



# Attenuation of trace elements in coal fly ash leachates by surfactant-modified zeolite

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## HIGHLIGHTS

- ▶ Fly ash contains environmentally available and leachable trace elements.
- ▶ Several unlined fly ash disposal sites pose environmental risk of contamination.
- ▶ SMZ was evaluated for its applicability as permeable reactive barrier (PRB).
- ▶ SMZ helped remove and retard anionic species of trace elements in leachate.
- ▶ SMZ could be used as a PRB for unlined fly ash disposal facilities.

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## ABSTRACT

Potential leaching of trace elements from older, unlined fly ash disposal facilities is a serious threat to groundwater and surface water contamination. Therefore, effective methods for containing the pollutant elements within the unlined coal combustion products (CCPs) disposal facilities are required to minimize any potential impact of leachate emanating from such facilities into the nearby environment. Because surfactant-modified zeolite (SMZ) has the potential to sequester both cationic and anionic trace elements from aqueous solutions, bench-scale batch and column experiments were performed to test its ability to remediate trace elements in leachates generated from both alkaline and acidic fly ash samples. Fly ash leachate treatment results showed the potential application of SMZ as an effective permeable reactive barrier (PRB) material to control the dispersion of heavy metals and metalloids from ash disposal sites. Quantitative comparison of the elemental composition of SMZ-treated and untreated leachates indicated that SMZ was effective in decreasing the concentrations of trace elements in fly ash leachates. Similarly, SMZ treatment column experiments showed the delayed peak leaching events and overall reductions in leachate concentrations of trace elements. The effectiveness of SMZ column treatments, however, decreased with time potentially due to the saturation of sorption sites.

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## 1. Introduction

Coal-fired power plants produce large volumes of coal combustion products (CCPs), including fly ash, bottom ash, boiler slag, flue gas desulfurization materials, and different gasses [1]. In 2010, 67.7 million short tons of fly ash were produced by coal-fired power plants in the US, accounting for 52.0% of the total CCPs [2]. Although the beneficial use of fly ash and other CCPs has varied in recent years (37.9% or 27.7 short tons of fly ash were recycled and used in 2010), the majority of the fly ash is buried in impoundment lagoons or dry landfills along with other unused CCPs [2]. Fly ash contains numerous trace elements which can potentially pose health hazards to humans; therefore, development of feasible and effective

techniques to control the dispersion of hazardous trace elements from older, unlined CCP disposal facilities to local hydrology is very important for the protection of potable water resources.

Several previous studies have attempted the treatment of municipal solid waste (MSW) fly ash [3–6]; however, there have been relatively few studies which focused on controlling the mobility of trace elements from coal fly ash [7,8]. Auer et al. [3] noted that the addition of reactive calcium aluminates to sulfate rich MSW fly ash resulted in the formation of ettringite-like minerals, partially sequestering some trace elements. A ferrous sulfate treatment method developed for fixing arsenic in a contaminated soil [9] was also tested for immobilizing trace elements in coal fly ash [7,8]. It was found that ferrous sulfate treatment at a 1:30 solid:liquid ratio was effective in decreasing the synthetic acid rain leachability of several trace elements associated with coal fly ash [8].

Zeolites are hydrated aluminosilicate minerals characterized by cage-like structures with high internal and external surface areas

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[10,11]. The availability, low cost (about \$60–\$100 per metric ton), and high cation exchange capacity make natural zeolites very useful material for treatment of contaminated water [12]. Although natural zeolites are effective in removing cationic species from aqueous solutions [13], they are not useful for removing oxyanions due to their negative surface charge [14]. However, the external surface of natural zeolite can be altered to make it suitable to adsorb oxyanions [14]. When natural zeolite is treated with cationic surfactant solution with concentration > critical micelle concentration (CMC), its surface becomes a positively charged surface suitable for adsorbing anionic counterions [14].

Despite the potential to sequester trace elements from aqueous solution and its relatively low cost (\$350–\$500 per ton [12,15]), SMZ has not previously been tested for remediation of trace elements in fly ash leachate. In the current study, we performed bench-scale batch and column experiments to evaluate the effectiveness of SMZ to remediate trace elements in fly ash leachates.

## 2. Materials and methods

### 2.1. Background soil

A yellow sandy background soil (5–20 cm) was collected from Fort Walton Beach, FL. The background soil was air dried, passed through a 2 mm screen to remove larger debris, and thoroughly mixed. Mineralogy of the soil was studied with X-ray diffraction analyses of bulk soil and clay-sized (<2  $\mu\text{m}$ ) soil fractions using a Brüker D8 Advance powder diffractometer. The clay-sized soil fraction was separated by flotation according to Stoke's Law. The soil pH was measured at 1:1 soil:water mixture [16]. The environmentally available elements in background soil were extracted by microwave-assisted partial acid digestion [17] and analyzed with a Perkin Elmer Optima 3000DV inductively coupled plasma-optical emission spectrometer (ICP-OES).

### 2.2. Fly ash samples and characterization

Three acidic (Class F) and an alkaline (Class C) fly ash samples were collected from four different coal-fired power plants located in the southeastern United States. The acidic fly ashes (HA, HB, and MA) and alkaline fly ash (PD) were the combustion products of Eastern Bituminous coals and the Powder River Basin coal, respectively. The fly ash samples were air-dried and homogenized prior to their use in experiments. The specific surface area of each fly ash sample was determined by the single-point BET method using a device with flow of 30%  $\text{N}_2$  in He using a Leybold-Infincon mass spectrometer to detect the gasses. Similarly, bulk mineralogy was identified with X-ray diffraction. The unburned carbon contents in fly ash samples were determined by loss-on-ignition tests [18]. Similarly, the environmentally available elements in the fly ash samples were extracted by microwave-assisted partial acid digestion [17].

### 2.3. Surfactant-modified zeolite

Natural zeolite was obtained from the St. Cloud Mining Company located in Winston, NM. St. Cloud zeolite is rich in clinoptilolite (74%) with smaller amounts of smectite (5%), quartz/cristobalite (10%), feldspar (10%), and illite [19]. Its external CEC was reported to be in the range of 70–90 mequiv./kg [19,20]. Quaternary amine hexadecyltrimethylammonium bromide (HDTMA-Br) with a CMC of 0.9 mM [21] was used for the zeolite surface modification. The HDTMA-Br has been used by several previous researchers [11,22,23] for surface modification of zeolites. Furthermore, Campos and Bucher [24] reported that HDTMA-modified zeolite was very effective in removing arsenic

from aqueous solution. At higher concentrations, HDTMA-Br selectively exchanges with inorganic cations on the external zeolite surface and forms a stable surfactant bilayer with anion exchange properties. It has been reported that this exchange occurs to the level of the zeolite's external CEC [11,14,22]. A method modified from Li et al. [22] was used for the surface modification of the natural zeolite. For the surface modification, zeolite was agitated for three days at 1:3.75 zeolite:0.04 M HDTMA-Br solution ratio in polypropylene bottles. The initial concentration (0.04 M) of surfactant in the surfactant solution was far greater than the CMC (0.9 mM) value [21]; therefore, the surfactant should have formed the HDTMA bilayer on the zeolite surface. After being allowed to settle for 24 h, the supernatant solution was discarded, and the SMZ was agitated with reagent water (>18  $\text{M}\Omega$ ) at 1:4 solid:liquid ratio for 24 h to remove the excess HDTMA-Br. The rinsed SMZ was finally collected by vacuum filtration, air dried at room temperature, and homogenized.

### 2.4. Fly ash leachate

Fly ash leachate solutions were prepared by equilibrating the fly ash samples with DDI water (>18  $\text{M}\Omega$  doubly de-ionized water produced by a Barnstead NANO pure system) at a 1:15 solid:liquid ratio. For each fly ash, 450 mL of DDI water were added to 30 g of fly ash sample in a 500 mL polypropylene bottle, and the mixture was agitated for 48 h. Then the leachate was filtered through a 0.2  $\mu\text{m}$  filter for use in the SMZ batch treatments. About 20 mL of each filtered leachate solution was reserved for chemical analysis.

### 2.5. SMZ treatment batch experiments

Fly ash leachate was treated with different amounts of SMZ in batch experiments. The batch treatments were conducted by equilibrating 40 mL of fly ash leachate in 50 mL centrifuge tubes with 0.027 g, 0.133 g, 0.267 g, 0.400 g, and 0.533 g of SMZ, which represent, respectively, 1%, 5%, 10%, 15%, and 20% by weight of the 2.667 g of fly ash that was used to generate 40 mL of leachate at a 1:15 solid:liquid ratio. A 24-h equilibration time was selected for use in the batch experiments, which has been used in previous studies [25,26]. Other studies of oxyanion adsorption have shown equilibration in substantially less time. For example, adsorption of  $\text{Cr}_{(\text{VI})}$  on surfactant-modified zeolite has been achieved in <10 min to 4 h [27–29]. Batch SMZ treatments were conducted in duplicate. All tubes were agitated at 200 rpm for 24 h. At the end of the experiments, the supernatant solutions were centrifuged at 8500 rpm for 20 min, filtered through 0.2  $\mu\text{m}$  syringe filters, acidified to 2% with OPTIMA  $\text{HNO}_3$ , and stored in a refrigerator until chemical analysis.

### 2.6. SMZ treatment column experiments

A representative acidic fly ash (HA) and the alkaline fly ash (PD) were selected for the SMZ treatment column experiments. For each fly ash, two columns were dry-packed into 40.6 cm long Plexiglas tubes with a large internal diameter (8.7 cm) to minimize the wall effects during unsaturated flow experiments. In one column, SMZ (5 cm), background soil (17.5 cm), and fly ash (17.5 cm) were packed, from bottom to top, while background soil (17.5 cm) and fly ash (17.5 cm) were packed into the other column (see Supplementary Fig. S1). To obtain the desired height for the fly ash layers, a total of 950 g of HA fly ash was used in each column (HA and HA-SMZ), while 1125 g of PD fly ash was used in each of the other two columns (PD and PD-SMZ). Similarly, 1400 g of background soil was used in each column. For each SMZ column, 400 g of SMZ was used. Loss of SMZ or background soil was prevented by placing a fabric filter reinforced with a 1-mm Teflon screen above a perforated stainless steel support plate at the base of each column.

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