

Composition and Morphology of Magnetic Microspheres in Power-Plant Fly Ash of Coal from the Ekibastuz and Kuznetsk Basins

OLGA M. SHARONOVA¹, NATALIA N. ANSHITS¹, ALEXANDER I. ORUZHEINIKOV², GALINA V. AKIMOCHKINA³, ALEKSEY N. SALANOV², ALEXANDER I. NIZOVSKII², OLGA N. SEMENOVA² and ALEXANDER G. ANSHITS¹

¹*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)*

E-mail: shar@icct.ru

²*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Lavrentyeva 5, Novosibirsk 630090 (Russia)*

³*Krasnoyarsk State Technical University, Ul. Kirenskogo 26, Krasnoyarsk 660074 (Russia)*

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Abstract

Using a multi-stage scheme including different sequences of the stages of magnetic separation, hydrodynamic and granulometric classification, magnetic microspheres of fixed composition containing the magnetic constituent at the level of 95–99 % were separated from the fly ash of coal from the Ekibastuz and Kuznetsk basins. The yield, texture characteristics, macrocomponent and mineral phase composition were determined and globules of three morphological types were described for close-cut fractions of magnetic microspheres. A general dependence of the properties of close-cut fractions of microspheres on ferric oxide content was revealed. It was demonstrated that for the mass concentration of total $\text{Fe}_2\text{O}_3 > 60\%$, mainly massive microspheres with various crystal microstructure are formed. With a decrease in iron content, the formation of porous microspheres becomes predominant. It is established that the governing factor in the formation of microspheres of morphological type is the viscosity of ferriferous silicate melt.

INTRODUCTION

High-temperature thermochemical transformations of the mineral constituents of coal during its combustion in heat power stations is accompanied by the formation of microspheric particles of several morphological types, which can be selectively isolated and used in the production of high-technology materials [1–3]. One of the kinds of microspheres exhibiting ferromagnetic properties is glass crystal microspheres based on Fe-spinelids formed from high-iron melts. Investigations of the magnetic particles of power-plant ash are limited mainly to the studies of individual globules or total mass of the magnetic product isolated by magnetic separation [4–7]. Investiga-

tion of individual globules by means of optical and electron microscopy, micro-probe analysis allows one to identify morphological features of magnetic particles, to determine their chemical and phase composition [1, 4, 6]. Forms of iron occurrence in fly ash, slag and in the magnetic fraction of ash are studied by means of Mössbauer spectroscopy [8–10]. The set of factors affecting the formation of ash magnetic particles in different power plants leads to broad variability of their morphology, mineral, granulometric and chemical composition.

In order to obtain products with required properties, it is necessary to develop methods of fine separation of the magnetic material with the isolation of microspheric components

of fixed composition. This allows predicting their properties and makes them competitive with synthetic microspheres in the production of ceramic and composite magnetic materials, magnetic media, pigments for polygraphy, toners, paint and varnish industry, in the production of magnetic biochemical preparations, heavy suspensions and magnetic liquids [11–13]. Development of adsorbents, catalysts and ion exchangers based on magnetic microspheres is also a promising area [14–17].

The goal of the present work is isolation of magnetic microspheres of fixed composition from fly ash formed in the coal-fired boiler combustion of coal from the Ekibastuz and Kuznetsk basins, investigation of their composition and physicochemical properties.

EXPERIMENTAL

The technology of the isolation of magnetic microspheres of fixed composition is based on the combination of magnetic separation, hydrodynamic and granulometric classification of dispersed power-plant ash [18, 19]. Two basic versions of the process for fly ash of different kinds of power-generating coal were developed: 1) hydrodynamic separation of ash into fine crystalline and coarse crystalline products with simultaneous or subsequent magnetic separation of each product; 2) magnetic separation of ash followed by hydrodynamic and granulometric classification of the magnetic concentrate. In the present work, the second version was used, including isolation of the magnetic concentrate and obtaining the products of fixed composition from it according to the following scheme:

- 1) Granulometric classification of the magnetic concentrate;

- 2) Hydrodynamic separation of the fractions of concentrate 0.1–0.063, 0.063–0.05 and <0.05 mm, and dry magnetic separation of the fractions of concentrate 0.4–0.2, 0.2–0.16, 0.16–0.1 mm;

- 3) Wet magnetic separation of each product.

The magnetic concentrate was isolated from the fly ash formed in coal-fired boiler combustion of the coal from the Ekibastuz or Kuznetsk

basins at the Heat Station No. 4 in Omsk. Fly ash was sampled from the 1st and the 2nd fields of electric filters of the dry purification system of the exhaust gases from power-generating units like BKZ-420-140 (coal from Ekibastuz) and BKZ-320-140 (coal from Kuznetsk). Coal was ground in ball or hammer mills: the residue on sieve R90 was 16 % for the coal from Ekibastuz and 6–8 % for the coal from Kuznetsk. Coal combustion was conducted with flame temperature within 1200–1700 °C. During this process, more than 80 % of the mineral part of coal passes into the fly ash; the residual part is removed as slag.

Magnetic separation of fly ash was performed using laboratory separator in which the pulp of ash was fed with controlled rate into the glass cylinder placed in magnetic field. The strength of magnetic field created by electromagnet was varied during experiments. The yield of concentrate was studied within the field strength range 0.065 to 0.65 T. The content of magnetic component in the resulting products was determined and their chemical composition was studied according to State Standard GOST 5382–91.

Granulometric classification of the magnetic concentrate was carried out with a vibratory set-up equipped with a set of sieves with the hole size of 0.4, 0.2, 0.16, 0.1, 0.063, 0.05 mm. Hydrodynamic separation of the fractions of concentrate was carried out in pulsed upward flow of liquid using a set-up described in [19]. The magnetic separation stage was performed in the air using 138T separator (TU 24-8-1054-77) or in water medium using the laboratory magnetic separator.

Macroelemental composition of the magnetic microspheres (Si, Al, Fe, Ca, Mg, Na, K, Ti, S, P) was investigated by means of chemical analysis according to State Standard GOST 5382–91. Mineral phase composition of the materials was determined by means of X-ray phase analysis using DRON-3 instrument with CuK_α radiation (tube voltage 30 kV, tube current 30 mA, sample volume $\sim 1 \text{ cm}^3$). Granulometric composition of fractions <0.05 mm was determined using conductometric Coulter's procedure with Coulter Counter TAI analyzer. True density of close-cut fractions of microspheres was determined in agreement with

State Standard GOST 2211-65 (ISO 5018-83), bulk density was measured using measuring tank method. Specific surface of microspheres (S_{sp}) was measured by means of thermal desorption of argon adsorbed at 77 K using Gasometr GKh-1 instrument (TU 25-0585.001-85). Surface structure and morphology of globules were studied with BS-350 (Tesla) scanning electron microscope with a resolution of 50 Å.

RESULTS AND DISCUSSION

Separation of magnetic concentrates from power-plant fly ash

Investigation of the effect of magnetic field strength on the characteristics of the isolated concentrate was carried out in order to determine optimal parameters to conduct the process both for the laboratory and for the experimental industrial scale. With an increase in magnetic field strength from 0.065 to 0.65 T, the yield of the concentrate increases from 7.5 to 10.3 % for the ash of the Ekibastuz coal and from 8.5 to 11.4 % for the ash of the Kuznetsk coal (Fig. 1). The content of magnetic part of the concentrates has a maximum at the magnetic field strength of 0.43 T for the ash of the Ekibastuz coal and decreases within the range 0.065–0.43 T for the ash of the Kuznetsk coal. The content of iron oxides changes cymbately with the magnetic constituent, while their mass concentration increases from 4–9 % in the initial ash samples to 12–33 % in magnetic concentrates. The experimental lot of the magnetic concentrate was manufactured from the ash of the Ekibastuz coal at the magnetic field strength of 0.43 T, and from the Kuznetsk coal at 0.215 T with the mass concentration of the magnetic constituent (41±2) и and (34±2) %, respectively.

Isolation of magnetic microspheres of fixed composition from the magnetic concentrate

In accordance with the above-described scheme, the magnetic concentrate of each kind of ash was classified granulometrically into 6 fractions, which were then subjected to hydrodynamic separation. The parameters of the

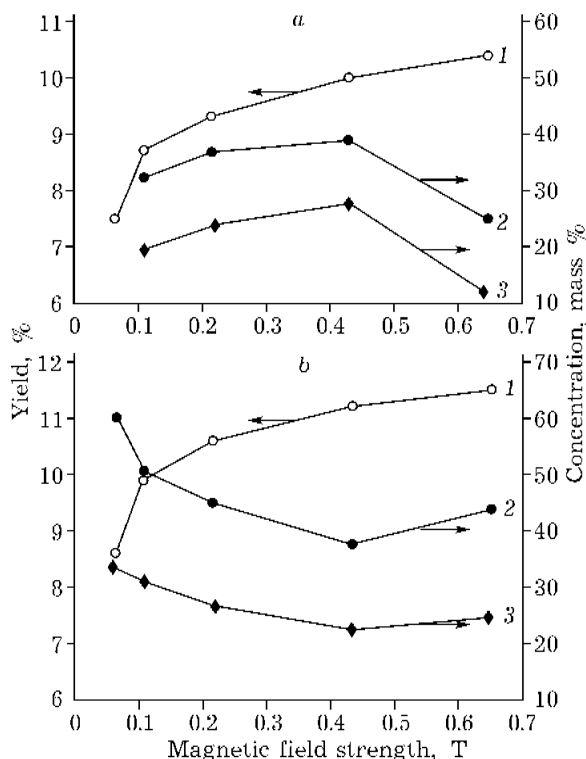


Fig. 1. Yield (1) of magnetic concentrate of ash of the Ekibastuz (a) and Kuznetsk (b) coal, obtained at different magnetic field strength, and the content of magnetic part (2) and total Fe_2O_3 in it (3).

process of separation into the fractions of the magnetic concentrate of the Ekibastuz coal ash are shown in Table 1. One can see that the efficiency of the process worsens substantially with an increase in particle size; this is especially true for concentrating the target product with respect to the magnetic constituent. Because of this, the concentrate fractions with particle size >0.1 mm (0.4–0.2, 0.2–0.16 and 0.16–0.1 mm) were processed by means of dry magnetic separation; as a result, magnetic microspheres with a purity of about 95 % were separated. Additional purification of the products from non-magnetic impurities is carried out by means of wet magnetic separation. As a result of three-stage separation of the concentrates of ash of the Ekibastuz and Kuznetsk coal, 12 products were isolated; they were magnetic microspheres of close-cut fractions with the purity of 95–99 % with respect to the magnetic constituent.

The yield of close-cut fractions of the magnetic microspheres of ash from the Ekibastuz and Kuznetsk coal is shown in Fig. 2. One can

TABLE 1

Parameters of mode and characteristics of the products of hydrodynamic separation of close-cut fractions of the magnetic concentrate of ash of the Ekibastuz coal

Fraction of magnetic concentrate, mm	V_{lin} , m/s	Specific load of column, kg/(h m ²)	Fraction of magnetic constituent, mass %	Isolation of magnetic microspheres, %
<0.05	0.0025	227	99	90
<0.05	0.0041	337	99	87
0.063–0.05	0.0041	404	95	86
0.1–0.063	0.0062	221	79	98
0.16–0.1	0.0062	237	63	81
0.2–0.16	0.0050	168	38	88

Note. Frequency and amplitude of pulsation of the ascending liquid flow are 10 pulses/min and 5 mm, respectively.

see that the maximal yield is observed in both cases for the fractions <0.05 mm: 40.7 and 56.6 %, respectively. The second largest and similar for the two kinds of ash is the yield of the fraction 0.1–0.063 mm (23.5 and 22 %, respectively).

For the ash of the Ekibastuz coal, relatively high is also the yield of the fractions 0.16–0.1 mm (17.5 %) and 0.063–0.05 mm (9.7 %); the lowest yield is observed for the two largest fractions: 5.2 and 2.7 %. For the Kuznetsk coal, the yield of fraction 0.063–0.05 mm is substantially higher (18 %), while the yield of fractions >0.1 mm does not exceed 5 % as a total and decreases with an increase in particle size (4, 0.7 and 0.3 %) (see Fig. 2). Granulometric distribution of magnetic microspheres is close

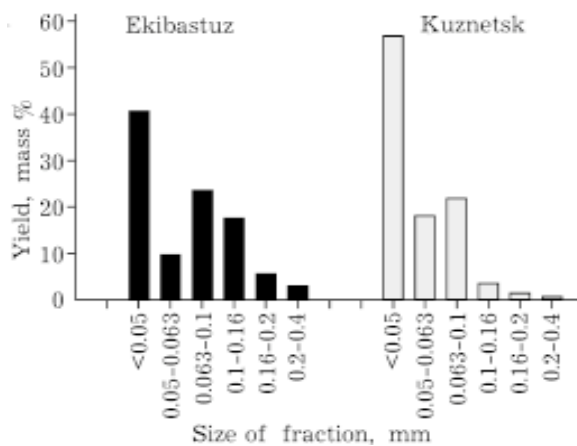


Fig. 2. Yield of magnetic microspheres of fixed composition isolated from the fly ash from the combustion of the Ekibastuz and Kuznetsk coal.

to the distribution of particles in the initial fly ash. So, the yield of close-cut fractions of magnetic microspheres varies from 40.7 to 2.7 % for the ash of the Ekibastuz coal and from 56.6 to 0.3 % for the ash of the Kuznetsk coal.

The analysis of electron microscopic images of the microspheric fraction <0.05 mm (Fig. 3, a) is the evidence of substantial non-uniformity of this material. One can see that the size of the particles varies from 0.001 to 0.05 mm. Because of this, we investigated numerical particle size distribution for the fraction <0.05 mm of the magnetic microspheres of ash from the Ekibastuz coal. The maximum of the distribution, determined using the data obtained by the two methods: Coulter and scanning electron microscopy (SEM), is about 0.043–0.045 mm (see Fig. 3, b). The volume concentration of the fraction 0.04–0.05 mm, calculating using these data, is 40 and 36 %; for the fraction 0.04–0.02 mm, 49 and 57 %; for the fraction <0.02 mm, 11 and 7 %, respectively.

On the basis of the data on the yield of products, a conclusion concerning higher dispersed state of the magnetic microspheres of ash from the Kuznetsk coal can be drawn. Comparison with the results reported in [3, 19] shows that the magnetic microspheres isolated from the fly ash of coal-fired boiler combustion of the Irsha-Borodino lignite are even more dispersed. In the latter, mass concentration of the particles less than 0.05 mm is 68–78 %; inside this fraction, 75 % of the particles have a size 0.001–0.005 mm.

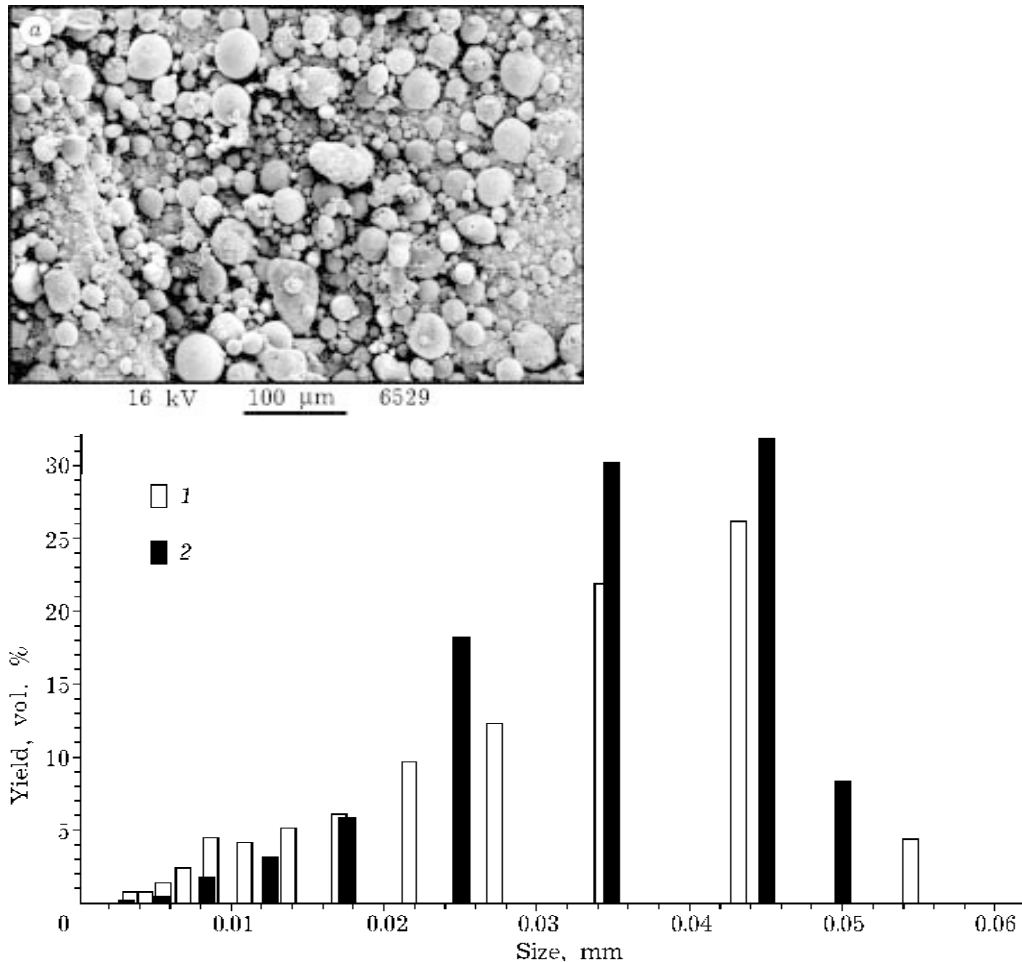


Fig. 3. Magnetic microspheres of ash of the Ekibastuz coal (fraction <0.05 mm): a – general view; b – particle size distribution (Coulter procedure (1) and scanning electron microscopy (2)).

So, 12 products of magnetic microspheres of fixed composition with the content of magnetic constituent 95–99 % were isolated from ash of the Ekibastuz and Kuznetsk coal. Depending on size, mass concentration of close-cut fractions is 56.6 to 0.3 %.

Physicochemical properties of the magnetic microspheres of fixed composition

Unlike ash and magnetic concentrate (Fig. 4, a), stabilized magnetic products are represented by microspheric particles of perfect and imperfect shape (see Fig. 4, b). Microspheric design of the magnetic particles is an evidence of their formation from melt enriched with iron. Chemical composition of close-cut fractions of magnetic microspheres formed with a yield ≥ 1 % is shown in Table 2. One can see

that total mass concentration of iron (Fe_2O_3) in magnetic microspheres varies within a broad range from 36 to 70 %; concentration of silicon and aluminium oxides decreases by a factor of 2; the trend of decreasing concentration of alkaline earth components is observed. Loss on ignition (LOI) corresponding to unburned carbon decrease by more than an order of magnitude.

Changes in the composition of melts cause changes in the properties of microspheres formed from those melts. In particular, the bulk density of the magnetic microspheres of different composition changes within the range 0.08–1.7 g/cm^3 ; true density varies within 2.6–3.6 g/cm^3 . The true and bulk density of magnetic microspheres isolated from the ash of two kinds of coal is described by a general dependence on the total iron content (Fig. 5).

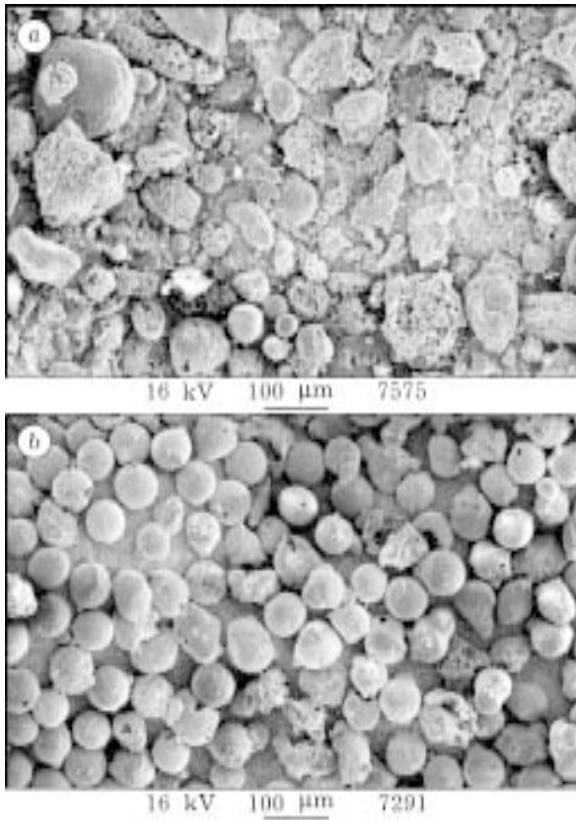


Fig. 4. Magnetic concentrate (a) and magnetic microspheres of 0.063-0.05 mm fraction (b) of the fly ash of the Ekibastuz coal.

The true density is in satisfactory agreement with the density of the melt near the liquidus point calculated with the help of the Melts software for thermodynamic calculations of

macrocomponent composition of the close-cut fractions of microspheres and overall composition of the magnetic products from ash of the Ekibastuz and Kuznetsk coal, shown in Table 2. Unlike overall composition (49.29 and 43.14 % Fe_2O_3), the scheme involved in the present work allowed us to carry out fine separation of the magnetic material which resulted in obtaining products substantially differing in composition and properties. In particular, a specific surface increases from 1.4 to 5.2 m^2/g with an increase in iron oxide content (see Table 2); morphology of magnetic microspheres changes.

The formation of globules of different morphology occurs in systems differing in chemical composition, first of all in iron content. Iron-containing compounds determine the mineral and phase composition of magnetic microspheres, which is represented by iron oxides in the form of ferrosphal of the following composition: $(\text{Fe,Mg})(\text{Fe,Al})_2\text{O}_4$ ($d = 2.96, 2.52, 2.09, 1.61, 1.48 \text{ \AA}$, predominant phase) and hematite $\alpha\text{-Fe}_2\text{O}_3$ ($d = 2.69, 1.84, 1.69 \text{ \AA}$; 5–15 % of the spinel phase). At the level of extrinsic phases, quartz $\alpha\text{-SiO}_2$ ($d = 3.34, 4.26 \text{ \AA}$) and mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($d = 3.39, 3.43 \text{ \AA}$) were identified; the intensity of their reflections increases with an increase in silicon and aluminium oxide content. It follows that the crystal structure of magnetic microspheres is

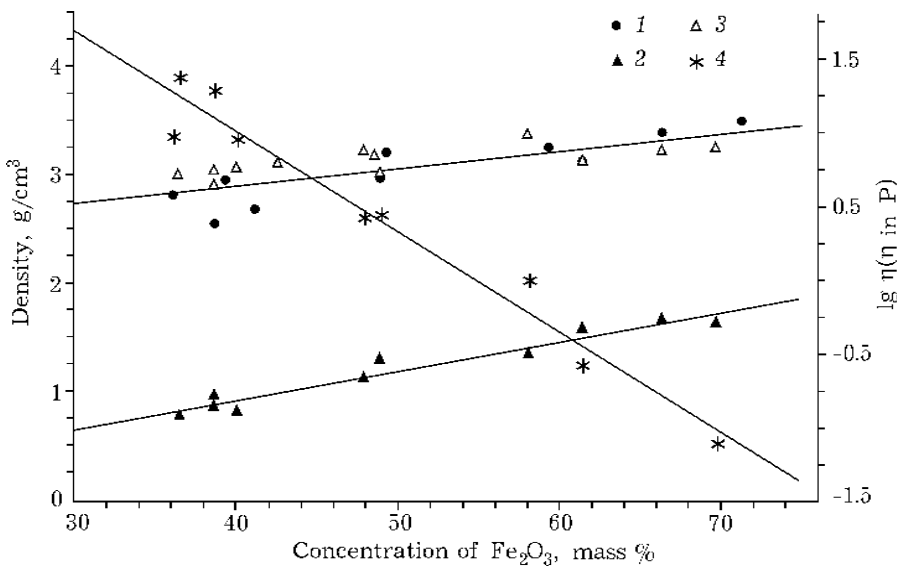


Fig. 5. Dependence of density (1 – true, 2 – bulk, 3 – calculated) and viscosity of melt (4) on total Fe_2O_3 content for magnetic microspheres of ash of the Ekibastuz and Kuznetsk coal.

TABLE 2.
Chemical composition of close-cut fractions of magnetic microspheres of the power-plant fly ash of the Ekibastuz and Kuznetsk coal

Fraction, mm	Concentration, mass %										$S_{sp}, m^2/g$	
	Calcina-	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂		Σ
	<i>Ekibastuz coal</i>											
0.4-0.2	2.5	39.0	15.6	35.6	3.6	1.3	0.6	0.4	0.3	1.1	100	4.9
0.2-0.16	1.6	35.9	14.7	40.1	3.2	1.6	0.7	0.8	0.3	1.1	100	3.1
0.16-0.1	1.2	37.8	16.0	38.7	2.8	1.6	0.4	0.3	0.2	1.0	100	3.1
0.1-0.063	0.3	32.2	12.4	48.0	2.6	1.1	0.6	1.2	0.3	1.3	100	2.1
0.063-0.05	*	25.8	9.2	58.2	2.8	1.0	0.6	0.9	0.2	1.3	100	1.6
<0.05	*	18.8	8.2	69.8	1.9	1.0	<0.1	0.1	0.1	<0.1	100	1.4
Magnetic product of ash from the Eki- bastuz Regional Hyd- roelectric Station [1]	-	32.0	14.0	49.3	1.5	1.3	0.3	0.5	0.9	0.2	100	-
	<i>Kuznetsk coal</i>											
0.16-0.1	4.1	38.1	13.1	36.1	3.8	2.9	<0.1	0.5	0.9	0.5	100	5.2
0.1-0.063	1.6	33.6	8.8	48.5	2.9	3.4	<0.1	0.7	0.5	<0.1	100	2.5
0.063-0.05	0	23.6	8.4	60.8	3.1	2.8	<0.1	0.8	0.4	<0.1	100	2.8
<0.05	0.1	20.5	6.6	65.8	2.9	2.8	<0.1	0.8	0.4	<0.1	100	1.7
Magnetic product of ash from the Belovo Regional Hydroelectric Station [1]	-	32.9	13.9	43.1	3.9	3.8	0.3	0.8	1.1	0.2	100	-

*An increase in mass is observed.

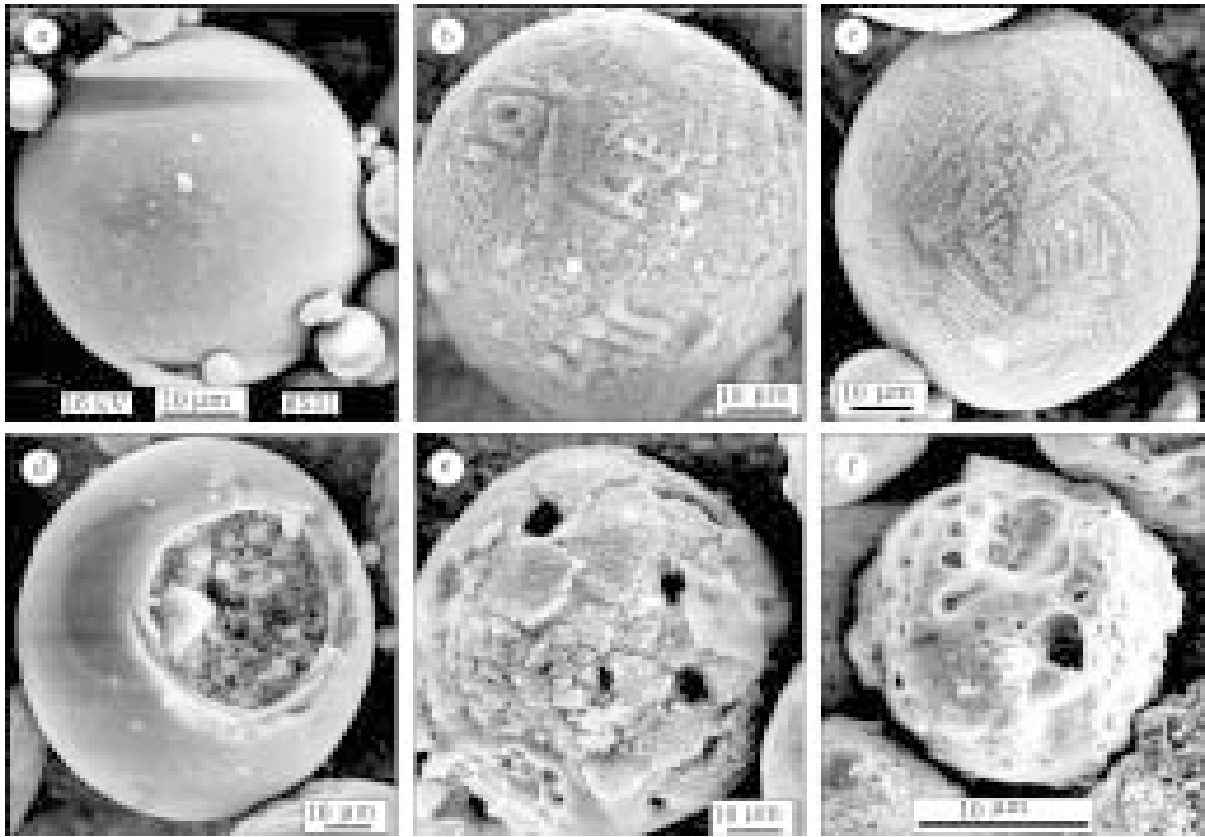


Fig. 6. Morphological types of magnetic microspheres of ash of the Ekibastuz coal: *a-c* – massive; *d* – plerospheres; *e, f* – porous.

formed mainly as a result of crystallization of iron oxide phases. The residual melt is enriched with silicon, aluminium, alkaline and alkaline earth components, which are crystallized from melt during cooling as quartz, mullite and form a glassy phase.

The viscosity of melts in the homogeneous state and under the conditions of crystal phase formation was calculated with the help of Melts software for the chemical composition of the close-cut fractions (see Table 2). The viscosity of melts in the liquidus point differs by more than 2 orders of magnitude (see Fig. 5). Low viscosity is characteristic of the compositions with high iron oxide content. The observed increase in viscosity occurs while the concentrations of silicon and aluminium oxides increase. During cooling the melts with low viscosity, active crystallization of iron oxide phases occurs, as well as release of gas inclusions, formation of dense heavy spherical particles. With an increase in the viscosity of melt, the growth of ferrosphenel crystallites and removal of gas

bubbles are hindered, which helps the development of porosity of microspheres.

On the basis of the data obtained by scanning electron microscopy, the main morphological types of globules were revealed, and estimation of their content in the products with different iron content was carried out. In particular, the following species are present in the magnetic microspheres of ash from the Ekibastuz coal: 1) massive globules of perfect spherical form with varied microstructure; 2) plerospheres (globules filled with particles <0.01 mm in size); 3) porous globules in the form of defect-bearing spheroids (Fig. 6).

Massive globules are characteristic of microspheres with high mass concentration of iron (>60 %). Their content decreases from 68 to 6 % with an increase in the mass concentration of Fe_2O_3 from 60 to 36 %. They possess diverse micro-relief depicting different character of crystallization of mineral phases. Among these microspheres, we did not discover monolithic magnetic globules with block structures

which are characteristic of magnetic microspheres with the mass concentration of Fe_2O_3 78–94 %, isolated from highly basic ash of the Irsha-Borodino lignite [3, 19]. In addition, we did not detect globules with uniform coarse crystalline dendritic or skeleton microstructure similar to those observed in microspheres of ash from the Chelyabinsk coal with ferrosphal content about 85 % [6]. In microspheres with Fe_2O_3 content about 70 %, most representative are ideal spheres with smooth or fine-relief surface (see Fig. 6, a); their structure is formed by micron and submicron inclusions of ferrosphal crystals in the glassy phase.

Along with them, the most frequently occurring sort is represented by globules with variations of fine crystalline structures, including oriented or disoriented attachments (up to 10 μm and more) of ferrosphal crystals and in combination with trans-crystallite structure (see Fig. 6, b, c). Combinations of structures of different types are described in [1] for magnetic microspheres with non-uniform composition, the crystal phases of which include magnetite (with inclusions of hematite and maghemite) and silicate minerals: quartz, mullite. Various microstructures of magnetic microspheres were also observed in [6] for particles with the volume fraction of glassy phase 20–50 %.

A special morphological version is plerospheres (see Fig. 6, d) which were also discovered in magnetic microspheres of ash from coal and brown coal from different deposits and in close-cut fractions of cenospheres [4, 9, 19, 20]. It is rather difficult to estimate the fraction of plerospheres in close-cut fractions because the outer wall can be continuous and in this case it will screen the inner part of a globule. Maximal fraction of plerospheres (about 16 %) was detected in the magnetic microspheres of ash of the Ekibastuz coal with Fe_2O_3 content about 48 %.

Porous globules in the form of defect-bearing spheroids occur in all the obtained products. Their fraction is about 26 % for Fe_2O_3 content 58 % and becomes predominant (82 %) in magnetic microspheres with decreased iron content (40 % Fe_2O_3) (see Fig. 6, e, f). Decisive factor in the formation of microspheres of morphological type is the viscosity of ferrifer-

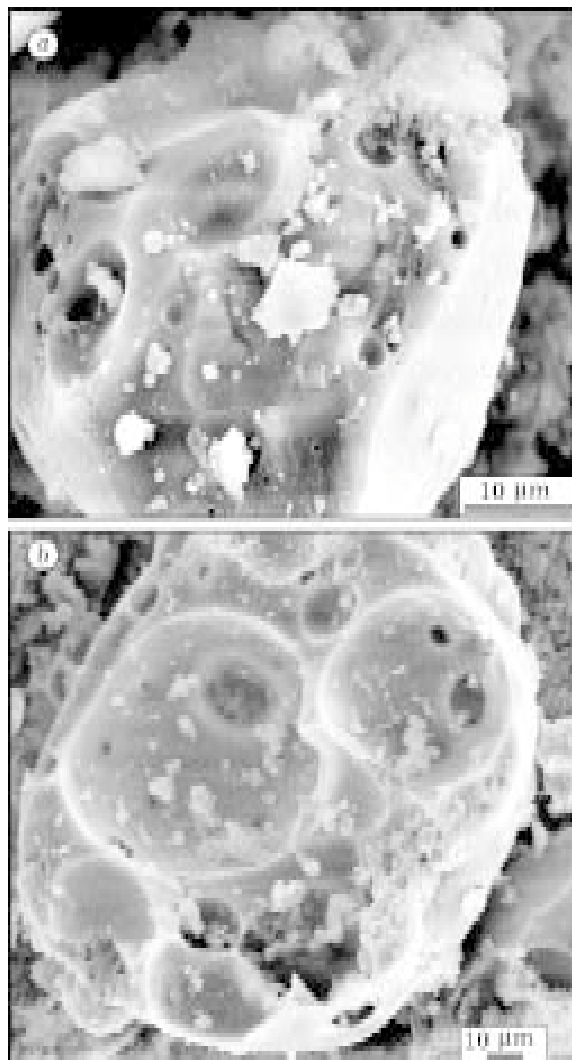


Fig. 7. Porous magnetic microspheres after destruction: a – in product with Fe_2O_3 content 58 mass %; b – in product with Fe_2O_3 content 40 mass %.

ous silicate melt, which depends mainly on total iron content (see Fig. 5). As the viscosity of the melts increases, macro- and microporosity of the resulting globules develops. The inner surface in which cavities and pores with a size up to 0.01 mm and rather low concentration are observed on the fracture surface of microspheres in the products with iron oxide content about 58 mass % and $S_{sp} = 1.6 \text{ m}^2/\text{g}$ (Fig. 7, a). With a decrease in the mass content of ferric oxide (40 mass %) and increase in the viscosity of the melt, macro-porosity develops in the form of many visible pores of different diameter and cavities with a size up to 0.05 mm (see Fig. 7, b), and contribution from micropores increases ($S_{sp} = 3.1 \text{ m}^2/\text{g}$).

CONCLUSION

Using the multistage scheme including different sequences of magnetic separation, hydrodynamic and granulometric classification, 12 products of magnetic microspheres of fixed composition with the magnetic constituent content 95–99 % were isolated with the yield of 0.3–57 mass % from the fly ash of coal from the Ekibastuz and Kuznetsk basins.

Texture characteristics, granulometric, macrocomponent and mineral phase composition of the products formed with a yield >1 % are investigated in detail; globules of three main morphological types are described. It is demonstrated that massive microspheres with various crystal microstructure are prevailing for the content of total Fe_2O_3 >60 mass %. With a decrease in iron content, the formation of porous microspheres becomes predominant. It is established that the determining factor in the formation of microspheres of morphological type is viscosity of ferriferous silicate melt.

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