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# Impact of Higher Temperature on Quartz Moulding Sand with Gypsum Binders

P. Paduchowicz \*, M. Stachowicz, K. Granat

Department of Foundry Engineering, Plastics and Automation, Wrocław University of Technology,  
ul. Smoluchowskiego 25, 50-372 Wrocław, Poland

\* Corresponding author. E-mail address: patrycja.paduchowicz@pwr.edu.pl

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## Abstract

This paper presents initial findings from research into the possibility of using gypsum binders in quartz moulding sand that could be used in the production of casting moulds and cores. For the purposes of the research two commercial types of gypsum were used as binders: building gypsum and gypsum putty. Dry components of moulding sand i.e. medium quartz sand and gypsum were mixed in proportion of 89/11 parts by weight. In order to achieve bonding properties for the binders, 5 parts by weight of water was added to the mixture of dry components. After 24 hours of adding water and mixing all the components, the moulding sand, naturally hardened, was subjected to high temperature. The moulding sand thus produced, i.e. with cheap and environmentally-friendly gypsum binders, was eventually analysed after heating (at temperatures of 300°C, 650°C and 950°C) and cooling in order to determine changes in the following parameters: LOI – loss on ignition, chemical composition and pH. Moreover, investigated were bonding bridges, before and after the moulding sand was roasted. The research results revealed differences in the structure of bonding bridges and the occurrence of automatic adhesive destruction for both types of gypsum binders. For two types of moulding sands under the investigation of the LOI exceeded 2.59wt.% (with building gypsum) or 2.84wt.% (with putty gypsum) and pH increased to ca. 12 as a result of increasing roasting temperature from 300°C to 650°C. Next, roasting at 950°C decrease value of LOI in both types of moulding sands. Moulding sand with building gypsum roasted at 950°C revealed a return to the value of pH parameter measured prior to annealing.

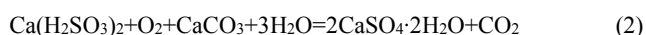
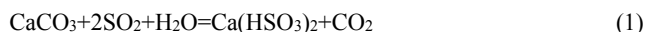
**Keywords:** Foundry, Building gypsum, Gypsum putty, pH, LOI

## 1. Introduction

Gypsum is a material used in the construction industry since about 9,000 BC. Archaeological excavations proved that in Europe it was first used 2,000–1,400 BC in Greece for wall facing and as a floor surface in the palace of Knossos. Between 4th and 6th centuries, burnt gypsum was used in Europe as a component of the gypsum mortar, for making stucco decorations, flooring, decorative boards, and sculptures [1].

This raw material is a waste in various technological processes. It is a reaction product of the cheapest and most common mineral acid: sulphuric acid, and most common bases: calcium and quick

lime [2]. Moreover, gypsum is a product of the flue gas desulphurisation reaction in power plants by means of wet limestone, dry, or two-alkali methods. The sorbent slurry is added to the flue gas. Sulphur dioxide SO<sub>2</sub> dissolves in water and reacts in the presence of oxygen with the sorbent according to the following formula [3]:



In Poland the flue gas desulphurisation [4] was introduced in 1994.

Gypsum is also produced in the process of neutralisation of acid waste containing  $H_2SO_4$  [5] in the salt and potassium salt industry and during the production of phosphorus. It is also regarded a waste in numerous industrial processes. The production of synthetic gypsum neither requires complex technologies, nor consumes much energy [6]. That is why, it is a cheap and generally available material [2].

This material can also be found in nature: in sedimentary deposits in salt lakes, in closed sea basins, lakes, and bays; in the vicinity of dolomites if calcium carbonate deposits were located on the bottom of evaporating sea basin; and as veins, interbeddings or single crystals created during chemical processes in the earth's crust [7].

In 2008 global gypsum production amounted to 180.943 thousand tonnes, in 2012 the amount increased to 190.051 thousand tonnes [4]. In 2008 in Europe, 43.466 thousand tonnes were produced, whereas in 2012: 36.823 thousand tonnes [4]. In Poland in 2008 a total of 3.077 thousand tonnes of gypsum was produced (including 1.596 thousand tonnes as a result of flue gas desulphurisation). Till 2012 the production output increased to 4.017 thousand tonnes (including 2.790 thousand tonnes as power plant waste) [4]. Moreover, we observe in Poland a considerable decrease in natural gypsum extraction. In 1993 (before lime was used for flue gas desulphurisation in power plants) 100% of gypsum was extracted from natural deposits. In 2012 only 30% [4]. Raw gypsum may be used directly after it has been produced (extracted) or it may be subjected to further processing [8, 9].

At present, gypsum is most often used for finishing works in the construction industry. 80% of its global consumption is spent on manufacturing gypsum prefabricated materials and elements e.g. Portland cement or gypsum plasterboards [4]. Furthermore, gypsum binders are eagerly applied in ceramics (for gypsum mould making), chemistry, jewellery casting and medicine [1]. Due to various additives like: talc, kaolinite [10], coal dust, bio-silica [6], citric acid or sodium carbonate [11] gypsum properties can be modified.

The presence of sulphur (see equation (2)) in moulding sand with gypsum binder, like in furan masses, may deteriorate the casting quality (the impact of sulphur on the casting quality is at present examined by numerous researchers) [12-16]. Unfavourable influence of sulphur present in furan moulding sands can be seen on the surface of cast elements made of spheroidal graphite cast iron. The diffusion of sulphur from moulding sand to the surface of hardening cast may result in degradation of spheroidal graphite to flake graphite [13-16], which has a negative impact on the mechanical properties of cast iron [13]. The assessment of sulphur diffusion is often supported by LOI (Loss on ignition) tests. This indicator is also applied for assessing broadly the degree to which moulding sand has been used up.

The loss on ignition is the difference between the remaining dry moulding sand (after binding), and the remaining sand after roasting [17]. In compliance with norm BN-70/4024-15 [18] the LOI test for moulding sand has been conducted for 1 g of moulding sand after it has been dried at 105°C (or any other temperature if necessary). Then the moulding sand should be roasted in a muffle furnace at a temperature of 900-1000°C [19].

## 2. Research objectives

The research aimed to establish whether gypsum binders can be added in the production of quartz moulding sands exposed to temperature of melt in the cavity of mould.

For the study, proposed three roasting temperature: 300°C, 650°C and 950°C. The reason behind roasting at 300°C was the release of water that was added in excess to moulding sand when the components were mixed. The reason behind choosing roasting at temperature of 650°C was following after behaviour of other inorganic binders (such as hydrated sodium silicate) in annealed and cooled-down moulding sands. Near the temperature of 650°C their residual strength [20,21] are the lowest, so they has good knock-out properties. The last roasting temperature (950°C) was choose according to literature data [18, 19] for LOI tests.

The analyses were made to determine how those fresh moulding sands behave at higher temperatures (from 300°C to 950°C) and which of available commercial types of gypsum (building gypsum or gypsum putty) will be possibly better for foundry industry as a cheap binder, also as an alternative binding material to the other organic and inorganic binders.

In order to assess the behaviour of moulding sands at higher temperatures, apart from the LOI tests, analysed were: the chemical composition and pH parameter. In the research were made observations of bonding bridges after roasting with the use of scanning electron microscope (SEM).

## 3. Research description

For the purposes of the analyses, was used popular in foundry applications medium quartz sand 1K from the Polish mine 'Grudzeń Las'. Sieve test was compliant with norm PN-H-11001:1985, and the size of grain was 0.20/0.315/0.16 measured on test sieves standardized with ISO 3310. Also, medium type of the foundry sand was selected based on author's preliminary successful study [22].

Two commonly available types of gypsum were added as a binder to produce:

- moulding sand GMS1 (Gypsum Moulding Sand) – made of 'Dolina Nidy' building gypsum [20] marked as A1 [23] in compliance with norm PN-EN 13279-1:2009;
- moulding sand GMS2 – made of 'Dolina Nidy' gypsum putty marked as B1 [24] in compliance with norm PN-EN 13279-1:2009.

On the basis of the author's preliminary study [22, 25] and the data given by the gypsum manufacturer [24], specified were the amount of particular components and how the moulding sand was to be produced. 89 parts by weight of the sand matrix and 11 parts by weight of loose binder were placed in the planetary mixer. Dry components were mixed for 2 min, then 5 parts by weight of water was added and the whole was mixed for another 2 min. After moulding and densifying, the strength of the moulding sand according to [25] after 5h amounted to:  $R_c = 0.60$  MPa,  $R_g = 0.19$ ,  $R_m = 0.09$  MPa. When additional microwave heating is applied [19, 22], the strength  $R_c^u$  may amount to ca. 1.7 MPa,  $R_m^u = 0.35$  MPa and  $R_g^u = 0.61$  MPa. The moulding sand GMS1 and GMS2 were prepared were than used to make a series of samples (ca. 10 g) for

LOI tests. The samples were placed in special ceramic containers and hardened naturally for 24h at a constant temperature (20°C) and air humidity 80% (relative humidity) in a climatic chamber KK 115 TOP+. It should be noticed that we departed from norm BN-70/4024-15, which recommended that the samples should not be completely cured at a temperature of 105°C. Then the samples were weighted to the nearest of 0.01 g using laboratory scales manufactured by OHAUS PA4102CM/1. At the next stage the samples were subjected to one-hour roasting at temperatures of 300°C, 650°C and 950°C in a chamber furnace manufactured by CZYLOK type PSK-10. After the samples were taken out of the furnace, cooled and weighted, the loss on ignition was determined. For each type of moulding sand, pH was established using ELMETRON CPC-401. Additionally, we made observations of bonding bridges between the matrix grains by means of scanning microscope by Hitachi TM-3000 with electron acceleration of 15 kV, equipped with EDS/EDX analyser.

## 4. Results

The results of the pH and LOI test and the binder chemical composition analysis are presented in Table 1 for moulding sand GMS1, and in Table 2 for moulding sand GMS2. The chemical composition analysis shows average values from at least 4 measurements. The spectra of exemplary chemical analyses at bonding bridges are presented in Figure 1.

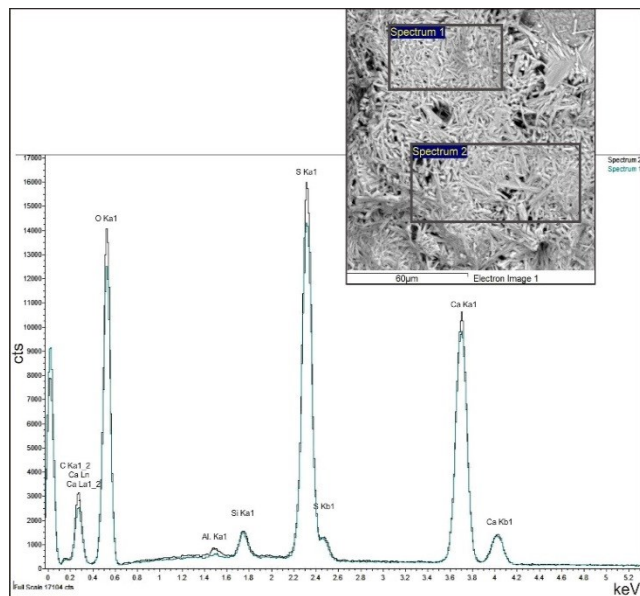


Fig. 1. Example locations of chemical analyses and elemental composition spectra for the binder in moulding sand GMS1

LOI tests (Table 1 and 2) was recorder that both types of binders show a tendency for mass reduction even at a temperature of 300°C. The greatest loss on ignition was recorder for moulding sand GMS2 at a temperature of 650°C - (2.84%), which may result from a further process of releasing chemically bound water. Similarly, for GMS1 the loss was the greatest (2.59%) at a

temperature of 650°C. At least, the samples were roasted at 950°C according to temperature recommended to LOI tests. At higher temperatures (950°C) this parameter slightly decreases for both types of moulding sand. It may be related to the diffusion of some elements from the environment to the samples of moulding sand (a change in the contents of Al, Si). However, the differences in LOI above 300°C to 950°C were small, never exceeding 1.02%. A high LOI parameter (above 2%) may affect the casting quality, but it can be eliminated by additional drying, e.g. microwave drying [22,25].

Table 1.

The pH parameter, LOI for moulding sand with building gypsum and chemical analysis at bridges bonding matrix grains.

Gypsum moulding sand GMS1				
Temperature	20°C	300°C	650°C	950°C
pH	8.867	7.853	11.756	8.905
Loss on ignition [wt.%]	-	2.00	2.59	2.25
Average element content [wt.%]				
O	61.513	57.921	53.859	57.286
Mg	-	0.104	0.075	0.083
Al	0.284	0.453	0.246	0.368
Si	1.160	6.285	0.946	1.138
S	17.218	17.344	21.028	19.729
Ca	19.826	17.894	23.845	21.396

Table 2.

The pH parameter, LOI for moulding sand with gypsum putty and chemical analysis at bridges bonding matrix grains.

Gypsum moulding sand GMS2				
Temperature:	20°C	300°C	650°	950°C
pH:	8.371	8.299	12.400	12.500
Loss on ignition [wt.%]:	-	1.49	2.84	2.51
Average element content [wt.%]				
O	54.883	51.733	56.915	53.357
Mg	0.103	0.086	0.170	0.200
Al	0.381	0.397	0.494	1.045
Si	3.168	3.794	2.037	2.113
S	12.557	18.324	18.076	19.265
K	0.162	-	0.147	-
Ca	28.746	25.666	21.931	24.020
Fe	-	-	0.231	-

In all cases, the pH was alkaline. The sulphur content, significant for the casting quality, maintained the same level for both types of gypsums (Table 1 and 2). The pH parameter for moulding sand GMS1 after roasting at 950°C is lower than after roasting at 650°C, which may indicate the presence of unidentified phenomena in the binder with building gypsum. In moulding sand

with gypsum putty (GMS2) an additional amount of iron and potassium was detected, which never happened in tests on moulding sand with building gypsum (GMS1). Gypsum moulding sand GMS2 contains more magnesium, aluminium and calcium, in moulding sand GMS1 a greater amount of sulphur is observed after roasting.

The results of chemical analyses were compared with SEM observations of bridges bonding matrix grains before and after roasting.

#### 4.1 Results of bonding bridges observations

The images of bonding bridges in gypsum moulding sand hardened in a natural way at a temperature of 20°C are presented in Figure 2a for GMS1 and in Figure 2b for GMS2. Figs. 3–5 demonstrate moulding sand after roasting. Figure 3 shows bridges after roasting at 300°C, and Figure 4 after roasting at 650°C, while Figure 5 shows moulding sand GMS1 and GMS2 after roasting at 950°C.

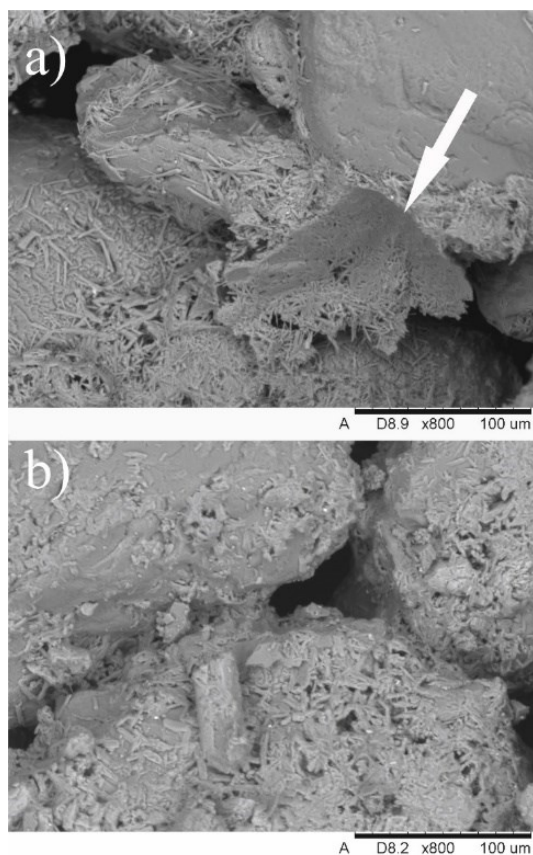


Fig. 2. View of bonding bridges in hardened moulding sand at a temperature of 20°C: a) GMS1 with a broken bridge in the contact area with the grain – adhesive type, and b) GMS2; Zoom: 800:1

The images of bridges (Fig. 2) demonstrate that in gypsum putty (GMS2) their structure is finer, needle-like, less compact, and consequently the pores are greater. In both GMS1 and GMS2

numerous lumps of gypsum binders can be seen; however, they make no direct and valuable contribution to the binding of matrix grains.

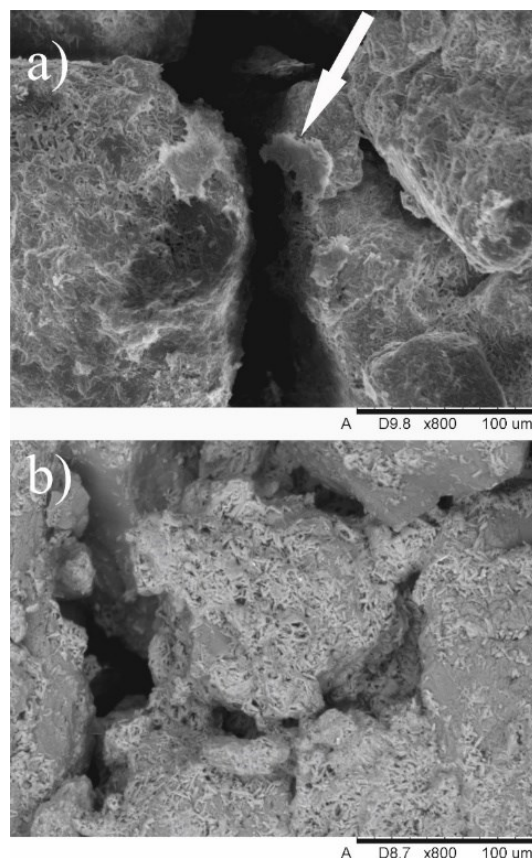


Fig. 3. View of bonding bridges in hardened moulding sand at a temperature of 20°C, and then roasted at a temperature of 300°C: a) GMS1 and b) GMS2; Zoom: 800:1

After roasting GMS1 and GMS2 at a temperature of 300°C (Fig. 3), the bridges with gypsum putty show numerous discontinuities (Fig. 3a) that appear spontaneously (as a result of higher temperature). The very structure and view of bonding bridges, apart from an increased amount of adhesive fractures (GMS1), was not changed.



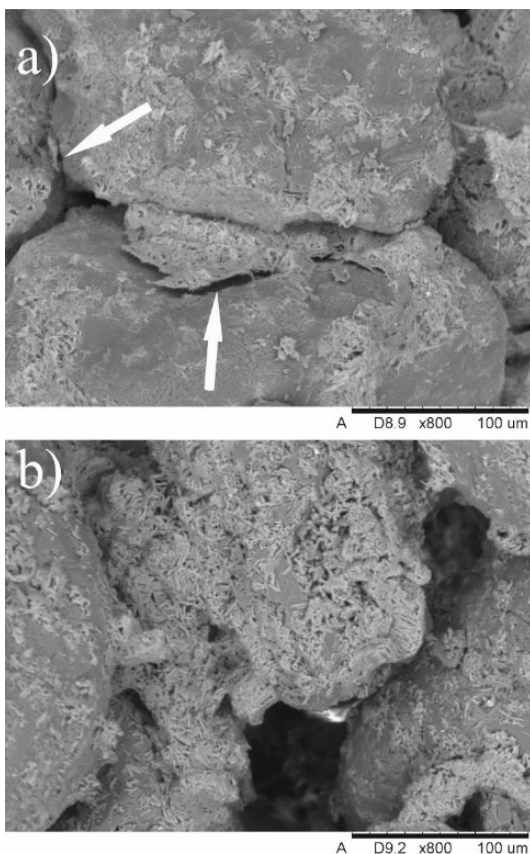


Fig. 4. View of bonding bridges in hardened moulding sand at a temperature of 20°C and then roasted at a temperature of 650°C: a) GMS1 and b) GMS2; Zoom: 800:1

In Figure 4a (gypsum moulding sand GMS1) adhesive fractures (indicated with an arrow) of bonding bridges as a result of high temperature can also be seen. The comparison of moulding sand GMS1 and GMS2 reveals noticeable differences in the size of needle-like components in the gypsum structure.

In Figure 5 the adhesive type of fractures in moulding sand GMS1 is clearly visible. The higher the temperature for roasting moulding sand with building gypsum binder is, the more visible fractures between the grains and the binders can be found. Adhesive fractures are also present in moulding sand GMS2, but they are not that distinct. When the samples for SEM test were prepared, their tendency to friability was less clear.

The observations demonstrate a capsule-like distribution of gypsum binders [18] and the creation of correct, favourable bridges binding the matrix grains due to the adopted method and order of mixing the components of moulding sand.

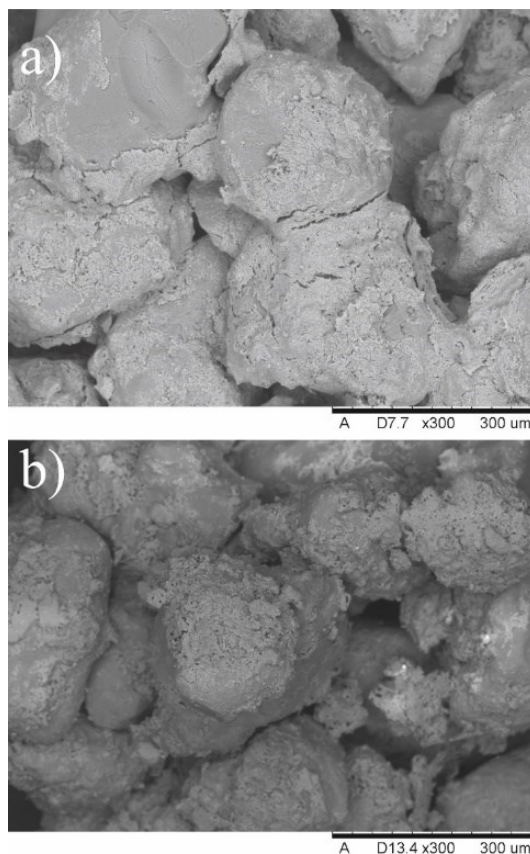


Fig. 5. Wide view of bonding bridges in hardened moulding sand at a temperature of 20°C and then roasted at a temperature of 950°C: a) GMS1 and b) GMS2; Zoom: 300:1

The comparison of bonding bridges in moulding sand cured at a temperature of 20°C and roasted (Fig. 2 - 5) shows that the roasting temperature has little effect on their structure, but it increases the tendency towards adhesive fractures. The reason behind the fractures can be found in the phenomena that accompany the polymorphous changes in the matrix, and in the presence of compounds with Ca and hydroxyl group as well as the process of releasing chemically bound water.

## 5. Conclusions

Research into the impact of higher temperature on moulding sand with gypsum binders yielded the following findings:

- all types of moulding sand are alkaline,
- moulding sand with building gypsum (GMS1) contains a greater amount of oxygen and sulphur, whereas moulding sand GMS2 with gypsum putty contains more aluminium, magnesium and calcium as well as iron and potassium,
- heating within the range from 300°C to 950°C caused no significant changes in the sulphur content, which encourages further research into the possibility of applying gypsum (both

- building gypsum and gypsum putty) in moulding sand binders,
- the values of loss on ignition at temperature within the range from 300 to 950°C fall from 2 to 2.9%; however, the highest values can be observed in both types of moulding sand after roasting at 650°C,
  - bridges bonding the matrix grains in gypsum moulding sand GMS1 with building gypsum have a very fine, needle-like structure,
  - the structure of bonding bridges in moulding sand GMS2 with gypsum putty contains thicker needles; the binder in moulding sand GMS2 is visible on the whole surface of grains; it is better distributed on the surface of grains when the described method of sand preparation is applied,
  - under the influence of temperature, bonding bridges in both gypsum binders show a tendency towards spontaneous fractures, which creates favourable conditions for regeneration and recovery of quartz matrix from the used moulding sand,
  - the occurrence of lumps in the binder, though the lumps participate neither in the creation of bonding bridges nor in transferring loads by moulding sand GMS1 and GMS2 should be eliminated as unfavourable in future studies.

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