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Environmental risk assessment of pyrometallurgical residues derived from electroplating and pickling sludges

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ABSTRACT

Pyrometallurgical residues from disposing of electroplating and pickling sludge (REPS), including copper (Cu) sludge (RCS), are often recycled as building materials in China. Although it is of great importance to assess the environmental risk of pyrometallurgical residues, few studies have been performed. In this study, REPS and RCS were analyzed from the aspects of metal speciation, concentration, leaching toxicity, and risk assessment (I_{geo}, *PER*, *RSP*, and *SQGs*), respectively. Results of metal concentrations showed that the sintered block and incinerated residue contained more potentially toxic metals (PTM) than the remainder of the slag. A significance analysis suggested that the Cu concentration in the pyrometallurgical residues was closely related to both the sludge type and its process, and the concentrations of chromium (Cr) and nickel (Ni) were mainly related to the disposal process, while the concentrations of other PTM were not correlated with sludge type or the process. Leaching toxicity analyses indicated that the incineration residues were hazardous wastes according to the Chinese standard and building materials made from such residues would be unqualified for extreme environments. Moreover, speciation and correlation analyses revealed that only speciation of Cu and cadmium (Cd) was strongly negatively correlated with leaching toxicity, and residual speciation was not the only factor determining metal stability. Thus, a new relative comprehensive assessment value (*F*), as a combination of metal concentration and speciation, was introduced to evaluate environmental risk of pyrometallurgical residues, which was more reliable than the results of existing assessments (I_{geo}, *PER*, *RSP*, and *SQGs*). Such an index indicates that the pyrometallurgical residues derived from incineration and sintering disposal processes presented the highest risk.

1. Introduction

Electroplating and pickling sludge (EPS), including copper sludge (CS), has been identified as hazardous waste because of the high-concentration of potentially toxic metals (PTM) (Kuo, 2012). Stabilization/solidification (Pileckaite et al., 2015), heat treatment, resource utilization (Chou et al., 2012; Tang et al., 2014), and biological treatment (Prabhu and Baskar, 2015) have been carried out to dispose of CS and EPS. Among these methods, pyrometallurgy has been commonly used to dispose of CS and EPS, as it extracts the heavy metals from the sludge to reduce sludge volume (Li et al., 2010) and avoids discharge into the environment (Cheng et al., 2005). These pyrometallurgical residues have been often treated by incineration, sintering, or melting (Rossini and Bernardes, 2006).

Pyrometallurgical residue is often recycled to manufacture building materials, including unburned brick and cement clinkers, after intensive investigation and particular treatments. A small amount of slag is reused for grit blasting (Morris, 2003). Many studies have reported that residues, such as steel slag, furnace slag, and some metal-containing slags, are frequently utilized as civil emerging materials (Mo et al., 2016; Pasetto et al., 2017; Sharma and Khan, 2017).

The elements inside any material will be released, so harmful building emissions are dangerous to human health and the environment (Kobeticova and Cerny, 2017). Severe problems have remained for large quantities of slags due to the existence of PTM. Hexavalent chromium (Cr^{6+}) with high potential environmental

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impact might exist in these pyrometallurgical residues (Beukes et al., 2017). Various experiments have been conducted to assess the environment risk of the residues with inconsistent results. Solubility and leachability of PTM in waste slag have been studied using a rainwater simulated solution and a weak citric acid solution (Ash et al., 2013) in a leaching column experiment (Houben et al., 2013). Many risk assessments, such as the geo-accumulation index (I_{geo}), ecological risk (E_r^i), Risk Assessment Code (*RAC*) and Hakanson Potential Ecological Risk Index Method, have been used to evaluate PTM contamination in a slag disposal area (Kasemodel et al., 2016) and a lead (Pb) and zinc (Zn) plant, from which the residues present serious potential risks to the environment according to the results of mineralogical analysis, the Community Bureau of Reference sequential extraction procedure, and a dynamic leaching test (Min et al., 2013). Therefore, such residues have indistinct effects on the environment but little research has investigated their risks from a comprehensive approach, such as total metal concentrations, leaching toxicity, metal speciation, and risk assessment.

Eight enterprises in Jiangsu Province, China use the pyrometallurgical process to treat CS and EPS, which caught the attention of the Solid Waste Supervision and Administration Center (SWSAC). In fact, China has substantial hazardous waste for disposal. Such residues have been reused as unburnt bricks or for grit blasting, cement clinkers, and as crane counterweights, but the relevant standards for reutilization as building materials are unclear. Therefore, comprehensive research is necessary to perform a systematic and integrated evaluation of the environmental risk of pyrometallurgical residues based on the SWSAC requirements.

In this study, metal concentration, leaching toxicity, and speciation of PTM were analyzed to assess whether the residues were suitable for resource utilization. Furthermore, a new comprehensive risk assessment method was developed to compare the risks of pyrometallurgical residues from eight enterprises.

2. Materials and methods

2.1. Samples

Pyrometallurgical residue samples marked RW, JF, YS, TY, SH, MF, and HJ were collected randomly seven times from eight enterprises in Jiangsu, China. RW, JF, YS, and TY were the CS residue samples (RCS), whereas SH, MF, HJ, and LK were the residue samples from EPS (REPS), among which SH was a sample from electroplating sludge and MF, HJ, and LK were samples from pickling sludge (Fig. 1). In this study, CS was specifically treated as an individual category for its main constituent of Cu.

The sludges from RW, JF, YS, SH, MF, and HJ have been disposed of through high-temperature smelting by adding additives, such as limestone, charcoal, iron ore, and dolomite, at ≥ 1300 °C (Kuo et al., 2011), while the oxides are reduced to a single element and the remainder becomes slags. The TY process involves directly sintering the sludge with coke into a sintered block, which demands further disposal. LK incinerates sludge with coke at the highest temperature of 900 °C and produces pyrometallurgical residues. The specific classification is shown in Table 1.

2.2. General analysis

The metal concentration of the PTM was measured after acid digestion with a mixture of nitric acid, perchloric acid, and hydrofluoric acid, using inductively coupled plasma mass spectrometry (ICP-MS). A 100 g portion of each sample was taken for leaching toxicity testing using a Chinese method (HJ/T299-2007, 2007). The sample was mixed with extractants (mixture of concentrated sulfuric acid and concentrated nitric acid at a mass ratio 2:1 and pH 3.2 ± 0.05) at a 1:10 ratio. After 18 h of oscillation at 23 °C, the filtrate was detected by ICP-MS. Then, the same experiments were carried out with the extractants at pH 1.0 to test leaching toxicity in an extreme environment. The leaching toxicity results were comparatively studied in accordance with the hazardous wastes standard of China (GB5085.3-2007, 2007).

2.3. Speciation analysis

Metal speciation is divided into exchangeable (F1), carbonate-bound (F2), Fe-Mn-oxide-bound (F3), organic-matter (F4) and residual fraction (F5), whose stability increases gradually with the decrease in eco-toxicity and bioavailability in the environment (Yuan et al., 2011). Based on the sequential extraction procedure proposed by Tessier et al. (1979), the five fractions of Cu, Cr, Ni, Zn, Pb, Cd, and arsenic (As) were extracted using different leaching agents in sequence (Bao et al., 2016; Kasemodel et al., 2016), and the filtrate was detected by ICP-MS.

2.4. Risk assessment

2.4.1. Assessment of PTM pollution

The geo-accumulation index, I_{geo} (Eq. (A.1)) (Muller et al., 2001) and potential ecological risk (*PER*) factor (Eq. (A.2)) (Hakanson, 1980) were selected to assess the environmental risk of the pyrometallurgical residues.

$$I_{geo} = \log_2 \frac{C_i}{1.5BE_n} \quad (A.1)$$

$$E_r^i = T_r^i \frac{C_i}{C_0} \quad (A.2)$$

Where C_i is the average PTM concentration (mg/kg) of sample i; BE_n and C_0 refer to the average geochemical background values, and As, Cd, Cr, Cu, Ni, Pb, and Zn contents are typically 10.0, 0.126, 77.8, 22.3, 26.7, 26.2, and 62.6 mg/kg, respectively in Jiangsu Province (CNEMC, 1990). T_i is the toxicity coefficient, and the values of As, Cd,

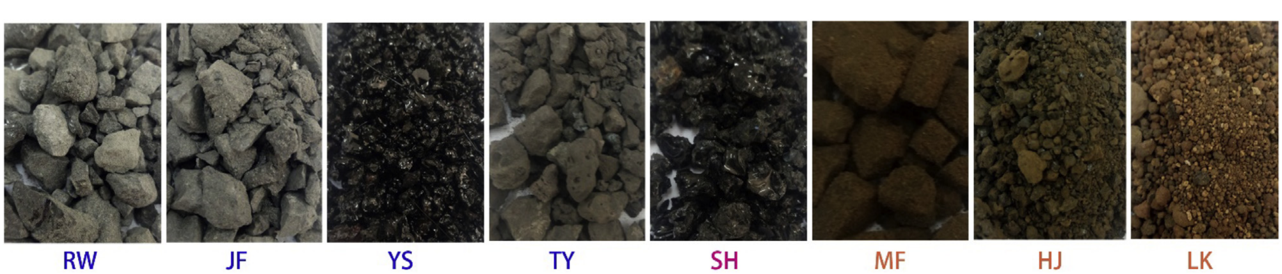

Fig. 1. Pyrometallurgical residue samples.