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Composition and Structure of Microspheres in Ash and Slag Wastes on the Far East of the Russian Federation (Case of the CHPP-2 plant, Vladivostok)

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Abstract. The results of laboratory studies of the composition and structure of microspheres of ash and slag wastes of Russian Far East energy enterprises (in particular, CHPP-2, Vladivostok) are presented in this scientific work. It has been established that the microspheres are concentrated in particles of technogenic wastes with a size of up to 500 μm , with the prevailing mass of valuable geomaterial (75-80 %) being in narrow granulometric classes from 71 to 100 μm and 100 to 200 μm . Part of the microspheres is represented by unusual technogenic metal alloys (for example, antimony with aluminium), has a density of more than 1g/cm^3 , and when wet enriched in water precipitates. From a practical point of view, the investigated microspheres cannot be considered a ready commercial product, since they contain a significant amount of carbon concentrate, which is unburned solid fuel particles. In this connection, it is required to develop effective technological solutions for the extraction and purification of microspheres from ash and slag wastes from the thermal power industry of the Far East of the Russian Federation.

1. Introduction

Ash and slag waste of the energy sector is an industrial, large capacity industry induced geomaterial containing a wide range of commercially valuable components.

Among the in-demand components of this waste are the microspheres, which are formed during the granulation of the of the gold-containing part of the solid fuel which is burned in in the boiler unit of the thermal power plant. The liquid melt of the inorganic component of the fuel segregates in the gas stream into discrete parts in the form of droplets, the shape of which is transformed by the expansion of the gases contained therein (carbon dioxide, ammonia, sulfur dioxide, nitrogen). In the case of equal gas pressure in the particles and the surface tension forces of the mineral melt, mineral formations of spherical shape are formed. Their mineralogical composition includes quartz, magnetite, hydromica, mullite, hematite, calcium oxide, and others. Regarding the chemical composition, silicon and aluminium compounds prevail; iron, potassium, and magnesium compounds are also present.

The average physicochemical and granulometric properties of microspheres are represented by the following indices: pH: 6.0-7.0; bulk density: 0.3-0.45 g/cm^3 ; true density: 0.34-0.5 g/cm^3 ; melting point: 1400-1500°C; Mohs' hardness: 6; coefficient of thermal conductivity: 0.08-0.20 W/mK ; particle diameter: from 20 to 500 μm ; high dispersity.



The primary fields of application of microspheres in industry are: 1) filler for the production of heat-insulating lightweight and radar-transparent construction ceramics; 2) additive to improve the performance properties of drilling and grouting mortars; 3) additive for the production of heat-insulating, heat-resistant concrete; 4) raw material for the production of thermoplastic spheroplasts [1-8].

2. Research methods

The present research chooses the ash and slag wastes of CHPP-2, Vladivostok, Far Eastern Russia as the subject of study. Two samples were taken from the ash dump: sample No 1 weighing 49.4 kg and sample No 2 weighing 83.2 kg. Using Labourette-27 sample divider, the research team managed to obtain two representative analytical weights: sample No 1 - 994 g and sample No 2 - 995.5 g.

The samples were then separated into light and heavy fractions using wet gravity enrichment. Semi-quantitative analysis of raw materials and products of enrichment required the use of the atomic emission multichannel spectrometer GRAND.

3. Results

According to the research findings, heavy fraction microspheres contain aluminosilicate ferrous composition, iron oxides and, less often, native iron. The particle size ranges between 50 and 150 μm .

The structural and textural features of the microspheres are quite diverse. They can be ideal microspheres and globules with a complex shape. Their surface can be smooth or tessellated resulting in the formation of microspheres from individual crystals or crystal nuclei (figure 1). The mosaic structure is more typical for microspheres of oxide composition.

The samples were researched according to the scheme represented in Figure 1. Initial ash and slag material was selected from energy enterprises ash dumps. The selected samples were grinded, quartered, and were sent to analytical researches.

The gold and noble metal content was determined by NAA and AAS methods, the chemical content of samples was determined by XRFA, morphology of gold micro-particles and noble metals micro-particles was determined by the SEM method.

The researches have revealed presence of gold and NM in a number of the examined samples. So, according to AAS data, gold was detected in 3 of 57 examined samples. The Au content varied from 0.04 to 0.18 g / t. At the same time, silver was found in 13 samples.

The highest silver content was noted in the sample from the polygon of TPP-2 - 29.7 g / t. According to NAA, gold was detected in 7 out of 57 examined samples. The Au content varied in the range 0.10-0.45 g / t (table).

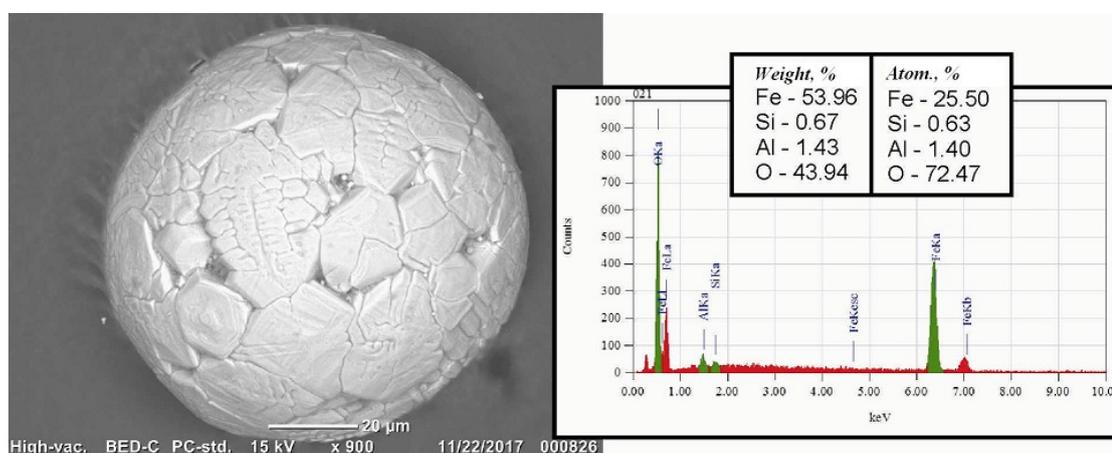
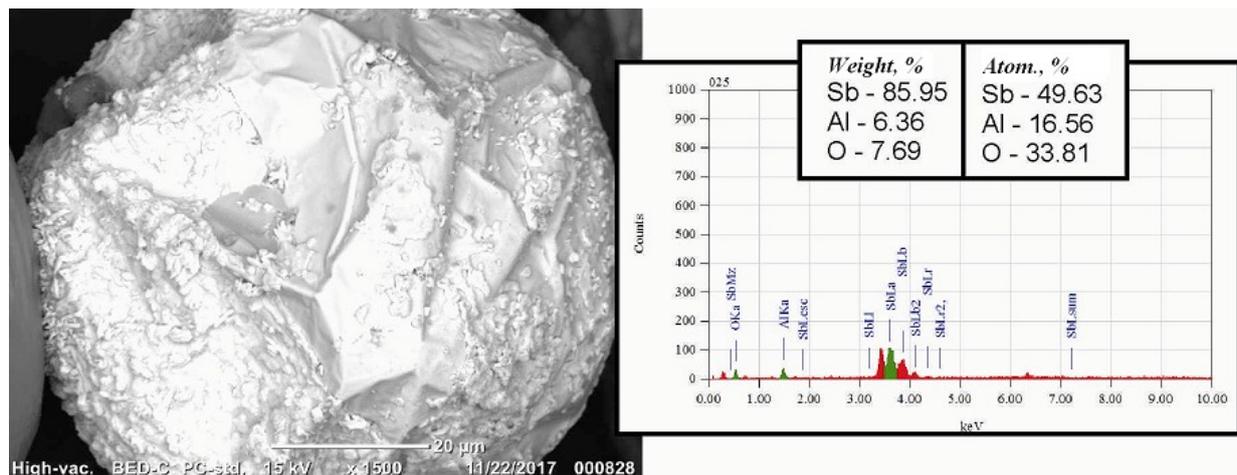


Figure 1. Microsphere (100 μm) with mosaic textural structural properties.

Table 1. The content of aluminosilicate microspheres according to grain size grades.

Grain size grade, mm	Mass content of the fraction		Mass of the floating fraction, g	The proportion of microspheres in the floating fraction	
	g	%		%	g
Sample 1					
+2	27,5	2,8	-	-	-
-2 +1	64	6,4	-	-	-
-1 +0,5	73	7,3	-	-	-
-0,5 +0,2	216,5	21,8	0,02	17	<0,01
-0,2 +0,1	186,5	18,8	0,04	80	0,03
-0,1 +0,071	90	9,1	0,04	75	0,03
-0,071	336,5	33,8	<0,01	85	<0,01
Bcero	994	100	0,1		0,06
Sample 2					
+2	32,5	3,3	-	-	-
-2 +1	111	11,1	-	-	-
-1 +0,5	141	14,2	-	-	-
-0,5 +0,2	218	21,9	0,34	15	0,05
-0,2 +0,1	185	18,6	0,11	82	0,09
-0,1 +0,071	125,5	12,6	0,07	87	0,06
-0,071	182,5	18,3	<0,01	89	<0,01
Bcero	995,5	100	0,52		0,2

Heavy ash fraction often contains irregular grains and microspheres of industry-induced alloys and, possibly, microspheres of not common natural alloys. For example, a microsphere formed by an alloy of antimony with aluminium (figure 2). The size of the microsphere is about 70 μm ; the surface is uneven due to soldered grains or crystals. Besides, there is a thin coating of grains (microns and micron fractions) of identical composition on the surface.

**Figure 2.** Microsphere (70 μm) formed by the industry-induced alloy of antimony with aluminium.

The light fraction is represented by aluminosilicate microspheres which often have a globular shape and sometimes they are regularly spherically shaped. The surface of the aluminium spheres is uneven containing buildups of microspheres and the thin microspheres, as well as interstices of various sizes and shapes (from rounded to irregular ones). The thickness of the walls of the hollow aluminosilicate

microspheres is 2-5 micrometres, the size of interstices ranges between decimals and 3-5 μm , rarely up to 10-20 μm . The number of interstices can reach 10-15%.

Visualization of microspheres was carried out with Axio Scope A1 microscope, JEOL scanning electron microscope (Japan) equipped with an energy dispersive analyzer "JCM-6000 PLUS". Photographs of microspheres in selective grain size grades 0.1 + 0.071 μm and -0.2 + 0.1 mm (samples No 1 and No 2) are shown in figure 3.4.

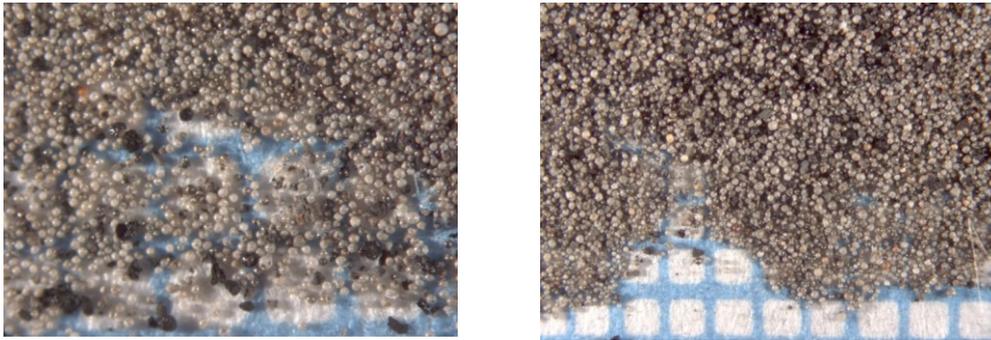


Figure 3. Light fraction microspheres with grain size grade -0.1 + 0.071 mm.

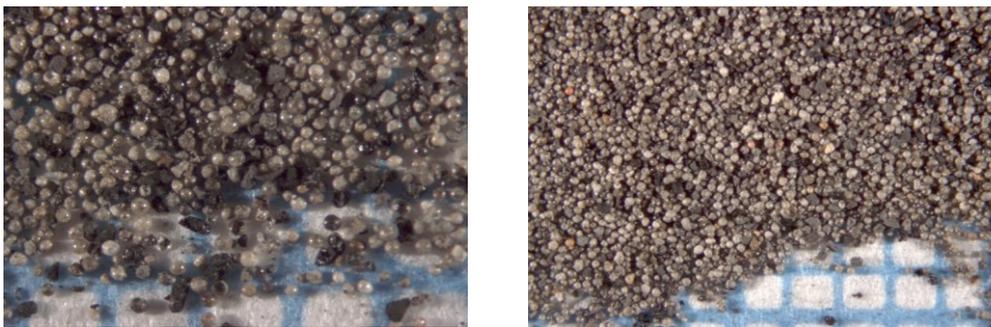


Figure 4. Light fraction microspheres with grain size grade -0.2 + 0.1 mm.

The study determined the content of microspheres in the grain size grades (from -0.071 mm to +2 mm) for each of the analyzed samples. The evaluation was carried out by counting the proportion of microspheres in the total mass of the floating fraction. The proportion of microspheres in the floating fraction was assessed visually. The table below exhibits the results.

4. Conclusion

- All microspheres are concentrated within the grain size grade - 0.5 mm.
 - The largest proportion of microspheres (from 75 to 80%) is recorded in granulometric classes of 0.1 + 0.071 mm and -0.2 + 0.1 mm.
 - A part of the microspheres is not concentrated in the floating fraction.
 - The significant content of carbon in microspheres does not allow the extracted material to be considered as a final product.
 - It requires the development of technological methods to separate the microspheres and unburned carbon.

5. References

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Acknowledgments

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