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Geochemical characterization of engineered coal-combustion byproducts (CCBs): Occurrence and mobility of trace elements, implications for interactions with acidic and ambient groundwater

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HIGHLIGHTS

- Four morphologic types of amorphous phase and their compositions were determined.
- Most trace elements are contained in the amorphous phase by sequential extractions.
- Bo and Cu have the highest mobility, while Ni and As have the lowest mobility in FSS.
- Little weathering has occurred at the base of FSS where in contact with coal refuse.

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ABSTRACT

Fixed scrubber sludge (FSS), is a coal-combustion byproduct composed of flue gas desulphurization sludge, fly ash, and quick lime. FSS has potential usages as structural fill and capping materials in mine land reclamation because of its low permeability and acid-neutralization capacity. Sediment cores extracted from an abandoned mine land reclamation site where FSS was used as a hydrologic barrier to groundwater recharge were analyzed in an effort to quantify the chemical phases (both primary and secondary) that constitute the FSS, and to evaluate any evidence of weathering that has occurred during the 18 years since emplacement. The primary solid phase is amorphous spheroids. Four different types were identified and their quantitative compositions were obtained, with SiO_2, Al_2O_3, and FeO being the primary components. Of special concern was the occurrence and mobility of trace elements within the solid phases. Sequential extractions using different chemical reagents were conducted to analyze the concentrations of As, B, Ba, Cd, Cr, Cu, Ni, Pb, and Zn in different fractions as indications of mobility. The highest concentration of the trace elements was contained in the residual fraction, which is consistent with the amorphous spheroids being very resistant to chemical weathering. The results also suggest that the mobility of the trace elements decrease in the following order: B, Cu > Cd, Zn, Pb, Cr > Ba > Ni > As. Comparison of samples collected from the weathered edges and unweathered portions of the FSS layer reveal that a more aggressive weathering environment exists at the upper boundary of the FSS, where it is in contact with oxygenated soil water. The quantitative chemical compositions, distribution of trace elements, as well as evidence of how trace elements are released provide background data for the development a reactive transport model to simulate long-term effects of placing FSS in the natural environment; and particularly in areas that are being subjected to abandoned mine land reclamation.

1. Introduction

The amount of coal combustion byproducts (CCBs) derived from power plants has increased during the past decades, because coal remains one of the world's primary energy sources. In 2014, more than 129 million tons of CCBs were generated in the United States, but only 48% were recycled or reused due to regulatory uncertainty and public concerns regarding health risks [1]. Many previous studies have been conducted on the physical and chemical properties of coal combustion byproducts [2–15]. Much attention has been placed on the morphology and mineralogy of coal ash as

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determined by X-ray diffraction (XRD) and scanning electron microscope (SEM) [11–14]. The minerals contained in CCBs are well studied and include quartz, mullite, magnetite, hematite, and ettringite. However, the amorphous spheroids within CCBs are less well understood. Sokol et al. [12] employed electron microprobe analysis to determine that the ferrospheres in their study consist of Fe_2O_3 (65–80 wt.%), CaO (2–8 wt.%), MgO (2–8 wt.%), SiO_2 (3–10 wt.%), and Al_2O_3 (1.5–4 wt.%). Ward and French [15] used quantitative XRD in their analysis of amorphous solids. They determined the chemical composition by subtracting the inferred chemistry of the minerals from the total ash. Their results showed that SiO_2 (43–70 wt.%), Al_2O_3 (16–30 wt.%), and Fe_2O_3 (3–18 wt.%) were the major components in amorphous phase.

Numerous leaching studies have also been performed to evaluate the mobility potential of toxic elements contained in CCBs. Kost et al. [6] analyzed 59 CCB samples from various locations and their leaching experiments using deionized water and dilute acetic acid revealed measurable concentrations of several trace elements, including Ag, As, Ba, Cd, Cr, Hg, Pb and Se in the leachate, but the concentrations were below drinking water standards. Praharaj et al. [16] used local rainwater to conduct leaching experiments on fly ash derived from bituminous coals in Orissa, India. Several trace elements that are known to exist in the study area, including Cd, Co, Cr and Ni, did not leach out at all, but total concentrations of As, Mn and Mo exceeded the World Health Organization (WHO) recommended values for drinking water, and concentrations of Fe, Mn and As were higher than the maximum allowable concentrations set by the US Environmental Protection Agency (USEPA). Fytianos and Tsaniklidi [17] conducted leaching tests of fly ash using liquids with pH of 4, 8, and >10. Their results showed that all ash samples exhibited strong alkaline reaction. Ca and Cd exhibited maximum mobility, followed by Pb and Cr, while the least leachable elements were Cu and Mn at all pH values. Although suggestive, such laboratory experiments may not be representative of field conditions, nor do they indicate much information about long-term interactions between CCBs and ambient groundwater. Also, while several sequential extraction experiments on fly ash [18–23] revealed the occurrence and concentrations of toxic elements in leachates, they do not provide detailed information about how those elements occur and react under different environmental conditions. For instance, Semeda and Zyrnicki [18] applied sequential extraction procedures to two certified reference ash samples to investigate the partitioning of boron (B) and metals Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Sr, V and Zn. Their results showed that the majority of these elements were contained in the residual fraction, but no information was given regarding the leaching potential of samples if exposed to ambient groundwater. Landsberger et al. [21] conducted sequential extractions to investigate the leaching characteristics of Ag, B, As, Ba, Cd, Cr, Hg, Pb, S, and Se. Analyses showed that the residual fraction was the most important host for these elements. Ag, As, Ba, Cd, Cr, Hg, Pb, and Se remained in dominantly insoluble forms, but B and S showed higher leaching levels.

CCBs may be useful as structural fill and capping materials in abandoned mine land (AML) reclamation because of their low cost, availability, and capacity for neutralizing acid mine drainage (AMD) [24]. By mixing flue gas desulfurization (FGD) sludge, fly ash, and lime, a virtually impermeable, cementitious substance—fixated scrubber sludge (FSS)—is generated [25,26]. Although the effects of using engineered CCBs in underground mines have been investigated in several studies [27–30], research on the long-term efficiency of using FSS at surface mined sites is limited [31–33]. A desirable long-term goal is to develop quantitative predictive models aimed at determining the rates of weathering and resulting changes in groundwater chemistry that occur when FSS is used as a hydrologic barrier and AMD inhibitor in surface coal mine settings. In order to achieve such a model, all of the solid phases, including their relative abundances, contained in FSS must be quantified. Most importantly, the occurrences and ease of mobilization of trace elements within the solid phases must be established.

In this paper, we present the findings of laboratory experiments aimed at: (1) examining the microstructure of FSS, (2) quantifying the elemental composition of the abundant amorphous phase, and (3) identifying the solid phases that contain trace elements and their relative solubility in the natural environment. The morphological and weathering differences in weathered vs. intact FSS samples collected from an AML site after nearly two decades of exposure to the environments are also analyzed, thereby gaining a more comprehensive mineralogical and geochemical understanding of how FSS is altered as a result of in situ weathering processes. A combination of SEM, electron microprobe (EMP) analysis, and sequential extractions were used to achieve these goals. Understanding the mineral phases, chemical composition, morphology, and distribution of trace elements in FSS is critical in assessing the risk of the releasing toxic trace elements into local ground and surface water. Moreover, the data obtained from these analyses are a necessary first step toward developing numerical models of the long-term effects that CCBs have on groundwater quality at coal mine reclamation sites.

2. Material and methods

2.1. Study site

The Midwestern Abandoned Mine Land Site in Pike County, Indiana, underwent reclamation in 1996. The site contained a large pyritic coal refuse deposit that was the main source of acidic drainage. Ponded ash was used as structural fill in highwall cuts and pit lakes, and the deposit of pyritic coal refuse was buried under a layer of FSS (Fig. 1). The FSS was, in turn, overlain by a 1-m-thick soil layer consisting of reworked overburden spoil with animal waste fertilizer to facilitate revegetation. For 18 years following reclamation, water monitoring was conducted and the samples of groundwater and streamflow were analyzed to determine any beneficial or deleterious effects that using FSS had on the hydrochemistry of the site [31]. Groundwater quality in the vicinity of the FSS was improved exhibiting an increase in pH and a decrease in total acidity, as well as decreases in the concentrations of toxic elements in the pore waters of the buried coal refuse. In 2012, cores were collected at several monitoring well sites using a Geoprobe. The cores which penetrated the FSS layer were described by Martin et al. [32] and also subjected to mineralogical and elemental characterization using XRD and X-ray fluorescence (XRF) analysis, respectively. The XRD analyses indicated that the FSS contains hannebachite, gypsum, calcite, mullite, quartz, ettringite, hematite and magnetite, as well as amorphous phases that exhibited no crystal structure to X-rays. Bulk chemistry data from XRF analyses showed many trace elements existed in the FSS, such as Ba, Cl, Co, Cr, Cu, Ni, Pb, Rb, Sr, and Zn. However, no further information was given about the composition of the amorphous phase and specific forms that contained trace elements. Martin et al. [33] described the observable weathering characteristics of the FSS and attempted to determine the degree of deterioration that has occurred along the outer edges of the FSS. Only the first few centimeters of the upper surface exhibited much evidence of weathering. The deterioration rate was determined to be less than 0.3 cm/yr. Although the bottom of the FSS layer was in contact with acidic mine water, there was no observable evidence of elevated trace element concentrations in the buried AMD aquifer that could be attributed to weathering of the FSS.