



Organic Moulding Sands for Production of Large-Size Castings

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Abstract

Recently, some major changes have occurred in the structure of the European foundry industry, such as a rapid development in the production of castings from compacted graphite iron and light alloys at the expense of limiting the production of steel castings. This created a significant gap in the production of heavy steel castings (exceeding the weight of 30 Mg) for the metallurgical, cement and energy industries. The problem is proper moulding technology for such heavy castings, whose solidification and cooling time may take even several days, exposing the moulding material to a long-term thermal and mechanical load.

Owing to their technological properties, sands with organic binders (synthetic resins) are the compositions used most often in industrial practice. Their main advantages include high strength, good collapsibility and knocking out properties, as well as easy mechanical reclamation. The main disadvantage of these sands is their harmful effect on the environment, manifesting itself at various stages of the casting process, especially during mould pouring. This is why new solutions are sought for sands based on organic binders to ensure their high technological properties but at the same time less harmfulness for the environment.

This paper discusses the possibility of reducing the harmful effect of sands with furfuryl binders owing to the use of resins with reduced content of free furfuryl alcohol and hardeners with reduced sulphur content. The use of alkyd binder as an alternative to furfuryl binder has also been proposed and possible application of phenol-formaldehyde resins was considered.

Keywords: Innovative foundry technologies and materials, Moulding sand, Organic binder, Furfuryl resin, Reduced sulphur hardener, Alkyd resin, Alphaset process

1. Introduction

Moulding sands of the second generation, i.e. sands bonded with binders, have the greatest application in foundry processes. This is due to their high technological properties and versatility, since they are applicable in the production of both foundry moulds and cores.

The latest trends in the production of castings are based on the attempts to reduce the casting weight by increasing the dimensional accuracy, due to the manufacture of foundry moulds

composed of core packages. This trend causes a significant increase in the demand for core sands made from 2nd generation sand mixtures [1].

The binders used in these technologies are mainly organic binders (based on synthetic resins) as well as inorganic binders, such as hydrated sodium silicate.

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castings (exceeding the weight of 30 Mg) for the metallurgical, cement and energy industries. The problem is proper moulding technology for such heavy castings, since their solidification and cooling may last even several days, exposing the moulding material to long-term thermal and mechanical loads [1].

Currently, foundries use moulding sands bonded with synthetic resins to make steel castings and the production of this type of castings has been dominated by loose self-hardening sands with furfuryl resin.

The reasons are as follows:

- ✓ the possibility of making castings with high dimensional accuracy,
- ✓ the possibility of making moulds with intricate shapes,
- ✓ binding process taking place at ambient temperature,
- ✓ easy process of making moulds and knocking out of castings,
- ✓ low content of binder,
- ✓ good collapsibility and possibility of mechanical reclamation.

The disadvantages of this technology include, first of all, the presence of very harmful gases that are released mainly during pouring of molten alloy [2].

Sands with furfuryl resins are suitable for the production of small and medium castings, while their use in the production of heavy castings may require significant modifications. This is very important, especially when the attitude of the European Union towards environmental problems and recent regulations on the content of furfuryl alcohol in resins are considered.

The composition of loose self-hardening sands with furfuryl resin includes base sand grains, furfuryl resin and an acidic hardener. Typically, silica sand and/or its reclaim are used as a base material. The silica sand should contain maximum 0.2% of the clay and its pH should be close to 7 [3]. The reclaim used as a component of the loose self-hardening sands with furfuryl resin should meet the following criteria:

- ✓ low loss on ignition: for cast steel less than 1.5% [3] (according to [4] 2.0%), and for castings made from grey iron and non-ferrous metals up to 3.0% [3];
- ✓ low content of clay binder, i.e. for cast steel up to 0.5%, and for castings made from grey iron and non-ferrous metals below 2.0% [3].

Furfuryl resins are obtained by polycondensation of furfuryl aldehyde (furfural $C_4H_3O \cdot CHO$) with phenol or ketones (especially acetone), or by polycondensation of furfuryl alcohol ($C_4H_3O \cdot CH_2OH$) with formaldehyde, urea, phenol or other compounds. Furfuryl resins cross-link under the influence of high temperature or chemical factors. In an acidic environment, furfuryl alcohol condenses with the release of heat, turning into a solid, hard but brittle substance. For this reason, plasticized resins containing furfuryl alcohol are used in combination with the components of other resins, mainly urea formaldehyde and resol resins [3].

Furfuryl resins and resins modified with furfuryl alcohol may contain from 7 to over 90% of furfuryl alcohol [3]. Usually, this addition is from 30 to 85% according to J.L. Lewandowski [3] or from 50 to 95% according to S. Bieda [4]. The higher is the content of furfuryl alcohol, the higher is the binding capacity and the faster is the resin curing process [3]. An equally important parameter is the nitrogen content in furfuryl resin, which can

range from 0 to 11%. Furfuryl resins with low nitrogen content (less than 1%) and low water content are used in the production of steel and aluminium castings [4].

In an acidic environment, the furfuryl resin condenses with the release of heat. Therefore, as a hardener for the loose self-hardening sands with furfuryl resin, organic and inorganic acids (usually a mixture thereof) are used. The acids used most commonly are organic sulphonic acids as well as inorganic sulphuric or phosphoric acids. Aromatic sulphonic acids are used in most hardeners, sometimes in combination with orthophosphoric acid [3]. Nitric acid (HNO_3) is not applicable due to the accumulation of nitrogen in the reclaimed sand. The situation is similar in the case of hydrochloric acid (HCl), which in combination with hydrocarbons at high temperature tends to form harmful compounds. Carbonic acid (H_2CO_3) or other acids such as formic acid ($HCOOH$) and acetic acid (CH_3COOH) are too weak and delay the curing process [4].

2. Moulding sands containing furfuryl resin with reduced content of furfuryl alcohol

Regulation of the European Parliament and of the European Council (EC) (No. 1272/2008 of 16 December 2008 on the classification, labelling and packaging of substances and mixtures), which entered into force on 1 December 2010, classifies furfuryl resins containing above 25% of free furfuryl alcohol as toxic, while furfuryl resins that contain less than 25% of free furfuryl alcohol are considered harmful [5]. Since 2010, changes in the classification of resins have been observed depending on the content of free furfuryl alcohol. This is illustrated in Figure 1 [6].

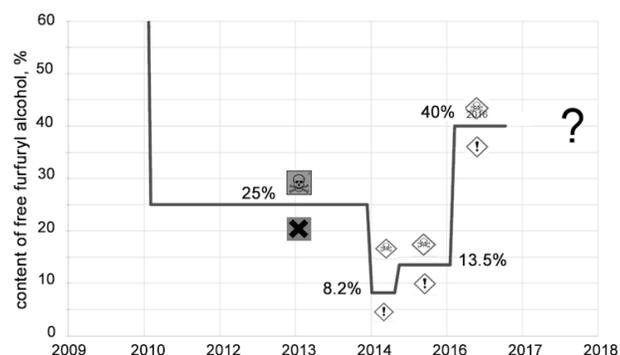


Fig. 1. Changes in the classification of resins depending on the content of free furfuryl alcohol [6]

Low content of free furfuryl alcohol in the resin can reduce the temperature and the temperature range of the beginning of the thermal destruction of the binder and shorten the sand life at high temperature, thus increasing the risk of the mould cavity deformation during metal pouring. Reduction in the content of free furfuryl alcohol can cause many foundry defects. They occur due to the thermal deformation of foundry mould and possible migration of sand components into the casting structure.

International corporations producing binders for the foundry industry are already proposing new solutions in this field. Hüttenes–Albertus has developed Kaltharz 8616 and 8700 series resins containing less than 25% of free furfuryl alcohol [7]. Unfortunately, the modifications cause an increase in water content and density and, above all, produce a rapid increase in viscosity. ASK Chemicals has developed a new Magnaset™ resin with less than 25% of furfuryl alcohol monomer [8].

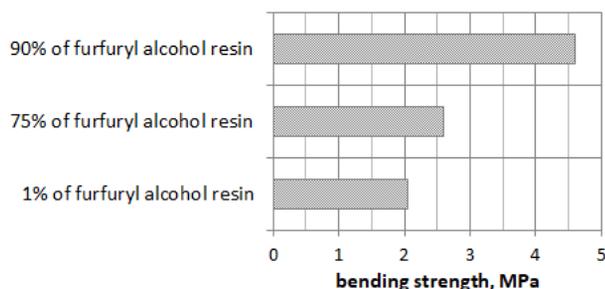


Fig. 2. The effect of furfuryl alcohol content in binder on the bending strength of sands tested after 24 hours of curing [1]

Recent research has shown (Fig. 2) that reducing the furfuryl alcohol content in the binder reduces the strength of the sand containing this binder. The sand with phenol-furfuryl resin containing 90% of free furfuryl alcohol is characterized by the bending strength of approx. 4.6 MPa, while the strength of the sand with the binder containing 1% of furfuryl alcohol is approx. 2.06 MPa. The sand with the resin containing 75% of furfuryl alcohol has a bending strength of about 2.6 MPa. This means that the strength of this sand is by about 45% lower than the strength of the sand with the resin containing 90% of furfuryl alcohol, but it still can be sufficient for the foundry purposes [1].

3. Moulding sands containing furfuryl resin and hardener with reduced sulphur content

Sulphur is another problem in sands with furfuryl resin. The possibility of reducing the content of this element in sand can make it more friendly to the environment, reducing at the same time also the risk of defects in castings associated with the diffusion of sulphur to their surface structure.

The problem of the diffusion of moulding sand components to the surface structure of casting is the subject of many studies [9–16] and applies especially to massive castings. Sometimes, in the production of ductile iron castings in moulds made from the loose self-hardening moulding sands with furfuryl resin, the spheroidal graphite suffers degradation on the external surfaces of the casting, combined with its transition into a flake form. This type of change is attributed to the diffusion of sulphur from the moulding sand to the surface of the solidifying casting. It can reduce the efficiency of the spheroidizer (magnesium) by bringing its content below the concentration level necessary to form spheroidal graphite.

The occurrence of sulphur in loose self-hardening sands with furfuryl resin has two sources. One of them is the hardener, which is a mixture of sulphonic acid and sulphuric acid, sometimes with the addition of phosphoric acid. The second source is the sand reclaim obtained in the process of mechanical reclamation. Sulphur from the hardener is transferred to the sand grains and accumulates there as a result of the process of mechanical reclamation. That is why it is so important to control sulphur content in the reclaim and systematically introduce the addition of fresh sand.

As a result of the use of sulphur hardeners, during pouring of moulds, gases such as H_2S , SO_2 , $(CH_3)_2S$ may evolve. The appearance of flake graphite in the structure of ductile iron is accompanied by the appearance of magnesium, sulphur and manganese [17]. Reducing magnesium concentration in the surface zone of casting leads to the formation of degraded flake graphite. In addition to other negative effects, this type of graphite can, especially in dynamically loaded castings, change its location and initiate the formation of cracks. Besides the precipitation of degraded graphite, this tendency will be additionally strengthened by the precipitation of sulphides [10].

One of the methods of eliminating the negative influence of sulphur transferred from the moulding sand to the casting surface is to limit the content of sulphur compounds introduced to the moulding sand. It is proposed to keep the amount of the added hardener at the lowest level possible or mix it with orthophosphoric acid, remembering, however, that also the content of phosphates in the sand based on reclaim should be kept under strict control. Pitting defects usually occur when the level of phosphates in sand exceeds 1.0% [15]. Phosphorus is deposited in the reclaim, which deteriorates the sand strength and reduces the refractory properties of sand grains [14].

The upper limit of sulphur content in the sand is estimated at 0.15%, and in the case of massive castings even at up to 0.07%, according to J. Baier and M. Köppen [11]. The content of sulphur compounds can be reduced at the expense of a more reactive resin, which is expressed by the abbreviation RS (reduced sulphur). Owing to the higher reactivity of the resin, a lower content of the hardener can be used [13].

The reduced content of sulphur in the loose self-hardening moulding sands with furfuryl resin is achieved mainly by reducing the content of p-toluenesulfonic acid in the hardener, which dissociates directly to SO_2 at 200°C [18], while sulphuric acid dissociates at a higher temperature (450°C) in an intermediate dissociation, first to SO_3 and then to SO_2 . Unfortunately, the use of sulphuric acid is limited due to its acidity and negative effect on the curing process. Too high content of sulphuric acid causes sand cracking (rapid polymerization of the resin) and breaking of the resulting bond bridges [18]. There is a decrease in the sand strength combined with the oxidation of sulphuric acid. The upper limit of sulphuric acid content in the hardener is about 15%. For technical and metallurgical reasons, nitric acid and hydrochloric acid are not applicable [18].

Another known method of eliminating the adverse effects of sulphur transferred from the moulding sand to the casting surface is the use of adsorbent coatings, which form a blocking system absorbing sulphur-containing gases and preventing their further migration to the liquid alloy.

It is assumed that in ductile iron sulphur has a negative effect [18] because the spheroidizing elements introduced into the cast iron easily react with sulphur and this process continues until the metal solidifies. The higher is the sulphur content in the cast iron before the spheroidizing treatment, the more of the spheroidizer will be needed. There is also a limit beyond which even a very large amount of the introduced spheroidizer will not be able to counteract the excessive amount of sulphur. Moreover, the reaction products can remain in metal in the form of inclusions [18].

As a result of the search for new solutions to reduce the negative impact of sulphur in the moulding sand, a new type of hardener with the reduced sulphur content (RS hardener) was elaborated. RS hardener is a newly developed hardener with the reduced content of p-toluenesulfonic acid (PTS) and trace amounts of sulphuric acid (p-toluenesulfonic acid 30 - 40%, sulphuric acid <0.23%) [18]. The tests were carried out on the sand mixtures based on fresh silica sand.

The following sand compositions were used:

- silica sand 100 parts by weight
- furfuryl resin 1.1 parts by weight
- standard hardener / RS hardener 0.55 part by weight

Hardeners with different content of converted sulphur were used, i.e. standard hardener with 10.94 - 13.73% S and RS hardener with the reduced converted sulphur content of 5.67 - 7.53% S. Figure 3 shows the effect of curing time on the bending strength of moulding sands with furfuryl resin and various hardeners. The values shown in the graph represent the average of three measurements not differing from each other by more than 10%.

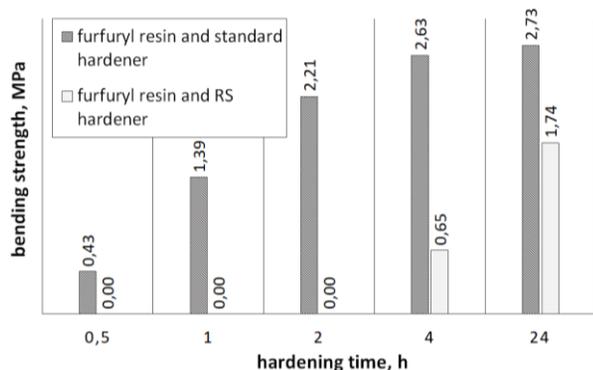


Fig. 3. The effect of hardening time on the bending strength of moulding sands containing furfuryl resin and hardeners with different sulphur content

Compared to standard hardener, the hardener with reduced sulphur content is a slow acting hardener, which means that the moulding sand with its addition is characterized by a long lifetime of initial curing. It was not possible to determine the sand strength after 0.5, 1 and 2 hours of curing. After 24 hours of curing, the strength of the moulding sand with RS hardener was by about 40% lower than the strength of the moulding sand hardened with a standard hardener.

The long lifetime of the sand is very useful in the preparation of sand mixtures based on the reclaim or in the summer, when the

sand bench life is much shorter. The long curing time of the sand is also beneficial in the preparation of large moulds and cores.

The research conducted in the Laboratory of Moulding Materials at the AGH Faculty of Foundry Engineering [9-10] included making test castings from ductile iron using loose self-hardening moulding sands with hardeners differing in sulphur content (standard hardener, RS hardener). The test moulding sand mixtures were based on:

- ✓ Fresh silica sand from Grudzen Las characterized by the following parameters: granulation 0.20/0.32 / 0.40; $d_{50} = 0.31$ mm; $pH = 7$. The composition of the sand mixtures based on fresh sand included:
 - silica sand 100 parts by weight
 - furfuryl resin 1.1 parts by weight
 - standard hardener / 0.55 part by weight RS hardener.
- ✓ Reclaim supplied by one of the Polish foundries. The reclaim was obtained by mechanical reclamation with separation of chromite sand in a 4-stage GUT device [18]. The reclaim with different sulphur content was used. The composition of the moulding sand mixtures based on reclaim included:
 - reclaimed sand 100 parts by weight
 - furfuryl resin 1.1 parts by weight
 - standard hardener/ 0.55 part by weight RS hardener.

The shape and design of test castings, as well as the sampling site were determined based on literature data [14, 18]. The aim of introducing the characteristic U-shape was to obtain the highest possible concentration of gas from the moulding material A scheme of the casting is shown in Figure 4.

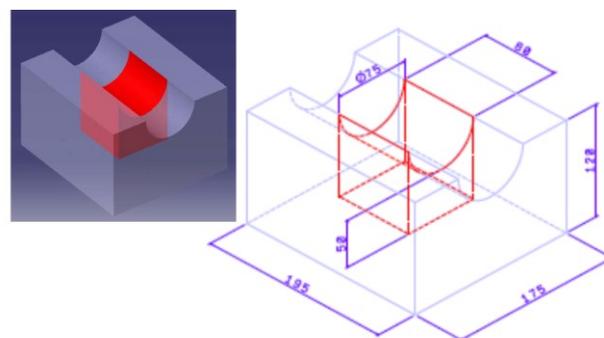


Fig. 4. The test casting with marked sampling site for metallographic examinations; dimensions of the casting 195×175×120 mm; dimensions of the sample: 80×50×50 mm [10, 18]

The conducted tests have shown that when the mixture based on fresh silica sand was used, even at a very high sulphur content (0.08%), the effect of spheroidal graphite degeneration did not occur [18]. On the other hand, a very pronounced effect of spheroidal graphite degeneration in the top layer of the casting was observed in the specimens cast in the sand mixtures based on reclaim [18]. The layer with the changed structure in castings made in the sand mixture containing 0.18% of sulphur was uneven on the entire casting surface, and its thickness varied from 200 to 600 μm . Very high roughness of the casting surface was

also observed. In some areas, at the casting top layer/core interface, thick elongated precipitates of graphite were present [18]. Analysis of the chemical composition showed that those were mainly sulphur compounds with magnesium and iron. Similar results were obtained for a sample taken from the test casting made in the sand with sulphur content of 0.22%. Also in this case, thickness of the degenerated graphite layer was uneven ranging from 200 to 600 μm and surface of the casting was characterized by a high roughness value. In the skin of the casting, the structure was composed of flake graphite embedded in a ferritic matrix, passing in more distant parts of the casting into the structure composed of spheroidal graphite in a ferritic-pearlitic matrix. The structure of this sample also contained thick elongated precipitates of graphite [18].

The test casting made in the sand with 0.30% of sulphur was characterized by an even thickness of the degenerated top layer amounting to about 600 μm . In the skin of the casting, apart from the flake graphite embedded in a ferritic structure, the precipitates of spheroidal graphite of various sizes and grey precipitates of an irregular shape were observed [18].

4. Moulding sands with alkyd resin

Moulding sands with alkyd resins are an important alternative for sands with furfuryl resins - also in the aspect of their application in the production of large-size castings. They are characterized by lower fragility and are more friendly to the environment. Currently, these moulding sands are mainly used for moulds in which massive steel castings are poured.

Alkyd resins belong to unsaturated polyester resins. They are a condensation product of the reaction taking place between difunctional phthalic acid and trifunctional glycerin. In the first stage of condensation, final -OH groups of glycerin react with -COOH groups of phthalic acid and a linear compound is formed. In the macromolecule of this compound, free OH groups remain from glycerin, and they can react further with phthalic acid, forming a cross-linked structure [3]. Pure phthalic resins are characterized by rather unsatisfactory properties - they are fragile, insoluble in oils and hydrocarbon solvents, and have poor resistance to water and weather conditions.

To confer to alkyd resins higher flexibility and better adhesion, they are usually modified with fatty acids, vegetable oils, etc. [3]. Modification with vegetable oils is more economical because the release of free acids from these oils is avoided.

When alkyd resins are used, the hardener, or rather the cross-linking compound, is a modified polyisocyanate. The sand bonding process takes place in two ways, i.e. by adding the polyisocyanate providing a polyurethane bridge bond or by bonding oil with oxygen from the air. In the process of curing polyester resins, compounds that accelerate the reaction of isocyanate groups with hydroxyl groups are of great importance. The commonly used catalyst is cobalt naphthenate added directly to the resin [3].

Currently, sands with an alkyd resin binder are one of the most competitive technologies with furfuryl resin sands, although even they have some limitations, to mention only problems with the curing time control, long setting time, and relatively high

viscosity of binder. The sand humidity is very important in the preparation of these sand mixtures. The water content of even 0.2% results in longer setting time and reduces the maximum strength of the sand [1].

The basic advantages of the sands with alkyd binder include the absence of nitrogen, formaldehyde and water in the binder composition; the possibility of using a very high proportional fraction of reclaim in the mixture (up to 90%); high plasticity of the sand during contraction of the steel casting (as opposed to phenolic and furfuryl resins); long bench life, which allows for unrestrained manufacture of moulds and cores for heavy and intricate castings even when the base material has a relatively high temperature; lower amount of BTEX (benzene, toluene, ethylbenzene and xylenes: ortho-, meta-, para-) gases emitted during pouring of molten metal (as opposed to furfuryl resins); and low level of the toxic compounds formed during mixing and setting of sands (as opposed to furfuryl resins) [1].

As part of the recently conducted research, the bending strength of sands with furfuryl resin binder and alkyd resin binder was compared. Tests were carried out on the sand with furfuryl resin and the composition shown in Chapter 3, and on the moulding sand with alkyd resin [1] having the following composition:

- silica sand 100 parts by weight
- alkyd resin 1.0 part by weight
- hardener 0.25 part by weight

The results of the tests carried out are shown in Figure 5. The values shown in the graph represent the average of three measurements not differing from each other by more than 10%.

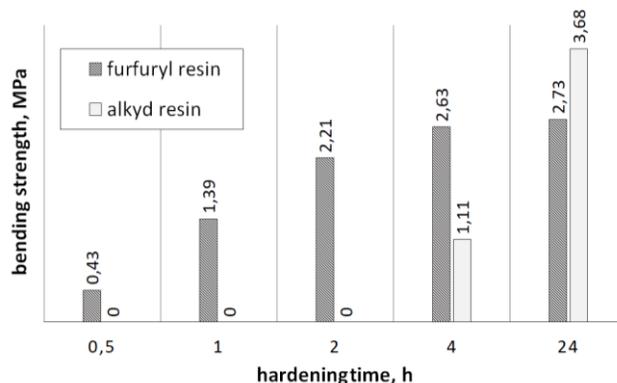


Fig. 5. The effect of hardening time on the bending strength of sands with furfuryl resin and alkyd resin

The conducted tests of the strength properties of the moulding sand mixtures showed that the moulding sands with alkyd binder were characterized by definitely longer bench life than the moulding sands with furfuryl binder. It was not possible to determine the strength of the sand with alkyd resin after 0.5, 1 and 2 hours of curing, while the strength after 4 hours of curing was more than twice lower than the strength of the sand with furfuryl binder. After 24 hours of curing, the alkyd binder sand has reached a bending strength by approx. 25% higher than the sand with furfuryl binder.

5. Moulding sands with phenol-formaldehyde resin (Alphaset process)

In this process, known as the Alphaset process, a resol type alkaline phenol-formaldehyde resin, containing below 1% of hydrous phenol and below 0.2% of free formaldehyde, is applied. As hardeners, esters are used, by means of which the hardening rate can be adjusted. An alkaline character of the process allows the use of all kinds of sands, including highly alkaline, as base material of the moulding mixture. Using more coarse sands requires the application of protective coatings (hydrous or alcoholic) [19].

The reclaimed material obtained from these moulding sands by means of mechanical reclamation should not have more than 1.5% loss on ignition and alkali content of maximum 0.15%.

The described above moulding sands can be used for moulds and cores poured with all alloys, and are especially advantageous for steel castings, in which hot cracks can occur [19].

Phenol-formaldehyde resin is obtained as a polycondensation product of phenol and formaldehyde. The synthesis process of this resin occurs in the presence of a catalyst, which can be of either a basic or acidic character.

Depending on the kind of the applied catalyst, that is, on the environment kind (acidic or basic) and the ratio of phenol to formaldehyde, products of different properties are obtained. In an acidic environment, the polycondensation is performed with a formaldehyde shortage and novolak (compound of a linear structure) is obtained. In a basic environment, an excess of formaldehyde is used and resols of a linear structure are obtained [19].

Phenol-formaldehyde resins of a resol type are used for making no-bake sands: loose self-hardening sands, loose fast-hardening sands and loose self-setting sands. In case of loose self-hardening sands, acidic hardeners are used, mainly sulphonic acids. In these sands, the resin can enter into a two-component binder (e.g. with phenolic polyisocyanate – Ashland's process) and then amines are catalysts. Loose self-setting sands are used in the hot box method. Hardening occurs due to a high temperature influence [19].

This paper presents the results of tests obtained for sand mixtures prepared by the technology of loose self-hardening sands.

The tests were carried out on moulding sands with the following composition [20]:

- silica sand 100 parts by weight
- phenol-formaldehyde resin 1.2 parts by weight
- hardener 0.3 part by weight.

The test results [20] are shown in Figure 6.

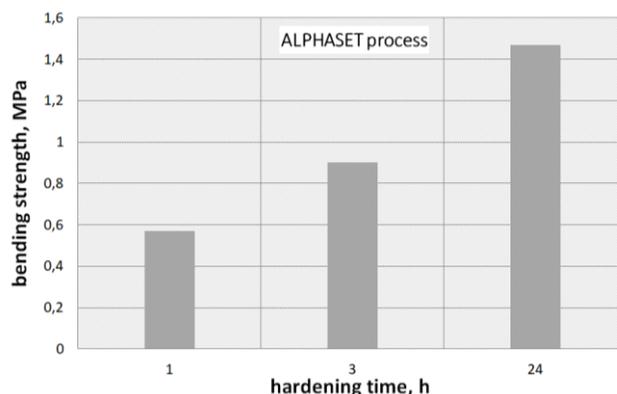


Fig. 6. The effect of hardening time on the strength of moulding sands made by Alphaset process [20]

The research [20] has shown that sands made by the Alphaset technology are characterized by relatively low strength properties compared to sands with furfuryl or alkyd resin. Their properties are similar to the properties of self-hardening moulding sands with inorganic binders, but the organic character ensures better knocking out properties and the susceptibility to mechanical reclamation. From the point of view of industrial practice, the strength obtained in the tested moulding sands is sufficient to make moulds for large-size castings.

6. Conclusions

The development of optimal moulding sands for the production of large-size castings, taking into account the restrictive requirements for environmental protection, is a very live issue from the point of view of the structure of the European foundry industry.

The analysis of literature data and the conducted research have shown that it is possible to make large-size castings using moulding sands with a furfuryl binder which has the reduced content of furfuryl alcohol. Reducing the furfuryl alcohol content in the binder reduces the strength properties of the tested sands, but it should be emphasized that the strength properties of the sand mixtures bonded with binders with the reduced content of total furfuryl alcohol are still sufficient for the needs of industrial practice,

It has also been shown that it is possible to use hardeners with lower sulphur content in the moulding sands with furfuryl binders, but in this case it is necessary to select a resin with appropriate properties, e.g. high reactivity.

As an alternative to sands with furfuryl binders, the Alphaset technology and moulding and core sands with alkyd binder have been proposed. According to the literature data, moulding sands with alkyd binder are characterized by very good technological properties, offering at the same time lower toxicity than the moulding sands with furfuryl binders. The conducted research and literature data confirm the long bench life and high strength properties after 24 hours of curing in the case of moulding sands with an alkyd binder. Moulding sands made by the Alphaset process are characterized by lower strength properties than

moulding sands with furfuryl or alkyd resins. Yet, from the point of view of foundry practice, their strength properties are satisfactory.

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