Functional Materials on the Basis of Cenospheres

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Cenospheres, that are hollow alumosilicate microspheres from flying ash of power stations, are a valuable industrial product due to a successful combination of their technical and commercial parameters, and can be used at creation of functional materials, including filled composites on the basis of inorganic and organic binders. Implementation of cenospheres is so various that today perhaps there is not an area of engineering or industry where possible implementation of cenospheres or materials with them would not be investigated[1, 2, 3].
Cenospheres have a rich combination of properties[4], and that provides their multifunctionality and makes them rather attractive in use. Variation of the diameter and thickness of the wall of cenospheres enables production of the material with the given structure. Fine-dispersion provides homogeneity of the material in a thin layer. Alumosilicate structure gives inertness and chemical stability to the material. A low density allows us to produce a light and heat-insulating material. A spherical shape and an alumosilicate structure provide high durability of the material in isotropic compression.
A complex of physical, chemical and mechanical properties allows implementing cenospheres in a condition of delivery as a material with an inert low-active surface. However, presence of a large amount of silicon and aluminium oxides within cenospheres enables some changes in chemical properties of the surface in the required direction and transformations of cenospheres into the material with an active surface.
Surface modification makes it possible to strengthen positive properties of cenospheres or to give them new ones that would lead to particular implementation of the material. For this purpose it is necessary to create some functional groups on the surface of cenospheres that would actively cooperate with inorganic or organic binders.
Various methods of surface modification for cenospheres have been studied lately in RFNC-VNIIEF aiming at their further use to create functional materials.
Reactive ability of silicas mainly comes from the presence of SiOH [5] silanol groups on their surface. The surface of cenospheres is fused under the influence of high temperatures, that is it is enriched with Si—O—Si siloxane groups that are much

less reactive that silanol ones. For siloxane groups to be able to interact with the molecules of modifiers, it is necessary to create more rigid conditions of interaction or implement very active modifiers.

Existing approaches to increase reactive ability of the silica surfaces are aimed at its clearing and obtaining maximum concentration of silanol groups. It is necessary to take into account that the surface of silicas is almost always covered with a polymolecular layer of physically adsorbed water, which, as a rule, interferes with modification. Therefore the standard procedure preceding the modification lies in chemical formation of additional silanol groups on the surface of silicas and the subsequent removal of physically connected water. All reactions of the further modification take place with implementation of silanol groups [5].

Because of this, the following ways to increase the concentration of silanol groups on the surface of cenospheres (Table 1) were tested: long processing in boiling water, processing with water steam at an elevated temperature, processing by boiling hydrochloric acid, deposition of active silica. When cenospheres were processed in boiling water during 60 hours the surface was cleaned from impurities and its re-hydroxylation [5, 6] took place. The same processes occurred at processing of cenospheres with water steam at the temperature of 180-200°C during 2 hours followed by drying at 150°C [7] and at processing in 0,1n and 1n solution of HCl at 100°C.

Table 1.
Concentration of SiOH groups at cenospheres.

Cenospheres	Specific surface, m^2/g	Concentration of SiOH groups/nm^2
Initial	0,923	1,96
Treated during 60 hours in boiling water	0,768	2,49
Treated with water steam	0,845	6,07
Treated in 1 n HCl	0,733	3,90
Treated in 0,1 n HCl	0,669	2,19
Coated with active silica	72,680	7,45

Concentration of silanol groups was determined with the help of chromatography by the number of methane produced during surface treatment of cenospheres with a dimethylzinc tetrahydrofuran (THF) complex [8]:

$$\equiv Si–O–H + Zn(CH_3)_2 \cdot 2THF \rightarrow \equiv Si–O–Zn–CH_3 + CH_4 + 2THF$$

Results of measurements show that the selected methods of treatment make it possible to increase concentration of reactive silanol groups on the surface of cenospheres.

On the basis of the modified cenospheres and a cement binder there was developed a promising a heat-insulated construction material called "Spherobeton" (“spherical concrete”) with the density of 0.8-1.0 g/cm^3 and the compression strength up to 21 MPa.

Implementation of cenospheres in the initial state for introduction into the matrixes of the inorganic nature,(cement in particular) is low effective because of low adhesion interaction of the surface of cenospheres with a cement clinker. The surface of cenospheres has low roughness, it is hydrophobic, so a potential contribution of a

mechanical component into the cement bond test with cenospheres can't be considerable.
To create "Spherobeton" there were used cenospheres with the active surface produced using different treatment techniques mentioned in Table 1.
Reactive silanol groups on cenospheres are significant for chemical interaction with components of Portland cement clinker. A proton of a silanol group is of low-acid character and can react and exchange with Ca^{2+} и Mg^{2+} cations.
One of the main properties of flying ash (including cenospheres) is its capability to react with calcium hydroxide, which is produced during cement hydration [9]. Products of hydration are calcium hydrosilicates and hydroaluminates.
Pozzolanic reaction of ash in concrete starts with the adsorption of calcium hydrate produced during hydrolysis of minerals, which are silicates of Portland cement, that happens on the surface of cenospheres. Between the coating of calcium hydrate and cenospheres that contain functional groups of SiOH thin water layers appear 0.5-2 microns thick, through which ions of calcium come to the surface and interact with its active components (Figure 1).

$$(-Si{-}O{-}H)_2O + 2Ca(OH)_2 \rightarrow {=}O(-Si{-}O{-}CaOH)_2 + 2H_2O$$

$$=Al{-}O{-}H + Ca(OH)_2 \rightarrow =Al{-}O{-}CaOH + H_2O$$

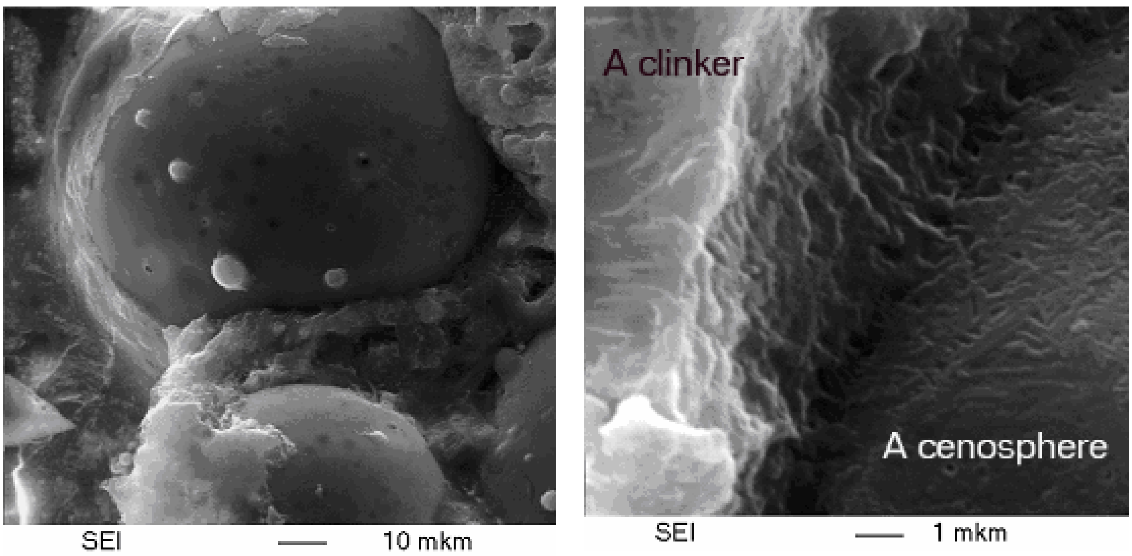

Figure 1 – Interaction pattern of cenospheres with a clinker.

Experimental verification of the adhesion interaction of cenospheres with inorganic binders was done using Portland cement of M-400 D 20 brand (State Standard

GOST 10178-85) and cenospheres from Cherepetskaya hydro-electric station. Most characteristic results are given in Table 2 and in Figure 2. All samples were made of Portland cement, and the cenospheres were taken in ratio of 60 wt % to 40 wt % (1000 g of cement and 668 g of cenospheres). The samples were tested for their static bend and pressure. A bending test was conducted in compliance with State Standard GOST 4648-71 (ST SEV 892-78) using samples 40×40×160 mm lying on two supports and loaded for short time in the middle between two supports. The distance between the two supports made l_0=100 mm. Here, bend breaking point σ_{Up} and the value of sagging ε_z at destruction of the sample were determined (Table 2). Compression tests were done in compliance with State Standard GOST 4651-82 (ST SEV 2896-81)using samples 40×40×62 mm. During the tests there was determined an ultimate stress at compression (σ_{Bp}) and strain at destruction (ε_c). During compression tests the fracture energy of the material was also determined. Table 2 gives the values of the work accomplished with the sample before pressure σ_{Bp} (A_{total}), and the values of the work calculated at the stage of destruction of the sample when the pressure value of 0,7σ_{Bp} (A_{total}) was reached.

Table 2.
Strength of “SPHEROBETON” at pressure and bend.

Number of the “SPHEROBETON” sample with cenospheres	Density, g/cm^3	Bend		Pressure			
		σ_{Up}, MPa	ε_z, %	σ_{Bp}, (MPa)	ε_c, %	Work, J	
						$A_{\sigma Bp}$	A_{total}
№ 1 (initial)	0,92	4,10	1,01	8,22	2,7	8,6	8,2
№ 2 (treated during 60 h by boiling water)	0,84	3,49	0,91	9,7	2,8	1,0	8,5
№ 3 (treated in 0,1 n HCl)	0,80	1,89	0,67	8,36	1,9	,1	8,7
№ 4 (treated in 1n HCl)	0,82	2,87	0,56	4,4	1,8	3,3	2,6
Foam concrete	0,84	0,51	0,43	3,27	1,0	,1	,8

Table 2 also gives tests results for light industrial material called “Penobeton” (foam concrete) for comparison; it is produced by creation of a cell structure along all the volume of the product at the expense of uniformly distributed air pores

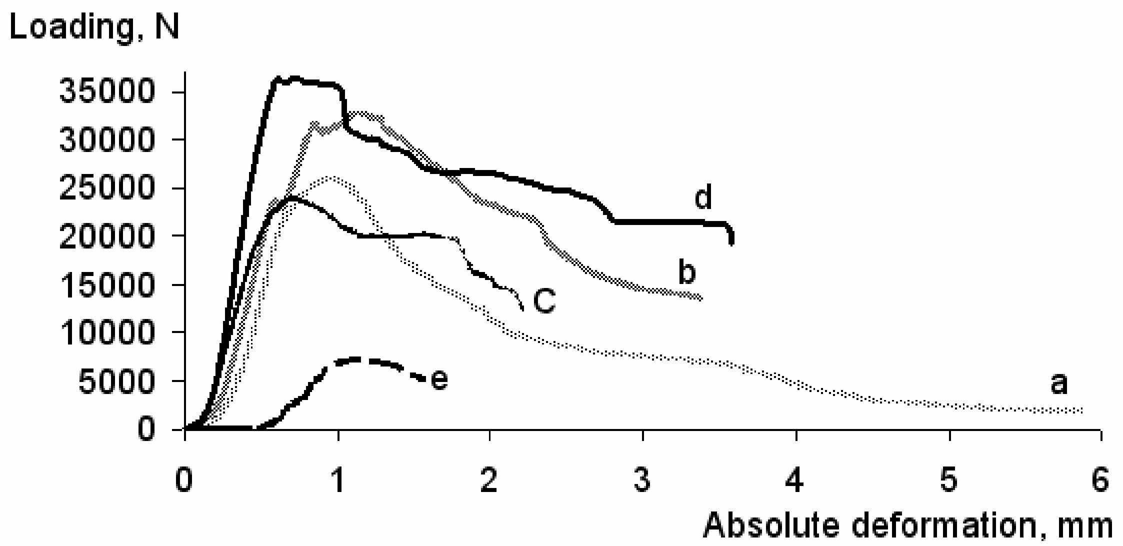

Fig. 2. Compression diagram for samples of “SPHEROBETON” and Foam Concrete.

a – spherobeton № 1
b – spherobeton № 2
c – spherobeton № 3
d – spherobeton № 3
e - penobeton

So, treatment of the microsphere surface with 1n HCl and 60-hour boiling changed the pattern of interaction of the clinker with microspheres. Compression strength σ_{Bp} with the cenospheres treated by boiling grew by 2.4 times and in the case of cenospheres treated with 1n HCl it grew by 1.8 times with some reduction of bend strength σ_{Up} (by 15 % and 30 %, respectively).

The produced results let us suppose that a new thermo-insulating and construction materials is developed on the basis of cement and modified cenospheres, which can be used in low industrial and civil construction. Besides, such material can be implemented in creation of protective layers in special-purpose containers, for example to transport and store fissile materials.

Composites on the basis of organic binders and filled with the modified cenospheres are also being developed and studied. Functional materials on the basis of cenospheres and polymers may be widely used in many areas of industry [3]. Introduction of cenospheres into polymers allows changing the properties of the composite in the needed direction not increasing the density of the produced material.

The material of floor cover with antiskid properties for means of transport is developed on the basis of polyvinylchloride filled with modified cenospheres. First of all it was found out that cenospheres in their initial condition have low adhesion with polyvinylchloride (PVC) used for these purposes, so later there was studied the material where there were introduced cenospheres finished with γ-aminopropyltrietoxisilan (AGM-9).

The performed research has shown that introduction of the finished cenospheres increases the compression strength and bend strength of the composite on the basis of PVC (see Table 3 and Figure 3).

Table 3.
Bending tests results for PVC filled with AMG-9-finished cenospheres.

Material	Density of the material ρ, g/cm^3	Bending stress $\sigma_{и\ 1.5h}$, MPa
Initial PVC	1,16	0,34
PVC + 5% cenospheres	1,12	0,35
PVC + 10% cenospheres	1,07	0,43
PVC + 15% cenospheres	1,03	0,56

Tests for static bending were performed using UP 5047-50 machine in compliance with State Standard GOST 4648-71 (ST SEV 892-28). The idea of the method is in the following. The sample to be tested lies freely on two supports; it is loaded in the middle between the two supports for short time. Here, flexural stress $\sigma_и$ at the given value of the sagging equal to 1,5 thickens of the sample is determined.

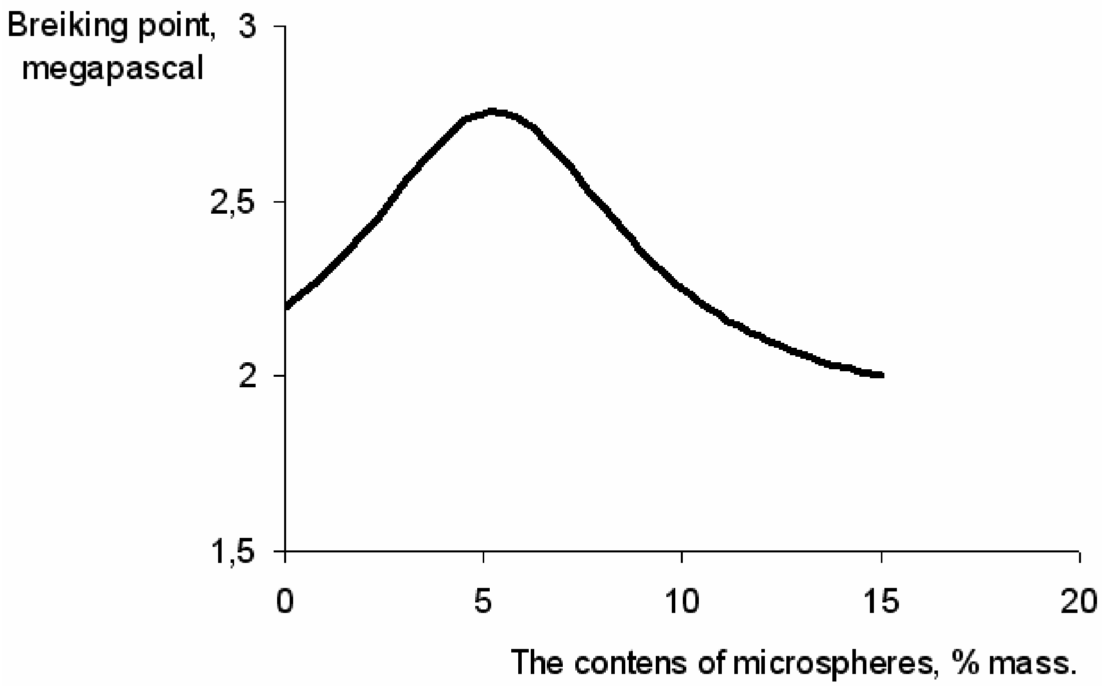

Figure 3. Ultimate stresses at compression σ_c as a function of the percentage of cenospheres.

Finished cenospheres, as a filler of polyvinylchloride, are a strengthening component. It is well illustrated by the concentration dependency of the compression strength on the mass content of the filler. So, maximum compression strength of polyvinylchloride is observed at 5% wt. content of the finished cenospheres, that is much more (28% more) than the strength of the not-filled material.
Samples of the sheet material containing 5 wt % of the finished cenospheres 180-300 microns in diameter were tested to verify their compliance with the requirements for the floor coating (cover). As for all physical and mechanical parameters, positive results were obtained (Table 4).

Table 4.
Physical and mechanical parameters of the sheet material.

№ п/п	Tests	Results
1	Shore hardness, units of scale	84-85
2	Breaking strength, MPa	20
3	Breaking percent elongation, %	215
4	Shrinkage in the longitudinal direction, %	0,5-1,0
5	Water absorption, %	0,026
6	Density, g/cm^3	1,37
7	Abradability, microns	32
8	Residual deformation, mm	0,14
9	Frost-resistance	Preserved flexibility at -50°C

Another way to use cenospheres is creation of sorbents on their basis to clean liquid radioactive wastes. The synthesized sorbents on the basis of cenospheres are easily loose granules, the surface of which is modified by various inorganic compounds with ion-exchange properties [10]. First of all, they are ferrocyanides of copper, iron, nickel, cobalt, zinc, vanadium, tungsten and zirconium, monoxides of manganese and zirconium, and tungstate zirconium.
Cenospheres contain chemically active groups on the surface that make it possible to fix these compounds on it. And the advanced enough and accessible surface of the cenospheres-sorbents has high kinetic characteristics and allows carrying out the process of sorption both in static and dynamic modes. The synthesized sorbents on the basis of cenospheres can be used for cleaning from radioactive nuclide of natural water sources and technological solutions in a wide pH range and salt background. The basic characteristics of cenospheres-sorbents are given in Table 5.

Table 5.
Main parameters of sorbents.

Parameter	Value
Inorganic modifier (wt. %)	2 – 5
Breakup, microns Average size, microns	20 – 300 90
Packed density, g/cm^3	0,35
Isotrope compression strength (50% level), Mpa	30
Floatation, %	~95
Radiation resistance, Gy	10^8
Operating temperature, °C	≤ 100
exchange capacity for radioactive nuclide, mg/g 1. static: Cs^{137} Co^{60} $Eu^{152, 155}$ Ce^{144} 2. dynamic Cs^{137}	 10 – 30 1 – 5 0,5 – 1 0,2 – 0,5 5 – 15

Sorbents are not toxic, not combustible, not explosive and are characterized by high chemical stability in alkaline and sour solutions, in the water and in an organic environment. They show high selectivity to radioisotopes of Cs, Co, Ce, Eu and other radioactive nuclides. Cenospheres, modified by a number of ferrocyanides appeared to be effective in relation to isotopes of Am, Np, Pa as well. At the same time, mechanical mixtures of sorbents have recommended themselves well. Using synthetic sorbents in various combinations it is possible to clean successfully the solutions from fission products and trans-uranium elements.
Sorbents have density less than 1 g/cm^3, and respectively good buoyancy (floatation), and can be placed on the surface of reservoirs, storing ponds, pools for the irradiated fuel. Besides sorbents are completely compatible with cement binders, and that ensures the possibility of their cementation for long disposal.
So, the cenospheres modified with inorganic ion-exchange compounds have good sorption parameters and physical and chemical stability of a natural mineral, they are rather manufacturable and can be used successfully for cleaning liquid radioactive wastes of various levels of pollution. Implementation of cenospheres as a carrier of sorbents provides not only technical advantages, but is also an effective ecological solution as in this case wastes of power-engineering industry are used for disposal of wastes of nuclear industry.
Thus, relying on the existing understanding of adhesive interaction of two and more component systems there were suggested technological ways of activation of the surface of cenospheres by creation of reactive groups on it. Changing the character of modification of the surface of cenospheres it is possible to expand areas of their implementation considerably. The above given examples of the created functional materials evidently confirm this opportunity.

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