STUDIU PRIVIND GIPSUL SINTETIC OBȚINUT PRIN DESULFURAREA UMEDĂ A GAZELOR DE ARDERE DIN TERMOCENTRALE

STUDY ON SYNTHETIC GYPSUM OBTAINED FROM WET FLUE GAS DESULPHURISATION IN THERMAL POWER PLANTS

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Synthetic gypsum $CaSO_4 \cdot 2H_2O$ (also called flue gas desulpurization – FGD gypsum) is a co-product resulted from the wet process of flue gas desulphurisation in thermal power plants. The gases are desulphurised with an injection of a lime or limestone suspension. The product that is initially formed by gas desulphurization is calcium sulphite. This, by forced oxidation, turns into calcium sulfate dihydrate - $CaSO_4 \cdot 2H_2O$, initially in the form of a suspension.

The article presents the main characteristics of synthetic gypsum obtained in the industrial environment comparative with natural gypsum. It also presents the opportunity to capitalize this co-product in the building materials industry.

În procesul umed de desulfurare a gazelor din centralele termice rezultă $CaSO_4 \cdot 2H_2O$, denumit gips de desulfurare sau gips sintetic. Gazele arse sunt desulfurate prin injectarea unei suspensii de filer de calcar sau var nestins. Produsul care se formează iniţial în urma desulfurării gazelor este sulfitul de calciu. Acesta, prin oxidare forţată, se transformă în sulfat de calciu dihidrat - $CaSO_4 \cdot 2H_2O$, iniţial sub formă de suspensie, a cărui umiditate este redusă prin filtrare sau centrifugare.

În acest articol se prezinta caracteristicile principale ale gipsului sintetic obţinut la scară industrială comparativ cu cele ale gipsului natural. De asemenea, se prezintă posibilitatea de valorificare a acestui produs secundar în industria materialelor de construcţii.

Keywords: *wet FGD, synthetic gypsum, clinker, cement*

1. Introduction

Flue gas desulphurization (FGD) is a specific process for large combustion plants that are using fossil fuels. After the combustion process pollutant emissions (SO_2, NOx, dust etc.) are discharged into the atmosphere with a significant impact on human health and environment [1,2]. From the point of view of SO_2 emissions, European Union norms state that starting with 2016, sulphur emissions will decrease to 200 mg/m^3 [3].

Flue gas desulphurisation is recognised as the most appropriate method for reduction SO_2 concentration systems. There are three desulphurisation processes: wet, semi-dry and dry [4]. Depending on the used desulphurisation process, SO_2 extraction from combustion gases is done with lime or limestone filler. The material resulted after the flue gas desulphurisation is synthetic gypsum (FGD gypsum).

Initially through the desulphurisation process calcium sulphite is obtained [2,5-7], after that, through forced oxidation [5,6] it is transformed into dihydrated calcium sulphate - $CaSO_4 \cdot 2H_2O$. In the case of a wet process, in the first step the resulted gypsum is in form of suspension (sludge). Further a separation of the solid phase takes place through centrifugation or vacuum filtration so that gypsum humidity is between 6-16% [2,7].

Environmental requirements imposed by the current legislation led to researches regarding valorification of waste from thermal power plants (synthetic gypsum and ash). A field with large valorification possibilities is represented by construction materials [7,16-20]. Internationally there are researches regarding use of synthetic gypsum from flue gas desulphurisation [7,13,14,16] and even information regarding its valorification in the manufacturing flow from construction materials field.

In Romania, there are thermal power plants that have desulphurisation installations, like Rovinari, Turceni, Isalnita, etc. Synthetic gypsum from Turceni power plant is used at manufacturing plaster boards [21].

The current study presents a comparison

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between synthetic gypsum obtained from flue gas desulphurisation and natural gypsum. To have a better overview on synthetic gypsum and its properties, the opportunity of using gypsum in the field of construction materials and in manufacturing Portland cement respectively was analysed. In this way research was done regarding the possibility of synthetic gypsum valorification as an setting regulator of type CEM I cement. The influence of using synthetic gypsum on chemical and physical-mechanical of cement, was comparatively analysed with the results obtained in case of using natural gypsum.

2. Materials and methods

Within this study th e following materials have been used: industrial clinker, synthetic gypsum from Rovinari power plant and natural gypsum from Cheia quarry.

The used materials were analyzed from chemical point of view according to SR EN 196-2 [9]. Also, in case of synthetic gypsum investigation were done regarding particle size distribution using laser sizer MARVEL MASTERSIZER 2000E. The $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ content was calculeted with the formulas (1) and (2) acording to STAS 4474/6-90 [22].

$$CaSO_4 \cdot 2H_2O = \%\ LOI \cdot 3.77850 + \%\ LOI \quad (1)$$

$$CaCO_3 = (\%\ CO_2 - \%\ MgO \cdot 1.09193) \cdot 2.27420 \quad (2)$$

The mineralogical components of synthetic and natural gypsum were identified through X ray diffraction by exposing the samples to a scanning interval 2θ between 5-70^0, using diffractometer DRON 3.

The synthetic gypsum sample, in the form of sludge, after water removal was dried in the drying chamber at a temperature of 40^0 C. The drying was done at this temperature to avoid the transformation of gypsum into anhydrite.

Type CEM I cements, according to [11], were done through simultaneous grinding of the components in a tubular laboratory mill with double beveled connes. Grinding was done in two steps. In the first step, preliminary grinding of raw materials took place up to a fineness expressed as Blaine specific surface area of about 3,700 cm^2/g. Taking into consideration that synthetic gypsum was characterized by an advanced fineness, this was added to grinding in the finishing step, to ensure an appropriate cement homogenization and a reduced energy consumption. Both cements (C1 and C2) were prepared by using 5% natural gypsum respectively synthetic gypsum as a setting regulator.

Cements C1 and C2, were analyzed from the point of view of chemical and physical-mechanical properties according to the specific method standards [8-10].

3. Results and discussions

3.1. Material characterization

- **Characterization of setting regulators**

The synthetic gypsum sludge, after drying, becomes a very fine grey powdery material (figure 1). Its particle size distribution is presented in Table 1.

Table 1

Sieve analysis of synthetic gypsum/
Analiza granulometrică gips sintetic

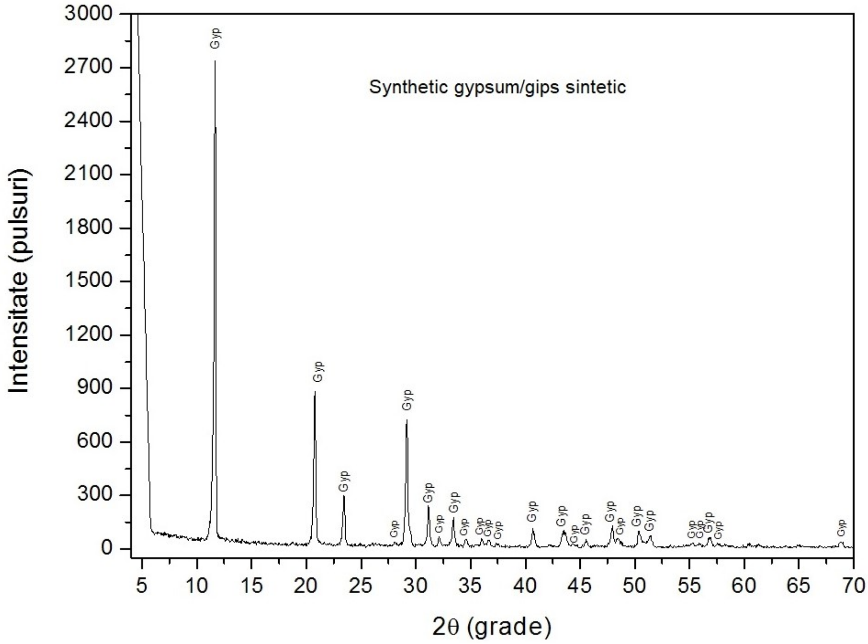
	Sieve size / *Clase granulometrice*	Cumulative passing / *Trecerea cumulată*, [%]
1	<1 µm	1.2
2	<1,5 µm	2.0
3	<2 µm	2.4
4	<3 µm	3.4
5	<4 µm	4.2
6	<6 µm	5.4
7	<8 µm	7.0
8	<12 µm	8.8
9	<16 µm	9.2
10	<24 µm	11.2
11	<32 µm	15.8
12	<48 µm	40.8
13	<64 µm	65.8
14	<96 µm	95.0
15	<128 µm	99.6
16	<192 µm	100.0
	Statistic parameter / *Parametru statistic*	
17	D50 [µm]	53.4

It can be observed (table 1) that the material has a particle size range relatively limited, more than 54% of the particles being between 48-96µm.

Fig. 1 - Synthetic gypsum sample / *Proba de gips sintetic.*

X ray diffraction analysis of the synthetic gypsum and natural gypsum samples (Figure 2), highlighted the presence of $CaSO_4 \cdot 2H_2O$.

Chemical properties of used gypsums are presented in Table 2.



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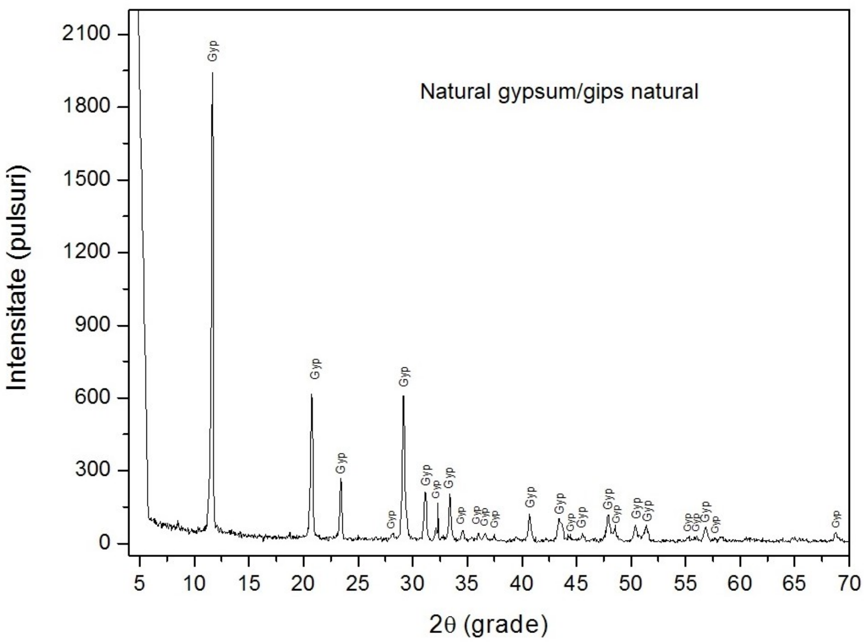

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Fig. 2 - X-ray diffraction patterns of gypsums / *Spectrul difractometric al gipsurilor.* a) synthetic; b) natural (Gyp, gypsum $CaSO_4.2H_2O$ assigned according to Powder Diffraction File PDF33-0311)

Table 2

Chemical analysis of natural and synthetic gypsum / *Analiza chimica a probelor de gips natural si gips sintetic*

Characteristic / Caracteristica	Gypsum sample / Proba de gips	
	Natural (wt %)	Synthetic (wt %)
LOI / *A.C.*	17.41	19.11
SiO_2	3.05	2.75
Al_2O_3	0.97	2.05
Fe_2O_3	0.32	0.55
CaO	32.36	30.97
MgO	< LD*	0.19
SO_3	41.89	42.77
Na_2O	0.58	0.20
K_2O	0.11	0.16
CO_2	2.39	0.87
$CaSO_4·2H_2O$	83.22	91.35
$CaSO_4$ anhydrite	5.41	0.47
$CaCO_3$	5.13	1.50
$MgCO_3$	-	0.40

*LD=0.12% (LD- Detection Limit)

The results of chemical analysis shows a high content of $CaSO_4 \cdot 2H_2O$, for both materials. This large content of gypsum is also confirmed through diffractometric analysis. The $CaSO_4$ and $CaCO_3$ content from natural gypsum couldn't be detected on the XRD analysis, beeing under the detection limit (6%). Analyzing comparatively the results, from the point of view of $CaSO_4 \cdot 2H_2O$ content, a higher proportion of it can be observed in case of synthetic gypsum. This fact is correlated with data highlighted through X ray diffraction pattern, additionally synthetic gypsum contains a lower anhydrite proportion (0.5 compared to 5.4) and calcium carbonate (1.5 compared to 4.3). Presence of carbonate in synthetic gypsum comes from not reacted limestone in the wet flue gases desulphurization process.

Also, a lower content of alkali can be observed for synthetic gypsum. Alkali content, expressed as Na_2O equivalent [12], is 0.31 in case of synthetic gypsum compared to 0.65 in case of natural gypsum. This represents an advantage, because cements with lower alkali content can be obtained that have benefits on the concrete durability with regards to alkali-aggregate reactions that can develop in time.

- **Clinker**

Oxide composition of clinker is presented in Table 3. In Table 4, the potential mineralogical composition (calculated with Bogue formulas) is also presented as well as the modular properties.

Table 3

Clinker chemical analysis / *Analiza chimică a clincherului*

Characteristic *Caracteristica*	Determined Value / *Valoare determinată*, (wt %)
SiO_2	21.12
Al_2O_3	5.18
Fe_2O_3	3.58
CaO	66.60
MgO	1.44
SO_3	1.04
K_2O	0.65
Na_2O	0.48
Free CaO, *CaO liber*	1.24
Insoluble residue / *Reziduu insolubil*	2.38

From the chemical, modular and mineralogical properties point of view, the clinker belong to the ordinary Portland cement clinker sorts, registering in the requirements from [11] namely:

Table 4

Mineralogical composition and modular characteristics of the clinker / *Compozţtia mineralogică și caracteristicile modulare ale clincherului*

Mineralogical composition / *Compoziție mineralogică* (%)		Modular characteristics *Compozţtie modulară*	
C_3S	70.66	M_{Si}	2.41
C_2S	8.54	M_{Al}	1.45
C_3A	7.68	LSF	98.56
C_4AF	10.88		

The clinker used is a normal Portland clinker,

- ✓ $C_3S + C_2S$: 79.2%, compared to 2/3 from the required mass;
- ✓ CaO/SiO_2: 3.15 compared to min. 2 required;
- ✓ MgO – 1.44% compared to max. 5% required.

3.2. Influence of setting regulator type on the properties of CEM I type of cements

The influence of setting regulator type on the chemical and physical-mechanical properties of cement, was studied for cement type CEM I. The cements were prepared by using 5% natural gypsum respectively synthetic gypsum and 95% industrial clinker. Cement C1, in which the setting regulator is natural gypsum, used currently in cement industry is considered as a reference cement.

3.2.1. Chemical properties

Chemical properties of the two cements (C1 and C2) are presented comparatively with conditions from SR EN 197-1 [11], in Table 6.

Analysing comparatively the results presented in Table 5, it can be observed that using synthetic gypsum as setting regulator does not influence significantly the chemical properties of the cement, values being comparable with the ones obtained in case of benchmark cement (C1). For both cements, chemical properties are classified in the conditions imposed by the standard SR EN 197-1 [11].

3.2.2. Physical and mechanical properties

Flexural and compressive strenght of studied cements are presented, comparatively with the conditions imposed by SR EN 197-1 [11], in Table 6 and Figures 3-4 respectively.

Table 5

C1 and C2 Chemical characteristics / *Caracteristicile chimice ale C1 și C2*

Determination / *Determinarea*	Cement / *Ciment*		Conditions impose by *Condiții impuse de* SR EN 197-1[11]
	C1	C2	CEM I 42.5R
LOI / *P.C.*, %	1.47	1.39	≤ 5.0
SO_3, %	2.91	2.94	≤ 4.0
Cl^-, %	0.009	0.011	≤ 0.10
Insoluble residue / *Reziduu insolubil*, %	0.27	0.27	≤ 5.0

Table 6

Physical-mechanical characteristics of cements / *Caracteristicile fizico-mecanice ale cimenturilor*

Physical caracteristics / *Caracteristici fizice*		Cement symbol / *Simbol ciment* C1	C2	Conditions imposed by/ *Condiții impuse de* SR EN 197-1
Finesses , expressed by Blaine surface specific area / *Finețe, exprimată ca suprafața specifică Blaine*, cm^2/g		3690	3710	-
Water for standard consistency / *Apă de consistență standard*, %		24.4	23.8	-
Setting time / *Timp de priză*	Initial / Inceput, min	190	250	≥ 60
	Final / Sfarsit, min	240	315	-
Soundness / *Stabilitatea*, mm		0.0	0.0	≤ 10

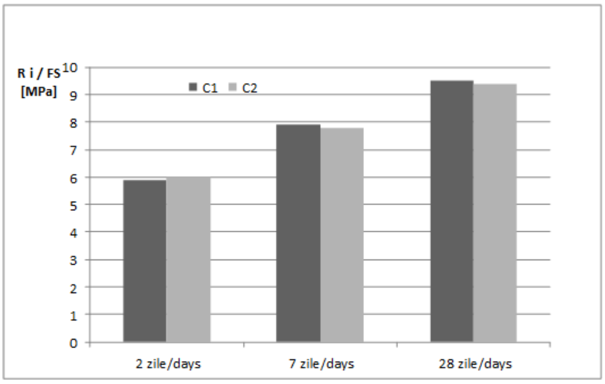

Fig. 3 -Flexural strength / *Rezistența mecanică la încovoiere*, MPa.

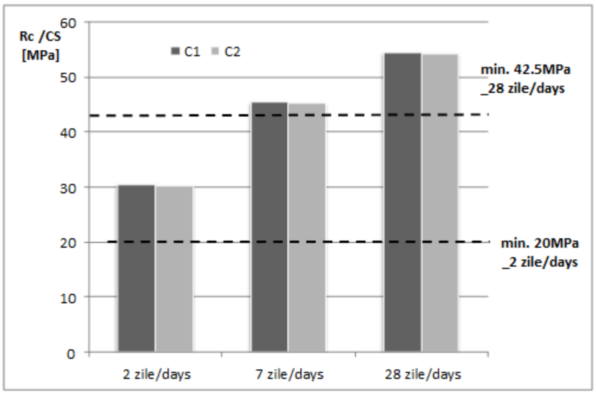

Fig. 4 - Compressive strength / *Rezistețta mecanică la compresiune*, MPa.

It can be observed that using synthetic gypsum generates a significant increase of initial as well as final setting time (approx. 60 min), compared to the situation in which natural gypsum was used; nevertheless SR EN 197-1 standard requirements are respected [11]. Results are in accordance with the ones reported in literature [13-16]. This behavior can be associated with a higher content of $CaSO_4 \cdot 2H2O$ in case of synthetic gypsum compared to the natural one, respectively 91.35% compared to 83.22%.

Analyzing the synthetic gypsum influence on the flexural and compressive strength it can be observed that the strength generated at the initial (2 and 7 days) and final (28 days) hardening terms are comparable with the ones of the reference cement. Both cements, according to SR EN 197-1, are classified in class CEM I 42.5R taking into consideration that compressive strength at 2 days is higher than 20 MPa and at 28 days exceeds 42.5 MPa.

4. Conclusions

Based on this study, the following conclusions can be drawn:

- from the point of view of chemistry of synthetic gypsum, this is appropriate for its use as setting regulator;

- from size distribution point of view, synthetic gypsum has a finesse that recommends it for grinding next to clinker without a preliminary crushing;

- synthetic gypsum influences the setting time, in the way of increasing it compared to the situation in which natural gypsum is used as setting regulator, but is within the limits required by SR EN 197-1;

- the value of compressive strength after 2 and 28 days allows including of cement with synthetic gypsum addition in the same class 42.5R as the reference cement, in which natural gypsum was used;

- using synthetic gypsum in cement industry would allow valorification of a waste generated by the thermo energetic industry with additional beneficial effect on the environment through conservation of gypsum natural deposits.

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MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS

Al XIII-lea SIMPOZION NAŢIONAL

INSTITUTUL DE CHIMIE FIZICĂ AL ACADEMIEI ROMÂNE

UNIVERSITATEA POLITEHNICA BUCUREŞTI

PULBERI CERAMICE
Bucureşti, 17.11.2017
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Acest simpozion, ajuns la a XIII-a ediţie, constituie un mod direct și eficient de informare a specialiştilor asupra principalelor noutăţi în acest domeniu.

Au fost invitaţi să participe toţi specialiştii care au preocupări în domeniul obţinerii sau utilizării pulberilor pentru producţia de materiale ceramice.

În acest an, s-au susținut 14 lucrări ale unor cadre didactice din cadrul Universității POLITEHNICA București, lucrări prezentate de câțiva studenți și masteranzi ai Facultății de Chimie Aplicată și Știința Materialelor, precum și de la Facultatea de Știința și Ingineria Materialelor lucrări ale multor cercetători din diverse instituții de profil: Institutul de Chimie Fizică ”Ilie Murgulescu” al Academiei Române (ICF), Institul de Cercetări Metalurgice (ICEM), Institutul Național de Cecetare Dezvoltare pentru Inginerie Electrică (INCDIE ICPE-CA), SC Ceprocim SA.

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