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HOLLOW MICROSPHERES OF COAL AND OIL SHALE ASHES

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The properties of hollow microspheres - ash species formed during burning coals and oil shales - are studied. Possibilities of their using are discussed.

Introduction

Wastes usually formed when burning coals in boiler units of heat-and-power stations are differentiated as ashes washed off from under the furnace units and as multicyclone ash the bulk of which is also discharged into the common hydraulic system conveying materials to ash ponds. As shown by practice, there exists a third type of ash which forms a floating foam product at the water surface of ash ponds. Examination of this product showed that the bulk of it was represented by finest aluminosilicate hollow microspheres [1, 2].

According to [1] the supposed mechanism of the microspheres formation is as follows: at elevated temperatures in the furnace chamber the mineral part of coals melts in the gas flow and thereafter the melt drops formed, especially the finest of them, distend from the inside due to the release of gaseous products of decomposition both of carbonates and sulfides present in the initial fuel and water vapour.

The hollow microspheres formed enter the ash ponds together with the main flow of the ash waste. Due to the low density of hollow compounds they float up there, forming a floating bed at the water surface of the ash ponds. According to the published data [1-3], the quantitative content of aluminosilicate hollow microspheres is not great and amounts to 0.01-1.2 per cent of the total mass of the ash waste.

However, considering the high capacities of present boiler units as well as long runs of their operation, the accumulation of the foam product in the ash ponds is great enough to discuss about commercial utilization of this material. Especially as the concentration of the microsphere fraction is realizable by relatively simple and cheap measures (through boiling out the foam, its filtration and drying [2, 3]). The relative ease of obtaining contributes to the moderate cost of this product, and that is why a number of companies have organized the industrial production of microspheres in the form of dry very flowing powder.

These powders are put on the market under the following names: cenospheres, globulite, localite, spherolite, fillite, armospheres, microshell, microballoon, floaters.

The demand for hollow aluminosilicate microspheres results from the fact that their low density and perfect shape make them an ideal filler for a great variety of composites [3, 4, 6, 7].

Basing on the experience gained at examination of foam products from coal ash ponds, the ash ponds containing kukersite combustion ashes were also studied. At the surface of these ash ponds also a foam product was observed.

In this paper, comparable results concerning kukersite-derived foam products and hollow microspheres taken from the ash dumps of heat-and-power plants of the town of Angarsk (the Irkutsk region) are presented. In Angarsk power plant a mix of coals from Cheremkhovsky and Azeisky coal fields (East Siberia) is burnt.

Experimental

Microspheres of Coals

The sample of the foam product taken from the ash dump of the Angarsk heat-and-power plant and dried at 105 °C represents an easily flowable dark-grey powder. Its chemical composition and the results of the chemical analysis of an averaged ash sample taken from the same ash pond are presented in Table 1.

As seen from the Table, the fraction of hollow microsphere (specimen No. 2) is characterized by a higher content of SiO_2 and Al_2O_3 and a lower content of Fe_2O_3 and CaO as compared with the composition of the average ash sample (specimen No. 1). This indicates the aluminosilicate composition of the specimen No. 2. A similar trend was noted in [1-4] when studying hollow ash microspheres of coals from other deposits in spite of their different origin and nature.

The phase-and-mineral composition of specimens Nos. 1 and 2 was determined with the help of transmitted-light microscopy and X-ray phase analysis by the instrument DRON-3.

Microscopic analysis of the specimen No. 2 showed that it is constituted mainly of spherical glassy particles, the refraction index of which is typical of glasses of the mullite composition. A partial fine-grained crystallization of mullite was observed at the surface of globules.

Table 1. **Chemical Composition of Hollow Microspheres Fractions and Averaged Ash Samples**

Specimen No.	Description	Oxide content, %							
		LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O
1	Averaged coal ash sample	3.61	52.92	23.82	6.66	8.92	2.19	3.19	1.77
2	Fraction of hollow microspheres separated from coal ash	0.95	58.50	30.93	3.65	3.15	2.03	-	1.80
3	Averaged oil shale ash sample	-	28.06	7.64	5.00	48.85	3.74	3.74	2.61
4	Fraction of hollow microspheres separated from oil shale ash	42.26	2.08	0.75	0.23	52.54	0.19	1.18	0.37

Table 2. **Physical Characteristics of Fractions of Hollow Microspheres and Averaged Ash Samples**

Specimen No.	Description	Apparent density, kg/m^3	Bulk density, kg/m^3	Glass density, kg/m^3	Microsphere wall thickness, μm	Melting temperature, °C	
						t_B	t_C
1	Averaged coal ash sample	2600	960	2500	-	1320	1400
2	Fraction of hollow microspheres separated from coal ash	540	290	2500	5-10	1400	1480
3	Averaged oil shale ash sample	2450	800	2650	-	1330	1360
4	Fraction of hollow microspheres separated from oil shale ash	485	232	-	0-5	-	-

Unlike the specimen No. 1, in immersion sections of the specimen No. 2 the round particles floated up indicating their low density. The spherical shape of the particles and their hollowness were fixed by the electron microscopy analysis. The thickness of the globule walls was 5-10 μm.

The main element of the diffraction pattern for the specimen No. 2 was a wide diffuse maximum over the interval of angles $2\Theta = 8...20°$ characteristic for glassy phases. Low diffraction reflexes of mullite and quartz were noted at its descending branch. A comparison of X-ray diffraction photographs of the specimen Nos. 1 and 2 supported the chemical analysis data about the aluminosilicate composition of the latter.

For the specimens Nos. 1 and 2 the bulk and apparent densities were determined and ash melting temperature measured. The results obtained are presented in Table 2. All determinations were carried out in compliance with the Russians standards. A drastic reduction in the density characteristics of the specimen No. 2 as compared with the average ash sample as well as its higher refractory characteristics can be seen from Table 2.

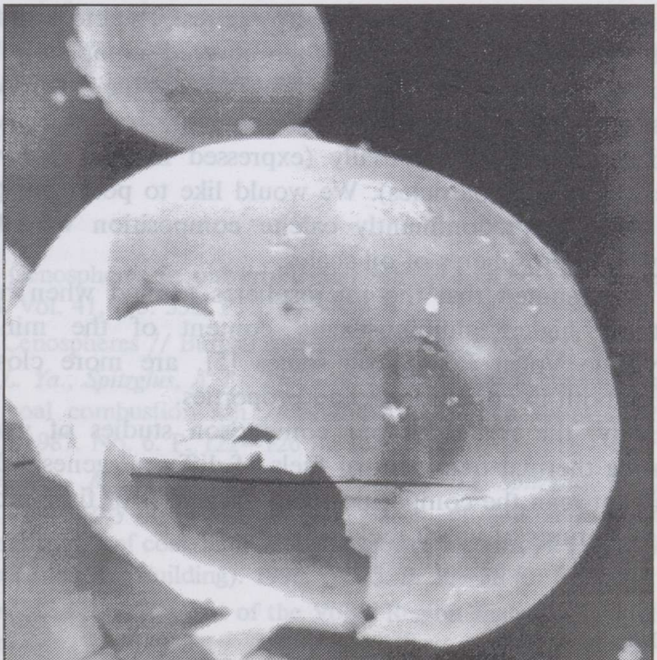
The grain-size distribution of the samples was determined with the help of the Analysette-22 sedimentograph of Fritsch GmbH. The prevalent size of globules of the hollow microsphere fraction was 80-120 μm.

The data obtained for the specimen No. 2 as to special features of the chemical and phase-and-mineral compositions, morphology of particles, their density and refractory characteristics are similar to those characteristics for a fraction of hollow microspheres of coal ashes from other deposits presented in publications [1-4].

Microspheres of Oil Shales

The sample under investigation was taken from the ash pond of the steam power plant of the town of Narva. After drying it represented a white easily flowable powder where spherical particles could be seen with an unaided eye. The comparison sample was made from the averaged ash sample taken from the same ash dump. In addition, similar materials - combustion wastes of the heat-and-power plant of Slantsy shale processing plant were studied. In Slantsy oil shale (kukersite) of the same Baltic deposit is utilized. Investigation of these two types of materials showed their practically complete identity which made it possible to present generalized results in this paper. It can be seen from the data of Table 1 that the sample No. 3 contains more CaO, but less SiO_2 and Al_2O_3 than the sample No. 1. By its chemical composition the sample No. 4 is even more closely approximating the calcium carbonate composition. This assumption was confirmed with the help of X-ray phase analysis.

The main reflexes in the X-ray diffraction photograph of the specimen No. 4 are related to $CaCO_3$. After the treatment of the sample with a diluted HCl solution to remove calcite, in the X-ray photograph of the insloluble residue one can see the reflexes of mullite and relict minerals of the initial raw materials of quartz and feldspar which pointed to there low content. The microscope study of the specimen No. 4 confirmed once again that the sample is made up of calcite. Round particles either consisting completely of calcium carbonate, or with a concentric zonal structure with the fine-grained mullite crystals can be observed in the central part of the zonal globules. Electron microscope analysis (РЭМ 100Y microscope) proved the hollowness of the particles of the sample No. 4 (Figure). As to density characteristics and refractoriness, the averaged samples of both ash types (specimens Nos. 1 and 3, Table 2) are very similar. This can be attributed to the high glassy particle content of both specimens, the glass composition of which correlates with that of the mullite as well as to the presence of the same relict minerals of fuel in the form of quartz and feldspar.



Micrograph of fraction of hollow microspheres (specimen No. 4) (РЭМ 100У microscope)

In regard to the specimen No. 4 it can be noted that by its density characteristics it not only differs radically from the specimen No. 3, but is also lighter than the specimen No. 2.

During refractoriness tests calcite of the specimen No. 4 completely dissociated at 950 °C, as evidenced by the results of the X-ray phase analysis of the dissociation products. Only CaO and relicts of quartz and mullite were found by the X-ray analysis.

The main size of globules in the oil shale microsphere sample was 150...250 μm, particles up to 500 μm also occurred, i.e. particles in this specimen were materially greater than in the specimen No. 2.

As to a probable mechanism of the formation of oil shale microspheres it may be suggested that it is in principle the same as that of coal microspheres. But since the mineral part of oil shales contained much less SiO_2 and Al_2O_3, the total yield of the melt was lower, and thus at distension of droplets from the inside thin-walled hollow globules with wall thickness of 0...5 μm were formed. But in this case the gaseous phase in the furnace will be over-saturated with CaO due to the high content of the latter in the initial fuel. It is believed that spherolites of the secondary calcium carbonate are deposited in large quantities on the aluminosilicate walls of the microspheres. This fact is responsible for the predominantly calcite composition of the oil shale microspheres. Therefore it seems as if the secondary calcium carbonate either covered completely the finest aluminosilicate frame (then the particles under the microscope may appear as consisting completely of calcite), or it covered the aluminosilicate frame only partially (expressed in the observed zonal-concentric structure of particles). We would like to point out that in the work [4] also the predominantly calcite composition was determined when studying microspheres of oil shales.

It may be assumed that the microspheres formed when burning oil shales with a higher aluminosilicate content of the mineral part, particularly, the Volga Region oil shales [5], are more close to coal microspheres both in composition and properties.

Accordingly, the results of our comparison studies of microspheres formed during thermal treatment of fuels of different genesis showed the relationship between the composition and properties of final products and the inherent features of initial rocks.

Conclusions

As already noted in the Introduction, the interest taken in the hollow aluminosilicate microspheres is connected with the fact that because of their low density and perfect shape they serve as ideal fillers for a great variety of composite materials. Compositions with these microspheres on the basis of organic and inorganic binders are known [6, 7]. It is worthy to note that they also possess advantages over such aggregates as ashes [8]. The aluminosilicate microspheres were utilized in heat-insulating concretes, facing tiles and other building materials [4].

The aluminosilicate microspheres not only reduce the mass of products, but they also exhibit a number of other valuable properties such as: high compressive and shearing strength, deformation stability, low values of dielectric permeability, high heat-insulating ability and so on. The introduction of the microspheres improves the quality of the composite materials and reduces their costs as compared with the unfilled materials. From this point of view the utilization of the microspheres under consideration appears to be especially promising as they are easily and cheaply attainable. There are suggested to utilize microspheres for making protective shields for oil storages, for columns filling as a sorbing and cleaning material, for filling interwall spaces to form heat-insulating layers, etc [6]. The oil shale microspheres appear to be the most suitable to use for that purpose because they are fragile and cannot be used in forced-action units.

The work carried out has revealed the necessity of the further investigation of the components of ash dumps of heat-and-power plants for gathering information on composition and properties of hollow microspheres, as well as for searching the ways of their commercial production, processing and utilization.

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