UDC 621.311:662.613:504.064.4

Part 3

ASH AND SLAG HANDLING

3.3. Ash and slag properties

3.3.3. HOLLOW MICROSPHERES FROM FLY ASHES OF POWER PLANTS

L.D. Danilin[1], V.S. Drozhzhin[1], M.D. Kuvaev[1], N.V. Maximova[1], I.V. Pikulin[1], S.A. Redyushev[1], M.Y. Shpirt[2]
Russian Federal Nuclear Center — All-Russian Research Institute of Experimental Physics, Sarov, Russia (1)
Institute of Combustible Resources — Science and Technology Center for Combined Processing of Solid Combustible Resources, Moscow, Russia (2)

ABSTRACT

A progressive tendency in material-consuming branches of industry is transformation of industrial wastes into the raw materials appropriate for industrial implementation. It can be fully referred to the microspheres from fly ash that can be considered as a side industrial product from operation of electric power stations. In the period of time since 1996 till 2002 specialists from RFNC-VNIIEF carried out technical monitoring at the electric power stations in the Russian Federation related to microspheres from the fly ash. The main goal of the monitoring was analysis of microsphere formation processes at the ash dumps of the electric power stations and study of the basic consumer properties of microspheres. As a result, they accumulated a summarized large material arranged now in the form of a computer program called «Ash Microspheres of the Russian Federation. Database» Thanks to the favorable combination of technical and commercial parameters microspheres of fly ash can be used in creation of various functional materials, including filled composites on the basis of inorganic and organic binders.

Under modern industry conditions production of the basic materials and items is to an increasingly greater extent estimated by the parameters characterizing the amount of the waste produced. Transformation of industrial waste into raw materials suitable for industrial application is a progressive tendency in primary and raw material intensive branches. This concerns the ash waste of electric power stations in full measure.

Microspheres (or cenospheres), which are a light fraction of fly ash, are one of the most valuable components of fly ashes. This fraction is a finely divided free-flowing powder consisting of hollow thin-walled spherical particles of aluminosilicate, the diameter of which is several tens or hundreds of microns [1—3]. At the electric power stations, where ash waste is removed in the form of an aqueous pulp, microspheres the density of which is less than 1 g/cm^3, float spontaneously to the surface of ash dump water ponds and remain there for a long time as «foam layers» of different thickness.

Specialists from England [4], the USA [5, 6], Poland [7], India [8] and the Ukraine [9] systematized the existing materials on fly ash microspheres, and now these countries have their own ash microsphere utilization industry. The Russian Federation also has some studies of fly ash microspheres [10—14], which will undoubtedly promote their industrial application development.

In 1996—2002 specialists of the Russian Federal Nuclear Center (RFNC-VNIIEF) carried out technical monitoring of fly ash microspheres from the electric power stations of the Russian Federation. The main objective of this monitoring was to study microsphere formation processes and to examine microsphere resources at ash dumps of electric power stations. Based on the studies, the following three key questions were to be answered: «Where, how many microspheres and microspheres of what quality are produced on the territory of Russia?» [15].

The Russian electric power stations usually use hydraulic transportation of ash and slag waste. Ash and slag are mixed with water and the produced pulp is pumped through pipelines to ash dumps. A heavy waste fraction settles down to the bottoms of water ponds and the floating fraction (microspheres) is distributed over the water surface. Thickness of the floating layer depends on the content of microspheres in the ash, on the duration of electric power station operation and on the design of engineering structures at the ash dump.

As previously derived information about the influence of various factors on microsphere formation processes was contradictory, the main criterion for the electric power station selection was the amount of the coal burnt there. From the references [3] it is known that ash microspheres may comprise 1…3 % of the total coal burnt at the industrial facility. Therefore, the electric power stations that burn 200…300 thousand tons of coal and less showed little industrial promise.

For the European part of Russia, where electric power stations of the mean capacity are concentrated, the limit on the burnt coal was set to be of not less than 400…500 thousand tons per year. For the Urals, Siberia and Far East, where large electric power stations make the basis of power engineering, the annual limit was set to be 800…1000 thousand tons of coal. The sampling volume included 42 electric power stations. The chosen electric power stations burn coals from the main coal-fields of the former USSR. These are Kuznetsk, Donetsk, Ekibastuz, Kansk-Achinsk, Pechora, Near Moscow and Maritime Territory coal-fields.

In fig. 1 the layout of the electric power stations, which were chosen in accordance with the above-mentioned criteria, is shown.

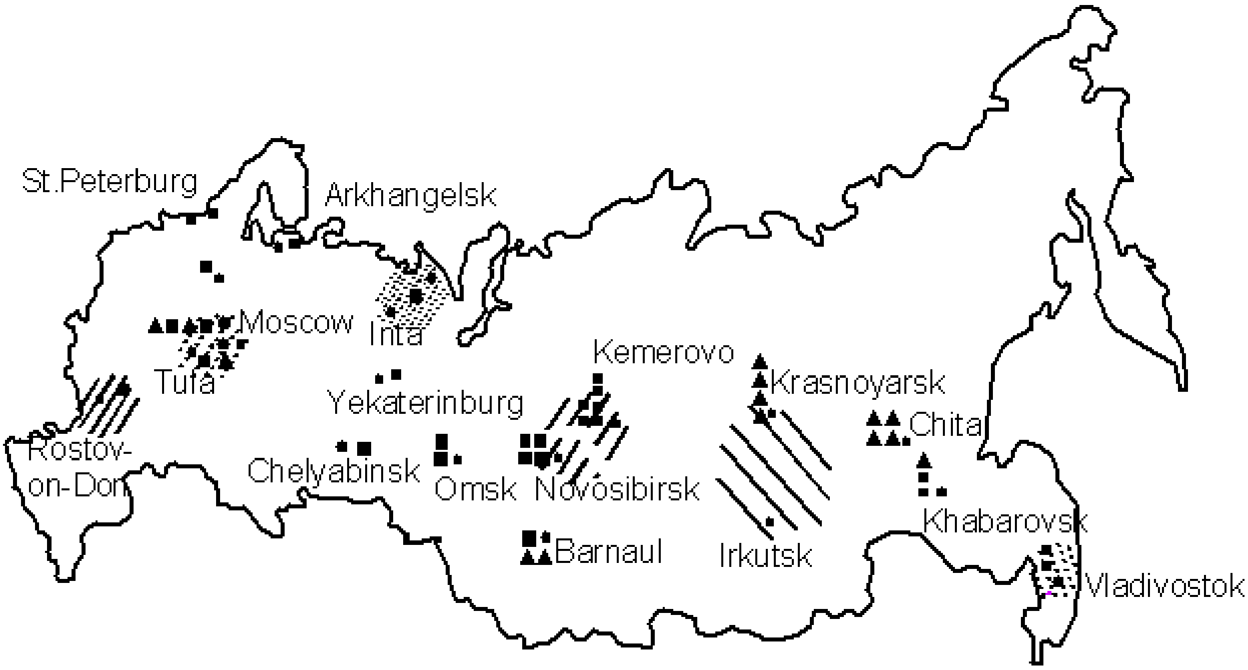

Fig. 1. Layout diagram of power stations examined in 1996—2002: ■ — power station with detected microspheres; ▲ — power station without microspheres.

Coal basins:

Based on the experiments, the approach was proposed, which establishes correlation between the amount of coals burnt at a power station and the amount of produced microspheres.

$N_m = N_c\, K_{ac}\, (1 - K_s)\, K_m,$

where N_m is the amount of microspheres produced in a unit of time; N_c is the amount of coals burnt out in a unit of time; K_{ca} is the dimensionless coal ash factor; K_s is the dimensionless mineral impurity slagging factor that shows the portion of the mineral impurities removed from the boiler in the form of slag; (1 — K_s) is the mineral impurities removed in the form of ash; K_m is the dimensionless microsphere formation factor, the fraction of microspheres in fly ash.

N_c, K_{ca} and K_s values are known for any electric power station. The factor K_m is determined from the relation between the masses of fly ash fractions floating and drowning in water. The annual «output» of microspheres and the calculations using the given ratio are shown for some electric power stations in table 1.

Table 1. **Estimation of microspheres formed at some power stations**

Power station	Coal basin	N_c, t/y	K_a	$(1-K_s)$	K_m	N_m, t/y
Barnaulskaya TPS-3	Kansk-Achinsky	$1{,}7 \cdot 10^6$	0,37	0,5	$0{,}07 \cdot 10^{-2}$	48
Tom-Usinskaya SRPS	Kuznetsky	$4{,}0 \cdot 10^6$	0,22	0,95	$3{,}35 \cdot 10^{-2}$	18,000
Omskaya TPS-5	Ekibastuzsky	$2{,}6 \cdot 10^6$	0,39	0,9	$0{,}22 \cdot 10^{-2}$	2000
Cherepovetskaya SRPS	Pechorsky (Intinsky)	$1{,}5 \cdot 10^6$	0,38	0,9	$1{,}21 \cdot 10^{-2}$	6200
TPS-1 of Arkhangelsk plant	Pechorsky (Vorkutinsky)	$1{,}0 \cdot 10^6$	0,2	0,9	$1{,}87 \cdot 10^{-2}$	3400
Novocherkaskaya SRPS	Donetsky	$4{,}6 \cdot 10^6$	0,28	0,9	$0{,}18 \cdot 10^{-2}$	2100
Artemovskaya SRPS	Maritime coals	$0{,}96 \cdot 10^6$	0,25	0,8	$0{,}9 \cdot 10^{-2}$	1900

This analysis supports the observations made at the electric power stations. Indeed, there are almost no microspheres at ash dumps of the electric power stations burning coals of Kansk-Achinsk coal-field. An extremely low ash content of coals, a high slagging factor and a small content of mineral impurities forming a glass phase make no contribution to formation of microspheres and their piling up at ash dumps. The electric power stations burning coals of Kuznetsk coal-field have the greatest amount of microspheres. This is well illustrated by the data on Tom-Usinskaya state relay power station (SRPS). Its microsphere formation factor is 3,35 %. These estimations are confirmed by the observations made at the ash dumps of Kuzbass electric power stations. In particular, the microsphere masses at Tom-Usinskaya state relay power station are as much as 1,5 million $м^3$.

Using the above scheme, the probable masses of microspheres formed at all power stations burning considerable amounts of coal were estimated. The data for the Russian Federation regions are presented in tab. 2.

Table 2. **Regional resources of microspheres in the Russian Federation**

Regions	Estimation of microsphere formations (t/y)
North European	15 000
Central European	18 000
Ural	12 000
West Siberian	74 000
Maritime Territory	5000

The regional distribution of the ash microsphere sources points to the fact that almost all basic industrial regions of Russia have the potential providing the possibility for production and use of ash microspheres either as raw materials for the local industry or large-capacity branches, or as export products.

Summarizing the data of tab. 2, it may be concluded that the total amount of ash microspheres annually produced at large electric power stations of Russia is 120 thousand tons.

Fig. 2 shows the panorama photographs of microsphere masses.

Similar masses were found at many electric power stations.

a)

b)

c)

d)

e)

Fig. 2. Masses of microspheres at ash dumps of power station:
a) shows the water pond of Cherepovetskaya SRPS ash dump. The right part of the photograph illustrates the microspheres floating on the pond surface. Metal pipes across the pond are the barriers preventing microspheres going to sewage wells (they are to the left); *b)* shows the water pond of Vorkutinskaya TPS-2 ash dump. The whole pond surface is covered with a thick layer of microspheres; *c)* illustrates disposal of ash and slag waste to Tom-Usinskaya SRPS ash dump; *d)* Severodvinskaya TPS-1 is shown. Dry microspheres are lying at the reserve pond bottom. At the center of the photograph initiation of the atmospheric vortex taking away the mcirospheres from the ash dump surface is clearly seen; *e)* shows Tom-Usinskaya SRPS. A thick layer of microspheres is over 50 cm. The layer of microspheres is so thick that can easily withstand people moving.

A great potential industrial resource of microspheres was established at nineteen power stations. The microsphere samples were taken from the ash dumps of these power stations, brought to RFNC-VNIIEF and subjected to thorough examination.

Formation of microspheres in the fly ash is a complex and multi-stage process [16]. Research on the composition and structure of the fly ash from different electric power stations made it possible to reveal basic tendencies in the processes of microsphere formation. Data from chemical and X-ray analysis of fractions of the fly ash allow us to make a conclusion on one type of physical and chemical processes that take place at formation of microspheres from mineral impurities of coals from various field. Comparative analysis of chemical composition of the fly ash from the basic coal fields, the samples of which were taken from particular power stations, and the chemical composition of microspheres from the same electric power stations shows that microspheres from all coal fields are close in their chemical composition, changes in the average composition of the fly ash affect them little.

This allows us to suppose that microspheres are formed from the mineral particles that are capable to form eutectic mixtures and glass-phase at the temperature higher than 1200 °C. Such particles comprise alumosilicate clay minerals and hydro-micas together with minerals with the increased content of SiO_2: quartz and feldspars. This also shows compliance of the density of these minerals and the density of the substance of the wall of microspheres. Such particles contain about 1…3% of substances at the level of additives that are capable of gassing, for example Fe or Ca compounds and crystallized water, that under high temperatures when the particles reach plastic state result into formation of hollow mono-cell spherical particles — microspheres.

Thermalphysic conditions where microspheres are formed are other basic factors that influence the quantitative content of microspheres in the fly ash. In particular it was found out that when burning coals of the same kind in the boilers with the slag-tap removal, which have higher temperature as compared to the boilers with bottom ash removal, a fraction of microspheres in the fly ash is much higher. Another group of factors that influence microsphere formation are conditions that provide thermal non-uniformity for the particles of the ash in the process of the coal burning in the turbulent gas disperse air stream.

It is thermal non-uniformity that result into the situation when various particles of the ash have quite different structural characteristics. Thermal non-uniformity is caused by not uniform temperature distribution at the cross-section of the boiler (in the center of the flame the temperature may reach 1700…1800 °C, in the area close to the wall it is 700…1300 °C). Difference in the mass of separate particles also has a large effect. The weight of the particles may vary within $10^{-9}…10^{-5}$ g, so the quantity of the heat to provide similar rheological characteristics should differ by a factor of 4. These factors allow estimating of thermal non-uniformity as it influences microsphere formation in the fly ash. Together with factors of chemical and phase-mineralogical character the process of microsphere formation in the fly ash is a complex statistical task, solution of which can bring practical use and is possible experimentally under real conditions for particular electric power stations.

Since ash microspheres are a multifunctional material, various properties of microspheres were examined. The chemical composition, structural, mechanical, thermal, dielectric properties, stability in aggressive media and the natural radioactivity level were analyzed. The studied parameters of microspheres totaled 24. When determining the properties of microspheres, the technical approaches developed for dispersed materials were used. However, in some cases, when the presence of an inner space produced a deciding influence, special methods and equipment were developed [13]. Tab. 3—7 shows the measurements of the ash microsphere parameters. These values were averaged for 19 power stations. At the same time some characteristics may have great variations depending on the specific power station.

Table 3. **chemical composition of ash microspheres**

Chemical compounds	Content, %
SiO_2	62
Al_2O_3	27
K_2O	3,39
Fe_2O_3	3,13
CaO	1,29
MgO	1,25
TiO_2	0,84
Na_2O	0,62
MnO	0,04
Cr_2O_3	0,02

Table 4. **structural and mechanical properties**

Density, g/cm^3 : bulk	0,34
real	0,64
Dispersed composition: diameters, μm	10…600
average diameter, μm	92
Strength	
uniaxial compression	
at 20 % deformation (P= 1,69 MPa),	
weight % of floating microspheres	85,0
at 40 % deformation (P= 3,49 MPa),	
weight % of floating microspheres	55,8
isotropic compression	
at P=10,5 MPa, weight % of floating microspheres	81
50 % strength level, MPa	30
Floatability, % weight	99
Angle of repose, degree	31,6

Table 5. **interaction with media**

Hygroscopicity, %	0,26
Chemical stability, %:	
alkaline solution, 10 % p-p NaOH	3,2
acid solution, 50 % p-p HNO_3	3,0
Bulk layer water absorption, %	96

For example, the average diameter of microspheres ranges within 60…200 μm, the real density varies from 0,5 to 0,7 g/cm^3, the hydrostatic strength — from 20 to 35 MPa, microspheres of some power stations are more stable in acid or alkaline media, etc. Such changes in the microsphere parameters are explained by the composition of mineral impurities in coals as well as by thermal microsphere formation conditions. The information about the whole range of microsphere parameters may favor optimum selection of microspheres for solution of specific technical problems.

The generated results suggest that due to their specifications and potential industrial resource ash microspheres may compete with some widely used materials such as industrial glass microspheres, light-weight heat-insulation materials, dispersed fillers of plastics and other composite materials.

Table 6. **Thermal properties**

Melting temperature, °C:			1000…1400
t_1- softening onset			
t_2- softening			1200…1500
t_3- liquid state			1300…1600
Specific heat, J/kg·°K (25 °C)			880…1700
Thermal conductivity, W/m·°K (25 °C)			0,121…0,232
Strength at elevated temperatures, MPa:			
at 20 °C	deformation level	20 %	1,4…2,1
		40 %	3,0…4,4
at 300 °C	deformation level	20 %	1,0…1,8
		40 %	2,3…3,6
Frost resistance			Withstood more than 20 cycles

Table 7. **Dielectric properties**

Dielectric constant	2,14
Loss-angle tangent	0,062
Specific resistance, Ohm×m	$1,61\times10^{11}$
Specific effective activity of natural ra-	

dionuclides, Bq/kg	208

In the course of technical monitoring and research of the properties of microspheres a vast scope of information about location of ash microsphere sources in the Russian Federation, probable volumes of their utilization, specifications of microspheres has been collected. The methods for control over these specifications have been also developed. To handle such a vast scope of information, to provide an efficient access to it and to give a vivid presentation of these data, a computer program «Ash Microspheres of the Russian Federation. Database» has been created. The information part of the database has two sections — technical and bibliographic. The technical section contains the information about location of ash microsphere sources, the actual data on microsphere masses in clarified water basins, the data on the properties of ash microspheres from 19 power stations of the Russian Federation as well as the methods for their determination. The bibliographic section contains the data on 200 literary sources pertaining to microspheres. The information search may be arranged through the alphabetic and subject catalogues. Each literary source is provided with the abstract and the list of key words.

The analysis of the technical monitoring results suggests that fly ash microspheres are actually an industrial by-product for many Russian electric power stations. There are real future opportunities for industrial utilization of this raw material and its application in various industries.

Application of microspheres is so diverse that there is hardly an area of science, engineering and industry where the possibility of applying cenospheres or materials containing them would not be studied. Microspheres are intermediate between artificial glass microspheres and lightweight building materials. In some parameters such as production technology, properties of microspheres, technical characteristics they join glass micropsheres. At the same time, in terms of their probable production output, cost characteristics and relative easiness of making they seem to be closer to lightweight building materials. On the one hand, they start to be used as fillers of plastics, and this is a conventional application field of glass microspheres. On the other hand, their application in lightweight concrete, mortars is being actively studied, and this is the field of such materials as claydite, swollen pearlite, etc.

In general it is possible to say that ash microspheres owing to specific combination of their technical and commercial properties are a multifunctional filler of materials. Variation of the diameter and thickness of the wall of microspheres enables production of the material with the given structure. Fine-dispersion provides homogeneity of the material in a thin layer. Alumosilicate structure gives inertness and chemical stability to the material. A low density allows us to produce a light and heat-insulating material. A spherical shape and an alumosilicate structure provide high durability of the material in isotropic compression.

In references [17, 18] the following areas of implementation of microspheres are described:

- application as lightweight fillers of various-purpose composite materials (light china, boot and shoe industry, building materials, wood making, etc.).
- production of explosives (sensitization of explosives, introduction of microspheres allows the density and detonation properties to be regulated);
- manufacture of sound- and heat-insulation materials (the application range of microspheres in this field is very wide — insulation of pipelines and electric cables, sound-absorbing panels, casting molds, bricks for coke ovens, insulation fills, etc.);
- materials providing floatability, the so-called syntactic foams;
- anticorrosion coatings (shipbuilding, construction of oil-rigs, motor-car construction);
- creation of protective surface layers to prevent volatilization of toxic and easily volatile liquid substances (oil, oil products) from open basins;
- manufacture of polymer compositions having special properties for electronics and electrical engineering (electromagnetic and radio frequency screens);
- various-purpose materials for automotive industry (body components, interior decoration, pneumatic tires, lamp reflectors, energy absorbing shields, bumpers, corrosion-resistant putties).

Specialists of RFNC-VNIIEF are developing some materials using microspheres. For example, based on inorganic binders (alumophosphate or sodium silicate) and microspheres as a filler a series of incombustible heat-insulation porous materials have been created [19, 20]. In a ready-made form a heat-insulation porous material is a low-density rigid material that is easily machined. The developed material is shown in fig. 3.

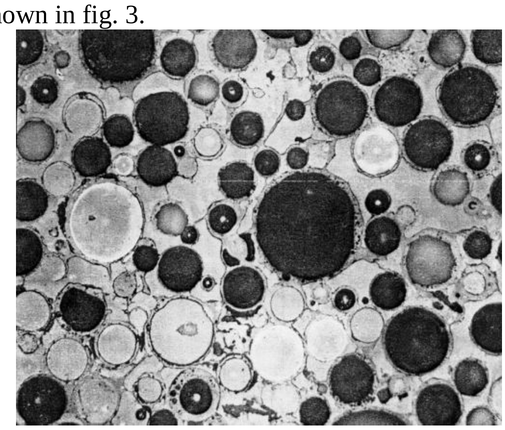

Fig. 3. Heat-insulating material

Basic specifications of heat-insulating material on fig. 3:
1. Density, kg/m^3 . . . . 80…520,
2. Compression strength, Mpa 3,6*
3. Bending strength, Mpa. 2,7*
4. Shock strength, kg/m^3. 0,25
5. Melting temperature, °C. 1100
6. Heat conductivity, V/mK. . . . . 0,081…0,191
7. Water absorption, wt. %. 19,6

*- For density values of 480—520 kg/m^3

It contains no combustible components. Its melting temperature is 1100°C. It is a good alternative for asbestos containing materials and may be used as a fire-resistant heat insulation in various engineering structures. The possibility of applying the developed porous material for fire-resistant panels has been studied. A high adhesion strength of the material and no shrinkage in its making allow its application in the form of sandwich-elements for producing multilayer panels.

Based on the cement binder and microspheres, a heat-insulation and structural material is being developed that can be used for making protective layers of containers designed for transportation and storage of fissile materials. The material under development includes portland cement with small amounts of other organic binders, microspheres as the main filler and a reinforcing filler. For comparison, tab. 8

shows the strength characteristics of this material and standard concrete made of portland cement-300 and quartz sand.

Table 8. **Strength characteristics of the materials with a cement binder**

Characteristics		Material	
		Standard concrete	«Spherobeton»
Density, g/cm^3		2,10	1,22
Binder, vol. %		25,0	40,0
Filler %		quartz sand 75,0	ash microspheres 60,0
Ultimate strength, MPa	flexural	5,16	4,37
	compression	24,2	23,8

From this table it can be seen that replacement of sand with microspheres resulted in greatly decreased density of concrete almost with no losses of its strength properties.

A promising application area of microspheres is their use as a sensitizer of emulsion explosives (EE). EEs sensitized with ash microspheres may be used for deep-hole charges or cartridges with the diameter as high as 90 mm. The studies show that for deep-hole charges $\varnothing > 60$ with the mass fraction of microspheres 9,0 — 9,3 vol. % (the detonation velocity of charges can make up 6 km/s). In comparison with standard industrial explosives, these EEs have some technical advantages such as the absence of toxic components, a low sensitivity to mechanical effects, a low content of toxic gases in explosion products, a higher explosion efficiency, an increased charging density, a higher water-resistance, etc. The existing EE cost estimations show that production of EEs may be cheaper than that of standard industrial explosives.

One more application of ash microspheres may be immobilization and isolation of radioactive wastes. Development of activities in nuclear energy has led to great amounts of radioactive wastes. One of the ways for solving the problem of radioactive waste disposal is creation of an ion-exchange material efficiently immobilizing heavy metals that make the basis of radioactive waste and capable of providing their subsequent isolation under long-term storage conditions [22]. Application of the known sorbents has certain limitations. These are a high cost of ion-exchange resins, organic matrix radiolysis, a tendency of some inorganic sorbents to hydrolysis, solubility change depending on pH medium, low filtration rates. An alternative approach to this problem solution is coating of a sorbent having the form of a thin layer on to the suitable carrier surface. In this connection application of microspheres as a sorbent carrier seems to be very promising. Using microspheres whose surfaces have been modified by various ion-exchange reagents, a new rather inexpensive ion-exchange material having a wide range of effects may be produced. It will provide optimum application of sorbents in a thin surface layer and have a physical and chemical stability of a natural silicate material. Microspheres surface modified by ion-exchange reagents are capable of adsorbing up to 70 Ci of Cs per 1 kg of microspheres. About 100 000 l of medium-active solution ($\approx 10^{-4}$ Ci/l) may be passed through the column filled with 1 kg of such a sorbent until it is completely free from radioactive components. A low hydraulic resistance of the microspheres layer allows using high linear velocities of fluid flows. Besides disposal of the atomic industry wastes, this material may be efficiently applied for utilization of the fuel and energy complex waste.

Analysis of modern tendencies and results of our own research make it possible to suppose that Russia has real perspectives for industrial utilization of ash microspheres and the efforts in this area will surely bring positive effect for all the parties involved.

This work has been done with a partial financial support of the International Science and Technology Center (ISTC), projects № 214, 478, 1582.

REFERENCES

1. **Raask E**. Cenospheres in pulverized-fuel ash // Journal of the Institute of fuel. 1968. Vol. 43. № 332, septembre. P. 339—344.
2. **Wandell T.** Cenospheres: from waste to profits // American Ceramic Society Bulletin. Vol. 75. № 6. June 1996. P. 79—81.
3. **Handbook** of Fillers and Reinforcements for Plastics. Ed. by Harry S. Katz, V. Milewski, New-York, Van Nostrand Reinhold Company, 1978.
4. **Raask E.** Particulate silicate minerals in boiler flame. Behavior. Problems and Remedial. 1985. P. 71—77.
5. **Rohatgi P.K., Guo R.Q**. Opportunities of using flu-ash particles for synthesis of composites // Material Dept., University of Wiskonsin-Milwaukee, Milwaukee, WI 53211, USA: Proc. Amer. Power Conf. 1997. Vol. 59(2). P. 828—833.
6. **Rose N.L**. Inorganic flu-ash spheres as pollution tracers // Environ. Pollut. 1996. Vol. 91(2). P. 245-252.
7. **Bledzki A**. Mikrosfery jako napelniacze kompozycji polimerowych // Polimerytworzywa wielkoczastecz Rowe. 1986. Vol. 30. № 11. P. 425-427.
8. **Pandey G.S., Gain V.K.** Cenosphere-load in coal ash discharge of thermal power plant. Res. Ind. 1993. 38(2). P. 99—100.
9. **Компоненты** зол и шлаков ТЭС/ Л.Я. Кизельштейн, И.В. Дубов, Л.А.Шпицглуз и др./ М.: Энергоатомиздат, 1995. 176 с.
10. **Здановский В.Г.** Опыт извлечения из золы микро-сфер для использования в промышленности. Энергетика, 1991. Т. 12. С. 11—12.
11. **Высокотемпературные** теплоизоляционные материалы на основе алюмосиликатных полых микросфер из золоотвала Апатитской ТЭЦ / Н.Н. Гришин и др. // Огнеупоры и техническая керамика. 2000. № 2. С. 19—25.
12. **Получение** ценосфер из энергетических зол стабилизированного состава и их свойства Т.А. Верещагина, Н.Н. Аншиц, И.Д. Зыкова и др. // Химия в интересах устойчивого развития. 9. 2001. № 3. С. 379.
13. **Cenospheres.** Properties and diagnostics methods/ V.S. Drozhzhin, I.V. Pikulin, G.G. Savkin et al. // Proc. SWEMP 2002, r. Ciccu (Ed). Cagliari, Italy, October 7—10. 2002. P. 1059—1068.
14. **Applications** of cenospheres, new materials on their basis. V.S Drozhzhin, I.V. Pikulin, N.V. Maximova and etc. //Proc. SWEMP 2002, r. Ciccu (Ed), Cagliari, Italy, October 7—10. 2002. P. 1183—1186.
15. **Technical** Monitoring of Microspheres from Fly Ashes of Electric Power Stations in the Russian Federation / V.S. Drozhzhin, I.V. Pikulin, M.D. Kuvaev et al. 2005 World of Coal Ash Conference, April 11—15, 2005, Lexington, Kentucky, USA, p. 113—114.
16. **Formation** Processes of Hollow Microspheres in the Fly Ash from Electric Power Stations. V.S. Drozhzhin, L.D. Danilin, M.Ya Shpirt and etc. 2005 World of Coal Ash Conference, April 11—15, 2005, Lexington, Kentucky, USA, pp. 115—116.
17. **Будов В.В.** Полые стеклянные микросферы. Приме-нение, свойства, технология // Стекло и керамика. 1994. № 7— 8.
18. **Functional** Materials on the Basis of Cenospheres. Drozhzhin V.S., Danilin L.D., Pikulin I.V. and etc. 2005 World of Coal Ash Conference, April 11—15, 2005, Lexington, Kentucky, USA, pp. 117—118.
19. **Bykova E.V., Korshunova G.H., Dorofeev A.A., Laricheva N.F.** Development of environmentally conscious noncombustible heat insulating material // Proc. of Twenty-Fifth Intern. Thermal

Conductivity Conf. Lancaster, Pennsylvania. Technomic Publishing Company. 2000. P. 361.
20. **Пат. России 2171241**, МПК7 С 04 В 28/24 // С 04 В 111:40. Силикатная композиция для получения теплоизоляционного пеноматериала / Э.В. Быкова, Г.Х. Коршунова, А.А. Дорофеев, Н.Ф. Ларичева // Открытия. Изобретения. 2001. № 21.
21. **Детонационные** характеристики эмульсионного ВВ с ценосферами // III Межотраслевая науч.-техн. конф. «Промышленные взрывчатые вещества (ПВВ): состояние, перспективы разработки и применения», А.А. Дерибас, В.В. Сильвестров, А.Г. Аншиц и др. 18 — 20 мая 2005 г., г. Дзержинск Нижегородской обл., ФГУП «ГосНИИ «Кристалл».
22. **Данилин Л.Д., Дрожжин В.С.** Неорганические сорбенты на основе модифицированных микросфер для очистки жидких радиоактивных отходов // VIII Междунар. конф. «Безопасность ядерных технологий: обращение с радиоактивными отходами», 27 сентября — 1 октября, 2004. С.-Петербург, России.