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Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals

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ABSTRACT

The fly ashes derived from three giant coal-hosted Ge deposits, Lincang (Yunnan of southwestern China), Wulantuga (Inner Mongolia of northern China), and Spetzugli (Primorye, Russian Far East), are unique because they are highly enriched in elements, including up to (on an organic-free basis): 4.66% Ge, 2.12% As, 1.56% F, 1.22% Sb, 0.56% W, 0.56% Zn, 0.55% Pb, 0.13% Sn, 0.12% Ga, 0.056% Bi, 0.04% Be, 0.028% Cs, 0.017% Tl, and 0.016% Hg. These high element concentrations in the fly ashes are due both to their high levels in the raw coals from which they were derived and their high volatility during the coal combustion process.

Rare earth elements and yttrium (REY) were fractionated during coal combustion. They are more enriched in fly ashes than in slag from the respective coals. Maximum REY enrichment may occur either in fine-grained fly ash from baghouse filters or in coarse-grained fly ash from electrostatic precipitators. Cerium and Eu are more enriched in the fly ashes than other REY, and yttrium is relatively depleted in the fly ashes in comparison with the slag.

Three types of unburnt carbon can be identified in the fly ashes: (1) carbon with well-preserved initial maceral structures (fusinite and secretinite), (2) isotropic and anisotropic carbon, and (3) secondary fine-grained carbon. The last type of unburnt carbon is characterized by embedded fine-grained Ge-bearing and other mineral phases. Ge oxides (e.g., GeO_2) are the major Ge carrier in the fly ashes. Other Ge-bearing mineral phases, however, were also identified, including glass, Ca ferrites, solid solutions of Ge in SiO_2, and probably elemental Ge or Ge (Ge-W) carbide, as well as previously-unknown complex oxides including $(Ge,As)O_x$, $(Ge,As,Sb)O_x$, $(Ge,As,W)O_x$, and $(Ge,W)O_x$. Some portion of the Ge occurs as adsorbed species in different types of unburnt carbon (Types 1 and 2) in the ash particles.

1. Introduction

Germanium is currently being industrially extracted as a raw material from three separate Ge-bearing coal deposits: Lincang (Yunnan province of China), Wulantuga (Inner Mongolia of China), and Spetzugli (Primorye, Russian Far East) (Fig. 1); together these account for more than 50% of the total industrial Ge production in the world. The abundance, origin, and mode of occurrence of Ge in high-Ge coals (Dai et al., 2012b; Du et al., 2009; Hower et al., 2002; Hu et al., 2009; Ivanov et al., 1984; Kostin and Meitov, 1972; Levitskii et al., 1994; Mastalerz and Drobniak, 2012; Qi et al., 2007; Seredin, 2003, 2004, 2006; Seredin and Danilcheva, 2001; Seredin and Finkelman, 2008; Zhuang et al., 2006), as well as the methods for Ge recovery from coal fly ash (Shpirt, 1977, 2009; Shpirt and Rashevskii, 2010; Yudovich and Ketris, 2004 and references therein), have been extensively studied in the last few decades.

However, coal combustion products (CCPs) derived from Ge-rich coals, especially from coals currently being used for industrial purposes, have rarely been investigated using modern analytical methods. There has been only limited information on concentrations of 14 trace elements in two fly ash and three slag samples from the Lincang deposit (Qi et al., 2011). In this paper, the mineralogy and geochemistry of various CCPs are reported for the first time for all the high-Ge coal deposits that are currently being industrially used in the world. Although only preliminary results from limited CCP grab samples are presented in

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Fig. 1. Locations of the currently mined high-Ge coal deposits.

this study, we believe that the data may provide some new information of the distribution and modes of occurrence of trace elements and minerals in CCPs derived from Ge-rich coals at a more generic level.

2. Ge-bearing coal deposits and sample collection

All three high-Ge coals have a low rank and low calorific values. For example, $R_r = 0.45\%$ for the Wulantuga coal (Dai et al., 2012b) and 0.48% for the Lincang coal ($R_r = 0.58\%$ for the Lincang coal as reported by Zhuang et al., 1998), and 0.39% for the Spetzugli coals (Medvedev et al., 1997); calorific values are 21.7 MJ/kg and 27.8 MJ/kg (air-dry basis) for the Wulantuga (Dai et al., 2012b) and Spetzugli coals (Medvedev et al., 1997), respectively. Huminite is the dominant maceral group in the Lincang and Spetzugli coals (80–90 vol.%), but the inertinite-group macerals dominate in the Wulantuga coals (52.5 vol.% on average; Dai et al., 2012b).

All these coals are combusted in small-scale power plants with different types of fly ash collection systems (Fig. 2A–C). All of the three plants only use the Ge-bearing coals as the feedstock. High-Ge fly ashes collected from baghouse filters of the plants are the raw materials for production of various Ge compounds and metallic germanium (Fig. 2D).

2.1. Wulantuga deposit

The Wulantuga high-Ge coal deposit is located in the Shengli Coalfield, Inner Mongolia, northeastern China (Fig. 1). The early Cretaceous No. C6 Coal, with an average thickness of 16.1 m, is the major host for the high Ge coal resources. Germanium concentration in the coal varies from a few hundreds of μg/g to more than 1000 μg/g, with an average of 240 μg/g (Du et al., 2009; Zhuang et al., 2006). Dai et al. (2012b) reported a very similar Ge concentration (273 μg/g) for the Ge-bearing coals, which were simultaneously collected along with the CCPs derived from the power plants. Du et al. (2009) estimated that 1700 t Ge could be extracted from this coal. The origin and modes of occurrence of Ge in the coal have previously been described by Dai et al. (2012b), Du et al. (2003, 2004, 2009), Li et al. (2011), Qi et al. (2007), Wang (1999), and Zhuang et al. (2006). It is considered that the Ge in the coal is dominantly organically-associated and its enrichment is due to hydrothermal fluids from the adjacent granitoids (Dai et al., 2012b; Qi et al., 2007).

The designed capacity for Ge production in the recovery plant at the Wulantuga deposit is 100 t per year, which is close to the annual world consumption of Ge in 2010–2011 (120 t; Guberman, 2012). The coals from the mine are crushed and then are fed into vortex furnaces for combustion. The combustion conditions are strictly controlled to ensure that Ge is mostly concentrated in the fly ash collected by the baghouse filters. For example, the combustion intensity and the boiler temperature are set at 156 kg/m^2 and 1200 °C, respectively. Two samples, representing relatively coarse fly ash from the electrostatic precipitator (FA(C)-W), and fine fly ash from the baghouse filter (FA(F)-W), were taken for the study from the fly ash collection system.

2.2. Lincang deposit

The Lincang high-Ge coal deposit is situated in southwestern Yunnan province of southwestern China (Fig. 1). The high-Ge coals are mined mainly from the Dazhai Mine, the Meiziqing Mine, and the Chaoxiang pit of the Zhongzhai Mine. Three Neogene coal seams (Nos. S1, Z2, and X3) are currently mined and are burned for Ge recovery. Qi et al. (2004) reported that the Ge concentration in the Lincang ore deposit ranges from a few tens of μg/g to about 2500 μg/g, with an average of 850 μg/g. However, we recently have found that the Ge concentrations of the Nos. S1 and Z2 seams in the Dazhai Mine are respectively 1345 and 1275 μg/g (based on 20 coal samples), with a weighted average of 1294 μg/g. Germanium in the Lincang coals is organically bound and was derived from Ge-rich granites by low-temperature hydrothermal solutions (Hu et al., 2009).

The ensured Ge reserves in the Dazhai, Meiziqing, and Zhongzhai Mines are 613 t, 76 t (both as of 31 December, 2009), and 39 t (as of 31 October, 2010), respectively. The Ge production of the Lincang Ge recovery plant is from 39 to 47.6 t per year.

The Ge-rich coals are fed into chain conveyer furnaces for combustion, and Ge-rich fly ash is collected by baghouse fabric filters after its temperature has been decreased to 110–120 °C by condensator cooling. The collection efficiency of the fly ash is around 99.8%. Two samples, one representing fabric filter fly ash (FA(F)-L) and one representing bottom ash deposited as a slag (SL-L), were collected for the present study.

2.3. Spetzugli deposit

The Spetzugli high-Ge coal deposit is located in the Pavlovka Coalfield of the southern Russian Far East (Fig. 1), where a small-scale open pit is being mined. Three Paleogene coal seams (Nos. II-low, II-up, and III-low) are currently being mined and burned for Ge recovery. According to the prospecting data, average Ge concentrations in the seams are 470, 480, and 620 μg/g, respectively (Sedykh, 2002), or 514 μg/g on average. However, based on 12 coal samples collected from drill holes and open pit in different years by Vladimir V. Seredin, the average Ge content in the seams is two times higher, 1025 μg/g. Like the mode of occurrence of Ge in the coals from the Chinese high-Ge deposits, the Ge in the Spetzugli coals is organically bound and was derived from granite basement by low-temperature hydrothermal solutions (Seredin, 2004, 2006; Seredin and Finkelman, 2008).

The ensured Ge reserves in the Spetzugli high-Ge coal deposit are about 1000 t. The designed capacity for Ge production is 21 t per year (http://www.geapplic.ru).

The coals from the mine are fed into a flare-layered boiler for combustion. The collection efficiency of the fly ash is similar to that for the Lincang deposit. Three samples, representing coarse fly ash from the cyclone (FA(C)-S), fine fly ash from the baghouse filter (FA(F)-S), and bottom ash (oolitic slag) (SL-S) were collected from the power plant.

Overall, the plant design and combustion conditions for the three coal-hosted high-Ge deposits are different. For example, based on the data