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Faculty of Applied Chemistry and Materials Science
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Doctoral Thesis

Abstract

Valorisation of end-of -life materials in the production of value-added construction materials

VALORIFICAREA UNOR DEŞEURI ÎN PRODUCEREA DE MATERIALE DE CONSTRUCȚII CU VALOARE ADĂUGATĂ

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Bucharest, 2022

CONTENT OF THE DOCTORAL THESIS

Keywords: waste, thermal insulation, sound insulation, recovery, circular economy

1. INTRODUCTION

Today, we are confronted with difficult choices related to the social and economic development, on the one hand, and the preserving of life quality, on the other hand. A high consumption of goods and services leads to the increase of the quantity of industrial and household waste and consequently to a rapid decrease in non-renewable natural resources.

The increase of industrialization and society requirements have led to the accumulation of many industrial and municipal waste, which generates numerous environmental problems as well as high costs for their neutralization. In this context, it is necessary to identify and implement measures which should steer the industrial sector towards a *circular economy*.

The European Union Commission has described the circular economy as an economy where the value of products and resources is preserved for as long as possible, while minimising the amount of wastes. This strategy is initiated right from the design stage of a product and focus on the use of efficient technologies and production processes as well as the preventing of improper management of any resulting wastes [1].

Since the protection of natural environment is a fundamental requirement, for the continuity of economic and social life, a comprehensive legislation has been developed at international and national level, that promotes the recycling / recovery of different types of waste and regulates the ways in which waste is stored, transported, and used. The numerous studies performed and the developed strategies aiming to recycle of different types of wastes have generated results; for several types of waste are now available standards and regulations which defines their essential characteristics, depending on their foreseen use.

In this context, the main objective of this doctoral thesis was to obtain and characterize construction materials for thermal and/or sound insulation, containing different types of municipal and/or industrial waste, as follows:

- portland cement-based materials with the addition of polyurethane waste and chopped electrical cables [2];
- materials based on calcium sulphate with waste addition: rubber or polyurethane waste, flue gas desulfurization gypsum (FGD gypsum), chopped electrical cables or ash resulted in the combustion of hydrocarbon-containing residues from petroleum industry [3-6];
- waste-based materials obtained by the alkaline activation of waste glass powder with slag, rubber and polyurethane addition [7,8].

2. *OBTAINING AND CHARACTERIZATION OF THERMAL INSULATION MATERIALS BASED ON PORTLAND CEMENT*

At national and international level, are currently available research results on the performance of materials based on portland cement and additions of waste such as rubber, cork, polystyrene, polyurethane, etc. Starting from the present state-of-the art, the study presented in this chapter aimed to obtain composite materials for thermal insulation, based on portland cement with polyurethane waste (P) and/or chopped electrical cables (E) additions.

To assess the influence of these waste on the main properties of cement-based composites, several compositions with 5 % polyurethane waste (R2P5) and/or 25-30% chopped electrical cables (R2P5E25 and R2E30) have been prepared and tested.

The partial replacement of portland cement with polyurethane waste and/or chopped electrical cables determined a significant decrease of the apparent density, correlated with the porosity increase, as compared to the reference sample – R2 (Figure 1).

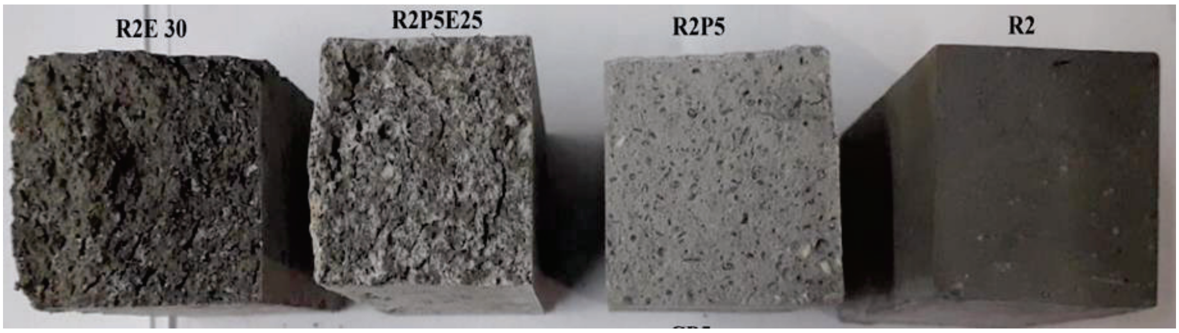


Figure 1. Cross-section (fracture) of cement specimens with/without wastes content

The increase of the porosity, in the case of cement composites with P and E waste, is due to several factors:

- substitution of portland cement with a waste with low density and high intrinsic porosity (polyurethane - P), as well as due to the increase of water/binder ratio used for the preparation of this composite;
- gas (hydrogen) generation in cement-based composites with chopped electrical cables (E), due to the interaction of aluminium (from waste E) with $Ca(OH)_2$ generated during the portland cement hydration. This gas is entrapped in the cement matrix and forms closed pores or/and cracks at the surface of the specimen.

The interconnected large-size pores, specific for the materials with P and E additions, produces an increase of capillary water absorption and a significant decrease of mechanical strengths.

The mechanical strengths of cement-based composites with waste content are smaller as compared to those assessed for the reference (R2), as follows:

- flexural strengths decreased by 60% for the materials with polyurethane waste (R2P5) and by 84% for the material with chopped electrical cables waste (R2E30);
- compressive strength decreased by 81% for the material with polyurethane waste (R2P5) and by 95.4% for the material with E waste (R2E30).

As expected, the coefficient of capillary absorption of water increases: for the composites with polyurethane waste (CP5), it increases by 48% as compared to reference (C). The coefficient of capillary water absorption for the compositions with chopped electric cables waste (CE30) and CP5E25) also increases, by 57% and 47%, respectively.

The thermal performance (thermal insulation capacity) of cement-based composites increases when cement is partially substituted with E and/or P wastes; the values of thermal conductivity (0.12÷0.18 $Wm^{-1}K^{-1}$) are close to or better when compared to the thermal conductivity of a concrete with perlite (0.20÷0.26 $Wm^{-1}K^{-1}$), which has an apparent density of 0.80 g/cm^3 [9].

3. *VALORIATION OF INDUSTRIAL WASTES IN THE PRODUCTION OF BINDERS AND COMPOSITE MATERIALS BASED ON CALCIUM SULPHATE*

3.1. Valorisation of different type of industrial waste to obtain thermal/sound insulation materials based on gypsum binder

The main objective of this study was to evaluate the influence of different types of waste (rubber, chopped electrical cables, and polyurethane) on the thermal and acoustic properties of composite materials based on gypsum binder.

The visual aspect of these materials (in fracture) is presented in figure 2.

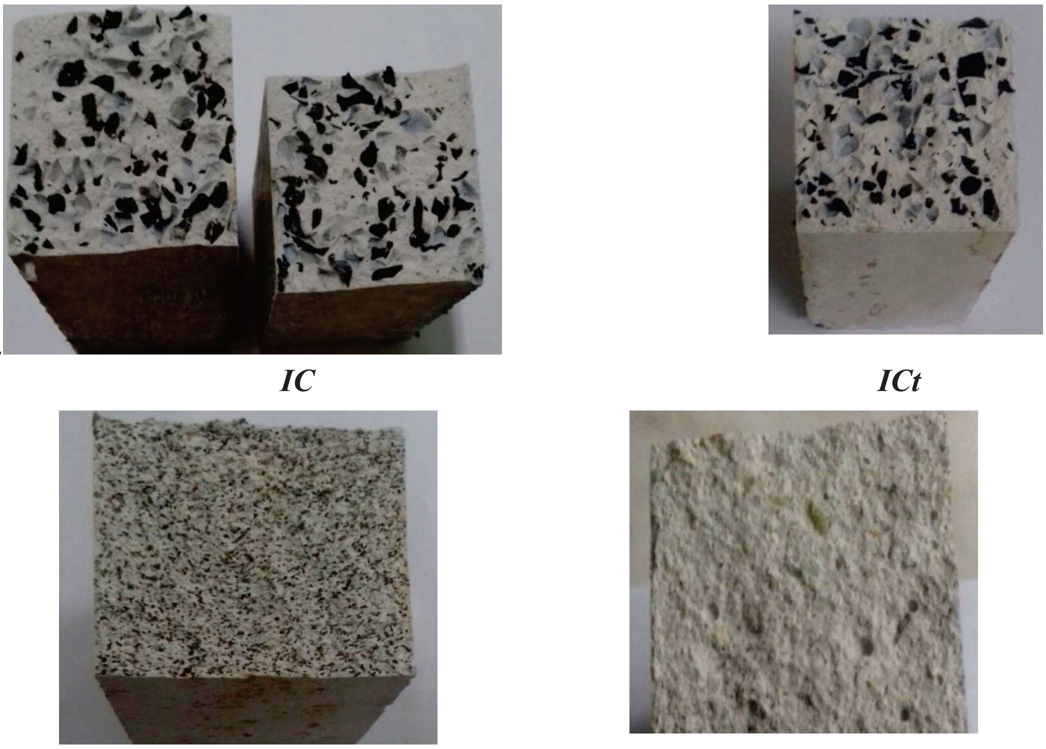
For the composite materials with rubber waste (IC), the adhesion of gypsum matrix to the surface of the rubber particles is small; the large voids which can be assessed in the matrix (figure 2) are due to the removing of rubber particles, when the specimens were tested for the assessment of flexural strength.

Partial substitution of gypsum with various types of wastes (rubber, polyurethane foam and chopped electrical cables) causes a significant decrease of the compressive strength; preliminary treatment of rubber waste (by immersion in NaOH 5M solution) does not have the expected a positive effect on the compressive strength of gypsum composite (ICt). This is due to the microstructure specific to the interfacial transition zone (ITZ) between the rubber particles and the binder matrix i.e. the rubber particles are embedded in the matrix formed by interconnected needle-like gypsum crystals; the increase of the surface roughness of the rubber particle (due to the previous mentioned treatment) does not improve the ITZ.

The apparent density of gypsum composite with waste content decreases due to the partial substitution of gypsum binder (and subsequently calcium sulphate dihydrate resulting from its hydration) with materials that have a lower density and high porosity.

The increase of porosity, noticed when studied wastes are added to gypsum binder, produces a decrease of thermal conductivity, and consequently an improvement of thermal insulation properties. The lowest value of thermal conductivity was obtained for the composite material with waste electrical cables (0.0951 $Wm^{-1}K^{-1}$). This value is close to the thermal conductivity of autoclaved aerated concrete (0.12÷0.14$Wm^{-1}K^{-1}$) and is smaller as compared with the one specific for a gypsum insulation plaster, with a density of 1000 kg/m^3, which has a thermal conductivity of 0.40 $Wm^{-1}K^{-1}$ [10].

The highest value of capillary water absorption coefficient was assessed for the composite with polyurethane waste, in good correlation with high porosity (low density) of polyurethane particles. On the opposite side, the substitution of gypsum binder with rubber waste and chopped electric cables determined a decrease of capillary water absorption coefficient. The highest value of this coefficient was obtained for the material with polyurethane waste – IP, corresponding to an increase of 9% with reference to gypsum plaster (I).



IC *ICt*

IE *IP*

Figure 2. Visual aspect (cross section - fracture) of composite materials based on gypsum plaster with different types of waste, hardened for 7 days.

The lowest values of compressive strength were recorded for the composite materials with rubber waste (IC and ICt); this can be due to the large size of rubber particles (1÷6 mm) as compared to those of chopped electrical cables (0.2÷1 mm) and of polyurethane waste (0.1÷2 mm). In all cases, the mechanical strength of composite materials with the addition of waste is with 69 ÷ 88 % lower than the one of the hardened plaster paste.

Composite materials with the addition of rubber waste also had a better sound-absorbing capacity compared to the plain gypsum.

The results obtained in this study highlight the possibility of recovering three types of waste (rubber particles, chopped electrical cables and polyurethane foam) in the manufacture of environmentally friendly materials, which can be used to achieve thermal insulation in construction; the lowest value of thermal conductivity and an adequate compressive strength, were obtained for plaster-based composites with chopped electrical cables addition.

3.2 Obtaining and characterization of composite materials based on gypsum binder and synthetic gypsum (FGD) with the addition of rubber waste

Another environmental problem is the generation in large quantities, in thermal power plants, of fly ash or synthetic gypsum (FGD), the last one resulting as a waste in the process of desulphurization of combustion gases [11].

The main objective of the study presented in this chapter was to valorise FGD gypsum and rubber waste, in the manufacture of gypsum-based materials with good thermal insulation properties.

In order to be able to substitute gypsum binder without significantly affecting the mechanical strength of the composite material, artificial gypsum (FGD) underwent a preliminary thermal treatment at 120°C, which led to the partial transformation of calcium sulphate dihydrate into calcium sulphate hemihydrate.

To design a composition based on the three above-mentioned materials, with good thermal insulating properties (low value of apparent density) and adequate mechanical strength, the design of experiment software - DesignExpert TM was used [12].

The experimental results obtained in this study, demonstrated that gypsum binder can be partially replaced by the thermally treated artificial gypsum FGD (FGDgp_t), without a significant negative influence on the compressive strength of resulted composite materials; the replacement of plaster with FGDgp_t, allows to obtain a binder that fulfils the requirements of European standard for gypsum binder - EN 13279-1 [13].

The addition of a small amount of rubber waste (5% wt.) has a positive effect on the thermal insulation capacity of these composite materials. The composite material with 5% rubber has a thermal conductivity of 0.157 $Wm^{-1}K^{-1}$, which is lower than the thermal conductivity of plaster panels i.e. 0.276-0.4 Wm^{-1}K-1 [8, 9].

3.3 Obtaining and characterization of thermal insulation materials with high porosity based on gypsum binder

This study presents the influence of three additions i.e., hydroxyethyl methyl cellulose (HEMC), sodium bicarbonate and flue gas desulfurization (FGD) gypsum on the main properties of gypsum binder-based materials (setting time, apparent density, open porosity, compressive strength and thermal conductivity).

The raw materials used for the preparation of these compositions were gypsum binder, artificial gypsum FGD, sodium bicarbonate ($NaHCO_3$) and hydroxyethyl methyl cellulose (HEMC).

The addition of HEMC to the gypsum binder - water system, determines an increase of the material's porosity due to its ability to stabilize the air entrained during the mixing of solid components with water; the average dimensions of the pores formed in this material, after curing, are comprised between 0.25÷0.75 mm.

The apparent density of the materials with addition of sodium bicarbonate decreases with the increase of $NaHCO_3$ dosage. In the binder matrix, numerous pores are formed due to the gas generated in the reaction of $NaHCO_3$ with water. For the samples with 0.5% and 1% $NaHCO_3$, the pore sizes are comprised between 10 microns and 1 mm. For the compositions with 2% $NaHCO_3$, was assessed the formation of large pores (>1 mm) with irregular shapes (due to the joining of several smaller pores).

As expected, the decrease of apparent density (and the porosity increase) of the studied materials determined a decrease of compressive strengths with reference to gypsum plaster i.e. by 37% for the composition with HEMC, and by 33÷75% for materials with sodium bicarbonate and FGD gypsum content. Still, for an adequate dosage of studied wastes (FGD gypsum and rubber particles), the flexural strength of the composite material exceeds 2 N/mm^2 and the compressive strengths exceeds 5 N/mm^2, which are the minimum values imposed by the European norm EN 13279-1 [13].

Thermal conductivity of gypsum-based composites with the studied additions, decreases by 9–18% with reference to gypsum plaster.

Based on the properties assessed for the studied materials, a potential application could be for the manufacture of lightweight gypsum blocks/panels for non-load bearing walls with improved thermal insulation properties and good reaction to fire.

3.4. Valorisation of a waste resulted from the combustion of petroleum residues in the production of inorganic binders with calcium sulphate content

Another type of waste with calcium sulphate content, studied in this doctoral thesis, is a waste produced during the burning of petroleum residues with a high sulphur content in the presence of limestone.

The aim of this study was to assess the possibility of using this type of waste (further denoted by A) to obtain gypsum-based binders.

Partial substitution of gypsum binder by 5 and 20% wt. waste A causes an increase of compressive strength, both after short (2 hours) and longer (7 days) curing times; however, the setting time of these compositions is much shorter as compared to the value imposed by the European norm specific for gypsum binder.

The increase of waste A dosage up to 30 % wt. causes a decrease of compressive strength (as compared with the compositions with 5 and 20 % wt.), but the values are comparable to those developed by gypsum binder.

The setting times of the composition with 5 and 20 wt.% waste A, are much shorter as compared to the value imposed by the specific norm for gypsum binders, therefore these compositions cannot be used in practice. The substitution of gypsum plaster by 30% wt. waste A delays the setting and the values of setting times are comparable to those specific to hardened gypsum binder.

The setting of the paste obtained by the mixing of waste A with water, is much longer as compared with the compositions based on gypsum binder; this is explained by the lower reactivity vs. water of the calcium sulphate anhydrite formed at high temperatures during the combustion of hydrocarbon-containing residues.

To accelerate the setting and hardening of waste A, two additives were used, i.e. K_2SO_4 and $FeSO_4$; the setting of these mixtures proceeds faster as compared to the setting of waste A paste. The values of setting time (initial setting time is 2-3 hours and final setting time is 5-6 hours) are closer to those specific for Portland cement, but much longer as compared to those specific for gypsum binder.

The use of accelerator additions increases the compressive strength of waste A paste by more than 130% (as compared to the compressive strength developed by waste A paste) and the values are comparable to those specific for gypsum paste.

4. *OBTAINING AND CARATERIZATION OF FIRE-RESISTANT THERMAL AND SOUND INSULATION MATERIALS BASED ON GLASS WASTE*

The researches presented in this chapter focus on the synthesises of alkali activated materials (AAM) based on waste glass powder and metallurgical slag with addition of rubber and polyurethane foam wastes.

4.1 Alkali activated materials with high porosity based on wastes glass powder and metallurgical slag

The main objective of this study was to obtain thermal and sound insulation materials by the alkaline activation of waste glass powder (WGP) with / without slag addition; the thermal treatment of these compositions (at different temperatures and plateaus) lead to an important increase of the material's porosity, thus improving its thermal insulation properties. Another advantage of these materials is their fire behaviour i.e. are non-combustible, due to the absence of organic substances in their composition.

All compositions contained soda-lime-silica glass powder obtained by the grinding of glass cullet (of different colours); the slag partially replaces the WGP (5% wt., 10% wt. and 20% wt.) and the alkaline activator was sodium hydroxide solution. These components were mixed and the resulting pastes were cast in cuboid moulds (15×15×60 mm) and cured at 60°C for 24h. The specimens were demoulded and cured in air at ambient temperature (20±2°C) for 7 days. The hardened specimens were thermally treated at temperatures ranging between 900°C and 1000°C, for 60 or 30 minutes.

The visual aspect of alkali activated materials, before and after thermal treatment, is shown in Figure 3.

before thermal treatment after thermal treatment at 900ºC/60 min.

Figure 3. Visual aspect of alkali activated materials

Before applying the heat treatment, the values of compressive strength are exceeds 25 MPa, for all studied AAMs. The increase of slag dosage determined an increase of compressive strength for the specimens obtained with a lower water to binder ratio (0.27).

The thermal treatment, causes a significant increase of the specimens volume (intumescence effect - specific to alkali-activated glass powder compositions), which leads to an increase of the material's porosity and a decrease of compressive strength; still, for some compositions the compressive strength can still be very high (for porous materials) i.e. 10 MPa.

The thermal conductivity of AAMs thermally treated at 900°C for 60 minutes, is comparable to the thermal conductivity of cellular glass (industrial product). Also, the values of thermal expansion coefficient are comparable to those specific to cellular glass, which demonstrates a good thermal stability.

The best acoustic performance was achieved at sound frequencies between 1200-1600Hz; the maximum sound absorption coefficients, recorded for these materials, are comprised between 0.98 and 1.

Due to the lack of organic compounds in the composition of studied AAMs, these materials can be classified in class A1 - reaction to fire.

Based on the determined performances, the studied materials can be used for thermal and sound insulation in construction.

4.2 Alkali activated materials based on waste glass powder and slag with addition of rubber and polyurethane waste

The study presented in this chapter, aimed to valorise rubber and polyurethane wastes to obtain alkali activated inorganic materials (AAM), with improved thermal insulating properties and a good fire behaviour.

Based on the results presented in the previous chapter, the AAMs were obtained by the by the alkaline activation of waste glass powder (G) or mixtures of waste glass powder and slag (G+Z). Rubber waste substituted 25% wt. and 30% wt. of G or G+Z, and polyurethane waste substitutes 5% wt. of G or G+Z. The water to solid ratio was 0.45 for the polyurethane waste compositions and 0.3 for the other compositions.

The obtained pastes were poured into moulds and cured for 24 hours at 60°C. Subsequently, the samples were demoulded and kept for 28 days in air at 23 ±2°C.

If the glass powder or the mixture of glass powder and slag were substituted with 5% wt. polyurethane waste, the values of the compressive strengths decreased by 62-63%. The higher strength loss was recorded for the AAMs with rubber waste (86-90%), and is mainly due to the large percentage of rubber waste used in these compositions to substitute G or G+Z (25 and 30% wt. compared to 5% wt. polyurethane). Also, the increase of ITZ between the AAM matrix and large rubber particles (4÷6 mm as compared with polyurethane particles - 0.1÷2 mm) contributes to this important strength loss.

The lower thermal conductivity was obtained for the AAM composite with polyurethane content. The thermal conductivity of AAM with rubber waste is slightly higher as compared to the one specific for an autoclaved cellular concrete (AAC) with similar apparent density.

The composite materials obtained in this study have a good fire behaviour – when put in direct contact with a flame for 90 minutes, these materials do not burn and do not present significant smoke emissions.

5. *GENERAL CONCLUSIONS*

The main objective of this doctoral thesis was to contribute to the valorisation of different types of end-of-life materials (waste) in the production of composite materials with thermal and sound insulation properties.

Seven types of composite materials, based on inorganic binder (portland cement, gypsum plaster) or alkali activated materials (AAM), containing different types of waste, were obtained and characterized from the point of view of composition, microstructure, physical and mechanical properties.

The properties of studied materials recommend them to be used for thermal and acoustic insulation in construction.

6. *MAIN CONTRIBUTIONS OF THE DOCTORAL THESIS*

The novelty and originality of the research carried out in the framework of this doctoral thesis can be summarized as follows:

- complex characterisation of the wastes used as alternative raw materials for the production of composite materials in terms of composition (oxide and mineralogical), particle size distribution, microstructure and apparent density. Assessment of the influence of preliminary chemical or thermal treatments of wastes, on the main properties of the studied composite materials;
- the design of materials containing different types and dosages of wastes, represents the first step in the manufacture (at laboratory level) of prototype products, having as intended use the thermal and sound insulation of various construction elements;
- obtaining and characterisation of composite materials with waste content, as well as carrying out comparative studies on the influence of the nature and dosage of each type of waste on the main properties of the newly obtained materials, in correlation with their intended use (thermal and sound insulation materials).

7. *PERSPECTIVES FOR FUTURE DEVELOPMENT*

The result obtained in the framework of this doctoral thesis can be considered as a first step in the design and manufacture of new eco-friendly composite materials with a good resistance to fire, to be used for thermal and sound insulations in constructions.

This information can be also used in the future development of specific production technologies.

The valorisation of industrial and municipal wastes to produce construction materials for thermal and sound insulations, contributes to the development of a circular economy, with a positive impact on the environment.

Thus, by implementing the newly developed technologies for the manufacture of these materials:

- natural resources (used as raw materials) will be replaced by different types of wastes (alternative raw materials) into the economic cycle,
- the cost for the landfilling of non-biodegradable waste will be reduced,
- environment protection, due to the elimination of potential burning of some of the studied wastes (rubber, polyurethane) as well as avoiding air and water contamination with fine waste powders, which are incorrectly landfilled.

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