Protolytic properties influence of the dispersion medium on the process of silicic acid polycondensation

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Abstract. The paper presents a procedure for the preparation of sodium polysilicate from silica hydrosol for use as an additional binding agent in the production of composite materials based on wood matrix. It is proved that 3-stages mechanical activation of low quality sand makes it possible to obtain silica particles with sizes on the upper boundary of the ultradispersed range (100 nm). The effect of dimensional characteristics, the zeta potential of the surface of silica particles, and the protolytic properties of the dispersion medium on the gel formation process is studied. The obtained dependence of the zeta potential of particles from the pH of diluent has shown that in acidic region have equivalence point and a low zeta-potential area in which the colloidal particles become unstable (which may lead to rapid gelification in the system). It is proposed to accelerate the process of depolarization of silica particles by maintain the pH value of the dispersion medium equal to 2-4, this will quickly produce a large yield of gel-like sodium polysilicate.

1. Introduction
It is known the property of colloidal silica to form a gel when interacting with acids, alkalis and the simplest alcohols [1-3]. Moreover, along with an increase in viscosity of the system and binding of particles occur imparting heat resistant properties to the material [4, 5]. In turn, this feature of colloidal silica allowed it to be used both for the production of new heat-shielding, fire-resistant nanocomposites, and for modifying the already known and traditional materials for the construction field [6, 7]. The regulation of the gelling process, in our opinion, in most cases should be limited to controlling the protolytic properties of the solvent (dispersion medium), which largely determine the aggregative stability of the dispersed phase substance. Therefore, the research task, described in this paper, was the study of the dispersion medium pH influence on the process of silicic acid polycondensation.

The appearance of a double electrical layer on the particles of the silica hydrosol is due to the ionization of their surface. The SiO2 molecules on the surface of the particles interact with the dispersion medium, they hydrate and form a silicic acid which is capable of ionizing:

\[ \text{H}_2\text{SiO}_3 = \text{SiO}_3^{2-} + 2\text{H}^+ \]

In this case, the silicate ions remain on the surface of the particle, which causes its negative charge.

\[ \{m[\text{H}_2\text{SiO}_3]n\text{SiO}_3^{2-}2(n-x)\text{H}^+\}^{2x+}2x\text{H}^+ \]
As the acidity of the dispersion medium increases (for example, due to the addition of $HCl$) on the surface of the nucleus excessive amounts of protons ($H^+$) are sorbed, because, according to the Fajans-Paneth rule, $H^+$ ions are part of the crystal lattice of the nucleus. As a result of this adsorption, excess surface energy is compensated at the interface between the phases in the "silicic acid" - "aqueous $HCl$ solution" system. The nucleus together with the adsorbed proton layer forms a positively charged aggregate. A part of the counterions ($Cl^-$) is adsorbed on the surface of the aggregate. The micelle formula in this case:

$$[n(H_2SiO_3)nH^+(n-x)Cl^-]^{+x}xCl^-$$

Under certain conditions (heating, mixing, addition of other electrolytes), the adsorption layers of ions on the nucleus are partially or completely destroyed. In this case, the compensation of excess surface energy at the interface between the phases occurs by aggregation (agglomeration of silicic acid particles). This process, leading to the coarsening of the phase particles without precipitation, is characterized by gelling.

With the addition of $NaOH$, it is possible to form a sodium silicate $Na_xSiO_4$ (soluble in water) as a solid phase. Further, due to hydrolysis, colloidal solutions are formed from the true solutions. Subsequently, a white precipitate is deposited from such systems.

2. Materials and methods

2.1. Materials
Dusty polymineral quartz-feldspar quarry sand from the Kholmoigorskoie deposit (Arkhangelsk region) was chosen as an object of study.

The sodium liquid glass with a density of 1.36 g/cm$^3$ and a silicate module of 2.6 was used for sodium polysilicate synthesis.

2.2. Methods
The mineral composition of sand was determined using X-ray fluorescence spectroscopy using the Shimadzu EDX-800 HS spectrometer.

The sand was mechanically activated in three stages: by mechanical dry grinding for 30 minutes at a rotor speed of 420 rpm by 2 cm large grinding balls in the Retsch PM100 planetary ball mill at the first stage; by mechanical wet grinding for 30 minutes at a rotor speed of 420 rpm by grinding balls of 1 cm in diameter in the Retsch PM100 planetary ball mill at the second stage; by mechanical wet grinding for 10 min at a rotor speed of 16000 rpm in the MK module (a colloid mill) of the Magic Lab portable mini lab equipped with the Micro-Plant attachment (product circulation equipment) at the third stage. The synthesized concentrated silica sol was diluted with water to the 16 Wt% silica hydrosol with a density of 1100 kg / m$^3$.

The silica particle size and their zeta potential were determined using the Delsa Nano C analyzer by photon-correlation spectroscopy and electrophoretic velocity measurement, respectively.

$NaOH$ and $HCl$ aqueous solutions were added to vary protolytic properties of the dispersion medium in the obtained silica sols. The Expert-001-3 fluid analyzer was used for pH control.

Sodium polysilicate was synthesized as follows: liquid glass was diluted with water to obtain a 20% aqueous solution of sodium silicate with a density of 1250 kg/m$^3$; then silica hydrosol was added at the ratio of 1:1.5 under continuous stirring at 95°C for 1 hour and aging at this temperature for 30 minutes.

In order to study the microstructure, gel test samples were placed on a specimen slide and left for 24 hours to self-level the surface. In total, 12 specimen samples were prepared for the study using the LOMO MICMED-6 light microscope. Macro and micrographs were made using the Nikon COOLPIX P500 digital camera.
3. Results and discussions

Table 1 shows the mineral composition of sand from the Kholmogorsko deposit expressed as oxides.

| Mineral composition of sand expressed as oxides. | The content of oxides, Wt. % |
| SiO₂ | MgO | Al₂O₃ | Na₂O | Fe₂O₃ | CaO | K₂O | other oxides |
|------|-----|-------|------|-------|-----|-----|-------------|
| 77.48 | 1.80 | 12.13 | 2.76 | 1.61  | 1.45| 2.09| 0.68 |

As is seen from the table, the SiO₂ content in sand is less than 90%, which indicates a low raw material quality. In addition, a significant amount of Al₂O₃ is observed, which indicates clay (aluminosilicate) inclusions.

Figure 1 specifies the average particle sizes of mechanically activated finely dispersed sand.

![Figure 1. Volume distribution of silica particles by size.](image)

The obtained data show that mechanical activation of sand makes it possible to obtain silica particles with sizes on the upper boundary of the ultradispersed range.

Figure 2 shows the functional relation between zeta potential change and pH of medium.

![Figure 2. Functional relation between zeta potential change and pH.](image)
It is known that the aggregative stability of colloidal silica is strongly influenced by the electrostatic barrier which in turn depends on the zeta potential level of particles. Therefore, an accelerated particle growth and subsequent gel forming should be expected in the system under low absolute values of $\zeta$.

According to experimental data, higher pH brings zeta potential of particles beyond boundaries of the low electrokinetic potential zone ($\zeta = \pm 30$ mV) where colloidal silica particles begin losing their aggregation stability according to the working hypothesis. In order to confirm this assumption, the particle sizes in suspensions were measured repeatedly after 24-hour aging. The experimental results are shown in figures 3, 4.

![Figure 3. Volume size distribution of silica particles after 24-hour aging (pH 2.4).](image1)

![Figure 4. Volume size distribution of silica particles after 24-hour aging (pH 9.0).](image2)

Repeated measurement results show that the particle size in the silica sol increases both in acidic and alkaline dispersion medium, however, particle size characteristics at pH = 2.4 are significantly higher than at pH = 9. In addition, particles of the original ultradispersed and finely dispersed range in amounts of 7.1% can be observed in the latter.

In contrast, the large sedimenting white flocks and residue visible to the naked eye were found in silica sol at pH = 2.4. This gel-like residue was extracted from the sol and moved to a specimen slide by a sampler for microstructure study (see figure 5).

The remaining samples with different pH values were used for sodium polysilicate synthesis. Upon synthesis completion, polysilicate identification, and further free water removal, all samples had gels formed in them at different times (see figure 6).
4. Conclusion

Thus, it can be concluded based on the conducted studies that low grade silica-containing raw materials can be used to produce finely and nanodispersed silica. In order to accelerate the particle depolarization process it is necessary to maintain the pH value of the dispersion medium in the suspension equal to 2-4.

References

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