Evaluation of fluorine release from air deposited coal spoil piles: A case study at Yangquan city, northern China

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ABSTRACT

The fluorine content of coal has been well documented, while such data of coal spoil are limited. In the present paper, fluorine in coal spoils and its releasing behavior were studied via leaching and combustion tests, as well as field investigation. Fluoride pollution in groundwater and soil occurred in the air depositing areas of coal spoils. The average content of fluorine in coal spoils was 525 mg/kg with the highest value of 1885 mg/kg. The only XRD detectable inorganic fluorine phase was fluorphlogopite. The absence of major fluorine bearing minerals in coal spoils suggested that bulk fluorine, rather than trace phases, resided in the mineral matrix. The major extracted species were water soluble fluorine and exchangeable fluorine in the coal spoils. Batch leaching tests illustrated that the leachable fluoride in coal spoils was widely distributed, ranging from 2.0 to 108.4 mg/kg. Column leaching tests showed a clear pH-dependent leaching behavior of fluorine: lower pH situation led to fluorine release from the mineral matrix; the loosely bound or easily exchangeable fluorine was also flushed out of the column. The higher ion strength or alkaline bicarbonate/carbonate rich leaching solution tended to free more fluorine into the acidic aqueous solution. The leachable fluorine in coal spoils was estimated as ca. 6%, based on the results of leaching tests. Also, our research found that over 90% of fluorine in coal spoils could be released into the atmosphere as a result of spontaneous combustion, accounting for over 40% of the total atmospheric fluorine emissions in northern China. Our investigation suggests that it is urgent to conduct comprehensive studies to assist the management and control of fluorine pollution at coal spoil banks.

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1. Introduction

High fluoride level can cause negative effects upon environmental quality and human health, such as dental fluorosis, skeletal fluorosis, impaired thyroid function, and lower intelligence in children. As reported by numerous researchers, fluorine in the environment had both natural and anthropogenic sources (Almeida et al., 2005; Alvarez-Ayuso and Querol, 2008; Ayoob and Gupta, 2006; Bressan et al., 1974; Codling et al., 2014; DAlessandro et al., 2008; Edmunds and Smedley, 2013; Farooqi et al., 2007; Prival and Fisher, 1974; Shvartsev and Wang, 2006). Natural sources of fluorine include volcanic gases, marine aerosols, and soluble fluorides in rocks (Agrawal et al., 1997; Tavener and Clark, 2006). Beside these natural fluorine emission processes, gaseous (e.g., HF and SiF_4) and particulate fluorides (e.g., $A1F_3$, $NaAlF_6$, and CaF_2) could be emitted from high temperature processing industries, such as the production of steel, aluminum, glass, China, phosphate fertilizer, brick, and tile, as well as coal burning (Greta et al., 2013; Jayarathne et al., 2014). The fluoride-containing

particulate may deposit in aqueous environments, causing fluorine contamination (Finkelman et al., 2002; Finkelman, 2004; Udeigwe et al., 2011; Zhu et al., 2013). In recent decades, anthropogenic sources have become more important in bringing fluorine concentration up to harmful levels in air, water, and food (Franzaring et al., 2006; Jayarathne et al., 2014).

Coal and coal waste combustion contributed significantly to anthropogenic fluorine emission (Conceicao and Bonotto, 2006; Godbeer et al., 1994; Liu et al., 2013; Lopez-Vilarino et al., 2003; Swaine, 1990), as coal remains the top energy source worldwide. In China, with the fast economic development over the last three decades, rapid growth of coal mining industry has resulted in accumulation of large amount of coal mining waste. As the largest coal production country in the world, China has a coal production capability of 2.5 billion tons in 2012 (The Ministry of Land and Resources P.R.C., 2013). According to Lv (2012), there were more than 1500 coal waste dumps and the total amount of solid waste was more than 5 Gt in China. There were more than 300 gobs in Shanxi Province, one of the biggest coal production bases in China (Zhao et al., 2008). And there the total amount of coal waste was more than 1.3 Gt in 2007, occupying a land area of 300 ha.

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Fluorine was classified as a potential toxic element in the development of coal resources (US National Research Council, 1980). Abnormally high content of F has been detected in coal spoils or stone coal, especially in its clay minerals (Finkelman, 2004; Sokol et al., 2002; Stracher and Taylor, 2004; Pone et al., 2007). It was reported that F content was fairly high in mudstone and shale interlayers of coal seams in fourteen provinces of China (Querol et al., 2008; Xu and Luo, 2012; Wang et al., 2014). For example, in Shanxi Province, fluorine content in coal spoils was reported from 20.6 to 912.5 mg/kg.

Toxic substances in coal and coal mining byproducts, including fluoride, trace elements, HF, SO_2 and particulate matter, are released into the aquatic and atmospheric environment due to combustion and leaching. It was reported that coal combustion accounted for ca. 10% of the total atmospheric fluorine emission in the United States (Fleischer et al., 1974). And a total of 66,398.5 t fluorine had been emitted due to combustion of 8 Gt coal in northern China (Luo et al., 2002). Results of our previous investigation demonstrated that a high portion of fluorine in coal spoils can be released into environment via leaching or combustion (Li et al., 2013). However, little has been known about the occurrence, pathway and contribution of air deposited coal spoil banks on environmental fluorine enrichment in China (Ao et al., 2008; Zhao et al., 2008).

The focus of this study is to characterize the release of fluorine from coal spoils banks via leaching or combustion. Coal spoils, soils, leachate, and groundwater samples were collected from depositing areas of coal spoils banks at Yangquan city. Batch and column leaching experiments, and combustion experiments were employed to evaluate the release of fluorine during natural weathering leaching and spontaneous combustion. The main objectives of this paper are: 1) to characterize the abundance and occurrence of fluorine in the coal spoils; 2) to assess the releasing behavior of fluorine under natural weathering leaching and spontaneous combustion; and 3) to estimate the environmental fluorine gained from air deposited coal spoils banks.

2. Geologic setting

The Yangquan coal mining district is located to the west of the town of Yangquan (Shanxi province, E113°36′ N37°53′). The total known reserve of coal at Yangquan is estimated to be 1.41 Gt, covering an area of 1400 km². The major periods of coal formation are Carboniferous (Taiyuan Formation) and Early Permian (Shanxi Formation). The Shanxi Formation mainly consists of sandstone, mudstone, and coal. T15 is the major coal seam in the Taiyuan Formation. The coal-bearing strata overlying the Ordovician and Cambrian limestone are overlain by the Xiashihezi Formation (Early Permian), the Shangshihezi Formation (Later Permian) and the Triassic System of clastic rocks. The major coal types include anthracite, meager coal, and little charred coal (Huang, 2004).

3. Samples and methods

3.1. Sampling and pretreatment

There are a total of 21 coal spoil banks produced by the six main coal mines (Fig. 1(a)). A total of 46 coal spoil samples were collected from the spoil banks in the two biggest coal mines (1) and (2) (Fig. 1(a), (b1), (b2), (d)), between December, 2006 and September, 2013. Samples of fired coal spoil (FCS) were quarried from the slope of the burnt banks (Fig. 1(b4)). The coal spoil fire gas minerals (CSFGM) were scratched from the gas vent at the top of the spoil banks (Fig. 1(b3)). All collected samples were stored in plastic bags after packaged with tin foil papers to prevent contamination.

Also, four shallow groundwater samples were collected, by digging pits with depth 1–2 m, along the front foot of the spoil banks (Fig. 1 (b), G1–G4 in Fig. 1(d)). Four leachate samples were collected at the foot of the spoil banks (L1–L4 in Fig. 1(b)–(d)). A total of sixteen surface soil samples were collected around the coal spoil banks with a distance of 5, 25, 50, and 100 m in four directions (E1–E4, S1–S4, W1–W4, and N1–N4 in Fig. 1(c)). Eight soil samples were collected far from the spoil banks (>3 km) which were representative of the background (B1–B8 in Fig. 1(a)). The coal spoil and soil samples were all dried in an oven at 75 °C overnight to remove excess moisture. Then, a portion of the dried coal spoil samples were crushed and sieved, and particles less than 74 μm were collected for the experiments.

3.2. Sample characterization

The mineral composition of the coal spoils, FCS, and CSFGM were analyzed using X-ray diffraction (XRD, Rigaku). Semi-quantitative XRD analysis was undertaken by using the Reference Internal Standard Method (Chung, 1974), with the analyze error of ± 10% for major minerals and ± 30% for minor minerals.

Total fluorine in the samples was analyzed by a pyrohydrolysis-ion-selective electrode (ISE) method, in accordance with the Chinese Standard for Determination of Fluorine in Coal (GB/T 4633-1997, Gao et al., 1984; Qi et al., 2000). Pyrohydrolysis, performed in a tube furnace at 1100 °C, was employed for sample decomposition prior to F determination. The fluorine ion was absorbed by DI water for further analysis. The detection limit of this method for fluorine is 0.2 mg/g. The difference of two consecutive measurements was less than 10%. All fluorine concentrations were reported on a dry mass basis.

3.3. Sequential extraction experiments

Sequential extraction experiments were performed based on the methods suggested by Tessier et al. (1979), to study the speciation of fluorine in coal spoils by soaking fresh spoil samples in different solutions: (1) water soluble fraction, 50 ml of H_2O (20 °C, coal spoil: DI water = 1:25, 30 min); (2) exchangeable fraction, 1 M $MgCl_2$ (pH 7.0, 20 °C, coal spoil: solution = 1:25, 30 min); (3) fluorine fraction bound to amorphous Fe–Al oxides, 25 ml 0.2 M NH_4OAc (pH = 3.25, 20 °C in a water bath, coal spoil: solution = 1:25, 4 h); (4) fluorine fraction bound to crystalline Fe–Al oxides, 25 ml 0.2 M NH_4Ac + 0.1 M ascorbic acid (pH = 3.25, 96 °C in a water bath, coal spoil: solution = 1:25, 30 min); (5) fluorine fraction bound to organic matter, 50 ml of 0.02 M HNO_3 + 30% H_2O_2 (coal spoil: solution = 1:25); and (6) residual fluorine fraction, the fluoride content in this step, was determined by subtracting the other five fractions from total fluorine content.

3.4. Batch leaching tests

Batch experiments were performed to evaluate the leaching potential of fluorine from coal spoils, when in contact with different electrolyte solutions. A solid to solution ratio of 1:4 was employed with DI water, or electrolyte solutions (nitrate as $NaNO_3$, bicarbonate as $NaHCO_3$, and carbonate as Na_2CO_3) with different concentrations (0, 50, 100, 300, and 500 mg/l), or artificially prepared rain water (APRW). Here, $NaNO_3$ solution was used as natural neutral electrolyte solution with different ionic strength (IS); $NaHCO_3$ and Na_2CO_3 solutions represented natural alkaline HCO_3^-/CO_3^{2-} rich water which was observed as another leaching source water in coal mine 2 (Fig. 1(b5)), except for precipitation. The chemical composition of APRW was prepared according to the rain water composition in Yangquan city (Gao et al., 2011), with 0.5 mg/l Na^+, 4.27 mg/l Ca^{2+}, 0.67 mg/l Mg^{2+}, 12.2 mg/l SO_4^{2-}, 1.28 mg/l Cl^-, and pH of 6.50 (adjusted with diluted HCl and/or NaOH).

Batch tests were conducted in triplicate and equilibrated for 72 h on a shaking table (HTR-02, Tianjing, China) at a speed of 39 rpm under room temperature, ca. 23 ± 1 °C. Following the 72-h reaction time, the coal spoil-solution mixture was used for F^- analysis by an ion-selective electrode (ISE, Leici, PF-1/PF-1-01, Shanghai INESA Scientific