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Technological and ecological studies of moulding sands with new inorganic binders for casting of non-ferrous metal alloys

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Abstract

The article presents the results of studies which form a part of broader research programme executed under the project POIG.01.01.02-00-015/09 "Advanced materials and technologies".
In a concise manner, the results of studies on the effect of chemical modification of inorganic binders on the technological properties of moulding sands containing these binders were presented.
Special attention was paid to the effect of modification of inorganic binders on their thermal destruction behaviour in the range of pouring temperatures of the non-ferrous metals and their alloys.
Also the results of comparative studies of the thermal emission of toxic gases and odours from moulding sands with new inorganic and organic binders were discussed.

Keywords: Innovative foundry materials and technologies; Inorganic binders; Modification; Technological properties; Thermal destruction

1. Introduction

Hydrated sodium silicate is one of the most popular inorganic binders. The foundry industry has been using it for over 50 years for the production of moulding and core sands. Although sands with sodium silicate are of a versatile nature, being moreover relatively cheap and characterised by numerous advantages, their indisputable drawback is too high residual strength and hence poor knocking out properties and difficult reclamation of the used, ceramic sand grains. The formation of sinters resulting from the tendency of an $Na_2O–SiO_2$ system to react with silica can be reduced by reducing the amount of binder in moulding sand on condition, however, that its binding properties are improved.

Some additives and modifiers, e.g. phosphates, improve the sand collapsibility after hardening. The used sand mixture knocking out properties and reclamability can also be improved with an addition of organic hardeners and modifiers, which allow the reduction of hydrated sodium silicate content in moulding sand, the best results being obtained when modifiers are introduced at the stage of autoclave digestion of sodium silicate glaze [1-6].

According to some researchers [4], the adverse properties of hydrated sodium silicate as a binder result, among others, from the fact that its wetting behaviour on the surface of sand grains is less effective than that of organic binders. The reason can be the absence of functional groups of the $–NH_2$, =CONH, $-CONH_2$, -COOH type in the structure of sodium silicate. The said groups activate the first stage of the formation and development of the structural strength of moulding sands. Therefore, the suggestion was to introduce these groups as modifiers to improve the properties of hydrated sodium silicate. With the hydrated sodium silicate they are forming the IPN type networks, that is, the Interpenetrating Polymer Networks. The consequence is reduced final strength and hygroscopicity of moulding sands produced with an addition of the modified solutions of hydrated sodium silicate.

2. Aim of studies

The purpose of the executed structural project is to introduce to the production of foundry moulds and cores, new ecological binders to replace the sands used so far for casting of non-ferrous metal alloys, i.e. the bentonite resin-bonded sands. The waste materials from these technologies have a negative impact on the environment [7]. The increasingly stringent environmental regulations and casting quality improvement requirements revive the interest in the high quality foundry sands with non-toxic inorganic binders [3,4,8].

From the analysis of mould and core technology used in domestic foundries, it can be concluded that the non-toxic inorganic binder (hydrated sodium silicate) has been previously used to a very limited extent only in the manufacture of moulds and cores for aluminum alloy castings. This fact was mainly due to the adverse characteristics associated with poor knocking out properties of the moulding sand, its low collapsibility and reclamability of the used sand grains.

The application of new binder is expected to definitely decrease the gas evolution rate, which is beneficial for both the environmental and work conditions at the moulding and casting stands.

3. Technological and ecological studies of moulding sands with new inorganic binders

3.1. Effect of chemical modification of hydrated sodium silicate on selected mechanical properties of moulding sand

Based on previous experience [9-13], two types of organofunctional and morphoactive organic modifying additives, referred to as modifier "A" (a synthetic thermoplastic polymer) and modifier "B" (a copolymer obtained by emulsion polymerisation) were selected. The modification consisted in introducing to the hydrated sodium silicate of modulus M = 2 and a density of 1.5 kg/m^3 the modifiers in an amount of 1.0% in respect of the total sum of oxides (Na_2O, SiO_2). The physical conditions under which the chemical modification was carried out included the changing mixing regime of the modifier - hydrated sodium silicate system, as well as a variable temperature, pressure and time of modification. As a result of the carried out modification, silicate binders, designated successively by symbols "B" 2, "A" 3, "B" 4, "B" 5, "A" 6, "B" 7, were obtained, while the standard unmodified reference binder was designated by symbol "0"1. Symbols "A" and "B" mean the type of modifier, while numbers indicate the method by which this modifier was introduced to the standard reference hydrated sodium silicate "0"1.

Using these binders and a hardener in the form of ethylene glycol diacetate (flodur1), moulding sand containing 2.5 parts by weight of binder and 10% of hardener (in respect of the binder weight) was prepared. As a reference moulding sand with an organic binder, the traditional moulding sand with X850 furan resin binder added in an amount of 0.9 parts by weight, hardened with 100T3 hardener added in an amount of 0.45 parts by weight was prepared. The reference sand was designated by symbol "Z". Figures 1 and 2 show the values of compressive strength and bending strength of the moulding sand samples prepared with the investigated binders.

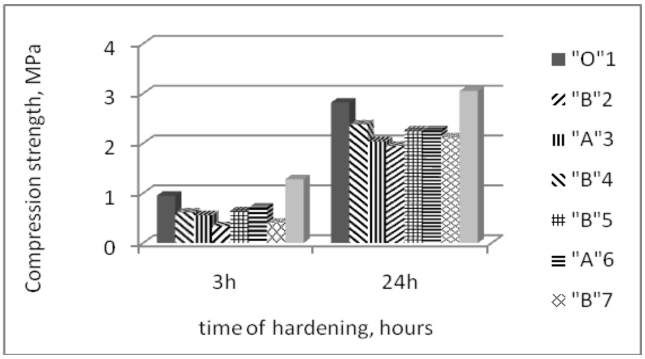

Fig. 1. Compression strength of moulding sands with different types of the soluble sodium silicate

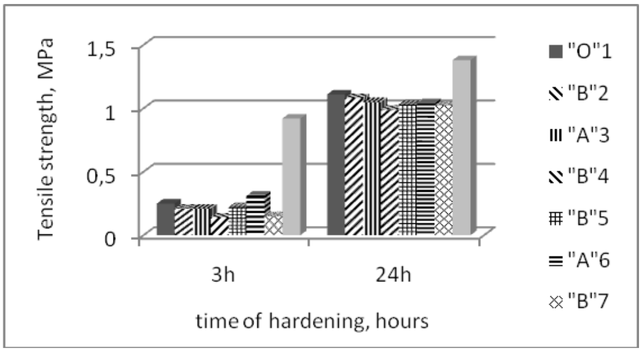

Fig. 2. Tensile strength of moulding sands with different types of the soluble sodium silicate

For each binder, tests were also carried out at elevated temperatures, with determination of the, so called, final strength, which is an indirect indicator of the sand knocking out properties. The results are shown in Figure 3.

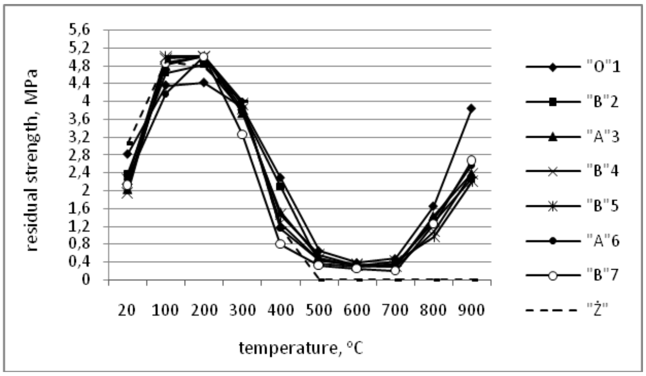

Fig. 3. Residual strength of moulding sands with different types of the soluble sodium silicate

It was found that the best final strength has the moulding sand prepared with modified hydrated sodium silicate designated by symbol "B" 7. It is true that within the temperature range of up to 200^0C, the final strength of the sand with binder "B" 7 is by about 11% to 13% higher respective of the final strength of the moulding sand with unmodified silicate binder "0" 1, but at the same time it is higher by only 5% respective of the final strength of the moulding sand with a resin binder designated by the symbol "Z". On the other hand, within the investigated range of temperatures, i.e. from 300^0C to 700^0C, the final strength of the sand bonded with binder "B" 7 is, for the same range of temperatures, lower than the final strength of the moulding sand with unmodified standard reference silicate binder "0" 1 - by about 15% at 300^0C, by about 65% at 400^0C, by about 45% at 500^0C, by about 30% at 600^0C, and by about 50% at 700^0C.

3.2. Measurements of the emission rate of aroma compounds during thermal decomposition of moulding sands

The currently binding regulations relating to the presence of toxic substances and the permissible limit of their concentration in the air refer either to the air pollutants emitted by industry, or to the air pollutants emitted by transport means (Regulation of the Minister of the Environment of 2008 on the permissible levels of certain substances in the air, the alert levels of certain substances in the air, and margins of tolerance for the permissible levels of certain substances, the regulation on the assessment of pollutant levels occurring in the air (Dz. U. 2008 Nr 47, poz. 281) or at workplaces (Regulation of the Minister of Labour and Social Policy of 29 November 2002 on maximum permissible concentrations and intensity of harmful factors in the working environment - Dziennik Ustaw Nr 217/2002 r., poz. 1833, (with later amendments - Dz. U. Nr 212/2005r. poz. 1769, Dz. U. Nr 161/2007r., poz. 1142, Dz. U Nr 105/2009r., poz. 873, Dz. U. Nr 141/2010r., poz. 950). In the majority of cases, the operative legal regulations provide the appropriate inspection services and regional authorities with the tools for effective intervention in the matters of the preservation of appropriate and safe for the local community standards of natural environment protection. In the case of the emission of unpleasant and often harmful odours, despite long-lasting works, such regulations are still lacking. Efforts are currently underway to speed up work on the so-called "odour law" that will allow legally protect the scented air quality.

In studies, the measuring equipment in the form of a portable gas chromatograph *zNose Model 4300 Ultra-Fast GC Analyzer* (Fig. 4), used for the characterisation of complex chemical compounds present in the gas phase, was applied.

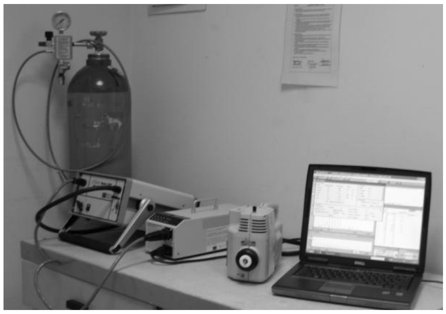

Fig. 4. The gas-chromatograph *zNose 4300 Model Ultra -Fast GC Analyzer*

The device for chemical analysis is also used for monitoring of air quality in real time. As a high-class sensor equipped with a SAW detector (quartz crystal) it provides rapid analysis of aroma compounds present in the air. The evolution rate of aroma compounds of this type from moulding sands prepared with the examined types of the hydrated sodium silicate and for comparison from the moulding sand made with the synthetic resin (moulding sand designated by symbol "Z") has been studied at temperatures of 500^0C and 800^0C. The study was conducted to detect the presence of organic compounds toxic or harmful to the human health. The concentrations of the aroma compounds evolved are expressed in Cts units. It can be concluded that the concentrations below 300 Cts are defined as very low, and the sensibility to compounds present in these quantities is negligible. Based on this, the aroma compounds of the highest relative intensity were identified, compared to each other and quantitatively characterised. The destruction of the examined moulding sands was carried out in a pipe furnace at temperatures of 500^0C and 800^0C, while the emitted volatile aroma compounds were collected with an "electronic nose" and analysed in real time in the form of chromatograms.

Very low concentrations of harmful substances evolved during thermal decomposition of the investigated sands were confirmed. The above mentioned aroma compounds are present in concentrations below 200 Cts at both applied thermal decomposition temperatures. The aroma compounds present most commonly during the thermal decomposition of moulding sands at both temperatures were: methyl laurate, estragole and propanol. It was also found that the temperature of thermal decomposition of the moulding sand has little effect on the amount of the evolved aroma compounds (their concentrations at 800^0C are slightly lower compared to concentrations obtained at 500^0C).

Based on the survey done it can be concluded that the concentration of aroma compounds evolved during thermal destruction of the moulding sand is so low that these compounds have no harmful effect on the human body. It should be noted, however, that not all chemical compounds could be identified due to the high level of specialisation of the electronic nose in identification of various types of the chemical compounds (the apparatus is not sensitive to all compounds emitted from the foundrysands).

The aroma compound emitted in largest quantities from all the tested sands is propanol. The maximum allowable concentration (MAC) and maximum instantaneous concentration (TWA) in the working environment specified for propanol (Dziennik Ustaw Nr 217/2002 r., poz. 1833 with later amendments) are: TLV = 200 mg/m^3, STEL = 600 mg/m^3. Propanol is flammable and irritating compound. It has a narcotic effect on the human body. Therefore, it is advisable to provide close monitoring of the concentration of this compound during the thermal decomposition of moulding sands with different chemical compounds. The hygiene standards have also been set for styrene, and are as follows: TLV = 50 mg/m^3, STEL = 200 mg/m^3. The concentration and the frequency of occurrence of styrene in the analysed sand moulds is very small, and therefore additional monitoring of its concentration is not necessary, as it is in the case of propanol.

The odour identification classifies the emitted chemical compounds as substances with the smell of wax, oil, resin, or solvent. Currently, no hygiene standards are available for other identified odorants. There are no additional indications for the use of other methods to mask the unpleasant odours since their nuisance is negligible.

3.3. Evaluation of the thermal destruction of moulding sand in terms of its harmful effect

The maximum allowable concentration (MAC) and maximum instantaneous concentration (TWA) for the examined chemicals at the workplaces are set out in Regulation of the Minister of Labour and Social Policy of 29 November 2002 - Dziennik Ustaw Nr 217, poz.1833, zał. 1A and in accordance with the amendments contained in Decree of the Minister of Economy and Labour of 10 October 2005 - Dziennik Ustaw Nr 212, poz. 1769, Decree of the Minister of Labour and Social Policy of 30 August 2007 - Dziennik Ustaw Nr 161, poz. 1142, Decree of the Minister of Labour and Social Policy of 16 June 2009 - Dziennik Ustaw Nr 105, poz. 873, and Decree of the Minister of Labour and Social Policy of 29 July 2010 - Dziennik Ustaw Nr 141, poz. 950. Therefore, any new binder system used in the moulding sand should be assessed in terms of its harmfulness to the environment.

Tests were conducted on moulding sands "0" 1, "A" 3 and "B" 4 and, for the sake of comparison, on sand "Z". The weighed sample of the tested moulding sand was introduced to a quartz tube placed in a resistance furnace, type PR-45/1200MF, heated to the required temperature. During decomposition, the air was flowing through the tube at a rate of 10 ml/min. The time of destruction was 30 minutes. The decomposition products pushed up to the surface by the jet of the flowing air were absorbed in the absorption bulb filled with proper absorbing solutions, or they were adsorbed in a layer of activated carbon in glass tubes and then subjected to chemical analysis, determining the evolving chemicals such as formaldehyde, acetic acid, ethylene glycol, ethyl acetate, carbon monoxide, nitrogen oxide and carbon dioxide. In the pyrolysis gases emitted from the tested moulding sand with resin binder (designated by the symbol "Z"), the following chemical compounds were determined: formaldehyde, ammonia, phenol, furfural, toluene, benzene, xylene, carbon monoxide, nitrogen oxide, carbon dioxide, sulphur dioxide. Formaldehyde, phenol and ammonia were determined by spectrophotometry. The content of acetic acid, ethylene glycol, ethyl acetate, furfural, toluene, benzene and xylene (mixed isomers) was determined by chromatography. Carbon monoxide, nitrogen oxide and sulphur dioxide were determined by direct measurement with MRU type gas analyser. The results are shown in Tables 1 to 3.

Table 1.
Thermal destruction of the moulding sands with soluble sodium silicate in the temperature 500^0C

Kind of the modifier	Kind of the impurities, mg/kg							
	Formalde hyde	Phenol	Acetic acid	Ethylene glycol	Acetate of the ethyl	Carbon monoxide	Nitrous oxide	Nitrogen dioxide
Without the modifier	1,0	p.o.	n.o.	n.o.	n.o.	37 930	p.o.	p.o.
„A”	1,0	p.o.	13,0	p.o.	p.o.	58 580	p.o.	p.o.
„B”	1,0	p.o.	n.o.	n.o.	n.o.	52 780	2680	p.o.

p.o. - below mark
n.o. – not mark

Table 2.
Thermal destruction of the moulding sands with soluble sodium silicate in the temperature 800^0C

Kind of the modifier	Kind of the impurities, mg/kg							
	Formalde hyde	Phenol	Acetic acid	Ethylene glycol	Acetate of the ethyl	Carbon monoxide	Nitrous oxide	Nitrogen dioxide
Without the modifier	p.o.	p.o.	n.o.	n.o.	n.o.	2 320	2 680	p.o.
„A”	1,0	p.o.	6,3	p.o.	p.o.	4 640	1 340	p.o.
„B”	p.o.	p.o.	n.o.	n.o.	n.o.	3 480	2 680	p.o.

p.o. - below mark
n.o. – not mark

Table 3.
Thermal destruction of the moulding sands "Ż" with resin binder in the temperature 500^{0}C and 800^{0}C

^{0}C	Kind of the impurities, mg/kg										
	1	2	3	4	5	6	7	8	9	10	11
500	p.o.	97,0	4,0	p.o.	34,4	5,1	2,1	648440	1 340	2 050	211 640
800	p.o.	193,0	3,0	p.o.	1,4	0,3	0,3	34800	1 340	2 050	660 660

1 – Formaldehyde, 2 - Ammonia, 3 - Phenol, 4 - Fural, 5 – Toluene, 6 – Benzene, 7 - Ksylene, 8 – CO, 9 – NO, 10 - NO_2, 11 - SO_2
p.o. - below mark
n.o. – not mark

From the obtained results it follows that the main pollutant emitted during the thermal decomposition at a temperature of 500^{0}C is carbon monoxide. Formaldehyde evolved from all the tested moulding sands prepared with an addition of the hydrated sodium silicate. Phenol and nitrogen dioxide were not observed to be present. Nitrogen oxide was found only in the pyrolysis gas emitted from sand "B"4. In the gas emitted from sand "A"3, acetic acid, ethylene glycol, and ethyl acetate were additionally determined, stating only the presence of acetic acid. During the destruction of hardened moulding sands containing hydrated sodium silicate which took place at a temperature of 800^{0}C, the compounds evolving in the largest amounts were carbon monoxide and nitrogen oxide. At this temperature, formaldehyde was evolving only from moulding sands "A" 3 and "B" 4. Phenol and nitrogen dioxide were not detected. From moulding sand "A" 3, acetic acid was evolving in an amount two times lower compared to the temperature of 500^{0}C.

The hardener used for hardening of the examined moulding sands was composed of ethylene glycol diacetate and ethylene glycol residues, acetic acid, and ethylene glycol monoacetate. The presence in the hardener of free acetic acid, ethylene glycol and its esters makes this hardener the potential source of the emission of acetic acid and ethylene glycol as early as during feeding of these compounds, and then during the sand preparation in mixers, moulding process and sand hardening. In the process of the thermal decomposition of the moulding sand that contains the hydrated sodium silicate as a hardener, new chemical combinations are forming, mainly from ethylene glycol, the concentration of which in the sand is increasing during the hydrolysis of esters. The main chemical transformations of ethylene glycol diacetate, taking place during the thermal decomposition of moulding sand with hydrated sodium silicate, include the following ones:

- oxidation of ethylene glycol to formaldehyde,
- dehydration of ethylene glycol to acetic aldehyde,
- oxidation of the newly formed acetic aldehyde to acetic acid.

At the next stage of the high temperature decomposition of the ethylene glycol diacetate components, carbon monoxide is formed. Based on the analysis of the results of the study, it has been observed that from the moulding sand prepared with hydrated sodium silicate and ethylene glycol diacetate, the emitted harmful substances mainly include formaldehyde, acetic acid and carbon monoxide; large amounts of these compounds are emitted at a temperature of 500^{0}C. It should be noted that the mechanism of thermal decomposition of ethylene glycol diacetate and the evolution rate of harmful substances, as well as their composition and quantity, depend on many factors such as the temperature, the duration of pyrolysis, the type of substances present in the moulding sand composition which can act as catalysts of the decomposition process, and the sample homogeneity.

To compare the harmful effect of moulding sands with inorganic binder (hydrated sodium silicate) and organic binder, the "Z" type moulding sand was selected. The main products of the thermal decomposition of this moulding sand include carbon monoxide and sulphur dioxide, where the evolution rate of carbon monoxide decreases with increasing temperature, while that of sulphur dioxide increases. Nitrogen oxides form minor components of the gas phase. The gaseous products of the destruction of the "Z" sand included ammonia, whose measured quantities were increasing with the increasing temperature of decomposition. The emission level of toluene, benzene and xylene was much lower at a high temperature (800^{0}C). The presence of formaldehyde and furfural was not detected in gases at any of the pyrolysis temperatures used. These compounds are mainly emitted during the process of moulding sand hardening.

The conducted research enabled determination of the coefficients of the laboratory toxicity T_L of the examined sands (Fig. 5), which on comparison showed that moulding sands containing hydrated sodium silicate hardened with ethylene glycol diacetate are far less toxic than the sands with an organic binder.

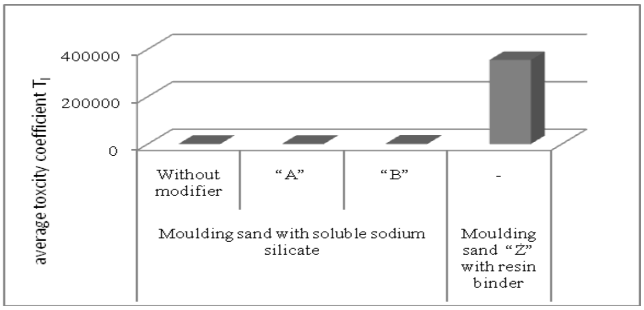

Fig. 5. Laboratory toxicity TL of the examined sands

Comparing the coefficients of the laboratory toxicity T_L of the examined moulding sands with water glass, little effect of the modification of binder and hardener on their harmfulness has been stated.

4. Conclusions

The technological properties of moulding sands with the inorganic binders of a new generation in the form of chemically modified hydrated sodium silicate, determined at ambient conditions, do not undergo any significant changes compared with similar properties of moulding sands with the unmodified silicate binder. An obvious improvement of their high-temperature technological properties has been stated, especially in the examined range of 400^0C to 700^0C, A considerable drop in the final strength of moulding sand in this temperature range, compared to the final strength of moulding sand made with the unmodified hydrated sodium silicate, enables these sands to be used in the manufacture of moulds and cores for casting of aluminium alloys. The research conducted on the gas evolution rate at 500^0C and 800^0C indicates that the type of the modifying addition has little effect on the toxicity index of moulding sand, compared to the toxicity index of moulding sand prepared with the unmodified hydrated sodium silicate. On the other hand, in the case of moulding sands made with an organic binder, the toxicity index of the sand has the value nearly 170 times higher compared to the toxicity index of the sand made with modified hydrated sodium silicate.

This proves once again that the idea to substitute for the sands with organic binders the sands based on modified inorganic binders is fully justified.

Acknowledgements

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