Materials Science-Poland, Vol. 24, No. 2/1, 2006

Influence of tribomechanical milling and activation of primary mixtures on the synthesis of calcium silicate hydrates

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Minerals of the tobermorite group with double [Al^{3+}+Na^+] substitutions were synthesized using both, non-ground raw mineral mixtures and mixtures ground in a colloidal mill. The synthesis of calcium silicate hydrate is more effective when dry primary mixtures ground in a colloidal mill are taken, because compositions of higher degree of crystallinity are synthesized under the same conditions. In the latter case, tobermorite is formed after 24 h. It is thought that grinding a mixture of CaO, SiO_2 and Al_2O_3 in a colloidal mill induces activation centres which later activate synthesis via hydrothermal processing. It is reasonable to grind dry reactants used for synthesising tobermorite in a colloidal mill before hydrothermal processing. Under our experimental conditions, tobermorite was formed more effectively when the specific surface was lower than 547 $m^2 \cdot kg^{-1}$. Use of finer particles of reactants does not enhance the reaction rate because of the stabilising influence of $(0.8–1.5)CaO \cdot SiO_2 \cdot (0.5–2.5)H_2O$ (C–S–H (I)) on the overall reaction rate of the synthesis of tobermorite.

Key words*: [Na^+ + Al^{3+}]- inserted tobermorite; hydrothermal synthesis; mechanical processing*

1. Introduction

Tribomechanics is a branch of physics investigating phenomena appearing during grinding in dynamic conditions. Tribomechanical milling and activation at room temperature has been investigated for several primary material mixtures ground in colloidal mills. The results have demonstrated that tribomechanical processing is the cause of a noticeable decrease in particle size, changes in particle distribution and increase of their specific surface area. Mechanical activation of solid-phase reactions was first investigated almost one and a half centuries ago. Along with the development of theo-

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retical mechanochemistry, its technical use in modifying mineral resources, chemical catalysis, and syntheses of new materials were studied.

Mechanical impact on reagents in solid phases comes in various forms: dispersing larger particles by grinding or by blows, pressing of powders, cold processing of metallic and non-metallic materials, forming by blast, etc. The practical importance of dispersion is that a decrease of the particle size results in an increase surface areas and, consequently, in shortening of the diffusion paths of the reagents. Due to this, several process occur as lower temperatures, hence the energy used can be lower [1, 2].

Of all activating methods, dispersion or grinding is used most often. A decrease of particle dimensions is not the only result of the grinding process. As the particle size decreases, the structure of the crystal lattice may change, energy levels are modified, and electron emission and other processes may appear.

Under forces exerted by grinding bodies, solid particles undergo elastic and, later, plastic deformation until the pressure becomes larger than the material can withstand. The particles then split into much smaller ones, and those smaller particles undergo a further dispersion at a certain rate. The mechanical energy is thus distributed into elastic and plastic deformations, while new surfaces appear due to breaking chemical bonds and movement of particles [1].

A reduction of particle size often causes an increase in the process rate because the id decreases the diffusion paths of reactants and products of a reaction to and from surfaces. In practice, the reaction rate depends on the sizes of particles of all reactants, in rare cases it depends on only one of the components [1]. Unfortunately, all mechanical dispersion methods have a common disadvantage which becomes especially noticeable while processing materials sensitive to micro-dashes. Therefore, along with mechanical milling, ultrasound and electro-erosive treatment is used [3].

Phases consisting of CaO, SiO_2, and H_2O are called calcium silicate hydrates (KSH). In industry, tobermorite is usually obtained by processing mixtures of $Ca(OH)_2$ and SiO_2 in an autoclave, at a temperature of saturated water vapour from 120 °C to 200 °C. In our experiments, tobermorite was synthesized by processing a mixture of CaO, SiO_2 and water, taken in various proportions of calcium hydroxide and silica, in a Fritch–Pubversirte planetary mill. The frequency of drum revolutions was 700 rpm. According to the chemical reaction of tobermorite synthesis

$$5Ca(OH)_2 + 6SiO_2 \rightarrow Ca_5(OH)_2Si_6O_{16}\cdot 4H_2O$$

the stoichiometric CaO to SiO_2 molar ratio is $C/S = 5/6$. The ratio of water to solid reagents was $V/K = 1/4$. Examining X-ray diffraction patterns, it was found that after 45 minutes milling, a peak for tobermorite appears, becoming more intense after 1.5 h, whereas the $Ca(OH)_2$ peak gradually fades. After 5 hours, the primary materials react almost completely and convert into tobermorite. This has been proved by comparing samples of tobermorite obtained mechanochemically with the ones obtained in the autoclave: deviations from stoichiometry were insignificant [4].

The effect of Al_2O_3 and NaOH on the formation of 1.13 nm tobermorite under hydrothermal conditions was studied. Also, the ion exchange capacity of tobermorites with and without Al^{3+} as well as with double $[Na^+ + Al^{3+}]$ substitutions in relation to heavy metal ions was investigated [7]. The effect of inorganic additives on the system $CaO–SiO_2–H_2O$ has been investigated by many authors [8–10]. Among inorganic additives containing aluminium and sodium, oxides play a significant role in the mechanism and kinetics of the synthesis of calcium silicate hydrate [11].

There has been a lack of data in the literature on the influence of mechanical activation of primary mixtures by using $[Na^+ + Al^{3+}]$ ions as additives in tobermorite synthesis. Therefore, the aim of this work was to synthesize tobermorite group minerals with $[Na^+ + Al^{3+}]$ ions inserted into the crystalline lattice and to investigate the influence of their mechanical processing on tobermorite synthesis.

2. Materials and methods of testing

Reactants of p.a. purity were used in this work: silica gel $SiO_2 \cdot nH_2O$ (loss on ignition – 23.5%, SiO_2 – 76.5%), amorphous Al_2O_3 (obtained by heating $Al(OH)_3$ at 550 °C for 0.5 hour, specific area $S = 505\ m^2 \cdot kg^{-1}$), calcium oxide (CaO – 98%, obtained by calcination of calcium carbonate at 1000 °C), NaOH aqueous solution (33.5 wt.%).

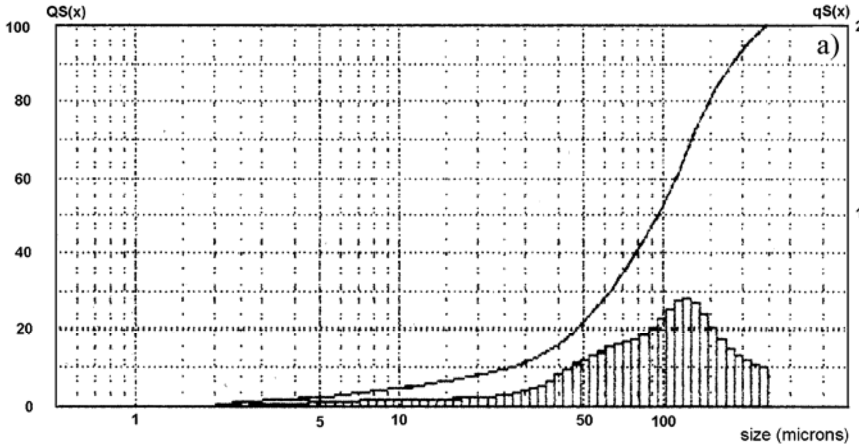
X-ray diffraction analysis was conducted with a DRON-6 diffractometer. The investigation was carried out within a 2Θ angle range of 4–60°, with Ni-filtered CuK_α radiation. A DuPont 990 thermal analyser was applied for differential scanning calorimetry (DSC) studies, with the rate of temperature increase of 10 °C/min and maximum temperature of 1200 °C. The specific surface area of the raw materials was determined by Blain's method. Particle distribution and the average diameter of grains were determined by means of a laser granulometer ("FRITCH Analysette 22", Germany). Samples were kept in water for 20 s. The mode of ultrasound dispersion was 250 relative units. The mixer turning speed was 300 rpm. The mode of pump operation was 200 relative units. The synthesis of calcium silicate hydrates was executed by mixing suspensions in a 250 ml autoclave, the turning speed of which was 16 rpm.

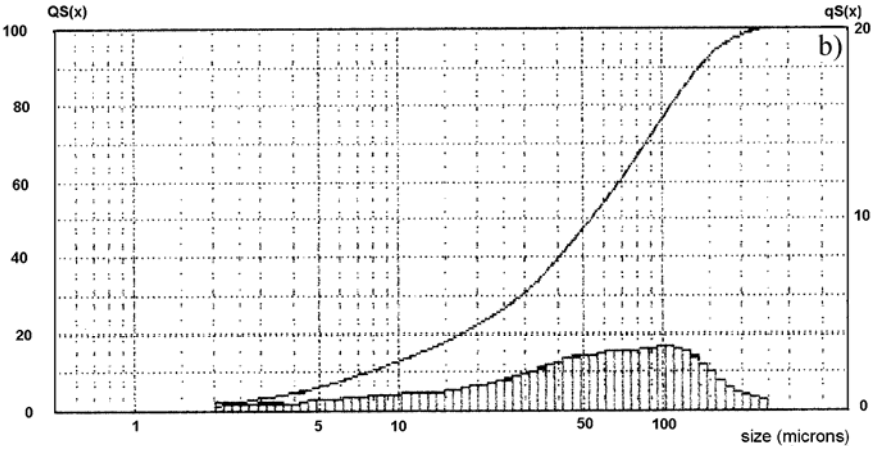
3. Results and discussion

The rate of reaction depends primarily on the particle sizes of primary components. For the synthesis of tobermorite with inserted $[Na^+ + Al^{3+}]$ ions, a mixture of primary components (1) ($S = 212\ m^2 \cdot kg^{-1}$) was used, its composition being: $C/(S + A) = 0.83$ and $A/(S + A) = 0.025$ in molar rations (here C, S and A stand for number of moles of CaO, SiO_2 and Al_2O_3, respectively). A part of the mixture was ground using different grinding modes in a colloidal mill, producing three additional mixtures (2), (3), and (4), with $S = 547$, 750, and $1040\ m^2 \cdot kg^{-1}$, respectively.

Results obtained on samples synthesised with $[Na^+ + Al^{3+}]$ added were compared with those obtained without the addition. In the latter case, the molar ratios were *C*/*S* = 0.83, and the specific surface areas were 230, 650, and 900 kg/m^2. The distribution curves and average grain diameters were determined for non-ground and mechanically processed mixtures 2, 3, and 4 (Fig. 1). According to granulometric analysis, it can be seen that although the character of the granulometric distributions is similar, in mixture 1 domensions of most particles range from 114 to 133μ, whereas in mixture 2 from 97 to 114 μ, in mixture 3 from 60 to 70 μ, and in mixture 4 from 50 to 60 μ.

According to the X-ray diffraction analysis, CaO prevailed in the non-ground mixture. After grinding in a colloidal mill, amorphous silica gel, CaO and $Ca(OH)_2$ prevailed (Fig. 2, curves 2, 3). Grinding, resulting in higher specific surfaces of the samples (mixture 4), causes almost all CaO convert into $Ca(OH)_2$ with H_2O taken from silica gel (Fig. 2, curve 4).





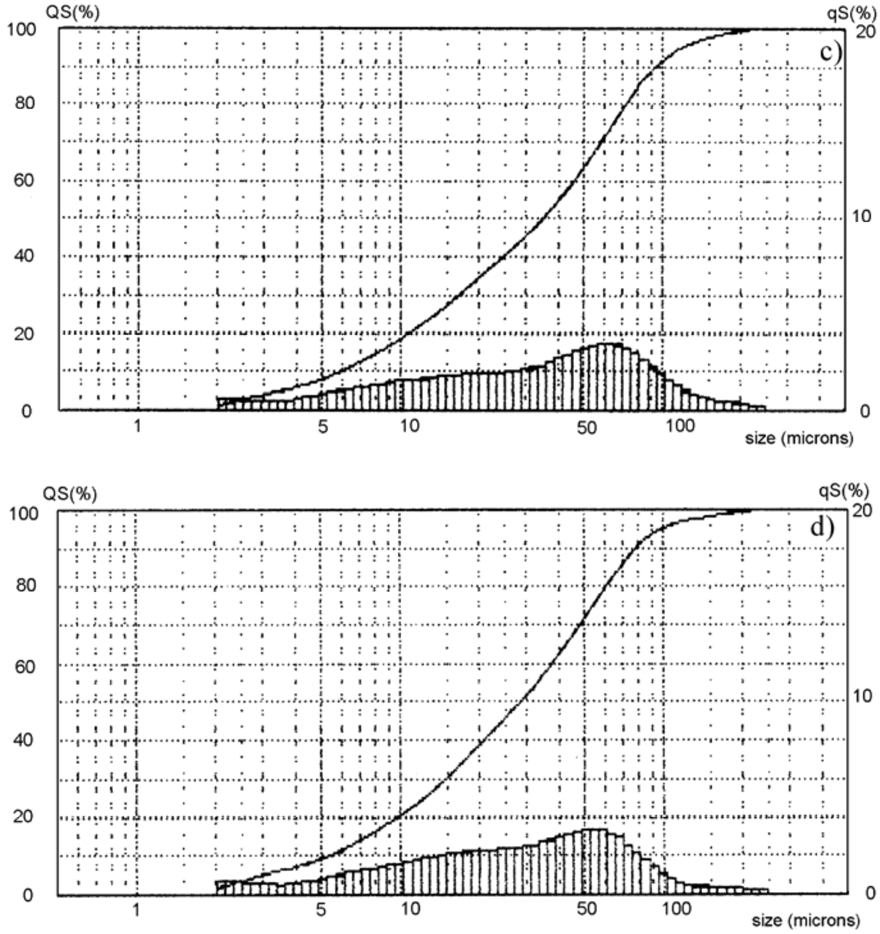


Fig. 1. Distribution of the particles in the mixture ($SiO_2{\cdot}nH_2O$ + CaO + Al_2O_3).
Specific surfaces *S* ($m^2{\cdot}kg^{-1}$) of the mixtures were: a) 212, b) 547, c) 750, d) 1040

Therefore, the cubic lattice of CaO in the primary mixtures transforms into the hexagonal $Ca(OH)_2$ lattice during grinding and dispersing due to the chemical reaction. According to the literature [5], the unit cell volume practically does not change during the transition. The noticed increase in the volume of the system is therefore related to the dispersion of CaO during the topochemical reaction and the increase in intergrain porosity.

After conducting the thermal analysis of the three dry mixtures, it appeared that the DTA and TG curves are nearly identical for all the mixtures (Fig. 2, b). The endothermic peak at 480 °C is due to the dehydratation of $Ca(OH)_2$. Since dry mixtures containing either CaO and $SiO_2{\cdot}nH_2O$, or CaO + $Ca(OH)_2$ and $SiO_2{\cdot}nH_2O$ were used, water in the silica gel had apparently reacted with CaO and formed $Ca(OH)_2$. For this reason, the DSC and TG curves of all mixtures were very similar.

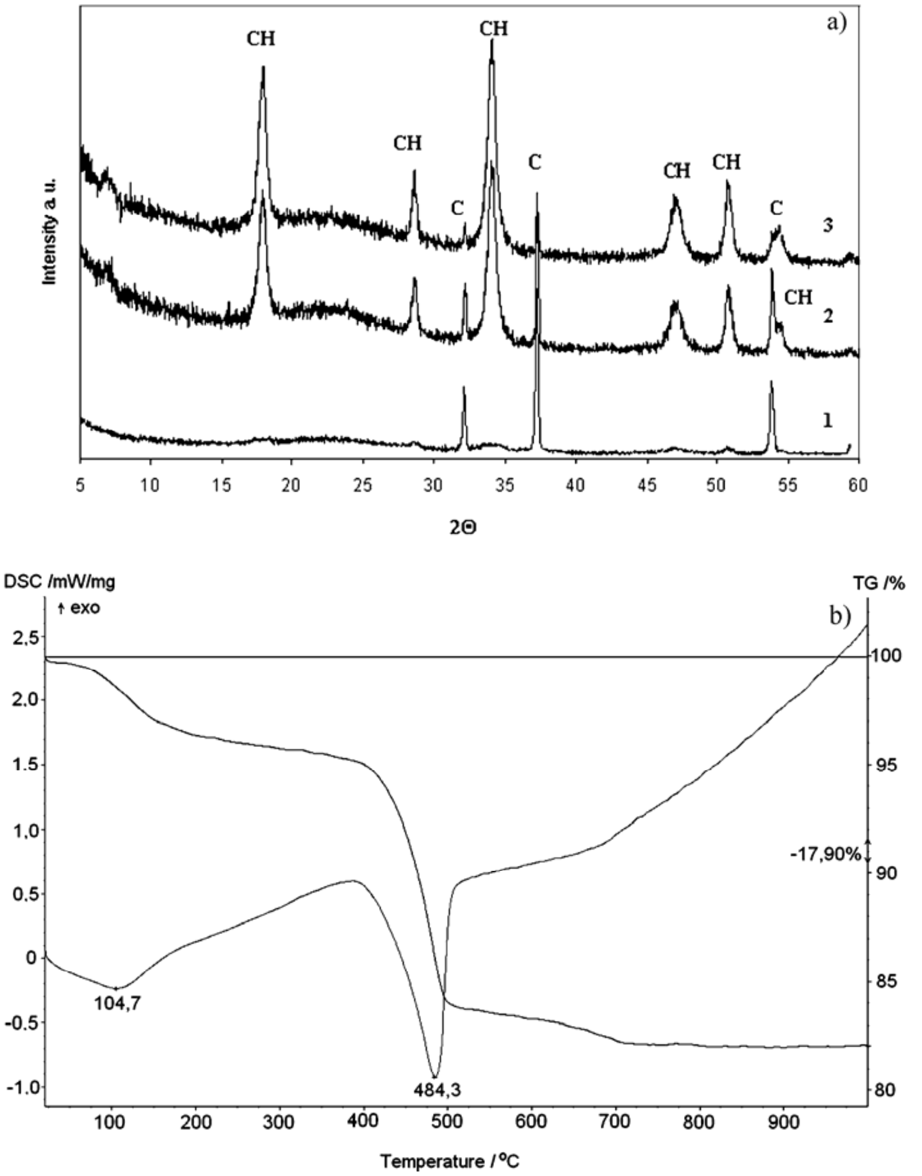


Fig. 2. X-ray diffraction patterns (a) and thermogram (b) of initial dry mixtures (CaO, amorphous $SiO_2 \cdot nH_2O$ and Al_2O_3): 1 – non-ground with $S = 212\ m^2 \cdot kg^{-1}$, 2 – ground to $S = 547\ m^2 \cdot kg^{-1}$, 3 – ground to $S = 750\ m^2 \cdot kg^{-1}$, 4 – ground to $S = 1040\ m^2 \cdot kg^{-1}$; CH – $Ca(OH)_2$; C – CaO

Mechanically activated primary mixtures necessary for KSH synthesis, of different degree of dispersion, were mixed with water in the water (W) to solid suspension (S) weight ratio $W/S = 10$. This was supplemented by an addition of 5% Na_2O according to the mass of the dry materials. The suspension so obtained was mixed before the synthesis. The hydrothermal synthesis was accomplished in 4, 6, or 24 hours, at

175 °C or 200 °C. After hydrothermal processing, the products of synthesis were filtered and dried at 105±5 °C.

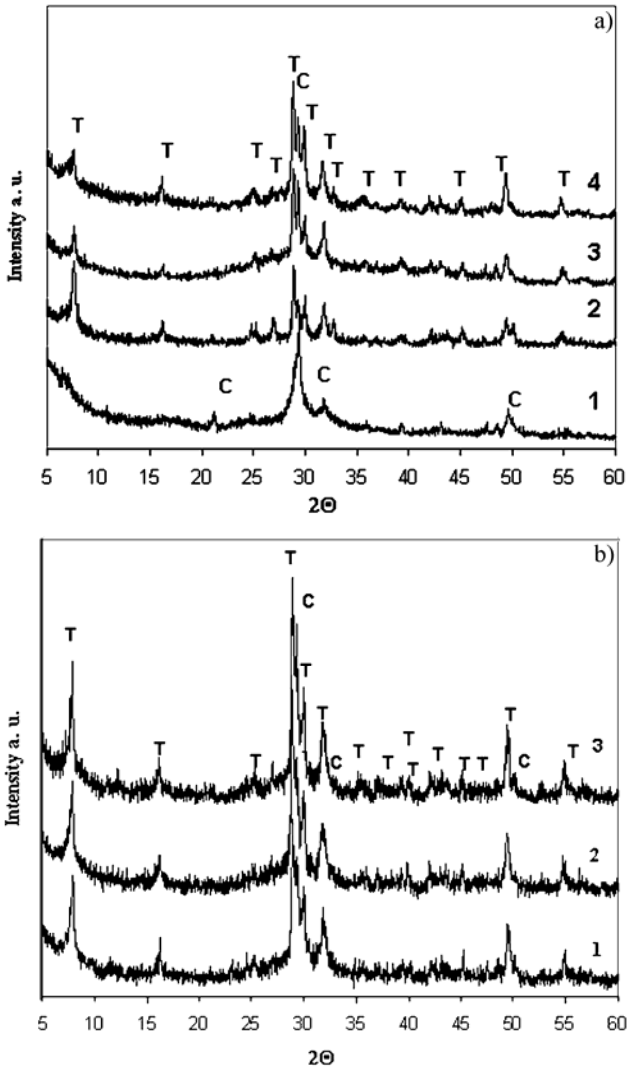


Fig. 3. X-ray diffraction patterns of calcium silicate hydrates modified with [Na^+ + Al^{3+}] (a) and without additives (b), synthesized for 24 hours at 175 °C. The specific surfaces S ($m^2 \cdot kg^{-1}$) were: a) 1 – 212, 2 – 547, 3 – 750, 4 – 1040, b) 1 – 230, 2 – 625, 3 – 900 .
T – tobermorite; C – (0.8–1.5)$CaO \cdot SiO_2 \cdot$(0.5–2.5)H_2O (C–S–H (I))

From a comparison of X-ray diffraction patterns (Fig. 3), it has been established that addition of [Na^+ + Al^{3+}] slows down tobermorite formation, and that the fineness of the reactant mixture affects the product formation. A large amount of crystalline tobermorite without any [Na^+ + Al^{3+}] addition (Fig. 3b) is formed in all cases and the effect of grinding is small. Using a non-ground mixture (curve 1) or the one with a 900 $m^2 \cdot kg^{-1}$ specific surface area (curve 3) results, however, in no tobermorite C–Si– H (I).

It can be noticed that the fineness of the reactant mixtures does affect $[Na^+ + Al^{3+}]$ substituted tobermorite synthesis. When using materials of a greater specific surface (750 and 1040 $m^2 \cdot kg^{-1}$) for synthesis (Fig. 3), calcium silicate hydrates of a lower degree of crystallinity were formed (the peaks in X-ray diffraction patterns are less intense 1.13; 0.297 0.280 nm), i.e. the processes proceeded more slowly and $(0.8–1.5)CaO \cdot SiO_2 \cdot (0.5–2.5)H_2O$ (C–S–H (I)) has not had time to recrystallise into tobermorite.

Butt and Raskovic [6] recommend using quicklime for silicate hydrate synthesis because fresh slack lime has a larger specific surface and exhibits a better reactivity, solubility, and activity than $Ca(OH)_2$ prepared in advance and well crystallised.

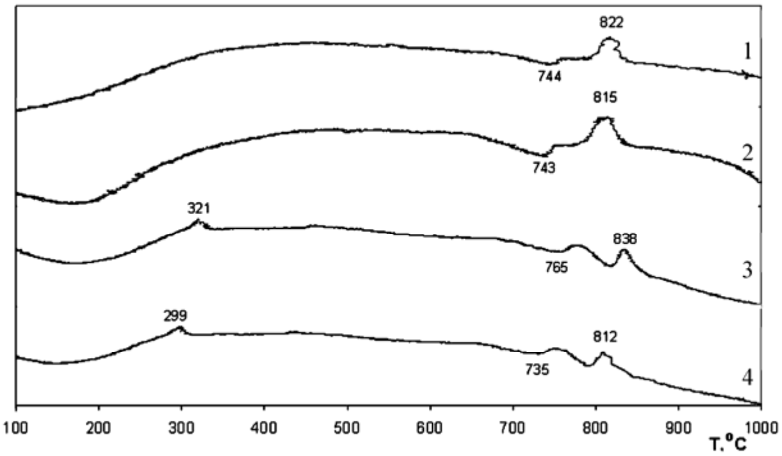


Fig. 4. Thermograms for modified calcium silicate hydrate for a primary mixture with the specific surface $S = 1040\ m^2 \cdot kg^{-1}$ and synthesis modes: 1 – 175 °C, 24 h, 2 – 175 °C, 4 h, and in case of a primary mixture with the specific surface of $S = 750\ m^2 \cdot kg^{-1}$: 3 –175 °C, 24 h, 4 –175 °C, 4 h

Along with X-ray diffraction pattern analysis, thermal analysis has also been conducted (Fig. 4). The analysis confirms the X-ray data: when the specific surface of the mixture is lower than 547 $m^2 \cdot kg^{-1}$, i.e. when CaO, SiO_2 and Al_2O_3 prevail in the mixture, products with a higher degree of crystallinity are synthesized. In the picture above, all the exothermic peaks in the range 812–838 °C suggest the crystallisation of C–S–H (I). The endothermic ones at 794 and 818 °C point to the decomposition of $CaCO_3$, and the peaks in the rage 735–765 °C are associated with the dehydration of tobermorite.

We can assert that in mixtures with large specific surfaces SiO_2 dissolves very rapidly in an autoclave while increasing the temperature, and reacts with $Ca(OH)_2$ while the semi-crystal C–S–H (I) is forming up. The crystallisation of this combination into 1.13 nm tobermorite takes a longer time. In addition, Al^{3+} ions insert themselves into the C–S–H(I) composition, and are located among the chains of the crystal grid thus, stabilising them.

4. Conclusions

It seems reasonable to grind dry component mixtures used for synthesising [Na^+ + Al^{3+}]-substituted tobermorite in a colloidal mill, before hydrothermal processing, but under experimental conditions of this work tobermorite was formed more effectively when the specific surface was lower than $S = 547\ m^2 \cdot kg^{-1}$. Use of mixtures of finer primary materials is useless because of the stabilising effect of C–S–H (I) on the kinetics of tobermorite formation.

It has been determined that the addition of [Na^+ + Al^{3+}] slows down tobermorite formation. In this case, the fineness of primary material mixture strongly influences product formation. High crystalline tobermorite forms in all cases without the addition of [Na^+ + Al^{3+}] and the grinding influence of the primary material mixture is small.

When a non-ground mixture of the primary materials (with [Na^+ + Al^{3+}] added) is synthesised for 24 h at 175 °C, products with a higher degree of crystallinity are formed than in case of mixtures ground in a colloidal mill. [Na^+ + Al^{3+}]-substituted calcium silicate hydrate synthesis is more effective when dry primary mixtures ground in a colloidal mill are taken because compositions with a higher degree of crystallinity are synthesized in the same conditions. In this case, [Na^+ + Al^{3+}]-substituted tobermorite forms after 24 h. It is believed that grinding a mixture of CaO, SiO_2 and Al_2O_3 in a colloidal mill induces activation centres which later activate the synthesis in the process of hydrothermal processing.

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Received 30 September 2005
Revised 21 February 2006