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ARCHIVES of FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 2020
Issue 2/2020

59 – 64

10.24425/afe.2020.131303

10/2

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Evaluation of the Chemical Composition, TG – DTA and Tensile Strength Tests of Commercial Gypsum Kinds for Foundry Sandmixes Application

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Received 08.10.2019; accepted in revised form 03.01.2020

Abstract

The paper presents the preliminary results of research on determining the possibilities of using available on the market commercial gypsum kinds as a binder for foundry moulding and core sandmixes. Construction gypsum and plaster gypsum, finishing coat and jewelry casting gypsum were tested. Elemental composition of gypsum kinds were carried out using a scanning electron microscope (SEM) with EDS/EDX probe, their crystal structure and phase composition was determined by analyzing the results of X-ray diffraction measurements (XRD) and thermogravimetric studies (TG-DTA). Evaluation of the mechanical properties of selected materials was carried out at the tensile strength test of the dog-bone samples after initial hardening of gypsum mortar at 25 °C for 5 h and drying at 110 °C for 24 hours. The impact of the properties of the used commercial gypsum kinds on the possibility of their use as a valuable binders in the manufacture of the foundry sandmixes for moulds and cores was evaluated. Construction gypsum and finishing coat have the highest tensile strength. Plaster gypsum and finishing coat have the longest setting time. In all tested types of gypsum, the initial water loss during heating occurs at a temperature of about 200 °C. The lowest valuable properties as a binder for sand moulding mixtures has jewelry casting gypsum mass.

Keywords: Foundry, Gypsum, Binding Material, Derivographic Studies

1. Introduction

Commonly used in many industries, gypsum ($CaSO_4 \cdot 2H_2O$) is a monomineral sulphate sedimentary rock, built almost exclusively from the mineral of the same name, with anhydrite, calcite and halite admixtures [1, 2].

The crystal structure of gypsum depends mainly on the conditions in which the raw material transformations took place and a specific phase (temperature and pressure) was created [3-6]. Figure 1 shows schematically, based on literature data [1 - 7], a number of transformations including calcium sulfate.

By dehydration of $CaSO_4 \cdot 2H_2O$ dihydrate gypsum at a temperature above 97 °C (Fig. 1), α-hemihydrate (α-$CaSO_4 \cdot 0.5H_2O$) is obtained, with some of it also forming during the burning of construction gypsum.

The industrial preparation of β-hemihydrate (β-$CaSO_4 \cdot 0.5H_2O$) consists in dehydrating the dihydrate in air or in a vacuum at a temperature below 100 °C. Occurs in technical

gypsum, more actively than α-hemihydrate reacts with water and dissolves better in it.

Anhydrite occurs in three varieties, as (Fig. 1):

- soluble α-anhydrite (α-$CaSO_4$III) formed in a vacuum during the dewatering process of the α-hemihydrate at 100 °C or in the range 110-129 °C at normal atmospheric pressure;
- soluble β-anhydrite (β-CaSO4III) obtained by dehydrating the β-hemihydrate in a vacuum at 100 °C or by treating the dihydrate at 200 °C in low humidity air;
- insoluble anhydrite (CaSO4II) occurs naturally.

The latter can be obtained synthetically as a result of roasting, for 2-4 hours at a temperature of over 350 °C β-anhydrite III, by heating at 220 °C α-anhydrite III or dihydrate in an aqueous medium at a temperature 42 °C.

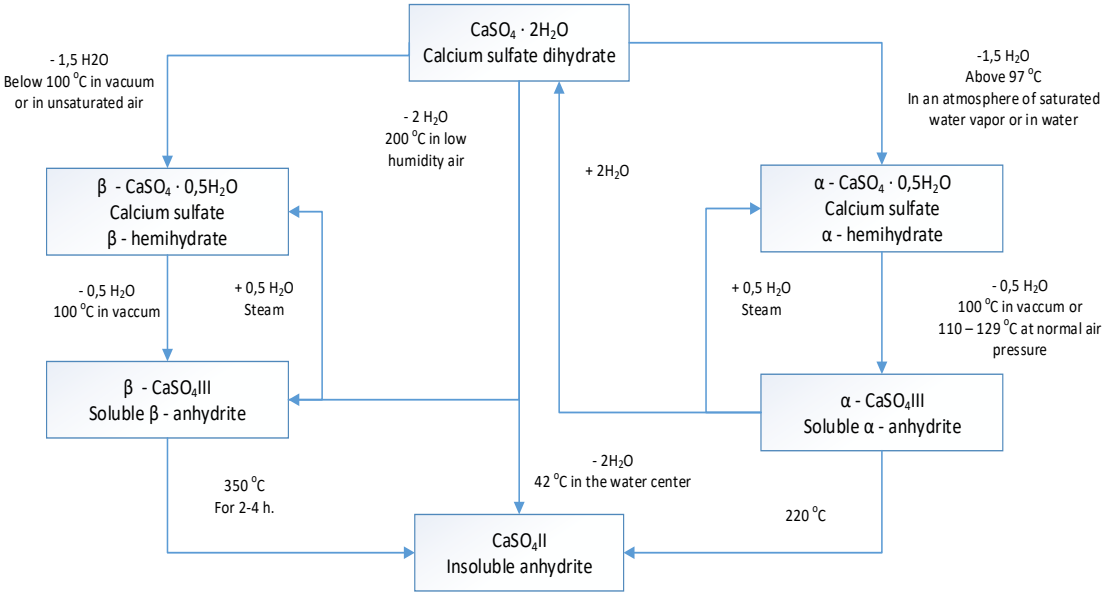


Fig. 1. Diagram of transformations taking place in calcium sulfate [1 - 7]

Gypsum compression depends primarily on its crystalline form and phase composition of the raw material, and thus the presence of α-hemihydrate in it provides even 2-3 [2] times greater strength than in the case of β-hemihydrate.

Gypsum strength is also affected by the degree of its fragmentation. Finer grain ensures compression and tearing. On the other hand, by increasing the total grain surface, it increases the water content, which deteriorates strength, while its plasticity increases, often required in technological processes [1].

The speed of setting plaster also depends on the size of its grain. Its binding time and hydration reaction speed are affected by the overall wetting surface, which depends on the proportion of small grains, and its increase causes an increase in the amount of water necessary to obtain the right consistency and affects the setting time of the gypsum binder.

The factor determining the possibility of using various gypsum mortar (gypsum and water) kinds in practice is very often their setting time. Maintaining proper plasticity of the gypsum mortar until its shaping process ends, and rapid crystallization after its completion, determine the technological parameters of production. Starting the process of binding the gypsum mortar before finishing its formation may lead to irreversible damage of the bonds between gypsum grains and deterioration of its expected properties [1].

Gypsum strength also depends mainly on the method of preparing utility mortars, e.g. by reducing water added to gypsum [8-9].

2. Purpose of the research

The aim of the presented research was to determine the possibility of using various commercially available gypsum kinds, including the jewelry casting gypsum as a binder for the moulding and core sandmixes [10-12].

Chemical composition (SEM-EDS/EDX), phase (XRD), tensile strength and thermogravimetric tests (TG - DTA) were determined for selected materials, which provided information on the effect of temperature on the course and intensity of their drainage process, binding of matrix grains and possible release of harmful reactions, i.e. sulfur trioxide SO_3.

The tests of tensile strength of gypsum mass were aimed at determining the practical application of gypsum as a binder for quartz, olivine, alumina or other moulding and core sands. The analysis of test results should show the relationship of individual properties of selected types of gypsum kinds with the possibility of their use in the processes of manufacturing sand moulds and foundry cores.

3. Description of the tests

The content of elements in selected gypsum kinds was determined using Hitachi TM-3000 scanning electron microscope

with EDS/EDX probe. The obtained results allow an unequivocal assessment of the diffraction patterns obtained for individual materials by the XRD method.

The analysis of the results of X-ray diffraction measurements of selected mortars was carried out using a copper lamp with the Ultima IV Rigaku 2008 device equipped with a Cross Beam Optics (CBO) optics system. Measurements were made in the 2Θ angle range of 5 ÷ 80°, measuring step 0.05° and time of 5 s. Mercury 3.7 and Origin 2019 programs and ICSD (Inorganic Crystal Structure Database) data were used to analyze the results.

Thermogravimetric tests DTA-TG were carried out using a Netzsch STA 449 F1 Jupiter thermal analyzer.

Tensile strength was determined on Multiserw Morek's LRuE-2e testing machine using standard octal (dog-bone) samples 70 mm length and 22.36 x 22.36 mm measuring cross-section in the narrowest part. Selected gypsum mortars were prepared in accordance with the manufacturer's recommendations in the planetary mixer. Five dog-bone samples: No.1(the 1st one) to No.5 (the last one) were made in time of 10 minutes, 2 min for each one. After 5 h of natural binding, the octal samples were dried at 110 °C for 24 h (experimentally determined time for complete drying of the samples, which ensures repeatable measurement of strength).

4. Results

For testing the following types of commercially available gypsum kinds for the expected application in foundry sandmix applications were selected: construction gypsum (CG), plaster gypsum (PG) "Dolina Nidy", finishing coat (FC) "Cekol C-45" and jewelry casting gypsum mass (JCGM) "R&R Argentum".

Table 1 shows the mass percentage content of elements found in tested with EDS/EDX probe gypsum kinds.

Plaster gypsum (PG) contains the highest participation of Ca among all tested raw materials.

By contrast, the finishing coat (FC) contains the most carbon and magnesium, and the least silicon and sulfur.

The highest silicon participation was found in jewelery casting gypsum mass (JCGM), while the lowest among the tested materials is carbon and calcium.

Examples of XRD patterns, mortars tested and identifiable compounds presented in them are presented in Figures 2-5.

The presence of $CaCO_3$ calcium carbonate and $CaSO_4 \cdot 0.5H_2O$ calcium hemihydrate was found in construction gypsum (CG) and plaster gypsum (PG).

Dolomite $CaMg(CO_3)_2$ and $CaSO_4 \cdot 0.5H_2O$ hemihydrate were identified in the finishing coat (FC).

Jewelry casting gypsum mass (JCGM) consists of significant amounts of SiO_2 silica, $CaSO_4 \cdot 0.5H_2O$ calcium hemihydrate and $CaCO_3$ calcium carbonate.

Figures 2-5 also compile TG - DTA charts, and Table 2 gives the transition temperatures and mass loss values of all raw, air-dry materials, carried out using a Netzsch STA 449 F1 Jupiter derivative in the temperature range from 30 – 1100 °C, at a heating rate of 20 K / min, with a sensitivity of recording a change in sample mass of 0.025 g. It contains the maximum temperature of thermal effects and/or intensive mass change (and its value) occurring in the tested gypsum mortars.

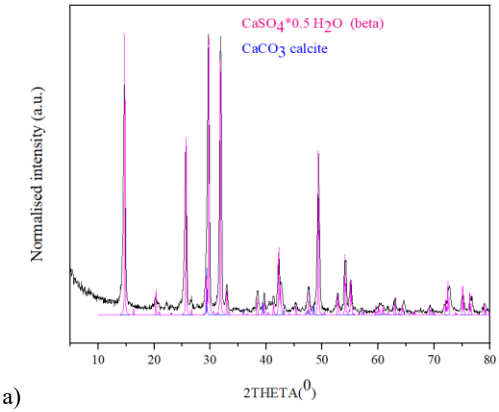
Table 1.
Percentage of ingredients in the tested gypsum kinds

Spectrum Number	Element %-wt.	Binder			
		CG	**PG**	**FC**	**JCGM**
1	C	8.47	8.88	13.23	3.79
2		9.91	10.66	11.44	3.30
3		9.97	9.61	11.96	3.98
4		8.44	12.21	9.11	4.06
Avg.		9.20	10.34	11.44	3.78
1	O	55.13	40.22	55.87	56.00
2		55.17	45.37	53.03	58.76
3		52.27	50.75	55.43	54.92
4		50.10	48.08	53.06	46.84
Avg.		53.17	46.11	54.35	54.13
1	Mg	0.16	0.40	6.17	-
2		0.35	0.19	6.27	-
3		0.65	0.15	5.60	-
4		0.36	0.04	5.13	-
Avg.		0.38	0.20	5.80	-
1	Al.	0.86	3.33	0.53	0.49
2		1.70	1.05	0.64	0.54
3		1.59	0.52	0.63	0.82
4		2.44	0.60	0.89	1.79
Avg.		1.65	1.38	0.67	0.91
1	Si	0.82	5.79	0.28	27.75
2		4.56	1.82	0.28	10.57
3		3.12	0.75	0.45	25.49
4		4.83	0.63	1.68	27.41
Avg.		3.33	2.25	0.67	22.81
1	S	16.27	16.17	7.06	5.92
2		13.30	14.68	5.10	12.77
3		14.71	17.76	7.74	6.70
4		13.86	13.81	7.57	7.43
Avg.		14.54	15.61	6.87	8.21
1	K	0.07	1.31	-	-
2		0.26	0.26	-	-
3		0.28	0.06	-	-
4		0.62	0.08	-	-
Avg.		0.31	0.43	-	-
1	Ca	18.10	22.49	16.87	6.05
2		14.46	25.51	23.25	14.07
3		17.12	20.28	18.20	8.09
4		18.69	24.29	22.55	12.47
Avg.		17.09	23.14	22.22	10.17
1	Fe	0.12	1.41	-	-
2		0.28	0.47	-	-
3		0.28	0.13	-	-
4		0.68	0.26	-	-
Avg.		0.34	0.57	-	-

The analysis of the TG – DTA data presented in Table 2 shows that for all gypsum kinds there is in the temperature range of 200-225 °C a large endothermic effect associated with the removal of H_2O, and its intensity Δg is more than 2.5 times greater in the case of construction and plaster gypsum than other . In the temperature range 175-225 °C, the $CaSO_4 \cdot 0.5H_2O$

hemihydrate gypsum is converted into $CaSO_4$ anhydrite [13]. Other large effects are observed during intensive weight loss at 800 and 890 °C and 870 and 1070 °C in the case of finishing coat (FC) and plaster gypsum (PG), respectively. The weight loss is caused by the decomposition of $CaSO_4$ anhydrite, resulting in the release of sulfur trioxide SO_3 [14], which can occur even at 650 °C [15].

In the temperature range of 260-580 °C, there are slight endothermic effects not related to weight loss, which in the case of construction gypsum (CG) are observed only during its intensive loss at temperatures of 790 and 875 °C.



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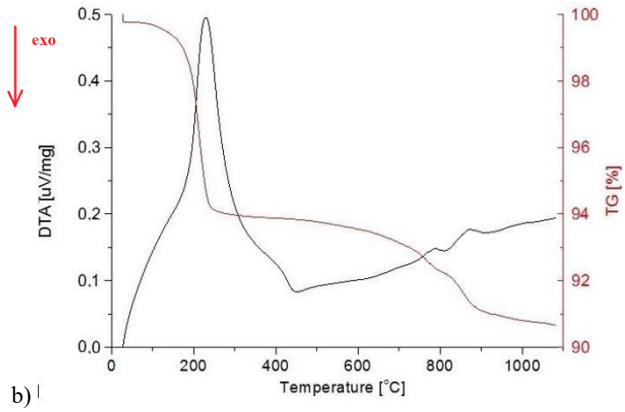
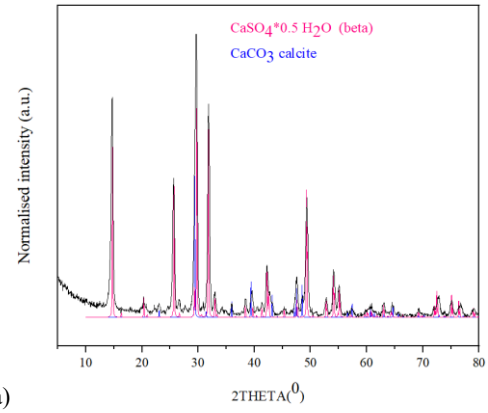


b)

Fig. 2. Analysis results of XRD (a) and TG - DTA (b) for construction gypsum (CG)



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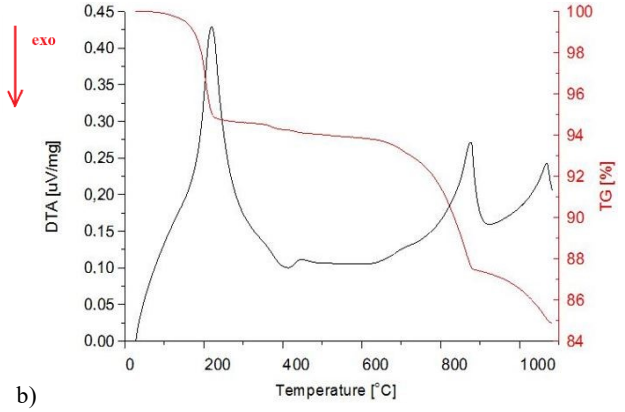

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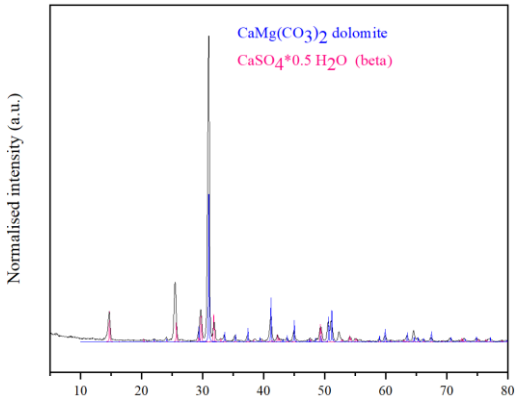
Fig. 3. Analysis results of XRD (a) and TG - DTA (b) for plaster gypsum (PG)



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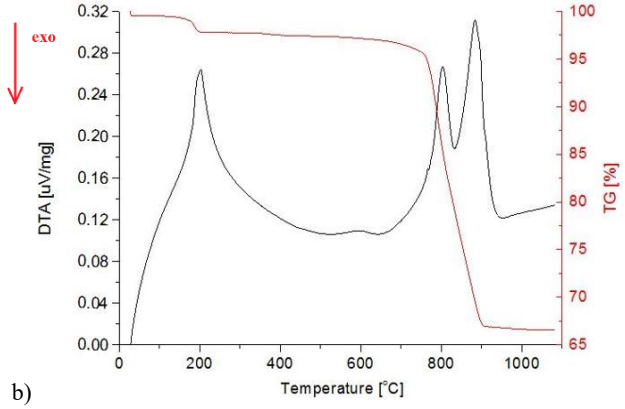
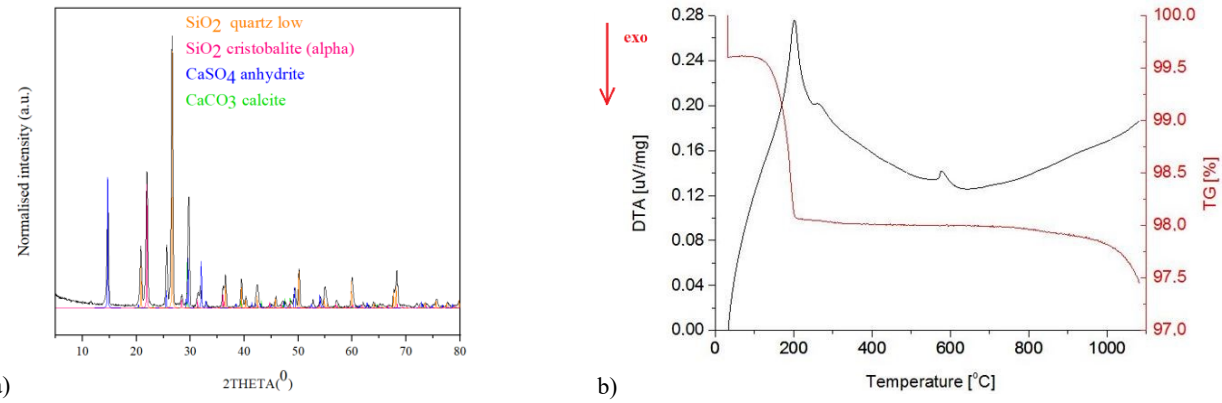


b)

Fig. 4. Analysis results of XRD (a) and TG - DTA (b) for finishing coat (FC)



a) b)

Fig. 5. Analysis results of XRD (a) and TG - DTA (b) for jewelry casting gypsum mass (JCGM)

Increased, sometimes very dynamic weight loss of the tested materials starts from 550 °C (CG) to 790 °C (JCGM). Finally, after completing the measurements, the smallest weight loss is observed in the case of JCGM (2.2%), while the remaining materials lose from approx. 9%, 15% to approx. 33% of the initial mass, respectively: CG, PG and FC.

Significant amounts of SiO_2 silica were found in the JCGM. Its addition ensures adequate permeability to the mass and also reduces temperature shrinkage during the conversion of β-quartz into α-quartz, which causes an increase in its volume [15].

Table 2.
Summary of TG – DTA analysis results

Effect	Parameter	Stuff			
		CG	PG	FC	JCGM
1	Temp. °C	**225**[1]	**220**[1]	**200**[1]	**200**[1]
	Δg %	5.8	5.2	2.0	1.6
2	Temp. °C				260[2]
	Δg %				1.6
3	Temp. °C		420[2]		
	Δg %		5.9		
4	Temp. °C	550[3]			580[2]
	Δg %	5.8			1.7
5	Temp. °C		660[3]		
	Δg %		6.3		
6	Temp. °C			760[3]	
	Δg %			4.2	
7	Temp. °C	790[2]		**800**[1]	790[3]
	Δg %	7.5		14.0	1.8
8	Temp. °C	875[2]	**870**[1]	**890**[1]	
	Δg %	8.5	12.5	30.5	
9	Temp. °C	1090	**1070**[1]	1090	1090
	Δg %	9.3	15.1	33.5	2.2

[1] large endothermic effect
[2] slight endothermic effect
[3] beginning of intensive change of sample mass

The tensile strength tests of air-dry setting gypsum mortars used in the work were carried out to supplement the information provided in the producers certificates about their mechanical compressive and bending resistance. Standard, octal samples were made from gypsum mortars prepared in accordance with the manufacturers' recommendations (Table 3).

Analyzing the R_m results presented in Table 3, a trend is observed in the change of strength in the order of preparation of dog-bone samples (No.1 – No.5), especially visible in the case of intensively binding construction gypsum (CG). It is necessary to take this fact into account when designing mould and core production technology using gypsum mortar as a binder for moulding sands.

Jewelry casting gypsum mass turned out to be the least favorable binder ($R_{m(avg.)}$ = 0.06 MPa), which confirms its low tensile strength (Table 3).

Table 3.
Tensile strength of tested gypsum kinds

Gypsum kinds:	No	R_m	R_m (avg.)	σ	Manufacturer's recommendations
		MPa			Ratio: gypsum/H_2O kg/dm^3
CG	1	0.72	0.55	0.12	**1 / 0.6**
	2	0.61			
	3	0.54			
	4	0.44			- binds after 3 min
	5	0.42			- use up to 10 min
PG	1	0.31	0.39	0.05	**1 / 0.7**
	2	0.36			- mix
	3	0.40			- wait 3-5 min
	4	0.41			- mix well
	5	0.45			- use up to 60 min
FC	1	0.38	0.42	0.05	**1 / 0.4**
	2	0.38			
	3	0.42			
	4	0.45			- binds after 60 min
	5	0.51			- use up to 60 min
JCGM	1	0.08	0.06	0.01	**1 / 0.4**
	2	0.06			
	3	0.06			
	4	0.06			- mix well
	5	0.05			- binds after 15 min

In the case of CG and JCGM in particular, each subsequent sample achieves lower tensile strength. In these two gypsum mortars, the binding process begins and runs faster than in the rest (FC and PG). Their setting and forming time is short. PG and FC mortars bind much slower, thanks to which the sandmixes with these binders are characterized by greater durability and can be used for a long time in the process of making moulds and cores.

5. Conclusions

Based on the analysis of the results of the tests, it was found that:

- Construction gypsum, which contains a lot of sulfur and calcium, is characterized by low weight loss during roasting and as the binder the highest tensile strength and short setting time, determining the service life of moulding sands prepared with it.
- Plaster gypsum contains a lot of β-hemihydrate, has a lower tensile strength than construction gypsum and longer setting time (life), which has a significant impact on the possibilities of its use as a binder for the production of sand moulds or cores.
- Finishing coat shows large roasting losses, especially at high temperature, and has a tensile strength similar to plaster gypsum and preferably a long setting time.
- Jewelry casting gypsum mass contains a very large amount of silica, is characterized by extremely low tensile strength and short setting time as well as a very small change in mass during roasting.
- In all tested types of gypsum, the initial water loss during heating occurs at a temperature of about 200 °C. The decomposition of $CaSO_4$, resulting in the release of SO_3 trioxide, takes place at the latest in plaster gypsum at 870 °C.
- The conditions to be used as a binder for moulding and core sands, tested mixtures are met by: construction gypsum, plaster gypsum and finishing coat. They are characterized by favorable strength properties and the possibility of choosing the length of binding time for a specific technology of mould and core production.

Acknowledgement

The research was financially supported by subsidies for statutory activity No. 0401/0015/18.

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