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Impact of Hardening Methods on the Moulding Sand's Properties with Gypsum Binder

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Abstract

The research paper presents the results of testing the strength and technological properties of molding sand with gypsum binder, the bonding process proceeded: naturally or conventionally. The tests included mass containing (parts by weight): 78 pbw. Grudzeń-Las quartz sand, 22 pbw. plaster gypsum "Dolina Nidy" and 9 pbw. water. Measurements of compressive strength, shear, tensile and bending as well as permeability and looseness were carried out on standard cylindrical samples kept in the air for 1 - 96 hours or dried at 110 oC for 1 - 8 hours. The results of the analysis were analyzed in connection with the mass structure and construction binding bridges warp grains observed with a scanning microscope (SEM). The influence of drying intensity on the bonding process and related mass properties has been demonstrated, especially from the point of view of the possibility of selection and / or intensification of a specific curing method for use in the production of gypsum binger molds and cores.

Keywords: Foundry, Gypsum Binder, Foundry and Core Masses, Mass Properties

1. Introduction

Commonly used in many industries, gypsum (calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$) consisting mainly of CaO, SO_3 and H_2O is a sulphate sedimentary rock, built almost exclusively of the same name' mineral, with anhydrite, calcite and halite admixtures [1].

The main source is natural stone (gypsum and anhydrite) occurring in the environment of salt deposits in Poland [2]. It also occurs as a waste product, e.g. in flue gas desulphurization processes [2], or during the processing of phosphorus into fertilizers as synthetic gypsum (phosphorogypsum) [2], which can be a source of raw material from an ecological point of view.

The crystal structure of natural and synthetic gypsum dihydrate is identical. Gypsum comes in three varieties, and its structure depends primarily on the conditions of transformation of the raw material and the formation of a certain phase (temperature and pressure) [3-8].

In addition to calcium sulfate dihydrate, there are:

- α-hemihydrate (α-$CaSO_4 \cdot 0.5H_2O$) as a dehydration product of $CaSO_4 \cdot 2H_2O$ dihydrate gypsum at 97°C;
- β-hemihydrate (β-$CaSO_4 \cdot 0.5H_2O$) obtained, among others in a vacuum at a temperature below 100°C, which occurs in technical gypsum and reacts more actively with water and dissolves better in it than α-hemihydrate.

Anhydrite also comes in three varieties, and so:

- α-soluble anhydrite (α-$CaSO_4$III), which is obtained in the process of dewatering the α-hemihydrate;

- β-soluble anhydrite (β-$CaSO_4$III), which is obtained by heating the dihydrate at reduced humidity;
- natural anhydrite ($CaSO_4$II), insoluble, which can also be obtained synthetically during thermal treatment of β anhydrite III, α-anhydrite III or $CaSO_4 \cdot 2H_2O$ dihydrate..

The gypsum binding process takes place in three stages: hydration, dissolution and crystallization. It ends with a complete conversion of the hemihydrate to the dihydrate.

Microscopic observations of gypsum hemihydrate found in the aqueous environment allowed to determine the mechanisms of its binding [1]. It was found that in the crystallization process it is transformed into the dihydrate, which precipitates in the form of coniferous crystals 10-40 μm long and 1.7-2.5 μm wide.

Observing changes in structure, a mixture of hemihydrate, water and finely ground quartz sand during curing, a slow increase of its strength was found for the first 4-5 minutes to the value of 0.15 MPa. The mixture produces dihydrate gypsum crystals. The thickening suspension consisted mainly of a hemihydrate, on the surface of which dihydrate crystals formed bound by Van der Waals forces. It was found that damage to such a structure during the first 3-4 minutes does not affect the strength of the mixture after the curing process. Further, continuous water binding and an increase in the amount of dihydrate gypsum crystals forming coagulation meshes leads to a rapid increase in its strength, which after approx. 30 min reaches 1.5 MPa [1].

The speed of setting gypsum depends primarily on the size of its grain, because the setting time and intensity of hydration reaction is affected by the overall wetting surface. Its increase causes an increase in the amount of water needed to obtain a grout with the right consistency, while affecting the setting time of gypsum [1].

The degree of fragmentation of gypsum also affects the mechanical strength of its components. Fine grain, by increasing the surface of mutual contact, ensures greater compressive and breaking strength. At the same time, there is an increase in water demand, which deteriorates strength, but improves the plasticity of plaster gypsum[1].

The factor determining the possibility of using different types of gypsum is their setting time, i.e. the period in which mass formation is possible without affecting its properties after the process [1,9,10].

In technological application, it is particularly important to maintain good plasticity of the molding sand until the element is shaped, and after its rapid crystallization. Earlier gypsum binding may lead to damage of the warp grain binding bridges and deterioration of the mold or core strength [1,9,10].

Gypsum compression and bending strength depends primarily on the crystalline form in which it occurs, and thus the α-hemihydrate has 2-3 times greater strength properties than β-hemihydrate. Therefore, it depends mainly on the phase composition of the raw material and the method of preparation of the masses. It is important for the quality of the gypsum mass to evenly mix all ingredients to thoroughly wet them with water [1,9,10].

The high mechanical strength of the gypsum element is achieved by using the smallest possible amount of water for grout preparation taking into account the granularity of the raw material and the associated water content [1].

2. Purpose of the research

The purpose of the presented research was to determine the change in strength and technological properties of gypsum binder mass, naturally hardened or dried conventionally, ensuring the necessary conditions for metal flooding of forms or cores [11].

The use of elastic, commercially available plaster gypsum [12,13] allowed, thanks to its specific features, to achieve further research objectives related to achieving favorable properties of molding sand from the point of view of its application in mold and core technology.

A characteristic, very important feature of the selected binder is a favorable crystallization process slowed down compared to Construction Gypsum, which does not change the elasticity and increases the service life of the mass during forming. In addition, thanks to the proven possibility of reducing the water content in the molding material, it is obtained a loose, non-sticking mixture and finally it is possible to shorten its hardening (drying) time [12].

3. Description of the tests

The tests were carried out for molding mass containing (parts by weight): 78 pbw. dry quartz sand Grudzeń-Las (main fraction 0.20 / 0.16 / 0.315, class 1K), 22 pbw. Plaster Gypsum: "Dolina Nidy" [13] (moisture content 4.1%) and 9 pbw. water [14-16].

The commercially available binder contains mainly $CaSO_4 \cdot 0.5H_2O$ β-hemihydrate and $CaCO_3$ carbonate as well as the quantity and type of additives modifying and regulating the binding time not determined in X-ray analysis [12,13].

The mass was prepared in a Garmin planetary device, mixing dry ingredients for 2 min and then dosing water, continuing the process for another 2 min.

In accordance with the recommendations of PN-83 / H-11070 [17], cylindrical, longitudinal and octal fittings were prepared, whose density was respectively: 1599, 1543 and 1663 kg/m^3.

By measuring the compressive strength R_c^s and shear R_t^s[18] and permeability P^s [19], the weight loss of the samples from their preparation to the moment of measurement was weighed each time, determining the time of their complete drying. Measurements of R_m^s tensile strength and R_g^s bending as well as S^s slurry were carried out using dried samples.

Studies on the influence of Plaster Gypsum binding conditions on mass properties were carried out on standard laboratory samples after their hardening (drying) [20,21]:

- natural, at a temperature of 25ºC and humidity of 56% during 1, 2, 5, 8, 24, 48, 72 and 96 hours, until the change in their mass ceases;
- conventional, at a temperature of 110°C and for 1, 2, 5 and 8 hours, selected from the point of view of using these parameters in the process of manufacturing foundry molds and cores;

After the flexural strength measurements, mass samples taken from the fracture area were observed using a scanning electron microscope (Figs. 1, 2).

4. Results

Analyzing the results of measurements for natural dried mass (Table 1), it was found [20]:

- systematic increase of its compressive strength R_c^s from 0.31 to 1.94 MPa after drying for 24 hours and a significant increase to approx. 3.6 MPa over 48 hours;
- R_t^s strength, initially increases (up to 8 hours) from 0.04 to 0.37 MPa, reaching a value of 0.71 MPa after 24 hours and after a longer time (≥48 hours) sets its final value around 1.15 MPa;
- the loss of primary mass of cylindrical samples ranges from 0.76% after 1 hour to 4.47% after 24 hours and reaches approx. 5% after 48, 72 and 96 hours;
- P^s mass permeability does not change significantly and ranges from 123 to 144 m^2/Pa·s, after 1 and 48 h, respectively, after which it decreases to approx. 110 m^2/Pa s, probably as a result of accumulation in spaces between warp grains of fine binder particles released during the measurement (Fig. 1);
- R_m^s and R_g^s strength, determined after 72 h for the determined mass loss of the sample is 0.72 and 0.75 MPa, respectively;
- the dry matter S^s of the dried mass for 72 h is 0.44%.

Table 1.
Strength R_c^s and R_t^s and permeability of naturally dried mass [20]

Time h	R_c^s	Σ	R_t^s	σ	P^s	σ
	MPa				m^2/Pa·s	
1	0.31	0.03	0.04	0.01	123	4.0
2	1.49	0.13	0.23	0.02	129	7.4
5	1.71	0.10	0.35	0.02	134	7.7
8	1.89	0.08	0.37	0.01	133	5.1
24	1.94	0.13	0.71	0.09	132	12.1
48	3.54	0.49	1.13	0.04	144	12.4
72	3.59	0.40	1.13	0.04	106	3.7
96	3.73	0.46	1.16	0.02	108	2.7

Favorable strength and technological properties of naturally dried mass result from the crystallization process of gypsum binder in a humid environment (Fig. 1). The gypsum hemihydrate is converted to the dihydrate, which precipitates as coniferous crystals. Residual moisture may lead to the formation of foundry incompatibilities when pouring molds, and in the case of alloys with a high melting point, for example the formation of hydrogen sulfide with calcium dihydrate breakdown products above 870 ° C [12].

Conventional drying in 110°C of the tested mass in the dryer showed that (Table 2) [21]:

- the strength R_c^s of the mass after 1 hour of drying equal to 0.27 MPa (as after natural drying) increases after 2 hours by approx. 50% and after 8 hours reaches 0.50 MPa;
- similarly, after 1 h, R_t^s strength, similar to naturally dried, increases after 2 h and finally reaches the value of 0.14 MPa;
- sample weight loss after drying for 1 h is 7.1% (90% of removed moisture), and after further heating up to 8.0%;
- the highest strength values R_m^s = 0.09 MPa after 2 hours, while R_g^s = 0.08 MPa after 5 hours of drying, are higher only in comparison with those determined after 1 hour of natural mass hardening;
- the permeability of the dried mass up to 2 h is about 100% higher than naturally cured and is about 250 m^2/Pa·s, and longer heating (≥2 h) causes a decrease in P^s, to the values measured after natural drying (117 - 142 m^2/Pa·s);
- the slurry S^s of the mass after 5 hours of drying equals 3.79%.

Intensive conventional drying in 110°C is not conducive to the proper crystallization of the binder (Fig. 2) and does not provide the mass with such favorable properties as natural, but after a period of ≥2 h allows almost complete drying of the mass (≤ 8%). The binder connecting warp grains gives the mass a certain strength, which in combination with a lack of moisture and good permeability makes it possible to use it in foundry technologies.

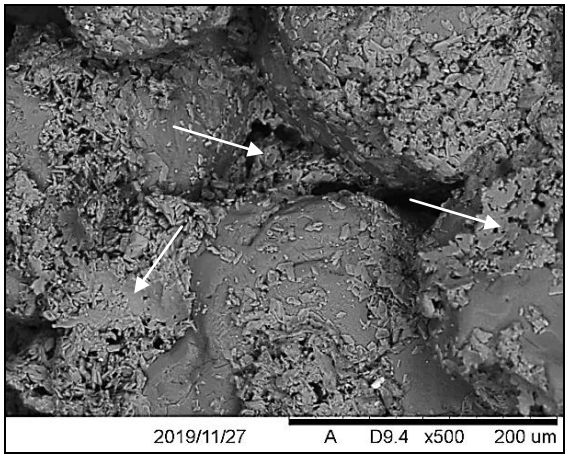

Fig. 1. SEM image of a naturally dried fracture surface 72 h mass, visible areas of detachment from the matrix of binding bridges and clusters of small, lumpy binder particles [20]

Table 2.
Strength R_c^s and R_t^s and permeability P^s of conventionally dried mass [21]

Time h	R_c^s	σ	R_t^s	σ	P^s	σ
	MPa				m^2/Pa·s	
1 h	0.27	0.01	0.06	0.01	256	5.5
2 h	0.41	0.03	0.09	0.01	248	4.5
5 h	0.44	0.01	0.14	0.01	142	2.7
8 h	0.50	0.02	0.12	0.01	117	2.9

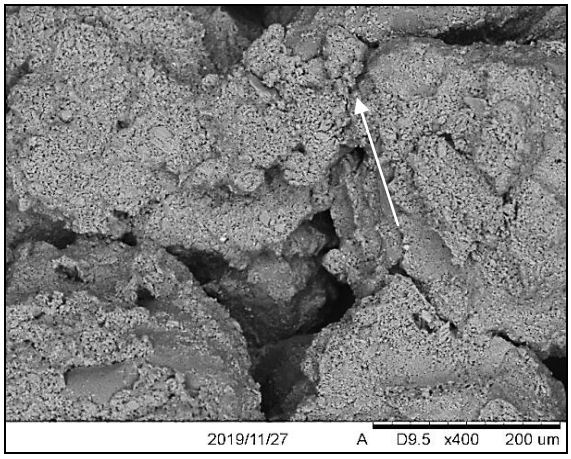

Fig. 2. SEM view of the dried matter breakthrough Surface conventionally for 2 h, fine, loose binder particles visible [21]

5. Results

Analyzing the results of the research carried out on the impact of the Plaster Gypsum binder drying method on its strength and technological properties, it is noted that:

- the natural process provides the mass with very good strength and technological properties, thanks to the correct crystallization and good connection with the gypsum binder matrix (Fig. 1). However, it does not provide complete removal of moisture (residual approx. 5%), which during pouring may cause foundry incompatibilities and, in combination with products of thermal decomposition of the binder, cause the release of e.g. hydrogen sulfide;
- accelerated conventional drying (≥ 2 h), which disturbs the proper crystallization of the binder used (Fig. 2) and does not provide the mass with such favorable properties as natural, but it can, however, give the mass a specific strength, combined with a lack of moisture and good permeability, make it possible application in foundry technology;
- applying, after achieving the proper mass after the natural binding process, drying or desiccation the molds and cores before flooding with metal, will shorten the time of their production and prevent the occurrence of foundry and harmful gas incompatibilities;
- slowing down the crystallization process of the applied Plaster Gypsum, provides the mass, without affecting the bonding process, good elasticity and extending the time of the forming process;
- analyzing the change in mass strength over time, the effect of reducing water content is observed, ensuring both a shortening of its hardening (drying) time as well as obtaining a loose, non-sticking mixture and ultimately the possibility of shortening the process of making molds and cores.

The presented research results may constitute guidelines for the development of ecological casting technologies based on gypsum binder sands, intended for industrial use.

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