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THE INFLUENCE OF SYNTHESIS PARAMETERS ON CALCIUM SILICATE SPECIES THERMAL CRYSTALLIZATION

A. R. ISAHAKYAN¹, N. H. ZULUMYAN¹, A. M. TERZKYAN¹,
S. A. MELIKYAN¹ and H. A. BEGLARYAN^{1,2}

¹M. G. Manvelyan Institute of General and Inorganic Chemistry of NAS RA

Bld. 10, Lane 2, Argutyan Str., Yerevan, 0051, Armenia

Fax: (374-10) 231275, E-mail: Isahakyananna@yahoo.com

²Yerevan State University

1, A. Manoukian Str., Yerevan, 0025, Armenia

This paper is devoted to the investigation of the interaction between a silica hydrogel species derived from a serpentine-group mineral $(\text{Mg}(\text{Fe}))_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ and calcium hydroxide $\text{Ca}(\text{OH})_2$ in aqueous medium in air at ambient pressure depending on stirring time and $\text{Ca}(\text{OH})_2$ concentration. The aim of the research was to study the influence of stirring time and $\text{Ca}(\text{OH})_2$ concentration on the yield and crystallinity of calcium silicate species, particularly, β -wollastonite produced by thermal crystallization of amorphous calcium hydro- and hydroxosilicates, which had been previously precipitated in the boiling aqueous suspension prepared from the mentioned reagents. The experimental data have revealed the optimal parameters guaranteeing the highest portion of β -wollastonite in the final product and have suggested possible mechanisms of processes occurring during the precipitation and thermal crystallization.

Figs. 6, references 29.

Owing to a series of remarkable properties, such as a low coefficient of thermal expansion, low thermal conductivity, thermal stability, low dielectric constant, low dielectric loss, shrinkage, as well as extreme whiteness, a synthetic β -wollastonite (β - CaSiO_3) has become an interesting material for various domains of modern engineering. It is used in ceramic [1, 2], as an insulator of high frequency [3], in medical materials for artificial bones and dental roots [4-6], in paint and frictional materials, as a filler in resins and plastics [7, 8].

One of the most popular routes to β -wollastonite synthesis consists of two steps: (i) the precipitation of intermediate solid phase in aqueous medium via the interaction of calcium hydroxide $\text{Ca}(\text{OH})_2$ or calcium salts with a silica-containing reagent (quartz, diatomite or various silica-

containing industrial wastes as well as tetraethoxysilane (TEOS) $\text{Si}(\text{OC}_2\text{H}_5)_4$, and (ii) calcination (900-1400°C) of the intermediate synthesized in the first stage [9-12]. Commonly, the intermediate phase is produced either by autoclave treatment [13-15] or sol-gel syntheses [11, 12, 16, 17] that are both energy-consuming.

Hydrothermal environments are required for the formation of infinite silicate chains with a three-tetrahedron repeat, similar to chains in wollastonite¹, which are intrinsic in such calcium silicate hydrates as tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18} \cdot 5\text{H}_2\text{O}$) and xonotlite ($\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$), that can be easily transformed into β -wollastonite by subsequent heating [18-20].

The sol-gel processing associated with wollastonite syntheses is a multi-step procedure frequently combined with *combustion techniques using organic compounds as a fuel* (sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, glycine $\text{C}_2\text{H}_5\text{NO}_2$) and a precursor of SiO_2 (TEOS), and calcium nitrate $\text{Ca}(\text{NO}_3)_2$ as a source of calcium cations [16, 17]. Naturally, subsequent gel evaporation and heat treatment of the synthesized intermediates at 900°C and higher for many hours (up to 12 hours) generate a large amount of gases as oxides of carbon CO_2 and nitrogen NO_2 that is undesirable [11, 16, 17].

Recent studies have shown that autoclave treatment and difficulties associated with the complicated sol-gel syntheses for β -wollastonite production can be avoided if a new species of silica xerogel produced from serpentinites² is involved in the precipitation process as a raw material with $\text{Ca}(\text{OH})_2$ in the presence of sodium hydroxide NaOH [21]. The latter promotes the faster and deeper progress of the reaction between the SiO_2 and $\text{Ca}(\text{OH})_2$ requiring less activation energy.

One of the main microscopic factors accounting for the small energy input for β -wollastonite production from the above mentioned silica xerogel is the *chain-like* silicate units bound up with each other by unsaturated (weaker) bonds inherent in this species of silica [21-23]. While being stirred with the silica xerogel and $\text{Ca}(\text{OH})_2$ in aqueous suspension, NaOH by penetrating into the structure of the SiO_2 interacts with Si-O-H silanol groups and simultaneously breaks the relatively weak $\text{Si-O}(\text{Si})$ siloxane bonds, thus reproducing silicate anions of different complexities [21]. The silicate anions released are easily involved in the interaction with $\text{Ca}(\text{OH})_2$. The amount of β -wollastonite synthesized from the intermediates by heat-

¹ Wollastonite is a calcium metasilicate belonging to the group of pyroxenoids, i.e. silicates with a chain structure of ilicon-oxygen anions.

² Serpentine is a rock largely composed of serpentine group minerals $(\text{Mg}(\text{Fe}))_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$ belonging to phyllosilicate group, layer-type silicates or sheet silicates in other words.

treatment is determined by the number of *chain-like* silicate anions produced during stirring [21].

The silica constitutes up to 6% of the silica hydrogel whence it is separated by dehydration. In turn, this silica hydrogel is produced by the polycondensation of silicic acids formed from ortho- $[\text{SiO}_4]^{4-}$, di- $[\text{Si}_2\text{O}_7]^{6-}$, $[\text{Si}_3\text{O}_{10}]^{8-}$, $[\text{Si}_4\text{O}_{13}]^{10-}$ and other silicate anions less polymerized and having oligomeric dimension which have been leached from the dehydrated structure of serpentine minerals [24-26]. Hence, the structure of the silica xerogel obtained from the silica hydrogel is made up of mono- $[\text{SiO}_4]$, one-, two-dimensional and oligomeric silicate units that distinguishes it from all other species of traditional silicon dioxide. Despite the fact that the Si–O(Si) bonds arisen between the silicate anions during the polycondensation are less saturated, i.e. weaker than the primary Si–O(Si) ones intrinsic in the silicate oligomers formed in magma prior serpentinization, they must have been marginally strengthened by the silica hydrogel dehydration, and NaOH addition is therefore required for both the cutting of siloxane bonds slightly strengthened and silicate anions releasing.

The knowledge about the structural particularities of the SiO_2 and a deeper insight into how NaOH affects the interaction mechanism of the SiO_2 with $\text{Ca}(\text{OH})_2$ have suggested replacing the silica xerogel with the silica hydrogel. This replacement has allowed excluding NaOH participation in the *β-wollastonite* synthesis thus simplifying the procedure of the intermediate phase precipitation at ambient pressure.

In order to find optimal parameters providing higher yields of *β-wollastonite* in the final product, a number of intermediates have been prepared by the interaction of the silica hydrogel derived from a serpentine group mineral with $\text{Ca}(\text{OH})_2$ changing the molar ratio of the initial reagents and stirring time. Thermal crystallization of the synthesized intermediates into calcium silicate species has been studied by differential thermal analysis (DTA), X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR) and scanning electronic microscopy (SEM).

Experimental

A serpentinite sample located in Shorja (Armenia) was used as a precursor for the silica hydrogel production using the method described in the work [24].

Reagent grade CaO 98% (248568 Sigma-Aldrich) previously annealed at 1000°C for 30 min was used as a raw material for the $\text{Ca}(\text{OH})_2$ production. A serpentinite sample located in Shorja (Armenia) was used as a precursor of the silica hydrogel.

Four samples of suspension with liquid/solid ratio of 15 were prepared from the primary mixtures of $\text{Ca}(\text{OH})_2$ and the silica hydrogel

with SiO₂ and CaO molar ratios (hereinafter referred to as S:C for short) of 1:1.0, 1:1.4, 1:1.6, 1:2.0. The S:C of 1:1.0 is the stoichiometric ratio required for wollastonite synthesis, the S:C of 1:1.4 used to be the optimal ratio providing the highest yields of β -wollastonite in the case of using the amorphous silica separated from the silica hydrogel, the S:C of 1:1.6 is the ratio allowing to study the effect of CaO excess on the calcium silicate species formation on heating, the S:C of 1:2.0 is the ratio which is supposed to lead to larnite Ca₂SiO₄ formation. When the silica hydrogel was metered, SiO₂ content in the hydrosilicagel that is 5.8% was taken into consideration in order to guaranty the appropriate molar ratio of SiO₂ to CaO and liquid/solid ratio. Each of the prepared samples was put into a vessel and heated up to the temperature of 95°C (boiling point). The boiling samples were stirred with mechanical stirrer in air for 15 *min* at ambient pressure. Then each of the slurries produced in the mixer was filtered and a gel-like mass remained in the filter was dried at the temperature of 60–80°C for 24 *hours* in a dryer type KBC G – 100/250 manufactured by Premed (Warszawa, Poland). As a result, a white precipitate powder was produced. The second, third, fourth and fifth series of experiments were repeated for all the four samples by increasing the stirring time: 30, 60, 90 and 120 *min*.

All the precipitate samples were studied in air by DTA from room temperature up to 1000°C. The mass of the test specimen was 300 *mg*. DTA and thermogravimetry (TG) measurements were performed by using a Derivatograph Q–1500D equipment (MOM company, Hungary) in air at a heating rate of 10°C *min*⁻¹. The samples of equal mass were investigated in platinum crucibles. The mass of the test specimen was 250 *mg*.

All the precipitate samples and the samples produced after DTA were studied in air by XRD analysis. Of the precipitate samples the four ones produced by stirring for 15 *min* were chosen to be annealed at different temperatures in the range from 700 up to 1000°C for 30 *min* and also subjected to XRD analysis. The temperature values were set and controlled by using High temperature muffle furnace type BR-14S-5 (China). The mass of the each test specimen was 220–240 *mg*. X-ray powder diffraction (XRPD) measurements were made on a Dron-3 diffractometer (Russia) equipped with nickel filter, under the following conditions: CuK α -radiation; power supply 25 *kV*/10 *mA*; angular range 2 θ =8–80° at the room temperature in air. All the reflections were identified and interpreted using the ICDD-JCPDS database of crystallographic 2008. The average crystallite size (*L*) in the final sample heated at 1000°C was automatically estimated by Match! software using the Scherer formula:

$$L = 0.94 \lambda / \beta \cos \theta,$$

where λ is the X-ray wavelength in Å, β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians [27].

The final product demonstrating the highest yield of β -wollastonite was studied by the FT-IR method. The FT-IR spectrum was recorded using “Nexus” spectrometer of the Thermo Nicolet Corporation (USA) (ATR method) in the range of 650–1600 cm^{-1} with the resolution of 2 cm^{-1} .

SEM analysis was also used to characterize the morphology of the synthesized product. It was conducted by scanning electronic microscope Tesla BS 300 (CZ). A small amount of the investigated powder was added in solvent such as ethanol and ultrasonicated for dispersion. A droplet of the suspension was dropped onto the thoroughly cleaned substrate. To avoid charge effect that will cause image distortion or drift, the sample was coated by thin layer of silver.

Results and Discussion

Independently of the molar ratios and stirring time, the reflections characteristic of calcium carbonate CaCO_3 (Card № 84–0654) are recorded for all the precipitate samples dried at 80°C (Fig. 1). There are no additional peaks in the diffraction patterns of the intermediates prepared from the initial reagents taken in the S:C of 1:1.0, 1:1.4 and 1:1.6. Besides CaCO_3 reflections, the ones of Ca(OH)_2 are traceable in the XRPD patterns of the sample with the S:C of 1:2.0 (Fig. 1). The more the stirring time, the less Ca(OH)_2 reflections intensity becomes. Because of the XRPD patterns identity for the intermediate samples with the S:C of 1:1; 1:1.4, 1:1.6 and 1:2.0 prepared by stirring for different time, the diffraction patterns of the samples precipitated by the thirty-minute stirring are represented (Fig. 1).

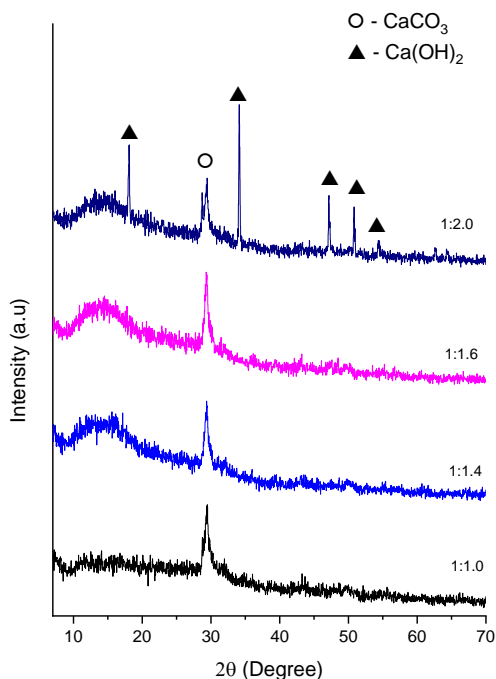


Fig. 1. XRPD patterns of the precipitate samples.

The XRPD patterns of all the precipitate samples produced after the DTA reveal that the gradual heating up to 1000°C results in the transformation of all the intermediates into calcium silicate species – largely, monoclinic *β*-wollastonite (Card №84–0654) and monoclinic larnite Ca_2SiO_4 (Card № 83–0460). The most intensive peaks of *β*- CaSiO_3 are fixed in the diffraction patterns of the samples with the S:C of 1:1.0 and 1.4. Particularly, *β*-wollastonite reflections of higher intensities are observable for the samples treated for 15 and 120 min. As for the rest of the samples, their XRPD patterns recorded after the DTA, demonstrate *β*- CaSiO_3 peaks of lower intensities along with the intensive reflections of monoclinic Ca_2SiO_4 and CaO. Moreover, additional diffraction peaks corresponding to another calcium silicate species, namely, triclinic Ca_3SiO_5 (Card № 31–0301), appeared in the diffraction patterns of the sample with the S:C of 1:2.0.

Based on the fact that the diffraction line intensity is proportional to the phase volume content, the relative concentration of each phase in the synthesized mixtures was estimated from the diffraction peaks intensities by the nonstandard method measuring the ratio of intensities of the different phases. The calculations were graphically represented in Fig. 2. According to the XRD analysis, there are some regularities between the stirring time/calcium hydroxide amount and calcium silicate species phases formation. Despite the comparatively big portion of *β*-wollastonite in the products produced from the suspensions stirred for 15 min, the increasing of

stirring time over 15 *min* leads to the reduction of β -wollastonite share in the synthesized product, but the extension of the reaction time up to 120 *min* promotes the increasing of β -wollastonite concentration in the final mixture again (Fig. 2). In turn, the increasing of Ca(OH)_2 amount in the initial solution is not desirable. The experimental results indicate, the number of CaO moles greater than 1.4 in the initial mixture (the S:C of 1:1.6 and 1:2.0) causes the appearance of CaO reflections and the formation of another species of calcium silicate abovementioned with the growth of larnite portion thereby decreasing β -wollastonite percent in the final products (Fig. 2). Thus, in the samples with the S:C of 1:1.6 and 1:2.0, Ca(OH)_2 is not completely involved in the reaction with the SiO_2 and therefore cannot provide the higher yields of larnite, its unreacted part is decomposed into CaO and H_2O on heating.

As β - CaSiO_3 peaks of higher intensity are observable for the samples with the S:C of 1:1.0 and 1:1.4 stirred for 15 and 120 *min*, the DTA curves of the samples produced after fifteen-minute stirring have been chosen for the demonstration (Fig. 3).

Each of the DTA curves for the precipitate samples chosen displays a number of endothermic events of different intensities and minima up to 800 °C and an intensive exothermic peak above 800°C (Fig. 3). The trend of the TG curves shows that all the endothermic processes are accompanied by mass loss whereas the exothermic ones occur without any mass change (Fig. 3). On the DTA curve of the sample with the S:C of 1:1.0 within the temperature range of 490-510°C there is no endotherm which is observable on the DTA curves of the samples with the S:C of 1:1.4, 1:1.6 and 2.0 (Fig. 3).

Both Ca(OH)_2 and CaO reflections recorded in the diffraction patterns of the precipitate sample with the S:C of 1:2.0 (Fig. 2) and the samples with the S:C of 1:1.6 and 1:2.0 after the DTA (Fig. 2), respectively, imply that this endotherm is referred to the decomposition of Ca(OH)_2 unreacted with the formation of H_2O and CaO. Ca(OH)_2 peaks absence in the diffraction patterns of the precipitate samples with the S:C of 1:1.4 and 1:1.6 is explained by its negligible amount formed which is detectable by the exothermic effects with minima barely traceable at 490 and 488°C for these samples, respectively (Fig. 3). The endotherm events set in the range of low temperatures 100-200°C (Fig. 3) are caused by the removal of adsorbed and crystalline water; the intensive endothermic peaks with minima at 783, 794, 800 and 788°C within the temperature range of 780-800°C on the DTA curves of these samples (Fig. 3) are produced by the process of dehydroxylation with the simultaneous formation of amorphous calcium hydroxosilicate species, the phases of which cannot be discovered by the X-ray analysis of the precipitates. These endotherms are immediately followed by the upward trend of the noticeable exothermic peaks over 800°C with

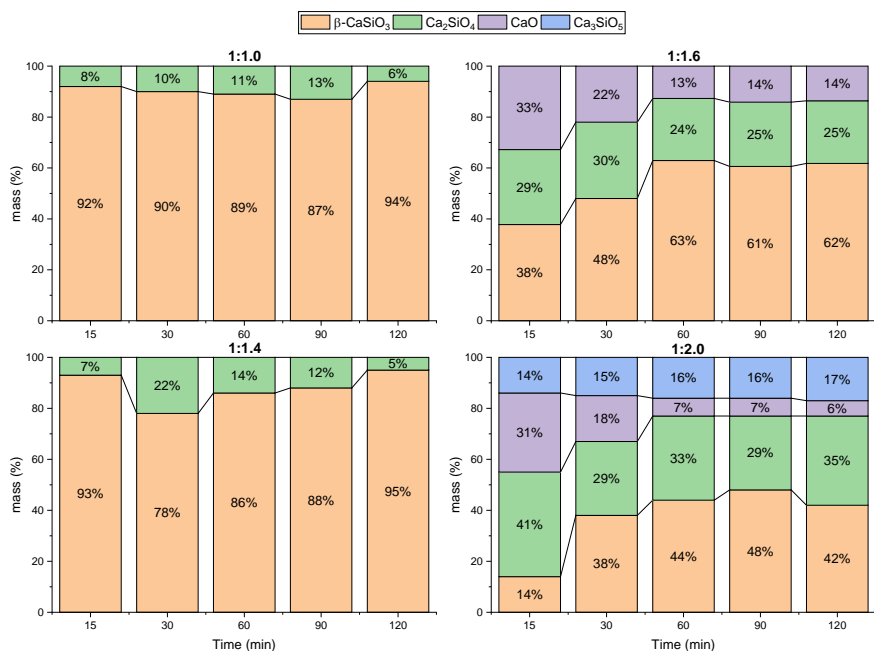


Fig. 2. Relative phase concentrations of the components in the products produced after the DTA of the precipitate samples depending on stirring time.

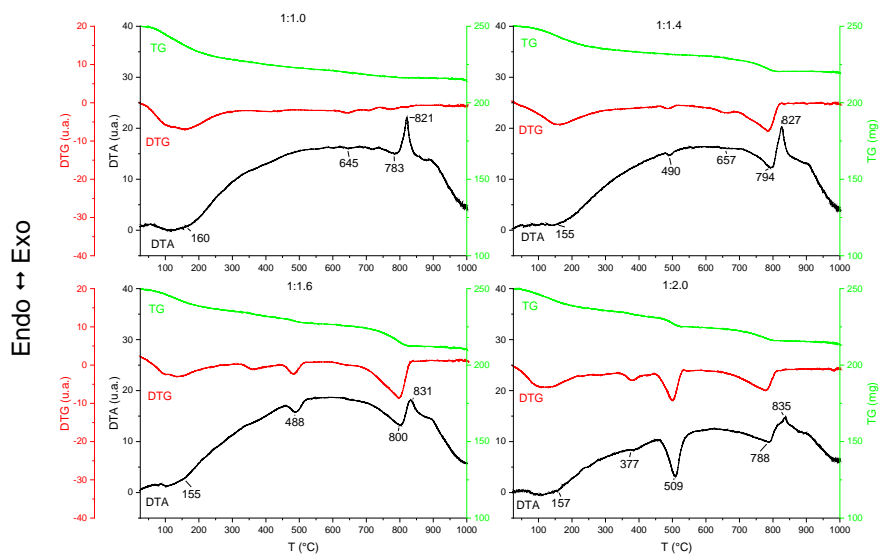


Fig. 3. Differential thermal curves for the precipitate samples produced by fifteen-minute stirring. TG thermogravimetric or weight loss curve, DTA differential thermal analysis curve. DTG differential thermal thermogravimetry curve. The vertical axis label applies to the DTA curve.

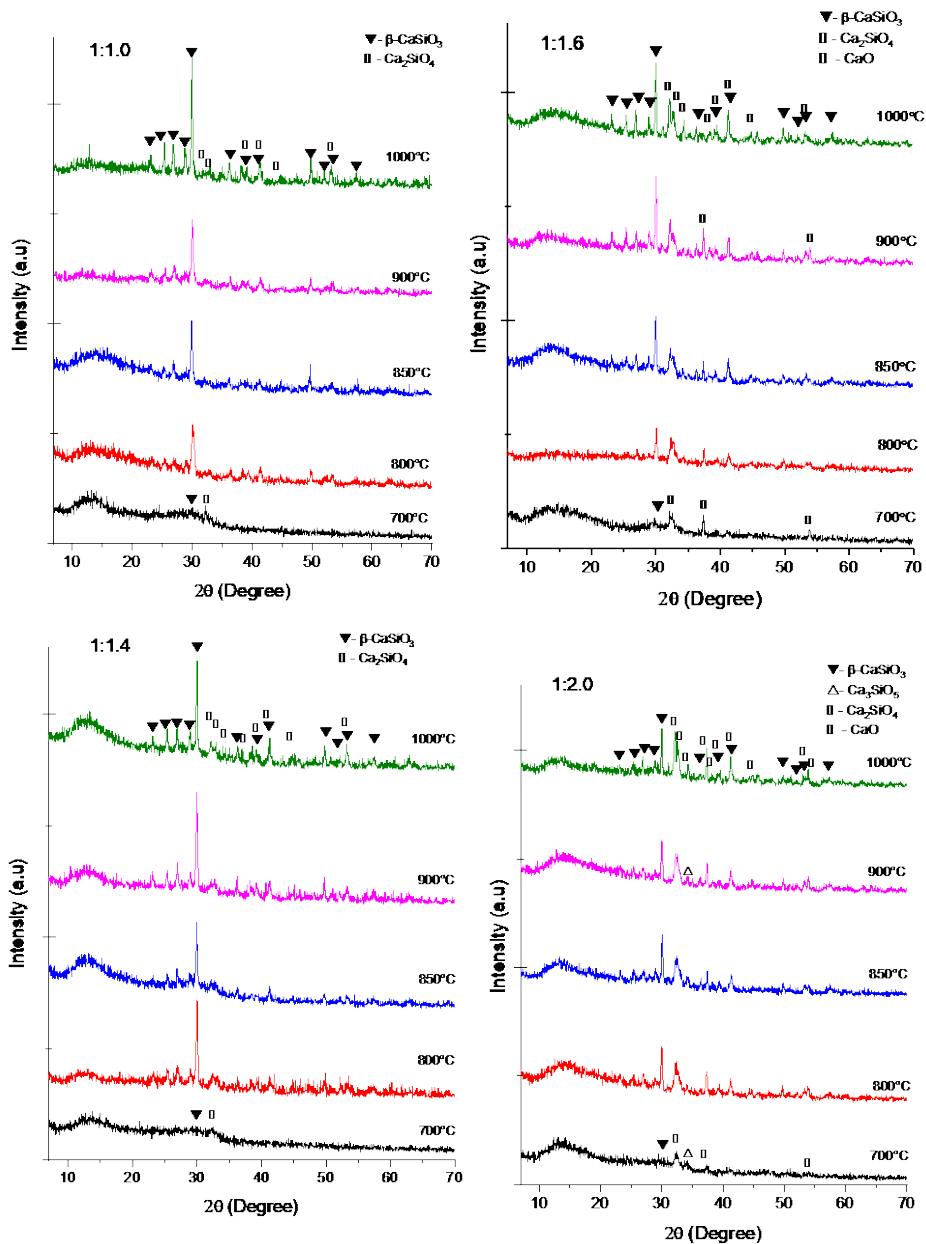


Fig. 4. XRPD patterns of the heated precipitate samples.

maxima at 821, 827, 831 and 835°C originated by the crystallization of the amorphous precipitate samples with the C:S of 1:1.0, 1:1.4, 1:1.6 and 1:2.0, respectively into calcium silicate species (Fig. 3).

In order to determine the feasibility of the fifteen-minute treatment for providing higher yields of β -wollastonite, all the intermediate samples synthesized by stirring for 15 min were examined at various heating rates. The XRPD patterns of these samples heated at different temperatures exhibit their crystalline state dependent on temperature and temperature-induced phase transformations on heating up to 1000°C.

Since on heating up to 700°C no phase changes are fixed, only the diffraction patterns of the chosen samples heated at 700°C and higher are shown (Fig. 4).

CaCO_3 reflections the intensity of which remains unchangeable on heating up to 600°C are not seen in the diffraction patterns of all the samples heated at 700°C and higher (Fig. 4).

Both the reflections of β -wollastonite and larnite are barely traceable in the diffraction patterns of the samples with the S:C of 1:1.0 and 1:1.4 heated at 700°C (Fig. 4). Subsequent heating over 700°C leads to the abrupt growth of β -wollastonite peaks at 800°C the intensity of which goes on increasing gradually up to 1000°C whereas the temperature increase over 700°C does not lead to any changes in the intensity of larnite reflections (Fig. 4). Only at 1000°C a slight increase in larnite peaks intensity is observed for the sample with the S:C of 1:1.4 (Fig. 4).

Besides the reflections of β -wollastonite and larnite, the ones of CaO, which is one of the products of the unreacted Ca(OH)_2 decomposition, are seen in the XRPD patterns of the intermediate samples with the S:C of 1:1.6 and 1:2.0 annealed at 700°C. Apart from these diffraction peaks, the ones corresponding to triclinic Ca_3SiO_5 (Card №31–0301) are recorded in the diffraction patterns of the sample with the S:C of 1:2.0 at 700°C (Fig. 5). As distinct from the previous samples, the more intensive reflections of larnite together with β -wollastonite peaks of lower intensity are recorded in the XRPD patterns of the sample with the S:C of 1:1.6 and 1:2.0 heated from 700 up to 1000°C (Fig. 4). As compared to the samples with the S:C of 1:1.0 and 1:1.4, the intensities of both larnite and β -wollastonite diffraction peaks of the sample with the S:C of 1:1.6 are gradually and simultaneously increasing from 800 up to 1000°C, whereas larnite reflections growth is mainly traceable in the same temperature range for the sample with the S:C of 1:2.0 (Fig. 4). CaO reflections disappear in the XRPD patterns of the intermediate sample with the S:C of 1:1.6 annealed at 1000°C, but they are observable in all the diffraction patterns of the sample with the S:C of 1:2.0 (Fig. 4).

As for calcium carbonate, its reflections disappear in the diffraction patterns of all the samples annealed at the temperatures over 600°C and at

higher temperatures no additional peaks are recorded but the ones of calcium silicate species and CaO. It is quite logical to suggest that on heating over 600°C CaCO₃ reacts with the SiO₂ that remained in an amorphous state, producing calcium silicate species and CO₂. The exothermic event that should be seen over 600°C and evidence calcium silicate species formation is most likely overlapped by the endothermic process of CO₂ releasing. As a result, no heat effects are detectable over 600°C on the DTA curves of all the samples.

As follows from the data of X-ray analysis, the fifteen-minute stirring turns out to be sufficient for guaranteeing higher yields of β -wollastonite. The higher concentration of Ca(OH)₂ in the initial mixture leads to the increasing of larnite and the formation of other species of calcium silicate in the final product on heating and therefore is not profitable for β -wollastonite high yields. The excess of Ca(OH)₂ remains unreacted.

Ca₂SiO₄ crystalline phase appearance in the diffraction patterns of the intermediate samples heated at 700°C and higher suggests the formation of amorphous calcium hydroxosilicate species largely made up of discrete orthosilicate units in the structure of synthesized precipitates, along with *chain-like* silicate units guaranteeing β -CaSiO₃ formation on heating.

According to the Scherer equation, the average particle size of β -CaSiO₃ is variable from 80 up to 100 nm.

In spite of the fact that both Ca₂SiO₄ and β -CaSiO₃ crystals immediately begin getting formed at about 700°C, in the samples with the S:C of 1:1.0 and 1:1.4, β -CaSiO₃ crystallinity is improved as the temperature is increased up to 1000°C, whereas the crystallinity of Ca₂SiO₄ crystals produced at 800°C remains almost unchangeable on subsequent heating. On the contrary, in the samples with the S:C of 1:1.6 and 1:2.0 heated at 1000°C there is a noticeable improvement in the crystallinity of Ca₂SiO₄.

The experimental data have allowed concluding that the fifteen-minute stirring of the boiling aqueous suspensions prepared from the silica hydrogel and Ca(OH)₂ taken in the S:C of 1–1.4 results in the formation of such amorphous calcium hydroxosilicate species the dehydroxylation of which at about 700°C is accompanied by their transformation into nano-sized β -CaSiO₃ crystals achieving final crystallization by the thirty-minute annealing at 1000°C.

According to IR spectroscopy data available in literature the three absorption bands at 680, 642, 566 cm⁻¹ produced by the symmetric stretching vibrations of three SiOSi bridges (ν_s SiOSi) and six absorption ones within the 900–1100 cm⁻¹ range (at 1087, 1056, 1019, 964, 952, 904 cm⁻¹) belonging to SiOSi, O⁻SiO⁻ asymmetric (ν_{as} SiOSi, ν_{as} O⁻SiO⁻) and O⁻SiO⁻symmetric (ν_s O⁻SiO⁻) stretching vibrations are characteristic of β -wollastonite [28, 29]. In the FT-IR spectrum of the final product, which was produced from the precipitate previously synthesized by fifteen-minute stirring of the sample

with the C:S of 1:1.0, β -wollastonite is easily identified by the main six absorption bands at 1065.7, 1026.2, 1010.5, 958.1, 931.65 and 891.3 cm^{-1} representing $\nu_{\text{as}}\text{SiOSi}$, $\nu_{\text{as}}\text{O}^-\text{SiO}^-$ and $\nu_{\text{s}}\text{O}^-\text{SiO}^-$ and two ones at 682 and 650 cm^{-1} corresponding to $\nu_{\text{s}}\text{SiOSi}$ (Fig. 5) [28, 29]. Hence, the FT-IR spectroscopic analysis of the above mentioned final product has also shown that the origins of all the absorption bands in the range of 650-1110 cm^{-1} can be definitely assigned to β -wollastonite.

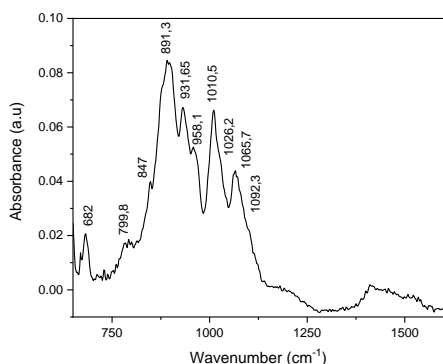


Fig. 5. FTIR spectrum of the final product.

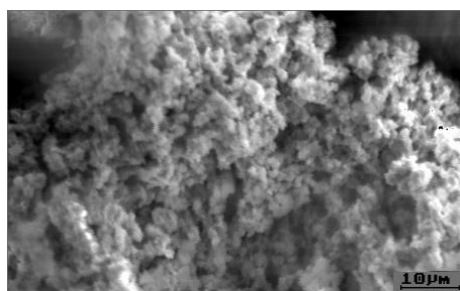


Fig. 6. SEM image of the final product.

The morphological features of the final product, which was synthesized from the precipitate sample with the C:S of 1:1 formed via fifteen-minute stirring have been studied by SEM. It is clearly seen that β -wollastonite represents agglomerates made up of nano-sized particles and has a uniform morphology (Fig.6).

The background information and previous findings allow to gain a deeper insight into the processes occurring during gelation.

The higher yields of β -wollastonite synthesized from the intermediates, which were prepared from the silica hydrogel and CaO with the S:C 1:1.0 and 1:1.4 without involving NaOH via the fifteen-minute stirring are indicative of the fact that the Si–O(Si) bonds arisen inside the structure of the silica during the polycondensation are really more weakened than the same ones after the silica hydrogel dehydration; and the short-time stirring is therefore enough to cut some of them without involving NaOH by releasing *chain-like* silicate anions, which are easily involved in the reaction with $\text{Ca}(\text{OH})_2$ resulting in β -wollastonite formation on heating. The extension of the stirring time over 15 min leads to the breakage of more number of siloxane bonds weakened and the separation of orthosilicate anions from the siloxane bridges of the silica thereby yielding larnite in the final product. Subsequent increase of the reaction time up to 120 min is most likely accompanied by silicate anions bonding providing the formation of extended silicate chains which is also promotive of β -wollastonite production. The experimental results gained for the samples with the S:C of 1:1.6 and 1:2.0

encourage to think that the higher concentrations of Ca(OH)_2 in the initial solutions also further the release of the more number of orthosilicate anions and prevent silicate anions from conformation and bonding thereby promoting the precipitation of a greater amount of amorphous calcium hydro- and hydroxosilicate species largely made up of orthosilicate units resulting in the growth of larnite portion and the formation of Ca_3SiO_5 in the final products. At the same time, the part of Ca(OH)_2 which does not participate in the reaction with the SiO_2 in the solution remains unreacted.

Consequently, the reactions development during gelation and the yields of calcium silicate species in the final products are determined by the number of ortho- and *chain-like* silicate anions released and involved in the reaction with Ca(OH)_2 during stirring. The amount of *chain-like* silicate anions dependent on the number of broken Si-O(Si) bonds can be controlled by the stirring time and the Ca(OH)_2 concentration.

Conclusion

The experimental data have confirmed the idea concerning the existence of comparably weakened Si-O(Si) bonds bonding silicate units of different complexities inside the structure of the amorphous silica constituting the silica hydrogel in comparison with the same bonds inside the silica xerogel separated from the silica hydrogel by dehydration. This type of siloxane bonds is the reason for avoiding NaOH involvement in the procedure of the intermediates preparation.

It has been revealed that the proportion between *chain-like* and ortho-silicate anions released in the solution is the main factor playing a major role in the development of the reactions of Ca(OH)_2 with the SiO_2 constituting the silica hydrogel resulting in the precipitation of various amorphous calcium hydro- and hydroxo- silicate species composed of the different number of meta- and orthosilicate units. The share of each calcium silicate species in the final products, namely $\beta\text{-CaSiO}_3$, Ca_2SiO_4 and Ca_3SiO_5 crystallized from the intermediates on heating is conditioned by the percentage of one or another compound variety synthesized in the precipitates. On heating, dehydroxylation of the compounds largely made up of *chain-like* silicate units is followed by their crystallization into $\beta\text{-CaSiO}_3$ which starts at about 700°C and completes at 1000°C , whereas the ones are comprised of orthosilicate units are either crystallized into Ca_2SiO_4 or Ca_3SiO_5 . The amount of meta- and orthosilicate anions released and involved in the reaction with Ca(OH)_2 in the suspension by stirring depends on both the number of broken Si-O(Si) bonds and the rate of the two processes – silicate anions releasing and bonding which can be governed by stirring time and Ca(OH)_2 concentration.

Proceeding from the experimental data, the higher yields of β -wollastonite having nano-sized particle dimensions 80-100 nm are expectable in the final products synthesized by the thirty-minute heat-treatment at 1000°C of the intermediates, which were previously prepared by the fifteen-minute stirring of the aqueous suspension prepared from the silica hydrogel and $\text{Ca}(\text{OH})_2$ where the SiO_2 and $\text{Ca}(\text{OH})_2$ molar ratio is 1:1÷1.4.

These investigations are of great interest and practical value because they create all the prerequisites required for the further development of a new cost-effective eco-technology for β -wollastonite production with the involvement of the silica hydrogel derived from a serpentine-group mineral.

ՄԻՆԹԶԻ ՊԱՐԱՄԵՏՐԵՐԻ ԱԶԴԵՑՈՒԹՅՈՒՆԸ ԿԱՅԻՈՒՄԻ ՄԻԼԿԱՏՆԵՐԻ ԶԵՐՄԱՅԻՆ ԲՅՈՒՐԵՂԱՅՄԱՆ ՎՐԱ

Ա. Ռ. ԻՍԱԿՅԱՆ, Ն. Ն. ԶՈՒՆՈՒՄՅԱՆ, Ա. Մ. ԹԵՐԶՅԱՆ,
Ս. Ա. ՄԵԼԻԲՅԱՆ և Ն. Ա. ԲԵԳԼԱՐՅԱՆ

Հոդվածը նվիրված է սերպենտինային հանքանյութերից $(\text{Mg}(\text{Fe}))_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ստացված սիլիկազոդի հիդրոքսիդի և կալցիումի հիդրօքսիդի ($\text{Ca}(\text{OH})_2$) ջրային միջավայրում միմյուրտային ճնշման տակ փոխազդեցության ուսումնասիրությանը՝ խառնման տեղումնից և $\text{Ca}(\text{OH})_2$ -ի կոնցենտրացիայից կախված: Այս ուսումնասիրության նպատակն է ուսումնասիրել խառնուրդի տեղումնից և $\text{Ca}(\text{OH})_2$ -ի կոնցենտրացիայի ազդեցությունը կալցիումի սիլիկատների, մասնավորապես, β -վոլաստոնիտի ելքի և բյուրեղացման աստիճանի վրա, որը ստացվել է կալցիումի ամորֆ հիդրո- և հիդրօքսոսիլիկատների ջերմային բյուրեղացմամբ, որոնք նախապես նստեցված են եղել վերոնշյալ ռեակտիվներից պատրաստված եռման ջերմաստիճանում գտնվող ջրային սուսպենզիայում: Փորձարարական տվյալները հնարավորություն տվեցին ստանալ օպտիմալ պարամետրեր, որոնք երաշխավորում են վերջնականում β -վոլաստոնիտի ամենամեծ չափաբաժինը և առաջարկել նստեցման և ջերմային բյուրեղացման ընթացքում տեղի ունեցող գործընթացների հնարավոր մեխանիզմ:

ВЛИЯНИЕ ПАРАМЕТРОВ СИНТЕЗА НА ТЕРМИЧЕСКУЮ КРИСТАЛЛИЗАЦИЮ СИЛИКАТОВ КАЛЬЦИЯ

А. Р. ИСААКЯН¹, Н. О. ЗУЛУМЯН¹, А. М. ТЕРЗЯН¹,
С. А. МЕЛИКЯН¹ и А. А. БЕГЛАРЯН^{1,2}

¹ Институт общей и неорганической химии
НАН Республики Армения им. М. Г. Манвеляна
Армения, 0051, Ереван, ул. Аргутяна 2-ой пер., д. 10
Факс: (374-10) 231275 E-mail: Hayk_b@ysu.am

² Ереванский государственный университет
Армения, 0025, Ереван, А. Манукяна, 1

Статья посвящена исследованию взаимодействия гидрогеля кремнезема, выделенного из серпентинового минерала $(\text{Mg}(\text{Fe}))_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ с гидроксидом кальция $\text{Ca}(\text{OH})_2$ в водной среде при атмосферном давлении в зависимости от длительности перемешивания и концентрации $\text{Ca}(\text{OH})_2$. Цель данного исследования заключалась в изучении влияния длительности перемешивания и концентрации $\text{Ca}(\text{OH})_2$ на выход и степень кристаллизации силикатов кальция, в частности β -волластонита, получаемого термической кристаллизацией аморфных гидро- и гидросиликатов кальция, которые были предварительно осаждены в кипящей

водной суспензии, приготовленной из упомянутых реагентов. Экспериментальные данные позволили выявить оптимальные параметры, гарантирующие наибольшую долю β -волластонита в конечном продукте, и предложить возможные механизмы процессов, протекающих во время осаждения и термической кристаллизации.

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