

The effect of processing parameters on the hydrothermal synthesis of wollastonite at low pressure

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In this research a hydrothermal method was applied to the synthesis of wollastonite. Silica, nano silica and calcium carbonate were used as the main raw materials and sodium chloride as a mineralizer. Six different slurries were prepared with SiO_2/CaO molar ratios of 0.54, 0.8, 1 and a solid content of 50 wt%. Then the slurries were hydrothermally treated in an autoclave for 12 h at 130°C at a pressure of 1.5 atm. In the next step, the samples were dried at 150°C for 8 h and then calcined at 1000°C for 5 h. The microstructures and phases analyses were investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Finally a three-stage mechanism was proposed for the hydrothermal synthesis of wollastonite. The results showed that by using nano silica, fine grain wollastonite was obtained.

Key words: Silica, Nano silica, Wollastonite, Hydrothermal synthesis, Mechanism.

Introduction

Investigations of calcium silicates, especially wollastonite, $\beta\text{-CaSiO}_3$, have attracted attention in recent years. This arises from the fact that calcium silicate ceramics can be used for many building construction and engineering applications because of their improved friction and wear behavior, enhanced fracture toughness, thermal shock resistance and machinability [1].

Wollastonite, a raw material mainly used for traditional ceramics, is also a candidate material for a high frequency insulator owing to its low dielectric loss at high frequencies [2]. Recently, wollastonite ceramics have been studied as bioactive materials for orthopedic applications and used to improve the mechanical properties of the biopolymers because of their good bioactivity and bio-compatibility [3-5]. A new field of application of wollastonite is in a bioactive ceramic material; as bioglass [6] for bone substitution and as coating [7].

Wollastonite occurs in three polymorphic forms; a low temperature triclinic form [1T], a monoclinic form or so called para-wollastonite [2M] and a high temperature form pseudo-wollastonite which occurs in a pseudo-hexagonal form. The conversion of the low temperature form to the high temperature form takes place at 1125°C [6].

Traditionally, wollastonite powders were prepared by precipitation or a solid state reaction method. Recently, a wet chemical method, such as hydrothermal process, was utilized to synthesize wollastonite fibers [2].

Nearly 50 years ago, Kalousek was one of the first researchers who studied the phases produced in autoclaved or hydrothermally cured lime-silica [8] and cement-silica [9] systems by employing thermal analysis techniques. Since then, numerous investigations have been conducted on the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system under hydro-thermal conditions due to its importance in relation to commercially-available construction materials [10]. The C-S-H system is highly complex with over 30 stable phases. This complexity is increased by the existence of many poorly ordered gels (e.g., C-S-H gel) and metastable crystalline phases (e.g., Z-phase). These compounds make experimental work in this system very complicated with a single-phase, pure, highly crystalline material difficult to synthesize. The mineral, tobermorite, is stable over a range of compositions from $\text{Ca/Si} = 0.8$ to $\text{Ca/Si} = 1$. This variation is possible due to the nature of the tobermorite structure and the intrinsic disorder within it. Xonotlite forms at higher temperatures than tobermorite, with the equilibrium phase boundary between the two minerals being at approximately 140°C , although tobermorite can be produced metastably at temperatures well above 200°C . The phase defined as the C-S-H gel is highly disordered [10].

In hydrothermal synthesis of wollastonite, in the first stage, calcium silicate hydrates with a SiO_2/CaO molar ratio of about 0.7 to 1.3, preferably about 1, are made by a hydrothermal treatment of an aqueous mixture of a source of CaO and SiO_2 . In the second stage, these calcium silicate hydrates are transformed into beta wollastonite by annealing in the range of 800°C - 1150°C . Depending on the SiO_2/CaO molar ratio of the starting mixture and the condition of formation, eleven different calcium hydrosilicates (CSH phases) occur in the system $\text{Ca}(\text{OH})_2\text{-SiO}_2\text{-H}_2\text{O}$ (CSH) [11].

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Table 1. Chemical compositions of the raw materials (wt%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	L.O.I	Total
Silica	98.6	0.09	0.05	0.01	0.12	0.04	0.02	-	1	99.94
Calcium Carbonate	-	-	0.15	0.05	55.65	0.15	-	-	44	100
Nano Silica	99.2	0.03	0.01	0.01	0.01	-	-	0.3	0.4	99.96

Table 2. Chemical compositions of slurries and hydrothermal treatment specifications.

Slurry Code	Raw Materials	SiO ₂ /CaO molar ratio	Solid Content	P (atm)	T (°C)	t (h)
HS54		0.54				
HS8	Silica	0.8				
HS1		1				
HN54		0.54	50%	1.5	130	12
HN8	Nano Silica	0.8				
HN1		1				

Experimental Procedures

In this research silica (30-40 μm), nano silica (< 100 nm) and calcium carbonate (40-50 μm) with a purity of over 98% were used as the raw materials (Iranian made). Chemical compositions of the raw materials are shown in Table 1.

In order to prepare the calcium oxide, calcium carbonate was calcined at 1000 °C for 3 h with a heating rate of 10 K/minute⁻¹. To avoid reacting the calcium oxide with CO₂, water was slightly added until the CaO was converted to Ca(OH)₂. Six slurries were prepared with SiO₂/CaO molar ratios of 0.54, 0.8, 1 and a solid content of 50 wt% from the raw materials. 5 wt% of NaCl as an additive was added to all the slurries.

For preparation of the slurries, all the raw materials were fast milled for 0.5 h and then sieved using a 63 μm mesh. Then the slurries were hydrothermally treated in an autoclave for 12 h at 130 °C at a pressure of 1.5 atm. The Chemical compositions of the slurries and treatment specifications are shown in Table 2.

After the hydrothermal treatment, the slurries were dried at 150 °C for 8 h and then calcined at 1000 °C for 5 h with a heating rate of 10 K/minute⁻¹. The powders before and after calcination were characterized using X-ray Diffraction (XRD: JDX-8030, JEOL, Japan). The morphology of the powders before and after calcination were investigated by a scanning electron microscope (SEM: VEGA É² TESCAN, Czechoslovakia).

Results and Discussion

XRD patterns of the hydrothermally treated samples with different SiO₂/CaO molar ratios of 0.54, 0.8, 1 and made of silica are shown in Fig. 1 (a, b, c), respectively. It is seen that in the case of the hydrothermally treated

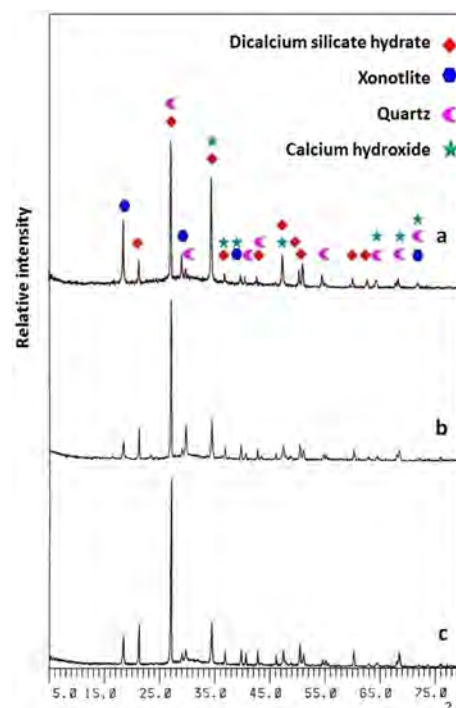


Fig. 1. XRD patterns of the samples made of silica and hydrothermally treated. a) SiO₂/CaO molar ratio of 0.54, b) SiO₂/CaO molar ratio of 0.8, c) SiO₂/CaO molar ratio of 1.

samples, quartz and dicalcium silicate hydrate are the dominant phases. In the sample with a SiO₂/CaO molar ratio of 0.54 (HS54), the sample with the highest amount of CaO and also close to the stoichiometric chemical composition of two moles of CaO and one mole of SiO₂, the main phase is Ca₂SiO₄H₂O (C₂SH) with small amounts of quartz. On the other hand, due to the existence of a high amount of CaO the possibility of Ca(OH)₂ formation increases. This issue can be easily distinguished by comparison of the Ca(OH)₂ peak intensity in this sample with the others. It should be noticed that for the sample with a SiO₂/CaO molar ratio of 1 (HS1), because of the higher amount of SiO₂ and minimum content of CaO in comparison to the other samples, the possibility of the C₂SH phase formation decreases. This is most probably due to being far from stoichiometric chemical composition of two moles of CaO and one mole of SiO₂. So it can be expected that besides the formation of lower amounts of C₂SH, quartz is the main phase.

XRD patterns of the hydrothermally treated samples with different SiO₂/CaO molar ratios of 0.54, 0.8, 1 and made from nano silica are shown in Fig. 2 (a, b, c)

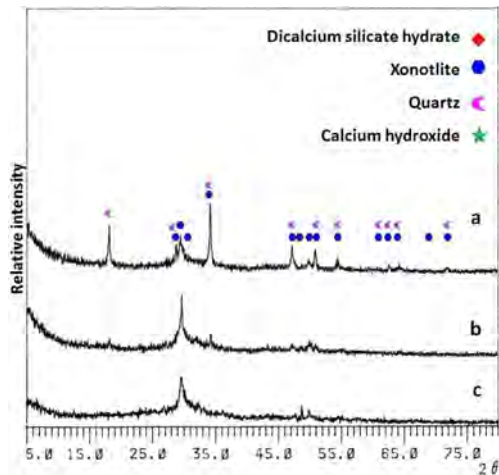


Fig. 2. XRD patterns of the samples made of nano silica and hydrothermally treated a) SiO_2/CaO molar ratio of 0.54, b) SiO_2/CaO molar ratio of 0.8, c) SiO_2/CaO molar ratio of 1.

respectively. It can be seen that xonotlite ($\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ or CSH) is the main phase that has been formed in the samples with SiO_2/CaO molar ratios of 1 (HN1) and 0.8 (HN8). In the case of the hydrothermally treated samples formation of xonotlite is favorable because as was stated by other researchers [12], xonotlite needs a lower activation energy for transformation to wollastonite than the other calcium hydrosilicates. The SiO_2/CaO molar ratio in the chemical composition of the CSH phase and wollastonite is similar, but in order for the transformation of C_2SH to wollastonite, one excess mole of CaO should be dissociated, so this decomposition reaction consumes extra energy and consequently produces extra CaO which remains as an impurity.

While non-completion of $\text{C}_2\text{SH} \rightarrow \text{CSH} + \text{CaO}_{\text{Free}}$ is inevitable, the most probable portion of this phase (C_2SH) will change to larnite (Ca_2SiO_4) in calcined products. By using nano silica instead of silica, some differences are clearly observed. By using nano silica, the higher activity and also reactivity of fine grained nano silica lead to a significant reaction progress and also a decrease in the amount of unreacted materials. Moreover a peak widening phenomenon is another consequence of using nano silica. It is well known that increasing the fineness of raw materials results in ample heterogeneous nucleation positions which lead to the formation of fine grained products. This issue is the main result of the peak widening phenomenon. It should be noticed that the formation of amorphous calcium silicate hydrate compounds can cause the peak widening phenomenon.

XRD patterns of the samples, made of silica, after calcination at 1000°C are shown in Fig. 3 (a, b, c). Wollastonite, quartz, larnite and calcium oxide were detected. As was mentioned previously, C_2SH together with small amounts of quartz are formed in the sample with a SiO_2/CaO molar ratio of 0.54 (HS54). Whereas in the case of the sample with a SiO_2/CaO molar ratio

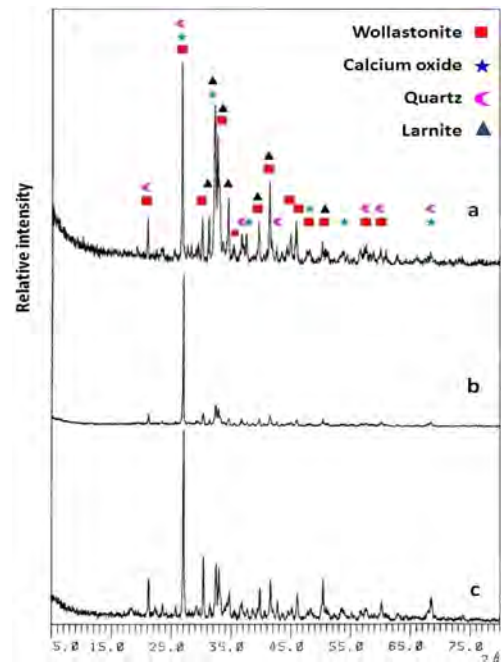
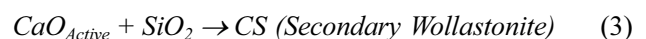
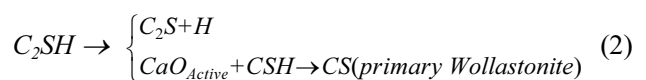


Fig. 3. XRD patterns of the samples made of silica and hydrothermally treated, after calcination at 1000°C for 5h. a) SiO_2/CaO molar ratio of 0.54, b) SiO_2/CaO molar ratio of 0.8, c) SiO_2/CaO molar ratio of 1.

of 1 (HS1) the results are opposite. So it is expected after calcination the larnite peak intensity in the sample (HS54) is much higher than that in the sample (HS1). This issue is completely compatible with results obtained from XRD patterns.

In order for wollastonite formation, CaO which is derived from the C_2SH decomposition reaction should react with a SiO_2 . In the sample with SiO_2/CaO molar ratio of 0.54, due to the lack of SiO_2 , free calcium oxide remains as an unreacted material in final products. Presumably, secondary wollastonite is formed in the sample with a SiO_2/CaO molar ratio of 0.8. In this case, despite the free CaO produced from the decomposition process, because of the reaction between CaO and SiO_2 , secondary wollastonite forms. In addition to secondary wollastonite, primary wollastonite is produced from calcination of the CSH phase and also decomposition of C_2SH . So it can be concluded that a SiO_2/CaO molar ratio of 0.8 is the optimum composition for the synthesis of wollastonite powder.

Based on the results, a three-stage mechanism is proposed for the hydrothermal synthesis of wollastonite.



As was mentioned previously, most probably in the

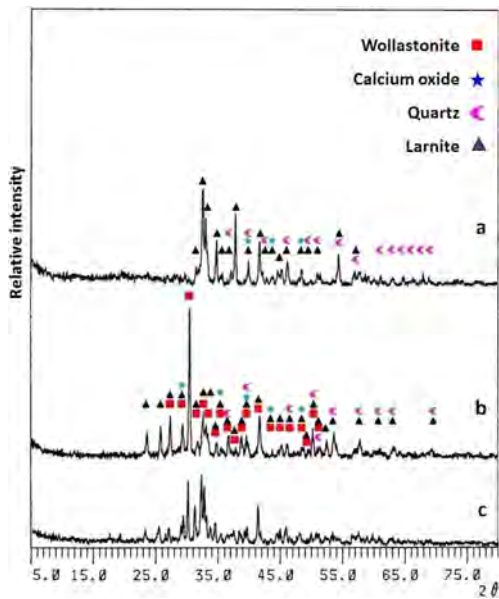


Fig. 4. XRD patterns of the samples made of nano silica and hydrothermally treated, after calcination at 1000 °C for 5h. a) SiO₂/CaO molar ratio of 0.54, b) SiO₂/CaO molar ratio of 0.8, c) SiO₂/CaO molar ratio of 1.

sample with the SiO₂/CaO molar ratio of 1, wollastonite is mainly formed from the calcination of CSH. In comparison with the sample with a SiO₂/CaO molar ratio of 0.54, there are two important differences:

1. Due to small amounts of C₂SH, the amount of wollastonite which is produced from the calcination of C₂SH is negligible.
2. Due to small amounts of CaO, produced from the C₂SH decomposition, the amount of secondary wollastonite which is produced by the $CaO_{Active} + SiO_{2System} \rightarrow CaO.SiO_2$ reaction is also negligible.

So it can be concluded in the sample with a SiO₂/CaO molar ratio of 0.8, because of the formation of primary and secondary wollastonite, the amount of wollastonite and impurities (CaO and SiO₂) are maximum and minimum, respectively.

XRD patterns of the samples, made with nano silica, after calcination at 1000 °C are shown in Fig. 4 (a, b, c).

It is seen in the sample with a SiO₂/CaO molar ratio of 0.8 (HF8N1), the amount of wollastonite is a maximum which is a confirmation for the proposed mechanism. Moreover, due to the high activity of nano silica and greater efficiency in the hydrothermal process, the amount of remaining unreacted materials was smaller than that using silica.

It was previously proved that at a high pressure of the hydrothermal synthesis, the suggested mechanism is the dominant mechanism [13]. It was mentioned that this three-stage mechanism is responsible only when silica is used as a raw material. In other words, by using silica, even at high pressure up to 7 atm, a SiO₂/CaO molar ratio of 0.8 was the optimum composition. But in the case of using nano silica, by increasing the pressure to 7 atm the optimum SiO₂/CaO molar ratio

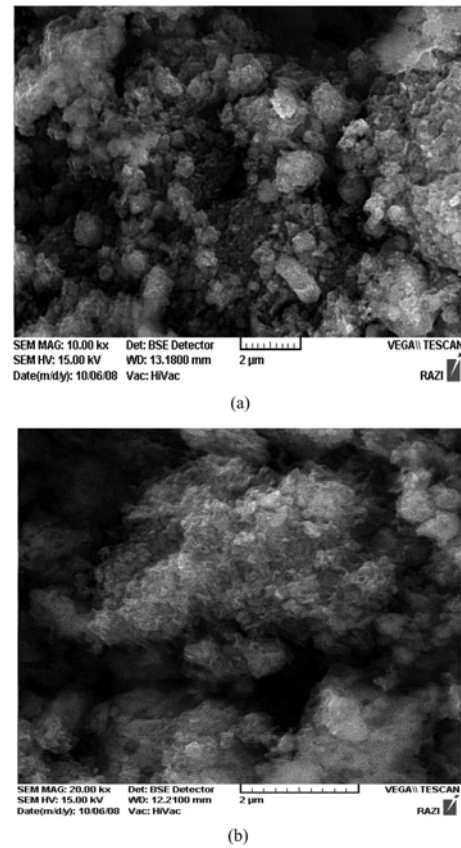


Fig. 5. SEM images obtained from hydrothermally treated samples. (a) Sample HS8, (b) sample HN8.

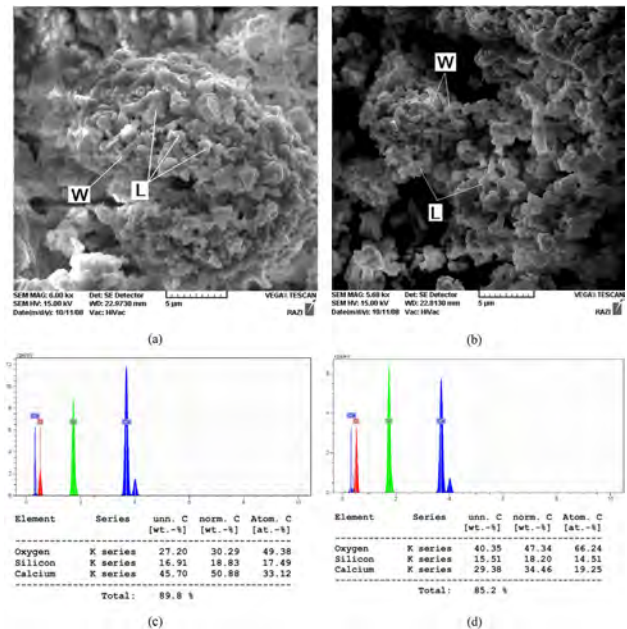


Fig. 6. SEM images obtained from hydrothermally treated and calcined samples. (a) Sample HFS8, (b) sample HFN8 (W = wollastonite, L = larnite) together with EDS results of (c) larnite and (d) wollastonite crystals.

changes from 0.8 to 1 [13].

SEM images of the samples with a SiO₂/CaO molar ratio of 0.8 and made of silica (HS8) and nano silica

(HN8) which were hydrothermally treated are shown in Fig. 5. Needle like crystals of xonotlite are clearly seen.

It is easily seen in the sample HS8 (Fig. 5-a), the amount of xonotlite and other hydrate phases are small. In other words, the quantity of raw materials such as coarse particles of quartz is noticeable. But in the sample HN8 (Fig. 5-b), when nano silica is used, more needle-like crystals of xonotlite are seen. Moreover as was anticipated previously, the size of the crystals is smaller than when silica was used.

SEM images of the above mentioned samples after calcination (HFS8 and HFN8) together with EDS analysis results are shown in Fig. 6. Wollastonite (W) and larnite (L) crystals were characterized from their morphology and chemical composition. Results of the EDS analyses from wollastonite and larnite crystals are also presented in Fig. 6. In both samples, wollastonite crystals are seen. But in the sample made with nano silica, these crystals are smaller and more abundant. This is probably due to fineness of the nano silica particles that cause the formation of fine-grained products. It is seen in the sample made with silica (Fig. 6-a), the amount of wollastonite crystals is not noticeable, while one can see that beside wollastonite, larnite and quartz particles are easily seen. But in the sample made with nano silica (Fig. 6-b), the density of calcined products, especially wollastonite, has significantly increased. This is directly related to the higher reaction efficiency of the hydrothermal process when nano silica is used. Using nano silica leads to the formation of more hydrate phases and consequently a greater amount of calcined products, wollastonite and larnite, after calcination.

Conclusions

1. Using silica and nano silica, a SiO_2/CaO molar ratio of 0.8 was the optimum ratio for producing the maximum amount of wollastonite at low pressure.
2. For a low pressure hydrothermal synthesis of wollastonite, a three-stage mechanism is dominant.
3. By using nano silica, in comparison to using silica, the reaction efficiency and also the amount of synthesized wollastonite increase significantly.

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