Investigation of interactions in the cenospheres-water system

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Abstract. Methods of chemical analysis, conductometric titration and pH measurement were used to study chemical composition and acid-base properties of cenospheres' surface. It has been established, that at the interaction of cenospheres and water anions of silicon acid, hydrocarbontes, cations of calcium, iron and aluminium are transferred to the solution. Recommendations were made regarding the use of cenospheres as a recyclable material for the production of aluminium and in coagulative water purification.

1. Introduction
Ash and slag are 80-90 % SiO$_2$, Al$_2$O$_3$, CaO, FeO, Fe$_2$O$_3$ and MgO. They also include compounds of sulfur, uranium, titanium, vanadium, germanium, gallium, and unburned fuel particles. Ash and slag waste can be used as a raw material to produce construction materials. For example, ash from thermal power stations is used to produce agglomerate, expanded clay and fly-ash gravel.
Ash and slag, formed at burning coal, shale and peat with calcium oxide content not less than 20%, are used as a cementing material in a lime-sand bricks production. At CaO content not more than 5%, they are used as a siliceous aggregate. Ashes containing significant amount of coal particles are used to produce red bricks. Depending on the used clay type, the content of the fed ash can be 15-80%.
Ash and slag waste with CaO content not less than 10% is used as a mineral additive in cement production. The concentration of flammables in these additives should not exceed 5%. Shale ash containing 14% of calcium oxide is used as a cementing material in the production of autoclaved aerated concrete, and ash from coal burning with 3-5% of flammable is used as a siliceous aggregate.
Ash and slag wastes are used in large quantities in road construction and in small quantities in mineral-cotton products manufacture. High content of calcium oxide in the ash of peat and shale allows it to be used for soil acidity reduction by liming. Plant ash contains potassium, phosphorus and other micro-elements; therefore, it is widely used as a fertilizer in agriculture. Certain types of ash and slag wastes can be used to purify waste gases from thermal power stations and industrial sewage.
One of the promising ways to solve the problem of utilizing ash and slag waste from thermal power stations is to produce cenospheres from it. Cenospheres are hollow vitro-crystalline aluminosilicate microspheres formed as a part of fly ash at coal combustion on thermal power stations [1-3]. They accumulate in the form of buoyant sludge in special pits. Cenospheres are good aggregates in manufacturing products from plastics, plaster, ceramic, lightweight cements, and etc. These products exhibit high wear resistance, lightness, high insulation properties, and low cost [3; 4]. Cenospheres can also be used as sorbents for wastewater treatment [5, 6] and conditioning of liquid radioactive waste [7] and in this case it is important to know their resistance to aqueous solutions.

2. Problem statement
The aim of our work was to study the interaction of cenospheres with water. To achieve the stated aim, the following tasks should be solved: 1) investigating chemical composition and surface morphology
of the cenospheres samples; 2) studying acid-base properties of their surfaces; 3) determining the composition of cenospheres' aqueous filtrates.

3. Research technique

Chemical composition of cenospheres' samples was determined by chemical analysis according to GOST 5382-91. The morphology and particle sizes were determined by scanning electron microscopy (SEM) by instrument JSM-6460LV "JEOL".

Acid-base properties of their surface were studied by conductometric titration. Investigated samples were placed in flasks with methylethylketone and after reaching adsorptive equilibrium they were titrated with potassium ethylate solution. According to the measurements, differential curves were built and the concentration of acid-base centers (g-\text{eq}/g) was determined on the cenospheres' surface by the formula:

\[
C_1 = \frac{C_2 V_2}{V_1 m},
\]

where \(C_2\) is a normal concentration of potassium ethylate; \(V_2\) is a volume of potassium ethylate used for titration; \(V_1\) is a volume of methylethylketone solution taken for the analysis; \(m\) is a weight sample of adsorbent.

The interaction of cenospheres with water was studied by chemical analysis. Cenospheres samples (1 g each) were placed in flasks with distilled water and left for 5 days. The resulting solutions were analyzed for the content of silicic acid, ions \(\text{Al}^{3+}, \text{Fe}^{3+}, \text{Ca}^{2+}\) and \((\text{HCO}_3)^{-}\) [8]. Ion meter ANION 4100 was used to determine \(\text{pH}\) value of cenospheres' water suspensions.

4. Experimental results and discussion

Cenospheres' chemical composition studies demonstrated, that they are a complex multi-component system \(\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{CaO} - (\text{Na}, \text{K})_2\text{O} - \text{TiO}_2 - \text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{CO}_2\) with principal content of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) (table 1). According to SEM studies (figure 1) cenospheres have a foam structure, the particle sizes varying from 0.05 to 0.2 mm.

| Component | CO\textsubscript{2} | Na\textsubscript{2}O | Al\textsubscript{2}O\textsubscript{3} | SiO\textsubscript{2} | P\textsubscript{2}O\textsubscript{5} | K\textsubscript{2}O | CaO | TiO\textsubscript{2} | Fe\textsubscript{2}O\textsubscript{3} |
|-----------|-------------------|-----------------|-----------------|-----------------|----------------|-------------|-------|----------------|-----------------|
| % wt.     | 8.4               | 0.5             | 32.5            | 50.5            | 1.8            | 0.6         | 2.6   | 1.3            | 1.8             |

Table 1. Chemical composition of cenospheres.

Figure 1. SEM image of cenospheres.

Changes in \(\text{pH}\) of cenospheres' water suspension with partial concentration 1 g/ 25 ml indicate the alkaline nature of the medium (figure 2). A constant \(\text{pH}\) value is set within 10 minutes.
The results of conductometric titration (figure 3) showed that 0.163 mg-eq/g of centres having the same nature are formed at the cenospheres surface as a result of water adsorption. These can be OH-groups. Chemical analysis of the solutions demonstrated that cenospheres dissolve in water. It was found that the water contained silicon acid (70 mkg/g), ions of Al+3 (8.4 mkg/g), Fe+3 (0.2 mg/g), Ca+2 (3.5 mg/g) and HCO3- (73.2 mkg/g). The water solubility of cenospheres is 76.9 mg/g for the sample. The presence of these ions in the solution in terms of cenospheres chemical composition can be explained by the following reactions.

$$\text{CaO + H}_2\text{O} \rightarrow \text{Ca(OH)}_2$$

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$

**Figure 2.** Changes in pH of cenospheres water suspension over time.

**Figure 3.** Differential curves of conductometric titration performed on cenospheres with potassium ethylate:1 – initial, 2 – soaked in water for 5 days.
When dissolved in water, silicon dioxide forms silicic acid anions that hydrolyze with release of hydroxyl ions:

\[
\text{HSiO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SiO}_3^- + \text{OH}^-
\]

Since aluminum oxide and iron oxide are insoluble in water, while chemical analysis demonstrates the presence of their ions in the aqueous solution, one may suppose that some oxides of Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), adjacent to the surface, form hydrox-penta-aquacomplexes when interaction with water and these complexes move into the solution under the influence of heat motion:

\[
\text{Fe}_2\text{O}_3 + 13\text{H}_2\text{O} \rightarrow 2[\text{Fe}({\text{H}_2\text{O}})_5(\text{OH})]^2+ + 4\text{OH}^-
\]

\[
\text{Al}_2\text{O}_3 + 13\text{H}_2\text{O} \rightarrow 2[\text{Al}({\text{H}_2\text{O}})_5(\text{OH})]^2+ + 4\text{OH}^-.
\]

Thus, interaction of cenospheres with water increases the amount of hydroxyl groups on their surface, and these groups are likely to be connected with atoms of silicon and aluminum.

5. Summary
Cenospheres surface morphology studies demonstrated that they have a foam structure. Their chemical composition is represented by oxides of silicon, aluminum, sodium, potassium, calcium, iron, titanium, phosphorus and carbon. Cenospheres dissolve at interaction with water. The ions of silicic acid, Al\(^{3+}\), Fe\(^{3+}\), Ca\(^{2+}\) and OH-groups enter the solution.

6. Conclusion
High contents of Al\(_2\)O\(_3\) in cenospheres allows them to be used as recyclable material to produce aluminum. Aqueous filtrates of cenospheres can be applied as a coagulant to purify natural and waste water from finely dispersed impurities.

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