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GYPSUM COMPOSITION FOR PREPARING MOULDS AND MODELS BASED ON LOCAL RAW MATERIALS

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ABSTRACT

The opportunity for obtaining gypsum compositions designed for plaster casts, which are based on local raw materials, has been explored. A study of physicomechanical and physicochemical properties of such compositions was conducted. An optimal composition has been found with regard to the compressive strength and shrinkage both before and after baking, following a certain technological regime.

Keywords: gypsum, gypsum composition, plaster casts, mould mass.

INTRODUCTION

The traditional application of gypsum and gypsum-based compositions is in the field of construction – mortars for masonry and plasters, gypsum blocks, panels, gypsum fiber products, ceiling components, etc. The gypsum setting substances have qualities, which determine their application in other industrial areas as well. The ability to produce complex configurations through preliminary moulded gypsum models on one hand and obtaining a smooth surface of the products, not requiring additional treatment, on the other hand, expands the scope of their application in metal casting and machine building. A prerequisite for their wide application is the ability for fast setting and hardening; hence, the production of gypsum moulds and models is distinguished by a short production and technological cycle. The technology of their production is easily realized, which is a precondition for the high productivity and low prime cost of products.

The lack of local production and the shortage of such materials are the main reasons for the interest towards them. The aim of the present study is to explore the capacity for obtaining gypsum compositions on the basis of local raw materials (hemihydrate, silicon dioxide) intended for casting of modules for the needs of the non-ferrous metal casting and machine building. When casting the forms, the behaviour of the mixture in the process of stirring and moulding is especially important, as well as the setting time, which characterizes the transition stage from the liquid gypsum mixture to its solid state.

In order to produce plaster casts with preset physicochemical and mechanical properties, various additives are added to gypsum. These additives may be differentiated in two main groups:

a/ additives regulating the setting time and consistency of the gypsum paste;

b/ additives changing the properties of the hardset gypsum.

The additives of the first group on its part are split to several classes [1]. One of these classes includes strong electrolytes with a homonymous ion of gypsum (Na_2SO_4, K_2SO_4) or without a homonymous ion (NaCl, KCl, KNO_3, $NaNO_3$). These electrolytes change the solubility of dehydrate and hemihydrate – increasing solubility leads to accelerated setting, while decreasing it causes a lagged setting. This class includes also weak electrolytes and non-electrolytes reducing the solubility of the hemihydrate – ammonia, ethyl alchohol, etc. Another class are surface-active substances (sulphate liquor) adsorpting on the hemihydrate and dehydrate, and lagging the formation of crystallization centers. This leads to setting time retarding, which is proportional to their concentration.

The additives of the second class, which may change the properties of the hard-set gypsum, are also an important element in the technology of the gypsum product preparation. Such additives are: the foaming agent Prawozell-N-BX (dry or 20% water solution), $Al_2(SO_4)_3$ combined with a foaming agent, hydrophobic additives, strength-increasing additives.

There are also requirements to the gypsum itself, related to: fine rate of grinding, setting time, volume expansion, content of non-soluble admixtures, compressive strength, etc.

In order to meet the set objectives, studies were conducted in the following directions:

• Finding an optimal gypsum composition (gypsum-hemihydrate, sand, setting retarder) in order to obtain casts having the necessary physicomechanical properties.

• Studying the influence of the technological regime of baking on the strength characteristics and the physicochemical properties of gypsum compositions.

EXPERIMENTAL

Materials

The following materials have been used in the study: Gypsum hemihydrate – produced by Gips EAD, Koshava village, Vidin region; Arenaceous quartz – from Burgas deposit.

Another material used was gangue quartz – from the Quartz Glass Plant, Sliven.

The mould mass of the KERR company, USA, intended for gypsum casts, containing crystobalit and gypsum was used as a standard sample [2].

The qualitative and semi-quantitative component composition of the gypsum from Koshava is given in Table 1.

According to the silicate analysis, the chemical composition of gypsum used in the experiments was as follows (in $\%_{mass}$): SiO_2 – 2,3; Ca – 19,7($CaSO_4$ – 67,0); Mg – 4,5; Al – 1,7(Al_2O_3 – 3,0); Fe – 0,8. The hygroscopic moisture content was 0,7 %; hydratation water – 5,5 %; heating losses at 1000°C – 9,0 %; fine rate of grinding – 4,2 % (screen oversize 0,2 mm). Gypsum was grinded to a fine rate of 0,063 mm for the experiment.

Data for the chemical composition of the arenaceous quartz are listed in Table 2.

The arenaceous quartz used was dried in advance and grinded in a ball mill to a fine rate of 100 % passed amount through a screen of 0,063 mm. The residual moisture content of the grinded arenaceous quartz at a temperature of 100°C and a delay of 3 h was $w < 0,05$ %.

The gangue quartz used contained ~ 99,99 % SiO_2. It has been grinded to a grain size under 500 μm.

Test methods

To find the optimal composition of the gypsum-arenaceous quartz mixture, i.e. the composition with the highest strength and the least shrinkage, both at the end of the setting time and after baking was the main objective of the studies conducted. Some advance studies have been carried out, taking into account the compressive strength as the main criterion in the estimations.

Three compositions have been studied:

- Composition 1 – gypsum 20 %, arenaceous quartz 80 % (1:4 in mass);
- Composition 2 – gypsum 25 %, arenaceous quartz 75 % (1:3 in mass);
- Composition 3 – gypsum 30 %, arenaceous quartz 70 % (1:2,3 in mass).

Similar compositions with gangue quartz have been studied.

For a comparison, studies with the mould mass of KERR have been conducted (Composition 4).

Table 1. Component composition of gypsum.

Ca	Si	Mg	Fe	Al	Mn	Pb	Ni	Cr	Ti	Ba	Sr	Na	Cu
>5	≅3	>1	≤1	≥1	≥0,01	$\cong 10^{-5}$	$\cong 10^{-5}$	$\geq 10^{-5}$	$\leq 10^{-2}$	$\geq 10^{-3}$	≥1	≥0.03	$\geq 10^{-4}$

Table 2. Chemical composition of arenaceous quartz.

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	Others
%	93,10	2,73	0,43	0,33	0,12	2,50	0,79

Table 3. Physical propertys before baking.

Sample №	Geometrical dimensions		Mass, g	Bulk density ρ_0, g/cm^3	Average value ρ_{0av}, g/cm^3
	ø, cm	h, cm			
1	1,43 (1,43)	1,53 (1,60)	3,01 (3,11)	1,22 (1,21)	1,20 (1,23)
2	1,43 (1,43)	1,63 (1,79)	3,19 (3,45)	1,22 (1,20)	
3	1,43 (1,43)	1,43 (1,65)	2,71 (3,40)	1,19 (1,28)	
4	1,39 (1,43)	1,80 (1,80)	3,20 (3,39)	1,17 (1,24)	

The experiments conducted for the composition's consistency determination indicated that the water content should be 29-31 % of the gypsum mass. Double vacuum treatment was performed after the composition preparation in order to avoid bubbles and other possible defects.

Four cylindrical samples of each composition have been prepared for the tests.

In order to use the moulds in the non-ferrous metallurgy (i.e. at temperatures of 900-1100°C) they should be heated at a temperature of 650-750°C in a time lag mode [2]. During this study, the samples have been baked in the way recommended by KERR [2]: 140°C – 2 hours; 370°C – 2 hours; 650°C – 3 hours.

The compressive strength was determined with the help of a special hydraulic press, and was calculated according to the following equation:

$$R_c = P \frac{A_0}{A}, \text{MPa},$$

where:

P – manometer reading upon sample destruction, MPa;

A_0 – area of piston, cm^2;

A – area of sample, cm^2.

The large number of procedures for the preparation of products – preparation of the mixture, vacuum treatment, transition from one mould to another – requires a prolongation of the setting time. This imposed additional studies to be conducted in order to find an appropriate retarder.

The most often cited crystalisation retarders, which at the same time increase the strength, are the organic acids (citric, tartaric, malic) [4,5]. When investigating the hydration of a gypsum paste obtained from a hemihydrate, it has been found that the citric acid additive retarded the gypsum hydration [6]. The penetration of water molecules into the gypsum particles is limited by the diffusion velocity.

It has been proved that the water-soluble polymers addition increases the mechanical strength and delays the setting [2].

The expediency of adding ammonium and ethanolamine salts with a water-soluble polymer acting as a hydromodifier at a higher temperature was proved – the setting time was reduced significantly, and the strength of products was increased by 40-70 % [7]. The influence of the following additives on the hydration kinetics and mechanical properties of gypsum has been

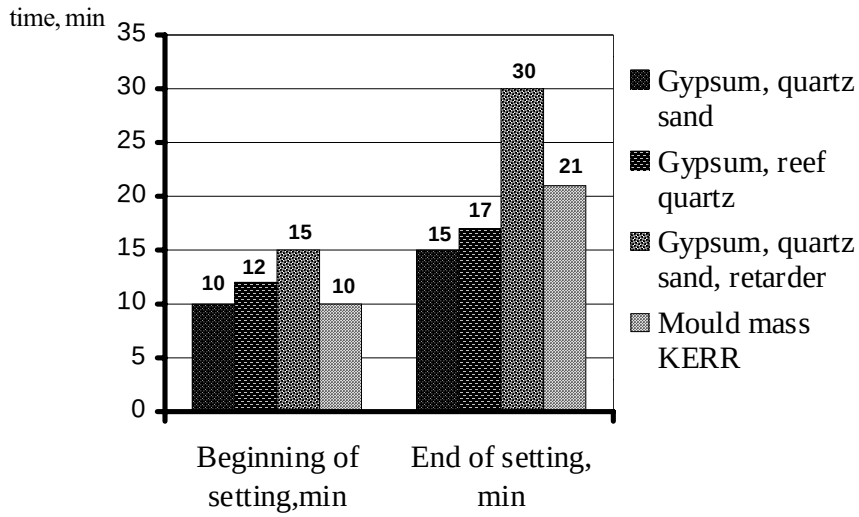

Fig. 1. Setting time.

studied: ammonium sulphate, tartaric acid, polyacrylic acid, sodium polyphosphate. An increased strength was registered with the first two additives, while the other ones caused decreasing of strength [8,9].

The experiments [10] performed with Na_2CO_3, citric acid and some polyoxides showed that the most appropriate additive is 20 % solution of polyacrylate disperser with the empirical formula $C_3O_2H_3Na$. The molecular mass of the disperser is 4500-5000, density – 1,3 g cm^{-3} and pH = 7,0-7,5.

The setting time of 3 compositions was determined with the Vikat device:

- Gypsum and arenaceous quartz;
- Gypsum and gangue quartz;
- Gypsum, arenaceous quartz and retarder - 20 % solution of polyacrylate disperser.

For the compositions studied, the ratio gypsum : arenaceous quartz = 1:3 (in mass), water being 31 % of the gypsum mass. For comparison, the mould mass of KERR was also tested.

RESULTS AND DISCUSSION

The compressive strength obtained for Composition 1 was 3,1 MPa, for Composition 2 – 6,4 MPa, and for Composition 3 – 4,0 MPa. The results for the compositions with gangue quartz were respectively: 2,9 MPa, 5,2 MPa, and 4,6 MPa. The test of the KERR material (Composition 4) indicated a compressive strength of 5,0 MPa.

The analysis of the results leads to the conclusion that Composition 2 (gypsum : arenaceous quartz = 1:3) has the best strength parameters. Therefore, the further studies were concentrated on the behaviour of this composition during moulding, setting and baking.

Table 3 and Table 4 show the results of testing of cylindrical samples of gypsum-arenaceous quartz mixture: the ratio between gypsum and arenaceous quartz = 1:3 (in mass), water being 31 % of the gypsum mass. Tests have been conducted before and after baking. The results in parentheses are related to tests of cylindrical samples prepared with the mould mass of KERR.

The analysis of samples of gypsum-arenaceous quartz mixture showed that as a result of baking the shrinkage in the radial direction was 0,7 % in average, while in axial direction it was 1,4 %. The loss of mass after baking was 7,3% in average. The average compressive strength was 6,53 MPa. Similar results were obtained when using gangue quartz instead of arenaceous quartz. The analysis of samples with KERR material revealed that the radial shrinkage was 1,1 %, the axial one – 1,6 %, the loss of mass was 9%, and the average compressive strength – 5,08 MPa.

The results obtained for the setting time of the compositions studied are presented graphically in Fig. 1. It is evident from the graph that for the compositions with arenaceous quartz, with or without a retarder, the retarder polyacrylate disperser lags the beginning of setting by 50 %, and the end – by 100 %. Compared to

Table 4. Physicomechanical properties after baking.

Sample №	Geometrical dimensions		Mass	Bulk density ρ_0, g/cm^3		Compressive strength R_c, MPa	
	ø, cm	h, cm		ρ_{0i}	ρ_{0av}	R_{ci}	$R_{c\,av}$
1	1,42 (1,41)	1,50 (1,58)	2,78 (2,89)	1,18 (1,17)	1,15 (1,16)	7,36 (5,09)	6,53 (5,08)
2	1,42 (1,41)	1,60 (1,75)	2,92 (3,12)	1,16 (1,14)		6,69 (4,75)	
3	1,42 (1,41)	1,41 (1,63)	2,51 (3,00)	1,13 (1,17)		6,03 (5,09)	
4	1,38 (1,37)	1,79 (1,77)	3,00 (3,00)	1,13 (1,15)		6,02 (5,39)	

KERR mould mass, for the composition with a retarder the beginning of setting is lagged by 50%, while the end is lagged by 65%.

Physicochemical characteristic of compositions

A differential thermal analysis (DTA) has been carried out for the composition with arenaceous quartz without a retarder and for the material of KERR. Two endoeffects have been noticed in the derivatogram of the first composition: at 110°C, when hygroscopic water is exuded, and at 180-230°C, when dehydration to anhydrite occurs. According to literature sources this effect occurs at the interval 170-220°C, but the availability of another phase here – SiO_2 - brings about a displacement of the peak to the right, i.e. the transition is realized at a higher temperature. The lack of thermoeffects up to 700°C indicates that no phase transitions occur in the process of the thermal treatment of samples. The DTA of KERR's material indicated that phase transitions occur at 140°C and 240°C, related to the transition of ?-hemihydrate into a soluble anhydrite.

X-ray phase analysis of the same compositions was made for comparison, which indicated that the phase composition of KERR's material was identical to the one being the subject of the present studies. Before baking, the following phases were identified: $CaSO_4.0{,}5H_2O$, α-crystobalit and quartz-hexagonal, while after baking the hemihydrate passed over to $CaSO_4$ (anhydrite).

CONCLUSIONS

On the basis of the experiments and the results obtained, the following conclusions may be drawn up:

- The optimal composition of the gypsum-arenaceous quartz mixture with respect to the main propertys – compressive strength and shrinkage of product – is gypsum : arenaceous quartz=1:3 (in mass) with an additive of 20% solution of polyacrylate disperser.
- Water amount providing the necessary consistency of the mixture in order to proceed with all supportive technological operations is 29-31% of the gypsum mass.
- The technological regime of baking the moulded products (2h at 140°C; 2h at 370°C, and 3h at 650°C) corresponds to the recommended one in the leaflet of KERR, thereby failing to reach a process of silicate-formation in the system.
- If the established technological codes and conditions are observed, the products will fully meet the demands of practice in the non-ferrous metal casting. By their main parameters, these products are in no way inferior to those obtained from the mould mass of KERR.

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