

Nanostructure of the soluble sodium silicate in the aspect of basic mechanical characteristic of the moulding sands

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Abstract. The paper describes the consequential advantages of the use of inorganic binders, particularly soluble sodium silicate, in the aspect of the environmental protection. Nanostructure of the soluble sodium silicate as a silicate colloid is described. Research of the structure of the soluble sodium silicate is executed with the use of the PCS method (*Photon Correlation Spectroscopy*). Characteristic parameters of the nanostructure of the soluble sodium silicate and the method of the estimation of the quantitative structure of the colloid are introduced. It has been proved that the nanostructure of the soluble sodium silicate has an essential influence on its proprieties as binders of the moulding sands. Mechanical characteristic of the moulding sands executed with this binder are dependent on the kind of the nanostructural characteristic of the soluble sodium silicate.

Key words: nanostructure, colloid, soluble sodium silicate, moulding sand, casting, environmental protection.

INTRODUCTION

About 80% of all foundry moulds are made in Poland from standard sands with bentonite binder and coal dust, or with lustrous carbon carriers. The processing plants for sands of this type are equipped with wet or dry dust collecting systems. The sludge or dust formed during mould preparation is an unnecessary burden for the foundry. Besides, the condensates of compounds are generally considered as *HAPs* (*Hazardous Air Pollutions*), they contain silica, deactivated bentonite, active bentonite and thermally non-deactivated particles of organic binder-hardener systems (sulphonic acids, pyridine derivatives, esters, isocyanates, amines, copper salts, ammonium salts, hexamethylenetetramine). Numerous studies [12,16] have proved that coal dust, organic lustrous carbon carriers, cores with organic binders and protective coatings based on alcohol or water are the main sources of hazardous air pollutions (*HAPs*), emitted during the process of casting production in standard moulding sands. The pollutants

emitted in the largest volumes include benzene, toluene, o-, m-, p-xylene, naphthalene, hexane, and their derivatives. When core sands with organic binders are used, others *HAPs* are formed, to mention only phenol and formaldehyde, both of which can occur in large amounts. Besides the above mentioned *HAPs*, the process of casting manufacture in standard moulding sands is the source of the emission of other compounds included in the group of *HAPs*, like acetaldehyde, acrolein, aniline, pyrokatechine, o-, m-, p-cresol, cumene, hexane, isophorone, methyl, indene, polycyclic organic compounds, propionaldehyde, styrene, triethylamine [11, 1, 3]. Other technologies of the casting production also generate injurious products of the thermal destruction [15, 19, 24]. It is the reason of great interest in inorganic binders, such as soluble sodium silicate. This is especially important in the case of producing casts from special alloys [20, 22].

The main advantage of soluble sodium silicate is low toxicity of this binder in all the processes of casting production - and thus - during the preparation of sands, pouring and knocking. The principal aim of these investigations is the limitation of quantity of soluble sodium silicate in moulding sands and cores, but at the same time the maintenance of their proper technological properties, especially the mechanical ones.

STRUCTURE OF THE SOLUBLE SODIUM SILICATE

A characteristic element of the structure of soluble sodium silicate is micella. The seed of this colloidal particle, possessing negative charge, is structural, individual – polijon ($\text{Si}_8\text{O}_{20}^{8-}$). Polijon enlarges as the result of condensing on his surface of ions of monomers and in final effect reaches the state of silicate poliparticle with the core in the form of molecular SiO_2 and with the

surface possessing negative charge due to groups OH. In certain circumstances, this kind of spherical particle has an ability of joining oneself to oneself (Si-O compounds). Adjoining molecules fix mutually one's own compound, due to which, in the final effect, they develop into porous, interlaced nets of fully extended chains. Thus, we can assume that the formation of structure in soluble sodium silicate is performed in three phases [4, 23]:

1. Mutual joining of monomers with rising spherical, colloid particles on warp of octamer ion.
2. Increase of spherical colloid particles.
3. Bonding of exchanged particles, at first in chains, and then in nets spreading in throughout the liquid medium and thickening it to the form of gel (naturally, this phase is reached in the situation of disturbing the state of equilibrium in a glass of water).

Molecules SiO_2 create the core of micel adsorbing ions $[\text{SiO}_3]^{2-}$ and in this way micels starts possessing negative charge. It absorbs the ions of opposite charge $[\text{H}^+]$, creating micels. Ions $[\text{H}^+]$, in absorption layer, create electric double layer. Adsorbing ions $[\text{H}^+]$, stepping out in further distances from core, they create dyfusion layer of micel. During the movement of micel in solution, part of adsorbing ions $[\text{H}^+]$ stays in solution, and a difference of potentials is created between the particle and the border free from its bounded ions. That is the so-called electrokinetic potential *Zeta* [5, 6, 14, 17, 18]. Potential *Zeta* usually qualifies the stability of the colloid

arrangement [14, 17]. So, we can ascertain, that the surface of particle occurring in soluble sodium silicate possesses negative charge and becomes surrounded with ions of opposite charge, strongly bounded with it. The layer of liquid surrounding the particle consists of two parts:

1. Parts determining internal area ("Stern layer"), in which ions are strongly bounded with particle.
2. Parts determining external area (diffusion layer), in which ions are considerably more weakly bounded with particle.

Inside diffusion layer extends the agreed border of area, of which antiions and colloidal particle of soluble sodium silicate create a stable part. When a movement of the particle occurs (e.g. under an influence of Brownian motions or gravitation), ions present in this area shift together from it. Ions staying outside the area do not perform movements together with the particle. Summing up – soluble sodium silicate - practical in foundring, is an electrolyte, and its ions are also present in hydration layer.

Characteristic build of colloid, which is soluble sodium silicate - will imply the use of *Photon Correlation Spectroscopy (PCS)*, to qualifications of size and decay of size elements of the structure of these binders [7, 10, 13].

The analysis of *PCS* determines a considerable progress in the area of measuring methods for determination of particle sizes. It makes it possible to investigate a sample in the natural state, does not cause its destructions or structural changes. In this kind of method, the measurement of stochastic Brownian motions takes place and on this basis the size of particles is analyzed.

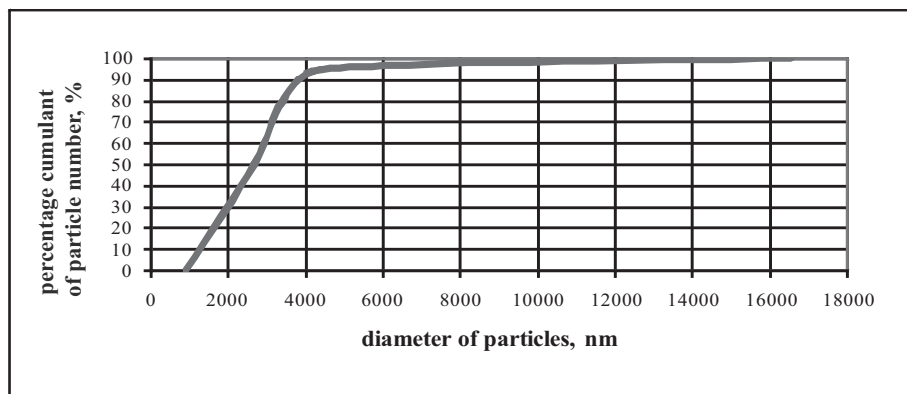


Fig. 1. Percentage cumulant of the number of particles in soluble sodium silicate $m_{2,1_1,45}$ after filtration by filter C

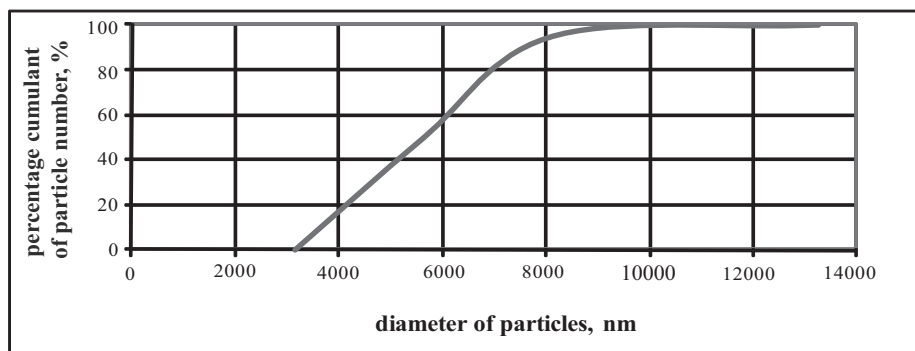


Fig. 2. Percentage cumulant of the number of particles in soluble sodium silicate $m_{2,3_1,40}$ after filtration by filter C

As an example, it is possible to present the results of investigations of soluble sodium silicate with modulus $M = 1,95; 2,1$ and $2,3$ - obtained from sodium-silicate glasses melted with the above values of modules. Every kind of soluble sodium silicate had the density $1,40; 1,45$ and $1,50 \text{ g} \cdot \text{cm}^{-3}$.

The second kind of soluble sodium silicate possesses analogous values of module and density, but is obtained from sodium-silicate glasses with modulus $3,3$ by the method of modification of chemical composition (using NaOH).

Considering the fact, that the investigated solutions were in the state of polydispersity and high polydispersity, it was necessary to use their filtration in order to ascertain the presence of elements of structure, which in basic solutions (not filtered) can be dominated by elements of large sizes [4].

An easier and more exact interpretation of the investigations results is possible by calculation and constructing the percentage cumulant of numbers of particles in dependences of sizes of their diameters. Figure 1 and 2 illustrate cumulants for samples $m_{2,3_1,40}$ (soluble sodium silicate obtained with the method of modification of chemical composition, with modulus $2,3$ and density $1,40 \text{ g} \cdot \text{cm}^{-3}$) and $m_{2,1_1,45}$ (soluble sodium silicate obtained with the method of modification of chemical composition, with modulus $2,1$ and density $1,45 \text{ g} \cdot \text{cm}^{-3}$) after filtration by filter C [4].

Qualification of characteristic parameters of the structure for the soluble sodium silicate is possible - values of average diameter of particles of the main fraction dG , halfwide dsG and range of particles of diffuse fraction dsR . (Fig. 3).

Description of characteristic parameters of structure, makes the so-called "partial indicator of structure WB_i " possible, calculated for solutions not filtered (nf) and for solutions obtained after filtration ($fA; fB; fC$). Diameters of pores of the used filters are: $A > B > C$:

$$WB_i = \frac{dG_i}{dsG_i + dsR_i} \tag{1}$$

Indicator WB , determining sum of indicators WB_i , became accepted as indicator of nothomogeneity of soluble sodium silicate:

$$WB = \sum_{i=nf}^{i=fC} WB_i \tag{2}$$

The second indicator of structure of the investigated samples of soluble sodium silicate - DWB , expresses the maximum difference of value of partial indicators WB_i . This indicator is characterized by a lack of homogeneities in arrangement, pointed out by indicator WB :

$$DWB = WB_i \text{ max} - WB_i \text{ min} \tag{3}$$

Values of indicators WB for different kinds of water glass are presented in Figure 4.

Investigations of the hydrations enables the qualification of dependence among the form of water (free water and bounded water), the quantity of this kind of water in a glass and the kind of its structure (Fig. 5). These investigations were performed by deriwatograph method. In the temperature from about 20°C to about 70°C and

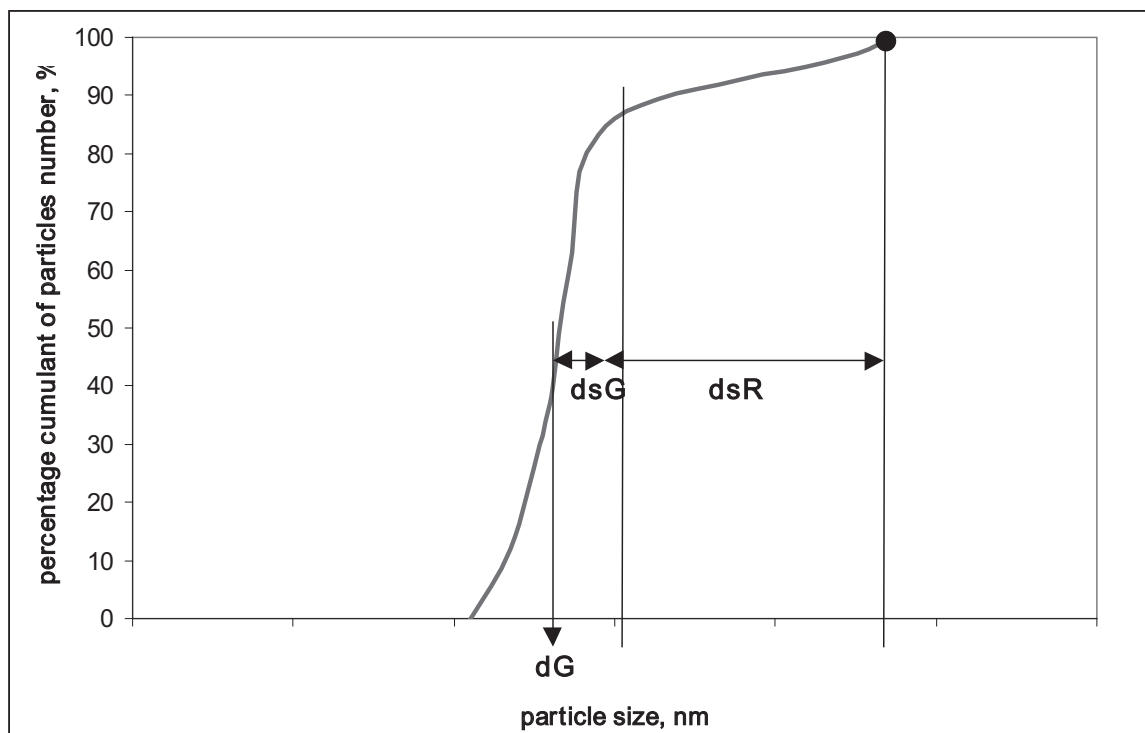


Fig. 3. Percentage cumulant of the number of particles

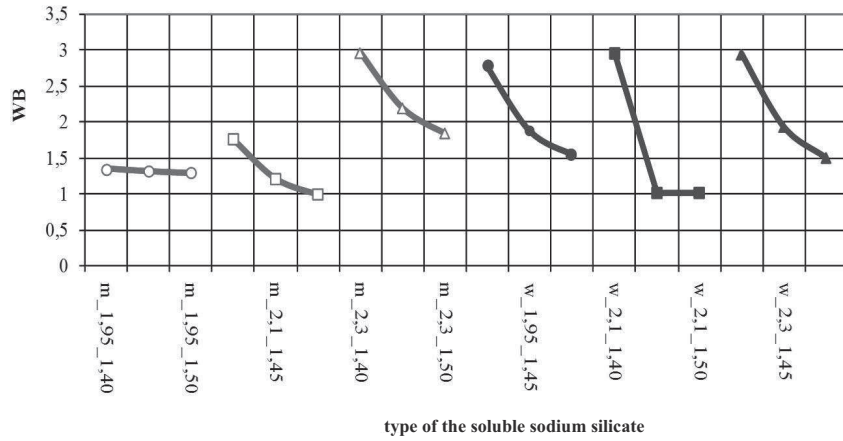


Fig. 4. Coefficient of structure WB for the soluble sodium silicates with different values of modulus and density, produced by different methods

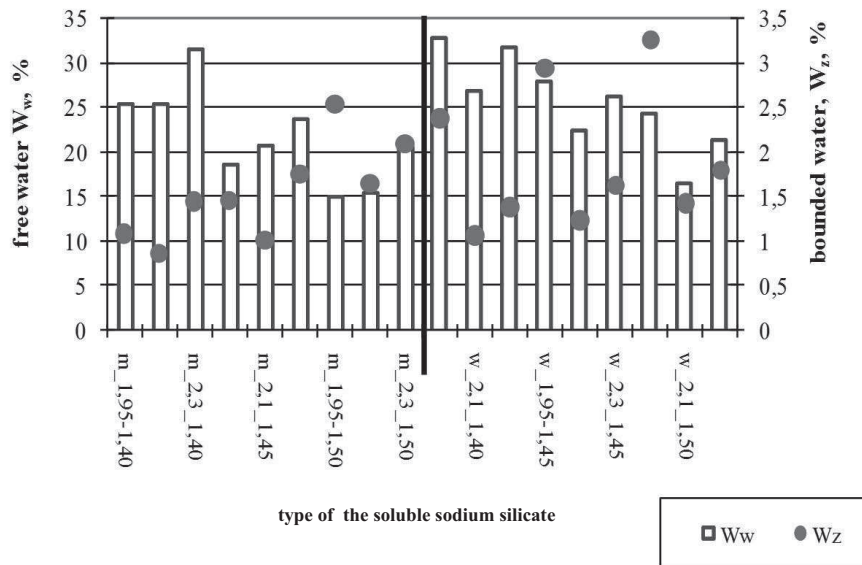


Fig. 5. Coefficient of structure WB for the soluble sodium silicates with different values of modulus and density, produced by different methods

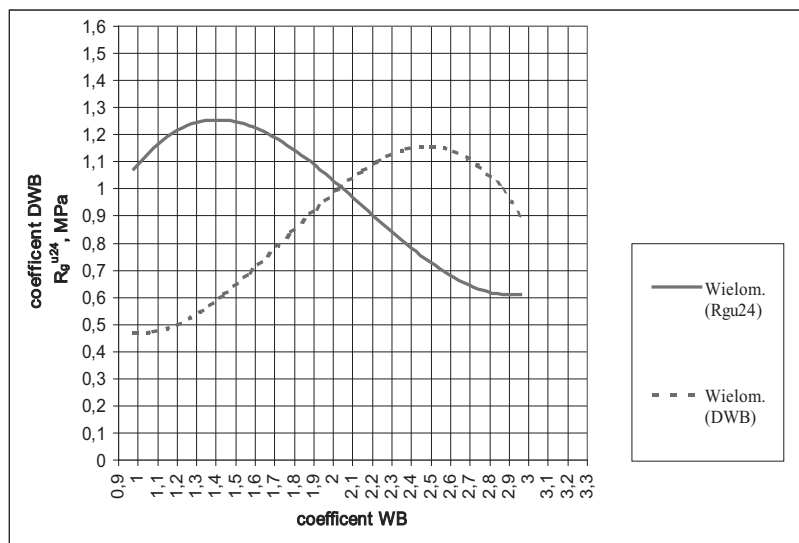


Fig. 6. Bending strength R_g^{u24} of moulding sand with soluble sodium silicate and ester, (after 24 hours of curing) and corresponding to them values of coefficient DWB , in dependence from values of coefficient of structure WB for different types of the soluble sodium silicate

from about 115°C to about 140°C, on *DTG* appears piques testifying about dehydration of soluble sodium silicate, related to a little endothermic effect on *DTA* [4].

Technological verification of investigations was performed. The moulding sands containing soluble sodium silicate with identical quantity sum of the oxides ($\text{SiO}_2 + \text{Na}_2\text{O}$), were cured with diacetate ethylene glycol. Moulding sands were made, cured and investigated in identical conditions of environment (20°C and 60% r. h.) in the climatical chamber. Figure 6 presents the dependency of strength properties of the moulding sands vs structure indicator *WB*.

CONCLUSIONS

1. We can accept, that in the range of the temperature from about 20°C to about 70°C, first the dehydration of soluble sodium silicate appears (loss of the free water W_w). In the range of the temperature from about 115°C to about 140°C, bounded water W_z is removed from the soluble sodium silicate.

2. It is very probable, that the content of the free water W_w has a great influence on the size of nanoelements in the soluble sodium silicate.

3. Two value of indicators *WB* and *DWB* can be defined as follows:

$$WB \in (3, 0; 1, 8) \text{ and } WB \in [1, 8; 1, 0),$$

$$DWB \in (1, 44; 0, 8) \text{ and } DWB \in [0, 8; 0, 13).$$

The most profitable strength properties of the moulding sands were obtained for the structures of the soluble sodium silicate with the values of indicators *WB* in the range up to 1,8 and *DWB* in the range below 0,8.

REFERENCES

- Baliński A. 2010.** *Advanced oxidation and adsorption modification of dust waste from standard moulding sands.* „Archives of Foundry Engineering”, vol. 10, issue 2, p. 5–8.
- Baliński A., Wisła-Walsh E. 2008.** *Fly ash from hard coal combustion as a ceramic base material of moulding sands.* „Polish Journal of Environmental Studies”, vol. 14, no. 3A, p. 44–48.
- Baliński A. 2010.** *Odpadowe pyły formierskie modyfikowane polielektrolitami.* „Archives of Foundry Engineering”, vol. 10, no 2, p. 9–13.
- Baliński A. 2000.** *Wybrane zagadnienia technologii mas formierskich ze spoiwami nieorganicznymi. Struktura uwodnionego krzemianu sodu i jej wpływ na wiązanie mas formierskich.* Kraków, s. 58–81.
- Baliński A., Janusz W. 2002.** *Changes of potential ζ in a system of „hydrated sodium silicate – ethylene glycol.* „Advances In Manufacturing Science and Technology”, vol. 26, nr 4, s. 21–25
- Baliński A., Janusz W. 2004.** *Potencjał ζ uwodnionego krzemianu sodu.* „Archives of Foundry”, vol. 4, no 11, p. 29–33.
- Baliński A., Wilkosz B. 1998.** *Examinations of the structure of sodium silicate and silica sols by the technique of photon correlation spectroscopy.* „Acta Metallurgica Slovaca”, no. 2, p. 113–117.
- Baliński A., Lewandowski J.L., Wilkosz B. 1999.** *Influence of the structure of water glass and modified silicate binders on the strenght proprieties of moulding sands.* „Acta Metallurgica Slovaca”, no 2, p. 70–74.
- Baliński A., Stechman M., Różycka D. 2003.** *Influence of modification of the soluble sodium silicate with morphoactive agents on the mechanical properties of the moulding sands in temperatures to 900°C.* „Materials Engineering”, vol. X, no 3, p. 271–275.
- Baliński A. 2004.** *Determination of size and size distribution of particles in hydrated sodium silicate and in silicate sols by photon correlation spectroscopy.* „Int. Journal of Cast Metals Research”, vol. 17, No. 2, p. 1–6.
- Cannon F.S., Voight R.C., Furness J.C. 2002.** *Non-Incineration Treatment to Reduce Benzene and VOC Emissions from Greensand System,* Final Report U.S. Department of Energy, DE-FC 0799 ID13719.
- Glowacki C.R., Crandell G.R., Cannon F.S, Clobes J.K., Voight R.C., Furness J.C., McComb B.AQ., Knight S.M. 2003.** *Emission Studies At a Test Foundry using an Advanced Oxidation-Clear Water System.* „AFS Transactions”, vol. 111, p. 579–598.
- Izdebska-Szanda I., Baliński A. 2011.** *New generation of ecological silicate binders.* „Engineering Procedia”. Published by Elsevier Ltd., vol. 10, p. 887–893.
- James R.O., Parks G.A. 1982.** *Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical proprieties.* „Surface and Colloid Sci.”, vol. 12, p. 119–129.
- Jankowski W., Żółkiewicz Z. 2003.** *A method to evaluate the permeability and strength of ceramic protective coatings applied on lost foam patterns.* „Archives of Metalurgy”, vol. 48, no 3, p. 277–283.
- McKinley M.D., Jefcoat I.A., Hertz N.J., Frederic C. 1993.** *Air Emissions from Foundries. A Current Survey of Literature, Suppliers and Foundrymen.* „AFS Transactions”, vol. 101, p. 979–990.
- Miller N.P., Berg J.C., O’Brien R.W. 1992.** *The electroforetic mobility of porous aggregate.* „J. Colloidal Interface Sci.”, no 153, p. 237–241.
- Parks G.A. 1965.** *The izoelectric point of solids oxides.* „Chem.Rev.”, no 65, p. 177–181.
- Pielichowski J., Sobczak J.J., Żółkiewicz Z., Hebda E., Karwiński A. 2011.** *Analiza termiczna polistyrenowego modelu odlewniczego.* „Transactions of the Foundry Research Institute”, vol. L, no 1. p. 15–22.
- Pirowski Z. 2011.** *Aplication of Nickiel Superalloys On Castings For Conventional Energy Equipmment Items.* „TEKA”, vol. XIC, p. 246–255.
- Pirowski Z., Gościanski M. 2009.** *Construction and technology of production of casted shares for rotating and fird plougs.* „TEKA”, vol. IX, p. 231–239.
- Pytel A., Stefański Z. 2011.** *An Inovattive And Environmentally Safe Method To Manufacture High-Quality Iron Castings For Possible Use As elements Of Agriculture Machines.* „TEKA”, vol. XIC, p. 256–263.

23. **Svenson J.I., Ohman L-O. 1986.** *Polysilicate equilibrium in concentrated solution of sodium silicate.* "J. Chem. Soc.", vol. 82, p. 3636–3672.
24. **Żółkiewicz Z., Żółkiewicz M. 2010.** *Characteristic properties of materials for evaporative patterns.* "Archives of Foundry Engineering", vol. 10, special issue, p. 289–292.