Intermediate Products of Selective Sampling High Calcium Volatile Ash Species and Obtaining Special Cements and Magnetic Microspheres on Their Base

O. M. SHARONOVA[1], A. G. ANSHITS[1,2], L. A. SOLOVYEV[1] and A. N. SALANOV[3]

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

E-mail: shar@icct.ru

[2]*Siberian Federal University, Prospekt Svobodny 79, Krasnoyarsk 660041 (Russia)*

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

Abstract

High calcium volatile ash species resulted from brown coal of the Berezovka open pit mine of the Kansk-Achinsk coal field selectively sampled from different ash collecting points (convection mine, premix chamber and each of four fields of electrical filters) at the Berezovka Heat and Electric Power Plant (BHEPP-1) were investigated. Differences are established between these intermediate products in chemical composition, dispersity, cementing properties. Within the system of volatile ash chemical classification the types were determined. It was demonstrated, that the ash of the Berezovka, Nazarovo coal taken from 1–4th fields of electrical filters differ from all known kinds of ash by an extremely high content of calcium. From $CaO-Al_2O_3-SiO_2$ phase diagram it follows, that the ash from electrical filters could result in the formation of hydraulically active phases similar to the basic phases of Portland cement clinker. In this case, owing to the difference in the ash composition, the ratio between these phases should change. Alongside with different dispersity level, this allows obtaining Portland cement with special properties on their basis. Six fractions of high purity magnetic microspheres were obtained, their chemical composition, quantitative phase composition and morphology were investigated, including the contribution of different globule types and structural texture features of the material; the methods of application, trends in of changing the structure and morphology with the change in fraction size were determined.

Key words: volatile ash species, structure, the dispersity level, cementing properties, magnetic microspheres

INTRODUCTION

In the world practice, volatile ash (VA) of heat and electric power plants (HEPP) are applied instead of natural raw material in the manufacture of Portland cement clinker and composite cements [1, 2]. This allows not only lowering the expenses for grinding the components due to high ash dispersity level, but also improving a number of ware properties in the use of VA as a mineral additive to cements: lowering thermal emission, shrinkage and swelling deformation, improve protective properties against gamma and neutron radiation, increasing resistance against corrosive media [3–5].

A steady trend of the last decade in the world is represented by improving ash quality due to the stabilization of their dispersity level and composition with the help of selective sampling [6, 7] or in the units for conditioning ash species (pneumoclassification, sieving, drying, grinding) [8]. Selective sampling in the system of ash collecting promotes the stabilization of ash granulometric, chemical, phase composition; therefore they represent intermediate products with constant quality. For example, the authors of [6] demonstrated the differences between aluminosiliceous ash species sampled from different fields of electrical filters (EF): particle size and the content of quartz decreases from 1st to 3rd to field, the amount of the amorphous phase grows, whereas the content of Al_2O_3 raises and the fraction of SiO_2 decreases in the composition.

For improving the properties of VA in the application as a filling material in cements, we selected much finer, chemically active fractions from the last three fields of EF [7]. Using the apparatus for pneumatic classification a product from VA is obtained that consists of 90 % particles with the size <5 μm, and of the 5–45 μm fraction that can be used as a filling material in polymer and a rubber industry [8]. The presence of microspherical components in VA promotes improving the plasticity of cement mortars, whereas in obtaining polymeric products this promotes moving the flow in the course of extrusion and casting procedures. In the rubber industry of the Republic of South Africa and the manufacture of plastics, they apply narrow VA fractions as a functional filling material to obtain the products of first-rate quality [7].

For obtaining cements, VA with the increased content of calcium are most promising, since this promotes decreasing CO_2 emissions in the manufacture of clinker due to replacing a carbonate component. Besides, the presence of cementing properties allows reducing the fraction of cement in cementing compositions or creating cementless cementing mixtures [9]. In the aggregate with the influence of microspherical particles, the application of high calcium VA as a substitute of cement in concrete modifies its properties, both in mobile, and in hardened condition, with improved placeability characteristics, shrinkage deformations, resistance against temperature impact and abrasion [10].

The key factors influencing the properties of microspheres in the course of hydration and hardening, behaviour in solid phase compositions and resistance against corrosive media, are presented by mineral phase composition and dispersity level. In this case, alumina-siliceous ash species are remarkable for weak microsphere crystalline phase structure dependence on the microsphere dispersity level and for close reactivity with respect to HF [11]. However, for fine fractions of high calcium ash microspheres it was identified as a minimum three types of microspheres differing by the content of calcium, reactivity with respect to acidic reagents and, to all appearance, by cementing properties [12].

One of the most widespread modifications of VA microspherical components resulting

from powdered coal combustion at heat power plants are presented by magnetic microspheres (MM) characterized by a high content of iron. The composition of MM differs to a considerable extent for alumina siliceous and high calcium ash [13, 14], which is demonstrated by the differences in the amount, structure and properties of magnetic ferrospinel phase and vitreous phase, the morphology of microspheres and the methods of their use.

The purpose of the present work consisted in studying the composition, dispersity level and morphology of intermediate products resulted from selective sampling high calcium VA of the Berezovka open-pit mine of the Kansk-Achinsk coalfield (KAC) and MM isolated from them, as well as studies on the potentialities of their application in obtaining special cements and magnetic microspherical materials.

EXPERIMENTAL

Research objects

As the subject of inquiry, we have chosen VA obtained in the course of the combustion of powdered B2 grade brown coal from the Berezovka open-pit mine of KAC. Samples were selectively taken in the system of ash collecting at the BHEPP-1 that belongs to the largest HEPP of Siberia with the power of 1460 MW, the consumption of coal being 4.535 million t/year and the VA production about 300 thousand t/year. The combustion was carried out in steam generating units P-67 with solid slag removal at the temperature of 1350–1450 °C. The ash level of the Berezovka coal was approximately equal to 7 % [15]. The fraction of volatile ash species is ≥95 %, that of slag is ≤5 %. The collecting of ash species was carried out using EGD2-128-9-6-4-200-5 electrical filters with the efficiency coefficient of 98.5 %. The sampling of ash intermediate products was performed in the convection mine (CM), pre-mix chamber (PC) as well as from each of four EF fields (1st–4th field) with the yield of 3.8, 5.1, 50.4, 25.5, 10.1 and 5.1 %, respectively.

The magnetic concentrate was isolated at the BHEPP-1 from joined products taken from CM and 1st EF field, its bulk density amounting to about 2.0 g/cm³, the content of Fe_2O_3 is equal
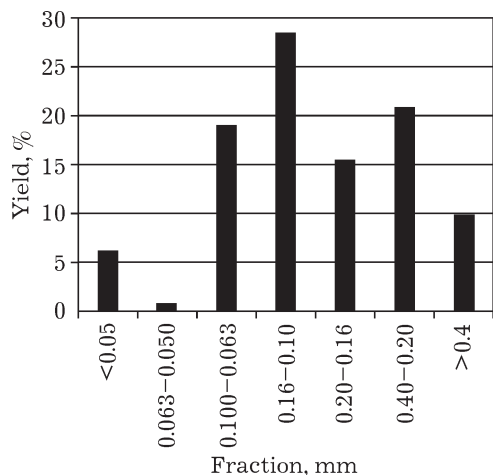
Fig. 1. Granulometric composition of the magnetic concentrate.

to 84.5 %. The granulometric composition of the concentrate is presented mainly by coarse fractions (Fig. 1), which allows obtaining high-purity fractions of MM according to three-stage scheme: 1) sieving the concentrate into six fractions; 2) dry magnetic separation of each fraction using 138T separator at the magnetic field intensity amounting to 0.3 T; 3) reference sieving each fraction. The yield of MM narrow fractions decreased with decreasing the particle size from 90 % for the fraction of 0.4−0.2 mm down to 44 % for the fraction <0.05 mm.

Methods of investigation

The sampling and preparation for the analysis was carried out according to the State Standards GOST 23148−98 [16] and the GOST 26565−85 [17]. The granulometric composition of materials was determined using the method of dry sifting a sample according to the GOST 18318−94 [18] on vibration apparatus VP-S/220, using a kit of sieves with mesh size amounting to 0.4, 0.2, 0.16, 0.1, 0.063, 0.05 mm. Particle size distribution was studied with the help of a Fritsch laser particle sizers Analysette Micro-Tec 22 plus.

The macroelemental composition and the calcination loss (CL) of intermediate products and the MM were determined using the methods of chemical analysis according to the GOST 5382−91 [19].

XRD patterns were registered using a PAN-alytical X'Pert PRO MPD system with a secondary graphite monochromator and solid-state detector includes an active pixel matrix. For minimizing the effect of microabsorption of ferriferous phases we used CoK_α radiation. The phase identification was performed with the use of an interactive search system [20]. The quantitative phase analysis was performed with the use of the Rietveld approach [21] and the method of minimizing derivative difference [22]. For determining of the content of an amorphous phase we used NaCl internal standard.

Studying the morphology on powder samples and polished cuts obtained by fixing microspheres in epoxide resin and by final polishing by 3M micropowder, were carried out using a LOMO Biolam optical microscope with Panasonic digital CCTV camera, as well as the method of using a LEO 1455 VP scanning electron microscope at accelerating voltage of 20 kV and with resolution up to 30 nm and a Tesla BS 350 SEM for 30 kV accelerating voltage.

RESULTS AND DISCUSSION

Ash intermediate product

The studies on ash chemical composition taken from six points of ash collecting demonstrated a considerable difference in the content of SiO_2, Fe_2O_3, CaO, SO_3, Na_2O and in the CL value (Table 1). In particular, in going from CM to the 4th to field of EF one can observe reducing the content of SiO_2 (2.3-fold) and of Fe_2O_3 (3.3-fold), however, there is an increase in the content of SO_3 (100 times) and Na_2O (4.8 times). The content of CaO is much lower in the products taken from CM (25.27 %) and PC (36.53 %), as compared to EF ash species (41.21−45.88 %). On the contrary, the highest CL values are observed in the products from CM (25.46 %) and PC (14.28 %) as compared to ash species from EF (6.3−12.2 %), exhibiting no steady tendency as a whole. The content of components K_2O, TiO_2 and MnO amounts to less than 0.5 % and, to all appearance, their influence upon ash properties is minimal.

A high content of calcium in ash species resulted from HEPP coal is observed, as a rule, only for low grade coal species (B1−B3), and not all the coal species of these grades are characterized by a high content of calcium in ash [23, 24]. Ash species with the content of CaO

TABLE 1

Chemical composition of intermediate products - volatile ash species from the Berezovka HEPP-1, mass %

Components	Point of sampling					
	Convection mine	Premix chamber	Field of electrical filters			
			1	2	3	4
SiO_2	26.18	19.02	19.58	15.40	11.85	11.26
Al_2O_3	8.15	7.05	9.86	9.45	8.41	9.87
Fe_2O_3	10.70	11.10	5.62	4.58	4.45	3.39
CaO	25.27	36.53	45.88	43.69	45.1	41.21
MgO	3.42	4.20	4.36	4.94	5.72	4.50
Na_2O	0.40	0.40	0.79	0.86	0.88	1.91
K_2O	0.47	0.24	0.31	0.33	0.24	0.36
TiO_2	0.10	0.33	0.13	0.05	0.10	0.06
MnO	0.30	0.30	–	–	–	–
SO_3	0.15	7.10	6.67	10.99	10.56	15.78
CL	25.46	14.28	6.30	9.20	12.20	11.20
Σ	100.28	100.32	99.51	99.50	99.51	99.54
$R = CaO/SiO_2$	0.97	1.92	2.34	2.84	3.81	3.66

>40 % occur very seldom, and their structure, properties and scopes are studied to a lesser extent. This is indicated also by data from the diagram of volatile ash classification (Fig. 2) [9]: the overwhelming part of ash species of 37 heat plants of the European Community [9] and 46 HEPPs of Russia and CIS countries [14, 23,

Fig. 2. Classification of volatile ash species according to chemical composition [9] into four types (S − alumina siliceous, FS − ferroaluminate siliceous, CS − calcium-alumina siliceous; FCS − iron- calcium-alumina siliceous): *1* − ash species taken from HEPPs of the European Community [9]; *2* − ash species from Russian HEPPs [13, 23, 24]; *3* − intermediate products from BHEPP-1.

24] belongs to alumina siliceous ash (type S, Sialic) which contain more than 77 % of sum $SiO_2 + Al_2O_3 + K_2O + TiO_2 + P_2O_5$, mainly due to a high (>70 %) content of $SiO_2 + Al_2O_3$. Within the narrow area located near the border with type S, there are ash compositions such as FS (Ferrisialic) which are characterized by an increased content of Fe_2O_3 (11−19 %). Ash species with an increased content of calcium − type CS (Calsialic) − exhibit a wide composition; they include also ash species resulted from brown coal of the Irsha-Borodino and Berezovka open-pit mines of KAC. Ash species from 1st and 2nd EF fields from coal of the Nazarovo open-pit mine [24] belong to FCS (Ferricalsialic) type.

Volatile ash species of selective sampling from BHEPP-1 belong to different types: those taken from CM and PC belong to FCS type; those taken from 1st−4th EF fields belong to CS type. In this case, ash species from 1st−4th EF fields resulted from the coal of the Bere-zovka and Nazarovo open-pit mines have no analogues in this diagram, since in their composition there is a maximal total content of (CaO + MgO + SO_3 + Na_2O + MnO), first of all, due to CaO. In the ash species with a high content of CaO there can be phases similar to the phas-es Portland cement (PC) clinker formed. The cementing properties of PC are caused by the content and properties of active clinker phas-
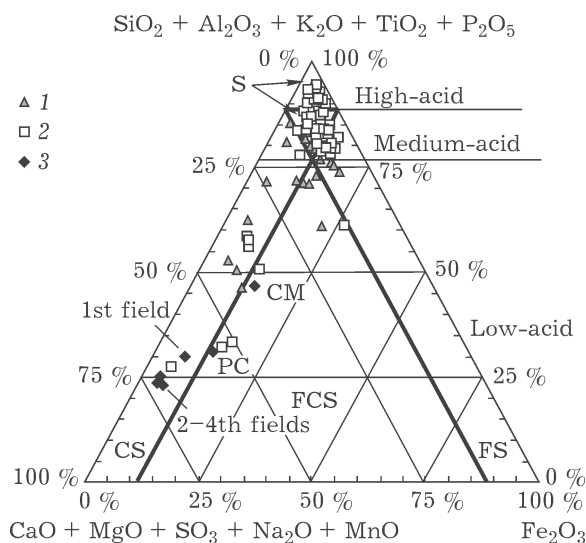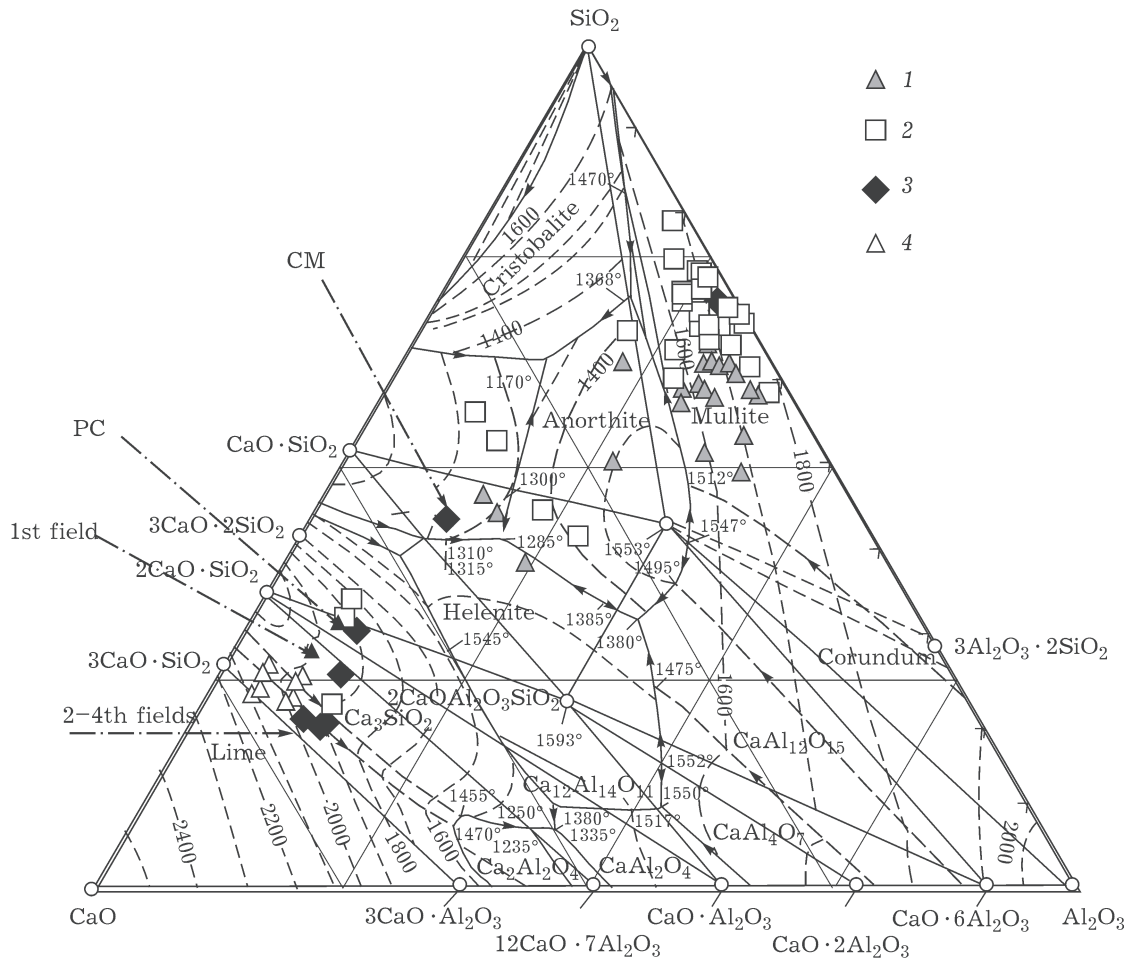
Fig. 3. State diagram for $CaO-Al_2O_3-SiO_2$ system [27] with indicated compositions: *1* − ash species from the European Community HEPPs [9], *2* − ash species from Russian HEPPs [13, 23, 24], *3* − intermediate products from BHEPP-1, *4* − Portland cement clinker [26].

es: Ca_3SiO_5 (42−65 %), Ca_2SiO_4 (10−50 %), aluminates (mainly $Ca_3Al_2O_6$ − 2−15 %) and calcium alumoferrite $Ca_4Al_2Fe_2O_{10}$ (10−25 %) [25, 26]. Basing on the chemical composition of clinker, one can conclude that the phase formation, determining its properties proceeds mainly in $CaO-Al_2O_3-SiO_2$ system whose componential content in the clinker exceeds 85 %. The majority of VA belongs to such systems, too.

For understanding phase formation under equilibrium crystallization, there were points put on the $CaO-Al_2O_3-SiO_2$ phase diagram [27] corresponding to different ash intermediate product compositions (Fig. 3). One can see that phase formation in ash species strongly differs, mainly, due to the differences in chemical composition. As it follows from data presented in Fig. 3, the products closest to Portland cement

clinker were taken from with 2nd−4th EF fields. Hence, in the course of phase formation, hydraulically active clinker phases such as Ca_3SiO_5, Ca_2SiO_4 and $Ca_3Al_2O_6$ would be formed therein. The development of the technology including directed phase formation, would allow one to use these products in full volume (120 thousand t/year) for obtaining clinker or composite PC.

A similar set of phases could be formed also in the case of ash species from 1st EF field, however Ca_2SiO_4 would prevail therein. The amount of such ash species at the BHEPP-1 amounts to about 150 thousand t/year, which in the aggregate with the products of 2nd−4th EF fields would allow 90 % reducing the annual supply of ash species for warehousing at an ash disposal area. In the ash species with

PC from active phases there could be only Ca_2SiO_4 formation possible, whereas in the case of CM ash species its formation is excluded. Hence, for the use of high calcium VA in obtaining the cementing materials it is necessary to carry out a selective taking of dry ash species from different points of an ash collecting installation at HEPP, which allows guaranteeing the quality of intermediate product and purposeful phase formation, including the ratio between hydraulically active phases.

The formation of phases in the ash species under investigation is influenced by the presence of SO_3 resulting in the linkage of the part of calcium into sulphate and sulphoaluminate. According to the GOST 31108−2003 [25], the content of SO_3 in constructional cements should not exceed 4 %. At the same time, the outlook of obtaining belite-sulphoaluminate cements on the basis of ash with a high content of calcium compounds and SO_3 was demonstrated for the temperature of sintering lower (1100−1350 °C) than the temperature of obtaining clinker (1450−1500 °C) [28, 29]. In their structure, calcium silicates are presented by belite Ca_2SiO_4, whereas the content of $CaSO_4$ ranges from 0.1 to 17 %. The cements obtained are characterized by increased stability in corrosive media. At a high content of Ca_3SiO_5 therein (more than 57 %) they can be used in obtaining unshrinkable and extensible cements.

One of requirements for VA consists also in the CL value which according to the GOST 31108−2003 [25], reflects the underfiring content and should amount to less than 5 %. The authors of [30, 31] demonstrated that the dehydration and/or decomposition of such minerals as portlandite, calcite, anhydrite and dolomite could result in a considerable error (5−500 %) in determining the content of unburned carbon. They proposed a thermogravimetric method which allows one to determine the contribution of carbon and mass loss due to the reactions of dehydration and decarbonization. Studies *via* the methods of thermal analysis [32] demonstrated that the content of carbon amounted to 7.25 and 7.36 % for CM and PC ash species, respectively, whereas for ash species from 1st−4th EF fields the main contribution to CL value is made by different forms of bound water: there is mass

loss from 3 to 7 % observed at the temperature ranging from 80 to 440 °C caused by the storage of ash species in humid atmosphere, as well as decomposition of a calcium carbonate (the mass loss from 2.5 to 5 % at the temperature values ranging from 500 to 720 °C), whereas the content of carbon particles did not exceed 1 %.

Thus, for ash from 1st−4th EF fields, the possibility of realizing phase formation with obtaining clinker phases was demonstrated at the temperature values below the temperature of obtaining PC clinker. Due to the differences in the structure of these ash species, they can be used as the components of cements with special properties. For example, in high-early-strength PC there should prevail tricalcium silicate and aluminate; in sulphate-resistant cement, on the contrary, the fraction of these compounds should be lower as compared to the fraction of dicalcium silicates and vitreous phases; in oil-well cement there should be contained more tricalcium silicate and calcium alumoferrite, whereas unshrinkable and extensible cements should be characterized by an increased content of calcium sulphate and sulphoaluminate [26, 33, 34].

It is known, that dispersity level of cements determines the activity of the latter in the course of the hydration and the formation of a fine-dispersed hydrosilicate matrix whose properties modulate the strength cement stone [35]. In particular, the fraction of 0−5 µm size
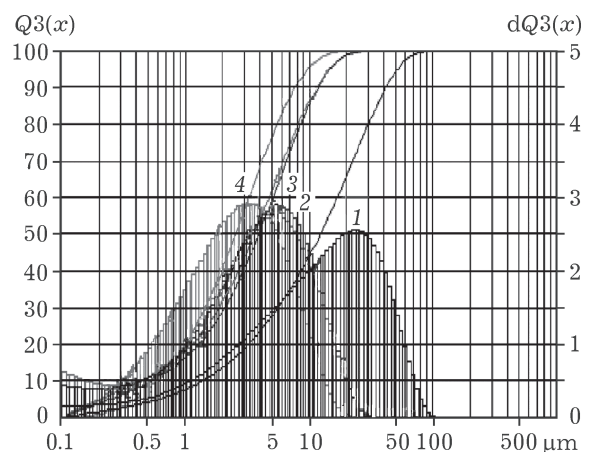

Fig. 4. Cumulative and differential size distribution for particles in the intermediate products of BHEPP-1 taken from 1st−4th fields of electrical filters (curves *1−4*, respectively).

exerts crucial influence within the first hours of hardening; the fraction with particle size of 5−10 µm influences the strength of products within 3−7 days, whereas the fraction of 10−20 µm determines the strength for the 28th day. The variation in the sizes of particles allows one to obtain different grades of cements.

The studies on granulometric composition revealed a considerable difference in the dispersity level between CM and PC ash and VA taken from the 1st−4th EF fields. So, the content of the fraction with particle size <0.063 mm amounts to less than 26 % in the case of CM, less than 46 % for PC and more than 95 % for the ash taken from 1st−4th EF fields [32]. In going from the 1st to the 4th EF field the dispersity level of ash increases, which is indicated by data obtained with the help of the laser analyzer of particles (Fig. 4). One can see that the maximum of distribution corresponding to 20−30 µm for the product taken from the 1st EF field is displaced towards 5−6 µm for the products taken from 2nd and 3rd fields and towards 3−4 µm for the products taken from 4th EF field. Within the same series, the contribution of particles submicron size increases. From these data it follows, that the dispersity level for ash taken from EF is comparable with those for PC, whereas the selective sampling allows one to obtain products with preset dispersity level, which is promising for making the cements of different grades, including fast-hardening and high-strength ones.

For ash species taken from the 1st, 3rd and 4th EF fields, according to the GOST 25094−94 [36], the testing of hydraulic activity concerning the time of cementation for the mixtures ash/CaO/gypsum = 28 : 7 : 1 with adding water to gain the density of normal paste.

TABLE 2

Hydraulic activity of the mixture additive/Ca(OH)$_2$/gypsum according to the GOST 25094−94 [36] (additive mass being 50 g, the mass of Ca (OH)$_2$ and gypsum being of 12.5 and 1.78 g, respectively)

Additives	Time of beginning solidification, h	Solidification time, h
400 Grade cement	0.62	3.66
Intermediate products:		
1st EF field	0.50	1.58
3rd EF field	0.68	0.90
4th EF field	0.61	0.65

The time of beginning the cementation of mixtures with ash species is comparable to those for cement of M400 grade (Table 2), whereas the period of cementation was much shorter decreasing from 1.35 to 0.39 h for ash in going from the 1st to 4th field. The major factor in this case, to all appearance, consists in increasing the dispersity level of ash going from the 1st to 4th field.

Thus, data concerning the chemical composition, dispersity levels, the hydraulic activity of ash species resulting selective sampling, as well as a comparative analysis of their composition and the composition of PC clinker allow one to conclude that ash species from the 1st−4th EF fields can be completely used for obtaining cements. Their total yield amounts to approximately 270 hundred t/year, which amounts to, for example, more than 35 % of the productivity of the Krasnoyarsk Cement Plant. Moreover, it would allow lowering the discharge of VA to ash-disposal area by 90 %. Selective sampling of ash products allows one to stabilize their structure, dispersity level, properties as well as to create efficient tech-

TABLE 3

Chemical and phase composition of the six fractions of magnetic microspheres, mass % (CL= 0)

Fractions, mm	Chemical composition									Phase composition			
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	TiO$_2$	SO$_3$	Spinel	Hematite	Quartz	Vitreous phase
0.4−0.2	4.00	1.90	85.20	8.69	1.00	0.25	0.07	0.18	0.25	64.7	10.1	1.3	23.8
0.2−0.16	2.48	1.20	88.42	7.43	0.81	0.20	0.05	0.19	0.21	63.6	18.7	1.3	16.4
0.16−0.1	1.26	0.83	92.52	4.90	1.30	0.11	0.04	0.17	0.27	65.8	24.6	0.7	9.0
0.1−0.063	1.30	0.92	90.47	6.60	0.90	0.20	0.06	0.18	0.28	54.8	22.6	0.5	22.1
0.063−0.05	1.35	1.02	89.25	6.70	0.81	0.24	0.10	0.12	0.28	44.6	35.6	0.5	19.3
<0.05	0.64	0.92	89.12	8.81	0.60	0.10	0.05	0.16	0.25	38.2	37.5	0.4	23.8

nologies for obtaining on their basis PC, including cements with special properties.

Magnetic microspheres

As it follows from data presented in Table 3, from high calcium ash intermediate products we obtained MM with the mass fractions of Fe_2O_3 equal to 85.2−92.52 % and an increased mass fraction of CaO (4.9−8.8 %) as compared to known microspheres [14, 23, 37−41]. At the same time, the content of SiO_2 and Al_2O_3 therein is much lower. At a close chemical composition, the difference in the properties of microspheres is determined by phase-mineral composition and texture-structural characteristics of the material of microspheres. The main phase of all the fractions of MM is presented by spinel phase on the base of magnetite whose mass fraction amounts to 38.2−65.8 % (see Table 3).

As against the mentioned papers [13, 14, 38, 40, 41], a high content of hematite α-Fe_2O_3 is inherent in the samples under investigation which content increases from 10.1 to 37.5 mass % with the reduction of fraction size and the decrease of the amount of ferrospinel phase. It should be noted that for microspheres the mass fraction of amorphous phase (9−23.8 %) is high, too, thus it contains more iron and calcium as compared to vitreous phase of the microspheres described in [39, 42].

The parameter of the unit cell for ferrospinel phase for the MM under investigation (8.395−8.3994 Å) is equal or exceeds that for magnetite (8.396 Å). A low (<1 mass %) content of Al_2O_3 and high (11−34 mass %) content of hematite are inherent in them, which could result in the formation of unsubstituted magnetite as well as the formation of faulted structure with oxygen vacancies.

The formation of microspherical globules occurs at the high temperature stage due to a complete or partial fusion of the material of microspheres, whereas the structural texture features depend, mainly, on the processes of phase formation inside a globule. It should be noted, that owing to the temperature gradient and features of phenomena occurring at the interface, surface structures could differ from the bulk ones, which to a greater extent is exhibited for coarse fractions of microspheres.

As against known data concerning the description of individual globules, the studies on a number of narrow microsphere fractions with maximal iron content (83−92 % Fe_2O_3) allowed establishing some tendencies in changing their morphological features observed as the diameter of globules reduced. According to the type of globules it was demonstrated that in the case of coarse fractions (>0.1 mm), plerospheres are the most typical, *i. e.* the globules with an external shell of different thickness and structure with an internal cavity filled by spheres, crystallites and carbon particles of much smaller size. The formation of plerospheres occurs under the conditions of significant temperature gradient, when the external layer has time for melting, whereas separate particles or units of sintered particles capsulate inside [43]. The thickness of plerosphere shell can range from $0.03d_m$ up to $0.75d_m$ (d_m is the diameter of a microsphere).

Plerospheres those have thin shell with different texture (Fig. 5, *a*), are inherent in the most coarse fractions of microspheres (0.4−0.2 and 0.2−0.16 mm). With reducing the fraction size, the contribution of thin-walled modifications decreases, the amount of plerospheres with thick dense or porous shell (see Fig. 5, *b*) and globules having a small cavity in the centre or in other sites of a microsphere. In the studies of individual plerospheres it was demonstrated [39] that the MM could be encapsulated in a shell composed of aluminium silicate (the content of Fe_2O_3 <5.46 %). At the same time, the authors of [38] demonstrated that the shells of magnetic plerospheres consist of ferrospinel crystals densely and homogeneously distributed within the Ca−Fe or Ca−Fe−Al basic glass.

As against the known data, in the microspheres under investigation there is a type of globules with concentric shells for the first time identified (see Fig. 5, *c*, *d*). They are observed for all the fractions, in this case the thickness of the shell increases as the diameter of microspheres decreases. Their textural features are similar to bulky microspheres, as well as plerospheres and can be different for different shells of one globule.

Among bulky globules of coarse fractions, the greatest contribution is made by globules with mixed and, in particular, with non-uniform structure, which is inherent in MM ash species from power plants [38−40, 44−46]. They
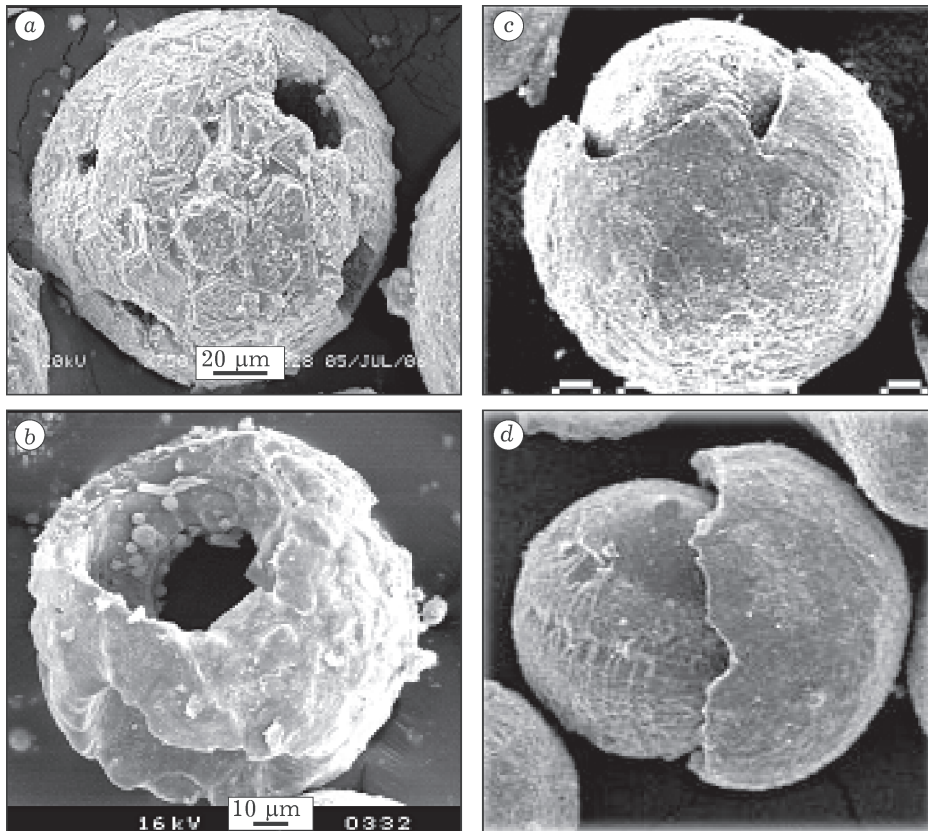
Fig. 5. Electron microscope images for plerospheres (*a*, *b*) and concentric globules (*c*, *d*).
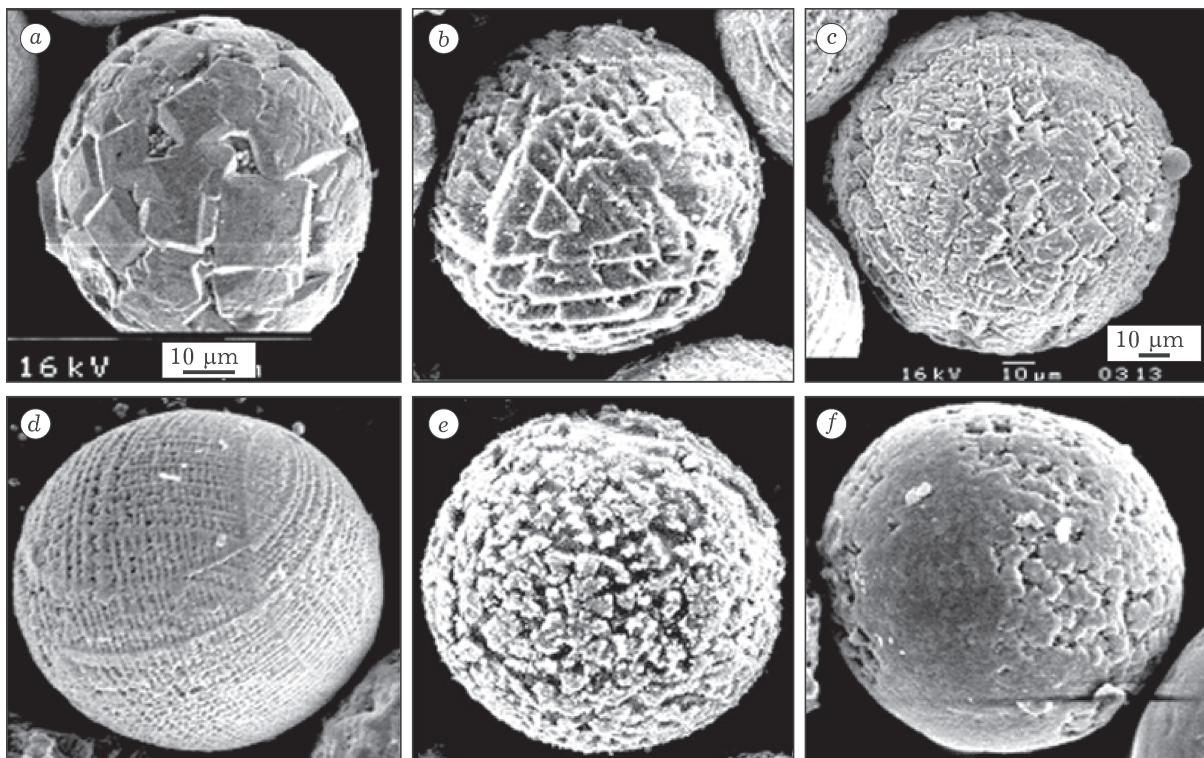

Fig. 6. Electron microscope images for bulky globules with different surface microstructure: *a*, *b* − block-like; *c*, *d* − skeletal-dendrite; *e* − granular; *g* − mixed non-uniform ones.

differ in the shape and size of crystalline individuals as well as in the amount and arrangement within the space of a microsphere.

With decreasing the size of microspheres, the contribution of globules with different shape of microstructures homogeneous enough (Fig. 6) increases. In particular, a block-like shape is observed which is formed, in opinion of the authors of [38], by crystallites whose growth occurs on the face {100} for cubic crystals of magnetite (ferrospinel) (see Fig. 6, *a*) or on the face {111} for octahedral crystals (see Fig. 6, *b*). Their size reaches 10−20 µm; in this case they have a maximal contact between each other.

With prevailing the growth rate of crystal individuals in one of the directions, there is the formation of crystallites is observed spatially oriented as skeletal, dendritic and skeletal-dendrite shapes (see Fig. 6, *c*, *d*). The studies of microspheres of 0.063−0.05 mm fraction in the form of polished cuts using method SEM method (Fig. 7) demonstrated that these struc-

tures range within all the globule volume, which was demonstrated also for individual globules by the authors of [38, 40, 42, 44].

Point crystallization with the formation of grains isolated from each other results in the formation of a granular structure, wherein crystalline individuals could considerably differ in shape and size, both for different globules, and within the range of one globule. In the microspheres under investigation there are homogeneous enough granular structures observed (see Fig. 6, *e*) with the size of grains from submicronic to approximately 10 µm, which corresponds to data from [39, 44, 46]. The globules with mixed non-uniform structure (see Fig. 6, *e*) are most widespread ones.

Thus, studying the shapes of crystal individuals and the structures of MM allows one to draw a conclusion on their wide variety, inherent in power-plant ash resulting from powdered coal combustion. As against known structures data concerning the description of individual globules, the investigation of some narrow MM fractions with maximal content of iron (83−92 % Fe_2O_3) has allowed establishing some tendencies in changing their morphological features observed as the diameter of microspherical globules decreases. In particular, for coarse fractions of microspheres, globules with mixed and non-uniform structure are most typical. With the reduction of diameter, microspheres become to occur with more ordered and homogeneous texture such as block-like, skeletal, dendritic, coarse-grained and fine-grained.

Highly ferriferous MM with the maximal content of ferriferous phases are most promising as catalysts or high-temperature carriers for catalysts applied in the processes of oxidative methane dimerization [47], oxidation of hydrocarbons [48], in heavy oil and black oil pyrolysis [49], for the decomposition of liquid radioactive waste products based on tributylphosphate with the immobilization of radionuclides within the structure of iron phosphate ceramics [50]. One of the ways for perfecting their properties could consist in high-performance separation according to the morphological types, whereas a necessary precondition for this consists in studying the features of the morphology and microstructure of magnetic microspherical globules.
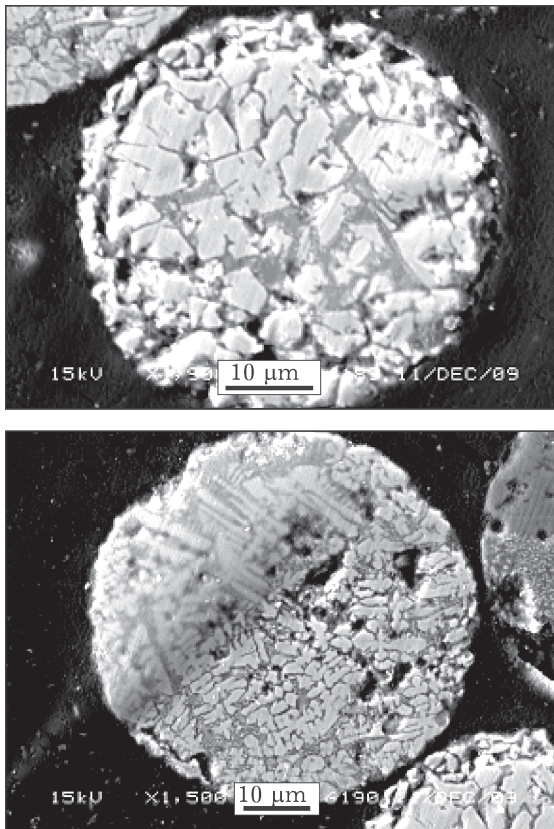

Fig. 7. Electron microscope images for polished cut of magnetic microspheres for 0.063−0.05 µm fraction: *a* − block-like, *b* − skeletal-dendrite ones.

CONCLUSION

1. High-calcium volatile ash species of brown the coal from the Berezovka open-pit mine of the Kansk-Achinsk basin selectively sampled from different points of the ash collecting unit at the BHEPP-1 (convection mine, premix chamber and each of four electrical filter fields) were studied. Considerable differences between these intermediate products in the chemical composition the dispersity level, cementing properties were demonstrated. Within the system of chemical classification for volatile ash species, their types were determined and it is established, that ash species resulted from the Berezovka, Nazarovo coal taken from the 1st–4th EF fields differ from all known ash species in an extremely high content of calcium.

The analysis of SiO_2 phase diagram has demonstrated that only the products from 1st–4th EF fields could result in the formation of hydraulically the active phases similar to the basic phases of the Portland cement clinker. Selective sampling of ash products allows one to stabilize their composition, dispersity level, properties as well as to create efficient technologies for obtaining on their basis PC, including cements with special properties.

2. In this paper, the composition and morphology of six high purity MM fractions isolated from CM and 1st EF field ash species were investigated. It was demonstrated that, as against known microspheres, they are inherent in a maximal content of iron (85.2–92.52 mass % Fe_2O_3) and calcium. Phase composition, alongside with the main ferrospinel phase (38.2–65.8 mass %), is characterized by a high content of hematite (10.1–37.5 mass %) and vitreous phase (9–23.8 mass %). The morphology of globules, including the contribution of different type globules were investigated, including structural and texture features of the material of microspheres.

It was demonstrated that in the case of coarse fractions (>0.1 mm), the most typical ones are presented by plerospheres with the shells of different thickness and with prevailing thin-walled modifications. For the first time, a type of globules with concentric shells was identified. With decreasing the size of fractions (<0.1 mm), there is thickening the shell of plerospheres and concentric globules observed, bulky globules are prevailing, with different microstructure – block-like, dendritic, skeletal-dendrite, fine-grained and coarse-grained one.

REFERENCES

1 European Coal Combustion Products Association. URL: http//www.ecoba.com
2 American Coal Ash Association. URL: http//www.acaa-usa.org
3 Cao Ch., Sun W., Qin H., *Cement and Concrete Res.*, 30 (2000) 71.
4 US Pat. No. 5573588, 1996.
5 US Pat. No. 2002129743, 2002.
6 Lee S. H., Kim K. D., Sakai E. and Daimon M., *J. Ceram. Soc. Japan*, 111 (2003) 0011.
7 Kruger R. A. URL: http//www.ecopower.ru
8 Levandovskiy V., Feuerborn H.-J. URL: http//www.ecopower.ru
9 Vassilev S. V., Vassileva C. G., *Fuel*, 86 (2007) 1490.
10 Atis C. D., Kilic A. K., Sevim U. K., *Cement and Concrete Res.*, 34 (2004) 99.
11 Hulett L. D. and Weinberger A. J., *Environ. Sci. Technol.*, 14 (1980) 965.
12 Enders M., *Cement and Concrete Res.*, 25 (1995) 1369.
13 Anshits A. G., Nizov V. A., Kondratenko E. V., Fomenko E. N., Anshits N. N., Kovalev A. M., Bayukov O. A., Sharonova O. M., Salanov A. N., *Khim. Ust Razv.*, 7, 1 (1999) 105.
14 Sharonova O. M., Anshits N. N., Oruzheynikov A. I., Akimochkina G. V., Salanov A. N., Nizovskiy A. I., Semenova O. N., Anshits A. G., *Chem. Sust. Dev.*, 11 (2003) 673. URL: http//www.sibran. ru/English/csde.htm
15 Vdovchenko V. S., Martynova M. I., Novitskiy N. V., Yushina G. D., Energeticheskoye Toplivo SSSR (Handbook), Energoatomizdat, Moscow, 1991.
16 GOST 23148–98. Poroshki, Primyenyaemye v Poroshkovoy Metallurgii. Otbor Prob, Moscow, 1998.
17 GOST 26565–85. Ogneupory Neformovannye. Metody Otbora i Podgotovki Prob, Moscow, 1985.
18 GOST 18318–94. Poroshki Metallicheskiye. Opredeleniye Razmera Chastits Sukhim Proseivaniyem, Minsk, 1994.
19 GOST 5382–91. Tsementy i Materialy Tsementnogo Proizvodstva. Metody Khimicheskogo Analiza, Moscow, 1991.
20 Yakimov I. S., *Nucl. Instrum. Methods Phys. Res.*, A282 (1989) 312..
21 Rietveld M. A., *J. Appl. Crystallogr.*, 2 (1969) 65.
22 Solovyev L. A., *J. Appl, Crystallogr.*, 37 (2004) 743.
23 Kizilshtein L. Ya., Dubov I. V., Shpitsgluz A. L., Parada S. P., Komponenty Zol i Shlakov TES, Energoatomizdat, Moscow, 1995.
24 Panteleev V. G., Larina E. A., Melentiev V. A., Sergeeva T. E., Mokrushin A. R., Sostav i Svoystva Zoly i Shlaka TES (Handbook), Energoatomizdat, Leningrad, 1985.
25 GOST 31108–2003. Tsementy Obshchestroitelnye. Tekhnicheskiye Usloviya, Moscow, 2004.

26 Volzhenskiy A. V., Burov Yu. S., Kolokolnikov V. S., Mineralnye Vyazhushchiye Veshchestva: Tekhnologiya i Svoystva, Stroyizdat, Moscow, 1979.

27 Sheludyakov L. N., Kosyanov E. A., Markonrenkov Yu. A., Kompleksnaya Pererabotka Silikatnykh Otkhodov, Nauka, Alma-Ata, 1985.

28 Ovcharenko G. I., Zoly Ugley KATEK v Stroitelnykh Materialakh, Krasnoyarsk, 1992.

29 Guerrero A., Goni S., Macias A. and Luxan M. P., *J. Mater. Res.*, 14 (1999) 2680.

30 Brown R. C., Dykstra J., *Fuel*, 74 (1995) 570.

31 Fan M., Brown R. C., *Energy & Fuels*, 15 (2001) 1414.

32 Sharonova O.M., Solovyov L. A., Oreshkina N. A., Yumashev V. V., Anshits A. G., *Fuel Proc. Technol.* (in press)

33 GOST 22266−94. Tsementy Sulfatostoykiye. Tekhnicheskiye Usloviya. Moscow, 1994.

34 Butt Yu. M., Sychev M. M., Timashev V. V., Khimicheskaya Tekhnologiya Vyazhushchikh Materialov (High school textbook), Vyssh. Shkola, Moscow, 1980.

35 Middendorf B., Singh N. B., *Cement Int.*, 4 (2006) 80.

36 GOST 25094−94. Aktivnye Mineralnye Dobavki dlya Tsementov. Metody Ispytaniy, Moscow, 1996.

37 Vassilev S.V., Menemdez R., Borrego A. G., Diaz-Somoano M., Martinez-Tarazona M. R., *Fuel*, 83 (2004) 1563.

38 Sokol E. V., Kalugin V. M., Nigmatulina E. N., Volkova N. I., Frenkel A. E., Maksimova N. V., *Fuel*, 81 (2002) 867.

39 Kukier U., Ishak C. F., Sumner M. E., Miller W. P., *Environ. Pollut.*, 123 (2003) 255.

40 Hower J., Rathbone R., Robertson J., Peterson G., Trimble A., *Fuel*, 78 (1999) 197.

41 Bayukov O. A., Anshits N. N., Balaev A. D., Sharonova O. M., Rabchevskii E. V., Petrov M. I., Anshits A. G., *Inorg. Mater.*, 41, 1 (2005) 50.

42 Dai S., Zhao L, Peng S., Chou Ch.-L, Wang X., Zhan Yg., Li D., Sun Y., *Int. J. Coal Geol.*, 2009, doi:10.1016 j.coal.2009.03.005.

43 Fisher G. L., Chang D. P. Y., Brumer M., *Science*, 192 (1976) 553.

44 Kutchko B. G., Kim A., *Fuel*, 85 (2006) 2537.

45 Gomes S, Francois M, Abdelmoula M, Refait Ph, Pelissier C, Evrard O., *Cement Concrete Res.*, 29 (1999) 1705.

46 Vassilev S. V., *Fuel*, 71 (1992) 625.

47 Anshits A. G., Voskresenskaya E. N., Kondratenko E. V., Fomenko E. V., Sokol E. V., *Catal. Today*, 42 (1998) 197.

48 Anshits A. G., Kondratenko E. V., Fomenko E. V., Kovalev A. M., Anshits N. N., Bajukov O. A., Sokol E. V., Salanov A. N., *Catal. Today*, 64, 1−2 (2001) 59.

49 RU Pat. No. 2375410, 2009.

50 Sharonova O. M., Akimochkina G. V., Rabchevskiy E. V., Kryuchek D. M., Anshits A. G., Mezhdunar. Konf. "Bezopasnost' Yadernykh Tekhnologiy. Obrashcheniye s RAO" (Proceedings), St. Petersburg, 2004, pp. 467−474.