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Metal leachability from coal combustion residuals under different pHs and liquid/solid ratios

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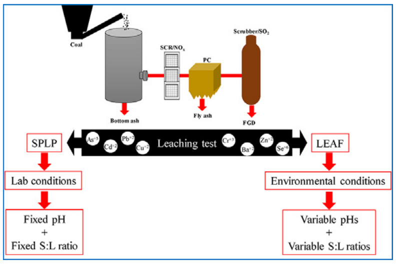
HIGHLIGHTS

- Comprehensive characterization of metal concentrations in coal combustion residues.
- First study to test the new USEPA LEAF Method 1313 and 1316 in fly ash..
- Ni, Zn and Pb were the highest with Pb being close to Florida industrial Soil Cleanup Target level.
- All metals except Cd showed amphoteric behaviors with increasing solution pH.
- All metal leaching excluding Ba and Pb decreased with increasing liquid:solid ratios.

GRAPHICAL ABSTRACT



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ABSTRACT

Coal combustion residuals (CCRs) contain variable amounts of trace metals, which can negatively impact the environment. We analyzed metal concentrations and leachability of CCRs from seven coal-fired power plants from Florida. The purpose of this study was to characterize and assess metal leachability in representative CCRs samples from coal-fired power plants, including As, Ba, Cd, Cr, Pb, and Se. The specific objectives were to: (1) measure metal leachability under different pH conditions and liquid-to-solid ratios using USEPA Leaching Environmental Assessment Framework (LEAF) Methods 1313 and 1316, and (2) compare their leachability with those obtained by the Synthetic Precipitation Leaching Procedure (SPLP). All metals excluding Cd showed amphoteric behavior, presenting higher concentrations at low and high pH using LEAF Method 1313. The highest Cd leaching was observed at pH 2–4 and decreased at pH > 7. SPLP results were highly variable when compared to the LEAF data. All metals except Ba exceeded the Florida Groundwater Cleanup Target Levels at all pH levels, however, metal leaching was low at typical soil pH of 4–9. Metal concentrations in fly ash decreased in most cases with increasing LS ratio. Therefore, due to potential leaching of some metals, evaluation is needed before beneficial use of CCRs.

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1. Introduction

Coal combustion residuals (CCRs) are one of the largest waste streams generated in the USA [1]. They are byproducts of coal combustion during electricity generation and consist of fly ash, bottom ash and flue gas desulfurization (FGD) residue [2]. In 2013, over 115 million tons of CCRs were produced in the USA, with ~51.4 tons being beneficially used for mine waste treatment, cement and concrete mixture, fill materials and metal recovery [3,4]. Due to updated Clean Air Act [5], CCRs production reached 140 million tons in 2015 [1,5].

Fly ash is fine in size (0.5–100 μm), which is generated during coal combustion and carried up with flue gas. To minimize its release into the atmosphere, emission control devices are used to separate fly ash in the flue gas from the air stream [6]. Bottom ash is the remaining residue in the boiler after fly ash removal and is formed in dry-bottom boilers and stokers [7]. FGD residues are produced by air-emission control devices, which contain lime-based materials to trap SO_2 as CaS or $CaSO_4$ to reduce its atmospheric concentrations [8]. In some cases, a selective catalytic reduction process is used to reduce NO_x gas emissions by spraying ammonia into the flue gas [9].

CCRs contain variable amounts of soluble salts and trace metals that may leach out and cause environmental problems [1,10]. Depending on the combustion process, CCRs can be enriched with trace metals such as As, Cu, Pb, Se and Zn [8,11,12]. Coal source impacts trace metal concentrations in CCRs [13]. For example, Appalachian and Illinois Basin coals have higher Pb, Cr, Ni, and As concentrations than coals from the Rocky Mountains and Northern Plains, while Gulf Cost coals show the highest Hg concentration [1,14]. Because different coals contain different metal concentrations and pH values, metal leachability from CCRs can vary widely.

Metal concentrations in CCRs are generally low, rarely reaching the hazardous levels based on USEPA's Toxicity Characteristic Leaching Procedure (TCLP) [15]. However, if not managed properly, CCRs have the potential to cause environmental contamination due to leaching of trace metals [11]. For example, trace metals including As, Se, B, Sr and Ba were detected in water from the impacted area 18 months after the collapse of the Kingston facility [12]. The collapse of another facility in 2014 released ~39,000 tons of ash into the Dan River, causing As, Se and Ba contamination in Duke river sediment [15,16]. Therefore, it is important to assess the potential risk associated with CCRs to minimize their impact on the environment.

The Synthetic Precipitation Leaching Procedure (SPLP) has been used to determine metal leachability under controlled laboratory conditions [17]. However, it does not consider site-specific conditions or leaching behavior over different time [1]. Leaching Environmental Assessment Framework (LEAF) methods were developed to examine metal leaching over a range of pHs (2–13; USEPA Method 1313) and liquid/solid ratios (0.5–10 mL/g; USEPA Method 1316), which help to assess metal leaching behavior in landfills or surface impoundments [15]. Combined with geochemical speciation modeling, LEAF methods can estimate metal leachability under different environmental conditions and land disposal characteristics [8,18]. Even though tests with wild range of pHs and L/S has been done in the past, they used different protocols and some report are incomplete, thus limited information is available regarding metal leachability of CCRs [19,20].

The purpose of this study was to characterize and assess metal leachability in representative CCRs samples from coal-fired power plants in Florida, including As, Ba, Cd, Cr, Pb, and Se. The specific objectives were to: (1) measure fly ash metal leachability under different pH conditions using LEAF Method 1313 (pH 2–13); (2) evaluate their leachability under different liquid-solid ratios using LEAF Method 1316 (0.5–10 mL/g); and (3) compare the LEAF results with those from SPLP.

2. Materials and methods

2.1. Chemicals, reagents and CCR samples

All chemicals were of analytical grade or better. Nitric acid (trace metal grade), H_2O_2, HCl and KOH were obtained from Fisher Scientific (Waltham, MA). Before use, all labware was washed and soaked in 1 M nitric acid for 24 h and rinsed several times with DI water.

Twenty four CCRs samples including 12 fly ash, 8 bottom ash, and 4 FGD residues were obtained from 7 representative coal-power plants in Florida. Composite samples were obtained following the in-stream and storage area methods. The in-stream method allowed collection of CCRs samples from transitory storage areas or conveyance systems. The storage area method allowed collection of CCRs samples from storage areas such as storage piles. All CCRs samples were subjected to total and SPLP analysis. Among those samples, 12 fly ash samples were analyzed using both LEAF methods (USEPA 1313 and 1316). All samples were derived from Bituminous type coal (Eastern, Central Appalachian and Illinois basin coal).

2.2. SPLP and LEAF tests

The pH was measured after shaking at a solid/liquid ratio of 1:10 (w/v) for 1 h and passing through 0.45 μm membrane filters. CCR samples were digested by USEPA Method 3050B for total concentrations [7]. Briefly, 1 g of sample was suspended in 15 mL 1:1 nitric acid and heated at 105 °C for 6 h. After cooling, 1 mL 30% H_2O_2 was added and digested for an additional 30 min before bringing samples to a 50 mL volume with double DI water. Concentrations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS NexIon 300, PerkinElmer Corp., Norwalk, CT).The SPLP was used to measure metal leaching behavior in CCRs samples. The SPLP was shaken at 1:20 solid/extractant ratio for 20 h in a rotary shaker. The resulting solutions were filtered (0.45 μm), acidified with concentrated HNO_3, and pH was measured before and after acid addition. The total content of As, Cd, Co, Cr, Cu, Ni, Pb and Se was analyzed by USEPA Method 6020 using ICP-MS [21].

LEAF Method 1313 uses dilute HNO_3 or KOH to adjust pH in nine parallel batch tests at a liquid/solid ratio of 10 mL/g, with the final pH values at 2, 4, 5.5, 7, 8, 9, 10.5, 12, or 13. The pH measurement was done within 30 min to avoid neutralization of the solution. An extraction with no acid/base addition was done to assess the pH of CCRs. LEAF Method 1316 is a five parallel batch extraction as a function of liquid/solid ratios. Water was added to 20 g of ash samples to reach 0.5, 1.0, 2.0, 5.0, or 10.0 mL/g. All samples were shaken for 24 h, followed by filtration and analyzed using ICP-MS. For LEAF methods, metals of most environment concern (As, Ba, Cr, Cd, Pb and Se) were chosen. All analyses were performed in triplicate.

2.3. Quality assurance

The QA/QC in SPLP and LEAF analyses included blanks, spikes and triplicates for every 20 samples. Recovery was determined using spikes (80–120%), and relative standard deviations of triplicate analysis were obtained. The performance of the ICP-MS was checked by running an intermediate calibration standard for every 20 samples. All calibration standard checks were within the acceptable range (80–120%).