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Heavy metals distribution characteristics of FGD gypsum samples from Shanxi province 12 coal-fired power plants and its potential environmental impacts

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ABSTRACT

Flue gas desulphurization (FGD) gypsum samples were collected from 12 power plants in Shanxi province in China. The total concentrations of Zn, Mn, Pb, Cr, Cd and Ni in FGD gypsum were determined. The chemical speciation and leaching toxicity were also analyzed. The total concentration ranges of Zn, Cr and Mn were at 40.1–96.1 mg/kg, 12.9–61.1 mg/kg and 2.1–56.1 mg/kg respectively. While the concentrations of Ni, Pb and Cd were relatively lower, with total concentration fell into the ranges of 0.7–31.7 mg/kg, 0.01–13.3 mg/kg and ND-1.6 mg/kg respectively. The average values appeared to follow the order of Zn > Cr > Mn > Ni > Pb > Cd. Synthetic Precipitation Leaching Procedure (SPLP) test results were all below the China's regulation level of leaching toxicity for heavy metals, while exceeded environmental quality standards for different classes of surface water in China. Selective sequential extraction (SSE) used for chemical speciation analysis showed that different heavy metals distributed variously in each extraction fraction. The bioavailability of major heavy metals for FGD decreased in the order of Mn > Zn > Cd > Cr > Pb > Ni, while their mobility decreased in the order of Cd > Mn > Ni > Pb > Zn > Cr. Risk assessment code (RAC) analysis suggested that heavy metals in all samples from Shanxi province posed risks to the environment. Especially, elements of Zn and Mn posed a very high risk. Estimation of annually leaching amount of heavy metals from FGD gypsum was calculated.

1. Introduction

Coal-fired power plant is the main electricity provider in China. Large amounts of byproducts including bottom ash, fly ash and flue gas desulfurization (FGD) gypsum have been produced [1] and different disposal and reutilization methods have been applied [2–4]. Coal contains all the elements existed in the natural environment [5], and during the combustion and the pollution control processes, elements in coal partition into different coal byproducts [6]. Therefore, elements in the byproducts, especially heavy metals, cause concerns about the process of disposal and reutilization.

It is reported in the literatures that chemical elements existed in coal can be divided into three groups [7–9]. The first group comprises of non-volatile elements and remains in fly ash and bottom ash, with the typical elements being Al, Ca, Co, Cr, Fe, Mg, Mn, Ni and Si. The second group includes volatile and condensable elements that are volatilized at high temperatures and can be transported by flue gases. As temperature drops these elements are condensed as droplets and/or are adsorbed to aerosols. Typical elements in this group are As, B, Be, Cd, Cu, Mo, Pb, Sb, Se, V, and Zn. The third group consists of volatile and non-condensable elements. During cooling of the flue gases, these elements stay in the flue gas and without adsorbing with aerosols and can be partly removed by a wet desulphurization step (F, Cl, Br and Hg). It can be expected that the elements released from coal combustion will enter different coal combustion byproducts according to their physicochemical properties. However, Diaz-Somoano et al. [10] classified Cr to Group II. Deng et al. [11] found most of the Cd, Pb, and Mn in coal was released into flue gas during coal combustion although they are not highly volatile elements. It was reported that heavy metals tended to enrich in finer particles which could escape from particulate control devices and removed by FGD progresses [8,12]. Therefore, the complicated behaviors of elements during combustion and pollution control progresses make their distribution differently.

In most countries, coal-fired combustion residues are defined as general solid wastes and have been stored on the ground or land filled except partially recycled. However, the adverse effects of the residues to the environment have been recognized. American Electric Power Research Institute (EPRI) evaluated the coal combustion product damage cases and confirmed the adverse effects of elements in the products on the groundwater, surface water and the organisms [13]. Many

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literatures also investigated the heavy metals in coal fly ash and bottom ash as well as their effects on the environment during the disposal and application [14–18]. There are relatively few studies on the environmental effects of heavy metals in FGD gypsum. And most of the studies on FGD gypsum focused on F, As, Se and Hg [12,19]. It had been reported that heavy metals such as Cd, Mn, Ni, Cu and Zn existed in FGD residues at various concentrations [20]. The mobility and potential release of heavy metals in FGD gypsum and their effects toward environment should be taken into consideration.

Shanxi province has a large amount of coal production and coal-fired power generation has been the major way of generating electricity. The number of coal-fired power plants in Shanxi province is more than that of other provinces [21]. Moreover, the average sulphur content in coal from Shanxi province is relatively high [22]. Therefore, FGD gypsum production is large. It is reported that in 2013 the FGD gypsum production in Shanxi province reached 6.68 million tons and the recycle rate was around 39%. By the end of 2013, the total accumulating pile-up of FGD gypsum in Shanxi province had reached 34 million tons [23]. Considering the heavy metals in FGD gypsum, it will be helpful to know the environmental risks of FGD gypsum and give a guide suggestion of treatment and disposal of the byproducts and minimize the environmental impact.

In this study, gypsum samples from 12 coal-fired power plants in Shanxi provinces were collected to determine Zn, Mn, Pb, Cr, Cd and Ni pollution characteristics. Total concentration and chemical speciation of the six elements with a selective sequential extraction (SSE) method were analyzed. Synthetic precipitation leaching procedure (SPLP) was also performed to evaluate the leachability of heavy metals in the FGD gypsum samples.

2. Materials and methods

2.1. Materials

FGD gypsum samples were collected from 12 coal-fired power plants, located in different cities of Shanxi province. All samples were collected according to standard procedures and stored in airtight plastic bags at −4 °C in the refrigerator.

2.2. Methods

2.2.1. Physical and chemical analysis of FGD gypsum

FGD gypsum samples were examined with X-ray diffraction (XRD, 18KW D/MAX2500 V+/PC, Rigaku Inc., Japan) at a scanning rate of 8 $^{\circ}\mathrm{min}^{-1}$ in the 2θ range from 10° to 80°. X-ray fluorescence (XRF-1800, Shimadzu limited., Japan) was performed to determine the major and minor elements in the FGD gypsum samples. FGD sample was ground and sieved through a #200 mesh sieve. The sample was mixed with boric acid and compressed to analyze the element composition with the XRF spectrometer.

An acid digestion method was used to measure the total concentration of Zn, Mn, Pb, Cd, Cr and Ni in FGD gypsum. FGD gypsum samples (n = 3) were placed into 60 mL PTFE tubes and digested with the mixtures of 10 ml HNO_3, 5 ml $HClO_4$ and 10 ml HF on a graphite digestion block at the temperature of 135 °C. Addition of the mixture of the acid was repeated a few times until the FGD samples were dissolved completely. The residual solution was filtered with a 0.45 μm cellulose acetate membrane filter and diluted to 50 mL in a volumetric flask with deionized water. And Ni, Cr, Zn and Mn were determined by ICP-AES (Inductively coupled plasma atomic emission spectroscopy) (Leeman prodigy, America), while Cd and Pb were determined by GFAAS (Graphite Furnace Atomic Absorption Spectroscopy) (Zeenit 600, Yena Germany).

2.2.2. Leaching toxicity

Leaching toxicity of the heavy metals from FGD gypsum was performed according to the US EPA's SPLP standard [24]. SPLP was designed to determine the mobility of both organic and inorganic analysts present in solid materials when exposed to the weathering conditions, such as rainfall [25]. The extraction fluid, concentrated sulfuric acid mixed with concentrated nitric acid (mass ratio 2:1) and adjusted with deionized water until the pH value equaled to 3.20 ± 0.05 were used as extraction fluid. The solution-to-solids ratio was 10:1. Samples were extracted at room temperature by end-over-end tumbling at 30 rpm for 18 ± 2 h. After extraction, the samples were centrifuged for 20 min at 3000 rpm, and the supernatant was filtered through a 0.45 μm cellulose acetate membrane filter. Filtration from the procedure was analyzed by ICP-AES and GF-AAS respectively.

Table 1
Selective sequential extraction procedure.

Steps	Speciation	Extraction solution and conditions
F1	Acid soluble fraction	0.11 mol/L acetic acid (v/w ratio = 40:l), 16 h extraction time
F2	Reducible fraction	0.5 mol/L $NH_2OH{\cdot}HCl$ in 0.05 mol/L HNO_3 (v/w ratio = 40:1), 16 h extraction time
F3	Oxidizable fraction	10 L concentrated H_2O_2, digested at 85 degree for 1 h1 mol/L ammonium acetate solution(pH = 2, v/w ration = 50:1), 16 h extraction time
F4	Residual fraction	Digestion procedure for total concentration of the heavy metals

2.2.3. Chemical speciation analysis of the trace elements by SSE procedure

A modified extraction procedure [26] was performed in this study to investigate the chemical speciation of trace elements in FGD gypsum. The procedure differentiated the elements into different behavioral classes. Details of extraction procedure are displayed in Table 1. The extracted fraction from each step was separated by centrifugation at 3000 rpm for 20 min, the supernatant was filtered with a 0.45 μm cellulose acetate membrane filter and the filtration was stored at 4 °C prior to determination by ICP-AES and GF-AAS.

2.3. Quality controls

The trace elements concentration was expressed as dry weight basis. All analyses were implemented in triplicates and the results were expressed as the mean ± standard deviation. To ensure the accuracy of the determination the standard addition method was applied during the total concentration measurement and the standard recovery rate was calculated. The recovery rates ranged from 75% to 121%. Blank samples were analyzed in each batch test to avoid the effect of impurities in the reagent.

2.4. Risk assessment code

Risk assessment code was normally performed to evaluate eco-risk of the labile fraction of heavy metals. According to the RAC[27], it considers that no risk when the heavy metal in the mobile fraction(F1 fraction) is less than 1% of the total concentration

low risks for 1–10%, medium risks from 11% to 30%, high risks for 31–50%, and very high risks for higher than 50%.

3. Results and discussion

3.1. Characterization of FGD gypsum samples

The properties of FGD gypsum from Shanxi province are reported in Table 2. Major elements determined by XRF included O, Ca, S, C and Si, while O, Ca and S were the predominant elements which accounted for more than 90% of total elements. There was no big difference for the major elements in FGD gypsum from different power plants. The water