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# THE EFFECT OF NANOSTRUCTURE MODIFICATION OF THE SILICATE BINDER ON ITS BINDING CHARACTERISTICS AND FUNCTIONAL PROPERTIES

# WPŁYW MODYFIKACJI NANOSTRUKTURY SPOIWA KRZEMIANOWEGO NA CHARAKTERYSTYKĘ JEGO WIĄZANIA I WŁAŚCIWOŚCI UŻYTKOWE

A method for the chemical modification of silicate binder (hydrated sodium silicate) affecting the distribution of its nanostructure elements was disclosed. The effect of silicate binder modification on the resulting technological properties of moulding sands, determined under standard conditions and at elevated temperatures in the range from $100^0$C to $900^0$C, was discussed. Modification of this type is done on inorganic binders in order to reduce their unfavourable functional properties. It is particularly important when moulding sands with the silicate binder are used for casting of low-melting alloys. Therefore special attention was paid to the impact that modification of inorganic binders may have on the knocking out properties of sands prepared with these binders, when they are used in the process of casting non-ferrous alloys.

*Keywords*: inorganic binders, chemical modification, knocking out properties

Przedstawiono sposób modyfikacji chemicznej spoiwa krzemianowego (uwodnionego krzemianu sodu) wpływającej na rozkład elementów jego nanostruktury. Omówiono wpływ modyfikacji spoiwa krzemianowego na uzyskane właściwości technologiczne masy formierskiej wykonanej z jego udziałem, określone zarówno w warunkach znormalizowanych, jak i w warunkach podwyższonej temperatury w zakresie od 100°C do 900°C. Zastosowanie tego rodzaju modyfikacji spoiw nieorganicznych ma na celu ograniczenie ich niekorzystnych cech użytkowych. Jest to szczególnie istotne w przypadku zastosowania masy formierskiej ze spoiwem krzemianowym do wytwarzania odlewów ze stopów metali charakteryzujących się małą wartością temperatury topnienia. Dlatego szczególną uwagę zwrócono na wpływ modyfikacji spoiw nieorganicznych na wybijalność mas z ich udziałem przy odlewaniu stopów metali nieżelaznych.

## 1. Introduction

Hydrated sodium silicate, described with the general chemical formula $x\mathrm{Na_2O} \cdot y\mathrm{SiO_2}$, is one of the most popular inorganic silicate binders used in the manufacture of foundry moulds and cores. Foundry sand mixtures prepared with an addition of this binder are relatively cheap and exhibit a number of advantages, but they are also characterised by a very high final strength, which makes the removal of cores from castings and of castings from moulds very difficult, creating also serious problems with reclamation of the used base sand [1,2]. Additionally, the $\mathrm{Na_2O-SiO_2}$ system tends to react with silica and the result is sintered moulding sand formed in contact with the hot liquid metal. These features are particularly unfavourable when thin-walled items are cast from the low-melting alloys.

The structure of sodium silicate in an aqueous solution is very complex due to the presence of hydroxyl ions and tetravalent silicon, adopting in silicate ions the coordination number 6.

Studies of electrical conductivity, refractive index , boiling point and freezing point of the aqueous solutions of sodium silicate confirm their colloidal character. The presence and the frequency of occurrence of the colloidal particles – polysilicate ions – are evident starting with the silicate modulus 2. In sodium silicate solutions with the modulus 2, besides monosilicate ions of $\mathrm{H_3SiO_4}$, disilicate ions of $\mathrm{H_4Si_2O_7^{2-}}$ are also present, and in solutions with the modulus value above 2, there is a mixture of polysilicate ions characterised by high degree of polycondensation [3].

At the earliest stages of expansion of the monomer particles (polymer formation), special role plays the, beneficial in terms of energy, formation of cyclic silicate tetramers of $\mathrm{Si_4O_6(OH)_6^{6-}}$ and $\mathrm{Si_4O_4(O)_4^{4-}}$ [4,5]. These are the components of octamer ions of a cubic structure $(\mathrm{HOSiO_{1,5}})_8$ with silicon atoms arranged in the corners of a cube. Each of them, operating via oxygen atoms, is bound to three other silicon atoms, and has the ability to ionise one SiOH group, leading to the formation of $(\mathrm{Si_8O_{20}})^{8-}$ octamer. This structural unit acts as a nucleus in the formation of colloidal particles. When ions of a monomer undergo condensation on its surface, the consequence is the formation of a particle with the $\mathrm{SiO_2}$ core and a negatively charged surface (SiOH) [4, 6].

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## 2. The effect of chemical modification of the hydrated sodium silicate on its nanostructure

Adverse properties of hydrated sodium silicate when used as a binder result, among others, from the fact that its ability to wet the sand grain surface is definitely much worse than that of the organic binders [7]. The reason may be the absence of the functional groups of the $-NH_2$, $=CONH$, $-CONH_2$, and $-COOH$ type in the structure of hydrated sodium silicate. These groups activate the first stage of the formation of the structural strength of moulding sands. Therefore it has been proposed to introduce these groups as modifiers improving the properties of hydrated sodium silicate and forming with this compound the Interpenetrating Polymer Networks (IPN). Modifiers added at the stage of the glaze dissolution can be divided into the following three groups:

1. catalysts which accelerate the dissolution of the glaze in water,
2. agents which improve plasticity and the adhesive and cohesive strength of the hardened binder,
3. modifiers which penetrate into the silicate micellae and, by decreasing the final strength of the binder, improve the sand knocking out properties and reclamability.

Agents included in the second group play the role of protective colloids, inhibiting the growth of the silica gel molecules and formation of new systems during hardening of the binder. They also act as additional bridges which bond the structure of the hardened binder and lead to the formation of internally interpenetrating networks.

Based on previous studies and experience [8,9], an organofunctional, morphoactive, organic modifying agent – a copolymer obtained by emulsion polymerisation – was selected and called "B7" modifier. The process of modification consisted in introducing into the hydrated sodium silicate of a modulus M = 2 and a density of 1.5 kg/m³, the modifier in an amount of 1.0% relative to the sum of oxides ($Na_2O$, $SiO_2$). The physical conditions under which the chemical modification was carried out involved a variable method of mixing the modifier - hydrated sodium silicate system, as well as a variable temperature, pressure and time of modification. As a result of modification, the silicate binder designated as "B7" was obtained, while the reference non-modified binder was designated as "O".

Structure was examined with a *Zetasizer Nano* apparatus made by Malvern Instruments. It is an analyser of the nanometric-sized particles (using the method of dynamic light scattering DLS) and of Zeta potential. Based on past experience, in measurements of the particle size, it was decided to use the solutions with an equal content (7%) of the sum of oxides ($SiO_2$, $Na_2O$), acting as the components of a dispersed phase forming the structure of hydrated sodium silicate [6,8-11]. To determine by DLS the characteristic features of the structure of colloids, which the hydrated sodium silicates are, it is necessary to determine parameters such as the refractive index of the dispersing phase $n_r$ and the refractive index of the dispersed phase (particulate) $n$.

The value of the refractive index of the dispersed phase in the hydrated sodium silicate was determined with an *RX-7007 α* refractometer by interpolation of the refractive index values obtained for aqueous solutions with the hydrated sodium sili-

cate concentration from 10% to 100% at a 10% gradation. The *Zetasizer Nano* apparatus was used to determine parameters such as the average particle size (*Z -Average*), the polydispersity index (*PDI*), the count rate, the average diameter of the particle fraction on which the laser light was scattered (*dI*), the average diameter of the particle volume fraction (*dV*), the average diameter of the particle number fraction (*DN*), the percent value of the laser light scattering, of the particle volume fraction and of the particle number fraction (*dI, dV, dN*), the value of the semi-range of the distribution of particles analysed in terms of the laser light scattering, volume fraction and number fraction ($W_{dI}, W_{dV}, W_{dN}$). The values of these parameters are collected in Table 1.

TABLE 1

Characteristic parameters of the structure of the examined hydrated sodium silicate variations

| Parameter | Hydrated sodium silicate variations | |
|---|---|---|
| | B7 | O |
| Z-Average, nm | 2673 | 2503 |
| PdI | 1.0 | 1.0 |
| Count Rate, kcps | 143.5 | 83.1 |
| dI, nm | 131.6 1.1 3.648 | 1.031 45.08 |
| dI, % | 53.9 38.1 8.0 | 55.4 44.6 |
| $W_{dI}$, nm | 9.663 0.1688 0.3682 | 0.1307 2.670 |
| dV, nm | 1.032 3.557 | 0.9883 |
| dV, % | 99.5 0.5 | 100.0 |
| $W_{dV}$, nm | 0.1891 0.5159 | 0.1611 |
| dN, nm | 0.9720 | 0.9467 |
| dN, % | 100.0 | 100.0 |
| $W_{dN}$, nm | 0.1680 | 0.1486 |

Average particle size (*Z -Average*), also called cumulative average, is in the dynamic light scattering technique (*DLS*) the most important and the most stable of all the quantities generated. It was found that in the examined, chemically modified, binders, *Z -Average* shows a clear trend of increasing values. It should be noted, however, that this parameter is calculated from changes in the intensity of laser light scattering on the surface of the investigated particles. Thus, in the case of broad distributions with the polydispersity index *PDI* >0.5 (common to all types of the binders tested), it is advisable to rely not only on the value of *Z –Average* but analyse also the distribution of the average particle diameters and determine the peak position. In the case of hydrated sodium silicate designated with the symbols "B"7 and "O", a monomodal and a bimodal, respectively, particle size distribution was stated. The chemical modification of "B"7 binder results in the formation of a small group of particles (or agglomerates) with a high value of the average diameter, amounting to about 131 nm.

These particles contribute a lot to the laser light scattering (about 53.9%).

## 3. The effect of hydrated sodium silicate chemical modification on selected mechanical properties of moulding sands [11,12]

Using chemically modified hydrated sodium silicate "B"7 and unmodified standard hydrated sodium silicate "O", moulding sands were prepared, each containing 2.5 parts by weight of binder and 10% of hardener in the form of ethylene glycol diacetate (*flodur 1*) added in respect of the binder weight. The base material was silica sand of 1K type from "Szczakowa" mine with the main fraction of 0,20 40/0,315. Figure 1 shows the compressive and bending strengths of samples of the moulding sand prepared with the binders tested.
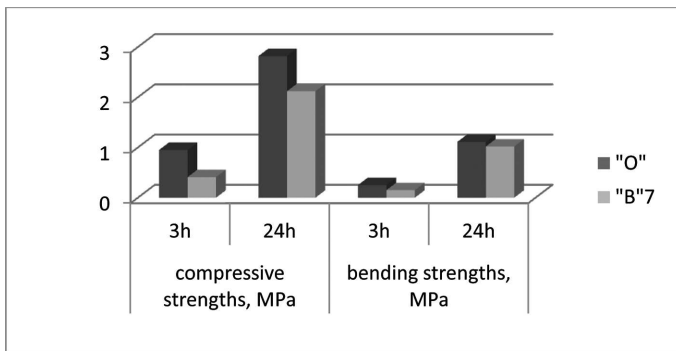


Fig. 1. Tensile properties of sands prepared with modified and unmodified binder

For binders "B"7 and "O", tests at elevated temperature were also carried out [12], determining the, so-called, final strength, which is an indirect indicator of the moulding sand knocking out properties. The test results are shown in Figure 2.
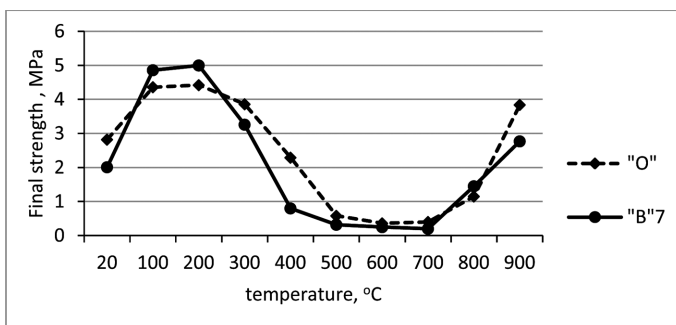


Fig. 2. Final strength of moulding sands with modified and unmodified binder

It was found that within the investigated range of temperatures, i.e. from 300°C to 700°C, for measurements taken at the same temperature, the final strength of moulding sands with binder "B"7 was reduced by about 15% at 300°C, about 65% at 400°C, about 45% at 500°C, about 30% at 600°C and about 50% at 700°C, compared with the final strength of moulding sands prepared with the unmodified reference silicate binder "O".

## 4. Testing of the sand knocking out properties

The chemically modified hydrated sodium silicate "B"7 was subjected to technological trials [13], involving its use as a binder in the manufacture of moulds tested for the knocking out properties in accordance with the Polish standard PN-85/H-11005. Moulds and cores for the knocking out test were prepared with the modified binder "B"7 and, for comparison, with the unmodified hydrated sodium silicate "O". The dimensions of foundry moulds made with these binders were 320x250x100/100. In these moulds, test castings were made from the AlSi9 and CuZn39Pb2 alloys. The temperature of alloy melt before removing the crucible from the furnace and pouring of moulds was 730°C and 1130°C for AlSi9 alloy and CuZn39Pb2 alloy, respectively; the metal weight in mould after pouring of the casting was 3 and 8 kg. The results of the knocking out tests are shown in Figures 3 and 4.
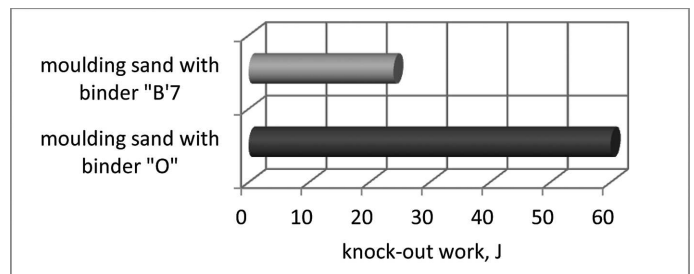


Fig. 3. The work input necessary to knock out the test castings made from Al alloy
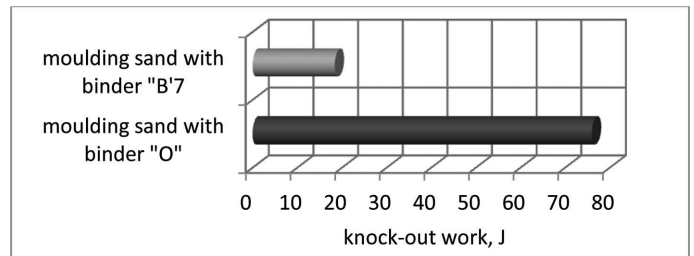


Fig. 4. The work input necessary to knock out the test castings made from Cu alloy

Compared with the unmodified binder, moulding sands prepared with the new type of binder are characterised by a much better knocking out properties, expressed in an almost three times lower work input during knocking out of castings.

## 5. Conclusions

1. The physico-chemical and structural studies conducted on materials included in a system called "moulding sand", containing an inorganic binder of new generation in the form of chemically modified hydrated sodium silicate, allowed selection of the modifying additive and development of a technique of its introduction into the hydrated sodium silicate.
2. Significant reduction of the moulding sand final strength in a temperature range of 400°C to 700°C, as compared to the final strength of moulding sands prepared with an addition of the unmodified hydrated sodium silicate, makes

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sands with the modified binder applicable in the manufacture of moulds and cores for casting of low-melting alloys (e.g. aluminium alloys).

3. Studies of the knocking out properties of foundry sands prepared with the new, chemically modified, hydrated sodium silicate proved that the use of silicate binders of new generation significantly improves the knocking out properties of moulding sands with these binders, which has further beneficial effect on the sand reclamability.

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