Applied investigation on the interaction of hazardous elements binding on ultrafine and nanoparticles in Chinese anthracite-derived fly ash

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ABSTRACT

A multifaceted instrumental approach was employed to determine the chemistry and mineralogy of pulverized-coal-combustion fly ashes from two Chinese power plants. Techniques included traditional optical microscopy, X-ray diffraction, and chemical analysis along with a variety of electron beam methods. The aim is to demonstrate and bring together the wide variety of procedures dealing with F as the key element of concern, and determining its location in the mineral nanoparticles.

The Hg content of the Anwen (Songzao coalfield) fly ashes is higher than that of the Diandong (East Yunnan) fly ashes, possibly owing to the greater C and Cl in the Anwen fly ashes. Both fly ash sources contain a variety of amorphous and nano-crystalline trace-element-bearing particles, both associated with multi-walled carbon nanotubes and as particles independent of carbons.

1. Introduction

China is both the largest consumer and producer of coal in the word (Dai et al., 2011a) with a coal production up to 3 Gt in 2009, of which the coal-fired power plants consumed 1.5 Gt (Zhao et al., 2011). The amount of coal fly ash (CFA) produced by the coal-fired power plants in China was ca. 375 Mt in 2009, while the CFA utilization rate is only 30% (Yang et al., 2010).

While knowledge of Chinese CFA characteristics is helpful with regards to its utilization, few studies have been conducted on the transformation of minerals and the associated trace elements in coal combustion from Chinese power plants. Inorganic matter in coal is the main source of CFA; the occurrence, distribution, and transformation of mineral matter can significantly affect CFA characteristics and the related environmental problems (Hower et al., 2005; Silva et al., 2009; Ribeiro et al., 2011; Silva and DaBoit, 2011). The transformations of major and minor inorganic elements have significant effects on the emission of particulate matter during coal combustion. Control of these emissions from coal power plants requires an understanding of the manner in which they occur in coal, their behavior during combustion, their form in the stack gas, as well as the final amount released into the atmosphere (Tian et al., 2011).

This investigation is the first study combining traditional CFA analysis (e.g. XRD, petrology, SEM, chemical composition by XRF and ICP-MS) and nanomineralogy (by HR-TEM/SAED/MBD/EDS) with aspects of the geochemistry and structure of hazardous elements from Chinese CFA. The results have implications for studying the potential health effects of nanominerals and ultrafine particles. Characterizing natural/anthropogenic mineral and particles assemblages is challenging, because it has been virtually impossible to isolate them free of artifacts.

2. Experimental

2.1. Sampling

The anthracite-combustion-derived fly ash samples were collected from two power plants: Diandong of eastern Yunnan and Anwen of Chongqing, in southwestern China. The fly ash samples from the Anwen and Diandong power plants were collected in July 2007

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and August 2009, respectively. The combustion conditions of two power plants are similar and the combustion temperature inside the boilers is about 1500–1600 °C. Both of the fly ashes were collected directly at the base of the electrostatic precipitator filter. In most cases, the ash samples were analyzed at the as-received particle size.

The Diandong Power Plant (capacity: 4×600 MW) is located in Fuyuan County of eastern Yunnan (Fig. 1). Four samples of fly ash (Sample nos. East Yunan 1 to 4) were collected at ash concentration units. The feed anthracite, from late Permian Longtan Formation coal, is mainly from the nearby Bailongsha Mine (Fig. 1).

The Anwen Power Plant (capacity: 2×660 MW) is located in Qijiang County of Chognqing (Fig. 1). The feed coals of the Anwen Power Plant are mainly from the late Permian Longtan Formation coals of the Songzao coalfield. The geological setting and coal characteristics were described in detail by Dai et al. (2010, 2011c). Two samples of fly ash (Sample nos. SZDC 1–2 and SZDC 2–2), one kilogram for each sample, were collected at ash concentration units. The present study was intended not only to help in assessing the environmental impacts associated with such dumping, but also to provide more definitive data that may assist in the application of mitigation measures.

Fly ashes from both the Diandong and Anwen power plants are mainly stored in piles and only a small portion has been used for landfill (2011, personal communication with Yongchun Zhao). Since some researchers reported that coals from eastern Yunnan and Chongqing of southwestern China contained high concentrations of toxic trace elements (Zhou and Ren, 1992; Dai et al., 2007b, 2008a,b; Zhuang et al., 2003; Wang et al., 2011), the combustion wastes of these coals may concentrate some toxic trace elements, which are potentially hazardous to human health or the environment.
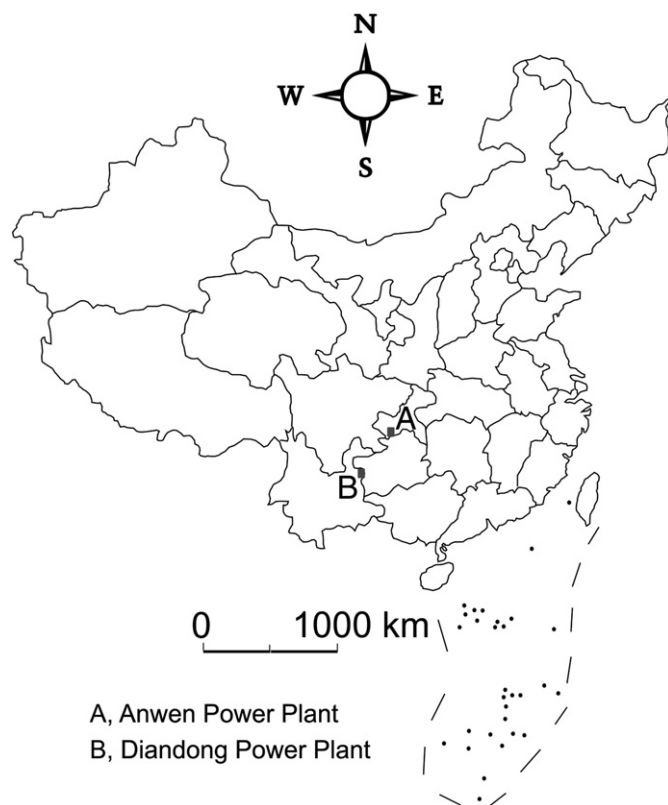

Fig. 1. Location of power plants and mines, China.

2.2. Analytical procedures

2.2.1. Ultimate analysis and mercury

An elemental analyzer (vario MACRO) was used to determine the percentages of C, H, and N in the CFA. Mercury analysis was performed in the University of Kentucky Center for Applied Energy Research (CAER) laboratories with a LECO AMA 254 instrument.

2.2.2. X-ray fluorescence (XRF)

Samples were crushed and ground to pass 200 mesh for geochemical analysis. X-ray fluorescence spectrometry (ARL ADVANT'XP+) was used to determine the oxides of major elements for each sample after high-temperature ashing (815 °C), as outlined by Dai et al. (2011c,d). For XRF analysis, the ash samples were prepared by borate fusion in an automated fusion furnace (CLAISSE TheBee-10). Each ash sample (1 g) was mixed and homogenized with lithium borate flux (10 g; CLAISSE, pure, 50% $Li_2B_4O_7$ + 50% $LiBO_2$). The mixture was melted in a Pt-Au crucible (25 ml; 95% Pt + 5% Au) and after fusion the melt was cast to a Pt-Au mould flat disk (diameter: 35 mm) (Dai et al., 2011c, under review). Such sample fusion could avoid particle and mineral influence on the element content. For matrix correction and calibration of XRF data processing, Uniquant software (Ver 5.46), a "standard-less" methodology based on a set of fundamental parameters and unique algorithms (Thermo Fisher Scientific — Kju, 2009), was used in this study. Although Uniquant allows us to analyze unknown materials without the need for matching standards or reference materials, references samples (NIST 2689, 2690, and 2691) were also integrated with Uniquant data processing. More details see UniQuant Cookbook (Thermo Fisher Scientific — Kju, 2009).

2.2.3. Inductively coupled plasma mass spectrometry (ICP-MS) and Cl and F analyses

Inductively coupled plasma mass spectrometry (X series II ICP-MS), in a pulse counting mode (three points per peak), was used to determine trace elements in coal samples, except for Hg, F, and Cl. The ICP-MS analysis and sample microwave digestion program, related to coal and coal-related materials, were outlined by Dai et al. (2011c). Arsenic and Se were determined by ICP-MS using collision cell technology (CCT) in order to avoid disturbance of polyatomic ions. Procedures for ICP-MS analysis follow Dai et al. (2011c). Multi-element standards (Inorganic Ventures: CCS-1, CCS-4, CCS-5, and CCS-6) were used for calibration of trace element concentrations. For ICP-MS analysis, samples were digested using an UltraClave Microwave High Pressure Reactor (Milestone).

Fluorine was determined by pyrohydrolysis with an ion-selective electrode, following the methods described in Chinese Standards GB/T 4633-1997 and GB/T 3558-1996. Chlorine was analyzed by ion chromatography at the CAER.

2.2.4. Optical petrography and particle size analysis

Samples for optical petrology were prepared as epoxy-bound particulate pellets prepared to a final 0.5-micron polish. Optical petrology was conducted on Leitz microscopes at the CAER with reflected-light, oil-immersion optics with a final magnification of 500×. Optical petrology complements the microbeam techniques discussed below. Each has their niche in the overall analysis of the samples.

Particle size was determined on a Malvern Mastersizer 2000 laser particle-size analyzer at the CAER.

2.2.5. X-ray diffraction (XRD)

The X-ray diffraction (XRD) analysis of the anthracite ashes was performed on a powder diffractometer with a Ni-filtered Cu-Kα radiation with a scintillation detector (D/max-2500/PC XRD). The XRD pattern was recorded over a 2θ interval of 2.6–70°, with a step size of 0.01°. X-ray diffractograms of the samples were subjected to quantitative mineralogical analysis using Siroquant™, commercial