

## Effect of thermal conditioning of silica-sodium glass on the kinetics of zeta potential changes during soluble sodium silicate gelation

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**Abstract.** The article describes the results of Zeta potential changes in the system „soluble sodium silicate - ester” according to the time of gelation. It was found out that the time of thermal conditioning of silica-sodium glass is important in terms of nanostructure elements stability of the soluble sodium silicate. Stability characteristics of these elements can affect the binding characteristics of silicate binder-quartz system, and thus their strength properties at ambient temperature.

**Key words:** soluble sodium silicate, silica-sodium glass, Zeta potential, thermal conditioning.

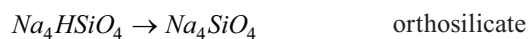
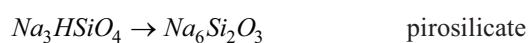
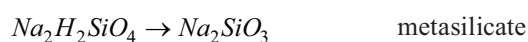
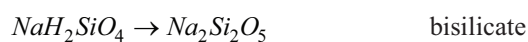
### INTRODUCTION

Soluble sodium silicate, or an aqueous solution of sodium silicate, is one of the oldest inorganic binders used in various industries. In the foundry it is a binder used in the production of the molding sands. The advantage of molding sands with the soluble sodium silicate is a good heat resistance of moulds and cores, which is especially important for medium and heavy cast iron alloy, and no emission of toxic gases in the preparation of the moulding sands, pouring forms and removing casting [4-10,11-17,19-23]. In addition to these environmental and technological considerations, economic considerations are also important. Molding sands with soluble sodium silicate are much cheaper than the moulding sands with the binder resin. Apart from the obvious advantages of moulding sands with the soluble sodium silicate, however, have several disadvantages such as too much residual strength, lower primary strength and tendency to formation of sinters. The sintering process can be reduced by reducing the amount of binder in the moulding sands, but this reduction is possible only if the improvement of its binding properties occurs.

Soluble sodium silicates usually form stable aqueous solutions, but from a chemical point of view, generally do not have a clear composition. They form durable com-

posite structures, which are defined complexes of sodium silicate and silicic acid. Their composition varies and ranges from 4 moles of  $\text{SiO}_2$  per 1 mol of  $\text{Na}_2\text{O}$  and 1 mol of  $\text{SiO}_2$  to 4 moles of  $\text{Na}_2\text{O}$ . Thus, the general formula of sodium silicate can be written as  $x\text{Na}_2\text{O} \cdot y\text{SiO}_2$ , and values for  $x$  and  $y$  vary from 1 to 4 [18].

The main parameter that allows to distinguish between the different sodium silicates is the silica module, which is the molar ratio of silicon dioxide contribution to sodium oxide in the considered system. There are known also sodium silicate crystal structure. They derive from a hypothetical silicic acid of the formula  $\text{H}_4\text{SiO}_4$ .



Some of them are in the form of readily soluble hydrates [3]. It may be noted that while the upper limit of module for soluble sodium silicate is 4, a sodium silicate for the defined limit value is the module 2. Understood is accepted hypothesis that sodium silicates, especially in aqueous solution, represent complex of silica sodium oxide, formed from simple silicates of module to 2 and silicic acid. The structural design of sodium silicate in aqueous solution is very complex due to the presence of hydroxyl ions and the adoption by the tetravalent silicon in the silicate ions sixth coordination number. Change in coordination number from 4 to 6 is facilitated by the presence of free silicon 3d orbitals, able to accept electron

pairs. This gives the connections of silicon (in particular with oxygen), specific properties. Investigation of properties of aqueous solutions of sodium silicate, such as conductivity, refractive index, boiling point and freezing point, confirmed their colloidal nature. The presence and frequency of polysilicate ions (colloidal particles) emerges clearly from the module silicate equal 2. In the sodium silicate solutions with module 2 there are monosilica ions  $[H_3SiO_4]^-$  - and bisilica ions  $[H_4Si_2O_7]^{2-}$ , and in solutions with higher modules there are a mixture of polysilicate ions with higher degrees polycondensation. Especially at higher concentrations of  $SiO_2$  and the modules  $M > 2$  identified the polymeric units containing from 4 to 8 or even 12 Si atoms [1-3].

In the solutions of sodium silicate, there is a progressive aggregation of silica from the molecular silicate to the colloidal and eventually solidified gels covering the entire solution. The possibility of interference with the rate of establishment of equilibrium in the aggregate, is used on an industrial scale to manufacture all kinds of binders and adhesives [1].

Examination of concentrated solutions of sodium silicate with module 2 to 4 by  $^{29}Si$ -NMR method [3] showed, that the number of groups  $Q^0$ ,  $Q^1$ ,  $Q^2$  decreases with increasing module, where  $Q$  is the number of siloxane bonds Si-O-Si, but increasing the number of groups  $Q^3$  and  $Q^4$ . For  $M > 1.5$  starts polymerization leading to the branched groups ( $Q^3$ ) of an average nuclearity 6 to 8, and with  $M > 3.5$  are formed three-dimensionally cross-linked units ( $Q^4$ ) with the surface units ( $Q^3$ ).  $Q^4$  units was observed only at  $M > 2.4$ . Assumed, however, that colloidal particles are formed at the module about 2 and at high concentrations [3].

## PURPOSE AND METHODS

To make sodium silicate glass with the assumed value of the module  $M = 3.3$  was used sand class 1A with the chemical composition:  $SiO_2 = 99.63\%$ ,  $Al_2O_3 = 0.19\%$ ,  $CaO = 0.09\%$ ,  $MgO = 0.035\%$ ,  $Fe_2O_3 = 0.016\%$ ,  $TiO_2 = 0.039\%$  and light soda with  $Na_2CO_3$  content =  $99.30\%$ . Assumed volatility of  $Na_2O$  equal  $0.59\%$ , which represents  $2.48\%$   $Na_2O$  loss in the melting process of glass. Oxide

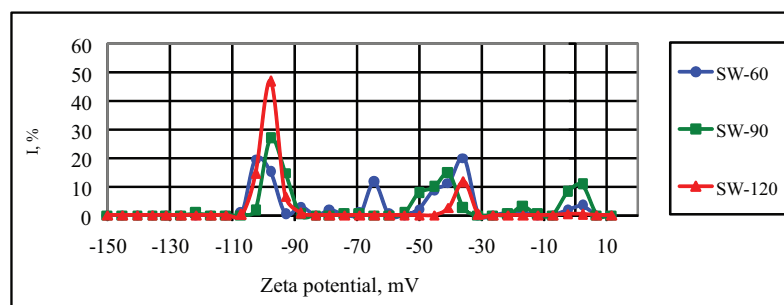
composition of the silica-sodium was:  $SiO_2 = 76.19\%$ ,  $Na_2O = 23.81\% + 0.59\%$  (for volatility) =  $24.40\%$ .

Melts of glass were performed in a gas furnace (oxidizing atmosphere), in the porcelain crucibles not glazed, with a capacity  $3\text{ dm}^3$ . For temperature measurement, thermocouples and optical pyrometers were used. Sets of sand and soda were dosed three times, every 40 minutes. After the last dosage alloys were kept in the crucibles at  $1350^\circ C$  for 60 minutes (sodium silicate glass from which the soluble sodium silicate SW-60 was made), 90 minutes (sodium silicate glass from which the soluble sodium silicate SW-90 was made) and 120 minutes (sodium silicate glass from which the soluble sodium silicate SW-120 was made).

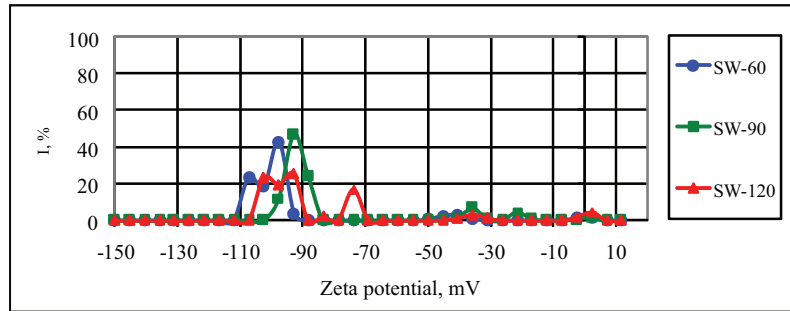
For the dissolution of the silica-sodium glass autoclave type VAIO-EWG 50 TR was used. Autoclavisation performed at a temperature of about  $160^\circ C$  and the corresponding pressure approximately  $6\text{ MPa}$ . For correction of the module of the soluble sodium silicate, sodium hydroxide was used.

Changes in the electrokinetic potential as a function of gel time was determined for samples of the soluble sodium silicate (SW-60, SW-90, SW-120) mixed with the ester (ethylene glycol diacetate). A sample of formed gel was collected after 20, 30, 40, 60, 80 and 100 minutes from the time of connection ester and a soluble sodium silicate, subjected to dispersion in NaCl solution (previously filtered through a membrane filter with a pore diameter of  $220\text{ nm}$  in order to remove insoluble impurities) and sonicated. Zeta potential was examined using the ZetaSizer 3000 apparatus.

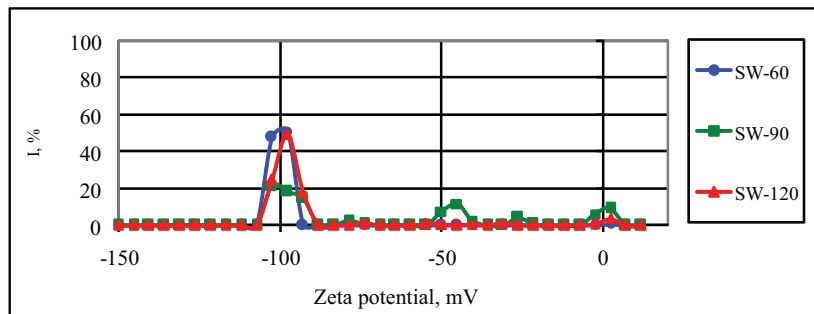
On the basis of measurements, determined the optimal composition of the electrolyte gel dispersion at which the recorded signal was the most favorable for scattered light and the measured values of Zeta potential were the same as when using larger dilution. After determining the pH value of the resulting solution, Zeta potential measurements were carried out. In order to characterize the sample, average potential distribution was calculated averaging the individual distributions (the sum of the individual channels and calculate the average). Two types of measurements were used in identifying changes in Zeta potential: as a function of gel time and after the gels, in order to characterize the surface properties of the resulting gel.



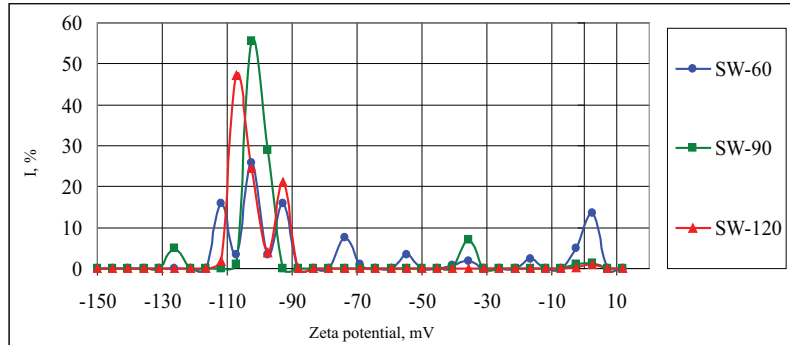
**Fig. 1.** Changes of the Zeta potential and the corresponding signal intensity  $I$  a laser light scattering on the surface elements of the structure formed after 20 minutes gelation process of the system "soluble sodium silicate (SW-60, SW-90, SW-120) - ethylene glycol diacetate"



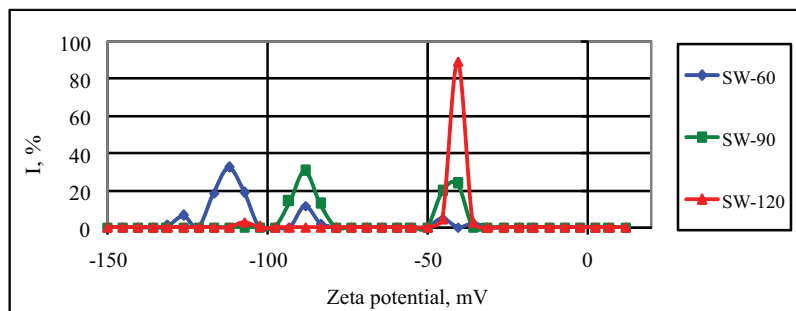
**Fig. 2.** Changes of the *Zeta* potential and the corresponding signal intensity *I* a laser light scattering on the surface elements of the structure formed after 30 minutes gelation process of the system “soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) - ethylene glycol diacetate”



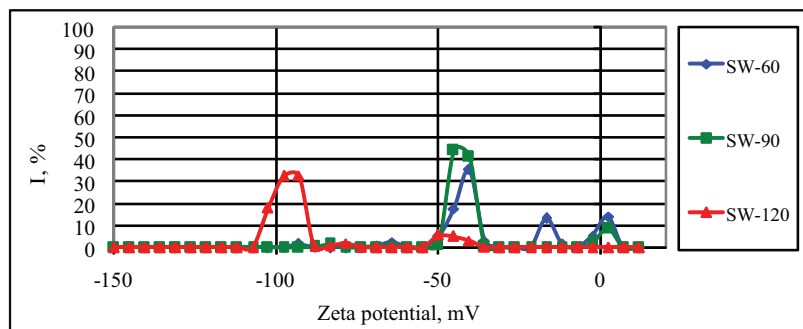
**Fig. 3.** Changes of the *Zeta* potential and the corresponding signal intensity *I* a laser light scattering on the surface elements of the structure formed after 40 minutes gelation process of the system “soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) - ethylene glycol diacetate”



**Fig. 4.** Changes of the *Zeta* potential and the corresponding signal intensity *I* a laser light scattering on the surface elements of the structure formed after 60 minutes gelation process of the system “soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) - ethylene glycol diacetate”



**Fig. 5.** Changes of the *Zeta* potential and the corresponding signal intensity *I* a laser light scattering on the surface elements of the structure formed after 80 minutes gelation process of the system “soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) - ethylene glycol diacetate”



**Fig. 6.** Changes of the *Zeta* potential and the corresponding signal intensity *I* a laser light scattering on the surface elements of the structure formed after 100 minutes gelation process of the system “soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) - ethylene glycol diacetate”

## RESULTS AND DISCUSSION

The results of studies described above are shown in Figures 1 to 6. They illustrate the changes on the *Zeta* potential and the corresponding signal intensity *I* laser light scattering on the surface elements of the structure formed after a certain time of the process of gelation of soluble sodium silicate (*SW-60*, *SW-90*, *SW-120*) under the influence of the ester.

The *pH* of the dispersion obtained from the gel varied from *pH*  $\cong$  11.0 for the shortest time of gelation, to the *pH*  $\cong$  10.3 for gel time of 100 minutes. The *pH* values for individual samples little differed and had no significant effect on the *Zeta* potential value. As shown in the placed figures, the initial stage of gelation gives rise of the structural elements with a relatively high value *Zeta* potential  $\cong$  -100 mV. The signal intensity *I* of laser light scattering on the surface of these elements is high for a longer gel time, then disappears for particles with the potential  $\cong$  -40 mV. In the case of the gel obtained by the reaction of soluble sodium silicate *SW-60* and *SW-90* with the ester by the time 80 minutes, the signal intensity of laser light scattering on the surface of structural elements with a high *Zeta* potential is less than 10%. In the case of the gel obtained by the reaction of soluble sodium silicate *SW-120* and ester, the signal intensity *I* of laser light scattering on the surface of structural elements with a high potential *Zeta* is significant after 80 minutes of the gelation process. As mentioned above, the signal intensity *I* of laser light scattering elements formed on the surface structure, can be a source of both the abundance of these elements, as well as their size and geometry of the surface (signal intensity *I* laser light scattering is proportional to the radius of the particles in the sixth power). It is also possible to notice the appearing and disappearing signal intensity of laser light scattering on the surface of particles contained in the reactants (soluble sodium silicate and ester). This effect is smallest in the case of gel obtained by the reaction of the ester and soluble sodium silicate *SW-120*, and the most visible in the gel obtained by the reaction of the ester and soluble sodium silicate *SW-60*. This may indicate the not full reaction of the gel reagent and a much slower reaction of soluble sodium silicate gel *SW-60* in comparison to the soluble sodium silicate

*SW-120*. The change was determined in the value of the *Zeta* potential versus *pH* for soluble sodium silicate gels *SW-60*, *SW-90* and *SW-120*. In the spectra signals were observed from particles of pollution of the reactants, and of the particles created in the process of nucleation. After analysis of the electrokinetic properties in the function of *pH*, *Zeta* potential values were selected for which the signal intensity *I* of laser light scattering on the surface elements of the structure was the biggest. The investigated electrokinetic properties of the systems resemble the properties of the “SiO<sub>2</sub> - electrolyte solutions” [18]. At the same time you can see some significant differences depending on the *Zeta* potential values of ionic strength. The increase in ionic strength of the carrier electrolyte causes the decrease in the absolute value of the *Zeta* potential, but does not move isoelectric point. These relationships are complex, which may indicate that the surface structure of the formed elements may have properties similar to the surface of a „hair”, occurring on some systems with the organic phase. Some impact on the *Zeta* potential dependence on *pH* can also increase the ionic strength of the electrolyte, due to the presence of electrolyte in the sample gel. As a result, the ionic strength of the electrolyte with the lowest carrier concentration is in fact higher than expected. Comparing the *Zeta* potential values for the gel samples, we can conclude that the elements of the structure of the gel obtained by the reaction of the ester and soluble sodium silicate *SW-90* showed the highest values potential at *pH* > 8, while elements of gel structure obtained by the reaction of the ester and soluble sodium silicate *SW-60* has the smallest value *Zeta* potential.

## CONCLUSIONS

1. *Zeta* potential distribution after 20 minutes of gelation. All the tested types of soluble sodium silicate have similar distribution *Zeta* potential range from about -110 mV to about -90 mV, but in the case of the soluble sodium silicate *SW-120* the corresponding signal intensity laser light scattering is the greatest. This may be attributable to a large number of particles, their large volume or the more developed surface

compared to other types of soluble sodium silicate, particularly *SW-60*. The largest slenderness ratio of the peak intensity of laser light scattering in this range of values of the *Zeta* potential indicates the greatest homogeneity of elements in its structure. The second distinct peak intensity of laser light scattering on the elements of the structure of soluble sodium silicate *SW-120* corresponds to the value *Zeta* potential from about -50 mV to about -30 mV and is the smallest, compared to the peaks of soluble sodium silicate *SW-60* and *SW-90*. It seems that the potential *Zeta* distribution in this period of gelation indicates the greatest stability of soluble sodium silicate *SW-120*.

2. *Zeta* potential distribution after 30 minutes of gelation. For all the investigated types of soluble sodium silicate the heterogeneity is increased of the structure elements formed in this gelation period, with the *Zeta* potential from about -110 mV to about -90 mV. In the case of soluble sodium silicate *SW-120*, elements of the structure are disappearing of the potential from about -50 mV to about -30 mV, for the benefit of structural elements with a potential from about -80 mV to about -70 mV. In the soluble sodium silicate *SW-60* practically disappearing are elements of the structure of the potential below -90 mV, while in soluble sodium silicate *SW-90* is an insignificant number of elements of the structure with the *Zeta* potential below -90 mV. The distribution of the *Zeta* potential after 30 minutes of gelation, suggests similar stability elements of the structure in all the tested types of soluble sodium silicate.
3. *Zeta* potential distribution after 40 minutes of gelation. Distribution of the values of *Zeta* potential show increased stability of elements of the structure in the soluble sodium silicate *SW-120* and *SW-60* and a slight decrease in the stability of these elements in soluble sodium silicate *SW-90*, for which again there are elements of structures with *Zeta* potential from about -10 mV to about +10 mV.
4. *Zeta* potential distribution after 60 minutes of gelation. Clearly increased heterogeneity can be observed of elements of the structure arising from the gelation process of soluble sodium silicate *SW-60*, with the *Zeta* potential from about -120 mV to about -90 mV. For this type of soluble sodium silicate, there are also elements of the structure with the potential from about -80 mV to about -70 mV, from about -60 mV to about -50 mV and from about -10 mV to about +10 mV. This suggests an increasing instability of the elements of the structure of the soluble sodium silicate *SW-60*.
5. *Zeta* potential distribution after 80 minutes of gelation. In the case of soluble sodium silicate *SW-120*, after the high stability of elements of the structure, there are mainly structural components of the *Zeta* potential from about -50 mV to about -40 mV, indicating a significant decrease in the stability of formed structure. Also the stability is decreased of the system in case of soluble sodium silicate *SW-90*, in which there are

elements of the structure of the *Zeta* potential from about -50 mV to about -40 mV, in addition to elements of the structure of the *Zeta* potential from about -100 mV to about -80 mV. The most stable arrangement of the structure of soluble sodium silicate *SW-60*, with the *Zeta* potential from about -130 mV to about -100 mV and from about -100 mV to about -80 mV. Distribution of the potential in the studied types of soluble sodium silicate indicates the highest growth of gelation speed in the soluble sodium silicate *SW-120*, a smaller increase in the speed of gelation in the soluble sodium silicate *SW-90* and the lowest speed of gelation in the soluble sodium silicate *SW-60*.

6. *Zeta* potential distribution after 100 minutes of gelation.

There has been a clear increase in the stability of elements of the structure in the soluble sodium silicate *SW-120*. In this silicate, elements of the structure disappeared with the *Zeta* potential lesser than about -90 mV, while there are elements of the structure of the *Zeta* potential from about -110 mV to about -90 mV. In the case of soluble sodium silicate *SW-60* and *SW-90* there is a reduction in stability of the system owing to elements of the structure of *Zeta* potential from about -50 mV to about -40 mV and from about -10 mV to about +10 mV.

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WPLYW KONDYCJONOWANIA TERMICZNEGO  
SZKLIWA KRZEMIANOWO-SODOWEGO NA KINETYKĘ  
ZMIAN POTENCJAŁU ZETA W PROCESIE ŻELOWANIA  
UWODNIONEGO KRZEMIANU SODU

**Abstract.** Opisano wyniki badań zmian potencjału Zeta układu „uwodniony krzemian sodu – ester” w zależności od czasu jego żelowania. Stwierdzono, że czas kondycjonowania termicznego szkliwa krzemianowo-sodowego ma istotne znaczenie w aspekcie stabilności elementów nanostruktury uwodnionego krzemianu sodu. Charakterystyka stabilności tych elementów może wpływać na charakterystykę wiązań układu spoiwo krzemianowe-kwarc, a tym samym na ich właściwości wytrzymałościowe w temperaturze otoczenia.

**Słowa kluczowe:** uwodniony krzemian sodu, szkliwo krzemianowo-sodowe, potencjał Zeta, kondycjonowanie termiczne.