

ASH AND SLAG HANDLING

3.3. Ash and slag properties

3.2.3. Bottom ash/slag removal

3.3.5. Novel functional materials based on ferroaluminosilicate microspheres from fly ashes of power-generating coals

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ABSTRACT

A systematic investigation of the relationship between the composition, structure, and physicochemical properties of narrow fractions of microspheres—ferrospheres and cenospheres separated from all known types of fly ashes of power-generating coals—has been performed for the first time.

It has been shown that microspheres separated from fly ashes of energy coals are promising for the use in the design of new functional materials: catalysts and diffusion membranes intended for the processing of the helium-bearing natural gas from the Eastern Siberia with the aim of producing ethylene and helium as target products, as well as sorbents for solidification of liquid radioactive wastes in the mineral-like form.

Examples are presented of the practical use of microspherical sorbents in the processes of purification and solidification of liquid radioactive wastes from the State Atomic Energy Corporation "Rosatom" and the United States Department of Energy.

1. INTRODUCTION

The physicochemical properties of components of the ferroaluminosilicate system synthesized using the sol-gel technology have been investigated in detail and continued to be investigated intensively, because they provide a basis for the synthesis of a large number of modern functional materials. At the same time, the physicochemical properties of microspherical components of the ferroaluminosilicate system formed under the conditions of high-temperature combustion of pulverized coal in thermal power plants are still not clearly understood.

Among the most commonly encountered modifications of microspheres in fly ashes are ferrospheres characterized by a high iron content and hollow aluminosilicate cenospheres with a low density. The granulometric, chemical, and phase compositions of concentrates of the ferrospheres, as well as the size of crystallites of mineral phases and the morphology of globules, depend on a large number of parameters, including the composition of the original coal, the regime of its combustion, the conditions used for cooling droplets of the melt, etc. [1–3].

The microspherical design and unique combination of high thermal stability, mechanical strength, and magnetic properties make microspheres attractive for the use as modern functional materials, which can replace expensive synthetic analogs. In particular, cenospheres can be used as microspherical membranes for the diffusion-sorption process of helium recovery from the natural gas [4, 5] owing to the high separation coef-

ficients of He/CH₄ mixtures, which are equal to 10⁵–10⁶ and exceed the separation coefficients of polymeric membranes by three to four orders of magnitude.

The most promising fields of applications of ferrospheres as catalysts are the processes where expensive traditional catalytic systems either are unstable or are rapidly deactivated at the expense of contaminants contained in raw materials or high temperatures providing the occurrence of the reactions involved. In particular, ferrospheres demonstrate a high efficiency in the process of thermolysis of heavy oils and petroleum residues into components of motor fuels [6], as well as in the process of oxidative coupling of methane [7].

The use of ferrospheres as catalysts in the high-temperature process of oxidative coupling of methane with the formation of ethylene and cenospheres as diffusion membranes, although offers obvious advantages, also presents serious problems associated with variations in the complex multicomponent composition of the Fe_xO_y-Al₂O₃-SiO₂-CaO system. It is clear that, for such systems, unambiguous conclusions regarding the functional properties of the active phase can be drawn only based on the results of a systematic investigation of a number of samples with revealing and elucidating the composition-structure-property relationship.

The purpose of this work is to reveal and elucidate the general regularities of the relationship between the major component and phase compositions, morphology, structural characteristics of crystalline phases, and functional properties of ferrospheres and cenospheres.

2. PREPARATION OF MICROSPHERES AND METHODS OF STUDIES

The use of the three-stage separation scheme, including the stages of the "dry" and "wet" magnetic separations, grain-size classification, and hydrodynamic gravitational purification of small fractions from foreign impurities [3, 8], has made it possible to obtain homogeneous narrow fractions of ferrospheres and cenospheres with different sizes from fly ashes, which, according to the classification [9], belong to the four known classes S, CS, FS, and FCS.

The chemical composition of the ferrospheres varies over a wide range: 30–90 wt % Fe₂O₃, 0.6–41.6 wt % SiO₂, 0–16.3 wt % Al₂O₃, and 2.0–9.1 wt % CaO. The chemical composition of the cenospheres with a stable low Fe₂O₃ content (less than 3 wt %) varies in the range: 55.6–66.8 wt % SiO₂ and 19.6–37.6 wt % Al₂O₃. In both cases, the range of variations in the major component

composition overlaps the range of variations in compositions of all the previously studied fractions of the microspheres, their concentrates, and individual globules.

Narrow fractions of the obtained microspheres have been investigated using the methods of chemical analysis, quantitative X-ray powder diffraction analysis within the Rietveld full-profile formalism with the derivative difference minimization method, Mössbauer spectroscopy, magnetic measurements, optical microscopy, and scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1. Composition and Structure of Ferrospheres

The formation of a globular structure of the microspheres proceeds in the reducing medium of the core of the flame, when almost all iron is stabilized in the form of Fe^{2+} . The major component composition of the prepared microspheres is presented in the ternary $FeO-SiO_2-Al_2O_3$ phase diagram (Fig. 1).

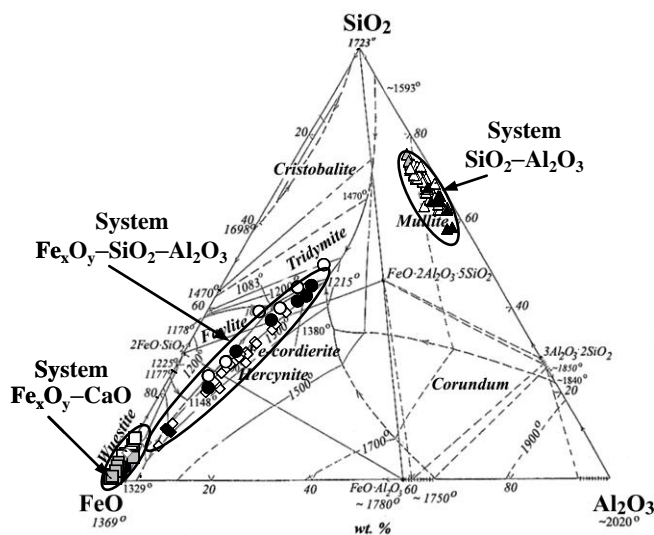


Fig. 1. Major component composition of narrow fractions of ferrospheres and cenospheres.

In this phase diagram, there is a region of compositions (the $SiO_2-Al_2O_3$ system), which characterizes non-perforated cenospheres with a stable low iron content.

The compositions of narrow fractions of ferrospheres correspond to the interface between the crystallization regions of the primary phases: wustite, fayalite, Fe-cordierite, and the hercynite phase. An increase in the oxidation potential beyond the melting zone leads to the oxidation and ferritization of the melt with the formation of the main phases: the ferrite spinel based on magnetite, the hematite phase, and the ferroaluminosilicate glass phase. It is obvious that the formation of the ferrospheres, which differ from each other in size and chemical composition, is determined by the viscosity of the low-temperature melts corresponding to the invariant points of the $FeO-SiO_2-Al_2O_3-CaO$ system [10]. In turn, for ferrospheres in the phase diagram, there are two regions of compositions corresponding to the $Fe_xO_y-Al_2O_3-SiO_2$ and Fe_xO_y-CaO systems, which dif-

fer from each other in the character of the relationship of the major component compositions, the morphology of globules, and the structure of ferrite spinel.

In the $Fe_xO_y-Al_2O_3-SiO_2$ system, the major component composition of narrow fractions of the ferrospheres and purified magnetic concentrates obtained from 14 heat and electric power stations in Russia, Ukraine, and Kazakhstan [1] are described by two regression equations $[SiO_2] = 65.71 - 0.71 \cdot [Fe_2O_3]$ and $[Al_2O_3] = 24.92 - 0.26 \cdot [Fe_2O_3]$ with the correlation coefficients of -0.99 and -0.97 , respectively (Fig. 2).

The general linear character of the relationship of the major component compositions of the ferrospheres obtained from the combustion of different types of coals allows us to conclude that, during the combustion of coals in thermal power plants, all iron forms of the mineral component of the coal participate in the formation of melt droplets whose composition after the partial oxidation and crystallization corresponds to the composition of the concentrates or narrow fractions of the ferrospheres. The composition and content of the iron-containing mineral forms of the coal affect only the yield of the magnetic concentrates and narrow fractions of particular sizes.

An increase in the iron content leads to a monotonic increase in the content of the ferrite spinel phase, in which the unit cell parameter also monotonically increases in the range from 8.3440 to 8.3897 Å. In this case, the main morphological types of microspheres change in the following order: porous, glass-like, dendritic, skeleton-dendritic, and block-like. In each of the aforementioned morphological types, there are plerospheres (from 5 to 10%) whose shells reflect the main morphological type and whose volume includes small globules with a variable composition (Fig. 2).

In the Fe_xO_y-CaO system, there is a linear correlation between the content of calcium oxide and the content of iron oxide, i.e., $[CaO] = 52.2 - 0.5 \cdot [Fe_2O_3]$ with the correlation coefficient $r = -0.97$. The phase composition of the ferrospheres includes the $(Ca,Fe)Fe_2O_4$ spinel, with the unit cell parameter exceeding the corresponding value for the magnetite, and defective hematite. Moreover, in the two main morphological types, the iron-containing phases undergo single-type surface and bulk crystallizations in the form of skeleton-dendritic and block-like structures.

3.2. Catalytic Properties of Ferrospheres in the Oxidation Reaction of Methane

The catalytic properties of the ferrospheres have been investigated in the reaction of oxidative dimerization of methane (ODM) at temperatures in the range from 650 to 750°C in a reaction mixture of the composition $CH_4 : O_2 : N_2 = 9 : 9 : 82$ vol %. The results obtained from the investigations of the phase composition, the structure of the ferrite spinel, and the catalytic properties allow us to draw the conclusion that, in ferrospheres of the $Fe_xO_y-SiO_2-Al_2O_3$ system, the catalytically active phase is the aluminoferrite spinel whose amount and lattice parameter increase with an increase in the iron content.

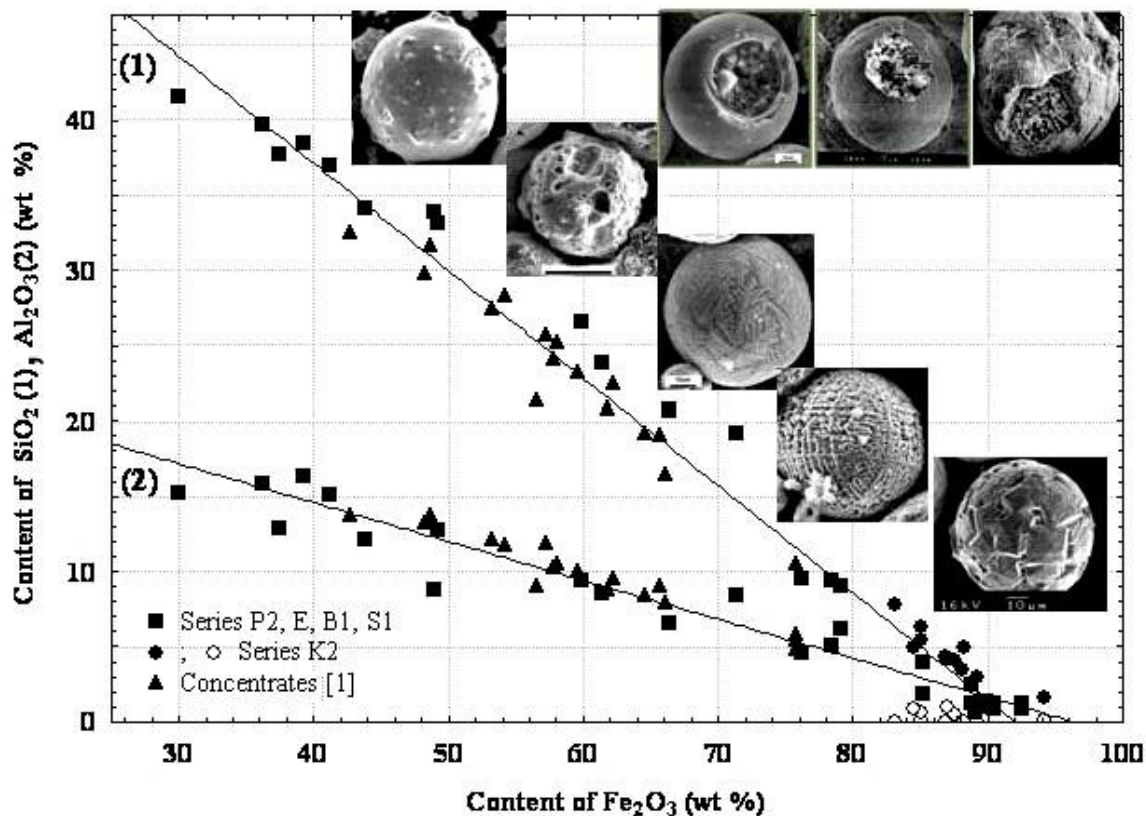


Fig. 2. Major component composition and the main morphological types of fractions of ferrospheres $-0.063 + 0.05$ mm.

The activity of the ferrospheres in the reaction of deep oxidation is determined by the content of the ferrite spinel and the glass phase. At a high content of the glass phase, the catalytically active component is blocked and the activity of the ferrospheres is decreased.

In the Fe_xO_y -CaO system, unlike the system considered above, the main route of methane conversion changes from the deep oxidation to the formation of C_2 hydrocarbons. The catalytically active component is the two-phase system, which includes the CaO-promoted ferrite spinel, with the unit cell parameter exceeding the corresponding value for the stoichiometric magnetite, and defective hematite. The high selectivity (up to 60%) of the formation of C_2 hydrocarbons for ferrospheres of this system is determined by the formation of active centers at the interface between the defective phases of the ferrite spinel and hematite.

A new type of catalysts for the reaction of oxidative dimerization of methane has been synthesized from ferrospheres, and their efficiency is not inferior to the best catalysts of this process [7].

3.3. Composition, Structure, and Helium Permeability of Cenospheres

The investigation of the relationship between the composition and structure of globules of narrow fractions of the non-perforated cenospheres in the SiO_2 - Al_2O_3 system has demonstrated that an increase in the Al_2O_3 content leads to a decrease in the SiO_2/Al_2O_3 ratio (Fig. 3). Moreover, for the non-perforated cenospheres produced from the combustion of coals from the Kuznetsk Basin (Russia) at different temperatures, the size of globules, the thickness of the globule shell,

and its porosity decrease in each of the series H, T, and M. The cenospheres produced from the combustion of coals from the Ekibastuz Basin (Russia) (series R) are characterized by the inverse dependence: with an increase in the concentration of aluminum oxide, on the contrary, the size of globules, the thickness of the globule shell, and its porosity increase. Furthermore, narrow fractions, in which the Al_2O_3 content is higher than 36 wt %, predominantly include globules with a network structure.

The most interesting region in the phase diagram of this system includes compositions with the Al_2O_3 content ranging from 30 to 34 wt %, where mullite on the outer and inner surfaces of continuous shells of the cenospheres undergoes planar crystallization, which should provide a high hydrostatic strength of the cenospheres (Fig. 3).

The helium permeability has been determined using narrow fractions of the cenospheres covered by a continuous shell with the thickness ranging from 2 to 3 μm . It has been demonstrated for the first time that the helium permeability coefficient of the cenosphere shells increases by more than three orders of magnitude when the Al_2O_3 content changes in the range from 25 to 30 wt %. The linear character of the dependence on the content of the mullite phase in the shell and the low activation energy indicate that the diffusion of helium occurs along the glass-mullite phase boundaries. It is important to note that the achieved values of the helium permeability for cenospheres with the high mullite content are one order of magnitude higher than the corresponding values for the well-known glass membranes.

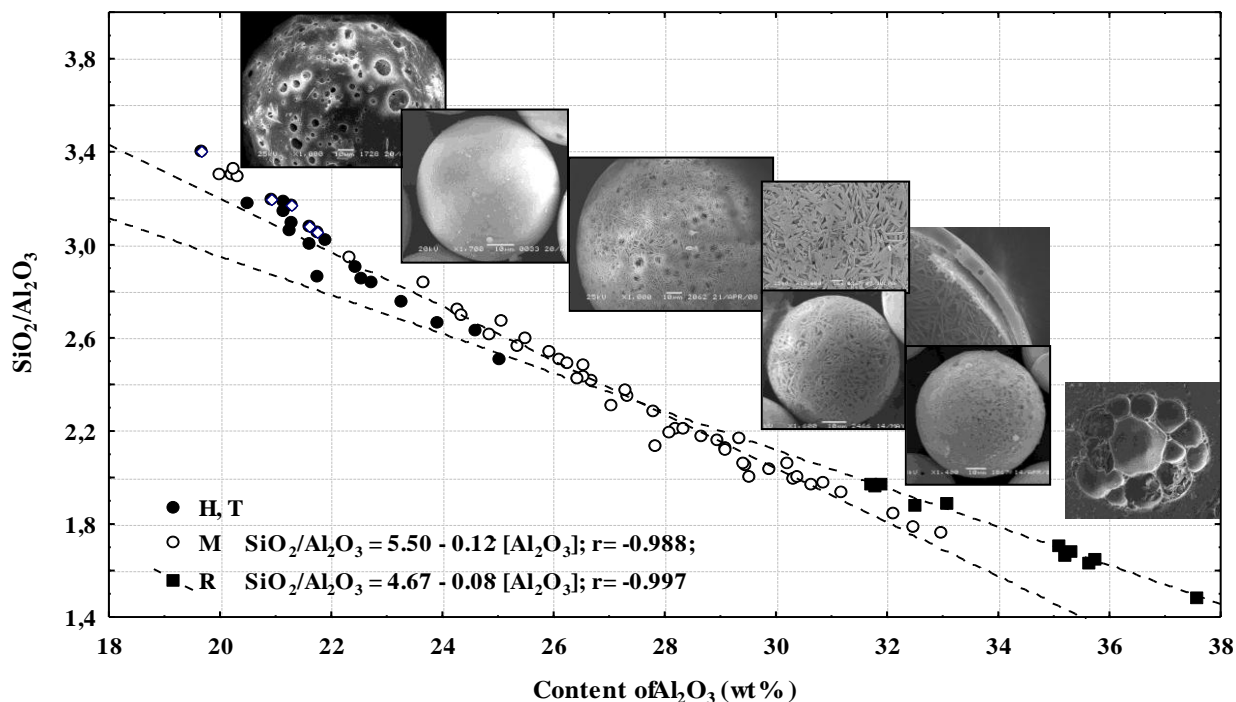


Fig. 3. Dependences of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the aluminum oxide content and the main morphological types of narrow fractions of cenospheres.

3.4. Cenospheres and Cenosphere-Based Microspherical Sorbents—Precursors of Aluminosilicate Minerals

The developed methods for stabilization of the composition of the cenospheres have made it possible to produce narrow fractions of the cenospheres of constant composition with the weight ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.5\text{--}3.4$ (Fig. 3) [3], which corresponds to the compositions of zeolites, feldspars, and feldspathoids. Since the major component composition of narrow fractions of the cenospheres is close to the composition of aluminosilicate minerals, they can be considered as precursors of mineral-like final isolation forms of ^{137}Cs and ^{90}Sr radionuclides [11]. A scheme has been proposed for radioactive waste solidification with the use of cenospheres, which is based on the sorption concentration of radionuclides in the bulk of the sorbent materials with their subsequent inclusion into the structure of mineral-like phases by means of heat treatment.

Various engineered forms of microspherical sorbents, namely, zeolites NaP1, NaX, и NaA [12], intended for the processing of neutral liquid wastes with a low salt content have been developed, as well as the composite sorbents with the addition of ammonium molybdophosphate (AMP/cenospheres) for the selective extraction of ^{137}Cs radionuclides from acidic wastes with a high salt background.

The properties of the zeolite sorbent NaP1 have been tested in the scheme developed for purification of non-technological liquid wastes from the Federal State Unitary Enterprise “Mining and Chemical Complex” (Zheleznogorsk, Krasnoyarsk region, Russia). The bench-scale testing of the sorbent AMP/cenospheres at the radiochemical plant (Idaho Falls, Idaho, United States) has been completed and the scheme for purification of high-salt acidic wastes from ^{137}Cs has been developed [13].

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