Influence of Various Types of Waste on the Main Properties of Gypsum Based Composites for Thermal Insulations

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In the last decade numerous research studies were performed in the attempt to recycle several types of industrial waste. This study has as main objective the obtaining and characterization of gypsum based composite materials with various amounts of industrial wastes (flue gas desulfurization gypsum and recycled rubber). The main properties assessed for these materials were setting time, compressive strength, apparent density and thermal conductivity. The gypsum binder was partially replaced with thermally treated flue gas desulfurization gypsum (FGDgp_t) without an important negative impact on the compressive strength; if the replacement amount is up to 40 wt.% the resulted binder still meets the requirements imposed for this property by specific norm for gypsum plaster - EN 13279-1. The substitution of gypsum plaster with FGDgp_t shortens the setting time, therefore it was compulsory to use also sodium citrate as retarder addition. The addition of 5 wt.% rubber waste has a positive effect on the thermal conductivity of composite materials based on gypsum binder with/without FGDgp_t. Consequently, these materials could be used for the manufacture of low cost, eco-friendly thermal insulation materials.

Keywords: flue gas desulfurization gypsum, recycled rubber, industrial waste, thermal conductivity

Raising living standards and technological development accelerate the consumption and rapid degradation of renewable natural resources, while increasing volumes of waste. The accumulation of large amounts of industrial waste causes numerous environmental problems and high costs for their neutralization. In these circumstances, manufacturers must identify and implement new measures to move towards a circular economy industry.

Thus, rubber wastes resulted from the automotive industry (tires or other rubber auxiliary components) cannot be recycled entirely through vulcanization processes. These types of wastes are not easily biodegradable and become a problem for the environment.

Several studies focused on the use of rubber waste as filler in concrete and mortar [1-3]. The obtained materials present improved flexibility, thermal and acoustic properties.

Correia *et al.* [1] studied the effect of rubber additions on the compressive strength of mortar mixtures. The natural aggregate was replaced by a maximum of 30% rubber waste, and the compressive strength after 28 days was 12-15 MPa representing 50-83% from the compressive strength of mortar prepared with natural aggregate [1].

Topcu and Demir [2] assessed the durability of concrete and mortar with addition of rubber waste and concluded that this type of waste should be used mainly in concrete destinated to be used in less harsh environmental conditions.

The incorporation of recycled rubber particles in a gypsum matrix was less studied. Herero *et al.* [3] studied the influence of rubber waste dosage and particle size on the mechanical, thermal and acoustic properties of mortars based on plaster with rubber additions. The best thermal and acoustical properties were obtained for the composites with the small size rubber particles (<0.6 mm).

Another environmental problem is raised by industrial wastes generated in electrical power plants such as fly ash or flue gas desulfurization gypsum. Up to now, numerous studies reported various valorization methods of fly ash in the building materials industry i.e. manufacture of portland cement (as alternative raw material or admixture), manufacture of concrete or geopolymers [4-9].

Flue gas desulfurization gypsum (FGD gypsum), waste generated in the desulfurization process of gases generated in power plants, raises also many environmental issues [10]. Several studies reported that FGD can be used in cement industry to replace natural gypsum as setting retarder [11] or for the total or partial replace of natural gypsum in the manufacture process of gypsum plaster [12].

In this context, this paper presents a new method to valorize FGD i.e. the use of FGD gypsum and recycled rubber for the manufacture of thermal insulation materials.

Experimental part

Materials

The materials used in this study were:

- gypsum plaster (G) for building purposes in conformity with EN 13279-1, with the main properties presented in table 1 [13];

- flue gas desulfurization gypsum (FGD) resulted from the desulfurization process of the combustion gases in a Romanian power plant; the main characteristics of FGD, according to the producer, are presented in table 2. In order to improve the binding properties of FGD gypsum, this waste was thermally treated at 120°C (FGDgp_t).

- waste rubber particles (R) from recycling of scrap tires, with a grain sizes comprised between 4-6 mm.

Table 1
MAIN CHARACTERISTICS OF GYPSUM PLASTER

Characteristics	SR EN 13279
Reaction to fire	Class A1
Fineness	99% under 315 µm
Content of calcium sulfate	>50 wt%
Initial setting time	10-15 min

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Table 2
CHEMICAL COMPOSITION OF FGD GYPSUM

Component	*wt%*	*Component*	*wt%*
Chloride	5.95	Potassium	0.83
Fluoride	0.34	Aluminum	0.009
Sulphate	65.70	Iron	0.002
Calcium	16.51	Manganese	0.003
Magnesium	7.64	Zinc	0.006
Sodium	2.76	Total organic carbon	0.25

Mixtures design

DesignExpert® software [14] was used to establish compositions based on the above mentioned three components (G, FGDgp_t and R), with: i) adequate mechanical strengths after 7 days of hardening, and ii) small values of apparent density required to provide good thermal insulation properties.

This software designed (generated) 16 mixtures. Three points were replicated: two of them in the corners and one on the side of the triangle; these replications are designed to identify and quantify experimental errors. Moreover, in the design of mixtures, the maximum rubber content was limited to 50% wt.

For the experimental program two main properties of these composites were selected:

- compressive strength of mixtures prepared with water to binder ratio of 0.5, assessed after 7 days of hardening;
- apparent (geometrical) density, assessed on mixtures hardened for 7 days.

The raw materials (G, FGDgp_t and R) were homogenized in dry state and subsequently mixed with water in a Hobart mixer. These compositions were cast in two types of moulds i.e. cubes (20x20x20 mm) and panels (300x300x10mm). The hardening was performed in air at 20+2°C.

Methods

The mineralogical compositions of FGD and FGDgp_t were assessed by X-ray diffractions (XRD). The XRD patterns were obtained using a monochromatic CuKα radiation (λ = 1.5406Å), range 2Θ from 10 to 60°.

Setting time and compressive strength of gypsum binder with/without FGDgp_t addition were determined in conformity with the methods presented in European Standard for gypsum binders and gypsum plasters [15].

Thermal conductivity (λ) was determined with an HESTO-Lambda-CONTROL A90-equipment; this equipment measures the heat flow through a specimen placed between two plates with different temperatures; the measurement accuracy is ± 3% in accordance with EN 12667 [16].

Results and discussions

Materials characterization

The mineralogical compounds identified by X-ray diffraction analysis (XRD) in FGD gypsum (fig. 1) are: calcium sulphate dihydrate ($CaSO_4 . 2H_2O$) and calcium sulphite hemihydrate ($CaSO_3 . 0.5H_2O$) [17, 18].

After thermal treatment at 120°C of FGD gypsum, XRD patterns shows the presence of calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$) resulted by the partial dehydration of calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) (fig.1).

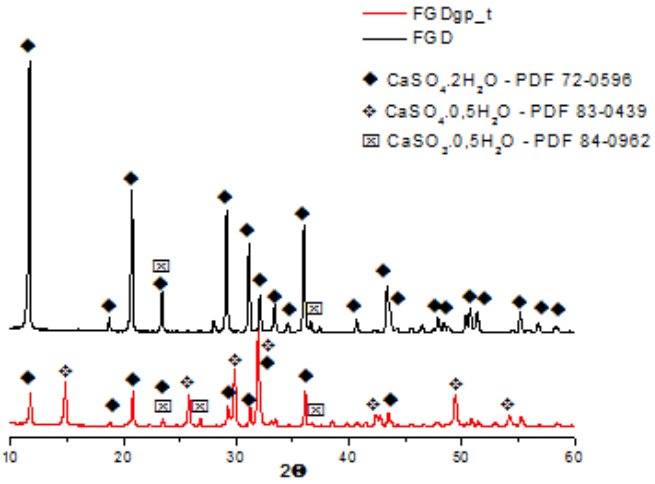

Fig.1. XRD patterns of FGD gypsum (FGD) and FGD gypsum after thermal treatment (FGDgp_t)

The values of compressive strength assessed after 7 days of hardening, on the designed 16 mixtures, were introduced in the software. For this property was chosen the Quadratic model (for which the standard deviation has the smallest value) and 97 solutions have resulted; these solutions were graphically processed as iso-property curves (contour plots) (fig.2a). In this model the correlation between experimental and calculated values is satisfactory (fig. 2b).

As it can be seen from figure 2, the compressive strengths assessed on these composites are comprised between 1.2 and 10 MPa, the lower values being recorded for the compositions in which gypsums is replaced by FGDgp_t (up to 25 wt.%) and the rubber dosage increase (up 25 wt.%); it has to be noted that the increase of rubber content over 25 wt% led to no recordable compressive strength values for all mixtures.

For the apparent density, the model chosen was linear and contour plots are presented in figure 3a. The values of apparent density are comprised between 0.96 g/cm^3 (for the compositions with higher dosage of rubber - 50%) and 1.5 g/cm^3 for the compositions with a higher amount of FGDgp_t.

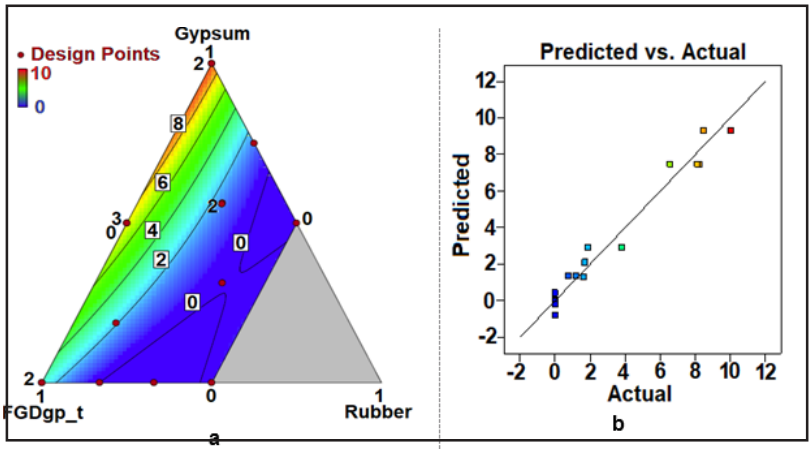

Fig. 2. Compressive strength: a) contour plots for compressive strength assessed on composite materials hardened for 7 days;
b) correlation between experimental and calculated compressive strength values

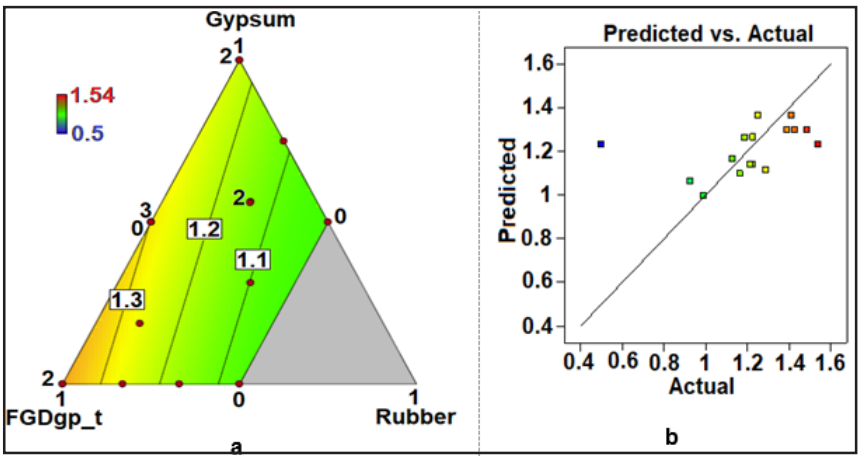

Fig.3. Apparent (geometric) density: a) contour plots for apparent density assessed on composite materials hardened for 7 days; b) correlation between experimental and calculated density values

However, the correlation factor between calculated and experimental values (fig.3b) is much smaller and is primarily due to the experimental errors, explainable when the geometrical density is assessed (a less accurate method as compared for example with helium pycnometer method).

Based on the data provided by these two models, it was selected a ternary composition (X) which comply with the requirement for compressive strength of gypsum binders. (i.e. higher than 2 MPa) [19] and has also a low value of apparent (geometric) density - below 1.3 g/cm^3. The selected composition (X) contains 47 wt.% gypsum plaster (G), 48 wt.% FGDgp_t and 5 wt.% rubber waste (R).

The compressive strength values assessed after 2 and 7 days of hardening and the apparent density of material with composition X are presented in table 3.

Another important property, for this type of composite materials based on gypsum binder, is the setting time (European Standard EN 13279-1 [19]). Thus, the setting time was determined for the composition without rubber waste corresponding to the composition X - hereafter referred to as X_1 (table 4).

The final setting time (6 min) assessed for this composition is too short as compared with the final setting time imposed by standard i.e. minimum 20 min [19]. Therefore, it is necessary to use also a retarder addition. Based on the results reported by Muller et al. [20] and Camarini *et al.* [21], sodium citrate was chosen to be used as retarder. The setting times, assessed on pastes with various amounts of sodium citrate (calculated with reference to G+FGDgp_t mixture), are presented also in table 4.

As it can be seen from the data presented in table 4, the increase of sodium citrate dosage determines, as expected, a delay of initial and final setting times. The composition with 0.08 % sodium citrate, which has a final setting time of 20 min, complies with the conditions stipulated in EN 13279-1 norm and is considered adequate. Although the composition with 0.2 wt% sodium citrate meets also the requirements of this norm, it was not selected due to the important delay of initial setting time which most probably has a negative influence on the mechanical strength values after short periods of time (2 h).

For the composition with 0.08 wt% sodium citrate it has been verified how this retarding additive influences the compressive strength values at different curing times and in parallel was studied the impact of rubber waste addition on the compressive strength. The results are presented in table 5.

As it can be seen from table 5, the addition of rubber waste (compositions X and X +0.08 wt.% sodium citrate) decreases the mechanical strength of this type of composite materials. The rubber particles have a porous

Properties/UM	Experimental	Predicted
Compressive strength after 2 hours/ (MPa)	2.27	-
Compressive strength after 7 days/ (MPa)	4	4.73±0.38
Density after 7 days/ (g/cm^3)	1.4	1.27±0.074

Table 3
EXPERIMENTAL AND PREDICTED PROPERTIES OF MATERIAL WITH COMPOSITION X

Binders	Setting time/ min	
	initial	final
X_1	4	6
X_1+0.04 wt.% sodium citrate	8	11
X_1+0.08 wt.% sodium citrate	14	20
X_1+0.2 wt.% sodium citrate	45	52

Table 4
SETTING TIME FOR THE COMPOSITION X_1 (WITHOUT WASTE RUBBER)

Compositions	Compressive strength (MPa) after:	
	2 h	7 days
X_1+0.08wt.% sodium citrate	2.65	4.62
X	2.27	4.00
X +0.08wt.% sodium citrate	1.75	3.5

Table 5
COMPRESSIVE STRENGTHS OF THE COMPOSITIONS BASED ON GYPSUM PLASTER AND FGDgp_t

Composition	Thermal conductivity 10°C (W/m.K)
G+5wt.% R	0.157
X+0.08% sodium citrate	0.206

Table 6
THERMAL CONDUCTIVITY OF THE COMPOSITE MATERIALS BASED ON GYPSUM PLASTER ASSESSED AFTER 7 DAYS OF HARDENING

surface therefore water can be partially adsorbed causing a decrease of workability of fresh paste; this decrease of workability will determine the decrease of compressive strengths. These results are in good agreement with those obtained in previous research works on gypsum plaster with waste rubber content [3].

The values of thermal conductivity assessed on the designed compositions based on gypsum binder are presented in table 6.

The thermal conductivity of the composites based on gypsum plaster (G) with 5wt.% rubber (R) content has a thermal conductivity of 0.157 W/m.K, lower as compared with the thermal conductivity reported in literature for gypsum plaster panels i.e. 0.276-0.4 W/m.K [21,22]. The thermal conductivity measured for the composition X with 0.08wt % sodium citrate is slightly higher as compared with the composition based on gypsum plaster but is smaller as compared with the thermal conductivity of FGD gypsum (0.47 + 10% W/m.K) reported by Tesarek *et al.* [22]. The decrease of thermal conductivity in the composition with rubber content was to be expected due to the increase of void space between rubber particles and binder matrix [1].

Conclusions

The results presented in this paper highlight the possibility to valorize two types of industrial wastes (i.e. FGD gypsum generated in electrical power plant and the rubber waste from scrap tires) in the production of building materials with good thermal properties.

Considering these experimental results, the following conclusions can be drawn:

- The gypsum plaster can be partially replaced with thermally treated flue gas desulfurization gypsum (FGDgp_t) without an important negative impact on the compressive strength; if the replacement amount is up to 40 wt.% the resulted binder still meets the requirements imposed for this property by specific norm for gypsum plaster- EN 13279-1.

- The setting time of gypsum binder with FGDgp_t content is too short (below 20 min - the minimum value stipulated in European Standard EN 13279-1) therefore it was necessary to use also a retarder i.e. sodium citrate (0.08 wt.% with reference to binder).

- The addition of small amount of rubber waste (5 wt.%) has a positive effect on the thermal properties of composite materials based on gypsum plaster with/without FGDgp_t.

References

1. CORREIA S.L., PARTALA T., LOCH F.C, SEGADAES A.M., Compos. Struct. **92,** Nr. 9, 2010, p. 2047.
2. TOPCU IB, DEMIR A., J Mater Civil Eng. **19**, Nr. 2, 2007, p. 173.
3. HERRERO S., MAYOR P., HERNANDEZ-OLIVARES F., Mater. Des. **47,** 2013, p. 633.
4. RASHAD A.M., Int. J. Sust. Built. Environ. **4**, Nr. 2, 2015, p. 278.
5. HEMALATHA T., RAMASWAMY A., J. Clean. Prod., **147**, 2017, p. 546.
6. TORRES-CARRASCO M., PUERTAS F., Rev. Rom. Mat. **47**, Nr. 1, 2017, p. 3
7. WACHTER, M.R., IONEL, I., NEGREA, A., CEBRUCEAN, D., MANZATU, V., CIOPEC, M.,Rev. Chim. (Bucharest), **66**, no. 11, 2015, p. 1881
8. CHENDES, R., BOB, C., BADEA, C., PODOLEANU, C.E., DAN, S., IURES, L.,Rev. Chim. (Bucharest), **67**, no. 9, 2016, p. 1868
9. IBRAHIM W.M.W, HUSSIN K., AL BAKRI ABDULLAH M.M., KADIR A.A. DERAMAN L.M., SANDU A.V., Rev. Chim. (Bucharest), **68**, no. 9, 2017, p. 1978
10. CÓRDOBA P., Fuel **144**, 2015, p. 274.
11. CAILLAHUA M.C., MOURA F.J., J. Mater. Res. Technol. 2017, http://dx.doi.org/10.1016/j.jmrt.2017.08.005, ARTICLE IN PRESS
12. LEI D.Y., GUO L.P., SUN W., LIU J., MIAO C., Constr. Build. Mater. **153**, 2017, p. 765
13.*** Technical Data Sheet - Rigips® Model Gips, Rigips Saint - Gobain [Internet] 2017. Available from http://www.rigips.ro/sites/default/files/Fisa_Tehnica_ RIGIPS_Model_Gips_ipsos_alb_modelaj_ stucaturi_2016_04_20.pdf (in romanian).
14.*** DesignExpert® Software [Internet] 2017. Available from http://www.statease.com /dx10.html.
15. *** European Standard EN 13279-2. Gypsum binders and gypsum plasters. Part 2: Test methods
16. *** European Standard EN 12667. Thermal performance of building materials and products - Determination of thermal resistance by means of guarded hot plate and heat flow meter methods – Products of high and medium thermal resistancee
17. GALOS K.A., SMAKOWSKI T.S, SZLUGAJ. J., Appl. Energ., **75**, 2003, p. 257.
18. ROWE G., 2012. Available from http://www.chemicalprocessing.com/assets/ wp_downloads/pdf/AZI-white-paper-LOD-vs-thermogravimetric-analysis.pdf
19.*** European Standard EN 13279-1. Gypsum binders and gypsum plasters. Part 1: Definitions and requirements
20. MUELLER M., FISCHER H.B., BORGARDT N., SOLOVEV S., SHLONKINA S., GARKAWI M.S., 2007. Available from http://leidykla.vgtu.lt/conferences/ MBM_2007/1pdf /Mueller_naujas.pdf
21. CAMARINI G., CAVALINI PINTO M.C, GOULART De MOURA A., REGGIANI MANZO N., Constr. Build. Mater. **124**, 2016, p. 383.
22. TESAREK P., DRCHALOVA J., KOLISKO J., ROVNANIKOVA P., CERNY R., Constr. Build. Mater. **21,** 2007, p. 1500.

Manuscript received: 17.01.2018