CONVERSION OF PLASTER MOLDS WASTES INTO THE NEW INORGANIC PRODUCTS BY THERMAL DEHYDRATION

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Abstract

Solving the environmental issues by reducing the waste generated by the industries of building and ceramic materials is a global priority due to their impact on the human health and ecosystems. Recovery of plaster molds wastes from fine ceramic industry is an important topic to address in order to reduce the use of natural gypsum resources and address environmental issues generated by solid wastes from landfill disposal. The main objective of this paper is related to the thermal behaviour study of the calcium sulphate dehydrate during the calcination and to determine the kinetic parameters for the dehydration reactions. Also, the effects of different heating rates on the course of dehydration are investigated, pointing out that the general state of dehydration does not change, although at a given temperature the mass loss is the same for different heating rate. On the other hand, the increase in the heating rate displaces the reaction towards high temperatures. Thus, based on the kinetic study carried out, it was established that the dehydration process needs to take place approximately 50 minutes at a constant temperature of 373 K. Finally, the dehydrated waste is used to obtain a new inorganic material, which can be used for geopolymer preparation. For geopolymeric mortar, 5 % and 10 % from fly ash was replaced with gypsum. The solutions of NaOH 5M and sodium silicate were used to activate the geopolymer. The obtained results indicated a good geopolymer structure formation.

Keywords: *gypsum-based solid wastes, kinetic study of thermal dehydration, geopolymers, fly ash replacing, new building materials*

1. INTRODUCTION

The Environment Action Programme foresees the development of a Thematic Strategy on the sustainable use of natural resources and management of waste [1, 2]. The industry-specific requirements as well as the ever-evolving needs of the three sustainability sectors (environmental, social, and economic) must be considered while developing the technological solutions [3]. The activities relating to waste valorization by recycling and reuse have risen in the frame of the best available techniques [4, 5], in the same time with the efforts for the research and industrial development in this area [6, 7].

Plaster of Paris, also known as calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), is widely utilized in the construction, ceramics, and medical industries [8, 9, 10]. Hemihydrate can be industrially produced in two different ways (α- and β-forms), with the α-$CaSO_4 \cdot 0.5H_2O$ form being created using a wet process (such as autoclaving) and the β-$CaSO_4 \cdot 0.5H_2O$ form being created through a dry process (such as calcining) [8, 11]. Gypsum plaster ($CaSO_4 \cdot 2H_2O$)is an important material in civil construction, widely used in pastes and mortars for renderings, as well as in the production of components, such as plasterboards and masonry blocks [11, 12].

Plaster molds used for manufacturing the fine ceramic products (plates and dishes, beautiful porcelain items, clay and sandstone items, etc.) are a significant type of waste [4]. These shapes are created from modeling plaster, which contains the calcium sulfate hemihydrate as its major component. The molds degrade throughout usage either as a consequence of pore clogging caused by the ceramic material penetrating inside of them or as a result of the pore size expanding as a result of heating cycles [13]. Calcinations at low temperature of the plaster molds issued from the fine ceramic industry is a promising technique, not only for recovering an economic value, but also for reducing its environmental impact if they are used as raw materials for obtaining new materials [8, 9, 10, 11, 12]. According to the literature [10], β-hemihydrate is prepared from the dihydrate by heating under a low water vapour partial pressure,

i.e., in dry air or vacuum, between 45 °C and 200 °C, whereas α-hemihydrate is prepared from the dihydrate under a high partial pressure of water vapour, e.g., above 45 °C in acid or salt solutions, or above 97.2 °C in water under pressure [8, 13].

In a previous study it is demonstrated that increased content modelling hemihydrate forms of waste can be achieved through a drying process of such waste, in concordance with the thermochemical processing system $CaSO_4 \cdot 2H_2O$ – $CaSO_4$ [13]. The recovering of the gypsum plaster molds presents an important issue for decreasing the consumption of natural gypsum resources and resolving the environmental issues related to the solid waste disposed on the landfills. No significant differences between the commercial and recovered gypsum was found, which indicates that this by-product can be used for building materials, and the conversion process proceeds without significant variations in composition at low energy consumption [11, 12, 14].

This waste can be calcined at low temperatures, which offers a viable method for recovering the economic value, minimizing the environmental impact of these solid wastes by using them as raw materials for obtaining of new products. In accordance with the chemical transformations in the system $CaSO_4 \cdot 2H_2O$ – $CaSO_4$, this paper presents a kinetic study of thermal dehydration using TG – DTA techniques, taking into account how the dehydration temperature and heating rate affect the behavior of the material undergoing thermal treatment. Finally, a new inorganic material created from the dehydrated waste is used to produce geopolymers. Gypsum was used to replace 5 % and 10 % of the fly ash (FA) in the geopolymic mortar. The geopolymer was activated using solutions of NaOH 5M and sodium silicate, while a good geopolymeric structure was formed.

2. MATERIALS AND METHODS

2.1. Materials

The fine ceramic molds made of pottery plaster have as main constituent the calcium sulfate β-semi-hydrate [13]. The quality requirements for the pottery plaster used in porcelain industry foreseen a high purity grade (min. 92 % $CaSO_4 \cdot 0.5H_2O$ – plaster of A quality) and whiteness – min. 82 % (in accordance with the Romanian standards SR 545-2:2000 [15], SR 4474-2:2000 [16], SR 4474-2:2000 [17], SR EN 13279-2:2005 [18]).

The fly ash (FA) used for preparation of the geopolymer was provided from a thermal power plant, located in North-East part of Romania. The activation was performed with NaOH and sodium silicate (Chemical Company, Iasi, Romania). For this study the samples were obtained by replacing 5 % and 10 % FA with gypsum GP5 and GP10, respectively. The samples preparation involved mixing the raw materials: fly ash, gypsum, slag, Bega sand, and rheological additives with liquid phase (5M NaOH solution, sodium silicate - for a proper Na:Si ration and water), under the stirring of 15 minutes [19, 20]. The solid/liquid report was imposed as a dependence of mixture workability. The samples (in triplicate) were molded after 24 h and kept for testing at different periods: 7, 14 and 28 days, respectively [21].

2.2. Measurements

2.2.1. Thermogravimetric analysis

The thermal behavior of some waste from the fine ceramics industry was analyzed using a Mettler Toledo TGA-SDTA851^e equipment [13]. This equipment allows the simultaneous recording of thermogravimetric (TG), derived thermogravimetric (DTG) and differential thermal (DTA) curves. The above mentioned curves were recorded under the dynamic conditions, in a nitrogen atmosphere with a flow rate of 20 mL/min, using the same sample amount of 6.39 ± 0.27 mg. The considered temperature was ranging between 25 and 250 °C, at four heating speeds: 5, 10, 15 and 20 °C/min, respectively. The reproducibility of the experimental results was verified by repeating the recordings for the same heating rate. The processing of the obtained curves was carried out using the STAR software from Mettler Toledo to establish the main thermogravimetric characteristics: T_{onset} – onset temperature at which thermal degradation starts, T_{peak} – temperature at which the degradation rate reaches its maximum, T_{endset}

– temperature at which the degradation process ends, W% - mass percentage loss per stage and the amount of residue.

2.2.2. Geopolymer characterization

The setting time and compressive and flexural strength were determined for GP5 and GP10, and the values were compared with geopolymer without gypsum.

Setting time of the obtained geopolymers were determined by using the Vicat apparatus [22], in accordance with the Romanian standards (SR EN 196-3:2017 [23]). After mixing, the geopolymers were cast into ebonite cone, and the initial setting time was considered when the needle entered up to 1 mm from the mold bottom. The final setting was measured as the time until the needle of the Vicat not leave a mark on the surface of geopolymer.

The compressive strength of the obtained geopolymers was measured in accordance with SR EN 1052-1:2005 [24], on the cub with 40 × 40 × 40 mm, at a loading rate of 0.5 mm/min. The compressive strength were measured at 7, 14 and 28 days of curing.

2.3. Methods

The kinetic study was carried out following the recommendations of the International Confederation of Thermal Analysis and Calorimetry (ICTAC) – ICTAC 2014 [25] and ICTAC 2011 [26]. Thus, special attention was paid to establishing the conditions for conducting the study both in terms of the amount of sample subjected to analysis, its homogeneity and the considered heating speeds. The amount of sample subjected to analysis was chosen according to ICTAC 2014 recommendations [25], so that it leads to a mass loss of approximately 1 mg. The recording was repeated under the same conditions considering half the amount of sample initially selected and it was found that there are no significant differences between the mass loss curves between the first and the second test. ICTAC 2011 [26] considers that at least three thermogravimetric curves recorded with heating rates lower than 20°C/min are necessary for the evaluation of kinetic parameters.

In our study we recorded thermogravimetric curves at the following heating rates: 5, 10, 15 and 20 °C/min and we kept according to the recommendations [25] approximately the same amount of sample subjected to analysis (6.39 ± 0.27 mg) and a constant flow of nitrogen (20 mL/min).

In the literature [26] there are several isoconversion methods for kinetic interpretation of thermogravimetric curves recorded at several heating rates. In this study, we chose to apply the integral method proposed by Vyazovkin [26, 27, 28], which is based on the numerical integration of equation (1) over short time intervals:

$$g(\alpha) \cong \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A \cdot \int_0^{t} \exp\left(-\frac{E_a}{RT}\right) dt \qquad (1)$$

where: α - the conversion degree, A – the preexponenţial factor, E_a - the apparent activation energy (J/mol), R – the gas constant (8.31 J/mol K), T – temperature (in K), t – time (in s).

This isoconversion method is presented in detail in the literature [26, 28, 29, 30, 31, 32] and allows the determination of the activation energy variation with the conversion degree, of the pre-exponential factor and of the functions f(∝) or g(∝).

Another important application aspect of the isoconversion method consists in the possibility of achieving kinetic predictions, respectively of estimating the time in which the dehydration of waste from the fine ceramic industry takes place using the following equation [27]:

$$t_{\alpha} = \frac{g(\alpha)}{A \cdot \exp\left(\frac{-E_a}{RT_0}\right)} \qquad (2)$$

where: t_α is the time required to reach a certain conversion degree at a given temperature T_0 in an isothermal step.

3. RESULTS

The kinetic parameters of the gypsum dehydration process were determined under nonisothermal conditions in nitrogen atmosphere, in concordance with the chemical transformations in the system $CaSO_4 \cdot 2H_2O$ – $CaSO_4$, considering the influence of the dehydration temperature and heating rate on the behaviour of the material subjected to thermal treatment.

The derived thermogravimetric curves (DTG), which were recorded at the following heating rates: 5, 10, 15 and 20 °C/min, are comparatively presented in Figure 1. The shift of the peak at which the dehydration rate is maximum can be seen with the increase in the heating rate from 125.4 °C to 146.3 °C. The differential thermal curves (DTA) presented in Figure 2 indicate the presence of two peaks that are shifted towards higher values of temperature with the increasing of the heating speed.

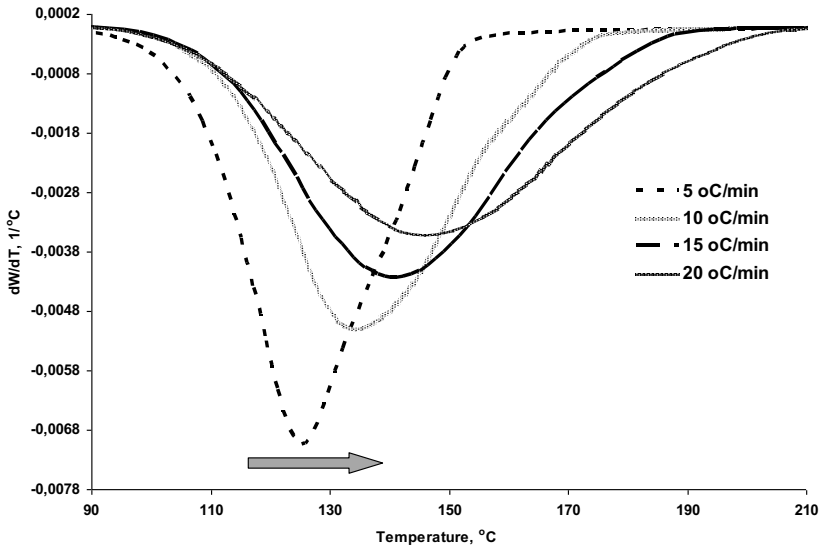

Figure 1. DTG curves

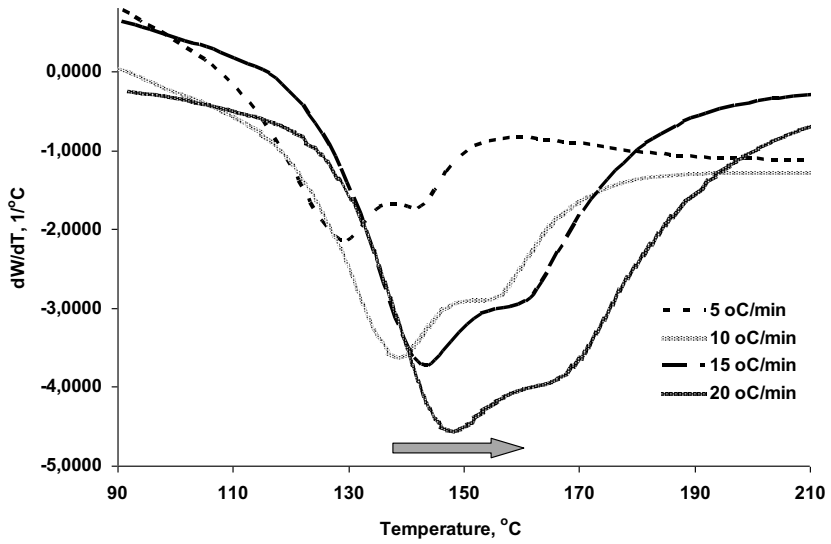

Figure 2. DTA curves

The existence of the two peaks in the DTA curves may indicate that the dehydration process of ceramic waste takes place in two stages according to the literature [8, 13, 33, 34, 35, 36]:

$$CaSO_4 2H_2O_{(s)} \rightarrow CaSO_4 0.5H_2O_{(s)} + 1.5\ H_2O_{(g)} \quad (3)$$

$$CaSO_4 \cdot 0.5H_2O_{(s)} \rightarrow CaSO_{4(s)} + 0.5\ H_2O_{(g)} \quad (4)$$

4. DISCUSSION

In this paper, the thermal behavior of some waste from the fine ceramics industry is analyzed, following the recommendations of the ICTAC 2014 [25] and ICTAC 2011 [26]. The obtained results in the frame of this paper represent a completion of the existing studies in the specialized literature, by applying for the first time of the integral isoconversion method (proposed by Vyazovkin) in the analysis of thermogravimetric data for this type of waste.

The kinetics of the dehydration process was analyzed by applying the integral method proposed by Vyazovkin [26, 28]. This method allowed us to determine the variation of the activation energy with the conversion degree and the calculation of the pre-exponential factor, which are graphically represented in Figure 3.

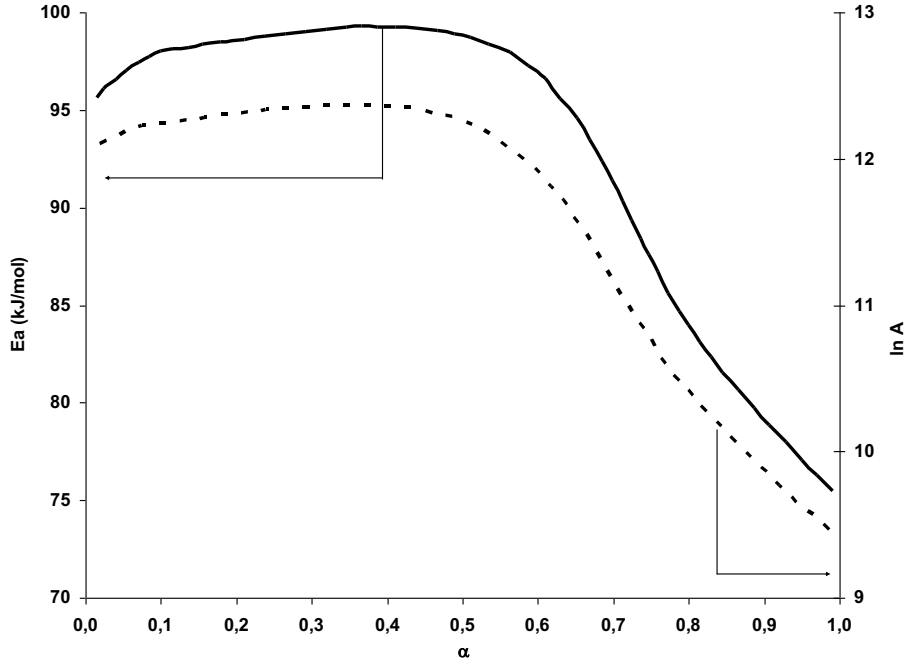

Figure 3. The activation energy and the pre-exponential factor variation with the conversion degree

At conversion degree values ranging between 0.1 and 0.6, the activation energy has an approximately constant value of 98 kJ/mol. At values higher than 0.6 for the conversion degree, the activation energy starts to decrease, reaching 75 kJ/mol when the conversion degree becomes 0.99. The values obtained for the activation energy are consistent with those obtained by other researchers applying other methods of kinetic interpretation of thermogravimetric data [37, 38, 39, 40].

The change in the activation energy value at conversion degrees higher than 0.6 confirms the fact that the dehydration process of ceramic waste takes place in two stages. The integral method proposed by Vyazovkin [26, 27] allowed us to establish the expressions of the functions f(∝) or g(∝) (Figure 4). It can be mentioned that in the kinetic study carried out in this work, all 13 models that are presented in reference [26] were tested. The best results were obtained by applying the contracting cylinder model named R2. López et al. [40] obtained by applying the Coats-Redfern kinetic interpretation method for a type of phosphogypsum of Spanish origin a Mampel type model (first order – F1) and for a type of phosphogypsum of Tunisian origin a three-dimensional diffusion model (3D) to describe the dehydration process.

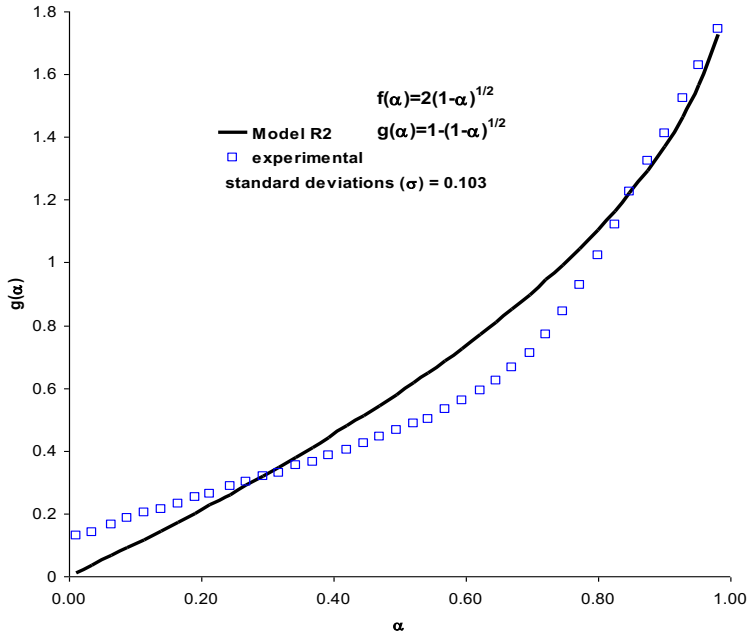

Figure 4. Function g(α) variation with the conversion degree

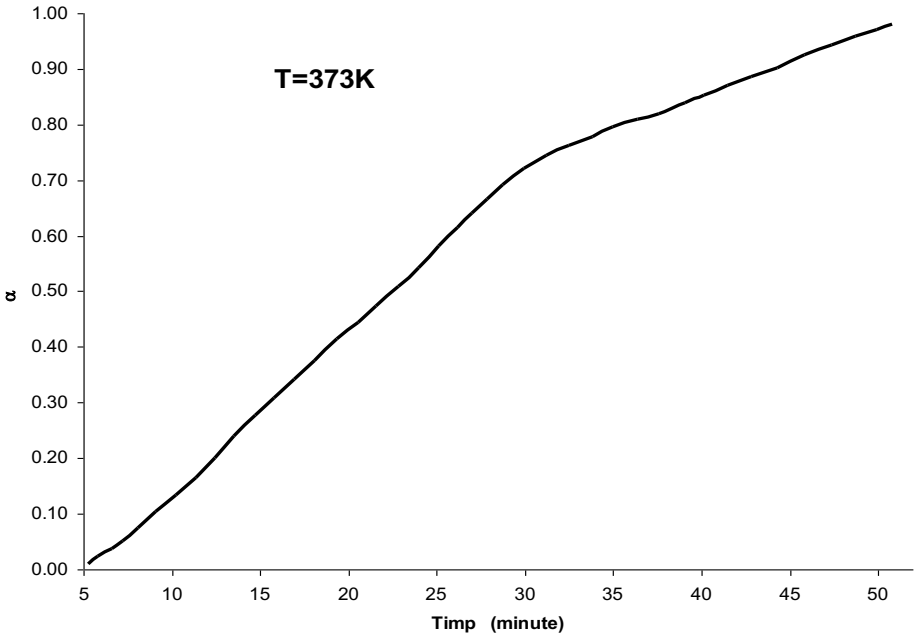

Figure 5. The variation of the conversion degree over time at the temperature of 100 ºC

However, in specialized literature [25, 26] the Coats-Redfern kinetic interpretation method is considered less accurate because it uses thermogravimetric curves recorded at a single heating rate. Another important aspect of the application of the isoconversion method proposed by Vyazovkin consists in the possibility of estimating the time in which the dehydration of the analyzed waste from the fine ceramic industry takes place. Thus, based on the kinetic study carried out by applying the relation (2), it was established that the dehydration process can last approximately 50 minutes at a constant temperature of 373 K (Figure 5).

For GP5 and GP10, a reduced setting time was observed with 2 % for GP5 and 4.5 % for GP10. One of the essential properties of the construction materials is the compressive strength [19, 20, 41], e.g. at 7 days, or later (at 28 days). Compared with geopolymers without gypsum the compressive strength of the GP5 and GP10 is improved, by over 7 % for GP5 compared to the control sample. This effect is due to the increased calcium ions content in GP10, as these can continue to react with dissolved Si^{2+} and Al^{3+} resulted by activation of fly ash to produce more C-(A)-S-H gels. It should be noted that C-(A)-S-H gel is the predominant aluminosilicate product due to high available calcium content [22, 42]. On the other hand, the contents of dissolved Si^{2+} and Al^{3+} were reduced due to the decrease in fly ash content (GP10), and therefore the generated C-(A)-S-H gels were decreased, which resulted in lower compressive strength comparatively with GP5.

5. CONCLUSIONS

The thermogravimetric and moving study carried out confirmed the fact that the dehydration process of the ceramic waste takes place in two stages: formation of calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5\ H_2O$) from gypsum ($CaSO_4 \cdot 2H_2O$) followed by formation of anhydrous calcium sulfate ($CaSO_4$). Shifts of the T_{peak} values towards higher temperatures take place as a result of increasing the heating rate. The integral method proposed by Vyazovkin allowed the determination of the variation of the activation energy with the conversion degree and the calculation of the pre-exponential factor. It was found that at values of the conversion degree ranging between 0.1 and 0.6, the activation energy has an approximately constant value of 98 kJ/mol, and at values higher than 0.6 for the conversion degree, the activation energy starts to decrease, reaching 75 kJ/mol when the conversion degree becomes 0.99. It was also established that the theoretical model corresponding to the dehydration process is of the contracting cylinder (R2) type, and the duration of the dehydration process is estimated at approximately 50 minutes at a constant temperature of 100 ºC.

The resulted gypsum was used in geopolimeric materials, by replacing 5 and 10 % from fly ash. The obtained materials have improved properties, in terms of setting time and compressive strength, which can contribute to the enhancement of their environmental performance, but more studies are necessary for establishing the influence over all properties and find the optimal percent of replacement.

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