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# Mineral changes and trace element releases during extraction of alumina from high aluminum fly ash in Inner Mongolia, China

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ABSTRACT

The mineralogy and trace element redistribution in the processes of extracting alumina from high aluminum fly ash in an industrial-scale production line (ISPL) in Inner Mongolia, China, are systematically investigated. Three samples were collected from the Togtoh power plant and ten samples from different processing sections in the ISPL. The mineralogy, chemical composition and morphology of the samples were characterized respectively by X-ray diffraction (XRD), X-ray fluorescence (XRF) spectrometry, and field scanning electron microscopy combined with energy dispersive X-ray spectrometry (FSEM-EDX). The trace element contents were determined by atomic fluorescence spectroscopy (AFS) and inductively coupled plasma-mass spectrometry (ICP-MS).

The results show that the minerals in the pre-desilication fly ash (PDFA) include mullite, corundum, quartz, and nosean, and that amorphous $SiO_2$ substantially disappears after the high aluminum fly ash (HAFA) is desiliconized. The minerals in the sintered fly ash (SFA) are sodium aluminate and larnite; most of the mullite reacts with $Na_2CO_3$ in the sintering process. Compared with trace element data for global hard coal ashes, elements that are slightly enriched elements in the HAFA are Li, Ga, Zr, Nb, Hf, Pb, and Th, and elements that are depleted include Ni, Ge, Rb, Sb, Cs, and Bi. The by-product silicon-calcium residue (SCR) is slightly enriched in Li, Zr, Nb, Hf, Ta, and Th, and depleted in Cr, Co, Ni, Cu, Ge, As, Rb, Mo, Cd, Sb, Cs, Ba, W, Hg, Tl, and Bi. Gallium shows a close affinity with $Al_2O_3$, and is strongly enriched (97 ppm) in the aluminum hydroxide (AH) product. For the whole ISPL, most of the trace elements are redistributed into the main SCR by-product, including Li, Be, Sc, V, Cr, Co, Ni, Cu, Sr, Zr, Nb, Cd, In, Hf, Ta, Bi, Th, U, and REY (rare earth elements and Y) (relative enrichment factor $>0.6$; relative enrichment factor is used to describe the distribution of trace elements that end up in the extraction process). Some of the trace elements are released to atmosphere at high temperature, such as Mo, Hg and Tl, and only small amounts of trace elements become redistributed into the product or other by-products.

## 1. Introduction

Thermal power generation is the main area of coal utilization in China, and coal fly ash (CFA), which is the principal by-product in coal-fired power plants, has become the most abundant anthropogenic solid waste (Yao et al., 2014; Saikia et al., 2015). Generation of CFA in China is still increasing per annum by 2015 (Yao et al., 2015), and a large proportion of the CFA in the north of China is treated simply as waste. However, coal combustion resides and coal itself in some cases contain valuable elements (e.g., Ge, Ga, U, rare earth elements and Y, Nb, Zr, Se, V, Re, as well as the base metal Al) occur at concentrations comparable to or even higher than those in conventional economic deposits (Arbuzov et al., 2014, 2016; Dai et al., 2015, 2016a; Hower et al., 2013, 2014, 2016a,b; Liu et al., 2015), and thus have attracted much attention as a source for these valuable metals (Seredin et al., 2013; Dai et al., 2016b; Franus et al., 2015; Hower et al., 2015). A number of methods have been proposed for high value-added utilization of fly ash (Zhang et al., 2004; Garg et al., 2005, Steveson and Sagoe-Crentsil, 2005; Chand and Vashishtha, 2000; Paul et al., 2007) including acid and alkali methods or salt activation method that have been developed to extract Ga and Al from high-$Al_2O_3$ fly ashes (Guo et al. 2013; Feng et al. 2014; Li et al. 2014; Li et al. 2016). Recycling of alumina is considered to be one of the most likely options (Seredin, 2012; Yao et al., 2015). In addition, extracting Ge, Ga, and REY (rare earth elements and Y) from some fly ashes is also promising for commercial production (Seredin, 2012; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Dai et al., 2014a; Franus et al., 2015; Rozelle et al., 2016). It has been reported that abundant coal resources containing high concentrations of alumina occur in southern Inner Mongolia and northern Shanxi province, China (Fig. 1) (Yao et al., 2014). The average alumina content in Chinese fly ash ranges from 20% to 35% (Ma et al., 1999), whereas the range in this specific area is as high as 40–50% (Dai et al., 2010, 2016b; Seredin, 2012; Yao et al., 2014). The annual output of high-aluminum fly ash in this area is approximately 80 million tonnes, which can yield 30 million tonnes of alumina and

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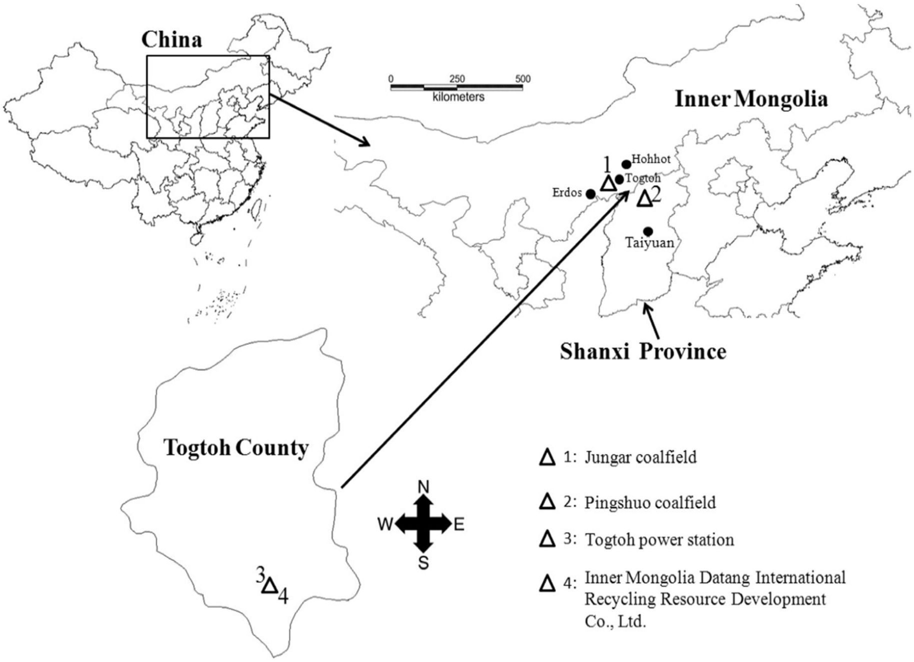

**Fig. 1.** Locations of samples and high aluminum coalfields.

33 million tonnes of active silica annually (Wang, 2014). The Jungar coalfield is located the northern Ordos Basin, and its geological setting and geochemical compositions have been described in a great detail by Dai et al. (2006a). The proven coal reserves in this area are 55.4 billion tonnes and the prospective reserves reach approximately 100 billion tonnes (Leng, 2006). The coal is also well-known for its high alumina content (Dai et al., 2010; Yao et al., 2014), which may represent a potential alternative resource of bauxite (Authier-Martin et al., 2001; Iyer, 2002; Seredin, 2012). An aluminum smelter has been built in 2007 and put into operation in Inner Mongolia, China; this is the world's first industrial-scale production line (ISPL) to extract alumina from high aluminum fly ash (Seredin, 2012; Yao et al., 2014).

A significant number of trace elements (TEs) are enriched in CFA, and some of these may be transferred to the atmosphere and water bodies, eventually leading to environmental and human health hazards (Finkelman et al., 2002; Dutta et al., 2009; Jones et al., 2012; Kostova et al., 2013; Saikia et al. 2015; Valentim et al. 2016). The environmental impacts of trace elements are probably related to their concentrations and affinities to organic or inorganic matrices, as well as the combustion conditions and pollution control systems (Xu et al., 2004; Vassilev and Vassileva, 2007; Guedes et al., 2008; Mardon et al., 2008; Huggins and Goodarzi, 2009, Mokhtar et al., 2014). The volatility of trace elements during coal combustion has been classified by some researchers (Meij, 1995; Meij and te Winkel, 2007; Dai et al., 2010, 2014b). Meij and te Winkel (2007) grouped the elements into three classes according to their volatility. Some elements, such as Se and Hg, are easily-vaporized during coal combustion (Rizeq et al., 1994; Meij and te Winkel, 2007; Dai et al., 2010). Gallium in some fly ashes is regarded as a potential resource for extraction and utilization (Dai et al., 2012a; Seredin, 2012). Although it is commonly regarded as a nonvolatile element during coal combustion, 20% of the Ga in Jungar coal may be volatilized at 1200 °C, mainly because a portion of Ga in this coal is hosted by the organic matter (Dai et al., 2006a,b, 2008; Zhang et al., 2008). Zhang et al. (2006) studied the distribution of trace elements in different inorganic matrices (ferruginous spheres, mullite-corundum, and glass substances) separated from high aluminum fly ash, and found that the TEs are more easily enriched in glass substances. The migration and emission of toxic trace elements or incorrect storage of the by-products during extracting alumina from fly ash may cause potential toxic trace element pollution (Han et al., 2013). However, the knowledge of the TEs distribution in the extraction process is limited (Zhang et al., 2006), due to that the overwhelming majority studies conducted have focused on improving the extraction method and the cost reduction (Matjie et al., 2005).

This study is aimed at understanding the mineralogy and trace element distribution associated with extraction of alumina from high aluminum fly ash in Inner Mongolia, China. It aims to provide comprehensive information on the mineralogy and trace element distribution in the industrial extraction of alumina from fly ash, and may provide insight for further utilization of high aluminum fly ash.

## 2. Samples and methods

### 2.1. Samples

The Togtoh power plant is located 50 km from the Jungar coalfield (Fig. 1). It is one of the largest power plants in China, with eight sets of 600 MW units and two sets of 300 MW units. Another two sets of 600 MW units have already been approved, which together would make it the largest power plant in Asia; its installed gross capacity will reach 6720 MW. The power plant partially combusts Jungar coal and generates 3.8 million tonnes of fly ash per year. The fly ash from the plant is provided to the Inner Mongolia Datang International Recycling Resource Development Co., Ltd. (DRRC) for utilization.

The DRRC facility (Fig. 2) was established in 2007, adjacent to the Togtoh power plant. It is an aluminum smelter that recycles alumina from the CFA and was the first industrial-scale production line (ISPL) put into operation in the world for this purpose. The plant adopts a pre-desilication and lime-soda sinter combination method for alumina extraction (Zhang, 2007), with an annual production capacity reaching 0.2 million tonnes of alumina and 0.2 million tonnes of active calcium silicate. A schematic of the ISPL is shown in Fig. 3.

In total, thirteen samples were collected, among which samples of feed coal (TFC), high aluminum fly ash (HAFA), and coal gangue (CG) were collected from the Togtoh power plant. Seven samples of the product or by-products in each process section were collected from the ISPL, namely, pre-desilication fly ash (PDFA) and active calcium silicate (ACS) from the pre-desilication process, sintered fly ash (SFA)

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