

Leaching Behavior of Fly Ashes from Power Plants

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Abstract The Yanzhou mine district, located in southwestern Shandong Province, is about 1300 km² with more than 8×10⁹ tons of proved coal reserves and there are 10 big power plants in this area. A large amount of coal ashes, which are regarded as waste materials, have been stockpiled in the area and have influenced the environment of the mine district. In this paper, analysis of fly ash samples from three power plants is carried out, the enrichment and concentration of trace elements, Pb, Zn, Cu and As, in coal ashes are analyzed, and petrological and mineralogical characteristics and chemical compositions of coal ashes are studied. The aim of this work is to provide basic scientific data for utilization of ashes and reduction of environmental pollutions.

Key words: fly ashes, trace elements, leaching experiment, power plants

1 Introduction

Coal plays an important role in consumed energy in many countries, especially in China, and the major consumed energy, at present and in the near future, is coal. *China Energy Annual Review* (1997) reported that coal will account for about 67% of the primary energy in 2020, dropping from the present 76% in China. The capacity of the coal-fired power plants is 93% of that of all thermal power plants. The principal usage of coal at present time is to provide heat energy through its combustion (particularly in the electrical power industry), but the coal-fired power plants not only produce heat and energy, but also have become one of the dominant pollution sources for environments. Therefore, many counties have paid attention to utilization of coal ashes from power plants (Sun et al., 1986; Henry et al., 1999; Yan et al., 1999).

Up to now, large mounts of fly ashes have been produced from the power stations in China. About 20% of them have been utilized in cement and construction industries, and the remainder disposed in lagoons, disposal mounts and landfill sites as waste material. Coal contains significant quantities of various trace elements and these elements are concentrated during and after the formation of coal. Many of the trace elements in the coal are partially or totally vaporized during combustion. The degree of vaporization determines how each element is partitioned between the solid phases and the flue gas, as well as the degree of surface association. Trace elements in coal can be classified as three groups by their behaviors during combustion. According to previous studies (Sun et al., 1986; Finkelman

et al., 1990; Helble, 1994; Rizeq et al., 1994; Liu, 2000; Liu et al., 2000a), Hg, Se and As are volatile, whereas Cr, Cu, Mo and Mn are less volatile. During combustion, trace elements tend to be enriched in fly ashes or associated with surface of ash particles due to evaporation and condensation as well as loss of carbon as carbon dioxide. So terrestrial disposal of fly ashes is regarded as a potential source of contamination due to the enrichment and surface association of trace elements in ash particles (Hassett, 1994; Liu et al., 1999; Liu 2000; Swaine 2000). Much attention has been paid to the leaching behavior and possible contamination, especially for the aquatic environment, when ash is in contact with water. The groundwater environment is more vulnerable than surface water due to the lower velocity under low permeability and the possible accumulation of leached elements in groundwater. In this case, not only more soluble sublimates on the surface of fly ash particles but also long-term dissolution of glassy particles which are unstable under natural conditions, is expected to influence the groundwater and soil environment (Liu and Yang, 2000b; Mehmet et al., 2001).

Many study results (Sun and Jervis, 1986; Finkelman et al., 1990; Helble, 1994; Rizeq et al., 1994; Cortland et al., 1997; Henry et al., 1999; Nathan et al., 1999; Yan et al., 1999; Liu, 2000; Liu and Yang et al., 2000a; Liu and Yang 2001) have pointed out that if coal ashes could not be utilized comprehensively or handled immediately the ashes will fly into the air, bringing about a great damage to the environment and life. Ashes can find their way into underground water, causing underground water pollution

during leaching actions (Finkelman et al., 1990; Hassett, 1994; Marcal et al., 1997; Wang and Ren, et al., 1999; Liu and Yang, 2000a, 2000b, 2003). Therefore, many researchers (Henry et al., 1999; Liu et al., 1999) from a number of countries have treated such a problem as how to make a comprehensive utilization of coal ashes.

The aim of this study is to investigate leaching behaviors of trace elements in fly ashes currently disposed in China and to assess the potential influence of fly ash landfills on groundwater composition. The methods adopted in the study include leaching tests in the laboratory.

2 Samples

Coal ashes have originated from the power plants in the Yanzhou mine district in Shandong Province. This district is an important basic area of coal industrial energy in eastern China. Fly ash samples were collected from three different power stations: FA1 from the Xinglongzhuang Power Plant, FA2 from the Dongtai Power Plant and FA3 from the Nantun Power Plant. All fly ashes were collected from electric precipitators of the power station.

3 Method

Mineralogy of the fly ashes were determined by the X-ray diffraction. The samples were prepared in different manners for determining trace elements. K, Na, Ca, Mg, Cu, Pb and Zn in ashes were determined by the ICP-MS and spectrophotometer for As. The chemical composition of ashes is listed in Table 1 and the concentration of the trace elements in ashes is showed in Table 2.

4 Experiments

In this study, Samples FA1, FA2 and FA3 were used in leaching experiments. The fly ash samples were treated by leaching with distilled water to evaluate the extractability of trace elements and the degree of surface enrichment.

Firstly, all vessels were dipped in dilute nitric acid (10%) for over 24 hours and washed with distilled water. Secondly, 15 g fly ash samples (FA) was placed in bottles with 1 liter polyethylene and mixed with 1 liter distilled water (pH=7). The bottles were shaken for 24 hours in a

horizontal shaker at room temperature. Then, the supernatants were decanted and filtered through a 0.025 μm micro-porous membrane filter at the end of the leaching experiment, and the final pH value in leaching solution was measured. The trace elements in solution were measured by the ICP-MS. The leaching test results are shown in Table 3. The process was repeated three times for the same sample. The higher the ratio between ash and water, the more difficult for solutions to achieve a saturation state and for all soluble materials to be dissolved out of the ashes. A relatively high ratio of ash to water was used to prevent the solution from achieving saturation and guarantee entire dissolution of all the water-soluble fractions in the ashes.

5 Results and Discussion

Fly ash looks like cement, grayish-white in color and powdered in form, generally less than 200 μm in particle size and mostly within the range of 50–100 μm . A mineralogical analysis by using the quantitative X-ray diffraction and scanning electric microscope gives the major composition and forms of minerals in fly ashes. Various kinds of particles can be observed in the fly ash samples, including non-crystalline material (vitreous bodies), crystal material newly-formed in the course of combustion, leftover minerals and incompletely-burnt carbon grains. Their characteristics depend on the composition of the particles.

5.1 Chemical composition of ashes

According to chemical composition, the ashes from the study power plants belong to the $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system (see Table 1). The chemical composition usually changes a lot along with different mineral components contained in coal. Analysis shows that the contents of the main minerals in coal are positively related to the chemical and mineral compositions of the ashes.

It can be seen from Table 1 that the main composition of the ashes are characterized by high contents of SiO_2 and Al_2O_3 , but low contents of Fe_2O_3 and CaO , and minor amounts of SO_3 , P_2O_5 , K_2O , Na_2O and TiO_2 . SiO_2 and Al_2O_3 are the main components of the ashes, which account for more than 60% of the total. This seems to be related to the composition of the parent rocks in the formation of peat

Table 1 Chemical Compositions of ashes (%)

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5
FA1	50.89	18.83	0.21	16.45	6.97	0.84	2.86	0.87	0.62	1.49
FA2	57.72	20.04	0.52	11.47	3.26	0.78	2.31	0.92	0.58	1.26
FA3	48.31	26.11	0.28	13.26	4.78	0.69	2.15	0.84	0.71	1.09

Table 2 Concentrations of trace elements in fly ashes ($\mu\text{g/g}$)

Sample	Cu	Pb	Zn	As
FA1	224.1	124.6	109.8	6.9
FA2	232.3	118.9	121.3	4.3
FA3	201.4	117.2	115.4	5.2

Table 3 Leachate concentrations of trace elements from the samples

Samples	Cu	Pb	Zn	As	K	Na	Ca	Mg
	$\mu\text{g/l}$				$\mu\text{g/l}$			
FA1-1st	17.92	1.98	6.56	1.8	8.7	6.7	106.8	1.1
FA1-2nd	9.13	1.12	4.13	0.6	3.2	0.8	4.7	0.4
FA1-3rd	11.21	0.87	2.32	0.3	1.2	1.1	1.5	0.1
FA2-1st	30.24	2.93	7.65	0.4	7.9	7.2	89.6	0.9
FA2-2nd	23.45	1.31	5.18	Nd	2.1	1.6	3.4	0.6
FA2-3rd	10.93	1.05	2.43	Nd	0.9	0.7	1.1	0.2
FA3-1st	26.85	1.86	7.08	0.6	9.2	5.4	115.4	1.3
FA3-2nd	14.22	0.97	5.36	0.3	3.2	0.6	6.3	0.7
FA3-3rd	7.31	0.83	2.16	0.2	1.5	1.3	2.1	0.3

Nd – Not detectable.

and coal, and also to the plant species involved in coal formation. The result (Liu et al., 1999) shows that Si is readily absorbed by herbal plants and then fixed on the cell walls, while Al is preferentially absorbed by ground pine-like plants. Plants are the material source for the formation of coal.

5.2 Trace elements in coal ashes

In coal, C, H, O, N and S, whose contents are usually more than 1000 ppm, are called major elements, which build up organic matrixes. Besides, elements such as Al, Fe, Mg, As, Zn, Cu, F, Th, V, whose concentrations are usually less than 1000 ppm, are usually named trace elements. The trace elements constitute inorganic matter in coal.

Coal is the most important energy source for heating and power generation. In the process of coal mining, washing, storage and transport, particularly combustion, some negative influences could be exerted on the environment (Swaine, 2000). Large amounts of SO_x , NO_x , CO_x and other environment-polluting gases will be produced, leading to redistribution of trace elements in coal, and transferred into the environment during coal combustion (Xu et al., 2000). Coal is used largely in power generation by means of combustion in large quantities. This means that most trace elements will be released and redistributed into ashes and gaseous phases. Up to about 20% of the original mineral matter is found in the bottom ashes and up to about 80% in the fly ashes.

The distribution of trace elements in the ashes from the Power Plants is listed in Table 2. According to studies (Xu et al., 1997; Liu et al., 2001), with decreasing sizes of the particles in coal ashes, concentrations of the trace elements will become higher and higher, i.e., their contents in ashes are negatively proportional to their particle sizes. Similar results were obtained in this study, that is, the contents of

Pb, Cu, Zn, As in fly ashes are high.

Trace elements are preferentially concentrated in fly ashes because of its small sizes and large specific surface. So much K, Na, Ca and Mg and part of Pb, Zn, Cu and As, which are adsorbed on the surface of fly ash have high concentrations, so in ashes of small size the contents of trace elements are generally high.

5.3 Leaching behavior of fly ashes

It is shown in Table 3 that Ca and Na concentrations in the initial leachate are high. This is because that Ca and Na are associated with the surface of fly ash particles as well as the main components of aluminosilicate glass fractions, along with other major elements including K and Al. So Ca and Na are thought to be from easily soluble sublimates on the ash particle surface. The Ca concentration is the highest for the first batch for all samples and then showed rather constant variations with leaching. Such a concentration variation seems to indicate that the Ca concentration is controlled by a solubility controlling solid phases. A large amount of K in the ashes can be attributable to glass associated fractions and the surface of particles, and the K concentration in leachate liquid changes as the same as Na. The Mg concentration in the leachate is relatively constant throughout the effluent and it is thought to be glass fractions rather than surface enrichment fractions that would control the Mg dissolution from fly ashes. When fly ashes are disposed in landfill, surface associated fractions might dominate the leachate chemistry during the early stage of fly ash disposal in contact with water. In the long-term leaching process, further weathering of aluminosilicate glass would release the trace elements incorporated within glass particles.

The Cu, Pb and Zn concentrations are lower than those of Na, Ca, K and Mg. Zn Shows a trend similar to that of Cu, but maintains a constant level. As is generally close to the detection limit, but is still detectable in all leaching solutions. Such continuous release of Cu, Zn, Pb and As might signify the dissolution of glass in ash particles.

The original pH is 7 and the final pH in leaching solutions ranges from 7.9 to 10.1. The latter is higher than the former because of the alkalinity of the fly ashes.

6 Conclusions

On the basis of study on chemical compositions and leaching experiments of trace elements in fly ashes, the following conclusions can be reached.

The major compositions of ashes include SiO_2 , Al_2O_3 , small amounts of Fe_2O_3 and CaO , and minor SO_3 , P_2O_5 , Na_2O , K_2O and TiO_2 .

The leaching behavior of fly ashes indicates that trace

elements in fly ash particles are mainly associated with the surface but some of them are incorporated within glass matrixes as well.

According to the characteristics of ashes, the authors suggest that the ashes in study area can be used to make cement, bricks, tiles and so on as pozzolanic admixture.

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