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Research and Utilization of Silica from Hydrothermal Solution

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ABSTRACT

Hydrothermal solutions contain the colloidal silica forming as a result of polycondensation of the molecules of orthosilicic acid. By ultrafiltration membrane concentration of solutions of Mutnovsky hydrothermal field (South Kamchatka, Russia), silica sols were obtained. We determined silica particles sizes, surface square and concentration of impurities. Utilisation of silica sols produced from hydrothermal solutions for concrete characteristics have been researched.

1. INTRODUCTION

Colloidal silica particles appear in a natural hydrothermal solution due to polycondensation of orthosilicic acid molecules (OSA) coming under the dissolution of silica-alumina minerals containing in the rocks under the increased pressure and temperature in deposits interior. When the solution raises to the surface the temperature and pressure reduce, the solution becomes supersaturated and nucleation and polycondensation of OSA molecules take place in it and they cause to the forming of colloidal silica particles of spherical form with the radii of 5-100 nm. Other components are also in the initial solution in addition to silica; their concentration is shown in table 1.

Nucleation and polycondensation of silicic acid molecules take place due to condensation of silanol groups, siloxane bonds formation and partial dehydration on the following reactions:

$$\begin{array}{ccccc} OH & & OH & & OH \quad OH \\ | & & | & & | \qquad | \\ OH\text{-}Si\text{-}OH & + & OH\text{-}Si\text{-}OH & \rightarrow & OH\text{-}Si\text{-}O\text{-}Si\text{-}OH + H_2O \\ | & & | & & | \qquad | \\ OH & & OH & & OH \quad OH \end{array} \quad (1)$$

$$Si_mO_{m-1}(OH)_{2m+2}+Si_nO_{n-1}(OH)_{2n+2}\rightarrow Si_{m+n}O_{m+n-1}OH_{2n+2m+2}+H_2O. \quad (2)$$

Finite sizes of silica particles first depend on the temperature and pH under which nucleation and polycondensation of OSA take place. Temperature increase of polycondensation results in increase of particles finite sizes. pH reduction results in increase of particles finite sizes too. During polycondensation the temperature was varied within the range from 20 up to 72 ^{0}C, pH – from 9.2 up to 4.0. At the same time finite mean radii of silica particles were within the range from 5 up to 100 nm subject to the temperature and pH.

Table 1. The concentration of the main components of the initial hydrothermal solution

Component	Na^+	K^+	Li^+	Ca^{2+}	Mg^{2+}	$Fe^{2+, 3+}$	Al^{3+}
Concentration, mg/dm^3	282	48.1	1.5	2.8	4.7	<0.1	<0.1
Component	Cl^-	SO_4^{2}	HCO_3^-	CO_3^{2-}	H_3BO_3	SiO_2	Cl^-
Concentration, mg/dm^3	251.8	220.9	45.2	61.8	91.8	780	251.8

To develop of the technology of membrane silica concentration the main stages must be worked out: nucleation and polycondensation of orthosilicic acid (OSA), sol filtering in membrane facilities and sol cleaning from electrolytes, sol stabilization (addition of stabilizing additives).

2.EXPERIMENTS ON MEMBRANE CONCENTRATION

After the completion of OSA polycondensation of hydrothermal solutions and formation of silica colloidal particles of given sizes the water removal was made by membrane filtration with a two-stage scheme discrybed in (Potapov V.V. et al., 2008; Generalov M.B., 2006; Brazhnikov S.M., Generalov M.B., Trutnev N.S., 2004; Generalov M.B., Trutnev N.S., 2006; Onopko K.D., Platov I.V., Trutnev N.S., 2008).

Under ultrafiltration silica colloidal particles were stopped by the membrane layer and water molecules and ions of dissolved salts passed through this layer. Thus, the electrolytes content reduces as silica was concentrated, it provided sols stability. Colloidal particles were concentrated in aqueous medium, at the same time SiO_2 content increased up to 10-62.2 mass %, and water content reduced up to 90-37.5 mass %.

The possibility of use of the main membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis for concentration of hydrothermal solutions were studied. The experiments with membranes showed the ultrafiltration advantage for the obtaining of stable concentrated silica sols. When nanofiltration and reverse osmosis were used both silica concentration and mean ions content increased, and the obtained sols were unstable. Microfiltrational membranes have a low selectivity on silica colloidal particles and they can't be effective during the initial concentration stages under a low SiO_2 content. So ultrafiltration or ultrafiltration with microfiltration were used to store a considerable sols volume. Ultrafiltration was used first, then during the later stages microfiltration was used. The ultrafiltration membranes of capillary type were used, the material of membrane layer was made of polyethersulfone and polyacrylonitrile. The diameters of the membrane layer pores were within the range of 2-100 nm. Ceramic microfiltration membranes were of tube type, mean pores size was 70 nm (0,07 micron). The concentration was made in three stages: SiO_2 content from 3 up to 10 g/dm^3 was obtained during the first stage, during the second stage it was 10-30 g/dm^3, during the third stage - 100-940 g/dm^3 (10.0-62.25 mass %). During the first stage the filters of a large standard size were used, during the second stage – the filters of a mean standard size, during the third stage – the filters of a small standard size. The sols density was in the range of 999-1510 g/dm^3, the dynamic viscosity was 1-150 mPa·s, diameters of silica particles were 5-100 nm, the particles zeta-potential was from -25,0 up to - 56,0 mV.

Electric power consumption E_m to obtain mass unit of silica consists of power consumption for pumps drive of membrane unit for sol concentration Power consumption for sol membrane concentration depends on selectivity of ultrafiltration membranes and process temperature. Power consumption for ultrafiltration membrane concentration was 0.18 - 1.0 kW·h/kg.

3. EXPERIMENTS ON USING OF SILICA FOR IMPROVEMENT OF THE KERBSTONE PRODUCTS

The aqueous medium containing orthosilicic acid H_4SiO_4 in concentration range of 600-800 mg/dm^3, was guided from the separators of geothermal power plant in reinforced concrete tank (cooler), where at a temperature 63°C occur a polycondensation of H_4SiO_4 with the formation of the silica particles. After cooling the separat was filed in baromembrane installation for concentration and to obtain a stable aqueous silica sol. Initial separat had the following characteristics: salinity - 702 mg/dm^3; pH = 9,73; the total content of SiO_2 C_t = 716 mg/dm^3;

Table 2. Characteristics of sol.

Appearance		Opalescent liquid
Density, g/dm^3		1072
Content of SiO_2, g/dm^3		115
pH		9,1
Material composition		Amorphous silica
Chemical composition, mass %	SiO_2	94
	CaO	0,9
	Na_2O	0,13
	Al_2O_3	0,5
	Loss on ignition	4,2
Content of the aqueous solution, g/dm^3		957

Characteristics of the silica sol are shown in table 2. The pressure difference across the membrane layer was 0.14 MPa, flow rate of solution passing through the membrane installation - 1.2 m^3/h. At the first stage of concentration was obtained silica sol with a density of 1015-1022 g/dm^3, C = 28-40 g/dm^3. In the second stage the density of sol increased to 1070 g/dm^3, and a - up to 115 g/dm^3.

In the conditions of the local climate of considerable interest is improvement of characteristics of kerbstone products BU 300.30.32: compression strength, water-resistance, freeze-thaw resistance, crack growth resistance, and reduction of porosity of the external surfaces. In order to improve the crack growth resistance and reduce porosity of the external surfaces of BU 300.30.32 products the Concrete Product Plant of Kamchatzhilstroy Co. modified M400 concrete by introduction of SiO_2 additive in the amount of 0.05 % of weight of the cement consumption if form of sol.

Composition of the concrete mix of the set quality was selected in accordance with state standart (GOST 27006) and account of standart GOST 8829-94 requirements to the concrete products. Two mixes, 1.5m^3 each, were in turn prepared in a fully automated concrete mix installation. As a binding agent Portland 400 cement was used in quantity 1560 kg.

Preparation of a concrete mix consisted in dispensing and mixing of its component materials. Its equipment incorporates JS1500 two-shaft horizontal mixer and automatic control, which ensures simultaneous and automatic dispensing of the inert materials. The central control system is a programmed controller with automatic or manual control and trouble detection function. Additional computer control is possible.

There is also a function of preservation of the set formulas and possibility of formation of detailed reports reflecting productivity with verification of the intervals and grades of concrete. Sand with crushed rock were delivered by an inclined conveyer, cement – by a screw conveyor. A water supply system with a tank ensured an uninterrupted water supply.

During mixing it is necessary to ensure a continuous enveloping of the filler grains' surface by the cement paste and a uniform distribution of the solution in the mass of a coarse aggregate. As a result the mix should have such uniformity, that all its mass would have an identical composition and uniform distribution of components. Vibro agitation in a forced mixer is carried out by means of rotating blades. To a great extent the quality of mixing depends on its duration (state standart GOST 7473-2010).

Transportation of a concrete mix to the place of formation of products should exclude completely any chance of its loss and stratification, loss of the cement milk, and should also prevent any derangement of the uniformity of the mix. During transportation the mix should be protected from the atmospheric precipitations and harmful influence of wind and solar beams. Otherwise its quality can decrease considerably notwithstanding accurate dispensing of the components and correct preparation of a mix.

Formation of products is a very important stage of manufacture of kerbstone products BU 300.30.32. The adopted method of formation ensures the set dimensions of the products, at that, the concrete must have a uniform strength in any section of the product. During the product formation process the reinforcement must not be shifted from the design positions. It is also desirable to eliminate the additional operations related to finishing of the product faces or reduce their number to a minimum.

Package horizontal forms (8 pieces in each) were applied by the number of the simultaneously produced products. A form consists of a pallet with steam jackets. Its design features include folding pivot-hinged opening boards and perimeter rigidity edges, allowing it to sustain without deformations the efforts arising during the formation and transportation of products. Nonprestressed reinforcement was installed in the required positions in a form without fixation. In order to avoid warps of forms during transportation of the formed products by cranes, cross bars with four hooks were provided.

Most methods of product formation are based on the fact that a concrete mix settles and thickens under the influence of vibration. Vibroplatform was used with the subsequent steaming of the products. When a product is taken out of the form, porosity is visible on its external surface.

Unloading of 3 $м^3$ of M400 modified concrete (silica SiO_2 in the amount of 0.05 % of the mass of the cement consumption) from a mixer was distributed in 2 cartridges with 8 forms in each. After formation without thickening on a vibroplatform the products remained in the shop during 12 hours in natural drying conditions and without protection from the formation of shrinkable cracks and maintenance of certain levels of temperature and humidity for gaining of strength by concrete. It was established that the external surface was smooth, without any popouts. Compressive strength of kerbstone product BU300.30.32 was equal to 15.5 MPa.

In general a product with SiO_2 additive (in the amount of 0.05 % of the mass of the cement consumption) has better characteristics than a product without the additive. This was proved in the laboratory conditions and when the product was installed on an asphalt road.

CONCLUSIONS

Ultrafiltration membranes have selectivity on colloidal silica about 1.0 without preliminary addition any coagulants and low selectivity on silicic acid molecules and ions. Therefore it is possible to get by ultrafiltration the solution with high SiO_2 concentration and low concentration of impurity ions – Na^+, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+, 3+}$, Al^{3+}, SO_4^{2-}, Cl^- . Thus, ultrafiltration has got the advantages before other membrane processes when the problem of obtaining of silica concentrated water sols is solved. Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest SiO_2 content.

One of the tendencies of silica sols use is their application as modifiers to improve the characteristics of concrete building materials: compression strength, water-resistance, freeze-thaw resistance, crack growth resistance, and reduction of porosity of the external surfaces.

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