Content and Distribution of Transition Metals and Rare Earth Elements in Magnetically and Mechanically Separated Brown Coal Ash

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Coal ash is known to contain a noticeable amount of valuable elements, including transition metals and lanthanides. Therefore it is quite actual problem to extract them for metallurgy and other applications. This paper presents the results of high gradient magnetic and mechanical separation, microscopy, element analyses and optical spectroscopy of brown coal ash taken from the combustion camera and chimney-stalk of Angren thermal power station. The separated magnetic fraction was 3.4 wt.%, where the content of Fe in ferrospheres increased to 58 wt.%. The highest contents of Fe and rare earth elements were found in the fine fractions of 50-100 μm. Optical absorption spectroscopy of water solutions of the magnetic fractions revealed Fe^{2+} and Fe^{3+} ions in the ratio of ~1:1. The separated coal ash could be used for cleaning of technological liquid waste by means of the high gradient magnetic field.

Keywords : coal ash, ferrospheres, high gradient magnetic separation, element analysis

1. Introduction

Thermal power stations (TPS) are the source of environment pollution, especially flu-ash spheres carried away in atmosphere over the world [1]. For example, at the present time dozens millions of brown coal ash have accumulated near TPS in Uzbekistan, that is why their utilization has become quite serious ecological problem. So far the ash is used as admixture in cement production. However, coal ash is well known to contain a large amount of valuable elements, including ferromagnetic fractions (> 3 wt.% Fe_2O_3 in Russian coal), which is magnetically separated for metallurgy [2]. Besides, it contains SiO_x and MgO microspheres having a wide application potential. For example, nanotechnology for manufacturing novel microphotonic devices is based on assembly of silica nanowires on silica aerogels [3]. Magnetic Fe oxide nanoparticles are of great interest [4, 5]. Both dry and wet magnetic separation techniques were implemented for coal and its fly ash [6-10]. Pyrites and > 70% ashes were removed from dry pulverized British coal by means of high gradient magnetic separation [6]. A two stage dry magnetic separator combined with pulverizer was employed for cleaning diamagnetic raw coal (SW Wyoming) from 75% FeS, 31% As and 72% Hg impurities [7]. Heavy and toxic elements distribution was studied in the magnetically separated fractions from coal fly ashes [8]. Fly ashes from three coal-burning power plants (Bulgaria) were subjected to wet low-intensity magnetic separation with new "cell" configuration filter to remove ferromagnetic iron [9, 10]. The author mentioned the following factors limiting the process: paramagnetic Fe-containing mineral, poly-mineral aggregates of magnetic and non-magnetic particles, amorphous matter. Literature analysis shows, that there is no sufficient data on magnetic separation of the bottom ash, were one may expect a higher contents of transition and heavy elements.

1.1. The Aim

This research was to do detailed element analysis and spectroscopy of brown coal ash magnetically and mechanically separated into fractions for extracting transition metals and rare earth elements and revealing potential applications. Standard experimental methods were used [11, 12].

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2. Experimental Results and Discussion

Two kinds of brown coal ash fractions were taken both from the combustion camera (bottom ash - BA) and chimney-stalk (fly ash - FA) at Angren TPS, because their contents, dispersion and specific weight were expected to differ significantly. Home made magnetic separator based on a permanent or pulse current magnet with the induction of 0.1 Tesla was used for extraction of a fraction containing ferromagnetic compounds from the BA fraction. Since high gradient magnetic separation turned out more effective [6, 9, 10], we used this method here too by means of ferrite balls of various diameters. Both magnetic and non-magnetic fractions were undergone to the following mechanical separation with the help of the standard screen grader into 7 classes from 400 to 50 μm. Figure 1 show microphotographs of FA fraction and magnetically separated BA fraction of the ash samples, taken also with infra-red microscope in the transmission mode.

2.1. Microscopic analysis

FA fractions dispersed on the water surface (Fig. 1(a), (b)) has shown that there are arranged white microspheres < 5 μm up to 150 μm with the specific weight less than that of water, so they must be hollow silica-alkali glass bubbles. And Fig. 1(c), (d) demonstrates the magnetic fraction with much higher specific weight, which consists of black ferrospheres of 10-50 μm size (C) and also tiny
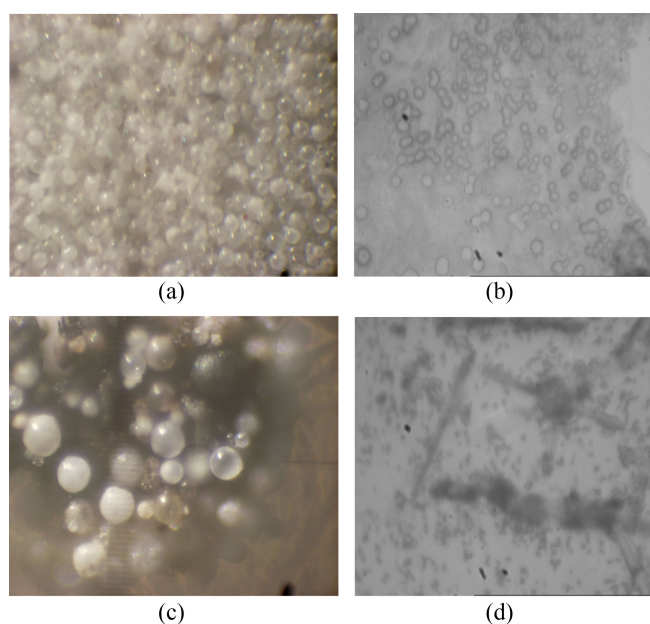
rods and ~1 μm particles (D). Since Fe was found in the BA fraction in the spherical shape, it was easier magnetically separated.

2.2. Element contents

Ash samples were determined by the instrumental neutron activation analysis (INAA) with the use of thermal and fission spectra neutrons in the WWR-SM nuclear reactor [12]. The techniques allowed determination of 37 elements, but Si couldn't be detected. Table 1 lists element composition of the two ash samples.

It is seen, that the both samples from the combustion camera (BA) and chimney-stalk (FA) contain dominating

Fig. 1. (Color online) Photo of FA (a, b) and magnetic BA (c, d) fractions of brown coal ash, taken with optical microscope 1 × 1 mm (a, c) and infra-red transmission microscope 0.12 × 0.12 mm (b, d).

Table 1. Element contents (INAA) of brown coal ash samples taken from the combustion camera (BA) and chimney-stalk (FA).

Elements	Contents of microelements, ppm	
	BA fraction	FA fraction
Sc	15 ± 1	22 ± 1
V	80.0 ± 8.0	110 ± 10
Cr	25 ± 1	27 ± 1
Co	4.6 ± 0.1	5.2 ± 0.1
Cu	31 ± 2	41 ± 2
Zn	512 ± 89	135 ± 15
As	27 ± 2	21 ± 1
Rb	101 ± 4	121 ± 8
Sr	414 ± 15	502 ± 17
Zr	630 ± 35	526 ± 42
Mo	20 ± 1	14 ± 1
Sb	3.9 ± 0.1	4.4 ± 0.2
Cs	34 ± 2	40 ± 1
La	57± 2	71 ± 2
Ce	104 ± 6	132 ± 6
Nd	52 ± 7	56 ± 4
Sm	8.4 ± 0.7	10 ± 1
Eu	1.6 ± 0.1	2.0 ± 0.1
Tb	0.85 ± 0.1	0.87 ± 0.06
Dy	6.8 ± 0.3	8.3 ± 0.3
Yb	3.7 ± 0.3	4.2 ± 0.1
Lu	0.67 ± 0.07	0.77 ± 0.1
Hf	11.4 ± 1.0	10.3 ± 0.6
W	61 ± 5.6	15 ± 2.0
Contents of macroelements, wt.%		
Na	0.25 ± 0.20	0.39 ±0. 04
Mg	0.94 ± 0.10	2.0 ± 0.1
Al	11.0 ± 0.5	16.5 ± 0.7
K	0.96 ± 0.20	1.48 ± 0.13
Ca	4.6 ± 0.1	5.2 ± 0.1
Mn	0.084 ± 0.006	0.10 ± 0.0 5
Fe	3.6 ± 0.3	3.0 ± 0.1
Ba	0.21 ± 0.01	0.20 ± 0.01

magnetic Fe impurities in close amounts within 3-3.6 wt.%, and much less contents of other metals. As expected, FA fraction is dominated with alkali and alkali earth metals Na, Mg, K. Comparing the data of Table 1 with those of [9, 10] for FA fraction, the contents of Na, Mg, K and also Fe is similar, but Angren ash has much more As and does not have Hg.

In the both kinds of samples the contents of 9 of 15 rare earth 4f-elements were also defined. It was impossible to determine the contents of the rest 6 lanthanides (Pr, Pm, Ho, Tm have odd Z and Gd, Er have even Z) with INAA techniques, because of their nuclear characteristics at the irradiation conditions chosen for the ash composition. Therefore they were calculated with the use of their ratio from the table data on an average prevalence of rare earth elements in the Earth crust by estimations of various authors [13]. The total amount of the rare earth elements in the BA fraction was $235.02+32.55^*$ and in the FA one was $285.14+41.63^*$ (the second terms with asterisk are calculated). Unlike our results, rare earth impurities were not found or determined in Bulgarian FA fractions [9, 10].

Figure 2 show distribution of rare earth elements in the FA and BA ash fractions, black squares mark the elements with contents determined experimentally by INAA, and white circles indicate those with calculated contents.

Express X-ray-fluorescence analysis (XFA) was implemented at the stage of mechanical separation of FA samples into 7 fractions of different dispersions with the use of Cd-109 and Am-241 sources [11, 12]. The techniques are effective for X-ray excitation of K-lines of elements with high Z or a few wt.% contents. Table 2 lists the element contents in relative units proportional to the intensities of their K-lines that allow one to compare the contents of each element in different fractions.

In order to obtain the ash fraction enriched with magnetic compounds, another BA sample of 500 g was taken from the combustion camera and processed with the high gradient magnetic separator. The magnetized ash fraction
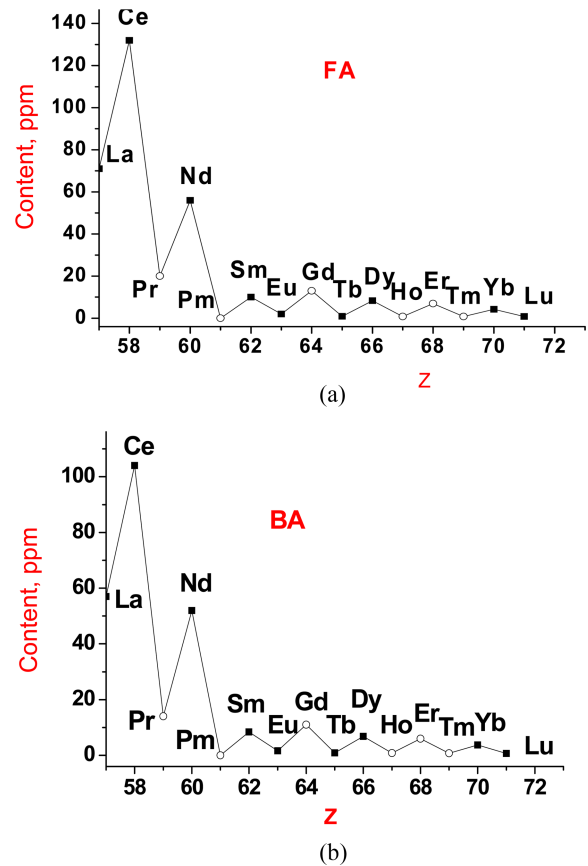

Fig. 2. (Color online) Distribution of rare earth elements over Z in the FA and BA fractions.

collected from the pole surfaces was 16.87 g (3.4 wt.% of the total sample mass). Then, it was mechanically separated into 7 fractions of different dispersions. As it is seen from Table 2, fine fractions of BA contain more heavy elements than coarse ones because of gravitation limit for their suspension in the combustion camera.

Table 3 shows element contents in the magnetized ash fractions as determined by XFA.

It is seen, that the magnetic fraction of 16.87 g contains

Table 2. Contents of elements determined with XFA in mechanically separated ash fractions.

Fraction, μm	Mass, g	Contents, wt.%	Contents of elements in relative units							
			Ca	Fe	Zn	As	Sr	Zr	Ba	Ce
> 420	38.0	8.3	7.2	1.1	9.1	8.6	15.7	25.3	7.1	1.5
> 300	57.09	12.5	5.0	1.3	10.2	4.2	34.5	25.8	9.7	1.6
> 210	107.12	23.4	4.7	0.9	1.6	2.6	31.1	35.0	11.8	1.9
> 105	163.91	35.8	6.2	1.2	12.4	5.2	42.6	29.4	18.2	2.3
> 62	58.42	12.7	8.2	1.3	13.6	7.2	53.2	57.7	26.7	2.1
> 53	3.95	0.8	6.4	1.6	15.9	2.2	50.7	70.6	34.4	2.6
< 53	28.93	6.3	5.5	1.6	19.3	3.8	46.0	54.5	32.2	2.4
Mass 457.42 ± 42.58 (8.5 wt.%)										

Table 3. Relative contents of Fe and heavy elements in the magnetized BA fractions.

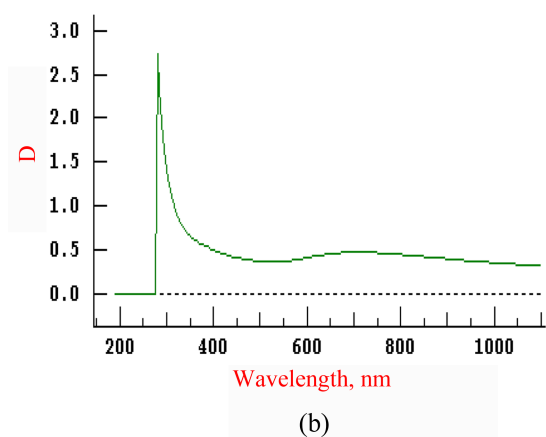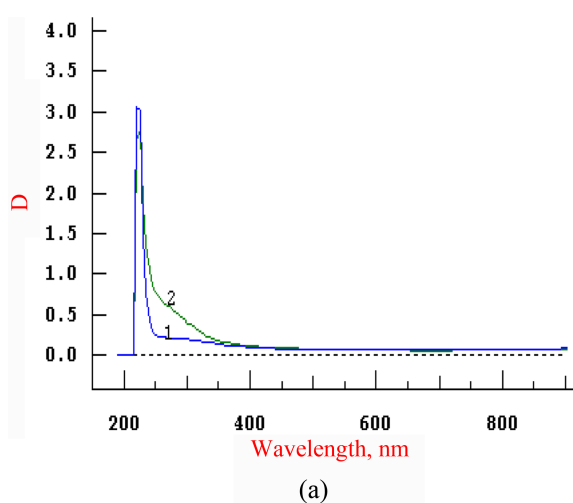| No	Fraction, μm	Mass g	Contents of Fe		Contents in relative units		
			g	wt.%	Sr	Zr	Ce
1	> 420	1.94	0.67	34.49	122	115	698
2	> 300	3.89	0.98	25.22	139	140	864
3	> 210	2.02	0.68	33.71	135	140	778
4	> 105	4.82	1.7	35.95	139	161	876
5	> 62	2.78	1.4	50.40	120	96	603
6	> 53	0.69	0.36	52.46	100	96	320
7	< 53	0.73	0.38	52.62	90	98	300
Total mass		16.87	Fe 6.17 g				

(a)

(b)

Fig. 3. (Color online) Optical absorption spectra D vs λ (nm) of brown coal ash specimens sieved and mixed with water: (a) curve 1 is for the glass cell with water, curve 2 is for FA fraction of SiO$_2$ microshperes, (b) magnetically separated BA fraction enriched with Fe.

6.17 g of Fe , the fine fractions (20-60 μm) turned out the most enriched (> 50 wt.%) with Fe, although their mass is only 2.2 wt.%. Tables 2 and 3 show the same distribution of Fe over the dispersion.

In order to examine the valence of iron ions, both in FA and magnetic BA fractions, each fraction was mixed with water to register optical absorption spectra in the range of 190-1100 nm at spectrometer SF-56 (LOMO, Russia). Figure 3 show optical absorption spectra D(λ, nm) of FA (A) and magnetically separated BA (B) fractions.

The empty glass cell gives only weak absorption < 200 nm, while water increases this band (A, curve 1), and the spectrum of FA fraction (curve 2), containing SiO$_2$ micro-shperes shown in Fig. 1(b), has an intensive narrow absorption peak at 220 nm related with the known oxygen deficient E'-centers accumulated on the defective surface of SiO$_2$ microspheres [5, 14, 15]. Two weaker broad over-lapping bands at 260 and 300 nm are attributed to elec-tron transfer from a metal to oxygen ligand. The spectrum (B) of BA fraction enriched with Fe (ferrospheres seen in Fig. 1(d)) begins from the intensive edge at 290 nm and consists of broad bands related with electron transitions in 3d-metals dominated by Fe^{2+} (~300 and 800 nm) and Fe^{3+} (~420 and 680 nm) ions attached to silica-alkali micro-spheres, with their ratio ~1:1.

3. Conclusions

Both bottom and fly ash fractions have similar element composition. Mechanical sieve separation has revealed that fine fractions contain more Fe and other heavy ele-ments than the coarse ones because of gravitation limit of microsphere formation. The light FA fraction (fly ash from chimney stalk) is dominated with silica-alkali micro-spheres, and the heavy magnetized BA fraction (from combustion camera) is enriched with ferrospheres.

After the high gradient magnetic separation of the bottom ash samples, the magnetic fraction was 3.4 wt.%, where the content of Fe increased up to 58 wt.%, especially in the fine fractions. Optical absorption spectroscopy of water solutions of the magnetic fractions has revealed the presence of Fe^{2+} and Fe^{3+} ions in the ratio of 1:1. The microspheres can be used for cleaning of technological liquid waste by means of the high gradient magnetic field.

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