

# Effect of Metal Oxides Nanoparticles on the Selected Strength Properties of Moulding Sand with Water Glass

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## Abstract

The modification of water glass with nanoparticles of metal oxides in organic solvents was attempted in the study. The results of investigations of moulding sands with water glass modified by nanoparticles of the selected metal oxides in organic solvents, are presented in the hereby paper [21]. Nanoparticles of ZnO, Al<sub>2</sub>O<sub>3</sub> or MgO in methanol, ethanol or propanol solutions were applied as modifiers of binding agents. Colloidal solutions of the modifiers were introduced into water glass in the amounts of 3, 5 or 7 mass %. Influences of the applied modifier and organic solvents as well as the modifier fraction in the binder on the selected strength properties of moulding sands were tested. On the bases of the analyses of the obtained results the probable mechanism of the water glass modification with nanoparticles of metal oxides was proposed.

**Keywords:** Innovative materials, Foundry technologies, Modification, Water glass, Nanoparticles, Tensile strength  $R_m$

## 1. Introduction

Moulding sands with water glass still constitute the basic group of moulding sands applied in technologies with inorganic binders. From the technological point of view, moulding sands with this binder are characterised by sufficient fluidity and compatibility. They have relatively long utility, which depends on the water glass modulus, moisture content and air temperature. Their positive side is the fact that castings produced with technologies based on moulding sands with water glass are usually of a good dimensional accuracy. However, the inconvenience, limiting their wide utilising in the foundry industry, is - first of all - a bad knock-out ability and difficult mechanical reclamation. Moulding sands with this binder exhibit also a relatively low strength. Therefore in several research centres [1-21] investigations on improvements of the selected

properties of moulding sands with water glass are currently being performed. This research is carried out in the following domains: matrix modification [1-4], developments of new hardening methods [5-9], binder modification [10-21]. According to Chun-xi [8] the best effects of improvements provides the direct binder modification.

One of the newer modification methods of water glass is introduction into its structure 'ultrafine powders' of particle sizes from 0.2  $\mu\text{m}$  to 3  $\mu\text{m}$ , which provides the binding force increase even up to 70 % [13].

A dynamic development of nanotechnologies created the possibility of using even smaller particles, namely nanoparticles, for the water glass modification.

Investigations concerning utilising nanoparticles in modifications of moulding and core sands binders have been

performed for some years already at AGH University of Science and Technology, Cracow, Poland [15-21].

The results of investigations of moulding sands with water glass modified by nanoparticles of the selected metal oxides in organic solvents, are presented in the hereby paper [21]. The obtained cohesion strength increase caused improvements of strength properties of moulding sands and of their knocking out ability [18,20,21].

## 2. Materials and methodology of investigations

Sodium water glass 'R 145' produced by Chemical Company Rudniki S.A. (Poland) of the following properties: density  $d_{20} = 1470 \text{ kg/m}^3$ , modulus  $M = 2.5$ , minimal content ( $\text{Na}_2\text{O} + \text{SiO}_2$ ) equal 41.6 % and maximum amount of water insoluble substances: 0.02 %,  $\text{pH} = 11.2$ , was subjected to modifications. The colloidal solutions of nanoparticles of zinc oxide (ZnO), aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and magnesium oxide (MgO) in methanol, ethanol or propanol, of a constant molar concentration  $M$  being  $0.3 \text{ mol/dm}^3$ , were water glass modifiers. The determined amount of the modifier colloidal solution was introduced into the water glass, and then mixed for 5 minutes by means of magnetic mixer to obtain a homogenous mixture. Nanoparticles were synthesized by the electrochemical method in the process of the anodic dissolution of metals: Zn, Al, Mg [22-24] in electrolyte. The structures of the synthesized nanoparticles were determined by means of the Transmission Electron Microscopy (TEM). Examples of the structure morphology and size of nanoparticles can be seen in photographs in Figure 1.

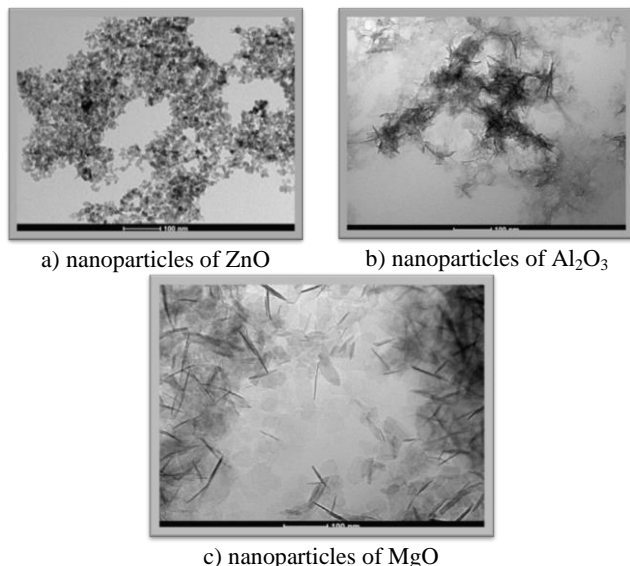


Fig. 1. a-c SEM (Scanning Electron Microscope) photographs of examples of the structure morphology and size of nanoparticles, electrochemically synthesized in the anodic metal dissolution process, utilised for the water glass modification [22-24]

Moulding sands were prepared on the high-silica sand matrix from the Sand Mine 'Szcakowa S.A.' (the main fraction: 0.32/0.20/0.16; AFS grain number  $L = 55.58$ ; average grain size  $d_L = 0.23 \text{ mm}$  and sand homogeneity index  $GG = 65 \%$ ).

In basic investigations aimed at the determination of the influence of the water glass modification with nanoparticles of metal oxides on the tensile strength  $R_m^u$ , moulding sands contained: high-silica sand 'Szcakowa' - 100 parts by weight; binding material (modified water glass) - 3 parts by weight; modifier: nanoparticles of metal oxides: 3, 5 or 7 mass % in the relation to the binder. Moulding sands were hardened in the air. Standard tensile test specimens, compacted by vibrations, were prepared from moulding sands with fractions of the modified water glass and subjected to tensile test  $R_m^u$ , after 24 h of hardening.

## 3. Investigation of the results and their discussion

Investigations of moulding sands with water glass were carried out in two directions:

- the first one was aimed at the determination of the influence of the water glass modification on the moulding sands strength at ambient temperature (e.g. tensile strength  $R_m^u$ ),
- the second direction was focused on probable mechanism of the water glass modification with nanoparticles of metal oxides [21].

Some examples of the obtained investigation results of moulding sands with water glass modified with nanoparticles of metal oxides in organic solvents are presented below. The results of tensile strength  $R_m^u$  of moulding sands with modified water glass are presented in Table 1.

Table 1. Results of tensile strength  $R_m^u$  of moulding sands with modified water glass (after 24 h of hardening) [21].

Organic solvent /Tensile strength $R_m^u$	Kind of nanoparticles / Fraction of the modifier solution in a binder, mass %		
	3	5	7
	<b>ZnO</b>		
Methanol/ MPa	1.41	1.47	1.51
Ethanol/ MPa	1.62	1.74	1.73
Propanol/ MPa	1.55	1.81	1.72
	<b>Al<sub>2</sub>O<sub>3</sub></b>		
Methanol/ MPa	1.69	1.48	1.60
Ethanol/ MPa	1.59	1.72	1.64
Propanol/ MPa	1.77	1.65	1.76
	<b>MgO</b>		
Methanol/ MPa	1.27	1.60	1.43
Ethanol/ MPa	1.27	1.27	1.46
Propanol/ MPa	1.55	1.72	1.71

\*  $R_m^u$  of moulding sand with not modified water glass was equal 1.44 MPa.

The most intensive increase of tensile strength  $R_m^u$  was found in moulding sands with the water glass modified with nanoparticles of metal oxides in propanol. Thus, the addition of 5 mass % of the modifier in a form of the colloidal solution of ZnO in propanol. The increase of  $R_m^u$  by approx. 23 % was obtained by moulding sands with additions of 3 mass % of the colloidal solution of  $Al_2O_3$  nanoparticles in propanol. There was an increase of 19 % increase in tensile strength  $R_m^u$  obtained moulding sands with the water glass modified by 5 mass % addition of the colloidal solution of MgO nanoparticles in propanol. In order to determine the influence of pure alcohol - used as a solvent for nanoparticles - on properties of moulding sands with water glass, the tensile tests of these sands were prepared in the same way, but with additions of 5 mass % of alcohols: methanol, ethanol or propanol. The obtained results indicated that additions of alcohol alone caused insignificant increases of the tensile strength as compared to moulding sands with not modified water glass. The determined strength was: for methanol: 1.48 MPa (approx. 3 %\*); for ethanol: 1.47 MPa (approx. 2 %\*) and for propanol: 1.56 MPa (approx. 10 %\*), respectively (\*the percentage increase tensile strength  $R_m^u$  moulding sand with modified water glass with respect to the tensile strength  $R_m^u$  of the moulding sands with water glass unmodified)<sup>21</sup>. Thus, it can be stated that an increase of the tensile strength  $R_m^u$  of moulding sands with modified water glass was mainly caused by additions of metal oxides nanoparticles. The obtained strength increases of moulding sands with the modified water glass an ambient temperature are most probably the effects of interactions between binder and modifier. Changing the physicochemical properties and the structure of the water glass under the application of modifiers in the form of metal oxide nanoparticles in organic solvents was presented in the works [15-21].

Shifting of absorption bands found in the FT-IR spectra [19,21] obtained for the modified and not modified water glass in the range of wave numbers corresponding to siloxane bonds Si-O-Si, is probably the results of the presence of added nanoparticles. This can be confirmed by the fact that - in case of the FT-IR spectrum obtained for the water glass with only alcohol added - no shifting was observed.

Taking into account the presented results of the properties of moulding sands with the modified water glass at ambient and increased temperatures, as well as the results of the previous investigations of the authors, concerning the influence of the modifications by means of the colloidal solutions of metal oxides nanoparticles in alcohols on the water glass properties, endeavours to develop the mechanisms of these processes were undertaken.

### 3.1. Probable mechanisms of the water glass modification with metal oxides nanoparticles

On the basis of broad fundamental investigations (FT-IR, XRD, SEM (Scanning Electron Microscopy), viscosity, wettability) that were carried out by the authors, concerning the application of metal oxides nanoparticles in alcohol solutions for the water glass modification, which were verified in technological tests, the probable mechanisms of the modification process - in dependence of the temperature - can be proposed:

- mechanism of the water glass modification causing an increased tensile strength  $R_m^u$  of moulding sands **at an ambient temperature**,
- mechanism of the water glass modification **at increased temperatures** (in mould that is filled with molten metal) [21].

### 3.2. Probable mechanism of the water glass modification with metal oxides nanoparticles at an ambient temperature

The mechanism of the water glass modification causing the tensile strength increase  $R_m^u$  of moulding sands **at an ambient temperature** consists of the following stages [21] :

- chemisorption of nanoparticles of metal oxides on water glass micelles,
- partial dissociation of metal oxides nanoparticles in the water glass environment as a result of acidic-base interactions between oxides, water glass and solvents (alcohols),
- hardening of water glass by hydrogen bonds and by carbonisation. This process was the most intensive when metal oxides nanoparticles in propanol were applied for water glass modification. For this alcohol the most intensive absorption bands, attributed to carbonate bonds vibrations, were observed in the FT-IR spectra.

The structure of the formed silica gel decides on the properties (including tensile strength) of the moulding sand with water glass. The proper internal built of a high cross-linking degree depends on the free and uniform polycondensation of silica in the whole moulding sand. The binding reaction of water glass is accelerated by the addition of substances (coagulant) causing shifting to the right the hydrolysis reaction equilibrium and - in consequence - the silica precipitation from the solution and its coagulation. In case of introducing the alcohol solution of metal oxides nanoparticles into water glass, alcohol works like coagulant agent. Admittedly, out of three alcohols tested as solvents (methanol, ethanol and propanol) the most acidic character had methanol, however the coagulation rate was in this case too high and the obtained structure of the hardened water glass did not provide the expected improvement of the moulding sand tensile strength. Moulding sands have the highest tensile strength when the colloidal solution of each metal oxide was in propanol, which means that this alcohol (out of the three tested ones) provides the optimal coagulation conditions. In addition propanol indicates the best adsorption ability of  $CO_2$  (its highest solubility) [25-28], due to which the hardening process of the modified binder is enhanced. Thus, moulding sands with water glass modified by propanol solutions of nanoparticles had the best tensile strength  $R_m^u$  (Table 1).

Another important feature of the colloidal alcoholic solutions of metal oxides nanoparticles is their degree of fineness, which allows their accurate distribution in the moulding sand and simultaneously the number of the silicic acid nucleation centres increases, simplifying the formation of the spatial structure of anhydrous silica. It means that the smaller sizes of nanoparticles introduced into the water glass structure the more nucleation

centres are formed and the coagulation process is easier. The tested oxide nanoparticles were of various morphology (dimensions, shape). The molar concentration of metal oxides nanoparticles in alcohol solutions was the same in all tests. Since ZnO nanoparticles were the smallest (globules of diameter:  $20 < d_{ZnO} < 50$  nm), their number was the highest (in the solutions of the same concentration), which caused the cohesion forces of the modified water glass increase (increase of tensile strength). As structural investigations of the modified water glass solutions (FT-IR) indicate - the positive influence of the reactions of nanoparticles of metal oxides with water glass on changes of physicochemical properties of water glass can not be excluded.

### 3.3. Probable mechanism of the water glass modification with nanoparticles of metal oxides at increased temperatures

The mechanism of the water glass modification **at increased temperatures (in mould that is filled with molten metal)** consist of stages:

- destruction of oxygen bridges between silicate tetrahedrons  $SiO_4^{4-}$  in a liquid state,
- thermal dissociation of metal oxides,
- building in of metal cations into the silicate network with the formation of the following bonds: Si - O - **Zn** - O - Si; Si - O - **Al** - O - Si; Si - O - **Mg** - O - Si [21].

### 3.4. Influence of temperature and modifier addition on the water glass structure

Within the temperature range 550 - 670 °C (in dependence on the water glass modulus) the effect of softening of sodium water glass occurs, which weakens bonds between matrix grains in moulding sands. After cooling, the moulding sand has the same structure, but of a smaller strength and therefore within the range 500 - 700 °C the minimum of the final compression strength of the moulding sand is observed. The temperature range 730 - 870 °C corresponds to the flow temperature, at which the water glass transition from a high-elastic state into a plastic and liquid state occurs. During cooling the transition from a high-elastic state (flow) into a glassy state occurs (glassy temperature  $T_g$  - temperature of transition from a high-elastic (flow) state into a glassy state, which occurs during cooling). In such case a strong water glass structure is obtained, which causes an abrupt increase of the tensile strength of the moulding sand with water glass at a temperature of approx. 800 °C.

In a liquid state tetrahedrons  $SiO_4^{4-}$ , present in the silicate structures, are joined with each other at corners (by means of oxygen bridges - in a similar fashion as in the solid state). However, after melting a regularity in a long-range order of structural elements decays, while an arrangement of tetrahedron in an intermediate-range order remains to a significant degree. In addition in a liquid state some corners become free. When basic oxides e.g. CaO or MgO, are added to liquid silicate, oxygen  $O^{2-}$  ions - formed due to the dissociation of these oxides - are joining

themselves to silica tetrahedrons causing breaking of oxygen bridges and entering the newly formed gaps, what in consequence breaks the structure. This process is shown according to the scheme at the example of magnesium oxide, MgO, in Fig. 2 [21]. MgO dissociates according to the reaction (1):



Oxygen atoms present in places of broken oxygen bridges have a charge<sup>1</sup>, and due to that, positively charged cations of  $Mg^{2+}$  situate themselves in their vicinity in empty spaces of the network.

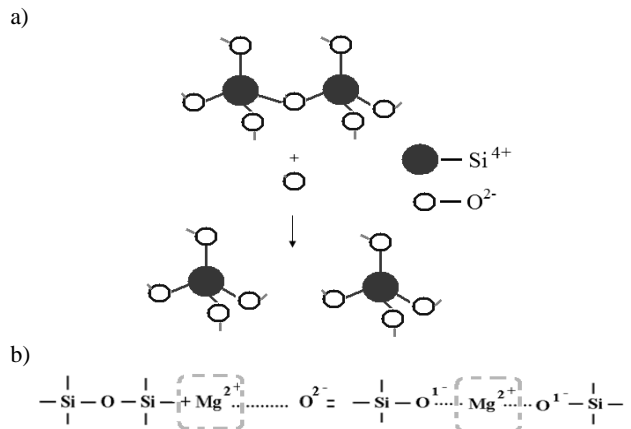


Fig. 2. a, b) Schematic presentation of processes occurring in the modified water glass at a temperature of the mould pouring with liquid metal a) Breaking of oxygen bridges in the oligomeric silicate network, type Q<sup>1</sup> by O<sup>2-</sup> ion, b) The process of magnesium cations  $Mg^{2+}$  building-in - by means of ionic bonds - into the silicate structure (presents schematically the ionic bond) [21]

The gradual structure transformation related to this process probably causes increasing of a flow/glassy temperature of water glass with additions of oxides and - in consequence - shifting the maximum retained tensile strength into a higher temperature (approx. 900 °C).

Magnesium oxide MgO which, out of the tested modifiers, due to its weakest oxygen attractive force [26 -28], is the easiest to return oxygen and in the  $Mg^{2+}$  cation form builds-in into the silica network by ionic bond. Zinc and aluminium oxides ( $ZnO$  and  $Al_2O_3$ ) dissociate not so easily (because in these oxides the bounding power between the cation and oxygen ion is stronger) and therefore the building-in of  $Zn^{2+}$  and  $Al^{3+}$  cations into the water glass structure occurs in a rather small degree.

Generally, the less basic oxide character the weaker its modifying influence on water glass. The knock out results of moulding sands with water glass confirm the above [21]. In order to confirm the proposed modification mechanisms of water glass (applied as the binder of moulding sands) by nanoparticles of metal oxides ( $ZnO$ ,  $Al_2O_3$  or MgO) - in organic solutions - it is necessary to perform additional studies, e.g. structural

Example of the structure and morphology of water glass (after modification process) with nanoparticles of MgO can be seen in photographs TEM (Transmission Electron Microscopy) in Figure 3.



**MgO  
nanoparticles**

Fig. 3. TEM (Transmission Electron Microscopy) photographs of examples of the structure and morphology of water glass (after modification process) with nanoparticles of MgO.

## 4. Summary

The foundry industry is not immune to increasing environmental requirements. This results in the search for new inorganic binders, mainly water-glass-based, or improving ones already in use. The most effective methods consist in directly modifying water glass. There are various methods of modifying it, but as this publication shows, modification with the use of nanoparticles of selected metal oxides is very effective. It boosts the strength parameters of the sand, which are the two key characteristics hindering the use of sands containing water glass. Based on the authors' wide-range research on water glass modification with metal oxides and the ion theory of the structure of liquid metallurgical silicate slag, the mechanism of nanoparticle effect was developed with a view to improving water glass properties. Two probable mechanisms operate here, depending on the process temperature:

- 1) The mechanism of the water glass modification causing the tensile strength increase  $R_m''$  of moulding sands at ambient temperature,
- 2) The mechanism of the water glass modification at increased temperatures (at the mould pouring with liquid metal) [21].

The proposed mechanism for the effect of metal oxide nanoparticles, a solution of water glass used as a binder needs further studies using modern methods, e.g. Raman spectroscopy.

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