

# Synthesis of hydrogarnets in the system $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2\text{-SiO}_2\text{-CaO-H}_2\text{O}$ under hydrothermal conditions

**ZDZISŁAW PYTEL** • AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Poland • pytel@agh.edu.pl

Érkezett: 2019. 11. 29. • Received: 29. 11. 2019. • <https://doi.org/10.14382/epitoanyag-jsbcm.2019.31>

**Zdzisław PYTEL**

is a Doctor in Department of Building Materials Technology, Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow, Poland. His special field is utilization of waste by-products (especially fly ashes) in ceramic building materials made from clays and in the range of cementitious materials in concrete technology. He has worked for many years projects connected with sand-lime bricks production.

## Abstract

The paper summarises the experimental data on the products of synthesis of mixtures containing metakaolinite ( $\text{AS}_2$ ), silica ( $\text{SiO}_2$ ) and lime ( $\text{CaO}$ ) in various proportions, under hydrothermal conditions at  $180^\circ\text{C}$ . The actual compositions of reacting mixtures were determined by the molar ratios  $\text{Ca}/(\text{Al}+\text{Si})$ ,  $\text{Al}/(\text{Si}+\text{Al})$  and  $\text{C}/\text{S}$ , in the respective ranges  $(0.75 \div 1.5)$ ,  $(0.2 \div 0.5)$  and  $(1.0 \div 3.0)$ . Compositions of the reacting mixtures correspond to stoichiometric ratios of particular oxides, being the components of hydrogarnets from the series  $\text{C}_3\text{AS}_3 - \text{C}_3\text{AH}_6$ , whose composition varies in accordance with the formula  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ , for  $x$  in the range  $(0.0-2.0)$ . The mineralogical characteristic of thus obtained products of synthesis are evaluated basing on XRD, DTA, TG, IR and SEM+EDAX test data. Results obtained to date reveal that the hydrogarnet  $\text{C}_3\text{AH}_6$  is the most frequent product obtained in the analysed systems. It coexists with other products of the synthesis, belonging to the group of hydrated calcium silicates, chiefly revealed as an amorphous phase C-S-H and tobermorite ( $\text{C}_5\text{S}_6\text{H}_5$ ).

Keywords: metakaolinite, hydrogarnets, hydrated calcium silicates, hydrothermal conditions

Kulcsszavak: metakaolinit, hidrogénhidrát, hidratált kalcium-szilikátok, hidrotermikus körülmények

## 1. Introduction

Hydrogarnets of the series  $\text{A}_3\text{B}_2\{[\text{TO}_4]_{3-x}(\text{OH})_{4x}\}$ ,  $x$  ranging from 1 to 3, have the structure of garnets in which the process of partial or complete isomorphic substitution occurs, referred to as 'hydrogarnet substitution', in accordance with the formula  $4(\text{OH})^- \leftrightarrow (\text{SiO}_4)^{4-}$ . Cations of metals A and B occur in respective configurations 8 and 6 and the tetrahedron, cation T is mostly silicon [1]. Because of the possibility of isomorphic substitution as a continuous process, a series of solid solutions will be formed, their names depending on extreme terms in the given series [2]. Grossular ( $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ ) - hydrogarnet ( $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ) is a well known hydrogarnet series whose elemental composition varies in accordance with the general formula  $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_{3-x}(\text{OH})_{4x}$  [3]. It is assumed that those structures in the series are most stable in which  $x = 1$ , for example hydrogrossular ( $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_2(\text{OH})_4$ ). This series is of great importance in the sector of manufacturing of construction materials based on mineral binders in the form of cement or lime [4-6]. This series is of particular importance for ceramic engineers since its components determine the functional features of those construction materials, particularly their durability and strength, in the context of their susceptibility to carbonisation. These impacts, however, are not clearly defined, as several aspects are involved, yet it is a well-established fact that the higher the silica contents in hydrogarnets, the better the chemical resistance of construction materials containing those mineral binders.

Depending on the extent of 'hydrogarnet substitutions', physical properties of individual components of the series of solid solutions will vary [7, 8]. In the case of the series  $\text{C}_3\text{AS}_3 - \text{C}_3\text{AH}_6$ , the increase in the number of substitutions of the tetrahedrons  $[\text{SiO}_4]^{4-}$  by the complex  $[(\text{OH})_4]^{4-}$  is accompanied by the continuous change (increase) of the elementary cell parameters,

from  $a_0 = 1.185$  for grossular to  $a_0 = 1.256$  for hydrogarnete. Furthermore, as the number of complexes  $[(\text{OH})_4]^{4-}$  increases, apart from the lattice parameters, the position and intensity of reflexes will change, too. Besides, some diffraction lines will disappear whilst new ones will appear instead. At the same time, the growth of the elementary cell is accompanied by the decrease of the refractive index 'n' from 1.743 for  $\text{C}_3\text{AS}_3$  to 1.605 for  $\text{C}_3\text{AH}_6$  and by the change of density. With the increase of the amount of water present in the hydrogarnete structure in the form of hydroxyl groups, the dehydroxylation effect becomes more intense and the temperature of its maximum on the DTA curve goes down from about  $750-850^\circ\text{C}$  for  $\text{C}_3\text{AS}_3$  to  $(350-500)^\circ\text{C}$  for  $\text{C}_3\text{AH}_6$  [9-11].

## 2. Materials

Reaction mixtures for the synthesis of hydrogarnets contain the following materials:

- metakaolinite METASTAR 501 (symbol ME) whose composition is shown in Table 1.
- burnt lime obtained by calcination analytically pure  $\text{CaCO}_3$  at the temperature  $1050^\circ\text{C}$  for 3 hours (symbol C)
- silica powder (manufacturer: Quartzwerke GmbH), commercially available as SIKRON-Feinstmehl SGL-300 (symbol S)
- analytically pure aluminium oxide  $\gamma\text{-Al}_2\text{O}_3$  (symbol A)
- distilled water (symbol H)

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{MnO}$	$\text{P}_2\text{O}_5$	L.I.O
52.22	41.41	0.08	0.26	0.49	0.01	1.73	0.01	0.01	0.13	1.66

Table 1 Chemical analysis of metakaolinite METASTAR 501  
1. táblázat METASTAR 501 metakaolinit kémiai elemzése

### 3. Experimental

The synthesis of hydrogarnets of the series  $C_3AS_3 - C_3AH_6$  was conducted under hydrothermal conditions. Chemical composition of the reaction mixtures was varied, determined by the relevant molar ratios: C/(S+A), A/(S+A) and C/S. Those molar ratios were determined by the complex value  $x$  present in the general formula defining the composition hydrogarnets of the given series. For each considered value of  $x$  a reaction mixture was prepared in the form of dry components, whose chemical composition would represent the theoretical hydrogarnet composition for the given value of  $x$ . Synthesis of hydrogarnets was conducted for the following values of  $x$ : 0; 1.0; 1.5; 2.0. Accordingly, the formulas expressing the composition of particular hydrogarnets and the corresponding molar ratios agree well with the data in Table 2.

Sample designation	Value of "x"	Hydrogarnet formula	Molar ratios		
			C/S	C/(S+A)	A/(S+A)
ME - 0	0	$C_3Al_2[SiO_4]_3$ ( $3CaO \cdot Al_2O_3 \cdot 3SiO_2$ , $C_3AS_3$ )	1.0	0.75 (3/4)	0.25 (1/4)
ME - 1	1.0	$C_3Al_2[SiO_4]_2(OH)_4$ ( $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ , $C_3AS_2H_2$ )	1.5	1.0	0.33 (1/3)
ME - 1.5	1.5	$C_3Al_2[SiO_4]_{1.5}(OH)_6$ ( $3CaO \cdot Al_2O_3 \cdot 1.5SiO_2 \cdot 3H_2O$ , $C_3AS_{1.5}H_3$ )	2.0	1.2 (6/5)	0.4 (2/5)
ME - 2	2.0	$C_3Al_2[SiO_4](OH)_8$ ( $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ , $C_3ASH_4$ )	3.0	1.5	0.5

Table 2 Chemical composition of synthesised hydrogarnets  
2. táblázat A szintetizált hidrogarnetek kémiai összetétele

Reaction mixtures are prepared in stabilised and reproducible conditions. The procedure involved weighing the required amounts of basic components: metakaolinite (ME) and lime (C). Furthermore, certain amounts of silica powder (S) or aluminium oxide (A) were added to make up for the deficiency of silica or aluminium in metakaolinite and to obtain the desired chemical composition of reaction mixtures, determined by the molar ratios given in Table 2. Afterwards the mixtures are homogenised in an agate mortar, in the first stage with no presence of water, and then with water added. The amount of distilled water added to the mixture is determined by the need to ensure the complete hydration of calcium oxide and to achieve such consistency of the slurry that the ratio of water 'w' to dry substances 's' should equal 0.8. Thus prepared slurry is then transferred to Teflon crucibles which are then placed inside pressure cylinders acting as laboratory autoclaves. The slurry is then subjected to hydrothermal treatment. The samples are autoclaved at the temperature 180°C, which corresponds to the saturated vapour pressure of 1.002 MPa, for a variable period of time: 8, 24 and 72 hours. The time required to reach the specified conditions is about 1.5 hours and the autoclaves are cooled down to the ambient temperature in an unconstrained manner.

The phase composition of thus obtained materials is analysed using the XRD, DTA, TG, IR and SEM+EDAX methods.

### 4. Results

The analysis of the phase composition of thus obtained products uses mostly the XRD data. X-ray tests were performed using an X-ray diffractometer (Philips PW 1040). X-ray patterns were registered in the angle range  $CuK_{\alpha}$  5 - 60° 2 $\theta$  and the presence of mineral phases was established on the basis of ICPDS-ICDD file Copyright 2005. Test results in the form of XRD data are compiled in Fig. 1.

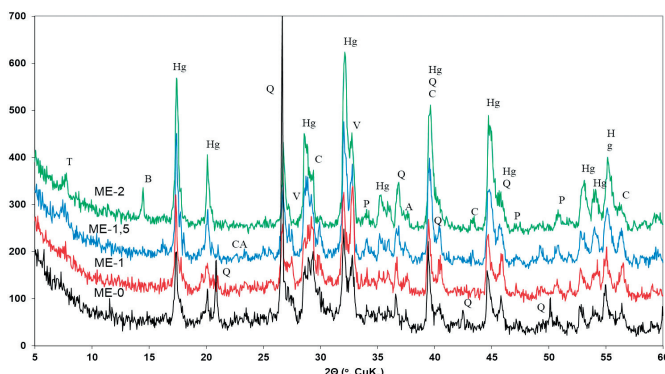


Fig. 1 XRD data of samples synthesised for 24 hours  
1. ábra A 24 órán át szintetizált minták XRD adatai

Designations: Hg-hydrogarnet; Q-quartz; P-portlandite; C- calcite; V-vaterite; B-boehmite; A- aluminium oxide; CA-carboaluminate; T- tobermorite;

IR spectra (400 – 4000  $cm^{-1}$ ) are registered using the standard technique involving the KBr tablet transmission. Measurements are taken with a Fourier spectrometer Bio-Rad FTS 60MV with the resolution capacity 4  $cm^{-1}$  for 256 repetitions. Test results in the form of IR spectra of the investigated samples are shown in Fig. 2.

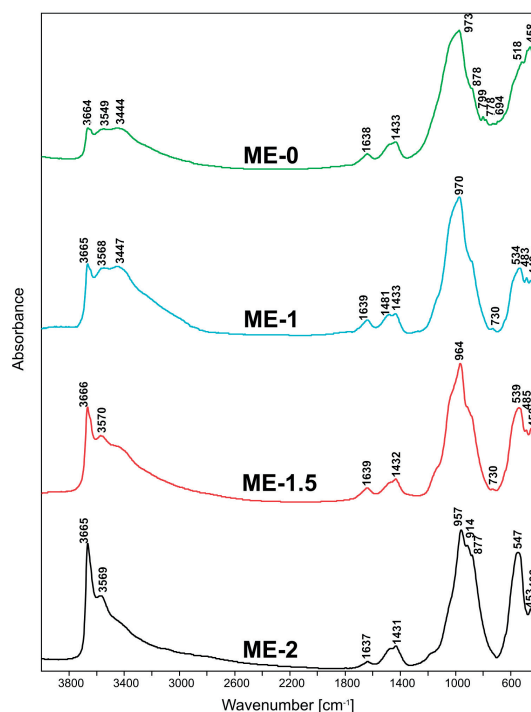


Fig. 2 IR spectra of the investigated materials  
2. ábra A vizsgált anyagok IR-spektrumai

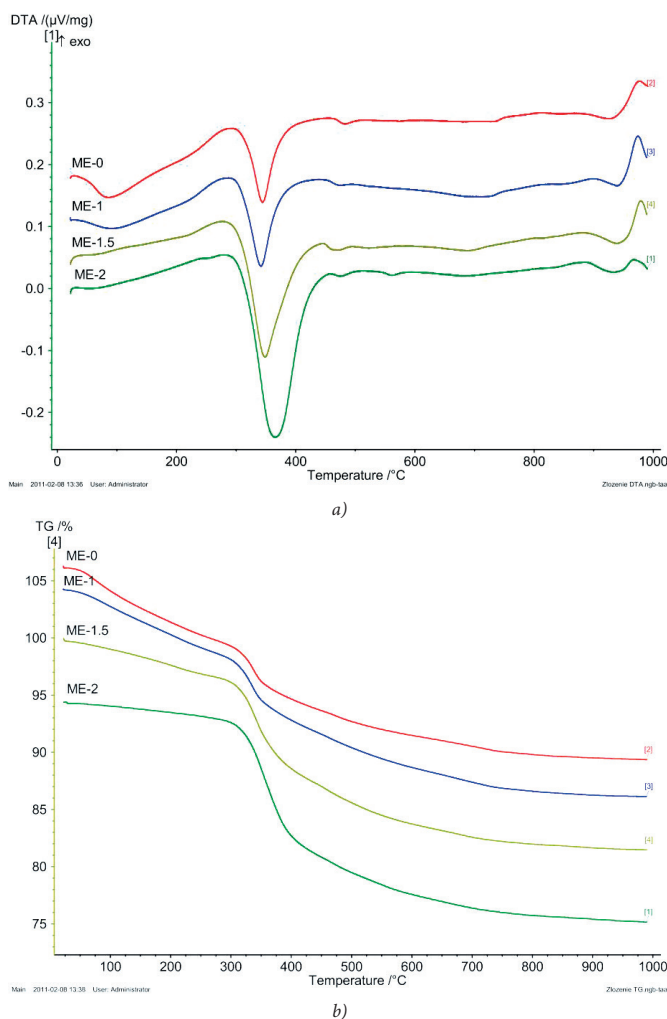


Fig. 3 Thermal treatment data: a) DTA curves; b) TG curves  
3. ábra Hőkezelési adatok: a) DTA görbék; b) TG görbék

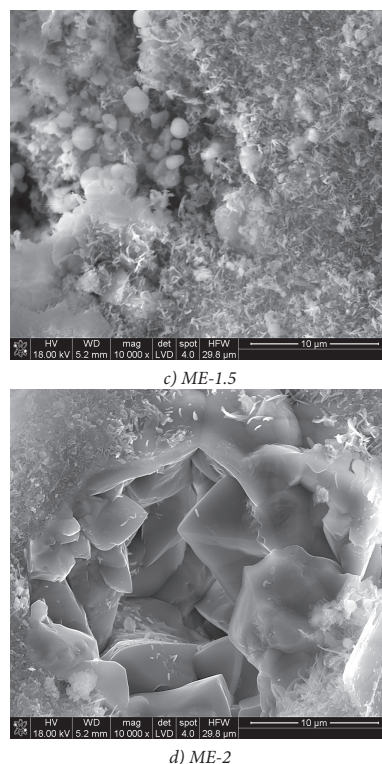
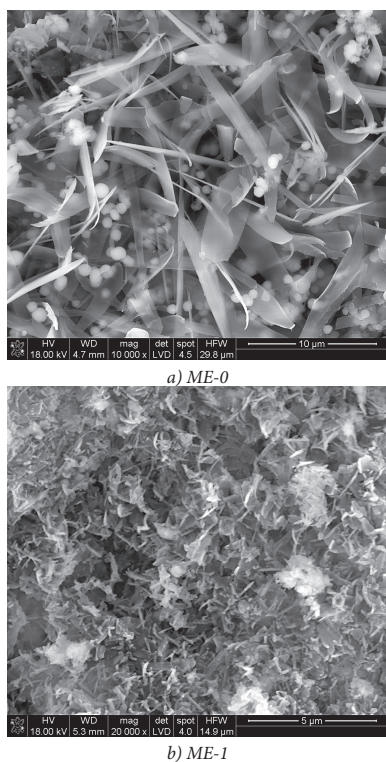


Fig. 4 Microstructure of investigated materials  
4. ábra A vizsgált anyagok mikroszerkezete

Investigations by the thermal methods DTA and TG are conducted using the device NETZSCH STA 449 F30 *Jupiter*. Measuring is done on the carrier DTA-TG, in the temperature range 20–1000°C, the heating rate 10°C/min, in the presence of air with  $\text{Al}_2\text{O}_3$  in the crucibles. Test results in the form of DTA and TG curves are shown in Fig. 3.

The microstructure of autoclaved materials is analysed using a scanning microscope NOVA<sub>NANO</sub> SEM 200 (FEI COMPANY) equipped with a micro-analyser EDAX. Samples to be tested are first sprinkled with coal powder. The most distinctive images of microstructure of investigated sample profiles are shown in Fig. 4.

## 5. Discussion

The analysis of X-ray test data (Fig. 1) reveals that for each investigated sample the basic product of synthesis will be hydrogarnete, accompanied by tobermorite. Furthermore, for hydrogarnets we observe most characteristic line shifting for the specified value of 'd', which evidences the formation of solid solutions. The locations of reflexes from the planes (2,1,1) and (6,4,0) and their half-width indicate that in each case we obtain a hydrogarnete, whose composition varies in accordance with the Vegard's law (correlation factor 0.999), for  $x$  ranging from 2.38 to 2.65. It is reasonable to suppose that the composition of this product falls between the compositions of hydrogarnets given by the formulas:  $\text{C}_3\text{Al}_2(\text{SiO}_4)_{0.62}(\text{OH})_{9.5}$  and  $\text{C}_3\text{Al}_2(\text{SiO}_4)_{0.35}(\text{OH})_{10.6}$ . Actually, that means that in each case the recorded extent of silica substitutions ('hydrogarnet substitution') is less than the predicted (theoretical) value [8, 12].



The analysis of IR spectra in Fig. 2 reveals that the band responsible for OH<sup>-</sup> group substitutions is that registered for the wave number 3666 cm<sup>-1</sup>. Its intensity grows with the increasing number of substitutions, and its small half-width is indicative of the fact that OH<sup>-</sup> groups are distributed in an ordered manner within the structure of the material. The spectral line 3570 cm<sup>-1</sup> displays similar though less pronounced behaviour. The spectral line corresponding to the wave number 3400 cm<sup>-1</sup> displays an entirely different behaviour and the large band half-width indicates that it can be associated with tensile vibrations of OH<sup>-</sup> groups, distributed in the statistical manner in the structure of the material, or, more probably, it can be associated with water molecules physically connected with the material's surface. This conclusion can be drawn from the changes of the band intensity correlated with that of the spectral line 1630 cm<sup>-1</sup>, associated with deformative vibrations of H-O-H within the water molecule [13].

The IR spectrum for the sample ME - 0 reveals a spectral line 973 cm<sup>-1</sup>, indicative of the occurrence of asymmetric tensile vibrations in Si-O and the spectral line 458 cm<sup>-1</sup> associated with bending vibration in SiO<sub>4</sub> tetrahedrons, which is a distinctive feature of ortho-silicates, including hydrogarnets. The spectrum also reveals the presence of a doublet of spectral lines 780-800 cm<sup>-1</sup>, indicative of vibrations symmetrically stretching the Si-O-Si bridges, which is a distinctive feature of β-quartz. This doublet is absent in subsequent spectra, which suggests that the samples do not contain free quartz. Furthermore, a spectral line is revealed corresponding to the wave number 914 cm<sup>-1</sup>, characteristic of Al-OH vibrations (LK<sub>Al</sub> = 6, octahedron). The band intensity tends to increase in subsequent spectra, which can indicate that a part of OH<sup>-</sup> groups are associated with aluminium, specifically with AlO<sub>4</sub> tetrahedrons. Of particular importance is the fact that position of a band with the highest intensity tends to shift from the wave number 973 cm<sup>-1</sup> (sample ME - 0) to 957 cm<sup>-1</sup> (sample ME - 2), which can indicate that substitutions of OH<sup>-</sup> groups in a large extent depolymerize the structure, which tends towards the ideally mono-silicate structure. Furthermore, the spectra reveal the lines for the wave number 1432 cm<sup>-1</sup>, associated with CO<sub>3</sub><sup>2-</sup> groups, which is confirmed by the presence of carbonates.

DTA and TG curves for the investigated materials, shown in Fig. 3, are very similar. That can indicate that the analysed samples have a similar composition in qualitative terms. Quantitative differences involve the intensity and temperature of the predominant endothermic peak associated with dehydroxylation of hydrogarnets. The enhanced peak intensity and the increase of its maximum temperature from 344.4°C (sample ME - 0, x = 0) to 366.4°C (sample ME - 2, x = 2) evidence the formation of the series of hydrogarnets with the decreasing number of silicate substitutions. However, the scale of the temperature increase suggests that the number of 'hydrogarnate substitutions' 4(OH)<sup>-</sup> ↔ [SiO<sub>4</sub>]<sup>4-</sup> seems inadequate in relation to the specified value of x, determining the composition of reaction mixtures. That is why the chemical composition of thus formed hydrogarnets does not represent their predicted (theoretical) composition [14].

The microstructural analysis of investigated samples (Fig. 4) reveals the co-existence of two basic products synthesised under hydrothermal conditions: tobermorite formed in the shape

of elongated crystals, and hydrogarnets with a typical crystal morphology. In a majority of investigated samples these products form a heterogeneous mixture of statistically distributed crystals.

One can conclude, therefore, that regardless of the initial composition of reaction mixtures, in each case the synthesis conducted under hydrothermal conditions will yield two products with crystalline structure: tobermorite and hydrogarnate, containing silicon. However, the extent of silicate substitutions in the structure of hydrogarnets is lower than expected and fails to reflect the chemical composition of mixtures used in the process of synthesis, no matter what the time of duration.

## Acknowledgement

*This study is a part of a research project sponsored by the Polish Ministry of Science and Education from the resources allocated for years 2011-2013, as a project No N506 282140.*

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## Ref.:

**Pytel**, Zdzisław: *Synthesis of hydrogarnets in the system Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>-SiO<sub>2</sub>-CaO-H<sub>2</sub>O under hydrothermal conditions*  
 Építőanyag – Journal of Silicate Based and Composite Materials,  
 Vol. 71, No. 6 (2019), 180–183. p.  
<https://doi.org/10.14382/epitoanyag-jsbcm.2019.31>