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Nanocomposites Based on Water Glass Matrix as a Foundry Binder: Chosen Physicochemical Properties

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Abstract

The nanocomposites based on water glass matrix were attempted in the study. Nanoparticles of ZnO, Al_2O_3 or MgO in organic solutions were applied into water glass matrix in the amounts of: 1.5; 3; 4 or 5 mas. %. Wettability of the quartz sad by the nanocomposites based on water glass matrix was determined by testing changes of the wetting angle θ in time τ for the system: quartz – binder in non-stationary state, by means of the device for measuring wetting angles. Wettability measurements were carried out under isothermal conditions at an ambient temperature (20 – 25 ^oC). The modification improves wettability of quartz matrix by water glass, which is effective in improving strength properties of hardened moulding sands. Out of the considered modifiers in colloidal solution of propyl alcohol water glass modified by MgO nanoparticles indicated the smallest values of the equilibrium wetting angle θ_r. This value was equal app. 11 degrees and was smaller no less than 40 degrees than θ_r value determined for not modified water glass. Viscosity η of nanocomposites based on water glass matrix was determined from the flow curve, it means from the empirically determined dependence of the shearing stress **τ** on shear rate **γ**: τ = f (γ) (1), by means of the rotational rheometer. Measurements were carried out at a constant temperature of 20 ^oC. The modification influences the binder viscosity. This influence is conditioned by: amount of the introduced modifier as well as dimensions and kinds of nanoparticles and organic solvents. The viscosity increase of the modified binder does not negatively influence its functional properties.

Keywords: Innovative technologies, Water glass, Nanoparticles, Wettability, Viscosity

1. Introduction

Wettability of solids by liquids and these liquids viscosity, is important in several technological processes, such as e.g. flotation, printing, catalysis, deposition of coatings, gluing, as well as preparation of moulding sands. In the case of moulding sands the main aim is making stable connections: matrix grains - binder, which are providing the casting moulds stability. These parameters can be controlled either by a matrix surface modification or by a binder modification [1 - 3]. In modifications of surfaces (high-silica sand) the chemical or physical agents, which significantly increase polarity and surface energy, are applied. Thus, due to the modification, it is possible to introduce into a material structure various functional groups increasing wettability [3, 4, 5]. These functional groups ensure formations of physical and chemical bonds since, as it is known, atoms being on interphase boundaries behave differently than atoms inside a phase. They are attracted from one side by atoms of their own phase and from the other side by atoms from the neighbouring phase. Thus, they are in an asymmetrical field of force.

Systems water glass - high-silica sand are characterised by a relatively weak wettability and therefore these systems are often modified. A wetting angle in this system changes in time up to the moment when the system obtains its steady state.

This process is influenced by two components: thermodynamic and dynamic. A thermodynamic component is caused by surface coarseness and heterogeneity. A different surface state can cause that a drop is in various metastable states, accompanied by various wetting angles. A dynamic component depends on time. It is effected by: e.g. interphase chemical influences of the type: liquid - solid, or the reorganisation of particles on a surface [3, 4].

In dependence of physicochemical parameters of a binder and a matrix, joints of these elements formed in a moulding sand can be of various geometry, corresponding to:

- Coating connection [2, 6], which occurs at a high viscosity of a binder where its majority is adsorbed on matrix grains surfaces forming a tight layer and only a small part flows to contact points forming a concave meniscus (Fig. 1 a, b),
- Non-coating connection [2, 6], which occurs at a small viscosity of a binder when only a small amount of a binder adsorbs on matrix grains surfaces forming a thin film, and its majority flows to contact points forming a concave meniscus (Fig. 2 a, b).

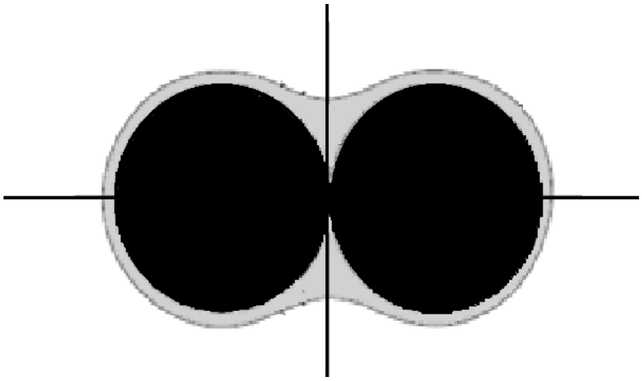

Fig. 1. a) Binder distribution on surfaces of matrix grains, corresponding to the so-called coating model [2, 6]

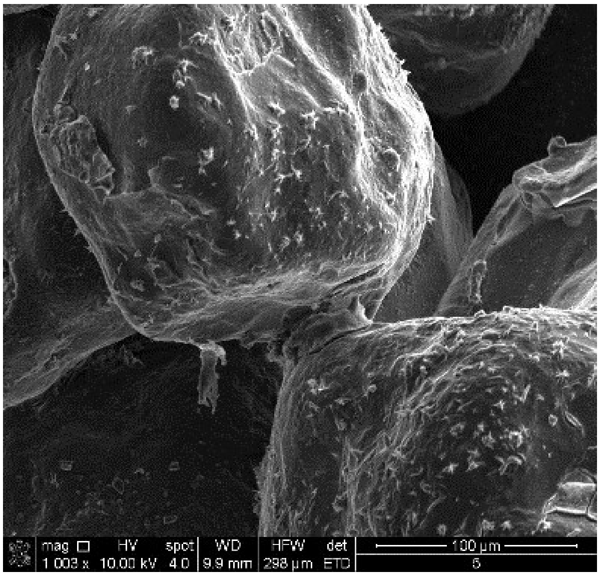

Fig. 1. b) Photo of the real system: high-silica sand - water glass [9]

2. Materials used for investigations

Materials used for investigations:

- Sodium water glass „R 145" produced by: Rudniki S.A. of the following properties: density d_{20} = 1470 kg/m^3, modulus M = 2.5, minimum content (Na_2O + SiO_2) equal 41.6 %, maximum amount of substances insoluble in water - 0.02 %, pH = 11.2.
- Modifiers of water glass constituted **colloidal solutions of nanoparticles:** zinc oxide **(ZnO)**, aluminium oxide **(Al_2O_3)** and magnesium oxide **(MgO)** in organic solvents of a constant molar concentration M, being 0.3 mol. Nanoparticles were synthesised by the electrochemical method [7].

3. Methodology of investigations

Methodology of investigations:

- The modification treatment of water glass consisted of the introduction of: **1.5**; **3**; **4**; **5** mas. % (in relation to water glass) of a colloidal solution of metal oxides in organic solvents, followed by a precise homogenisation of the mixture.
- The ability of wetting of the high-silica matrix of modified binders was determined.

Wettability of the matrix by a binder was determined by testing changes of the wetting angle θ in time τ for the system: quartz – binder in non-stationary state, by means of the device for measuring wetting angles. Wettability measurements were carried out under isothermal conditions at an ambient temperature (20 - 25 ^{o}C).

Viscosity η of binders was determined from the flow curve, it means from the empirically determined (1) dependence of the shearing stress $\boldsymbol{\tau}$ on shear rate $\boldsymbol{\gamma}$:

$$\tau = f(\gamma) \quad (1)$$

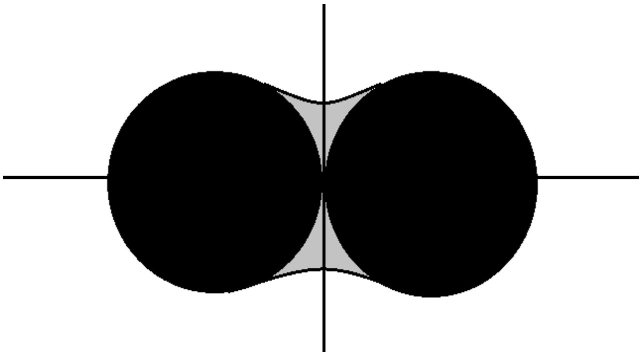

Fig. 2. a) Binder distribution on surfaces of matrix grains, correspondingto the so-called non-coating model [2, 6]

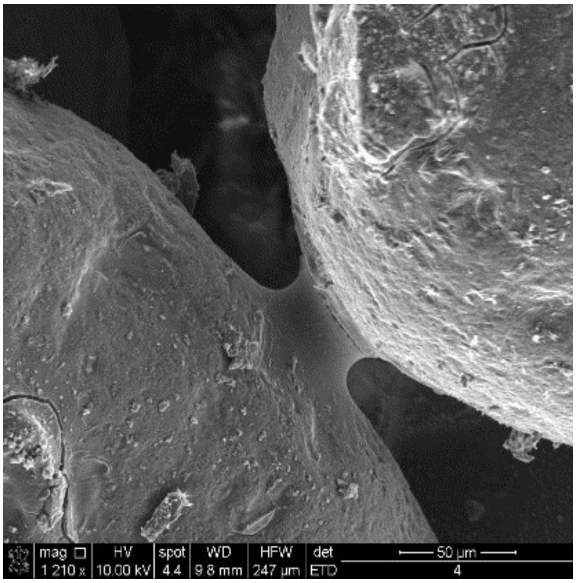

Fig. 2. b) Photo of the real system: high-silica sand - nanocomposite based on water glass matrix [9]

by means of the rotational rheometer. Measurements were carried out at a constant temperature of 20 ^{o}C. On the basis of the obtained flow curve the dynamic viscosity value of a binder η.

4. Investigation results and their discussion

4.1. Wettability in the system: quartz - water glass

It was shown by investigations that when there is the same modifier addition and the same organic solvent it is possible to notice an influence of the kind of nanoparticles on the quartz wettability. However, the in-depth analysis of this process is hindered by various structures of nanoparticles (globules, flakes and viscers).

As an example: time functions θ = f (τ) for the system: quartz - water glass modified by colloidal solutions of: ZnO, Al_2O_3 and MgO in propyl alcohol, are presented in Figure 3. Measurements were carried out at a constant modifier additions Q = 5 mas. % and the same solvent.

Out of all considered modifiers (Fig. 3) in the colloidal solution in propyl alcohol the smallest value of the equilibrium wetting angle θ_r indicated water glass modified by MgO nanoparticles. This value was equal app. 11 degrees and was lower by app. 40 degrees from θ_r , determined for not modified water glass. The modification by the remaining nanoparticles, i.e. ZnO and Al_2O_3 in propyl alcohol, much less improved the quartz surface wettability. The equilibrium wetting angle values were 22 and 18 degrees, respectively. The performed investigations indicated that out of considered nanoparticles, the addition of MgO to the water glass structure influenced to the highest degree the improvement of the quartz surface wettability.

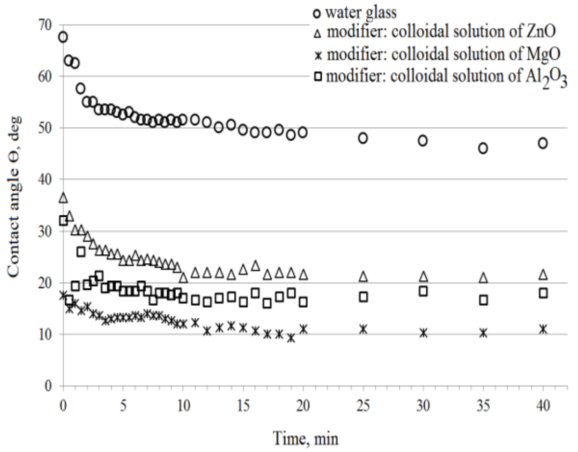

Fig. 3 . Influence of the kind of nanoparticles on the wetting angle changes versus time, in the system: quartz – water glass with various oxides nanoparticles in organic solvent. Modifier mass fraction Q = 5 mas. %, solvent - propyl alcohol [9].

4.1.1. Influence of the organic solvent kind on the wettability in the system: quartz - water glass

The performed investigations indicated the influence of the kind of the applied alcohol (methyl, ethyl, propyl) on the quartz surface wettability. The compiled results of the quartz wettability by water glass modified by 5 mas. % of colloidal solutions of ZnO nanoparticles in organic solvents: methyl, ethyl and propyl alcohol, are given in Table 1. It can be seen - from the presented compilation - that the best solvent for the considered nanoparticles is propyl alcohol. The binder modified by the colloidal solution of nanoparticles in propyl alcohol is characterised by the lowest value of the equilibrium wetting angle being app. 22 degrees, while in ethanol and methanol these values are equal app. 35 and 45 degrees, respectively. Nevertheless, they are still slightly lower than the analogous value for not modified water glass (θr = 48 degrees).

Table 1.
Compilation of the results of the quartz wettability by nanocomposites based on water glass matrix, with a constant mass fraction (5 mas. %) of ZnO nanoparticles [9].

Kind of solvent	$\theta_{0\ average}$ [deg]	$\theta_{r\ average}$ [deg]	τ_r [min]
Unmodified water glass	67	48	~14
Methyl,	55	45	~12
Ethyl	44	35	~ 12
Propyl	33	22	~ 9

θo: initial wetting angle directly after the binder deposition on the quartz surface (degrees)
θr: equilibrium wetting angle (degrees)
τ_r: time of reaching the steady state by the system: quartz - binder (min.)

This can be explained by different length of the hydrocarbon chain. The longer hydrocarbon chain of the solvent the better adsorption of the modified water glass on the quartz surface and the better its wettability [8, 9]. The longest hydrocarbon chain among the considered alcohols has propyl alcohol (of a structural formula CH_3-CH_2-CH_2-OH) and this is the reason of the best wettability. Wettability properties correlate well with moulding sands strength properties [9].

4.1.2. Influence of the modifier fraction on the wettability in the system: quartz - water glass

The compilation of the results of investigations of the quartz wettability by water glass modified by: **1,5; 3, 4 or 5** mas. % of a modifier, in a form of colloidal solution of nanoparticles of: ZnO, MgO or Al_2O_3 in propyl alcohol, is shown in Table 2.

Table 2.
The compilation of the results of the quartz wettability by nanocomposites based on water glass matrix. Kind of nanoparticles: ZnO, MgO and Al_2O_3 in propyl alcohol [9, and unpublished research].

Modifier addition [mas. %]	$\theta_{0\ average}$ [deg]	$\theta_{r\ average}$ [deg]
Unmodified water glass	67	48
1.5: ZnO	62	38
3 : ZnO	60	43
4 : ZnO	37	26
5 : ZnO	33	19
1.5: Al_2O_3	29	14
3: Al_2O_3	30	15
4: Al_2O_3	33	16
5: Al_2O_3	36	17
1.5: MgO	32	21
3 : MgO	31	18
4: MgO	24	16
5 : MgO	18	11

Investigations indicated that the ability of quartz wetting by colloidal solutions of ZnO and MgO in propyl alcohol increases with an increased modifier addition (Table 2). This property correlates with the strength results of these moulding sands, since they were of the highest tensile strength R_m^u [9].

Also in case of water glass modified by nanoparticles of Al_2O_3 in propyl alcohol an increase of the modifier fraction to 5 mas. % causes an increase of the equilibrium wetting angle θ_r from 15 to 17 degrees.

4.2. Water glass viscosity

4.2.1. Influence of the kind of nanoparticles on the water glass viscosity

The compiled results of viscosity values of modified binders (Table 3) indicate an insignificant influence of the nanoparticles kind on the viscosity value. As it results from the performed tests, modifiers in a form of colloidal solutions of ZnO and MgO nanoparticles in methyl alcohol, cause similar increases of the water glass viscosity (by app. 33 %). Whereas modifiers containing colloidal solution of Al_2O_3 nanoparticles in methyl alcohol caused app. 17 % increase of this parameter in relation to not modified water glass.

Table 3.
The compilation of the results of viscosity of the water glass modified by 5 mas. % colloidal solutions of nanoparticles ZnO, MgO and Al_2O_3 in methyl alcohol [9]

Kind of nanoparticles	η [Pa•s]
Unmodified water glass	0,12
ZnO in methyl alcohol	0,16
MgO in methyl alcohol	0,16
Al_2O_3 in methyl alcohol	0,14

4.2.2. Influence of the kind of organic solvent on the water glass viscosity

Apart the modifier fraction, dimensions and kind of nanoparticles, also the kind of organic solvent influence the water glass viscosity. Measurements were performed at constant dimensions of nanoparticles, d_{ZnO} app. 50 nm and a constant modifier fraction Q = 5 mas. %. At constant values of Q and d the highest influence on the binder viscosity had colloidal solutions of nanoparticles in propyl alcohol while the smallest influence had colloidal solutions of nanoparticles in butyl acetate (Table 4). Apart from the length of the hydrocarbon chain the solvent polar properties influence molecular interactions. Out of the discussed solvents the highest polar properties has propyl alcohol (dipole moment μ_{20} = 3.09 D). This leads to electrostatic attraction of particles and efficient increase of its dimensions and - in consequence - to obtaining the binder of as high as possible viscosity. Polar properties of butyl acetate (dipole moment μ_{20} = 1.87 D) and methyl alcohol (dipole moment μ 20 = 1.6 D) are similar, and therefore intermolecular influences are also similar.

Table 4.
The compilation of the results of viscosity of the water glass modified by 5 mas. % colloidal solutions of nanoparticles ZnO in: methyl, propyl or butyl acetate [9]

Nanoparticles of ZnO	Ƞ [Pa•s]
Unmodified water glass	0.12
Methyl	0.16
Propyl	0.25
Butyl acetate	0.14

4.2.3. Influence of the modifier solution fraction on the water glass viscosity

Modifying water glass by colloidal solutions of nanoparticles of metal oxides influences also its viscosity. This influence depends on the following factors: modifier fraction, dimensions of nanoparticles, nanoparticles and organic solvent kind.

Measurements were carried out at a constant temperature (20 ^{o}C) and the same organic solvent. Rheological investigations indicate that the flow curves are straight lines starting from the origin of the coordinate system: (γ, τ), which indicates the Newtonian character of binders ($\tau = \eta \cdot \gamma$) with the rheological parameter - viscosity η , characteristic for this type of fluids.

The binder viscosity increases when the amount of the introduced modifier increases. As an example: the water glass viscosity modified by: **1.5; 3; 4 or 5** mas. % of ZnO nanoparticles in methyl alcohol equals app.: 0,13 Pa•s; 0.14 Pa•s ; 0.15 Pa•s and 0.16 Pa•s, respectively.

A viscosity increase, after modifying the binder by the colloidal solution of nanoparticles in methyl alcohol, can be explained by the coagulation process occurring under an influence of alcohol. Another probable factor influencing a viscosity constitutes building-in of metal cations into the binder matrix with forming a new phase of larger dimensions (as compared with micelles of not modified water glass) causing an increase of the internal friction, which measure constitutes the binder viscosity. A similar effect is observed in case of the modifier in a form of the colloidal solution of Al_2O_3 nanoparticles in methyl and propyl alcohol. Cumulative results of viscosity measurements for binders with the discussed modifiers are given in Table 5.

Table 5.
The compilation of the results of viscosity of the water glass with different oxide nanoaprticles in methyl or propyl alcohol [9, and unpublished research]

Modifier addition [% mas.]	Ƞ [Pa•s]
Unmodified water glass	0.12
1.5: ZnO in methyl	0.13
3: ZnO in methyl	0.14
4: ZnO in methyl	0.15
5: ZnO in methyl	0.16
1.5: Al_2O_3 in methyl	0.128
3: Al_2O_3 in methyl	0.13
4: Al_2O_3 in methyl	0.137
5: Al_2O_3 in methyl	0.14
1.5: Al_2O_3 in propyl	0.16
3: Al_2O_3 in propyl	0.17
4: Al_2O_3 in propyl	0.156
5: Al_2O_3 in propyl	0.15

The water glass viscosity increase after its modifying does not disqualify this binder with regard to functional properties, since - as indicates the author of paper [10] - the recommended value of this parameter under industrial conditions should not exceed 1 Pa•s.

5. Conclusions

The performed investigations of the water glass modification by colloidal solutions of metal oxides: **ZnO, Al_2O_3 or MgO in** organic solvents indicated that:

- The modification **improves wettability** of quartz matrix by water glass, which is effective in improving strength properties of hardened moulding sands [9].
- Out of the considered modifiers in colloidal solution of propyl alcohol water glass modified by MgO nanoparticles indicated the smallest values of the equilibrium wetting angle θ_r. This value was equal app. 11 degrees and was smaller no less than 40 degrees than θ_r value determined for not modified water glass.

The modification influences on the **binder viscosity**. This influence is conditioned by: amount of the introduced modifier as well as dimensions and kinds of nanoparticles and organic solvents. The viscosity increase of the modified binder does not negatively influence its functional properties [9].

The research presented in [9] showed that the modification of water glass by metal oxide nanoparticles improve the knocking out properties of the moulding sands. This is confirmed by parallel studies using R_c^{tk} and the Polish Standard PN-85 / H-11005. Probably this is due to changes in the structure of the binder after the modification process by nanoparticles at high temperature [9].

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