Technical Monitoring of Microspheres from Fly Ashes of Electric Power Stations in the Russian Federation

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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 produced waste. Transformation of industrial waste into raw materials suitable for industrial application is a progressive tendency in primary and raw material intensive branches. This in full measure concerns the ash waste of electric power stations, whose annual amount in Russia is no less than 25 million tons.

Microspheres (or cenospheres), which are a light fraction of fly ash, are one of the most valuable components of fly ashes. This fraction has the form of 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, 2, 3]. At the electric power stations, where ash waste is removed in the form of an aqueous pulp, microspheres whose density 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 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 deals with the studies of fly ash microspheres [10, 11, 12, 13, 14], which will undoubtedly promote their industrial application development.

In 1996 through 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?”

The Russian electric power stations usually apply 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. The thickness of the floating layer depends on the microsphere content of

ash, on the electric power station operation duration and on the design of engineering structures at an ash dump.
Since the previously derived information about the influence of any factors on microsphere formation processes was contradictory, the main criterion for the electric power station selection was the amount of burnt coal. 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 burning 200 ÷ 300 thousand tons of coal and less showed little industrial promise.
For the European part of Russia, where mean capacity electric power stations are concentrated, the limit on the burnt coal was set to be no less than 400 ÷ 500 thousand tons per year. For the Ural, Siberia and Far East, where large electric power stations are 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 figure 1 the layout of the electric power stations, which were chosen in accordance with the above criteria, is shown.

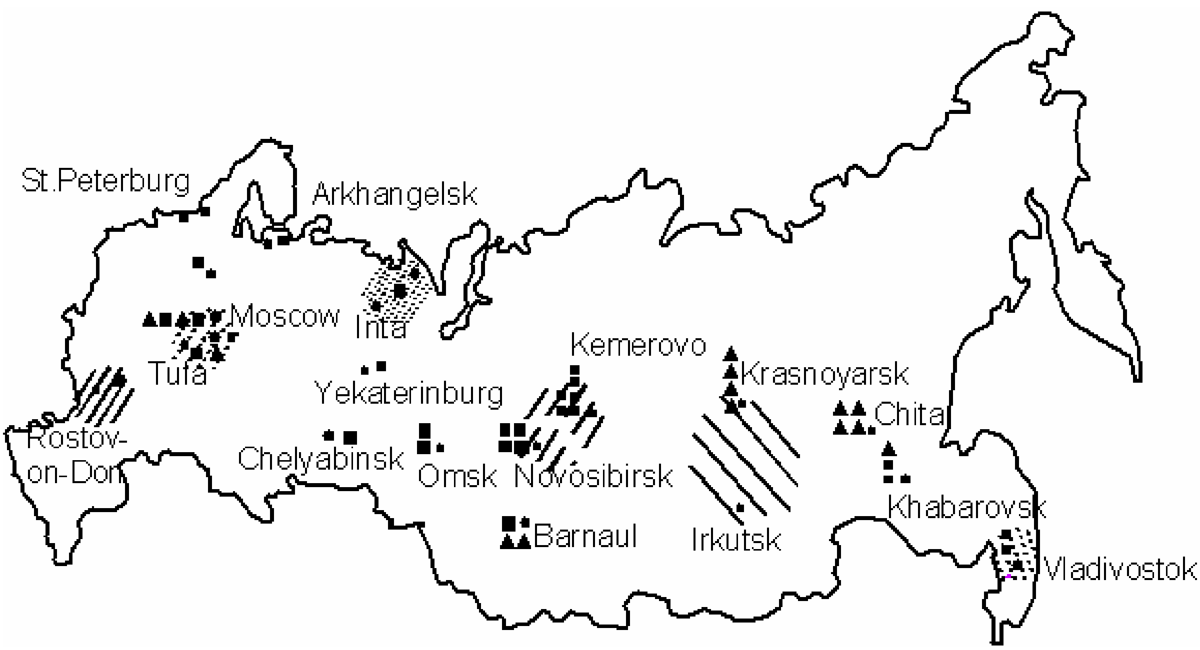

Figure 1. Layout diagram of power stations examined in 1996-2002

■ Power station with detected microspheres

▲ Power station without microspheres

Coal basins:

Pechora
Donetsk
Kansk-Achinsk
Near Moscow
Kuznetsk
Primorski

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.

$N_m = N_c \cdot K_{ac} \cdot (1\text{-}K_s) \cdot K_m$, 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;
$(1\text{-}K_s)$ 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	$(1\text{-}K_s)$	K_m	N_m, t/y
Ryazanskaya SRPS	Near Moscow	$5.5 \cdot 10^6$	0.08	0.8	$0.31 \cdot 10^{-2}$	5000
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 table 2.

Table 2
Regional resources of microspheres in the Russian Federation

Regions	North European	Central European	Ural	West Siberian	Maritime Territory
Estimation of microsphere formations (t/y)	15,000	18,000	12,000	74,000	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 producing and using ash microspheres either as raw materials for the local industry or large-capacity branches, or as export products.
Summarizing the data of table 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.
Figure 2 shows the panorama photographs of microsphere masses.
Similar masses were found at many electric power stations.

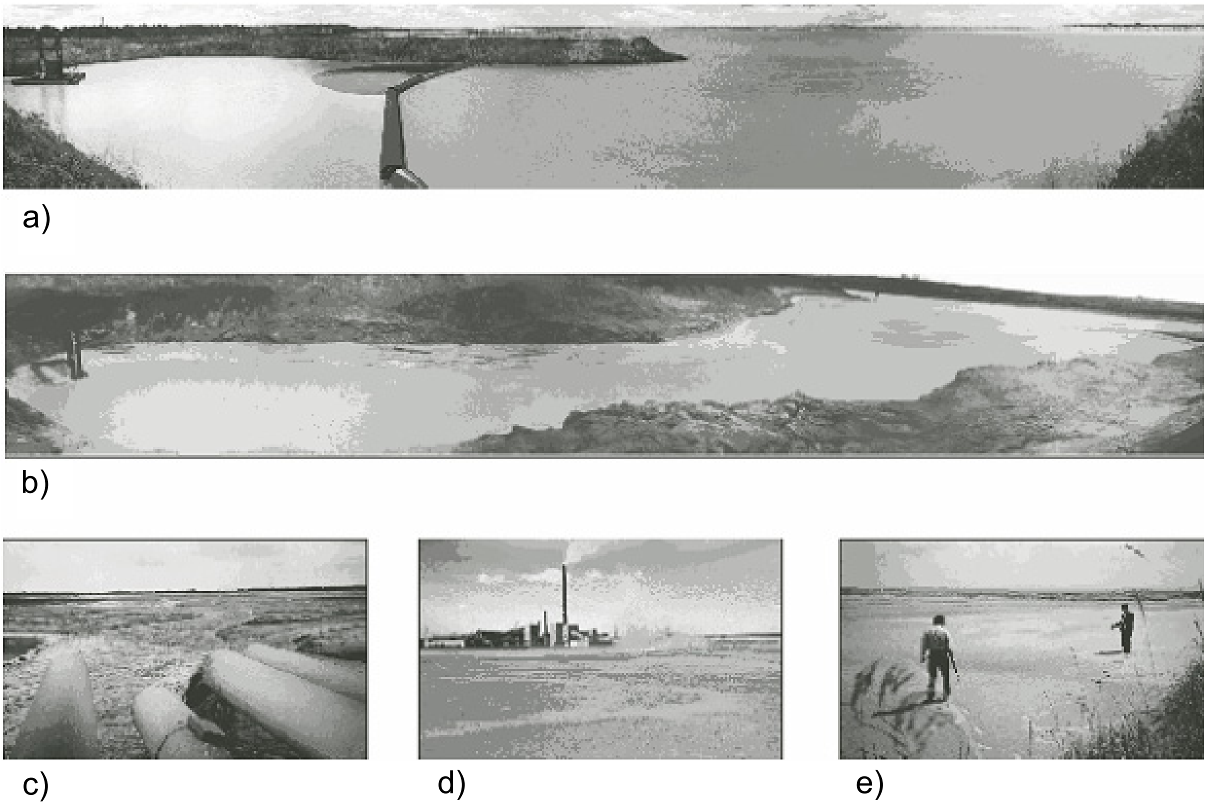

Figure 2. Masses of microspheres at ash dumps of power station.

Figure. 2 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 limiting access of microspheres to sewage wells (they are to the left). Figure 2 b) shows the water pond of Vorkutinskaya TPS-2 ash dump. The whole pond surface is covered with a thick layer of microspheres. Figure 2 c) illustrates disposal of ash and slag waste to Tom-Usinskaya SRPS ash dump. In figure 2 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. Figure 2 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.

Such power stations might in future become microsphere sources on the industrial scale.

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. 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]. Table 3 shows the measurements of the ash microsphere parameters.

Table 3
MAIN SPECIFICATIONS OF ASH MICROSPHERES

CHEMICAL COMPOSITION OF ASH MICROSPHERES			
SiO_2 - 62	K_2O - 3.39	MgO - 1.25	Na_2O - 0.62
Al_2O_3 - 27	Fe_2O_3 - 3.13	TiO_2 - 0.84	MnO - 0.04
CaO - 1.29	Cr_2O_3 - 0.02		
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
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
THERMAL PROPERTIES			
Melting temperature, °C:		t_1- softening onset	1000 ÷ 1400
		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
DIELECTRIC PROPERTIES			
Dielectric constant			2.14
Loss-angle tangent			0.062
Specific resistance, Ohm×m			1.61×10^{11}
Specific effective activity of natural radionuclides, Bq/kg			208

These values were averaged for 19 power stations. At the same time some characteristics may have great variations depending on the specific power station. For example, the average diameter of microspheres ranges within 60 - 200 μm, the real density varies from 0.5 g/cm^3 to 0.7 g/cm^3, the hydrostatic strength – from 20 MPa 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.

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 “Cenospheres 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 developed control program allows formation of the data for their review on the computer screen in the form convenient for a user. It also makes it possible to perform input-output, search and sorting operations. The database control program uses both Russian and English languages. The program provides for the data protection and information export into files of different formats. The software is designed for operation under control of WINDOWS 95 operational system and using a personal computer of IBM PC type.

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.

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