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The mechanism of improving the knock-out properties of moulding sands with water glass

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Abstract

The article concerns a trial of explaining the mechanism of improving the knock-out properties of moulding sands with water glass made in ester technology after using the new additive called Glassex. Within the labour, the variety of technological and basic researches were done, including the researches evaluating the chemical influence of the new additive.

Keywords: Moulding sands; Water glass; Knock-out properties; New additive Glassex

1. Introduction

Loose self-hardened moulding sands with water glass are the most widespread moulding sands from the group of moulding sands with inorganic binder. According to the pro-ecological character of binder, the meaning of these moulding sands becomes very crucial for industrial practise. However the inorganic binder makes the knock-out properties of these moulding sands weaker.

The authors elaborated a new Glassex for moulding sands with water glass. It is an inorganic additive consisting of SiO_2 (65 – 75%), Al_2O_3 (10 – 18%), $K_2O + Na_2O$ (6 – 9%), MgO + CaO (2 – 6%), Fe_2O_3 (1 – 5%) and water (2 – 5%). Moulding sands with this additive are described with patent no. P-365723.

Previous publications (1-4) showed the influence of Glassex additive on the knock-out properties of moulding sands with water glass. Fig 1 shows the influence of the additive on the knock-out properties of moulding sand with water glass measured according to PN-85/H-11005 and fig. 2 presents the influence of the additive on the knock-out properties of moulding sand with water glass estimated on the basis of moulding sand's retained strength measurement.

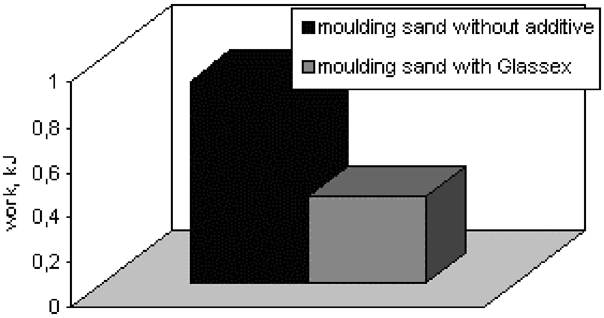

Fig. 1. The influence of Glassex additive on the knock-out properties of moulding sands with water glass, described according to PN-85/H-1100

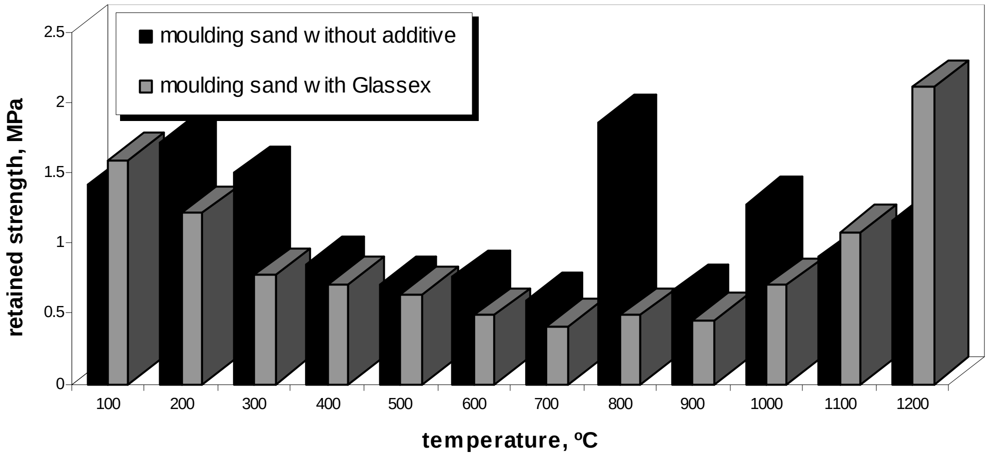

Fig. 2. The influence of Glassex additive on retained strength of moulding sand with water glass

Inserting the Glassex additive to moulding sand with water glass leads both to double improvement of its’ knock-out properties defined according to PN-85/H-11005 (fig. 1) and to lowering the retained strength of moulding sand in measured range of temperature (fig. 2)/. Moreover, the change of retained strength curve of moulding sand has been noticed after the Glassex additive was inserted. On the curve, there is no maximum by the temperature of 200°C, which is characteristic for moulding sands prepared in ester technology, and the second maximum by the temperature of 800°C is moved into direction of higher temperatures.

The article (5) widely explains the influence of Glassex additive on the phenomenon of moulding sand’s thermal expansion. Presented researches proved that inserting the new additive into moulding sand causes the stop of researched moulding sand’s thermal expansion, lowers the pressures and improves the knock-out properties. The question is: whether the influence of this new additive has only the mechanical character, so it causes the relaxation of internal stresses or does this influence also the chemical character. Within the frames of this article, authors present the conclusions of further basic researches, tending to explain the mechanism of the additive’s influence.

2. Researches

These were researches of moulding sands based on quartz sand with water glass R-145 in quantity of 3 part by weight, and ester hardener – flodur – in quantity of 0,3 part by weight. The Glassex additive was inserted into moulding sand in quantity of 1,0 part by weight.

2.1 Spectroscope researches

The method of spectroscope in infrared was chosen to explain the influence of Glassex additive on hardening process of water glass. This method gives the possibility of analysis in the whole volume of fine-grained material, as the moulding sand.

These researches were made with Digilab Excalibur FTS 3000 Mx Spectroscope with DTGS detector, electrically cooled. The spectroscope is equipped with ATR unit with ZnSe crystal for multiple reflection and transmission unit. The samples for transmission measurements were prepared in the form of KBr pills pressed in matrix under the thrust of 7Mg. The pill was then out into the measuring chamber of FTIR spectrometer.

Transmission spectrum of samples examined in range of 4000 – 400 cm^{-1} were registered. The number of scans was chosen depending on the level of received signal within the range of 32-64 scans. The correction of base line of received spectrums was run with MERLIN (FTS 3000) software.

Structural examination of liquid water glass was run with ATR method. Fig 3a shows the spectrum of water glass. The spectrum includes absorption bands, standing for stretching vibrations of –OH groups in range of 3700 – 2800 cm^{-1}

By 1643 cm^{-1} there is an absorption band standing for bending vibrations H_2O. In the range of wave numbers below 1200 – 900 cm^{-1} , there are bands characteristic for silicate lattices complying with Si–O–Si and O–Si–O vibrations.

Band 1732 cm^{-1} seen on the spectrum stands most probably for asymmetrical stretching vibrations Si=O, and 1376 cm^{-1} band for symmetric stretching vibrations Si=O.

ATR technique was used for structural researches of ester hardener – flodur.

Achieved spectrum is presented on Fig. 3b. Very weak and blurred band by the 3479 cm^{-1}, standing for ν–OH vibrations, can be seen in the spectrum of flodur. As well as weak band by 2959 cm^{-1} of stretching vibrations C-H can be noticed. Characteristic band by 1736 cm^{-1} 1736 cm^{-1} complying with stretching vibrations C=O in esters (–CO–O–CH_2–). Moreover, the absorption bands complying with bending vibrations C–H (1443 cm^{-1}, 1373 cm^{-1}) and band characteristic for stretching vibrations C–O (1215 cm^{-1}).

Further examinations were run for water glass hardened with flodur. Transmission technique was used for this researches. Received spectrum is presented on Fig. 3d.

In the spectrum of water glass hardened with flodur, there is a displacement of band's maximum from 3341 cm^{-1} to 3431 cm^{-1}, which is connected with creation of influences of physical-culombus type (hydrogen binder). As a result of hardening the water glass with flodur, there is a decay of bands 1732 cm^{-1} (from water glass) and 1736 cm^{-1} (from flodur).

However, there is a new band 1568 cm^{-1} connected with the reaction of crosslinking. The displacement of 991 cm^{-1} band to 1049 cm^{-1} is also ^{1} connected with the reaction of crosslinking.

Structural examinations of Glassex additive were run using the transmission technique. Received spectrum is seen on Graph 3c. In the spectrum of Glassex additive, bands characteristic for symmetrical stretching groups –OH (Si–OH, Al–OH, Fe–OH) can be seen. By 1634 cm^{-1} there is an absorption band complying with bending vibrations H_2O. In the range of wave numbers 1163 –789 cm^{-1}, there is a presence of bands characteristic for Si–O–Si, Si–O–Al and Si–O–Fe vibrations.

Structural examinations of water glass with Glassex additive, hardened with flodur – were run with transmission technique. Received spectrum is shown on Graph 3e. During the hardening of water glass with Glassex additive by flodur, there can be seen some changes of bands' location, connected with the reaction of water glass with hardener. After hardening, there are some noticed changes on the spectrum:

- Displacement of a band → 3447 cm^{-1} with appearance of additional arms in this band: 3285 cm^{-1}, 3161 cm^{-1},
- Displacement of a band → 2984 cm^{-1}
- Appearance of an additional band 1690 cm^{-1},
- Appearance of band 1564 cm^{-1},
- Displacement of two bands → 1414 cm^{-1} and 1413 cm^{-1},
- Band covered by other bands in ~1200 cm^{-1},
- Displacement of band → 1196 cm^{-1}.

Creation of additional arms in 3285 and 3161 cm^{-1} can be caused by crosslinking of oxides, coming from the Glassex additive during the hardening process. These are the bands characteristic for systems with crystal structure. There can be few parallel reactions resulting in creating new bindings, that have an influence on the appearance of new band in 1690 cm^{-1}. Table 1 presents the compilation of received results.

Results of structural examinations confirmed the chemical influence of Glassex additive on the structure of water glass hardened with flodur (Fig. 3d and 3e). Displacements of already existing bands on the spectrum of water glass hardened with flodur and the creation of additional bands after insertion of new additive, is connected with creation of additional bindings after hardening the water glass.

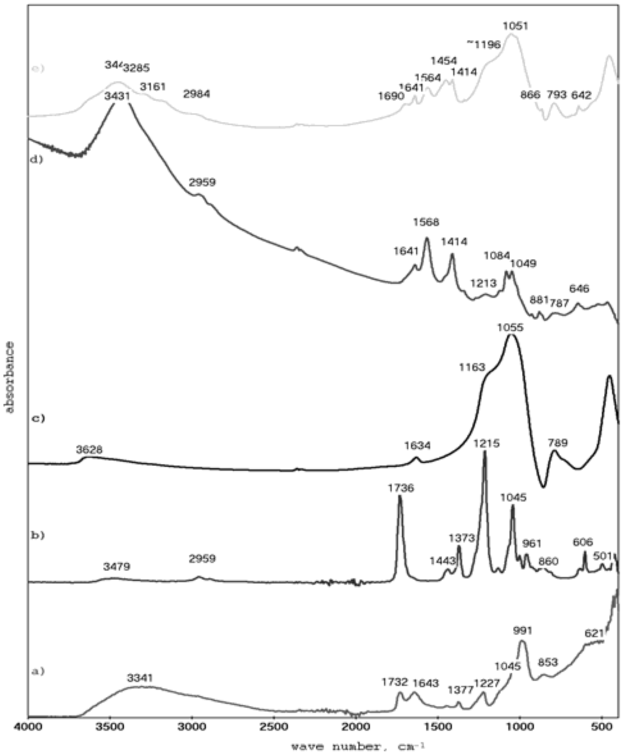

Fig. 3. Spectrums FT-IR: a) water glass, b) flodur, c) Glassex additive, d) water glass hardened with flodur, e) water glass with Glassex additive, hardened with flodur

2.2. Identification of phase γ-Al_2O_3

Basing on the literature [6, 7] , it is supposed that the interaction of new additive in increased temperatures is caused by insertion Al_2O_3 into moulding sand.

I.S. Syčev [6] and P. Jelinek [7] have been elaborated the topic of Al_2O_3 additive's influence on the knock-out properties of moulding sands with water glass. They suggest, that after insertion of Al_2O_3 additive, caused by temperature of liquid foundry alloy, there is a creation of active γ-Al_2O_3 phase, which makes the displacement of II maximum on the curve of retained strength into direction of higher temperatures.

They proved, that some materials consisting of Al_2O_3, such as ile and boxite displace the II maximum of retained strength in the direction of higher temperatures. (above 1000°C).

Because of the fact, that the creation of molten glass causes the presence of II maximum, the displacement in the direction of higher temperatures results in transition from the double system Na_2O – SiO_2 into triple system Al_2O_3 – SiO_2 – Na_2O with high melting point. Such a system is presented on Fig.4 [8].

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Table.1
Characteristic absorption bands in spectrums FT-IR of examined samples and their interpretation

Water glass[cm^{-1}]	Flodur [cm^{-1}]	Glassex [cm^{-1}]	Glass+Flodur [cm^{-1}]	Glass+Flodur+Glassex [cm^{-1}]	Element of structure
3341	3479	3628	3431	3447 3285 3161	ν-OH OH···O-Si-O O-H···O-H O-H···O=C
–	2959	–	2959	2984	C-H (stretching)
–	–	2360	2342	2359	
–	1736	–	–	~1690	ν-C=O in esters
1732	–	–	–	–	ν -Si=O
1643	–	1634	1641	1641	Vibrations bending H_2O
–	–	–	1568	1564	C=O···H
–	1443	–	–	1454	C-H (bending)
–	1373	–	1414	1414	C-H (bending)
1376	–	–	–	–	ν_s-Si=O
1227	1215	–	1213	~1200	Si-O in water glass C-O (stretching, assym.)
1045	–	1163	1084	1196	Si-O-Me: Si-O-Al
–	1045	1055	1049	1051	Si-O-Si
–	961	–	881	866	
991	–	789	787	793	Si-O-Si Si-O-Me: Si-O-Al

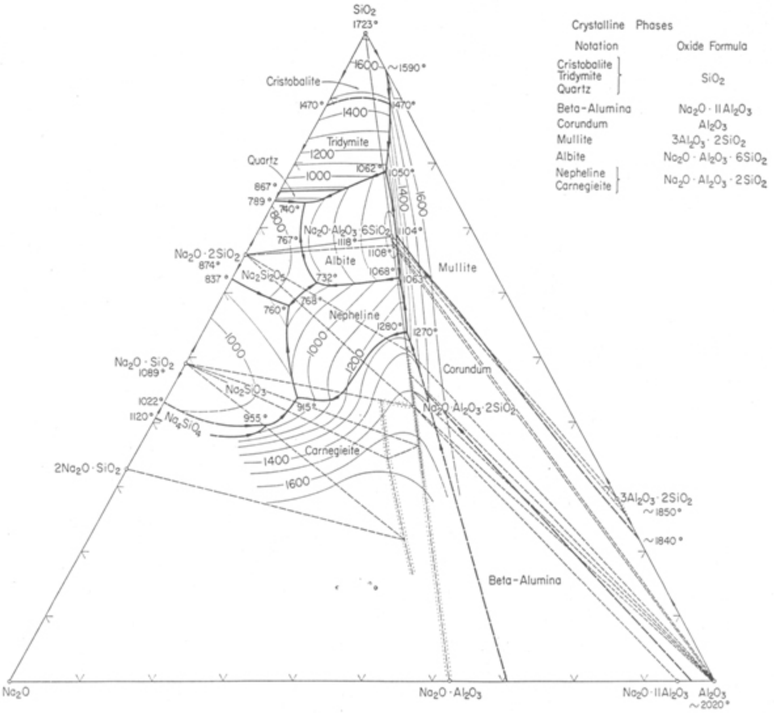

Fig. 4. Triple system Na_2O – Al_2O_3 – SiO_2 [8]

The next beneficial effect of Al_2O_3 influence on knock-out properties, can be α–SiO_2 stabilisation in transition direction in cristobalite, which is connected with constant expansion growth of volume of moulding sand with quartz matrix. Literature data show, that γ-Al_2O_3 phase can be identified while carrying out the examination of X-ray diffraction of examined material [9]. Fig.5 presents typical X-ray diffraction of Al_2O_3 phase.

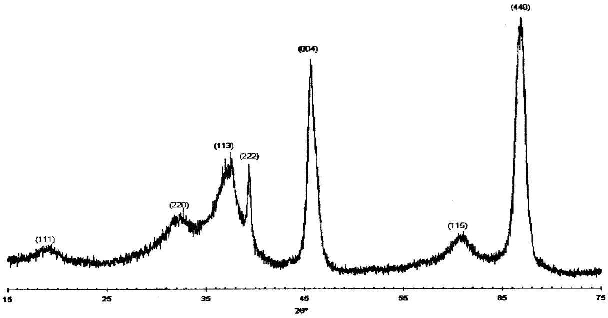

Fig. 5. Typical curve of X-ray diffraction of γ-Al_2O_3 phase [9]

2.3. X-ray examination

X-ray diffraction examination was carried out using the X-ray photograph Krystalloflex 4H from Siemens.

Fig. 6 presents the curve of X-ray diffraction of Glassex additive in the initial state. Peaks characteristic for γ-Al_2O_3 phase couldn't be found here, which may suggest that this phase may not be present in Glassex additive. Curve of X-ray diffraction of Glassex additive heated in temperature of 800°C (fig.7) was also carried out, just to make sure that the phase didn't create just after heating of additive. Literature sources present that γ-Al_2O_3 phase forms after heating till the temperature of 720°C.

Diffraction pattern is presented on Fig.7. Also here, the peaks characteristic for γ-Al_2O_3 phase haven't been noticed.

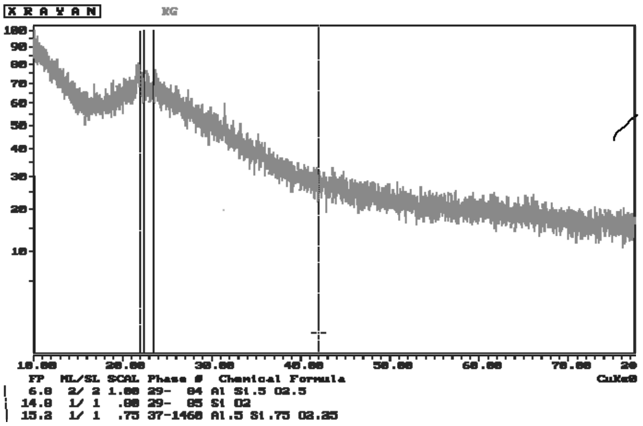

Fig. 6. Diffraction pattern of Glassex additive in initial state

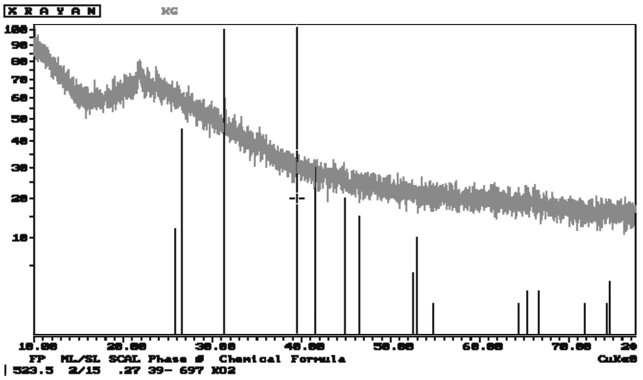

Fig. 7. Diffraction pattern of Glassex additive heated in temperature of 800°C

It results from the analysis of achieved curves, that there is a presence of complicated multicomponent silicates in Glassex additive. Definition of kind of silicates would take a precise analysis of oxides system, present in Glassex additive and creating the data base of diffraction patterns for possibly forming silicates. Glassex additive is an amorphous material , so the interpretation of X-ray diffraction's curves is quite difficult. However it didn't show the presence of reactive γ-Al_2O_3 phase in new additive.

3. Conclusions

Spectroscope examinations presented in the article, showed the chemical influence of applied, new additive on the structure of binder (water glass). So, for the improvement of knock-out properties of moulding sands with such binder, there can be used the additives influencing both on the relaxation of stresses in moulding sand after thermal exposure and on chemical properties of binder itself. The trial of using the X-ray examination for identification the γ-Al_2O_3 phase - which according to literature sources is responsible for the effects of additives' action - failed. It can lead to the fact that this phase doesn't form in moulding sand and that it's not responsible for the mechanism of improving the knock-out properties of moulding sand with water glass. Further examinations should lead to the full recognition of mechanism of knock-out properties of moulding sands with inorganic binders, which will be a basis for elaboration of rules and selection's procedures of composition of these ecological moulding sands.

Acknowledgments

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