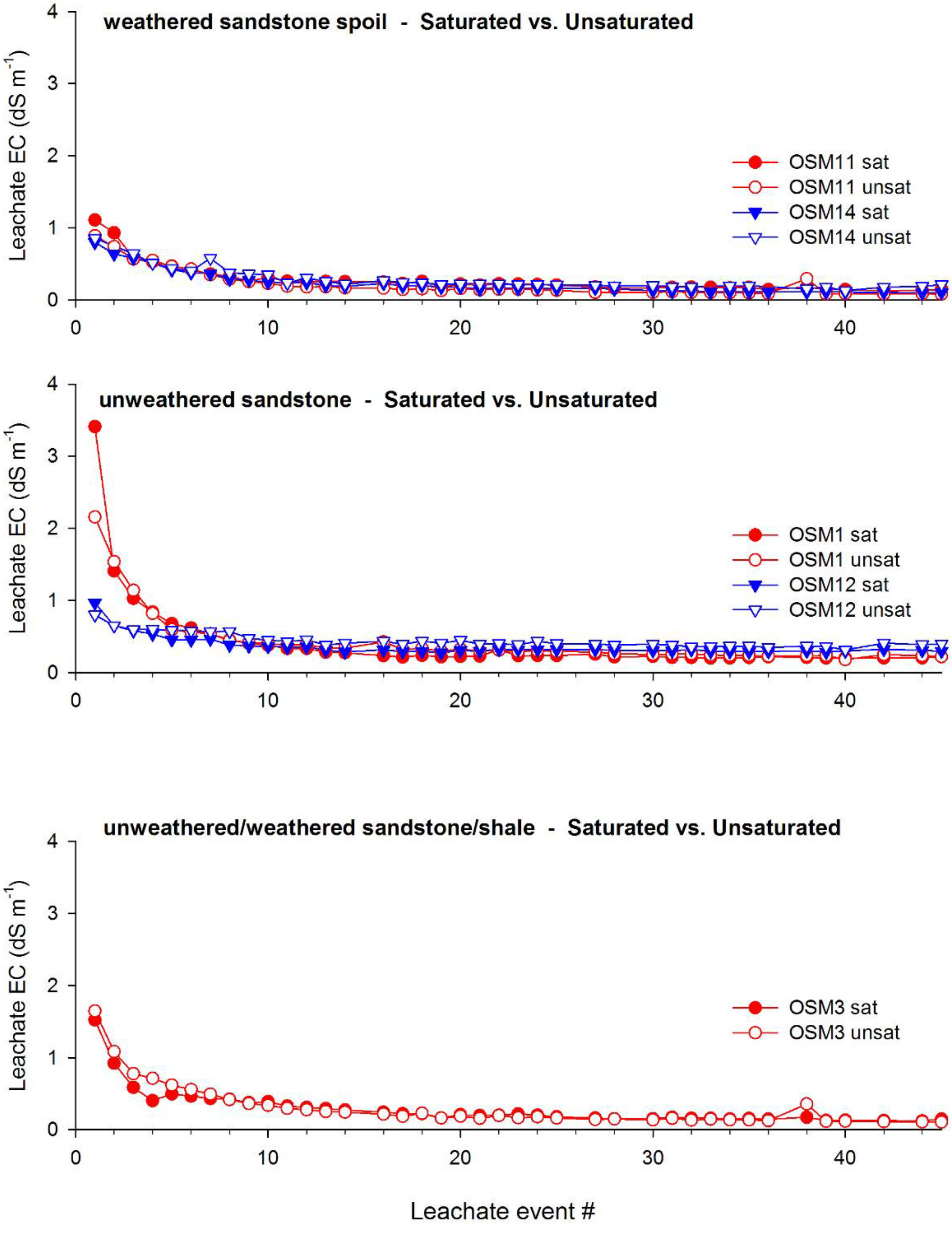

Figure 4. Leachate EC from weathered and unweathered sandstone spoil, and mixed spoil material, under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for EC graphs the Y-axis range is 0 – 4 dS m$^{-1}$ for Figs. 4 and 5, and 0 – 10 dS m$^{-1}$ for Fig. 6.

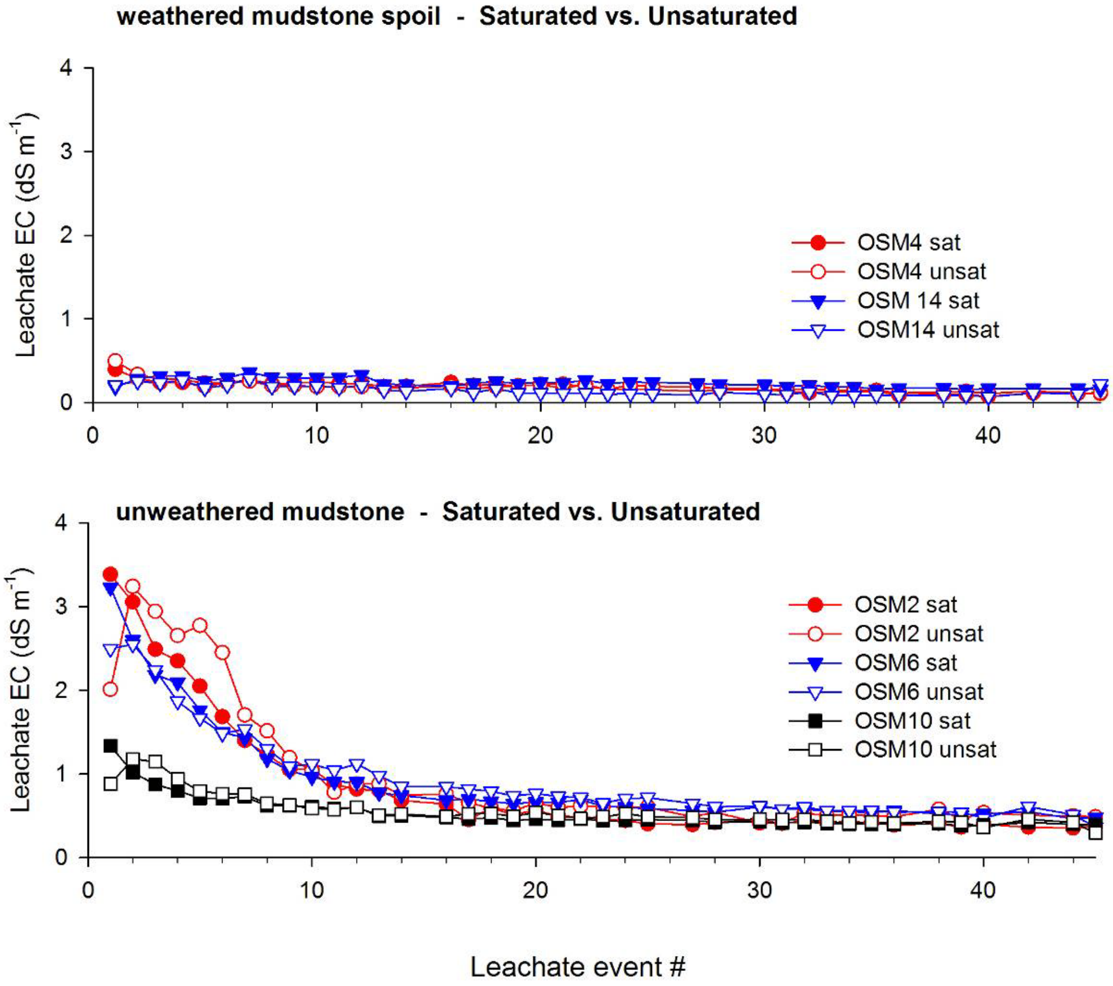

Figure 5. Leachate EC from weathered and unweathered mudstone spoil under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for EC graphs the Y-axis range is 0 – 4 dS $m^{-1}$ for Figs. 4 and 5, and 0 – 10 dS $m^{-1}$ for Fig. 6.

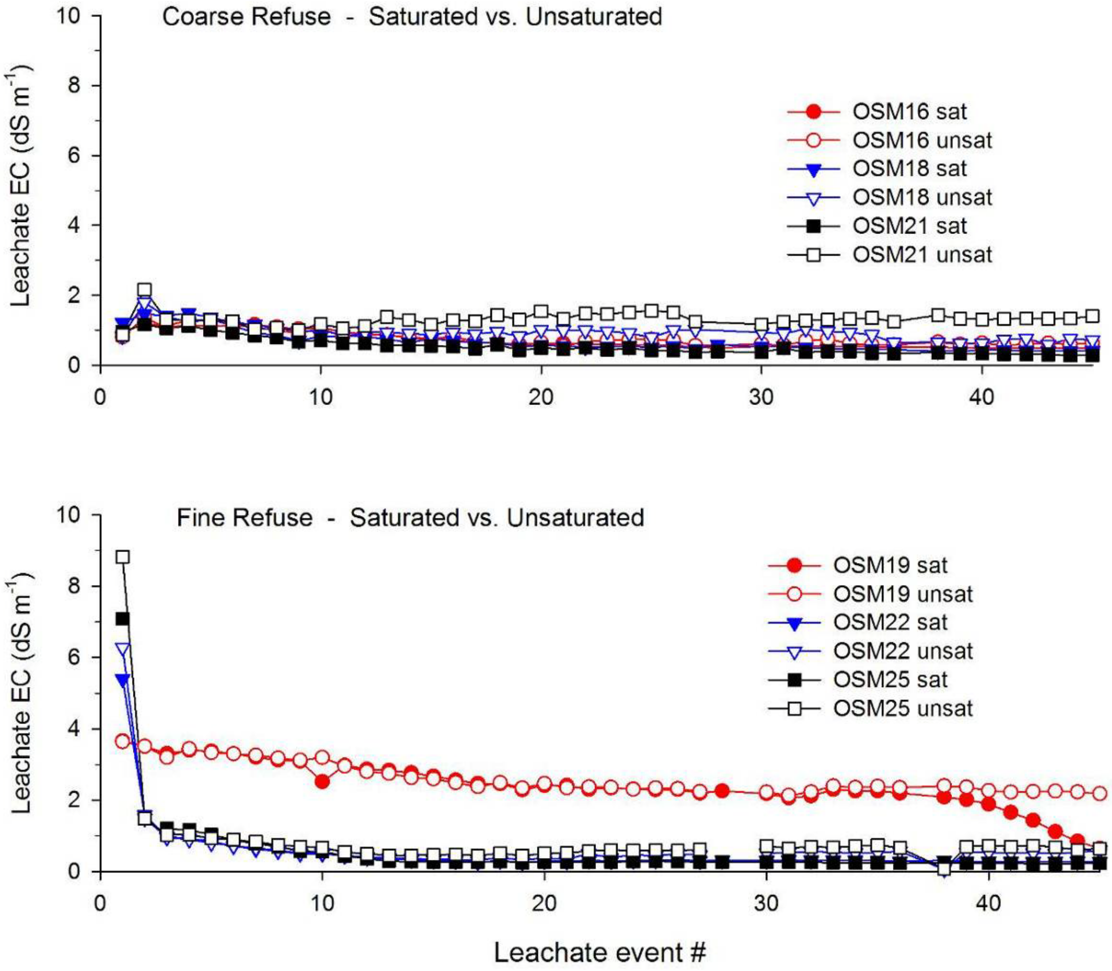

Figure 6. Leachate EC coarse coal refuse and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for EC graphs Y axis range is 0 – 4 dS $m^{-1}$ for Figs. 4 and 5, and 0 – 10 dS $m^{-1}$ for Fig. 6.

The most apparent effect of saturated versus unsaturated conditions on EC was observed in the coarse refuse samples, particularly OSM 18 and OSM 21, where EC was considerably higher from the unsaturated columns (Fig. 6). While EC for the saturated treatments showed a steady decline from approximately 1.5 to 0.5 dS $m^{-1}$ over the course of the study, the EC of the unsaturated materials remained fairly steady between 1.0 to 1.5 dS $m^{-1}$. Elevated EC levels observed in the unsaturated columns were related to sulfide oxidation, sulfate elution, and complex interacting geochemical processes that occur with materials containing acid producing and acid neutralizing compounds. For example, coarse refuse OSM 21 had the highest PPA of all samples, but also contained an apparent surplus of CCE neutralizing capacity. Based on these data, it appears the rate of carbonate dissolution was sufficient for approximately 8 to 10 leaching cycles to neutralize the acid sulfide reaction products, but the rate of pyrite oxidation eventually exceeded the carbonate dissolution rate, leading to the subsequent progressive drop in pH and increase in EC (Figs. 3 and 6). In the case of fine refuse sample OSM 19, the same source/mechanism for salt generation was present under saturated and unsaturated conditions, but it finally became suppressed under saturated conditions after 38 leachings as indicated by a distinct decline of EC.

Finally, the high EC/TDS values from OSM 2 and 6 probably represent the presence of a highly reactive sulfide (framboidal?) that even though present in relatively low amounts (0.23% and 0.14% S) reacted quickly with substrate carbonates to produce prolonged sulfate release over the extent of this experiment. Collectively, this acid-base reaction control on leachate chemistry was also reflected in leachate bicarbonate, sulfate, and Ca concentrations as discussed below.

Bicarbonate. The release of bicarbonate (Fig. 7) reflected the effects of saturated versus unsaturated conditions more than any other measured parameter in this study. Bicarbonate analysis was completed on all fine and coarse refuse samples, but only 3 spoil samples. Vastly more bicarbonate was leached under saturated conditions for both mine spoil and coarse refuse materials. The lower levels from the unsaturated columns presumably reflect acid neutralization reactions, even when relatively low amounts of S were present. The differences due to saturation were not as pronounced for the fine refuse materials and bicarbonate release was much more uniform among the different fine refuse materials compared to the mine spoils and coarse refuse. This was likely due to the finer texture of the fine refuse materials limiting oxidation in the unsaturated columns relative to the coarser spoils and coarse refuse.

Sulfate. Sulfate release patterns (Fig. 8-10) reflect the acid-base reactions discussed above which are due to fundamental differences in the geology/mineralogy of the samples and reflect the total-S content of the materials (Table 2). In SW Virginia, where most of these samples originated, the vast majority of strata within the Pennsylvanian system are fluvial-deltaic facies which are generally low in pyritic-S. Many of the massive sandstones that dominate the Lee, Norton, and Wise formations contain secondary carbonate cementing agents (Howard et al., 1988) which offset the relatively minor amounts of sulfidic minerals found in most geologic sections (like OSM 11). Significant accumulations of sulfides do occur in coal seams and

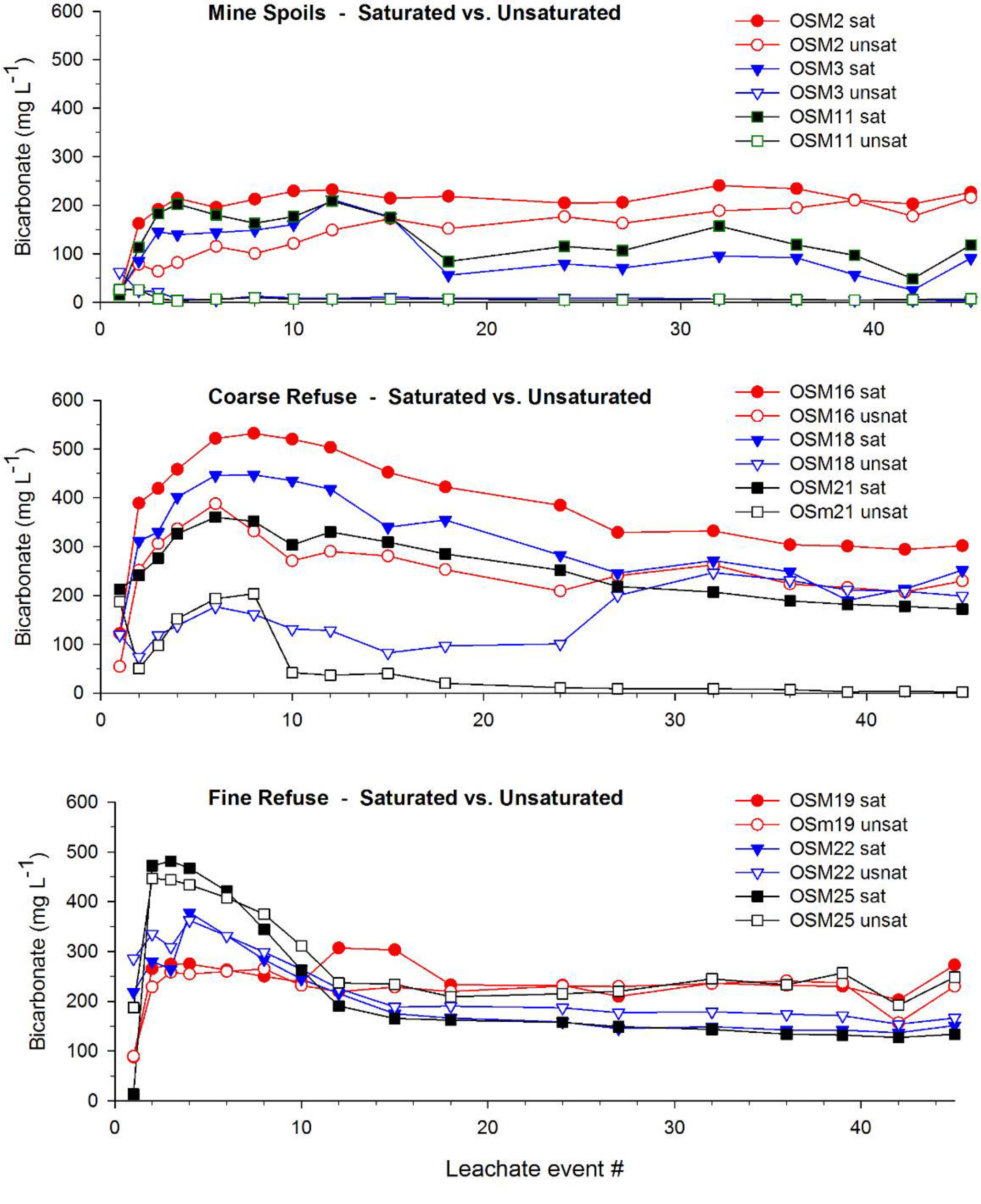

Figure 7. Bicarbonate leached from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks.

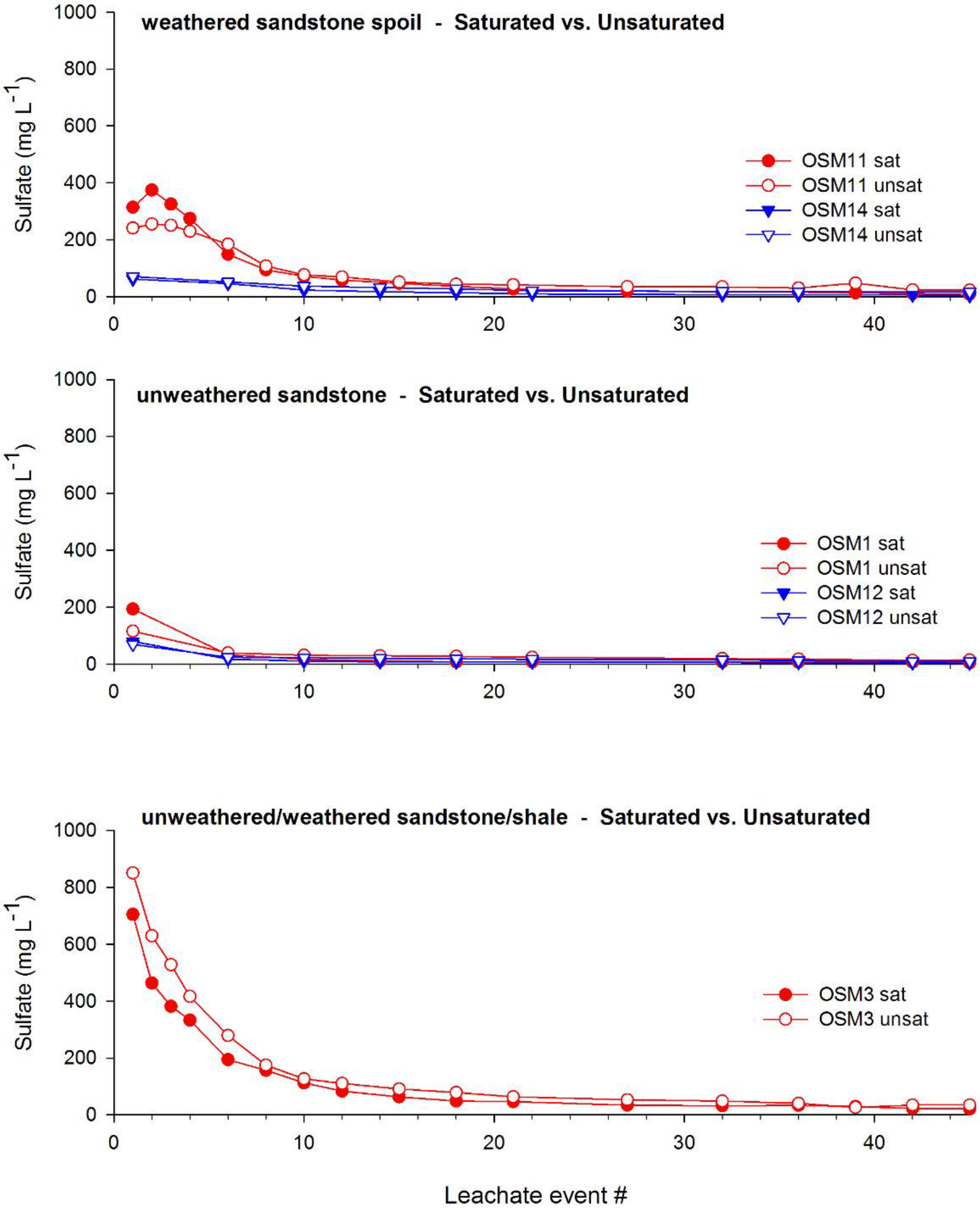

Figure 8. Sulfate leached from weathered and unweathered sandstone, and mixed spoil material, under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Sulfate graphs Y-axis ranges from 0 – 1000 mg $L^{-1}$ for Fig. 8, 0 – 3000 mg $L^{-1}$ for Fig. 9, and 0 – 5000 mg $L^{-1}$ for Fig. 10.

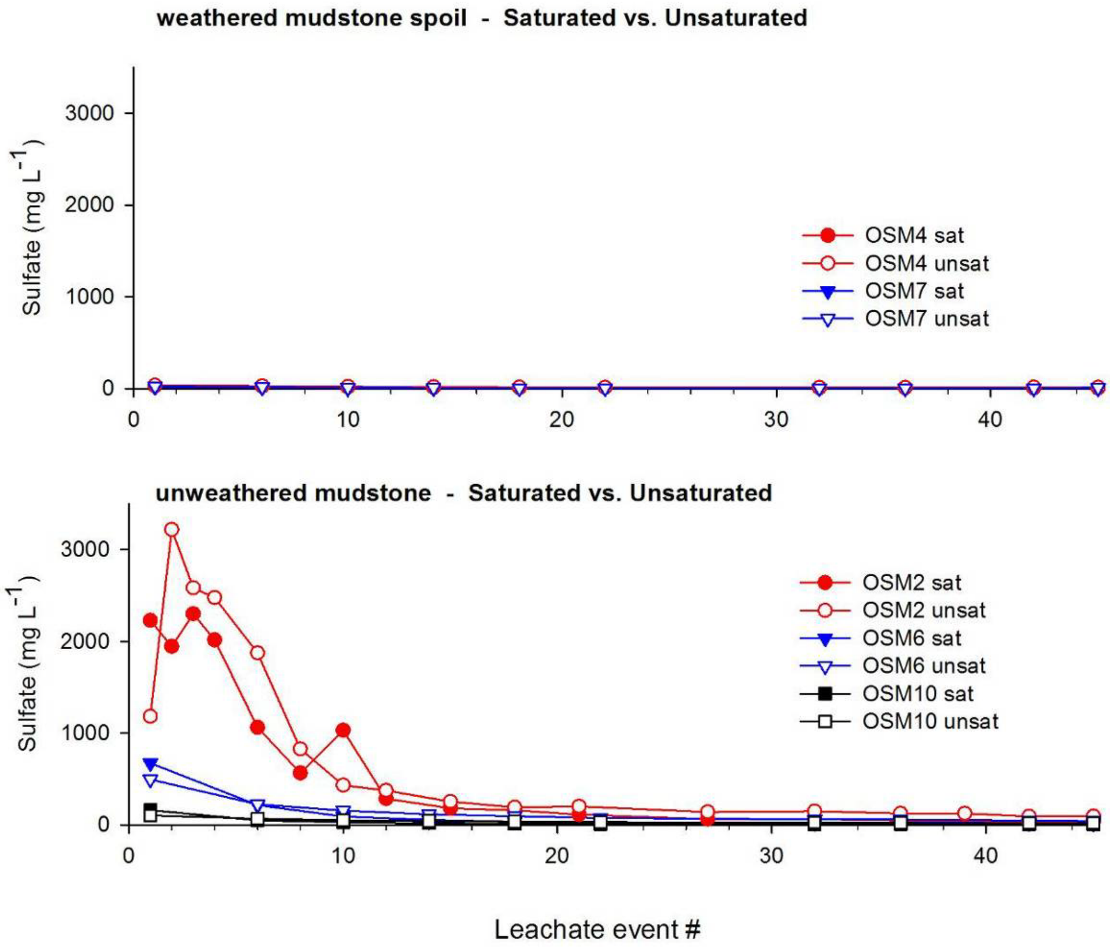

Figure 9. Sulfate leached from weathered and unweathered mudstone under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Sulfate graphs Y-axis ranges from 0 – 1000 mg $L^{-1}$ for Fig. 8, 0 – 3000 mg $L^{-1}$ for Fig. 9, and 0 – 5000 mg $L^{-1}$ for Fig. 10.

underclays throughout the region; however, these seams are relatively thin (< 3 m). Also, several relatively minor sections of overburden in Virginia (e.g. the Standiford seam interburden of the middle Wise formation) generate spoils with significant (>20 Mg/1000 Mg) levels of potential acidity (Orndorff & Daniels, 2004). For most spoil samples used in this study the majority of sulfate release occurred within the first month (10 leachings). The greatest sulfate release occurred from OSM 2, a mudstone from the Breathitt Formation in eastern Kentucky. This formation has been noted and studied for its acid forming potential (Barnhisel and Massey, 1969).

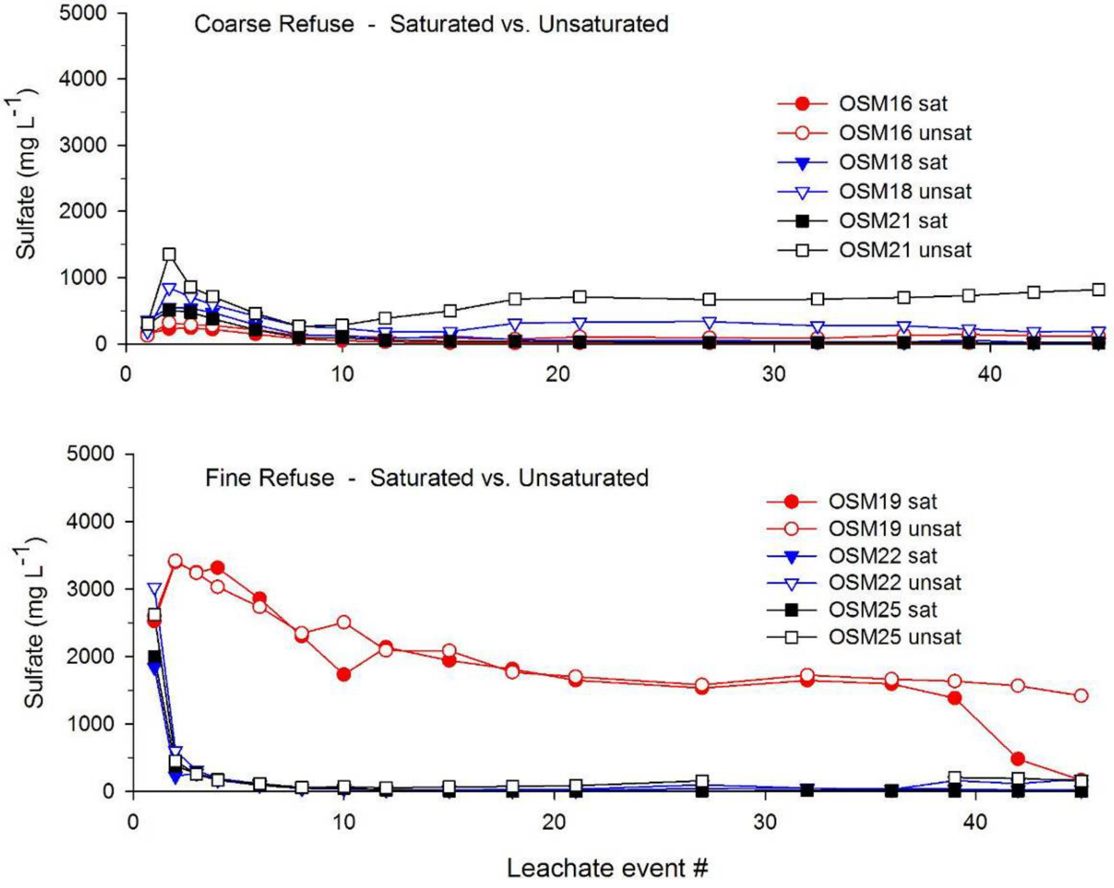

Figure 10. Sulfate leached from selected coarse coal refuse and fine coal refuse mine spoils under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Sulfate graphs Y-axis ranges from 0 – 1000 mg $L^{-1}$ for Fig. 8, 0 – 3000 mg $L^{-1}$ for Fig. 9, and 0 – 5000 mg $L^{-1}$ for Fig. 10.

The pairing of the coarse and fine refuse samples (by the source of the materials) resulted in two pairs (OSM 16/22 and OSM 18/19) with low total-S and PPA in the coarse fraction and high total-S and PPA in the fine fraction, and the reverse being the case for the third pair, OSM 21/22 (Table 2). These differences were clearly reflected in higher sulfate concentrations in leachates. The total-S content among the fine refuse samples was similar (Table 2) as were sulfate concentration in initial leachates. However, fine refuse OSM 19 produced significantly higher and sustained sulfate release than the other two samples. While this sample was not significantly higher in total S vs. CCE, it did test higher in PPA, indicating a potentially more reactive sulfide type or size.

The effect of saturated conditions on sulfate leaching was apparent in the coarse refuse materials (Fig. 10) due to the fact that pyrite oxidation rates are controlled by oxygen gas diffusion (Xu et al., 2008) when the pH is > 4.5. Thus, the better aerated coarse refuse readily promoted pyrite oxidation in the unsaturated columns, although a certain amount occurred initially in the saturated columns as well. Subsequently, the solubility and release of other ions such as Ca, Fe, and Zn would be affected by the interaction of $O_2$ diffusion rates, sulfide oxidation, carbonate dissolution, and bulk solution pH (Malmstrom et al., 2006).

Calcium (Ca), Iron (Fe) and Manganese (Mn). Calcium leaching patterns (Figs. 11-13) for the mine spoils followed the pattern of sulfate very closely. As expected, unweathered spoil materials released greater amounts of Ca than did the weathered materials. The release patterns of the coarse and fine refuse samples (Fig. 13) are characterized by changes associated with oxidation of sulfidic material and the corresponding changes in pH and TDS/EC as discussed earlier.

The Fe release patterns (Fig. 14) did not mirror those or other pyrite oxidation reaction products like sulfate. Due to the relatively high pH of the leachates, the vast majority of Fe was precipitated and retained within the columns in various oxy-hydroxide forms. However, the leachates from certain columns (e.g. OSM 21) did exhibit a red Fe-oxide coloration that became more pronounced as the pH dropped over time. The relatively high release of Fe from one saturated weathered mudstone spoil (OSM4) and one saturated weathered sandstone spoil (OSM 11) is notable and may be the result of reduction of original Fe-oxides to soluble $Fe^{+2}$ over time. The other spoil materials, released only low concentrations of Fe over the course of the study.

Overall, leachate Mn concentrations were higher than Fe due to the higher solubility of Mn than Fe in this pH range (Fig. 15). Furthermore, Evangelou (1995) pointed out that amorphous $Mn^{+4}$ oxides may serve as an alternative electron acceptor (oxidizing agent) in moderate pH sulfide oxidation environments which can lead to large amounts of water soluble $Mn^{+2}$ being mobilized. The Mn release patterns from refuse were closely related to Ca and sulfate as seen in the high release from fine refuse OSM 19 and the increasing release from OSM 21. This similarity also was seen for some spoil materials, particularly OSM 3 and OSM 1, however, the opposite was true for the Kentucky shale (OSM 2) which did not release notable amounts of Mn. This is presumably due to differences in the inherent Mn oxide forms in the differing spoils. For both Mn and Fe, the most notable releases from spoil materials occurred under saturated conditions.

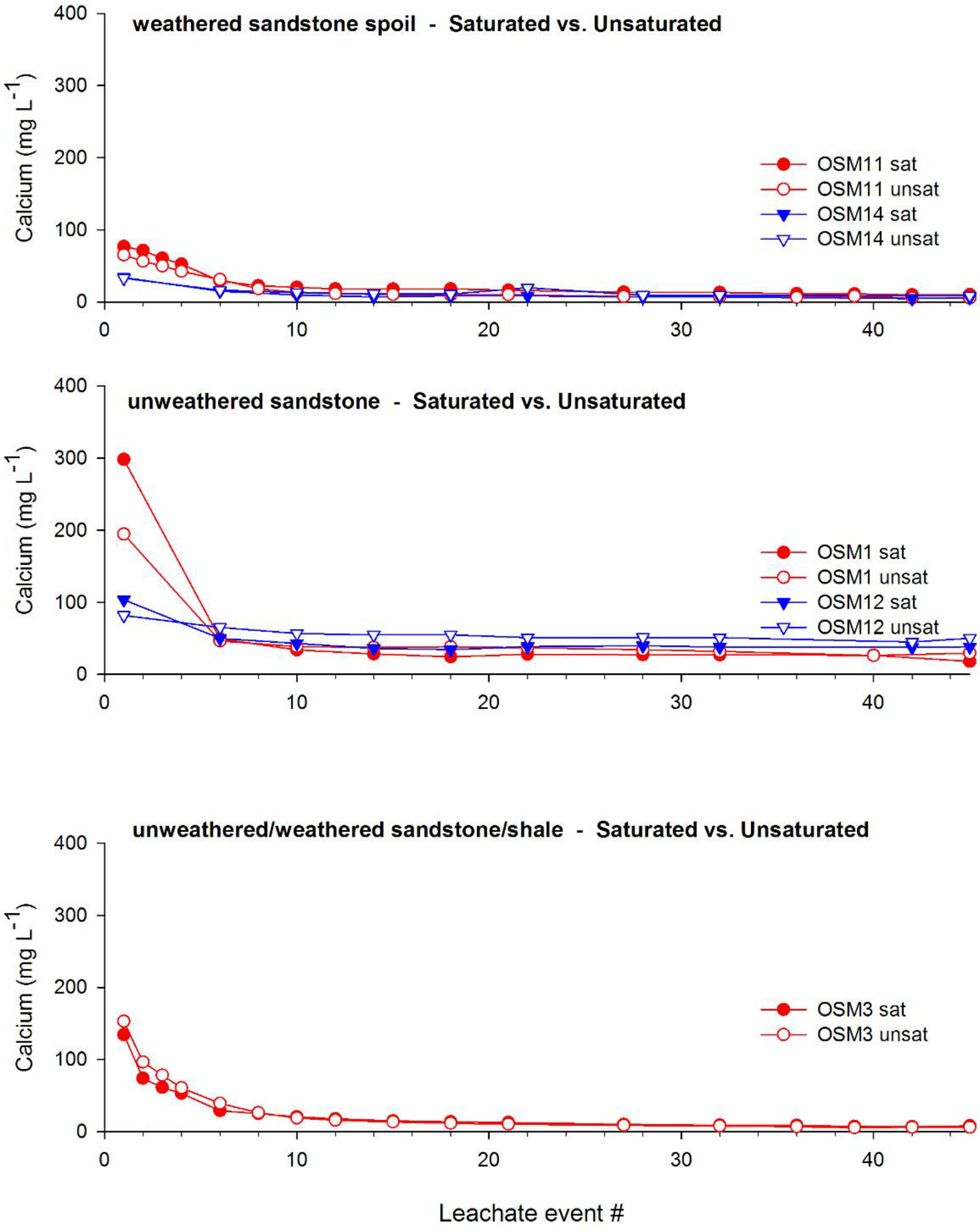

Figure 11. Leachate Ca from weathered and unweathered sandstone spoil under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Ca graphs Y-axis ranges from 0 – 400 mg $L^{-1}$ for Fig. 11, and 0 – 800 mg $L^{-1}$ for Figs. 12 and 13.

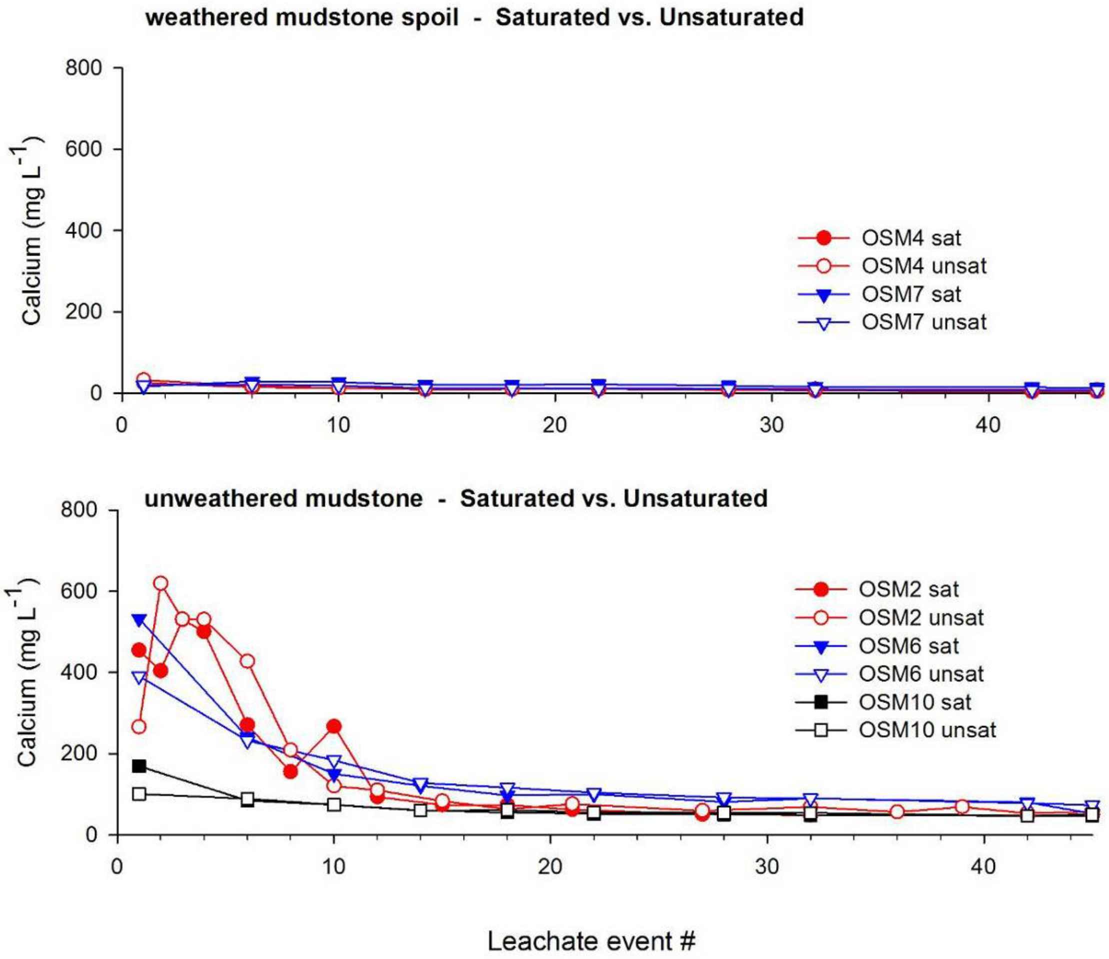

Figure 12. Leachate Ca from selected weathered and unweathered mudstone under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Ca graphs Y-axis ranges from 0 – 400 mg L$^{-1}$ for Fig. 11, and 0 – 800 mg L$^{-1}$ for Figs. 12 and 13.

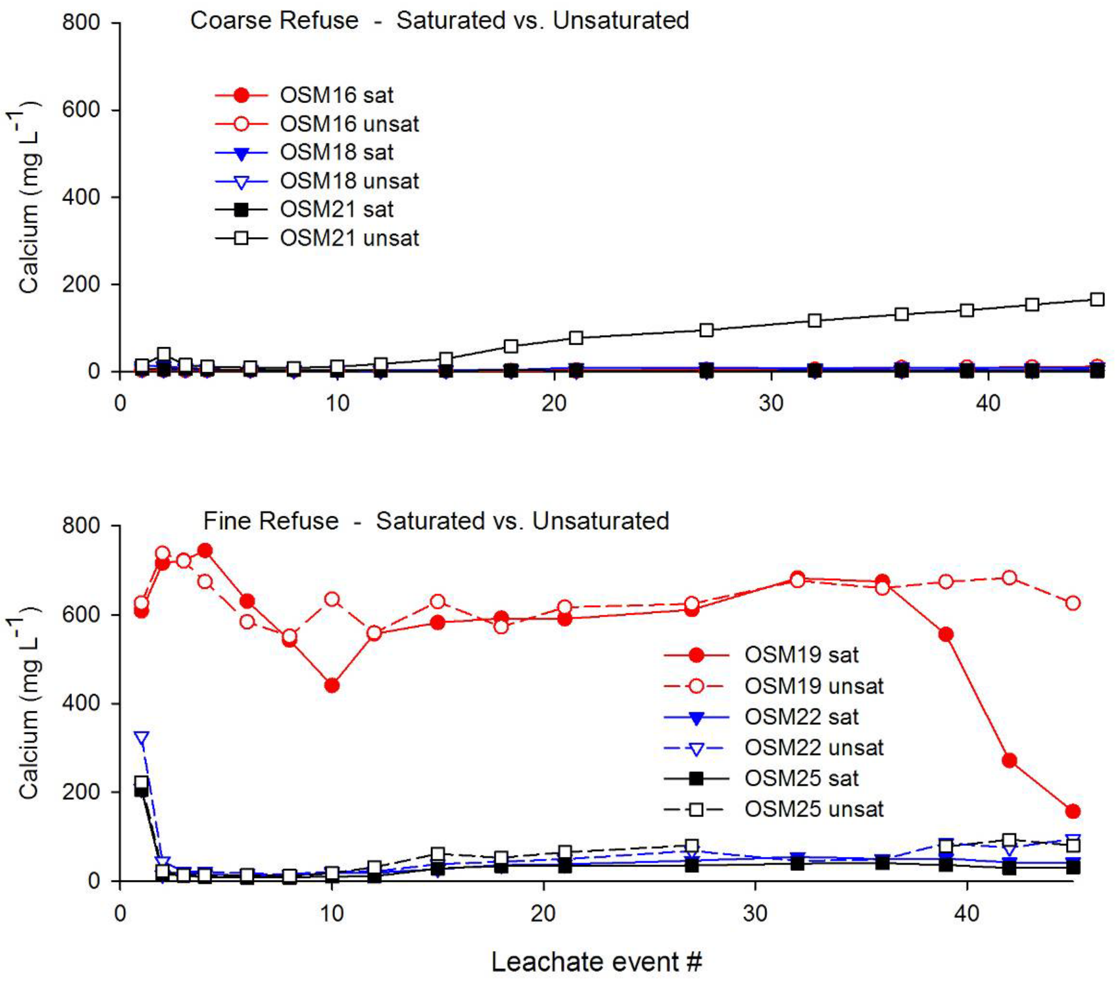

Figure 13. Leachate Ca from selected coarse coal refuse and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: for Ca graphs Y-axis ranges from 0 – 400 mg $L^{-1}$ for Fig. 11, and 0 – 800 mg $L^{-1}$ for Figs. 12 and 13.

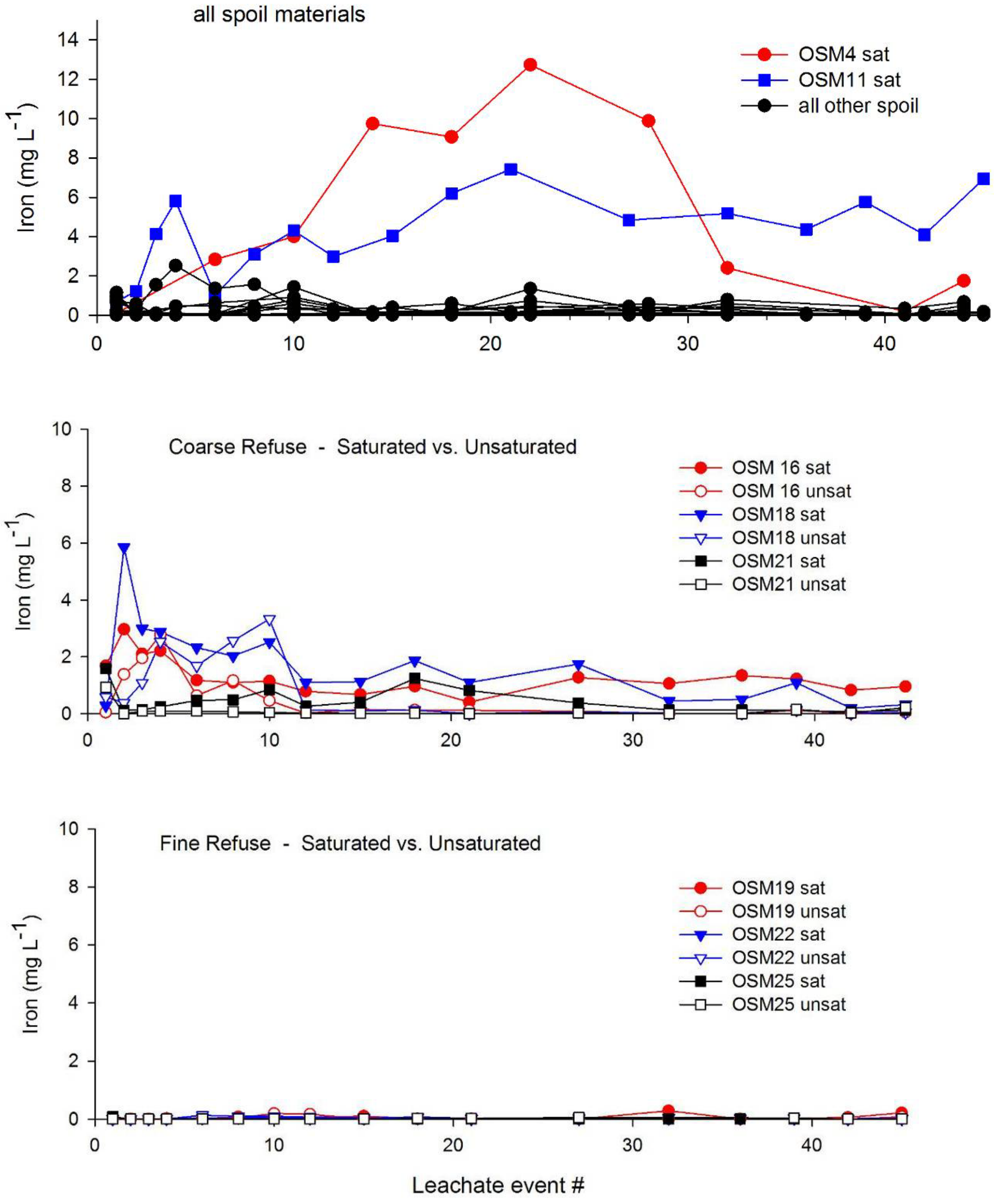

Figure 14. Leachate Fe from all spoil materials, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks. Note: Y-axis ranges from 0 – 14 mg $L^{-1}$ for spoil materials, and 0 – 10 mg $L^{-1}$ for refuse materials.

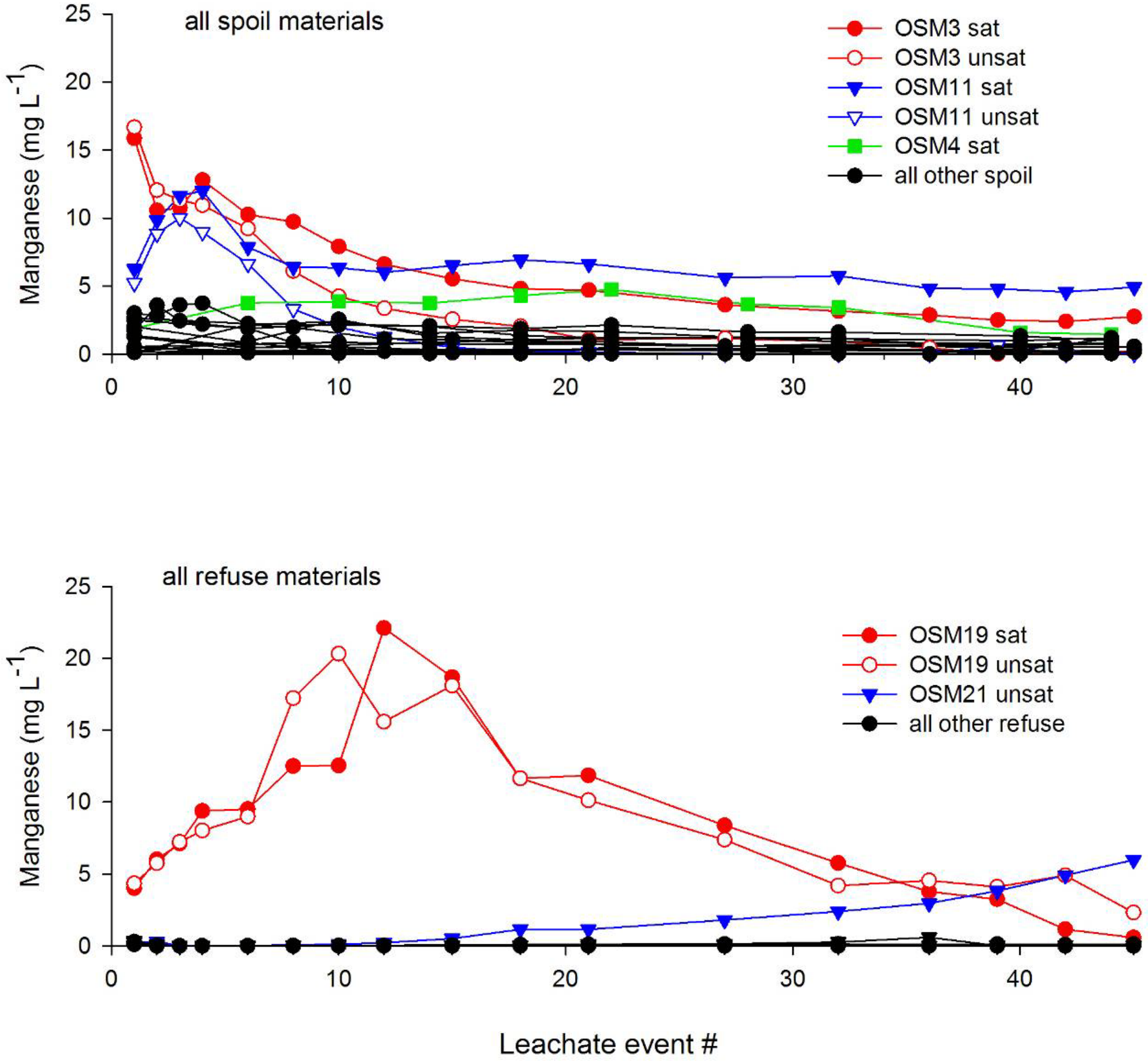

Figure 15. Leachate Mn from all spoil materials, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 22 weeks.

## Summary and Conclusions

The mine spoils sampled in this study were typical of surface mined overburden in the central and southern Appalachians in that they were largely non-acid forming and moderate (> 6.0) in initial pH and moderate in prolonged leachate pH. The 10 coal refuse samples (5 pairs of coarse & fine) were more variable with potential acidities ranging from 0 to -31 tons of CCE lime demand per 1000 tons material and 0.21 to 1.27 % total S. The CCE of all materials tested was supposedly high enough to completely offset acid generation by sulfides. Although the majority of samples did maintain a moderate pH (6.0 to 8.0) in leachates over the full study period (22 weeks), one sample (OSM 21) generated net acid drainage and several produced substantial sulfates. This reinforces the fact that standard acid-base accounting approaches to predict acid drainage are subject to a number of potential errors including their underlying assumption of similar rates of sulfide oxidation vs. carbonate dissolution. In this study, even though none of these samples were strongly acid forming, the version of the $H_2O_2$ oxidation test used (PPA) was a better predictor of which materials would produce large amounts of sulfate salts and TDS over time at the moderate pH levels observed in our columns. As expected, mine spoils that were significantly pre-weathered were lower in pH than unweathered materials of similar geology.

Most samples eluted considerable TDS as indicated by high EC (> 2.0 dS $m^{-1}$) over their initial leaching cycles. Although EC values dropped rapidly for most samples, this behavior would support continued TDS loadings to discharge waters on active operations that continued to disturb and place fresh spoils or refuse materials over extended periods of time. Samples that contained higher amounts of reactive sulfides continued to elute high TDS levels for the duration of the study, regardless of their leachate pH values. Of the materials studied here, the fine refuse materials had the highest initial EC values, but these values rapidly dropped in two of the three samples tested. Prolonged elevated leachate EC was most prominent in the third fine refuse sample, and to a lesser extent in the unsaturated coarse refuse samples, and two of the unweathered mudstone spoils (saturated and unsaturated). Differences in TDS release were clearly related to basic sulfide oxidation reactions with subsequent generation of sulfate and other reaction and dissolution products.

The relative concentrations of bicarbonate, sulfate, Ca, Fe, and Mn in column leachates over time were controlled primarily by acid-base reactions, pH solubility controls, and relative saturation. Bicarbonate was the one parameter most affected by saturated versus unsaturated conditions, with release being lower from unsaturated columns presumably due to consumption by acid neutralization reactions. Calcium and sulfate release patterns were very similar to each other; this was most apparent in samples OSM 2 and OSM 19 due to their noticeable fluctuations. Iron release was dissimilar to Ca and sulfate release presumably due to the precipitation and retention of iron oxy-hydroxides within the columns. Iron release was most notable from OSM 4 and OSM 11, both weathered samples, under saturated conditions and likely represents the reduction and subsequent dissolution of iron oxides present in the materials. Manganese release patterns were comparable to Ca and sulfate release for the refuse samples, but only for some of the spoil samples. Like Fe, the highest instances of Mn release occurred under saturated conditions. Surprisingly, this study revealed no major significant or consistent differences between coarse and fine refuse materials for any parameter of long term leaching concern.

## Acknowledgments

This research was supported by the OSM Applied Science Program with oversight by Nancy Pointon and Lois Uranowski of the Appalachian Regional Office in Pittsburgh. Components of this work were also supported by the Powell River Project with oversight by Carl Zipper. We appreciate the assistance of Julie Burger, Pat Donovan, and Athena Tilley in our labs at Virginia Tech. Finally, we want to thank our numerous industry cooperators in the Virginia and Kentucky coalfields who assisted us with sample collection.

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