

CHARACTERIZATION OF COAL COMBUSTION BYPRODUCTS FIFTEEN YEARS AFTER EMPLACEMENT IN AN ABANDONED MINE LAND SITE¹

L.C. Martin², T.D. Branam, S. Naylor, and G.A. Olyphant

Abstract. Coal combustion byproducts (CCBs) have potential as structural fill and capping materials in abandoned mine land (AML) reclamation because of their acid-neutralization capacity. However, the potential for these materials to leach constituents of potential concern (COPCs) into groundwater hinders their use by AML program managers. In 1996, the Midwestern AML site in southwestern Indiana was reclaimed using fixated scrubber sludge (FSS) cap composed of flue gas desulfurization sludge, fly ash, and lime. The cap was placed over a pyritic refuse deposit, an unreclaimed spoil ridge, and highwall lakes that were filled with ponded ash. Post reclamation analyses of groundwater chemistry showed that alkalinity and pH levels increased below the cap, indicating that the CCBs helped to neutralize the preexisting acid mine water. Concentrations of COPCs initially increased below the cap, but dropped back to near or below pre-reclamation values over the past 10 years. For example, boron that initially increased to 13,000 µg/L decreased to pre-reclamation values (300 µg/L) with time. X-ray diffractometry was conducted on core samples containing FSS and ponded ash collected from the site in 2011 to identify mineralogical changes since emplacement. Oxidation of hannebachite (calcium sulfite hemihydrate) produced gypsum and calcite in the upper 1 to 4 cm of the 1 to 3 m thick FSS cap. No oxidation zone was observed at the bottom of the cap. Sediment cores of ponded ash reveal little change with depth, possibly because leaching had already occurred as a result of stockpiling at the power plant. The results of this study indicate that FSS did contribute COPCs, including boron, molybdenum, chromium, and arsenic, to groundwater for short periods and in the immediate vicinity of emplacement. Nevertheless, a lack of significant oxidation and declining trends in groundwater contamination represent long-term favorable outcomes for use of CCBs in AML reclamation.

Additional Key Words: Flue gas desulfurization sludge, fly ash, mineralogy, and reclamation.

¹ Paper was presented at the 2012 National Meeting of the American Society of Mining and Reclamation, Tupelo, MS *Sustainable Reclamation* June 8 – 15, 2012. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502

² Luke C. Martin, Geological Sciences, Indiana University, 1001 E 10th St, Bloomington, IN 47405, Tracy D. Branam, Research Scientist; Shawn Naylor, Director; and Greg A. Olyphant, Research Affiliate/Professor, Indiana Geological Survey Center for Geospatial Data Analysis, 611 N. Walnut Grove Ave., Bloomington, IN 47405.

Proceedings America Society of Mining and Reclamation, 2012 pp 346-358

DOI: 10.21000/JASMR12010346

<http://dx.doi.org/10.21000/JASMR12010346>

Introduction

Production of coal combustion byproducts (CCBs) from coal-fired power plants has steadily increased for decades causing concern over the disposal and beneficial use of CCBs. Some beneficial uses of CCBs have been questioned because of their potential to contribute constituents of potential concern (COPCs) to the environment. The Environmental Protection Agency (EPA) suspended active participation in the Coal Combustion Products Partnership (C2P2) program in 2010 while they reviewed CCB contaminant concerns. Since the establishment of the EPA's Acid Rain Program in 1990, SO₂ emissions from coal-fired generators were reduced by 51%, but the reduction of emissions inevitably increases solid waste production (EPA, 2010). Use of the solid waste created during coal combustion remains of pivotal importance in the effort to minimize impacts of coal-fired power plants. In 2009, U.S. CCB production was over 125 million tons, and more than 44% was used in various beneficial applications such as concrete and gypsum products, structural fill, and waste stabilization; 12% of total production was used in mining applications (ACAA, 2011), some in reclamation.

Coal combustions byproducts are used in abandoned mine land (AML) reclamation because of their low costs, availability, and acid-neutralization capacity (Sajwan et al., 2006). In 1996 one AML site in southwestern Indiana, the Midwestern site (Fig. 1), was reclaimed in part by applying a fixated scrubber sludge (FSS) cap (previously called Poz-o-Tec) that was composed of flue gas desulphurization sludge (FGD), fly ash, and lime. One to three meters of capping material were placed over 1) a central pyritic refuse deposit (gob) that generates acid-mine drainage (AMD), and 2) adjacent highwall ponds filled with ponded ash (a mixture of bottom ash and fly ash). Subsequent hydrologic monitoring indicated that the FSS successfully reduced recharge of oxygenated water into the underlying pyritic refuse (Naylor et al., 2012).

In this study, a mineralogical analysis of the FSS and ponded ash was conducted to determine if geochemical alterations occurred since reclamation and to assess the potential of CCBs to leach COPCs into the groundwater after emplacement. Water samples were analyzed to see how much of an effect the CCBs may still be having on groundwater chemistry. Mineralogical changes following emplacement paired with groundwater chemistry should shed light on the relative stability of FGD-ash mixtures, as discussed by Lecuyer et al. (1996). Mineralogical

stability of the FSS cap is also important for understanding any negative effects of different ash mixtures versus their advantages in mining reclamation, storage/disposal, and other applications.

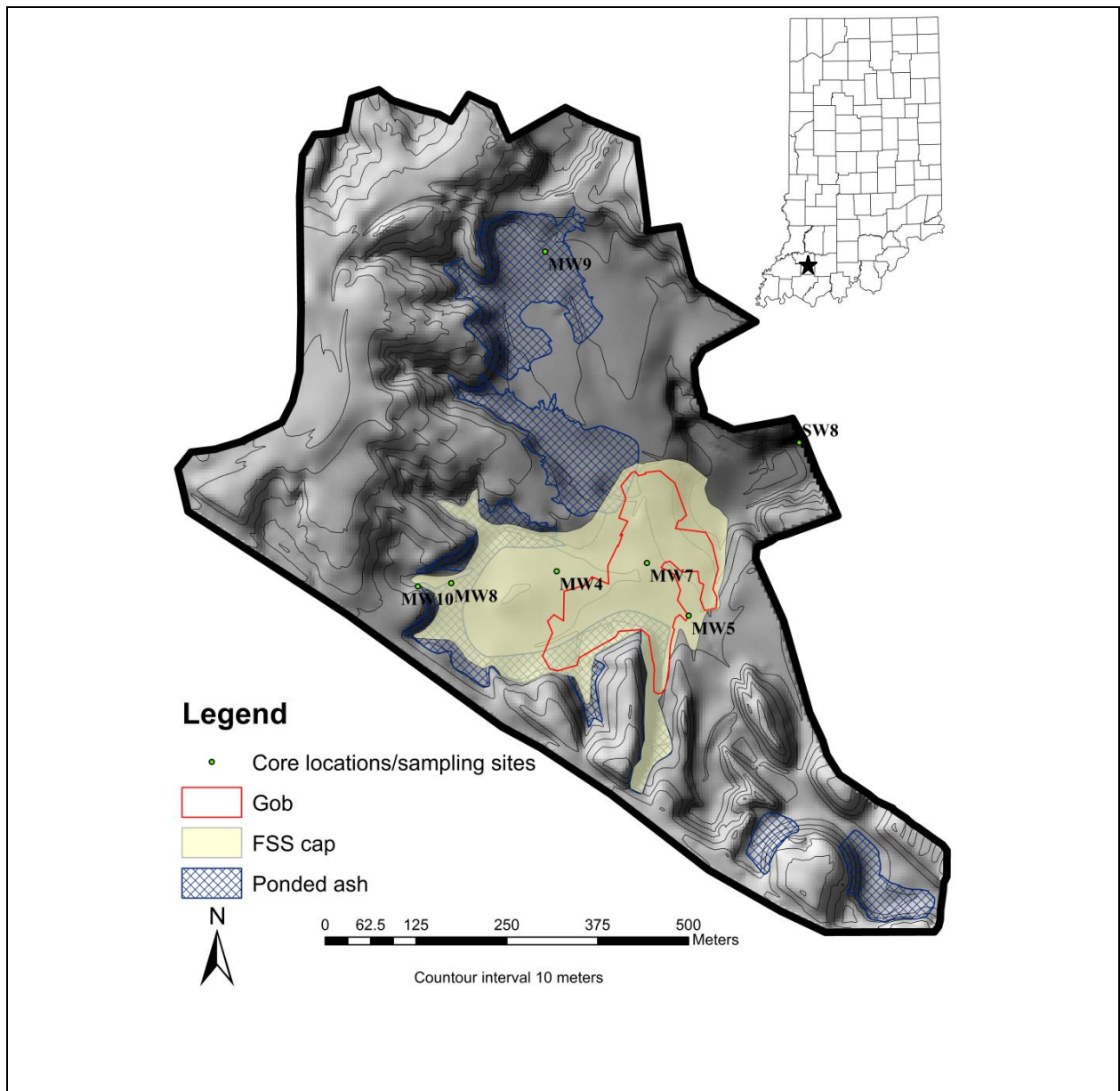


Figure 1. Location and site map of Midwestern showing the monitoring well (MW)/core location, outlet (SW8), and areas covered by FSS, ponded ash, and gob.

Methods

Solids

In March of 2011, eight 4 to 8-cm-diameter cores were collected at six sites at Midwestern using a Geoprobe[®] (Fig. 1). Each core represented a different type of vertical sequence of CCBs

and, where applicable, the underlying coal refuse deposits (Table 1). Samples were extracted from the cores at different depths (Table 2 and Fig. 2) to observe any vertical or zonal mineralogical changes in the FSS or ponded ash. All the extracted samples were dried in an oven at 65°C for 24 hours and stored in airtight containers cf., Phillips et al. (2002). One sample of FSS collected from the Petersburg Generating Station (the source of FSS and ponded ash used at Midwestern) was mixed with deionized water and cured for 28 days to allow the pozzolonic reaction to complete. Prior to mineralogical analysis, the samples of ponded ash were first ground in a steel ring mill and thereafter with a Retsch Muhle motorized agate mortar and pestle mill, using acetone as a wetting agent. FSS samples were ground only with the agate mortar and pestle.

Table 1. Shows depth and thickness of materials recovered from cores at Midwestern. Fill material is made up of topsoil and overburden available onsite

Site	Depth (m)	Thickness (m)	Material
M4	0 - 1.0	1.00	Fill
	1.0 - 2.25	1.25	FSS
	2.25 - 4.0	1.75	Gob
M5	0 - 1.43	1.43	Fill
	1.43 - 1.88	0.45	FSS
	1.88 - 3.66	1.78	Spoil
M7	0 - 1.0	1.00	Fill
	1.0 - 3.63	2.63	FSS
	3.63 - 6.0	2.37	Gob
M8	0 - 1.40	1.40	Fill
	1.40 - 3.23	1.83	FSS
	3.23 - 6.0	2.77	Pond ash
M9	0 - 4.07	4.07	Fill
	4.07 - 7.30	3.23	Pond ash
M10	0 - 1.32	1.32	Fill
	1.32 - 3.96	2.64	FSS
	3.96 - 5.0	1.04	Pond ash

Mineralogical characterization was determined solely by X-ray diffraction (XRD) with Cu K α radiation and a 2 θ 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 α Al₂O₃ as an internal reference to compare with the other peaks in the pattern allowing for

quantitative analysis. The internal reference also allows for quantification of the amorphous component of the pattern.

Mineralogical analysis was paired with X-ray fluorescence (XRF) for bulk chemical analysis. Samples were prepared for XRF by weighing out 5-6g of sample and heating for one hour at 1000°C to remove carbon (LOI). An X-Press hydraulic press was used to compress the samples to 20 tons/in². Samples were then sent to University of Cincinnati and analyzed on a 3070 wavelength dispersive X-ray fluorescence spectrometer. Major elements and trace elements analyzed were Ba, Cr, Co, Cu, Mo, Nb, Ni, Pb, Rb, Sr, U, Th, V, Y, Zn, and Zr to concentrations in the ppm range. Si, Fe, Al, Ca, Na, K, Mg, Mn, P, and Ti values were recorded as oxides in weight percentages.

Water

Samples of groundwater were collected at wells installed in the core locations (Fig. 1) quarterly for 1 year before and 5 years after reclamation. Samples were collected only intermittently between 2001 and 2011, but quarterly sampling recommenced in 2011. A sonde was used to analyze samples in the field for temperature, pH, dissolved oxygen, specific conductivity, and Eh and were then filtered, acidified, and refrigerated pending analysis. Ion concentrations in water samples were analyzed using atomic absorption spectroscopy (AAS) for Fe, Mn, K, Mg, Ca, Na, As, Cr, Cd, Mo, Ni, and Se. Boron and Al concentrations were obtained from Astbury Water Technology, Inc. using inductively coupled plasma optical emission spectrometry (ICP-OES). Ion chromatography (IC) was used to determine sulfate and chloride concentrations.

Results and Discussion

Minerals identified in the FSS were hannebachite, gypsum, mullite, quartz, hematite, magnetite, calcite, and ettringite, and mineraloids (Table 2). Pondered ash contained feldspar, mullite, hematite, magnetite, quartz, cristobalite, diopside, calcite, and amorphous material.

There may be unidentified mineral phases due to the large unidentifiable component that the model in TOPAS attributes to the generic amorphous component commonly referred to as mineraloids (minerals having no crystal structure to diffract X-rays). The amount of gypsum is an order of magnitude greater at the soil cap-FSS boundary and the amount of calcite is high as

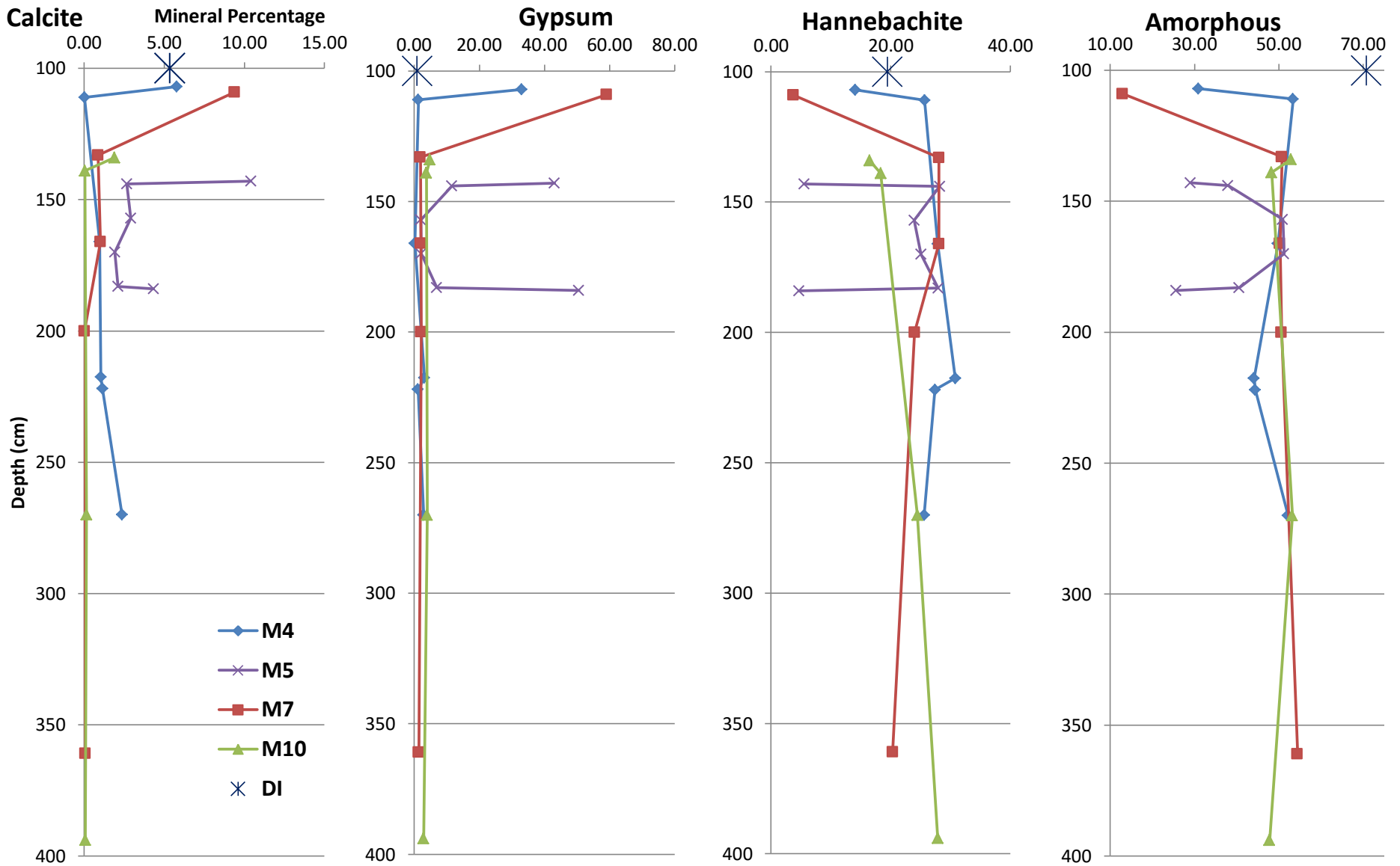


Figure 2. Graph showing vertical change in mineral percentages in FSS. DI refers to a sample of FSS preserved with deionized water, an example of FSS prior to emplacement.

well because of oxidation and hydration (Equation 1). This increase in gypsum and calcite is accompanied by a comparable decrease in hannebachite and amorphous material as oxidation and hydration occur (Fig. 2). Mineralogical data from cores M4 and M5 suggests that there is a change in mineralogy with depth occurred only in the upper 1 to 4 cm of the FSS cap (Fig. 2 and 3 and Table 2). The increase in gypsum may be accounted for by oxidation of hannebachite to gypsum in the top of the FSS cap as shown in Equation 1.

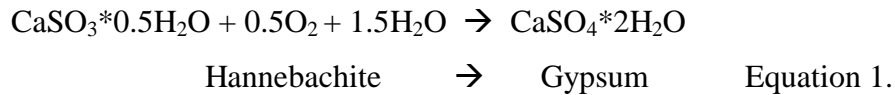


Table 2. Shows percentages of mineral phases identified in FSS (mineraloids are represented by the amorphous component).

Core-depth	Amorphous	Calcite	Ettringite	Gypsum	Hannebachite	Hematite	Magnetite	Hem + Mag	Mullite	Quartz
M4-107	30.99	5.76	0.00	33.05	14.03	3.31	1.26	4.58	7.49	4.11
M4-111	53.41	0.03	0.56	1.35	25.69	3.13	1.10	4.23	8.88	5.85
M4-166	49.76	0.95	0.75	0.14	27.86	3.49	0.89	4.38	13.48	2.71
M4-217.5	44.10	1.04	1.89	3.09	30.81	4.13	0.15	4.28	10.90	3.89
M4-222	44.41	1.14	0.69	1.15	27.38	3.65	0.98	4.63	11.80	8.83
M4-270	52.18	2.35	0.58	2.91	25.63	3.71	0.99	4.70	8.68	3.00
M7-109	13.00	9.38	0.00	59.13	3.73	2.19	1.71	3.90	5.99	4.89
M7-133	50.74	0.85	0.64	1.94	28.05	3.54	1.18	4.71	9.86	3.23
M7-166	50.30	1.00	0.68	2.06	28.04	3.31	1.80	5.11	8.80	4.01
M7-200	50.66	0.01	0.63	2.11	24.00	3.78	1.10	4.88	13.15	4.58
M7-361	54.49	0.06	1.14	1.46	20.35	3.20	1.70	4.90	14.26	3.36
M10-134	52.95	1.89	0.45	4.90	16.49	2.71	1.96	4.68	9.09	9.56
M10-139	48.26	0.04	0.40	3.79	18.31	3.06	1.85	4.91	13.96	10.33
M10-270	53.19	0.14	0.94	3.94	24.49	3.68	0.93	4.60	9.90	2.83
M10-394	47.81	0.08	1.00	2.91	27.90	3.78	0.94	4.71	14.23	1.36
M5-143	29.11	10.41	0.00	43.01	5.49	0.00	0.00	0.00	8.65	3.33
M5-144	38.00	2.66	0.38	11.64	28.18	3.54	0.20	3.74	13.16	2.25
M5-157	50.96	2.91	0.66	1.98	23.95	3.48	1.80	5.28	10.68	3.60
M5-170	51.24	1.90	0.51	2.14	25.06	3.38	1.51	4.89	10.70	3.56
M5-183	40.59	2.10	0.54	6.91	27.91	3.10	0.84	3.94	14.84	3.16
M5-184	25.66	4.33	0.00	50.51	4.65	0.86	1.45	2.31	7.26	5.28

The conversion of hannebachite to gypsum is very important because of the higher solubility rate of gypsum in water (2.1 g/L compared to 0.054 g/L for hannebachite at room temperature; Lee et al., 2007). Core M5 is an exception because it shows an increase in gypsum and calcite at the bottom and top of the core. This is because the FSS cap is much thinner at M5, which is near the edge of the FSS (Fig. 1). The thinner part of the cap may allow more water and oxygen to

react with the edge of the FSS cap. Lack of oxidation at the bottom of all other cores provides evidence that the FSS cap is preventing further oxidation of the underlying pyritic refuse. There does not appear to be any significant change in mineralogy laterally within the FSS or ponded ash (Fig. 2). The ponded ash at M8 and M9 showed little to no variation with depth.

Possible trace element contributions from FSS and ponded ash used at Midwestern were analyzed by ATEC Associates for major components and trace elements from 30-day leaching tests. ATEC reported that the ponded ash leached larger amounts of trace elements than the FSS (Fig. 4) (Branam et al., 1999). Bulk chemistry data from XRF analysis shows that ponded ash contains higher concentrations of many trace elements, but little variation vertically or laterally (Fig. 3 and 5). Following reclamation, concentrations of barium, boron, chromium, and molybdenum immediately increased. Concentration of COPCs was greatest at MW7 because it was screened within the refuse pile underlying the FSS (Fig. 1).

Boron and Mo concentrations increased dramatically after reclamation, indicating that they are leached from CCBs (Fig. 4 and 6). Boron increased in groundwater after reclamation more than any other trace element, suggesting boron is the best indicator of CCB leaching (Fig. 6). Molybdenum concentrations had the largest proportionate increase (nearly two orders of magnitude) following reclamation (Fig. 6). This suggests that CCBs contribute most of Mo to the groundwater system, but is not as useful an indicator of

As a result of CCB leaching with abundant Fe, relatively insoluble ferrous molybdate absorbs Mo from aqueous solutions and thus exerts a significant control on Mo concentration (Hem, 1997). Molybdenum attenuation by this method is apparent at MW7, which has high levels of Fe coupled with low Mo and high B levels (Fig. 6 and 7). Owing to formation of ferrous molybdate in the presence of Fe, Mo is not as good an indicator of leaching as B.

Two years after reclamation, trace element and COPC concentrations decreased to near pre-reclamation values or below, with the exception of boron at M8 (Fig. 6). Acidity, Fe, and Al levels decreased significantly following reclamation owing to reduced oxygenation in the pyritic refuse. Alkalinity and pH increased significantly at MW7 and the outlet (Fig. 7). It is difficult to quantify the contribution of some COPCs from CCBs, most notably arsenic, in groundwater owing to their presence in CCBs and AMD; however, there is an overall decrease of COPCs at Midwestern (Fig. 8).

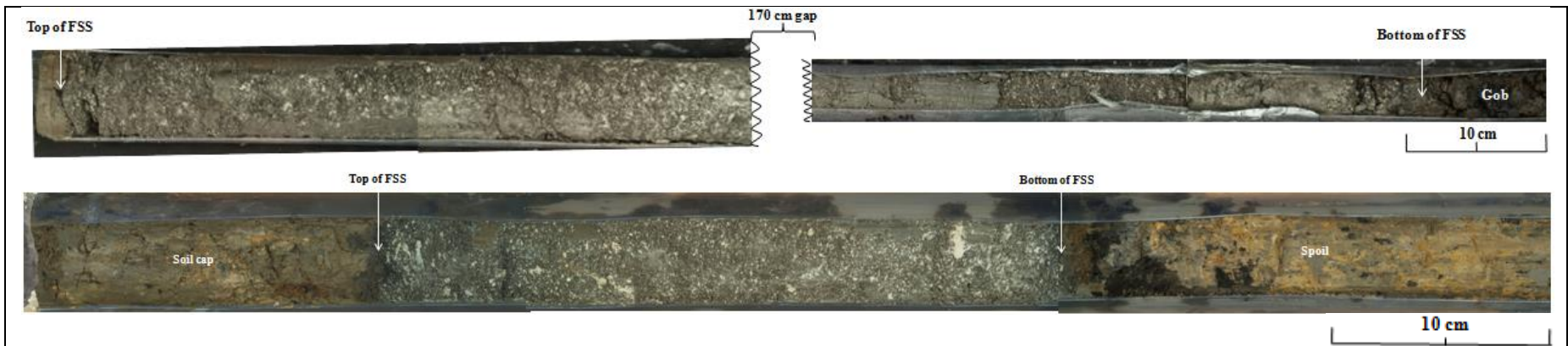


Figure 3. Photographs of cores M7 (top) and M5 (bottom). Core M7 has little to no reaction zone at the top of the FSS cap with less gradational color change and no reaction zone at the bottom in contact with the gob. Color differences throughout the core appear localized from spoil/fill material in contact with the FSS. The core liner size had to be decreased because of expansion in the borehole during drilling. Part of the core was removed from the photo. Core M5 displays a well-defined reaction zone at the top of the FSS cap with a distinct color change. Note the similar reaction zone at the bottom of the FSS cap.

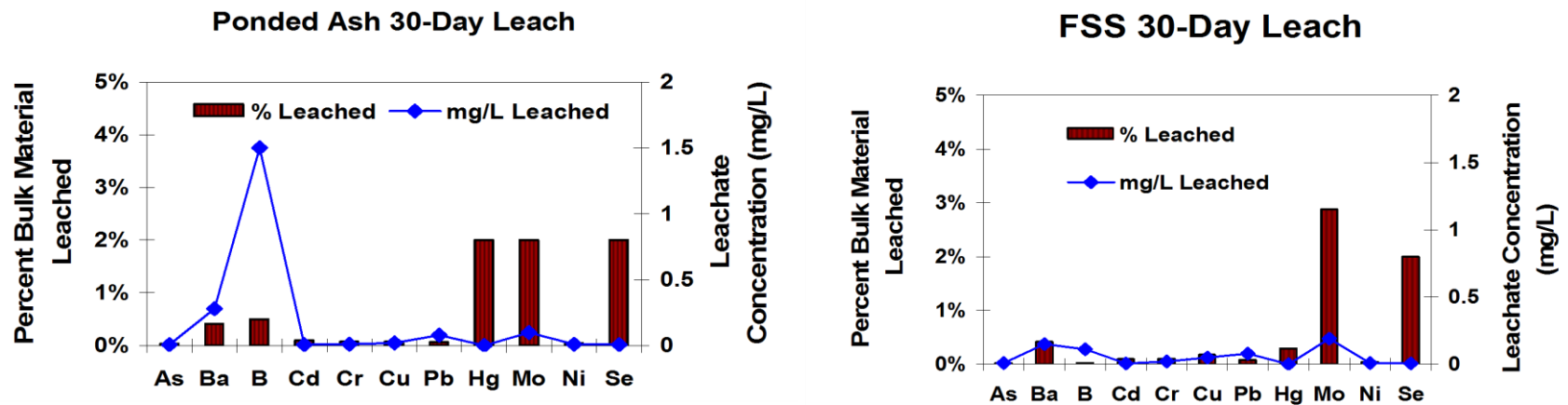


Figure 4. Graphs showing concentration of trace elements leached from FSS and ponded ash during 30-day leaching experiments (Branam et al., 1999).

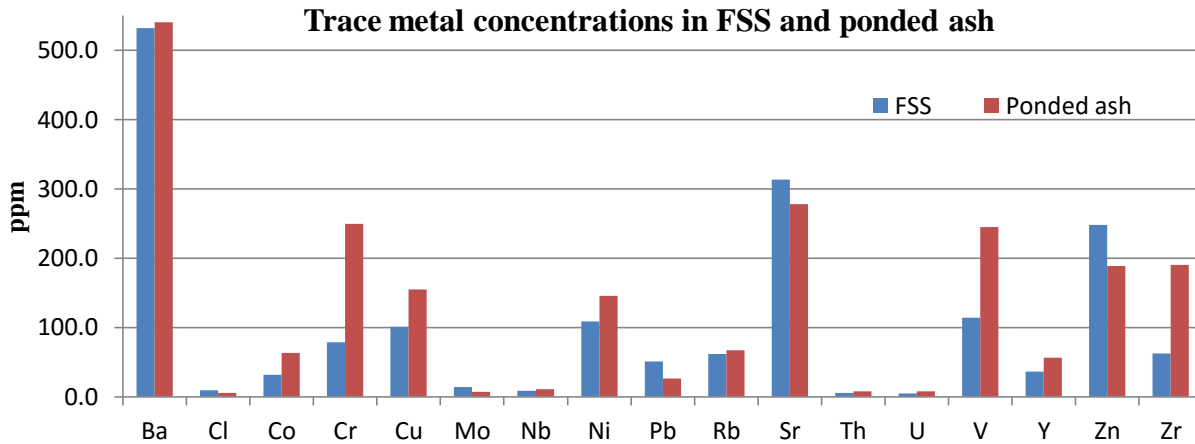


Figure 5. Graph showing average concentrations of trace elements in FSS and ponded ash based on XRF analysis.

Conclusions

At the Midwestern AML site in southwestern Indiana, the lack of change in mineralogy in the coal combustion byproducts used as capping material and structural fill indicates that leaching of COPCs was minimal in the 15 years following reclamation. Ponded ash was not an initial concern because of the length of time the ash was exposed to weathering prior to use at the site. It should, therefore, be rather nonreactive. However, FSS contained relatively fresh fly ash and was of greater concern. A large reaction front propagation rate for Equation 1, based on the size of the reaction zones, would be 1/3 cm/yr, but could be as low as 1/15 cm/yr as shown at M4.

Previous research at Midwestern (Naylor et al., 2012) indicated that the aquifer with the pyritic refuse is now confined by the FSS, surface run-off increased, and recharge to the refuse aquifer decreased. This study supports the conclusions that FSS is an impermeable, oxidation-reducing, and alkalinity-generating material. Leachate studies, Midwestern water chemistry, and bulk chemistry all show that water from FSS and the ponded ash at Midwestern is not concentrated enough in COPCs to be of concern. The positive influences of the FSS cap outweigh the minor amount of leaching that took place immediately following reclamation.

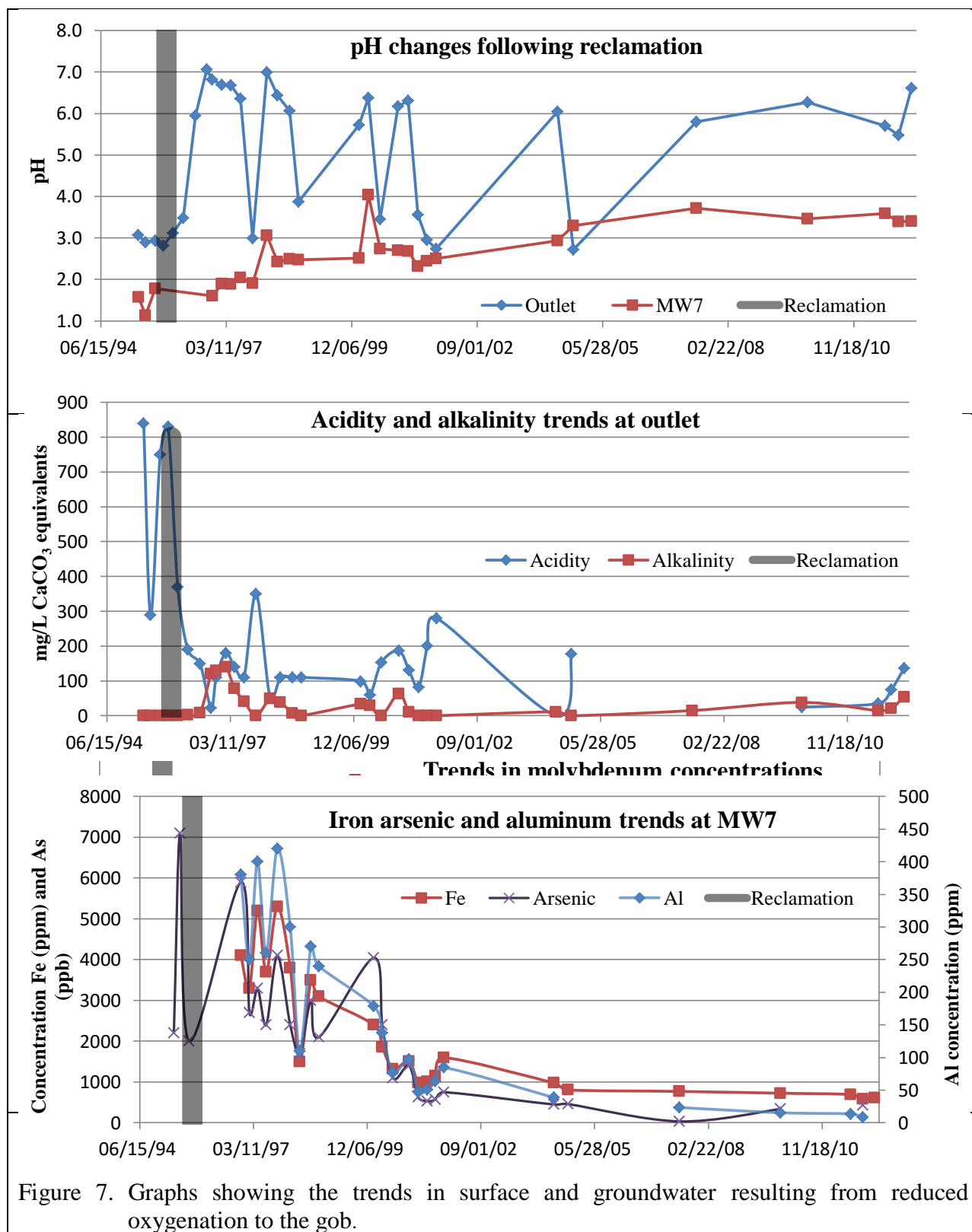
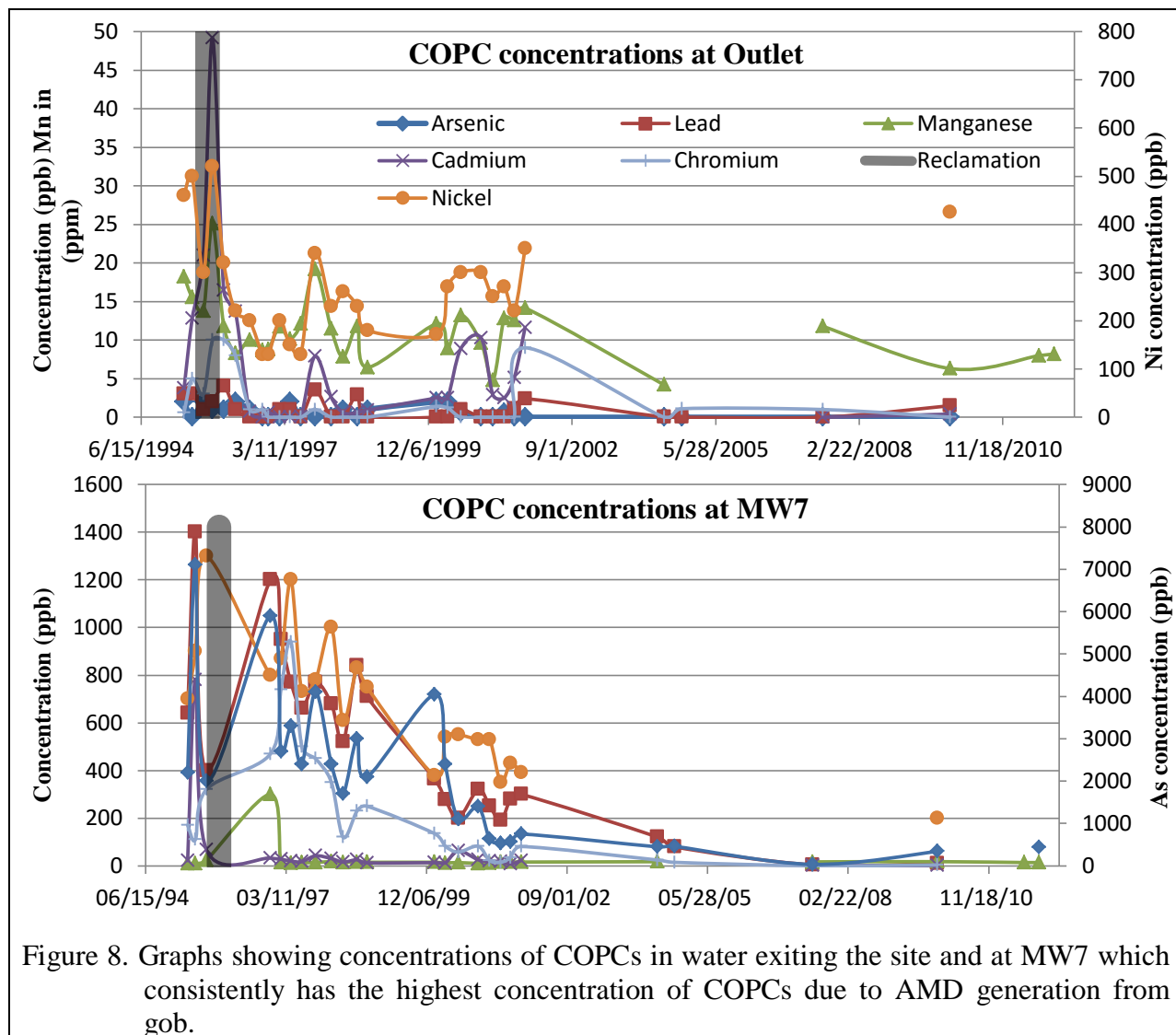


Figure 7. Graphs showing the trends in surface and groundwater resulting from reduced oxygenation to the gob.



Literature Cited

- American Coal Ash Association (ACAA), 2011, Revised 2009 CCP Production & Use Survey Report, <http://www.acausa.org/associations/8003/files/2009_Production_and_Use_Survey_Revised_100511.pdf> Accessed October 6, 2011.
- Branam, T.D., R.T. Smith, M.V. Ennis, J.P. Rybarczyk, and J.B. Comer, 1999, Trace element partitioning in ground water at an abandoned mine-land site reclaimed with coal combustion products: Proceeding of International Ash Utilization Symposium: Materials for the next millennium (Lexington, KY, October 18-20, 1999).
- EPA, 2010, The Clean Air Act - Highlights of the 1990 Amendments, <http://www.epa.gov/air/caa/CAA_990_amendments.pdf> Accessed September 29, 2011.

- Hem, J.D., 1977, Reactions of metal ions at surfaces of hydrous iron oxide: *Geochimica et Cosmochimica Acta*, v. 41, p. 527-538. [http://dx.doi.org/10.1016/0016-7037\(77\)90290-3](http://dx.doi.org/10.1016/0016-7037(77)90290-3).
- Laperche, V., J.M. Bigham, 2002, Quantitative, Chemical, and Mineralogical Characterization of Flue Gas Desulfurization By-Products: *Journal of Environmental Quality*, v. 31, p. 979-988. <http://dx.doi.org/10.2134/jeq2002.0979>.
- Lecuyer, I., S. Bicocchi, P. Ausset, and R. Lefevre, 1996, Physico-Chemical Characterization and Leaching of Desulphurization Coal Fly Ash: *Waste Management and Research*, v. 14, p. 15-28. <http://dx.doi.org/10.1177/0734242X9601400103>.
- Lee, Y.B., J.M. Bigham, W.A. Dick, F.S. Jones, and C. Ramsier, 2007, Influence of Soil pH and Application Rate on the Oxidation of Calcium Sulfite Derived from Flue Gas Desulfurization: *Journal of Environmental Quality*, v. 36, p. 298-304. <http://dx.doi.org/10.2134/jeq2006.0050>.
- Naylor, S., T.D. Branam, and G.A. Olyphant, 2012, Physico-chemical assessment of a fixated flue-gas desulfurization sludge cap emplaced along with other coal-combustion residues to abate acid mine drainage: *Journal of Contaminant Hydrology*, v. 132, p. 37-48. <http://dx.doi.org/10.1016/j.jconhyd.2012.01.012>.
- Phillips D.H., B. Gu, D. B. Watson, and Y. Roh, 2002, Impact of Sample Preparation on Mineralogical Analysis of Zero-Valent Iron Reactive Barrier Materials: *Journal of Environmental Quality*, v. 32, p. 1299-1305. <http://dx.doi.org/10.2134/jeq2003.1299>.
- Sajwan K.S., T. Punshon, J.C. Seaman, and A.K. Alva, 2006, *Coal Combustion Byproducts and Environmental Issues*: New York, Springer Science-Business Media, p. 3-20. http://dx.doi.org/10.1007/0-387-32177-2_1.