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Study of aluminosilicate microspheres using SEM – EPMA

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ABSTRACT
This work discusses the studies based on the microstructural properties of the improved ash and slag materials obtained after flotation enrichment with SEM-EPMA analysis (Scanning Electron Microscope and Electron Probe Microanalysis). According to the results of the analysis aluminosilicate microspheres was found in all four samples with a certain concentration and their similar morphology were identified. The microspheres are characterized by a spherical shape and a rough shell surface. Moreover, the shells are characterized by different morphology, which is typical after flotation enrichment. The size of the microspheres is less than 100 microns. The chemical composition of all four samples are inhomogeneous and was found by linear EDS (Energy-dispersive X-ray spectroscopy) analysis. However, the average values of the content of elements are quite close to each other. The special significance of the work is emphasized by the cross section of the shells of microspheres, which are similar to the crystallization structure of molten metal. They play an important role as materials in the construction industry. According to the results of SEM-EPMA studies, it is recommended to apply ash and slag materials, containing aluminosilicate microspheres, obtained after flotation enrichment, in construction industry.
Keywords: Ash and slag waste, aluminosilicate microspheres, scanning electron microscope, microstructure, microanalysis.

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Introduction

The current state of solid waste processing at thermal power plants is extremely low today, which leads to a significant accumulation of bottom-ash waste in ash-disposal areas. When burning coal in a boiler furnace at a state district power station, the composition of flue ash waste can consist of 95-98% of mineral compounds of aluminum oxides, silicon, calcium, titanium, iron, alkali oxides, sulfates, and sulfides. Processing of such ash products can be converted into valuable goods [[1], [2]], such materials as aluminosilicate hollow microspheres. several times lower than that produced by industrial methods.

For several decades, microspheres have been widely used all over the world in construction:

The aluminosilicate microspheres formed during the combustion of coal in power plant boilers as a result of granulation of the melt of the mineral part of the coal and the splashing of crushed small droplets with internal gases have a diameter from 10 to several hundred micrometers, on average about 100 microns. The wall thickness is from 2 to 10 microns, the melting point is 1400-1500°C, the density is 580-690 kg/m^3. The microspheres' properties are close to hollow microspheres which are obtained from melts by industrial methods. It is essential that the cost of hollow ash microspheres is

special cements, masonry mortars, plasters, liquid concrete; in the automotive industry: tires, brake friction pads, casting molds, body fillers; in the oil industry: plugging materials, drilling fluids, grinding materials; in ceramics: refractories, tiles, aluminum cement, insulating coatings, etc.

Any technical problem where weight reduction is required with low thermal conductivity, high strength and volume savings, increased resistance to erosion, and aggressive media can be solved with the use of aluminosilicate microspheres.

In connection with the above, we have studied aluminosilicate microspheres using SEM-EPMA. This SEM-EPMA technique with a special electron probe microanalyzer will provide information on the chemical composition of the sample in an arbitrarily chosen area of microscopic dimensions with high accuracy.

Research method

The studies were conducted using JXA-8230 electron probe microanalyzer (JEOL) at an accelerating voltage of 25 kV and an electron beam current of up to 5 nA (Fig. 1). The technical capabilities of the device correspond to its passport data, according to which the detection of impurities or components of a substance (from boron to uranium) and the calculation of their concentrations are performed with standard methods based on JEOL own EPMA program. The dimensions and current of the electron beam were selected empirically to provide sufficient statistics for the collection of characteristic X-ray radiation (CXR) pulses, and the so-called “dead time” ranged from 10 to 30%.

The mounting corresponded to the perpendicular position of the sample concerning the electron beam, which makes it possible to obtain the results of automatic calculation of the detected pulses with high reliability.

The backscattered electron mode (COMPO), which gives better images of such objects compared to the observation and shooting mode in secondary electrons (SEI) was used for all areas selected for scanning electron microscope (SEM) studies. The main feature of the SEM contrast in the backscattered electron mode is the known fact of brighter emission of particles with a large atomic number in comparison with particles that make up the general background [3].

All automatic calculations in the EPMA program, which are used in the JXA-8230 electronic microanalyzer, are performed from the approximation of an absolutely flat surface located perpendicular to the electron beam. The most important consequence of not meeting flat

Figure 1 – JEOL JXA-8230

Table 1 – Chemical composition of samples of aluminosilicate microspheres

Elements compounds	Al_2O_3	SiO_2	SO_3	CaO	TiO_2	Fe_2O_3	Na_2O	P_2O_5
weight %	18.850–20.770	42.224–48.231	0.128 – 0.421	2,058 – 2.922	1.024 – 1.117	4.698 – 12.975	0.226 – 0.447	0.285 – 0.461

surface requirements are the loss of accuracy for sample analysis. The work used the techniques used in IMOB JSC.

Research results and their discussion

Samples of aluminosilicate microspheres produced after flotation concentration of ash from burning coal in TPP from various deposits in Kazakhstan were taken for the study.

The chemical composition of the samples (Table 1) is represented mainly by oxides of aluminum, silicon, iron, calcium, titanium, sulfur, sodium, and the content varies considerably depending on the composition of the original ash. As a result of the research, micrographs were produced in the mode of backscattered electrons and secondary electrons at magnifications from X100 to X3500.

Samples are free-flowing powder in the form of various particles of irregular shape, various structures and globules with a variety of morphological features: ideal spheres with an intact smooth or perforated surface, hollow spheres filled with small particles, in the form of fragments, and all kinds of porous grains of irregular shapes. The size range of the observable particles is from 1 to 150 microns.

The sample presented in Figure 2 demonstrates the most characteristic differences in the shape and morphological features of individual globules: ideal spheres with an intact smooth and rough surface, hollow spheres, and aggregates of small spheres on the surface or in cavities and dimples of large globules. According to COMPO data, the particles size is on average 1-150 microns. (Fig. 2). EDS analysis from the surface of the microspheres showed that the main elements of the shells consist of Al, Si, Ca, Fe, K, S, Ti, Mg, Mn, Cu, Zn. (Fig. 3).

It should be noted that the composition of the material is very heterogeneous for all samples, and this heterogeneity is also manifested for particles of the same sample with the same morphological characteristics. Figure 2 shows the EDS spectra of the particle morphology of microspheres of samples No. 1,2,3,4, which demonstrate a different set of elements.

The average elemental composition of the microsphere material according to the EDS analysis is shown in Table 2.

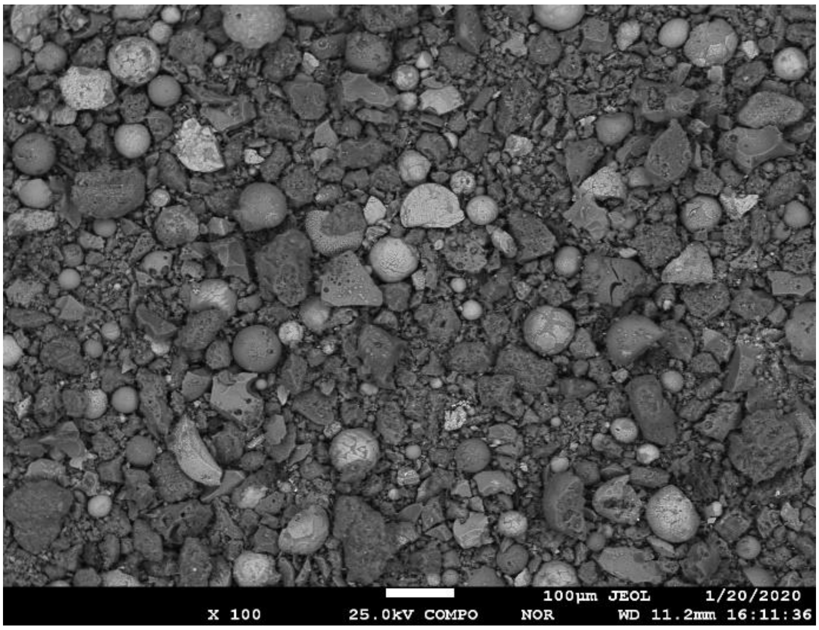

Figure 2 – General view of the accumulated aluminosilicate microspheres (X100)

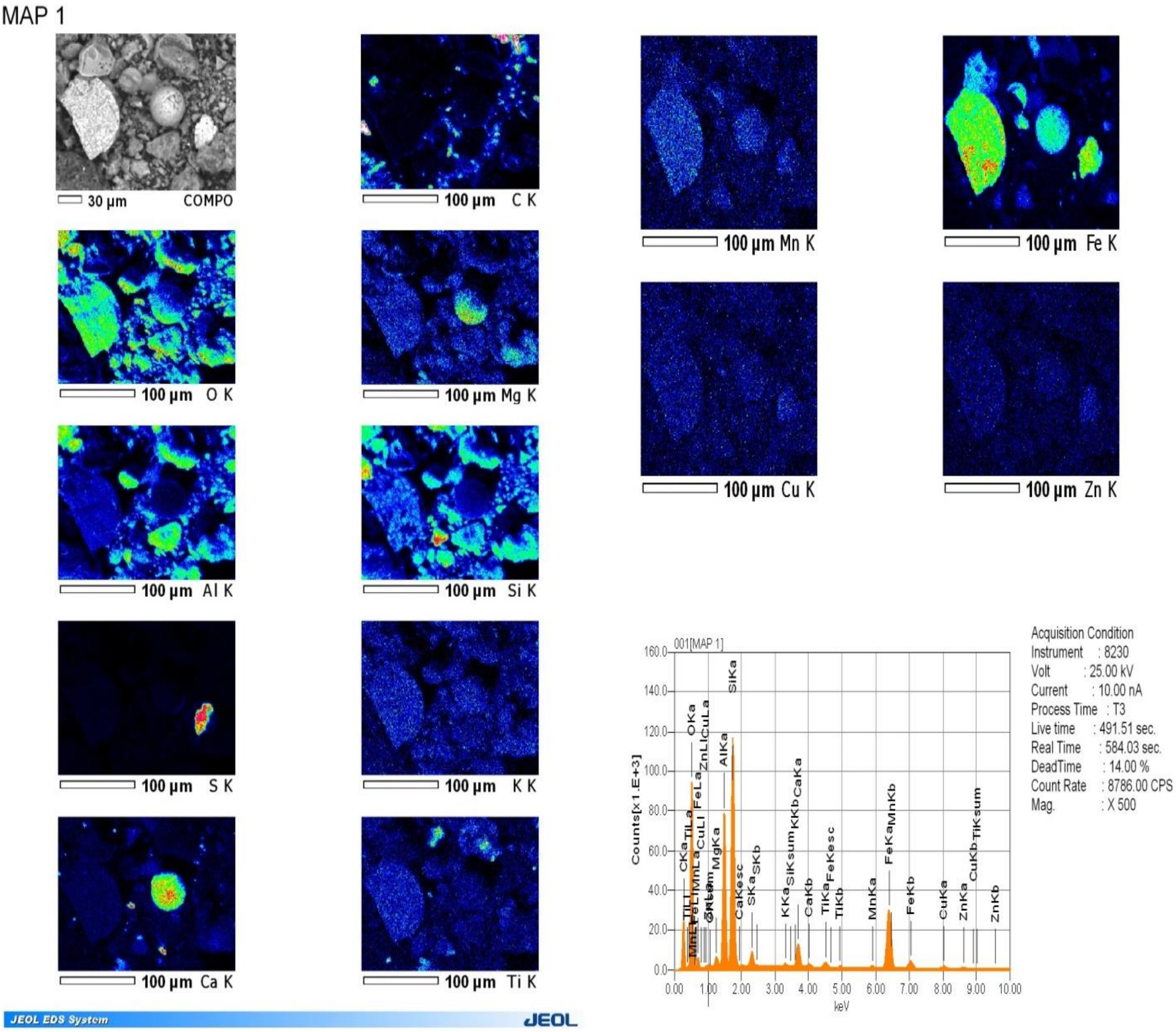

Figure 3 – EDS analysis from the surface of microspheres (X500)

Table 2 – Average elemental composition of the surface of microspheres

Element *(in % wt)*	**Sample No. 1**	**Sample No. 2**	**Sample No. 3**	**Sample No. 4**
O	50.15	51.42	49.54	47.34
Mg	0.65	0.34	0.48	0.69
Al	7.05	6.98	8.95	8.12
Si	9.85	12.11	13.98	13.76
S	0.81	0.07	0.05	0.03
K	0.12	0.32	0.29	0.27
Ca	1.41	0.11	1.29	2.45
Ti	0.44	0.27	0.65	0.32
Mn	0.28	0.18	0.04	0.87
Fe	8.85	3.44	2.45	28.78
Cu	0.62	0.57	0.69	0.51
Zn	0.41	0.39	0.55	0.42

These samples are characterized by an almost spherical shape and a rough surface of the shell, which have different morphologies. The microspheres are less than 100 µm in size (Fig. 4).

More detailed results of the analyzes are given in our work [4].

In previous works, the study of aluminosilicate microspheres from the ash and slag waste of the Aksu State District Power Plant is considered, which the chemical and elemental composition revealed using scanning electron microscopy with an X-ray spectral microanalyzer confirm the same composition. The paper [5] also states that the use of ash and slag waste (ASW) from thermal power plants brings the technology of thermal power plants closer to waste-free by 80%. When coal is burned from the Ekibastuz deposit, about 40-50% of silicon ash is formed. Alumina can be obtained from this ash, and cement can be obtained from alumina production waste.

However, despite the heterogeneity of the chemical composition of the samples, the averaged values for the content of elements are quite close (Table 2).

You can also see spheres with shells similar to the crystallization structure of the molten metal [[6], [7], [8]]. From Table 2 and Figure 4, the chemical composition of the areas marked with a yellow cross may indicate the content of phases resembling fayalites, magnetites, hortonolites, ferrites, spinels, ganites, or hypoeutectic silumins [[9], [10]].

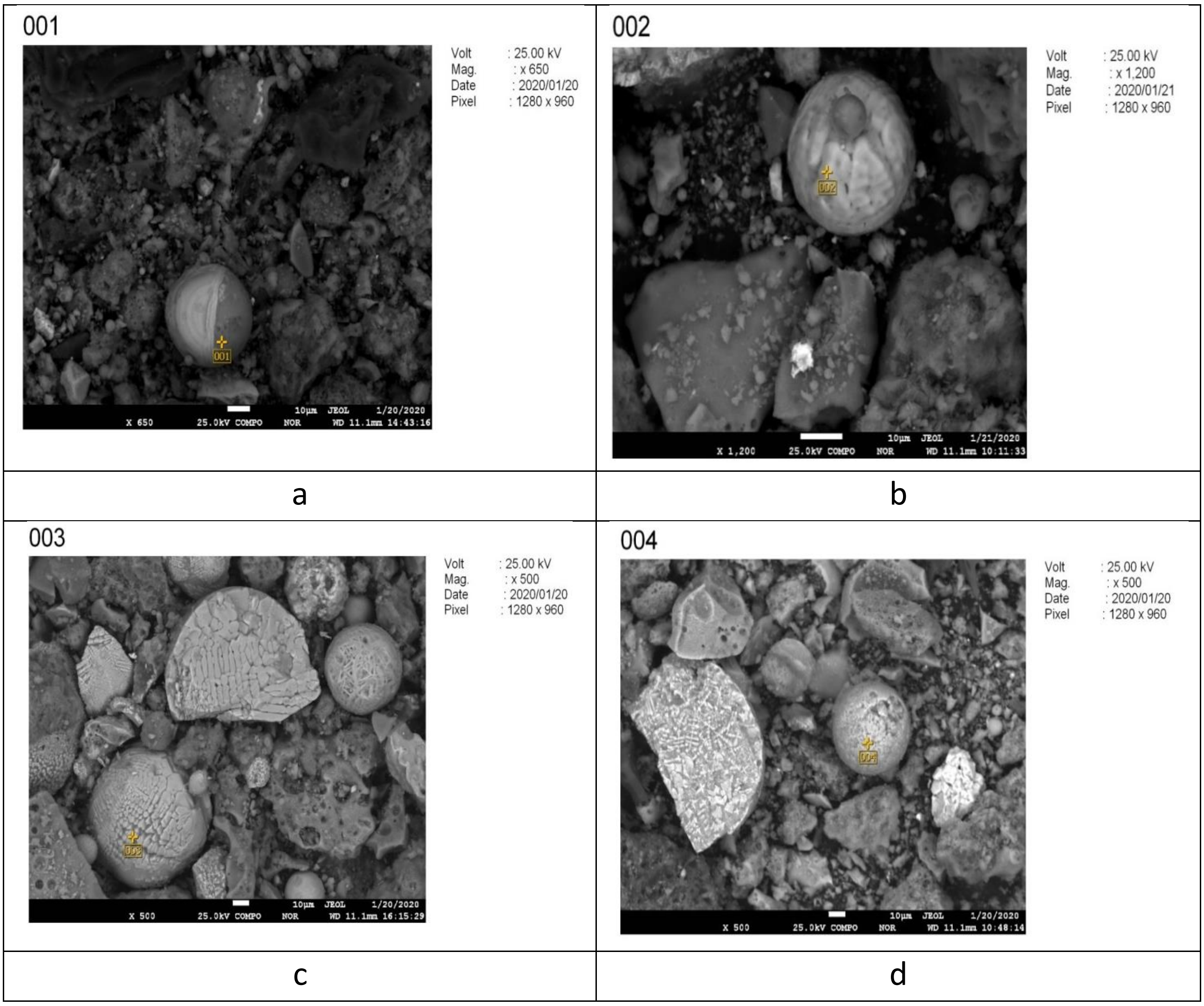

Figure 4 – Photographs of microspheres in enlarged form from X500 to X1200 (a - sample No. 1 (X650), b - sample No. 2 (X1200), c - sample No. 3 (X500), d - sample No. 4 (X500))

From the point of view of greater detail, it is recommended to perform X-ray diffractometric measurements with large statistics after the separation of the components in the ash.

Conclusions

The research results indicate that aluminosilicate microspheres from bottom-ash waste from state district power stations can be used as ready-made microspheres after flotation ash concentration. Its use in the industry and the construction industry is one of the strategic ways to solve environmental problems. Ash has good prospects for widespread use to save resources that are to solve economic problems associated with the preservation of natural resources, building materials, non-ferrous, rare metals, and other materials.

The paper presents new data on the concentration composition associated with the microstructure. The microstructure gives us the ability to visually predict the general state of the microspheres, which is applicable to the construction industry. In the construction industry, aluminosilicate microspheres are used as a filler in: inorganic building materials, lightweight structural materials and ultralight concretes, wall blocks, dry mortars, lime mortars, cement, plaster, high-strength wear-resistant floor coverings for industrial premises, paint, insulating roofing and soundproofing materials, finishing and plaster gypsum for insulation of external walls of buildings, sound and heat insulating coatings, decorative materials, as well as for mastics when sealing cracks and joints, fillers, sealants, etc.

Studies have shown that our microsphere is superior in quality to imported ones, and its acceptable cost leads to a reduction in the cost of finished products and a direct economic benefit to the manufacturer. So, expensive lime and cement can be replaced with aluminosilicate microsphere up to 50 wt.%, and the plasticizer up to 30 wt.%, while the properties of the materials are improved.

According to rough estimates, the cost of such microspheres is ten or more times lower than that of microspheres produced by industrial methods.

Conflicts of interest

On behalf of all authors, the author declares that there is no conflict of interest.

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РЭМ-РСМА көмегімен алюмосиликатты микросфераларды зерттеу

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ТҮЙІНДЕМЕ

Мақалада флотациялық байытудан кейін алынған күл-шлак материалдарын микроқұрылымдық зерттеу нәтижелері келтірілген. Растрлық электронды микроскопияны және рентгендік спектрлік микроанализді (РЭМ-РСМА) талдау нәтижелері бойынша белгілі бір концентрациясы және ұқсас морфологиясы бар алюмосиликатты микросфералар анықталды. Барлық төрт сынамада анықталған микросфералар сфералық пішінмен және қабықтың өрескел бетімен сипатталады. Сондай-ақ, қабықтар флотациялық байытудан кейін тән әр түрлі морфологиямен сипатталады. Микросфералардың мөлшері 100 мкм-ден аз. Сызықтық ЭДС (Энергодисперсиялық рентген спектроскопиясы) анализімен анықталған барлық төрт үлгінің химиялық құрамы біркелкі емес. Алайда, осыған қарамастан, элементтердің құрамы бойынша орташа мәндері өте жақын. Сынамалардың бетін сканерлеу элементтер мен олардың пішіндерінің орналасуын көрсетті. Жұмыстың ерекше маңыздылығын балқытылған металдың кристалдану құрылымына ұқсас микросфералардың қабықтарының көлденең қимасы баса көрсетеді. Олар құрылыс саласындағы маңызды материалдар болып табылады. Балқытылған металдың кристалдануы сияқты шығу тегі параллель жүретін екі қарапайым процестерден тұрады: кристалдану шоғыры және осы кристалдану шоғырының өсуі. РЭМ-РСМА зерттеулерінің нәтижелері бойынша өнеркәсіпте және құрылыс индустриясында алюмосиликатты микросфералары бар флотациялық байытудан кейін алынған күл-шлак материалдарын қолдану ұсынылады.

Түйін сөздер: Күл-шлак қалдықтары, алюмосиликатты микросфералар, растрлық электрондық микроскоп, микроқұрылым, микроталдау.

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Исследование алюмосиликатных микросфер с помощью РЭМ-РСМА

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АННОТАЦИЯ

В статье приведены результаты микроструктурных исследовании золошлаковых материалов, полученных после флотационного обогащения. По результатам анализов растровой электронной микроскопий и рентгеноспектрального микроанализа (РЭМ-РСМА) выявлены алюмосиликатные микросферы с определенной концентрацией и схожей морфологией. Обнаруженные микросферы во всех четырех пробах характеризуются сферической формой и шероховатой поверхностью оболочки. Также оболочки характеризуются различной морфологией, которой свойственно после флотационного обогащения. Размер микросфер составляет менее 100 мкм. Обнаруженные линейным ЭДС анализом химический состав всех четырех проб неоднороден. Однако, несмотря на это, усредненные значения по содержанию элементов достаточно близки. Сканирование поверхности проб показал расположение элементов и их формы. Особую значимость работы подчеркивает поперечное сечение оболочек микросфер, похожие на структуру кристаллизации расплавленного металла. Они являются важными материалами в сфере строительства. Такие происхождения как кристаллизация расплавленного металла состоит из двух элементарных параллельно протекающих процессов: зарождения зародышей, или центров кристаллизации, и роста этих центров кристаллизации. По результатам РЭМ-РСМА исследований рекомендуется применение золошлаковых материалов полученных после флотационного обогащения, с содержанием алюмосиликатных микросфер в промышленности и строительной индустрии.

Ключевые слова: Золошлаковые отходы, алюмосиликатные микросферы, растровый электронный микроскоп, микроструктура, микроанализ.

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