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Full Length Article

Leaching characterization of dry flue gas desulfurization materials produced from different flue gas sources in China

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HIGHLIGHTS

- Leaching behaviors of DFGD materials from major sources in China were tested.
- B, Mo and Se are the most readily leachable COCs under percolation scenarios.
- Cr and Tl showed the highest cumulative releases among COCs under diffusion.

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ABSTRACT

By-products produced from dry flue gas desulfurization (DFGD) have been used in many engineering applications. Structural fill and/or mine reclamation applications utilize more than 74 and 22% of the annual DFGD production in Europe and the United States, respectively. In China, although there are reports showing the applications of DFGD materials in the production of bricks, precast concrete, highway construction, and agricultural applications, large-scale, high-volume uses have developed slowly. One of the major roadblocks to high-volume utilization is lack of knowledge regarding the associated utilization issues. In order to better understand the environmental response of Chinese DFGD materials, this study compared the leaching characteristics of three typical DFGD materials produced from different flue gas sources (i.e., coal-fired boiler, iron and steel sintering plant, and circulating fluidized bed (CFB) boiler). The goal of this study is to characterize the release of inorganic constituents of concern (COCs) under the leaching conditions (i.e., pH dependence, percolation column, and diffusion-controlled conditions) representing different potential application scenarios. Except for Se, the maximum concentrations of all selected COCs (Hg, B, Mo, As, Ba, Cd, Cr, Pb, Sb, Co, and Tl) under all tested leaching conditions were lower than the toxicity levels. The high release of Se observed under acidic conditions in the pH-dependent leaching tests might be adversely promoted by nitric acid induced oxidation of sparingly soluble selenite minerals to soluble selenate counterparts. Rapid initial releases of Mo, Se, B, and Tl were found during the early stages of the percolation column leaching tests. B, Mo and Se were found to be the most readily leachable COCs under the scenarios when the leaching is equilibrium-controlled. Under a diffusion-controlled leaching environment, Cr and Tl showed the highest cumulative mass release among the COCs.

1. Introduction

The dry flue gas desulfurization (DFGD) process, e.g., spray dryer absorber (SDA) and circulating desulfurization scrubber (CDS), is an alternative sulfur dioxide (SO_2) emission control technology to the most commonly used wet process. A DFGD system captures SO_2 from the flue gas using hydrated lime and the by-product is captured in a particulate collector. Fly ash in the flue gas may be captured prior to a DFGD system or mixed with the desulfurization by-products containing residual hydrated lime and collected with the DFGD material.

Due to its better calcium utilization efficiency, higher operation flexibility, and multipollutant emission control capability, the DFGD process, especially the CDS system, has been increasingly used in many industrial installations [1,2], such as pulverized coal

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(PC) coal-fired power plants, iron and steel sintering plants, and circulating fluidized bed (CFB) boilers [3]. In addition, no wastewater is produced from the DFGD process. The recent restrictive implementations in the United States Environmental Protection Agency's (USEPA) *Steam Electric Power Generating Effluent Guidelines* requires coal-fired power generation utilities to adopt newer treatment technologies for their wastewaters. Currently, only limited treatment options are available to effectively reduce the concentrations of regulated constituents in the coal-fired power plants' wastewaters to the levels required by effluent guidelines.

By-products produced from DFGD processes have been used in many engineering applications [2,3]. In the U.S., approximately 22% of the annually produced DFGD by-products are used in mining applications and the oil/gas services, according to American Coal Ash Association [4]. In Europe, more than 74% of the annually produced DFGD by-products are utilized in structural fill/infill application and reclamation [5]. No statistical data are available in China. However, there are reports showing that DFGD materials have been used in the production of construction materials, highway construction, agricultural applications, and filling materials in mine land reclamation [3]. In China, high-volume utilizations of DFGD materials have been developed slowly. One of the major barriers is lack of systematic evaluations on potential environmental issues associated with reutilizations.

A number of testing protocols, e.g., Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), and ASTM D-3987, are commonly used to evaluate the potential environmental impacts associated with utilization of coal combustion residuals. For example, in a comprehensive characterization study carried out by Kost et al. [6], the leaching potentials of 59 samples collected from 13 DFGD systems representing a wide range of DFGD technologies used in the U.S. were studied using ASTM D-3987 and TCLP. Results obtained from these testing protocols provide valuable information on the comparisons of the leachate concentrations among samples representing different DFGD operation conditions, as well as to regulatory standards. However, these testing protocols were based on single-point pH and did not consider the amount of liquid infiltration occurring during management of the material [7]. These testing protocols might be inappropriate to evaluate the leaching potential of DFGD materials based on how they are actually managed [7,8].

In China, one of the potential high-volume applications of DFGD materials is use as a structural fill. In addition to the field hydrological conditions, the release of COCs under such structural fill application scenarios can be affected by the chemical properties of the water (e.g., infiltrate and groundwater) that might come into contact with the materials. To better assess the potential environmental impacts associated with high-volume structural fill applications, the release of constituents from DFGD materials were studied under different pHs, liquid-to-solid ratios, and mass transfer conditions. Three DFGD materials provided by Lonjing Environment Technology Co. Ltd. in China were evaluated in this study. The study was carried out using a series of leaching protocols of Leaching Environmental Assessment Framework, i.e., LEAF. The leaching conditions created by the LEAF's protocols are thought to better represent the field conditions of how the DFGD material is to be utilized when compared to TCLP, SPLP, or other commonly used leaching procedures.

2. Materials and methods

2.1. Dry flue gas desulfurization materials

The three DFGD materials, i.e., LYS1, MSS2, and S3, tested in this study were produced from the circulating fluidized-bed flue gas desulfurization processes (CFB-FGD) equipped in three different flue gas sources. Sample LYS1 was taken from a 110 MW coal-fired power plant located in Liaoyang, Liaoning, China. Sample MSS2 was provided by an iron and steel sintering plant with an effective sintering area of 400 m^2 in Nanjing, Jiangsu, China. Sample S3 was collected from a 200 MW circulating fluidized-bed boiler (CFB) using a CFB-FGD system as a polishing unit (CFB + CFB-FGD) in Pingyao, Shanxi, China. All three CFB-FGD processes are CDS systems. These materials represent the by-products produced from three major DFGD installations in China [3]. In both the LYS1 and MSS2 plants, fly ash in the flue gases was removed by particulate collectors prior to the CFB-FGD systems, where hydrated lime was injected to control SO_2 emissions. The DFGD by-products were then collected by the secondary particulate collectors. In the S3 plant, limestone ($CaCO_3$) was injected into a CFB boiler with coal. The limestone was converted to CaO at 850–950 °C in the flue gas and reacted with SO_2. After leaving the boiler, the flue gas was directly introduced to a CFB-FGD absorber, a "polishing" unit where hydrated lime was sprayed into the flue gas to further remove SO_2. The DFGD by-product was collected by a downstream particulate collector.

The complete elemental analysis was carried out as per EPA method 3052 with a microwave-assisted heating method. In summary, about 300 mg of DFGD material was first digested in a 20 mL solution that contained 6 mL of deionized (DI) water, 9 mL of concentrated HNO_3, 2 mL of concentrated HCl, and 3 mL of concentrated HF. An inductively coupled plasma atomic emission spectroscopy (ICP-AES, Prodigy Dual View ICP spectrometer, Teledyne Leeman Labs, New Hampshire, USA) and a cold vapor atomic fluorescence spectroscopy (CVAFS, CETAC M8000 Mercury Analyzer, CETAC Technologies, Nebraska, USA) was used for elemental analysis.

The mineral compositions of the three tested DFGD materials were identified using powder X-ray diffraction (XRD) analysis. Each sample was air-dried overnight before being ground to less than 50 μm. The ground sample was mounted in a holder as a randomly-oriented powder. The mounted samples were then scanned in a Rigaku Geigerflex diffractometer (Rigaku MSC, The Woodland, TX) with CuKα radiation at 35 kV and 20 mA. Step-scanned data were collected from 6 to 60° 2θ with a fixed time of 3 s per 0.05° 2θ. All data were analyzed using a semi-quantitative data reduction software (WinJade, version 5.0) from Materials Data Inc. (Livermore, CA).

2.2. Leaching characteristics under different application scenarios

In China, one of the potential high-volume utilizations of DFGD materials is as the fill material for road construction or mine land reclamation. The release of constituents under such structural fill application was conceptualized as water either percolates through or flows around the fill depending on how the hydraulic conductivity of the DFGD fill compared to the surrounding strata or geotechnical materials. To assess the leaching potentials of the materials under the conceptualized leaching conditions, three scenarios similar to the ones developed by Pasini and Walker [9] were adopted. Scenario One simulates the release of constituents under a percolation-controlled condition when DFGD materials are used as structural fills. Scenario Two was set to represent the release of constituents during mine land reclamation where a DFGD fill is in contact with infiltration with various pH under a chemical equilibrium condition. Scenario Three represents a field condition where a DFGD fill is surrounded by materials with higher hydraulic conductivities. The presence of high-permeable materials around the DFGD fill can direct the groundwater or rainwater flow around the FGD fill. A diffusion-controlled release condition is expected under such scenario [10]. The setups of the leaching experiments