

A Study of Ferrospheres in the Coal Fly Ash

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Abstract

Coal fly ash is an industrial by-product, produced from coal combustion in thermal power plants. It is the most complex anthropogenic materials, which consists of combination of minerals originated from different sources. Coal fly ash and its byproduct has become an environmental concern over the World. Therefore, there is a pressing and ongoing need to investigate the structures and some properties of coal fly ash and develop new recycling methods for it. The amount of silica, aluminum, calcium, potassium, magnesium, sodium, titanium and phosphorus oxides contained in power plant fly ash was determined by X-ray flouresecence (XRF) analysis. Concentration of heavy metals in fly ash was in sequence of Pb > Zn > Cu > Cr > Ni. As results of Scanning Electron Microscopy (SEM), except for porous and hollow particles, large and small microspheres were observed. These particles are classified as ferrospheres. X-ray diffraction (XRD) analysis show that fly ash consists of the following crystal phases: quartz, albite, anorthite and hematite.

Keywords

Fly Ash, Ferrospheres, Quartz, Albite, Anorthite, Hematite

1. Introduction

Fly ash was firstly used as mineral filler in road pavement in 1930. The "Fly ash" contained in concrete was published in a research paper of Concrete Institute of USA in 1937. Today, electric utilities in the US annually burn billion tons of coal and generate over 100 million tons of large-volume coal combustion products. Only a quarter of these coal combustion products are used and others are stored underground. Utilization of coal combustion products have following results: 1) Reducing land degradation, 2) Saving environmental resource, 3) Harmless effect in environment, 4) Decreasing carbon dioxide, 5) User-saving, 6) Decreas-

ing price of electricity. These results are the world tendencies to use coal combustion products and slag [1]. The chemical elements, mineral composition, particle forming condition and physical chemical properties of fly ash have been studied by SEM [2] [3]. The fly ash container of Thermal Power Plant III, Ulaanbaatar city, Mongolia will be filled to capacity in the coming years; therefore it is a good opportunity to study for ways to reuse the fly ash as a raw resource for roads, building material or agriculture and to verify if the power plant has changed its combustion procedure. Power Plant III burns brown coal from Baganuur, this coals general properties are: humidity: 28% - 33%, ash-flow: 15% - 20%, calorie: 3300 - 44,200 kcal/kg, sulfur: 0.7% - 0.8%. The physical and chemical properties of Baganuur coal deposit make it usable exclusively for Thermal Power Plants and also with processing it has been proven through research that it can be used for syngas, liquid and patent fuel, and raw materials for the chemical industry. The properties of fly ash depend heavily on the coal mine, mode of operation and other parameters.

The main objective of this research is focused on the obtaining new types of materials with the use of modern technological methods (for example, bricks, lightweight concrete, geopolymer and etc.) based on the detailed structural analysis of the ferrospheres from coal fly ash-industrial byproduct materials and further develop technological backgrounds of it.

2. Experimental

2.1. XRF Analysis

Sample was measured by X-ray Fluorescence Spectrometer (Rigaku, ZXS Primus II). Results of the analysis are shown in Table 1.

As can be seen in **Table 1**, fly ash contains silicon dioxide (62.53%), aluminum oxide (15.36%), calcium oxide (8.84), ferric oxide (5.84%), potassium oxide (2.26%), magnesium oxide (1.33%), sodium oxide (1.04%), titanium dioxide (0.61%), manganese oxide (0.11%), phosphorus oxide (0.08%) respectively. Except for these elements, low content of (ppm) Sr, Ba, Zr, Pb, Rb, Zn, Cu, Cr, Y, Ni, Co, Th, Ga and Nb were observed. Among these elements, Pb, Zn, Cu, Cr, Y, Ni, co, Ni are considered seriously. On the other hand, a sample of the fly ash is classified as F class, because silicon oxide, aluminum oxide and iron oxide are contained more than 70% of the ash (according to the ASTM C 618 standard).

Table 1. Chemical composition of coal fly ash.

(a)													
Compounds	SiO	2 A	l_2O_3	CaO	K	2 ₂ O	MgO	Na	₂ O	${\rm TiO}_2$	Mn	0	P_2O_5
Value, wt. %	62.5	3 1	5.36	8.84	2	.26	1.33	1.0	04	0.61	0.1	1	0.08
(b)													
Elements	Sr	Ba	Zr	Pb	Zn	Cu	Cr	Y	Ni	Co	Th	Ga	Nb
Value, ppm	518	461	166	132	69	47	47	37	31	26	23	18	14

This fly ash is pozzolanic in nature, and contains less than 7% lime (CaO). Since the calcium oxide content of this sample was higher than 7% (CaO, 8.84 wt.%) this sample is might to be defined to be the C Class fly ash. This class is formed when burning younger lignite or sub-bituminous coal [4].

2.2. SEM Analysis

SEM (Energy dispersive x-ray spectroscopy (EDX)) was applied to characterize the form of the fly ash particles. Results are depicted in **Figures 1-3**.

Except for porous large particles, individual large and small microspheres were observed in fly ash (Figure 1). As a result of analysis of microsphere A (marked red in Figure 1), following elements were determined (Figure 2).

As can be seen in **Figure 2**, microsphere A contains Ca (11.5 wt. %), Si (34.8 wt. %), Al (10.3 wt. %), Fe (43.4 wt. %). Therefore this sphere can be called a ferroshperes.

Except for porous large particles, individual large and small microspheres and hollow microspheres were observed in fly ash (**Figure 3**). As a result of analysis of porous sphere B (marked red in **Figure 3**), following elements were determined (**Figure 4**).

As can be seen in **Figure 4**, porous sphere B contains Fe (75.3 wt. %), Si (11.1 wt. %), Ca (4.1 wt. %), Br (9.4 wt. %).

Except for hollow large particles, individual large and small microspores were observed in fly ash (Figure 5). As a result of analysis of hollow particles C (marked red in Figure 5), following elements were determined (Figure 6).

As can be seen in **Figure 6**, hollow particle C contains Fe (47.1 wt. %), Si (30.3 wt. %), Ca (13.6 wt. %), Al (9.0 wt. %). As mentioned before this sphere can be

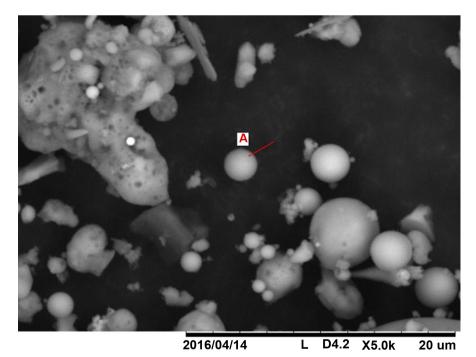


Figure 1. SEM micrograph of Coal fly ash $(20 \times \mu m)$.

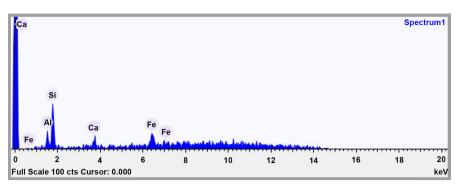
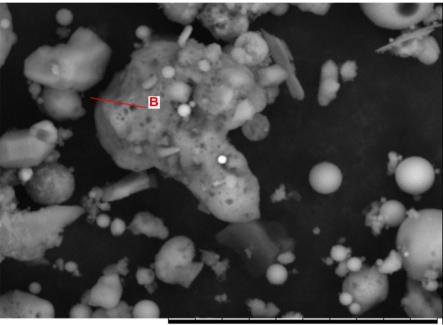


Figure 2. Chemical elements of individual microsphere A.



2016/04/14 L D4.2 x5.0k 20 um

Figure 3. SEM micrograph of fly ash $(20 \times \mu m)$.

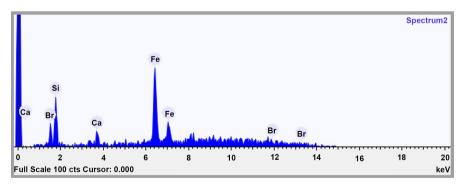
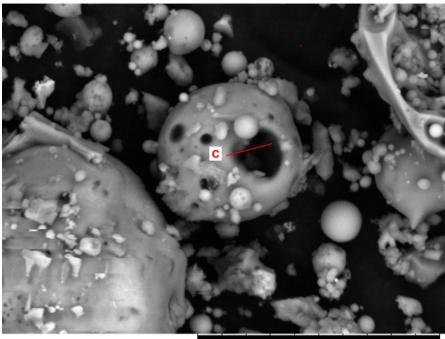


Figure 4. Chemical elements of porous sphere B.

also called a ferroshperes. On the basis of the analysis, it can be said that, the main component of all microspheres are iron (Fe = 43 - 75 wt.%). Other components are Ca (4 - 13 wt.%), Si (11 - 35 wt.%), Al (9 - 10 wt.%). These observed particles are in agreement with other researcher's investigation [2] [3].



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D4.2 x3.0k 30 um

Figure 5. SEM micrograph of fly ash $(20 \times \mu m)$.

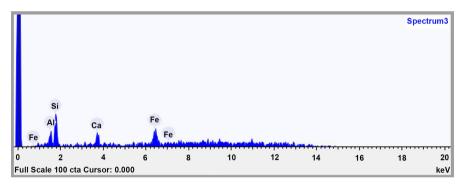


Figure 6. Chemical elements of hollow sphere C.

2.3. XRD Measurements

XRD measurements were carried out at ambient conditions on a X-ray powder diffractometer (Enraf Nonius Delft Diffractis 583). A step size of $0.05^{\circ} 2\Theta$, an integration time of was 2 s per step and scan range from 13° to 80° were used. Phase analysis was done by < Match! Crystal Impact > program [5]. The x-ray powder diffraction pattern of samples is shown in **Figure 7**.

The interatomic distances was calculated by using equation $2d\sin\Theta = n\lambda$ and compared to International Powder Diffraction File (ICSD, PDF-4). Then types of minerals and amounts were determined (**Table 2**).

As can be noticed (**Table 2**), crystal phase of fly ash consists of 54.74% of α -quartz SiO₂, 27.55% of monoclinic albite (K[AlSi₃]O₈), 9.21% of monoclinic anorthite Ca (Al₂Si₂O₈), 8.49% of rhombohedral hematite (α -Fe₂O₃) respectively. The iron oxide is detected by hematite. However, low content of K, Mg, Ti, Mn,

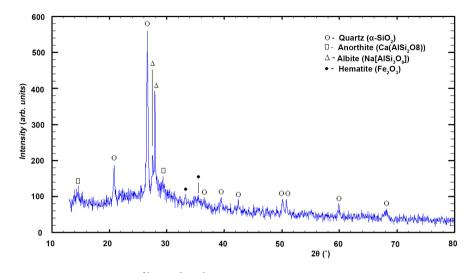


Figure 7. X-ray pattern of burned coal.

N	2-theta	d, Å	Minerals	Chemical formula and	Crystal symmetry, space group
				amount of minerals	and lattice parameters (Å)
1	20.83	4.25		SiO ₂	
2	26.19	3.34	Quartz	SiO ₂	Hexagonal, P3 ₂ 2 ₁ , a = 4.91, c = 5.40
3	27.50	3.23		Na[AlSi ₃ O ₈]	
4	27.87	3.19	Albite	Na[AlSi ₃ O ₈] (27.55%)	
5	29.44	3.03	Anorthite	$\begin{array}{c} \text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)\\ (9.21\%) \end{array}$	Monoclinic, I(-1), a = 8.18, b = 12.86, c = 14.16
6	33.12	2.70	Hematite	α -Fe ₂ O ₃ (8.49%)	Rhombohedral, $R(-3)c$, a = 5.03, c = 13.74
7	35.48	2.52		α -Fe ₂ O ₃	
8	36.38	2.45		SiO ₂	
9	39.37	2.28		SiO ₂	
10	42.36	2.12		SiO ₂	
11	50.00	1.81		SiO ₂	
12	50.69	1.79		SiO ₂	
13	59.86	1.54		SiO ₂	
14	67.44	1.36		SiO ₂	

Table 2. Phase composition and crystal structural parameters of coal fly ash.

2-theta—scattering angle, d—interatomic distances.

P, Sr, Ba, Zr, Pb, Rb, Zn, Cu, Y, Ni, Co, Th, Ga and Nb elements were observed in results of XRF analysis, these elements does not form crystal phase in results of XRD analysis, because of equipment resolution. The results of XRD measurements are in agreement with chemical analysis (Table 1).

The above-described phases of albite and anorthite are quite stable and ordered compounds. From these perspectives, these phases are used to be as not only filler materials in concrete but also applied for the strengthening the concrete. The results of x-ray phase analysis made on coal fly ash were in good agreement with the results from the investigations within the frame of the Project "Utilization of Coal Fly Ash" realized at Florida University in 1992 [1].

3. Conclusions

As a result, it can be concluded that

- Baganuur coal ash that are used at the Thermal Power Plant III of Ulaanbaatar city, Mongolia contains 8.84 wt% of calcium oxide (CaO), it can be classified as C Class fly ash. Therefore, due to its low content of calcium this type of fly ash is possible for use of the production of geopolymer material.
- However, according the US standard ASTM C 618, this type of fly ash is defined to be classified to be F Class fly ash.
- Microspheres in the coal fly ash samples were successfully observed by the SEM method. Since these microspheres contain a large amount of iron (Fe, 43 75 wt%) it is possible to separate them with magnetic separation method.

X-ray diffraction analysis shows that the major compound, which represents the iron phase in microspheres are the hematites (α -Fe₂O₃, 8.49 wt%).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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