Weathering and Leaching Characteristics of a Fixated Scrubber Sludge Cap at an Abandoned Mine Site in Pike County, Indiana

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ABSTRACT

In 1996 an abandoned mine site containing a coal refuse pile, ash-filled highwall lake, and spoil was capped with fixated scrubber sludge (FSS) obtained from a nearby coal-fired power generation station. The FSS is a blend of flue-gas desulfurization sludge from an oxygen-inhibited scrubber unit, fly ash, and lime. Core samples of the FSS cap were collected and lysimeters were placed above and below the cap near monitoring wells screened in the refuse and ash fill. Mineral compositions of cores were determined, and samples of weathered and unweathered FSS were subjected to laboratory leaching experiments of 3-week duration. The experiments employed ultrapure water, synthetic regional groundwater, and synthetic acid mine drainage.

Mineralogical analysis of core samples determined that the primary weathering indicators are increases in gypsum and calcite coinciding with decreases in hannebachite ($CaSO_3 \cdot 0.5H_2O$), the dominant sulfur-capture mineral phase generated in an oxygen-inhibited flue gas scrubber from which the bulk of the FSS is derived. Weathering appears to be minimal since the 1996 emplacement and confined to the top of the capping material. Laboratory studies demonstrate that weathered FSS leachate generated more sulfate, boron, molybdenum, and arsenic than unweathered FSS leachate, and less aluminum, barium, nickel, and selenium. Both synthetic solutions enhanced calcium, sulfate, nickel, and boron, and suppressed aluminum, arsenic, and selenium in leachate. Weathering characteristics observed for the FSS cap after 15 years suggest negligible water interaction based on comparisons of field data with laboratory leaching potential from continuous exposure to synthetic equivalents of locally present water.

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Introduction

Flue-gas desulfurization (FGD) methods employed at coal-fired power plants that use crushed limestone and lime-based reaction processes generate significant residues. Depending on the configuration of the stack gas scrubbers, the residues can consist primarily of gypsum ($CaSO_4 \bullet 2H_2O$) or hannebachite ($CaSO_3 \bullet 0.5H_2O$). The product of forced oxidation scrubbing, gypsum can be used in a variety of applications in the fields of agriculture and engineering. As a product of inhibited oxidation scrubbing, hannebachite has fewer beneficial applications and is more commonly treated as a waste material that is fixated with fly ash and lime prior to landfilling. This fixated scrubber sludge (FSS) has found some use in abandoned mine land (AML) reclamation due to its low-permeability and acid-neutralization properties. The main use in mine reclamation to date has been as a grout for filling underground mines to diminish acidic discharges and prevent subsidence (Bulusu et al. , 2005, Taerakul et al., 2004). Another less commonly employed application of FSS at AML sites is as a low-permeability capping material for sealing acid-generating, coal refuse deposits from exposure to water and oxygen (Bryenton & Gasper, 1996). This is to inhibit the formation of acid-mine drainage (AMD) which is initiated by the oxidation of pyrite through the following reaction (Stumm & Morgan, 1981):

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad [1]$$
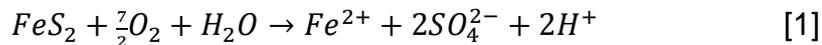
Reducing the amount of oxygenated water infiltration into coal refuse deposits containing high concentrations of pyritic materials is an important step in long-term prevention of AMD formation. One of the lingering questions regarding this strategy is how long will the FSS cap remain impermeable given that one of the primary mineral phases, hannebachite, can oxidize to the more soluble mineral gypsum as shown by reaction 2 (Laperche & Bigham, 2002).

$$CaSO_3 \cdot \tfrac{1}{2}H_2O + \tfrac{1}{2}O_2 + \tfrac{3}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad [2]$$
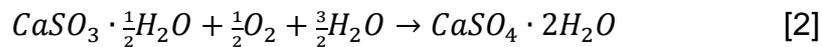
In addition to the formation of gypsum, the solubility of hannebachite has been shown to be pH dependent, increasing under acidic conditions (Hao & Dick, 2000; Lee et al., 2007). An increase in hannebachite dissolution will also provide a mechanism for conversion to sulfate in the presence of oxygen by the following reactions (Lee et al., 2007):

$$CaSO_3 + H^+ = Ca^+ + HSO_3^- \qquad [3]$$

$$HSO_3^- + \tfrac{1}{2}O_2 = HSO_4^- = SO_4^{2-} + H^+ \qquad [4]$$
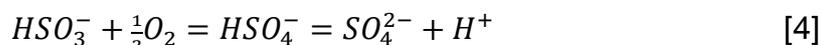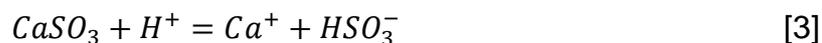
The potential of reactions 2-4 occurring creates a concern regarding the usage of FSS as a capping material for acid-generating materials as the top of the cap would be

susceptible to mineral conversion in the presence of oxygen and water to a more soluble phase while dissolution of a primary mineral component at the base of the cap would increase if it encounters acid solutions.

A negative impact from the deterioration of FSS as a capping material would be the potential release of trace metals sequestered in the FSS. Previous studies have documented the occurrence of trace metals in the FSS components of FGD filter cake, fly ash and lime as well as the final product (Laperche & Traina, 1999; Cheng et al., 2007; Lee et al., 2007). And though trace element concentrations can vary significantly between FSS components (Sanchez et al., 2008), in most cases there are sufficient concentrations of constituents of potential concern (COPC) to warrant some apprehension regarding their use as a capping material in AML reclamation. As a result, a key factor to evaluating the successful resistance of FSS to environmental deterioration is by monitoring for increased mobilization of COPCs at sites where FSS is used. The purpose of this study is to identify the nature of COPC mobilization or attenuation at an AML site reclaimed 15 years ago using CCRs, through mineralogical alterations of FSS and water chemistry from the site coupled with lab simulations of water-material interactions designed to replicate field conditions.

In 1996, an abandoned mine land site in Pike County, Indiana located in a small headwater catchment of the Patoka River Basin underwent reclamation that included the use of CCRs both as fill (ponded fly ash/bottom ash blend) and capping material (FSS consisting of 0.6 – 1:1 ratio, fly ash: FGD sludge with 1.5 to 2.0% quick lime) (Fig. 1). An area of 9 ha was covered with the FSS, including a coarse-grained refuse pile referred to as gob (~3 ha) and an ash-filled highwall lake. Water-monitoring wells and surface drainages were sampled quarterly for the first year prior to and first five years after reclamation. At the conclusion of this monitoring activity intermittent monitoring occurred until quarterly monitoring was reconvened for one year beginning in July, 2011. The initial post-reclamation monitoring established that only the constituents of boron, molybdenum and potassium were noticeably mobilized from CCRs out of a component set that also included major ions and the trace elements arsenic, cadmium chromium, lead, mercury, nickel and selenium (Branam et al., 1999). Longer term monitoring data indicates decreasing trends in 10 of the components measured in the gob pile water table under the FSS cap, including arsenic, cadmium, lead, iron, sulfate and boron (Naylor et al., 2012). Soil moisture profiles and water-level data indicated the presence of a short-duration, wet weather-generated, perched water table above the FSS cap (Naylor et al., 2012). The potential for cap deterioration exists as a result of water interaction at the site yet the lack of long-term, elevated concentrations of FSS-leached constituents found in water samples collected from the gob aquifer suggests that the cap has experienced minimal deterioration at that location. By 2011 the FSS cap had been in place 15 years. A study was undertaken to determine the degree of

FSS deterioration and how various water interactions influence the mineralogical and leachate composition.
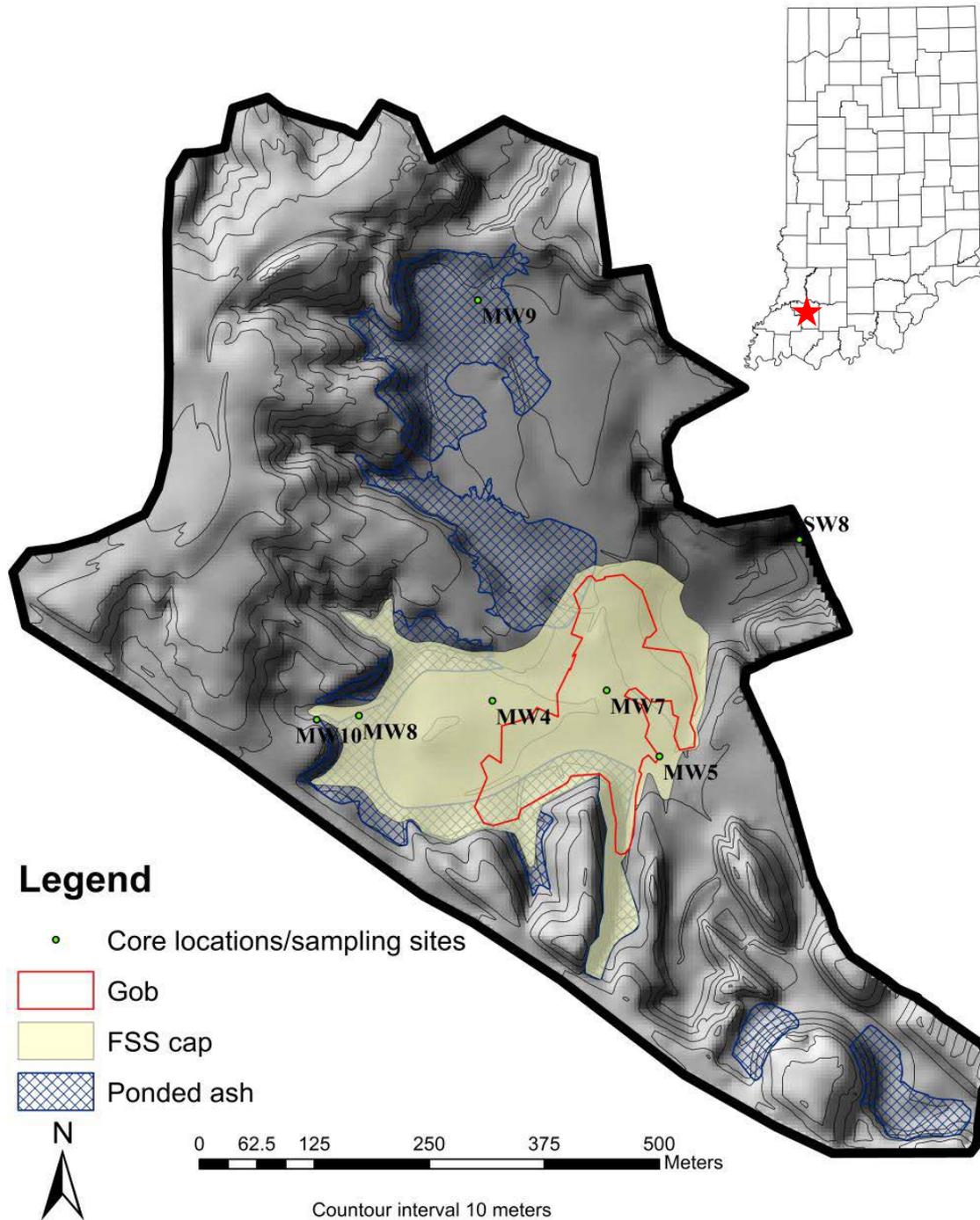

Figure 1 Location of AML reclamation site, CCR placement, and monitoring well locations where cores were extracted.

Methods

<u>Solids</u>

In March of 2011, eight 4 to 8-cm diameter cores were collected at six locations within the Midwestern Reclamation site using a Geoprobe® (Fig. 1). Each core represented a different vertical sequence of CCRs and underlying materials (Table 1). For mineralogical analysis samples were collected at the top, bottom and multiple locations along the length of the FSS portion of the cores. Samples were dried in an oven at 65°C for 24 hours and stored in airtight containers. Prior to mineralogical analysis, samples were ground with an agate mortar and pestle (Martin et al., 2012).

Mineralogical characterization was determined by X-ray diffraction (XRD) with Cu Kα radiation and a 2θ range of 2-70° on a Bruker D8 Advance X-Ray Diffractometer with a solid-state detector. Observed peaks were matched to known minerals using DIFFRACplus EVA software. Quantitative Rietveld analysis was conducted on all samples using DIFFRACplus TOPAS software. All samples were spiked prior to grinding with 20% by weight pure αAl_2O_3 as an internal reference for quantitative analysis.

<u>Water Monitoring</u>

Monitoring wells from which water samples were collected (Fig. 1, Table 2) were originally installed during the reclamation phase of the Midwestern project (Branam et al., 1999), with the exception of MW10, which was completed after core samples were extracted in March, 2011. Vacuum lysimeters were installed at sites MW4, MW7, MW8 and MW9 (Table 2). Multiple lysimeters were installed at sites MW7 and MW8 at depths just above and below the FSS cap where interactions with ambient surface and groundwater occur. Water samples were collected quarterly from July, 2011 to May, 2012. Field measurements were taken for pH, conductivity, ORP, DO and temperature using a YSI 600XL multiparameter sonde coupled with a 650 DMS data logger. All samples were field-filtered and stored in separate aliquots depending on the required preservation protocols for analytes to be measured, and transported to Indiana University. Laboratory analyses were conducted in the Geological Sciences Department for Cl, SO_4, Ca, Mg, Fe, Na, K, Mn, As, Cr, Ni and Se. Aliquots were shipped to Astbury Water Technology, Inc. in Indianapolis where Al, B and Mo were determined.

Table 1Depth and thickness of materials recovered from cores at the Midwestern Reclamation Site. Soil cap consists of top soil on spoil.

Site	Depth (m)	Thickness (m)	Material
MW4	0 – 1.0	1.00	Soil cap
	1.0 – 2.25	1.25	FSS
	2.25 – 4.0	1.75	Gob
MW5	0 – 1.43	1.43	Soil cap
	1.43 – 1.88	0.45	FSS
	1.88 – 3.66	1.78	Spoil
MW7	0 – 1.0	1.00	Soil cap
	1.0 – 2.7	1.7?	FSS
	2.7 – 6.0	3.3?	Gob
MW8	0 – 1.40	1.40	Soil cap
	1.40 – 3.23	1.83	FSS
	3.23 – 6.0	2.77	Ponded ash fill
MW9	0 – 4.07	4.07	Soil cap/spoil fill
	4.07 – 7.30	3.23	Ponded ash fill
MW10	0 – 1.32	1.32	Soil cap
	1.32 – 3.96	2.64	FSS
	3.96 – 5.0	1.04	Ponded ash fill

Table 2 Well and lysimeter depths compared to approximate depth interval of FSS cap as determined from core recovery. Lysimeters are coded with "SL" in ID column.

Well/Lysimeter ID	Well/Lysimeter depth (m)	Material	FSS depth interval (m)
MW4-SL	0.9	Spoil/FSS Interface	1.0 – 2.25
MW4S	1.0	Soil/FSS top	1.0 – 2.25
MW4D	2.4	Spoil/Gob?	1.0 – 2.25
MW7-SL3.33	1.0	Spoil/FSS Interface	1.0 – 2.7
MW7-SL8.75	2.7	FSS base	1.0 – 2.7
MW7D	4.1	Gob	1.0 – 2.7
MW8-SL3.9	1.2	Spoil/FSS Interface	1.4 – 3.23
MW8-SL9.75	3.0	FSS/Ponded Ash Interface	1.4 – 3.23
MW8	6.1	Ponded Ash	1.4 – 3.23
MW9-SL18.5	5.6	Ponded Ash	---
MW9	11.3	Ponded Ash	---
MW10	4.6	Ponded Ash	1.32 – 3.96

Leachate Experiments

Four leachate experiments were conducted on core samples taken from FSS at site MW8. Core fragments were approximately 7 cm in length and 3.5 cm in diameter, weighing ~300 g. Three fragments were extracted from the middle of the FSS core from site MW8 to ensure they have been minimally altered from exposure to water and oxygen. One fragment was taken from the bottom of the FSS core interval from site MW8 where color and textural differences indicated mineral/chemical alteration. All leachate experiments were conducted using a 1L Ace glass reaction vessel that allows for continuous flow of liquid. FSS fragments were placed in mesh nets and suspended in the reaction vessel from a glass hook. The reaction vessel was connected to inflow and outflow peristaltic pumps. The inflow pump was connected to a 20 L reservoir tank and the outflow pump connected to a 1.3L collection tube. Gas lines were connected from the reservoir tank and reaction vessel to cylinders of N_2 and CO_2 for purging the fluid of oxygen and increasing the partial pressure of CO_2 as needed. YSI multiparameter sondes in flow-through chambers were placed in line between the inflow pump and the reaction vessel, and the outflow pump and the collection tube for measuring pH, DO, conductivity, ORP and temperature for both inflow and outflow, respectively (Fig. 2). The sondes were programmed to collect continuous data at one hour intervals. The reaction vessel and flow-through cells were filled with leaching solution and the pumps started. Flow rates were maintained at ~1L per day (~0.7 ml/min). Flow velocity was calculated to be approximately $2x10^{-5}$ cm/sec. All leaching experiments were allowed to continue for a duration of 3 weeks.

The first two leachate runs were conducted on one unweathered FSS fragment and the apparent weathered FSS fragment. Both fragments were leached with ultrapure water under a constant nitrogen purge. The third run was performed on a second unweathered fragment leached with a synthetic groundwater (SGW) containing calcium sulfate, magnesium sulfate and calcium carbonate. CO_2 gas was bubbled through the stock solution until all of the calcium carbonate was dissolved. The experiment was conducted under a continuous purge of N_2 and CO_2 to maintain both a low O_2 concentration and an elevated alkalinity characteristic of regional spoil aquifers (Branam & Harper, 1994). The fourth leachate experiment consisted of preparing synthetic acid-mine drainage (SAMD) of similar composition occurring in the gob aquifer at the reclamation site. Sulfate salts of iron (II), aluminum and calcium were dissolved in ultrapure water that had been purged of dissolved O_2 for 24 hours with N_2 gas. Sufficient sulfuric acid was added to the solution to adjust the pH to 3.5 – 4.0. The stock tank and reaction vessel were kept under a constant N_2 gas flow to maintain low O_2 levels such as found in the gob aquifer, where Fe(II) is the predominant iron species.

The collection tube was emptied on a daily basis, with the collected leachate filtered, partitioned and preserved for analysis. Alkalinity titrations were performed in

house and aliquots of all samples were transported to the Indiana Department of Health laboratories in Indianapolis for determinations of Cl, SO_4, Ca, Mg, K, Na, Fe, Mn, Zn, Sr, Ba, Al, B, Mo, Ni, As, Cd, Cr, Pb, Hg, and Se.
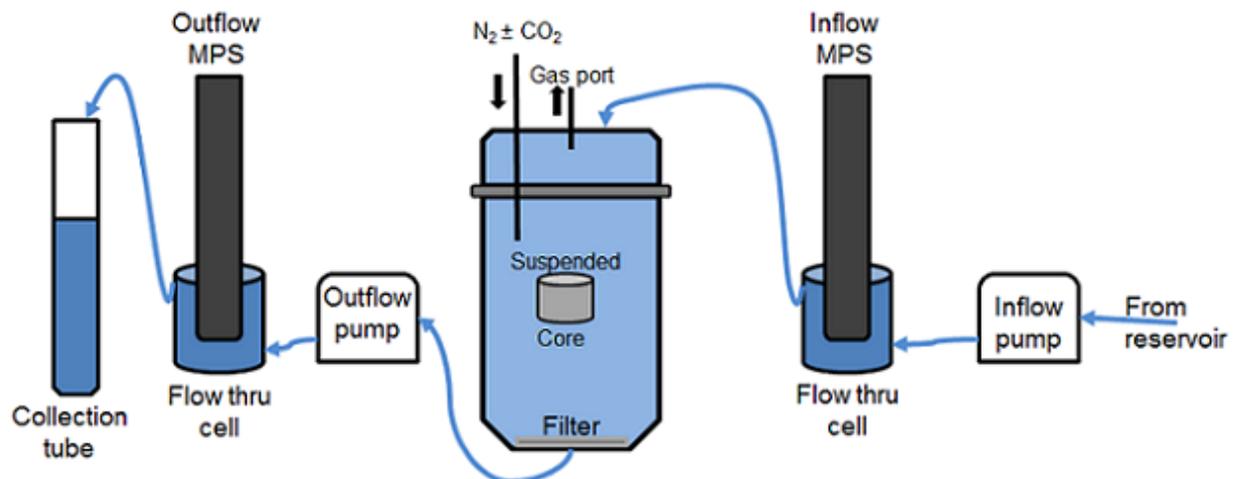

Figure 2. Schematic of experimental design for continuous flow leaching of fragments taken from FSS core extracted from reclamation site. MPS - multiparameter sonde for measuring pH, ORP, DO, SpC and T°C.

Results

XRD data for the FSS core samples extracted from the reclamation site identified the mineral phases of hannebachite, gypsum, mullite, quartz, hematite, magnetite, calcite, and ettringite (Martin et al., 2012). A significant unidentifiable component was assigned a generic amorphous classification by the XRD instrument software. For the thickest FSS cores collected at sites MW4, MW7 and MW10, the spatial distribution pattern showed the highest occurrence for calcite and gypsum was at the top of the FSS, rapidly dropping off to minimal or undetected throughout the rest of the core, while the distribution of hannebachite and ettringite show an opposite pattern with the lowest amounts found at the top of the FSS (Fig. 3). The FSS cap at MW5 was much thinner (Fig. 1, Table 1) as it was located at the edge of the cap overlying spoil. The pattern for FSS cap at this location shows an increase in calcite and gypsum at the top and gypsum the dominant mineral phase identified at the bottom (>80%) while ettringite and hannebachite are depleted at both the top and bottom relative to the interior of the core.
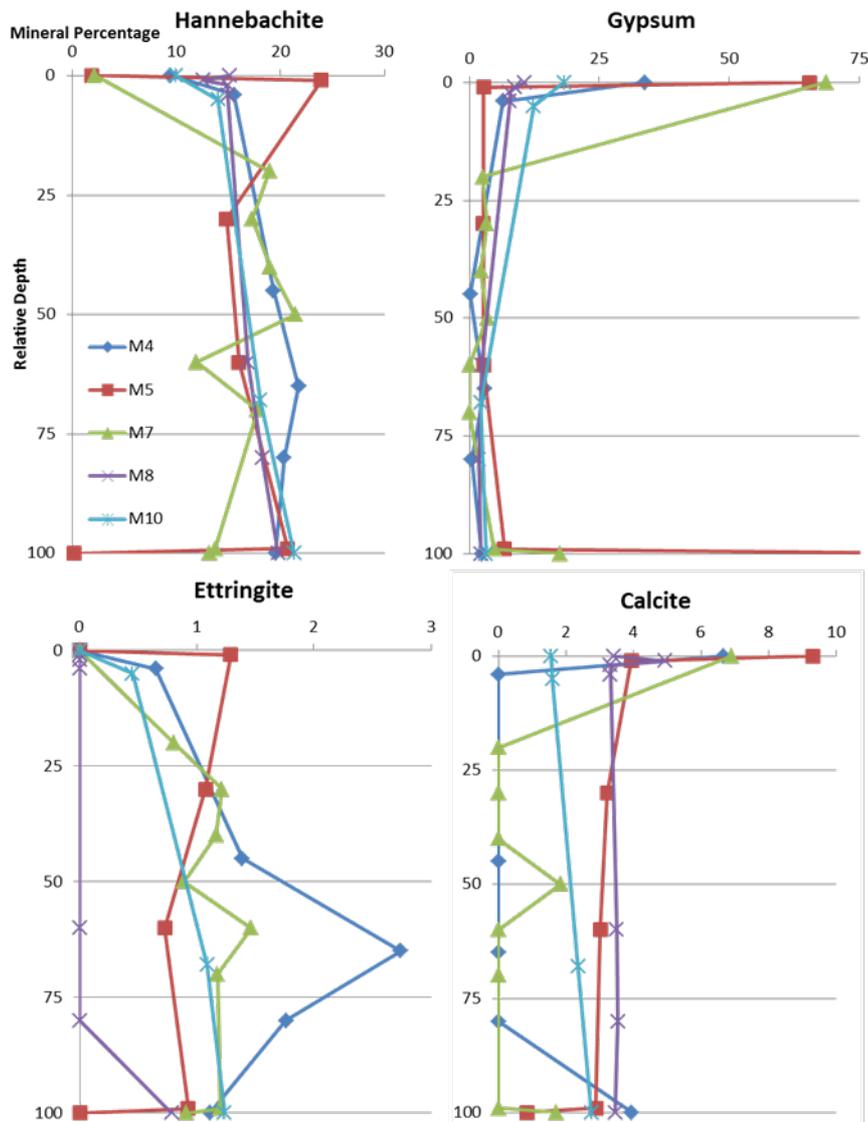
Figure 3 Mineral distributions in FSS cap determined for extracted core from 5 locations at reclamation site (from Martin et al., 2012). Horizontal axis is mineral percentages. Vertical axis is relative depth of FSS portion of core.

Water samples collected from the monitoring sites were either characterized as calcium-sulfate, calcium-magnesium-sulfate, or iron-calcium-sulfate with the majority of samples plotting in the calcium and sulfate areas on a Piper trilinear diagram (Fig. 4). A better delineation of the FSS influence on water chemistry is derived from plotting calcium, magnesium and iron on a ternary diagram (Fig. 5) and calculating the Ca/Mg molar ratios (Table 3). Using these relationships, shallow depth lysimeters differ from the deeper lysimeters in the amount of magnesium present as indicated by the much smaller Ca/Mg ratios for the shallow lysimeters which extract pore water from materials

above the FSS cap. The deeper lysimeters installed at the base of the FSS cap contain minimal magnesium resulting in much higher Ca/Mg ratios.
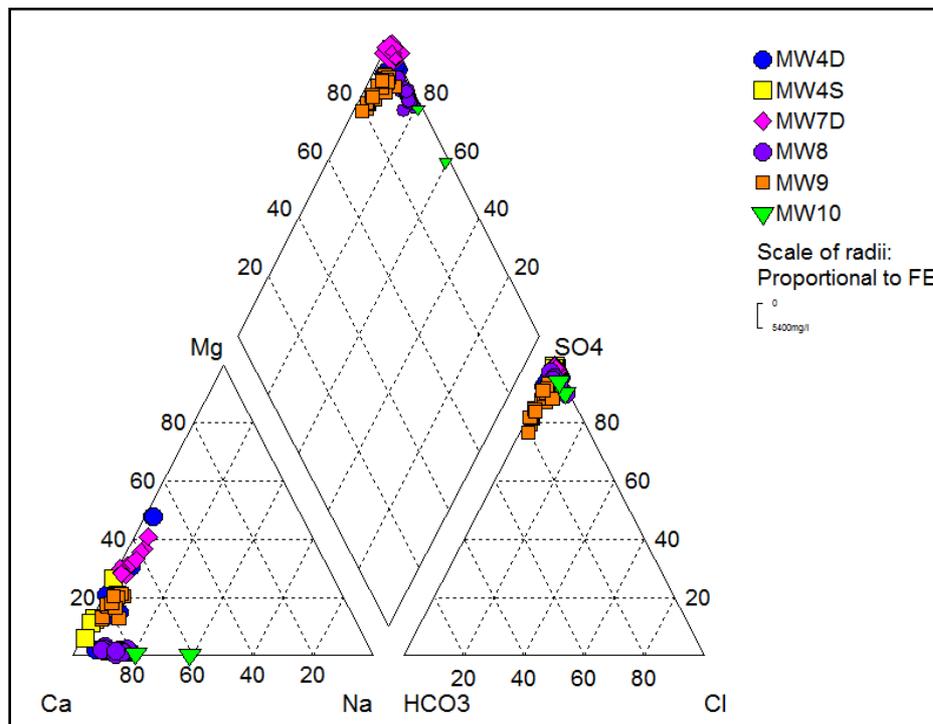

Figure 4 Piper Trilinear diagram showing prevalent chemical character of groundwater collected from monitoring wells at the Midwestern Reclamation Site. Symbols in central diamond graph are proportional in size to the amount of iron in water samples.

There is a significant difference in the major water chemistry at the two well locations beneath the FSS cap in shown in Figure 5. The well MW7 is screened in gob material, a primary source for acid-mine drainage and is the only sampling site dominated by the cation Fe^{2+}. A trend in major cation composition at MW7 from completely iron-dominated to a more mixed composition represents a period of time when samples were collected immediately after cap emplacement (iron dominant) to the most recent samplings of 2011-2012 (mixed). In contrast to this well, MW8 has a dominant calcium metal component throughout the post-reclamation interval from which samples were collected. MW8 is placed in an ash-filled lake bed (table 2) consisting of a blend of fly ash and bottom ash that had been previously ponded at the coal-powered facility prior to transport and emplacement at the reclamation site. Under these conditions much of the soluble mineralogy of the ash had been depleted prior to placement (Martin et al., 2012).
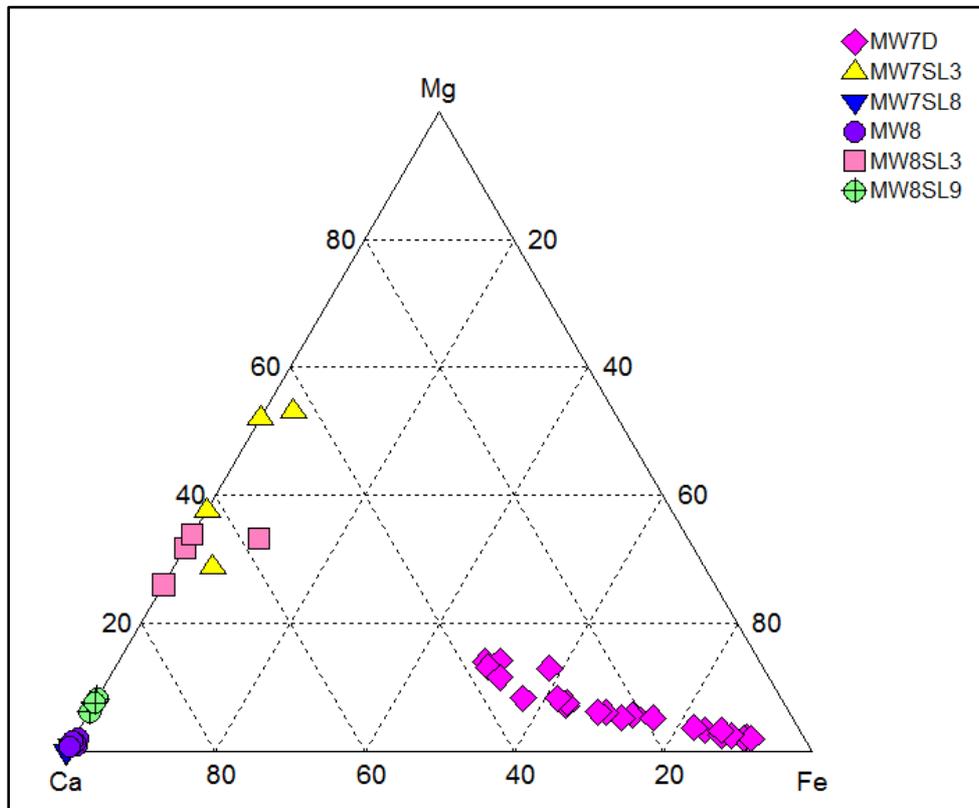
Figure 5 Ternary diagram showing proportion of calcium, magnesium, and iron for well and lysimeter clusters at sites MW7 and MW8.

Table 3 Average Ca/Mg molar ratios for well and lysimeter clusters at sites MW7 and MW8. Monitoring wells MW7D and MW8 show two averages, one for the first 5 years of quarterly monitoring, and the most recent year of quarterly monitoring. Bold type indicates below FSS cap.

Sample ID	N	Average Ca/Mg molar ratio
MW7-SL3.33	4	0.9
MW7-SL8.75	4	**1009**
MW7D (1996-2001)	17	**2.3**
MW7D (2012)	4	**1.6**
MW8-SL3.9	4	1.3
MW8-SL9.75	4	**7.6**
MW8 (1996-2001)	17	**70**
MW8 (2012)	4	**57**

The results of the leaching studies are summarized in table 4. The data show the cumulative amount of components extracted from the FSS cores for each leaching experiment, and the relative amount gained or lost from three leaching experiments

compared to the first experiment which leached unweathered FSS with ultrapure water. This initial experiment (UFSS+H_2O, Table 4) is treated as a baseline and relative amounts of extracted components from subsequent leaching experiments are represented by positive or negative percentages of baseline results. Extracted amounts of chemical components less than the baseline values obtained from unweathered FSS with ultrapure water are indicated by negative percentages. For synthetic solutions reacted with unweathered FSS, a reduced component extraction is attributed to the chemical composition of the solution suppressing the mobilization of a component. Reductions in components exceeding -100% of baseline results indicate that depletion from the initial leaching solution concentrations have occurred. For the weathered FSS leached with ultrapure water, changes in extracted components are attributed to mineralogical changes in the weathering of the FSS. In table 4, comparisons of unweathered versus weathered FSS leaching with pure water indicates that sulfate, boron and molybdenum concentrations are the most elevated components leached from weathered FSS. At the opposite end of the leaching spectrum, aluminum, nickel, barium and selenium concentrations indicated less leaching for these species in the weathered FSS fragment experiment. Since the same leaching solution, ultrapure H_2O was used for both experiments the implication is that these elements must be readily leached from FSS under the elevated pH conditions that prevail when unbuffered water encounters FSS.

While more sulfate is extracted from the weathered FSS fragment, there is virtually no change in the amount of calcium leached. Calcium/sulfur molar ratios for the two water-leaching experiments produced an average ratio of 1.8 for the unweathered FSS fragment, and an average ratio of 1.1 for the weathered fragment. Since the molar ratio of calcium to sulfur is 1 for gypsum this would comprise the likely soluble source of calcium and sulfate in the weathered sample. The higher Ca/S average value obtained from unweathered FSS indicates another source of calcium contributing to the total leached amount. The most likely possibility is believed to be the lime that was mixed with the CCRs to create the fixated material.

Comparisons of unweathered FSS leachate from water with the two synthetic solutions indicate significant mobility reductions for arsenic in both solutions and molybdenum in the synthetic AMD. Major increases in mobilizations of zinc and nickel occurred in both synthetic solutions and significant increases in boron and barium were also observed. Both aluminum and iron in the synthetic AMD experienced major decreases in solubility while a small amount of iron was extracted from the FSS with synthetic groundwater. Both solutions were strongly buffered within a narrow pH range, the synthetic groundwater solution within the bicarbonate buffering range, and the synthetic acid-mine drainage by sulfuric acid (Table 4).
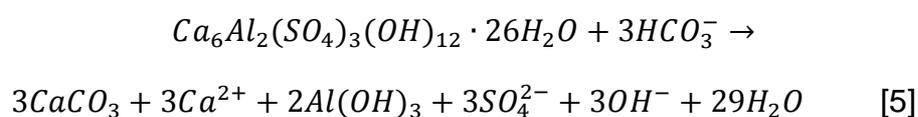
Table 4 Comparison of leaching results of pure water on unweathered and weathered FSS, and synthetic solutions on unweathered FSS.

| Parameter | Approximate cumulative leached quantity after 3 weeks @flow rate of 1L/day | | | | % component leached compared to UFSS+H$_2$O | | |
	UFSS[1] +H$_2$O	WFSS[2] +H$_2$O	UFSS +SGW[3]	UFSS +SAMD[4]	WFSS +H$_2$O	UFSS +SGW	UFSS +SAMD
Sulfate mg	936	1524	1230	6920	63	32	639
Calcium mg	670	640	1300	2640	-5	94	294
Potassium mg	190	170	220	100	-8	18	-47
Sodium mg	44	38	44	bdl[5]	-13	1	-100
Iron mg	9	bdl	57	-1520	-100	530	-16940
Manganese µg	bdl	bdl	890	390			
Zinc µg	3.6	3.3	200	650	-9	5360	18000
Barium µg	85	60	930	740	-29	990	770
Strontium mg	1.02	1.13	2.63	4.02	11	160	290
Aluminum mg	50	25	2.6	-540	-50	-95	-1170
Boron mg	2.85	3.97	16.0	12.1	39	460	325
Molybdenum µg	710	890	960	13	26	35	-98
Nickel µg	59	25	1540	1710	-57	2540	2830
Arsenic µg	130	140	5	bdl	15	-96	-100
Selenium µg	43	31	bdl	bdl	-28	-100	-100
pH range	10.4 – 10.8	10.2 – 10.3	5.8 – 6.7	3.7 – 3.9			

[1]UFSS – unweathered fixated scrubber sludge; [2]WFSS – weathered fixated scrubber sludge; [3]SGW – synthetic groundwater; [4]SAMD – synthetic acid-mine drainage; [5]bdl – below detection limit

Discussion

The mineralogical changes observed at the top of the FSS where calcite and gypsum are more abundant while hannebachite and ettringite decrease coincides with the mineral transformation described in reaction 2 above along with the carbonation of ettringite (Laperche and Traina, 1999):

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O + 3HCO_3^- \rightarrow$$

$$3CaCO_3 + 3Ca^{2+} + 2Al(OH)_3 + 3SO_4^{2-} + 3OH^- + 29H_2O \qquad [5]$$

The cores extracted where the FSS cap is at its maximum thickness range (>1.5 m) exhibited these mineralogical changes only within 4 cm of the top of the FSS. Assuming the rate of weathering is constant over the course of one year in order to account for seasonal fluctuations, then over the 15 year span of the caps' existence, the rate of FSS deterioration could be estimated to be occurring by an average of < 0.3 cm per year. The lack of a more aggressive deterioration by this process can be attributed to the 1 m layer of vegetated soil that effectively prevents sufficient dissolved oxygen from reaching the FSS and accelerating the rate of deterioration (as in equations [2] and [4]).

Although soil-moisture data indicate that short term desaturation may occur in refuse below the cap (Naylor et al., 2012), there is little mineralogical evidence at the base of the FSS cap to indicate deterioration from hannebachite to gypsum alteration. This is attributed to there being minimal oxygen available beneath the cap for reaction 2 to proceed sufficiently to generate similar concentrations of gypsum observed at the top of the FSS cap. Dissolution of hannebachite by reaction 3 is a more likely mechanism for eroding the base of the FSS layer, especially where the FSS is exposed to acidic water. Hannebachite dissolution should lead to increased proportions of the more stable phases identified in the FSS such as hematite, magnetite, quartz and mullite, but this was not observed, implying very little interaction with acidic waters that would increase hannebachite solubility. However, aqueous evidence does suggest that there is some mineral influence of the FSS chemistry on pore waters beneath the cap. As shown in figure 5 and table 3, pore waters beneath the FSS cap are characterized by containing predominantly calcium with virtually no magnesium in these pore waters which contrasts with the unsaturated zone in the soil layer on top of the FSS. The lack of magnesium ions in pore waters at the base of the FSS cap is attributed to the leaching of only calcium ions from lime, hannebachite and to a lesser degree, gypsum in the FSS with no discernible contributions from magnesium-bearing sources that might exist in gob, spoil or ponded ash underlying and adjacent to the FSS. The effect on the acidic gob aquifer Ca/Mg ratio in the vicinity of monitoring well 7 (MW7D) appears to be minimal (Table 3) due to the apparent low ratio of impacted pore water to aquifer volume. At an average depth of less than a meter below the cap base (Naylor et al., 2010), the gob aquifer is adequately close enough to the FSS base to undergo a noticeable major cation composition change if sufficient pore water leachate were to be mixed with the aquifer. However, the water chemistry trend at MW7 towards a more mixed Ca-Mg-Fe cation composition as shown in figure 5 is primarily attributed to a decreasing trend in soluble iron (Naylor et al., 2012) and is credited to diminishing pyrite oxidation under the less oxygenated conditions that now prevail in the gob beneath the cap.

The leaching experiments provide some corroborating information regarding how much influence FSS leachate has on aquifer chemistry. The Ca-Mg-Fe cation relationships shown in figure 5 were replicated in figure 6 so that the major cation

character for synthetic solutions plotted on either the Ca-Mg axis or the Ca-Fe axis, similar to the monitoring sites shown in figure 5. A synthetic AMD solution (SAMD), characterized as Fe-Ca-SO$_4$ water generated a pattern similar to MW7 after exposure to the FSS (Fig. 6) in which a minor increase in major cation composition towards more calcium was observed. According to the cumulative chemical changes shown in table 4, this appears to be the result of both calcium dissolution and iron precipitation. Individual daily samples collected from the FSS+SAMD contained calcium increases relative to the initial concentration that ranged from 25-61% and averaged 41%. This is believed to be the result of constant interaction of calcium-bearing minerals such as lime, hannebachite and gypsum with an acidic solution. As previously noted there appears to be little evidence that direct contact of the FSS material with the underlying acidic gob aquifer in the vicinity of MW7 has occurred. The results of a Mann-Kendall statistical trend analyses performed on data collected from MW7 did not find an increasing trend for calcium (Naylor et al., 2012), which would be expected from dissolution of calcium-bearing minerals. So even though continuous exposure of FSS to AMD in a laboratory setting appears to produce the same kind of major cation change observed in water chemistry data collected from monitoring sites, the means by which this change is generated are not the same.
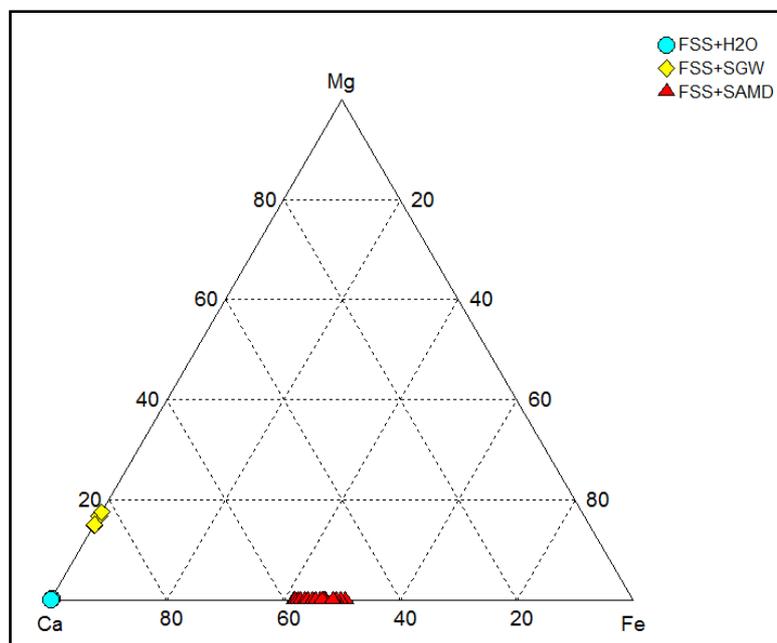

Figure 6. Ternary diagram for leaching experiments illustrating correlation of leachate chemistry with dominant cation in the system Ca-Mg-Fe. Legend defined in Table 4.

A synthetic groundwater (SGW) was used to represent leaching from water characterized by major ion composition of Ca-Mg-SO_4-HCO_3 which has been observed to develop in coal-mined spoil deposits in Indiana (Branam and Harper, 1994). The shallow lysimeters placed in the spoil cover overlying the FSS cap at MW7 collected a pore-water chemistry of similar character, with the dominant cations consisting of calcium and magnesium (Fig. 5: MW7SL3, MW8SL3). The leaching experiment of FSS with synthetic groundwater (FSS+SGW) produced a major cation chemistry that also plots along the Ca-Mg axis (Fig. 6). The total cumulative calcium leached with SGW was nearly double what was extracted with ultrapure H_2O, but only half of that extracted with SAMD (Table 4). These results suggest that there is some dissolution of mineral phases associated with the FSS by water of this composition, and since this would occur at the top of the FSS cap where perched water tables episodically occur (Naylor et al., 2012), the likelihood is quite high. However, as seen from mineralogical examination of the FSS material, the rates of reactions appear to be extremely slow due to the limited depth of mineral alterations observed.

In contrast, the Ca-SO_4 water chemistry observed at MW8 was duplicated by leaching FSS with ultrapure water (Fig. 6, FSS+H_2O). The leaching tests show that the prevalent cation character of buffered aquifer solutions in materials associated with this site (gob, spoil) are not appreciably altered from interactions with FSS (Fig. 6, FSS+SAMD and FSS+SGW) and that only weakly to unbuffered aquifer solutions will produce a Ca-SO_4 water chemistry. This would then imply that the prevalent Ca-SO_4 water chemistry of the aquifer in the ponded ash beneath the cap at site MW8 is the result of a lack of any strong buffering or attenuating capacity within the ponded ash materials The inference is that the ponded ash fill does not contain sufficient reactive mineralogy differing from that of the FSS cap to prevent the water table from acquiring the characteristics of FSS leachate.

A similar finding was determined from the relationship between trace components. Boron is a highly conservative component exclusively attributed to CCR leaching in this particular setting (Branam et al., 1999). Molybdenum is similarly derived exclusively from CCR leaching but becomes much less soluble in the presence of iron. Manganese is believed to be primarily derived from either carbonate or sulfide minerals, but has low solubility in high pH solutions that are associated with lime-fixed scrubber sludges. Using this knowledge, a ternary diagram was constructed that indicates: (1) which sampling sites are located where FSS leachate is most prevalent, characterized by a boron-molybdenum association (Fig. 7A – MW8, MW8-SL9, MW7-SL8; 7B – UFSS+H_2O), (2) the result of FSS leachate reacting with AMD groundwater, shown by a boron-manganese trend (Fig. 7A – MW7D; 7B - SAMD), and (3) where minimal FSS leaching has occurred, characterized by no boron or molybdenum (7A – MW7-SL3; 7B – initial SAMD). In summary, the most likely place to encounter FSS leachate is either in

the unsaturated zone immediately beneath the FSS layer, or in an aquifer with minimal soluble minerals capable of attenuating or masking the FSS leachate chemistry, such as occurs in the ponded ash aquifer beneath the FSS cap at the Pike County reclamation site in Indiana. Given that AMD has a strong potential to significantly increase the solubility of several components sequestered in FSS (Table 4: zinc, barium, strontium, boron, and nickel), the lack of significant increases in the concentration of these components iin water samples from the AMD aquifer beneath the FSS cap, nor any noticeable mineralogical changes at the base of the FSS cap is evidence that there is minimal interaction between the FSS and the AMD aquifer at this reclamation site. The net result is that the cap is only undergoing deterioration at the top, and only then at a very slow rate.
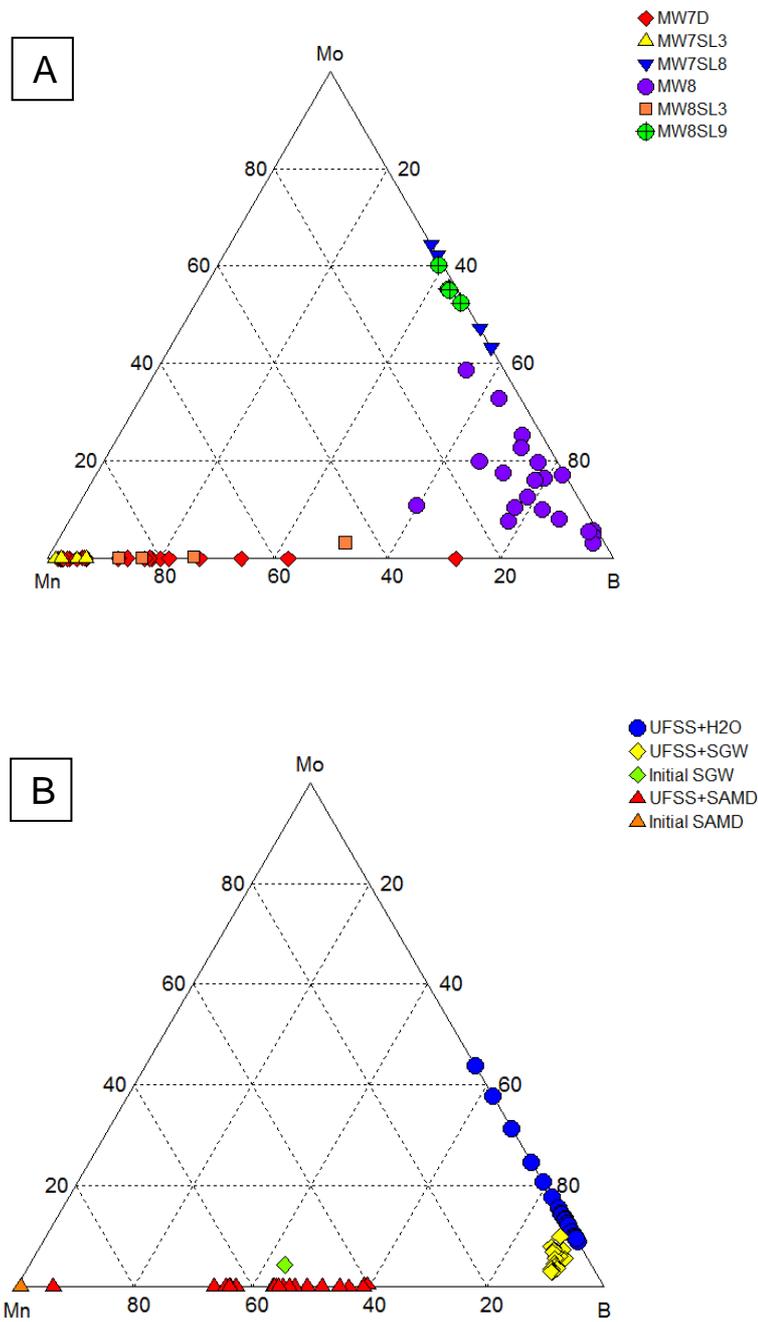
Figure 7 Ternary diagrams showing associations of boron, manganese and molybdenum for (A) saturated and unsaturated zones at monitoring sites MW7 and MW8; and (B) leaching of unweathered FSS fragments with water and synthetic solutions. Legend for graph B defined in Table 4.

Conclusions

Flue-gas desulfurization sludge, generated in an oxygen-inhibited stack gas scrubber producing a predominantly calcium sulfite material, was combined with lime and fly ash and placed over coal refuse and coal-ash fill at a reclamation site as a low-permeability barrier in 1996. After 15 years of emplacement an evaluation of mineralogical changes in the barrier and water chemistry monitoring of the unsaturated zones above and below the barrier along with underlying aquifers was undertaken to determine the degree of deterioration that has occurred to the barrier. Mineral alterations detected within a few centimeters of the top of the fixated scrubber sludge (FSS) cap indicate an extremely slow, oxidative reaction of hannebachite to gypsum is occurring. The base of the FSS cap is not undergoing the same hannebachite oxidation reaction due to a lack of dissolved oxygen reaching this region of the cap. Hannebachite dissolution is possible as an alternative weathering process at the base of the cap but because of the low solubility of hannebachite the deterioration of the FSS at this location will be slow. Leachate studies indicate that under constant exposure to AMD, dissolution of hannebachite would be accelerated, and the release of sequestered components would significantly increase in the AMD aquifer. The lack of observable elevated concentrations in the underlying AMD aquifer for the COPCs found in FSS are evidence that there has been insufficient contact of the cap with AMD to allow significant concentrations of COPCs to develop. Unsaturated zone water chemistry shows leachate from the FSS barrier occurring at the base of the cap but mineralogical changes are neither sufficient to alter the cap mineralogy nor allow the release of significant quantities of FSS-derived components to manifest a change in the underlying acidic aquifer. The results of this study regarding the degree of deterioration after a 15 year period suggest that the integrity of the 1.5+ meter-thick FSS cap is likely to continue for several more decades under the current conditions to which it is exposed. Under the conditions in which the FSS barrier was placed at an abandoned mine site in southwestern Indiana, this has proven to be a beneficial capping technique for reclaiming an abandoned mine-land site that contained exposed acid-generating coal refuse. This research indicates that mineralogical characterization and leaching experiments with synthetic groundwater comparable to ambient conditions can be important tools when assessing the feasibility of CCR emplacement.

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