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Digesting high-aluminum coal fly ash with concentrated sulfuric acid at high temperatures

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ABSTRACT

The decomposition of coal fly ash (CFA) digested with concentrated H_2SO_4 at a high temperature has been proven to be an efficient way to leach aluminum in view of extracting useful metals from solid wastes. In this research the reaction between the CFA collected from Jungar in Inner Mongolia, China, and concentrated H_2SO_4 was studied to get a high level of leaching efficiency, which is industrially applicable to extract aluminum. The microstructures, mineralogical transformation and mass transfer were investigated by means of X-ray diffraction, chemical composition analyses, polarization microscopy, electron probe micro-analysis, scanning electron microscopy, and transmission electron microscope observation. The surface of CFA spheres consisting mainly of crystalline phases, e.g., mullite, corundum, was found to be digested by concentrated H_2SO_4 much easier than the vitreous phases. Most of the CFA spheres can be disrupted at high temperatures ($T > 230\,^{\circ}C$). The mineralogical transformation in this art follows a route as mullite, corundum + $H_2SO_4 \rightarrow$ millosevichite ($Al_2(SO_4)_3$) $\rightarrow$ leached metal ions + residues rich in SiO_2. Base on the EPMA analyses the element of chromium that was distributed as substitutions in mullite or corundum was found to be enriched in form of chromium oxide. The maximum leaching efficiency of aluminum reaches 86.0% under the optimized conditions as $T = 300\,^{\circ}C$, $t = 110$ min, and molar ratio of H_2SO_4:CFA = 1.2. A modified shrinking core model was used to describe the diffusion controlled kinetics, and the apparent rate constant (k_d) were found to be $1.18–1.89 \times 10^{-3}\,min^{-1}$ at the temperature of 230–300 K. The activation energy of the internal diffusion-controlled reaction in the digesting reaction was evaluated to be 19.23 kJ mol^{-1}.

1. Introduction

Coal fly ash (CFA) is one of the most abundant anthropogenic wastes that were produced in the coal-firing power plants. The disposal of CFA is becoming a great concern because the landfill of such wastes would not only take up a great deal of land, but give serious problems to environment (Yao et al., 2014). Recycling coal fly ash can be a good choice. Methods in utilizing CFA have been in pursuit for several decades (Blissett and Rowson, 2012). Reports in this area authored by Chinese are growing because China is suffering from damages of huge accumulation of CFA (0.63 billion tons in 2017). On the other hand, China is poor in bauxite that is used in the present aluminum industry. The content of alumina (Al_2O_3) in Jungar CTA, collected in Ordos Bain, Inner Mongolia, China, was found to reach 51.18% which is comparable to that of bauxite (Ma et al., 2010). This high content of Al_2O_3 makes Jungar CFA as a substitute for bauxite (Bai et al., 2011). Up to date, means of extracting alumina from CFA includes the alkali-assisted digestion followed by dissolving/crystallizing (Matjie et al., 2005; Bai et al., 2010), the low-temperature acid leaching (Guo et al., 2013a, 2013b), and sequential treatments by acid/alkali to produce alumina (Bai et al., 2011; Guo et al., 2013a, 2013b; Wang et al., 2014). Unfortunately, the alkali-assisted digestion requires high energy-consumption (temperature, $T > 800\,^{\circ}C$), and this art was demonstrated to produce more amount of solid wastes than the starting CFA (Wu et al., 2012). The acid digesting procedures are featured with lower temperature ($T < 350\,^{\circ}C$), amendable operations, and capable of recycling acidic fumes (SO_3), which affords this method as a technical reliable and economically profitable to extract aluminum (Guo et al., 2013a,

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2013b). Based on previous findings including ours (Guo et al., 2013a, 2013b; Mu and Zhai, 2010) the concentrated sulfuric acid (H_2SO_4, > 98% wt.) was proven to be an efficient way to digest the CFA.

It was usually believed that the leaching of aluminum (Al^{3+}) and/or other cationic elements (e.g., Fe^{3+}) from CFA with H_2SO_4 involves a rate controlling step of mass transport. The diminishing of CBF particles follows a shrinking core model with respect to a layer formation of $CaSO_4$. This layer plays roles in the self-inhibition in the digesting step. Examples were found for the decomposition of mullite by concentrated H_2SO_4, and the mullite crystallites were found to be decomposed within 16 h at about 230 °C (Bai et al., 2011; Li et al., 2011). An elegant work is of Shemi et al.'s (2015) in which the CFA were treated with H_2SO_4 via a multiple leaching procedure. To the best of our knowledge, the published reports were lack of evidences for compositional details in micro-areas of samples digested from CFA and H_2SO_4. The corrosion of CFA imposed by H_2SO_4 is still to be clarified. To understand this digestion reaction as well as improve the Al^{3+} leaching efficiency, it is necessary to conduct the temperature-dependent reactions as well as study the mineralogical transformation. In this research the concentrated H_2SO_4 was chosen to digest CFA due to its strong acidity, oxidant capacity and possibility in reclaiming acidic fume (SO_3). Parameters that affect the leaching efficiency of Al^{3+} were investigated on the Jungar CFA, and details such as microstructures and phases were identified. By studying the mineralogy, morphologies of residues after leaching the Al-species, and factors such as reaction time, temperatures, and stoichiometry of H_2SO_4:CFA were optimized to get a higher leaching efficiency. The reaction between CFA and concentrated H_2SO_4 was confirmed as a typical solid-liquid diphase reaction which involves the heterogeneous corrosion and formation of $Al_2(SO_4)_3$ at the CFA surface. Although the shrinking core model has been usually used in describing the fluid-solid reactions (Song et al., 2013; Weingarten et al., 2012; Gbor and Jia, 2004), this model is found for the first time to be applicable in the high-temperature and viscous system consisting with CFA and concentrated H_2SO_4.

2. Experimental

2.1 Materials The CFA was sampled from thermal power plant No.x of Guohua Co., located at Ordos, in Inner Mongolia, China. The average particle of the raw CFA (d_{50} = 8.0 μm) and the pulverized sample (d_{50} = 3.0 μm) were tested on a Mastersizer 2000 analyzer, and the plot of size-distribution was shown in Fig. 1. The chemical compositions are listed in Table 1. The content of alumina is 51.8% wt. demonstrating the CFA was a type of high-aluminum ashes. According to the X-ray diffraction (XRD) analyses and polarized microscopy, the major phases

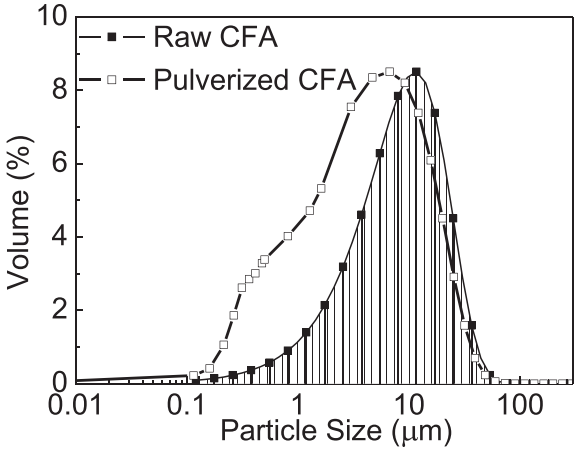

Fig. 1. Plots of particle size-distribution of CFA and the pulverized sample collected from one of the thermal power plants of Guohua Co., located at Ordos.

Table 1
Chemical composition of the raw CFA collected from Guohua Co. and the solid residue after leaching (fraction%, wt.)

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	K_2O	Na_2O	MgO	LOI[a]
Raw CFA	40.70	51.18	1.96	1.72	1.35	0.35	0.22	0.10	1.08
Residue	69.97	14.94	0.92	1.28	0.85	0.19	0.033	0.13	9.48

[a] Loss of ignition.

were identified as amorphous (aluminosilicate glass), mullite and corundum. There were almost no XRD peaks indexed to quartz or SiO_2 authigenic minerals. Sulfuric acid (H_2SO_4) used in this research is of industrial grade with concentration of 98% wt. Other chemicals that were used in these measurements were of analytical grade purchased from Beijing Chemical Factory.

2.1. Brief description of the procedure

The whole procedure in extracting aluminum from the Jungar CFA includes the following four steps: (1) The CFA was homogeneously mixed with H_2SO_4 (98%, wt.) at certain ratios of H_2SO_4:CFA (0.2–1.6). For example, 10.0 g coal fly ash mixed with 10.28 mL H_2SO_4 (98% wt.) was evaluated to be a molar ratio of H_2SO_4:CFA (Al_2O_3, 51.2%) = 1.2 in stoichiometry; (2) The homogeneous mixture was digested in a three-necked flask, and the reaction was performed at a particular temperature (220–320 °C) for some period of time (30–120 min). A condensate reflux device was installed on the flask to recycle SO_3; (3) After digestion the clinker was dissolved in boiled de-ionized (DI) water under turbulent stirring, and the leaching was kept for a period of time. The leachate was separated by vacuum filtration followed by washing with hot water (80–90 °C). The liquor ($Al_2(SO_4)_3$) was collected and analyzed via a volumetric method. The extraction yield of alumina was calculated according to the equation, $\eta = m_{LE}(Al^{3+})/m_{CFA}(Al^{3+})$, where η is the extraction efficiency of aluminum, $m_{LE}(Al^{3+})$ and $m_{CFA}(Al^{3+})$ denote the mass of Al^{3+} in the leachate and in the raw CFA, respectively. The residue was washed five times with hot water followed by drying at 120 °C for 24 h; (4) The solution of aluminum sulfate was heated to 115–117 °C, and the $Al_2(SO_4)_3{\cdot}18H_2O$ crystalloids were obtained after evaporation. After drying the $Al_2(SO_4)_3{\cdot}18H_2O$ was dehydrated at 370 °C, and further calcined at 870 °C. $Al_2(SO_4)_3$ was decomposed into SO_3 and γ-Al_2O_3. The fume SO_3 was reclaimed, and could be reused. The final γ-Al_2O_3 was to be produced. The schematic diagram of this art was illustrated in Scheme 1. For the study of CFA treated with concentrated sulfuric acid at high temperatures, this article was focus on the digesting (2nd) and leaching (3rd) steps.

2.2. Characterizations

The XRD was conducted on a DX-2007 instrument (Dandong Haoyuan Co., China) linked with a Cu-Kα radiation (1.5419 Å) with 35 kV and 25 mA. The scattering angles were set within 5–80°, and scanned at a speed at 0.02° per minute. For phase identification, thin sections of 75 mm × 50 mm in size with thickness of 30 μm were prepared via an abrasive method. The sample was primarily immersed into fluidic plastics with hardening agent, then mixed by stirring, and then vacuumed in a vessel to degas from the past. After consolidation, the hardened plastics were made into thin section. The petrographic study was carried out under a polarization microscope (59XC-PC, Shanghai Optical Instrument, China). For compositional inspection a certain micro-area, samples were selected and characterized by an electron-probe micro-analyzer (EPMA) using a JEOL JXA-8600 Superprobe linked with a LINK 860 X-ray spectroscopy (EDS) detector (Harding et al., 2014). The scanning electron microscopy (SEM) images were also captured by a Quanta-200 at the voltage of 25 kV. The energy-dispersive X-ray spectroscopy (EDX) analysis was performed by using an