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Investigation of hydrothermal synthesis of wollastonite using silica and nano silica at different pressures

Arash Yazdani, Hamid Reza Rezaie* and Hossein Ghassai
Department of materials and metallurgical Engineering,Iran University of Science and Technology, Tehran, 16844, Iran.

In this research a hydrothermal method was applied to synthesis of wollastonite. Silica, nano silica and calcium carbonate were used as raw materials. 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 2 h at 200 °C at pressures of 3, 5 and 7 atm. In the next step, the samples were dried at 150 °C for 8 h and then were calcined at 1000 °C for 5 h. The microstructure and phase analyses were investigated using SEM and XRD. The results showed that by using both silica and nano silica, with increasing pressure, the amount of wollastonite increased. At all pressures using silica, slurry with 50 wt% of solid content, SiO_2/CaO molar ratio of 0.8 gave the optimum results while by using nano silica the optimum SiO_2/CaO molar ratio was 1.

Key words: silica, nano silica, wollastonite, hydrothermal.

Introduction

Studies of calcium silicates, especially wollastonite, â-$CaSiO_3$, 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 behaviors, enhanced fracture toughness, thermal shock resistance and machinability [1]. Wollastonite is a brilliant white to gray or brown calcium meta silicate, $CaSiO_3$, with a composition of 48.3% CaO and 51.7% SiO_2. Wollastonite is rarely found in the pure state since it is associated with manganese, magnesium, iron and strontium. It occurs predominately as a contact metamorphic deposit formed between limestones and igneous rocks, often associated with garnet, diopside, epidoite, calcite and quartz [2]. Wollastonite crystallizes in three polymorphic forms; low temperature triclinic [1T], monoclinic 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 to the high temperature form takes place at 1125 °C [3]. Because of its cleavage properties, wollastonite breaks down during crushing and grinding into needle-shaped particles. The aspect ratio, or the ratio of needle length to its diameter, is a measure of the acicularity of the wollastonite product and is a key market specification. Wollastonite has a wide range of uses such as in ceramics, wollastonite-based glazes, plastics, paints, asbestos replacement, abrasives and glasses [4].

*Corresponding author:
Tel : +98-9121025394
Fax: +98-2177240480
E-mail: hrezaie@iust.ac.ir

There are several methods for the synthesis of wollastonite such as using diatomite [5], SiO_2 dust from filters [6], slag [7], synthesizing at low temperature [8], a solid state reaction [9], fusion [10] and a hydrothermal process [11].

In the hydrothermal method, in the first stage, calcium silicate hydrates with a SiO_2/CaO molar ratio of about 0.7 to about 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 $Ca(OH)_2$-SiO_2-H_2O (CSH) (Ohnemuller and Solf, 1975).

In this paper the hydrothermal synthesis of wollastonite using silica and nano silica at different pressures, was investigated and finally the results were compared.

Experimental Procedure

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

In order to prepare of calcium oxide, calcium carbonate was calcined at 1000 °C for 3 h with a heating rate of 10 Kminute^{-1}. To avoid reacting the calcium oxide with CO_2, small addition of water were made until the CaO was converted to $Ca(OH)_2$. Eighteen slurries were prepared with SiO_2/CaO molar ratios of 0.54, 0.8, 1 and a solid content of 50 wt% from the raw materials. For the preparation of the slurries, all the raw materials were fast milled for 0.5 h and then sieved using 63 μm mesh. Then

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

SiO_2	AL_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L.O.I	Total	
98.6	0.09	0.05	0.01	0.12	0.04	0.02	-	1	99.94	Silica
-	-	0.15	0.05	55.65	0.15	-	-	44	100	Calcium carbonate
99.2	0.03	0.01	0.01	0.01	-	-	0.3	0.4	99.96	nano silica

the slurries were hydrothermally treated in an autoclave for 2 h at 200 °C at pressures of 3, 5 and 7 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 were calcined at 1000 °C for 5 h with a heating rate of 10 Kminute^{-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: Cambridge S360, UK and VEGA II TESCAN, Czechoslovakia).

Results and Discussion

Samples with silica

It is well known that compositional and processing parameters have significant effects on the formation of hydrothermal and calcined phases. So here, we discuss the various effects of the SiO_2/CaO molar ratio and processing pressure on the XRD patterns of the samples. Due to the major importance of the characterization of hydrothermal phases, including type and quantity, all analytical experiments should be carried out before and after calcination.

Table 2. Chemical compositions of slurries and hydrothermal treatment specifications

t (h)	T (°C)	P (atm)	Solid content	SiO_2/CaO molar ratio	Raw material	Slurry code
2	200	3	50%	0.54	Nano-silica	H54N3
				0.8		H8N3
				1		H1N3
				0.54	Silica	H54S3
				0.8		H8S3
				1		H1S3
		5		0.54	Nano-silica	H54N5
				0.8		H8N5
				1		H1N5
				0.54	Silica	H54S5
				0.8		H8S5
				1		H1S5
		7		0.54	Nano-silica	H54N7
				0.8		H8N7
				1		H1N7
				0.54	Silica	H54S7
				0.8		H8S7
				1		H1S7

XRD patterns of the hydrothermal treated samples at pressures of 3, 5 and 7 atm are shown in Fig. 1(A, B, C) respectively. Also XRD patterns of the samples, after calcination at 1000 °C are shown in Fig. 2(A, B, C) respectively.

In the case of the hydrothermally treated samples formation of xonotlite is favorable because as has been stated by other researchers [12], xonotlite ($Ca_6Si_6O_{17}(OH)_2$) needs a lower activation energy for transformation to wollastonite than the other calcim hydrosilicates. As these figures show, at pressures of 3 and 5 atm no xonotlite was formed and the only product phase was dicalcium silicate hydrate. The main tall peaks show overlapping of the raw materials and dicalcium silicate hydrate. Probably they belong to unreacted material such as calcium hydroxide and quartz. In other words, at low pressures the amounts of hydrated produced phases were negligible. By increasing the pressure to 7 atm, the desired xonotlite was formed. It is obviously seen that tall peaks have been replaced with short ones. At low pressures, with coarse particles of the raw materials and a low specific area, unreacted materials are probably the main cause of the sharp peaks, thus at these pressures, with none of the ratios, no xonotlite was formed. By increasing the pressure, the driving force of the reaction increases or in the other words increasing the pressure compensates the negative effects of the coarse particles of the raw materials, an increasing amount of production is expected, so the intensity of all peaks of the raw materials decreases. It can be concluded that because the raw materials consumption and formation of product phases, the peaks have been shortened. So by increasing the pressure, the reaction efficiency increases. At all pressures, with a SiO_2/CaO molar ratio of 0.8, the amount of unreacted raw materials and desired xonotlite are minimum and maximum respectively.

After calcination, in all the XRD patterns, the maximum peaks show an overlapping of the peaks of the raw materials and produc phases. It has been stated that with a low pressure treatment, hydrothermal reactions do not proceed significantly, so it is expected that after calcination, the amount of wollastonite and other calcined phases to be negligible. So similarly to the state before calcination, tall and sharp peaks belong to the raw materials such as quartz and calcium oxide, but at pressures of 7 atm, because of the formation of xonotlite, the amount of wollastonite is increased significantly. Another phase which forms in most of the calcined samples is larnite. Larnite (Ca_2SiO_4)

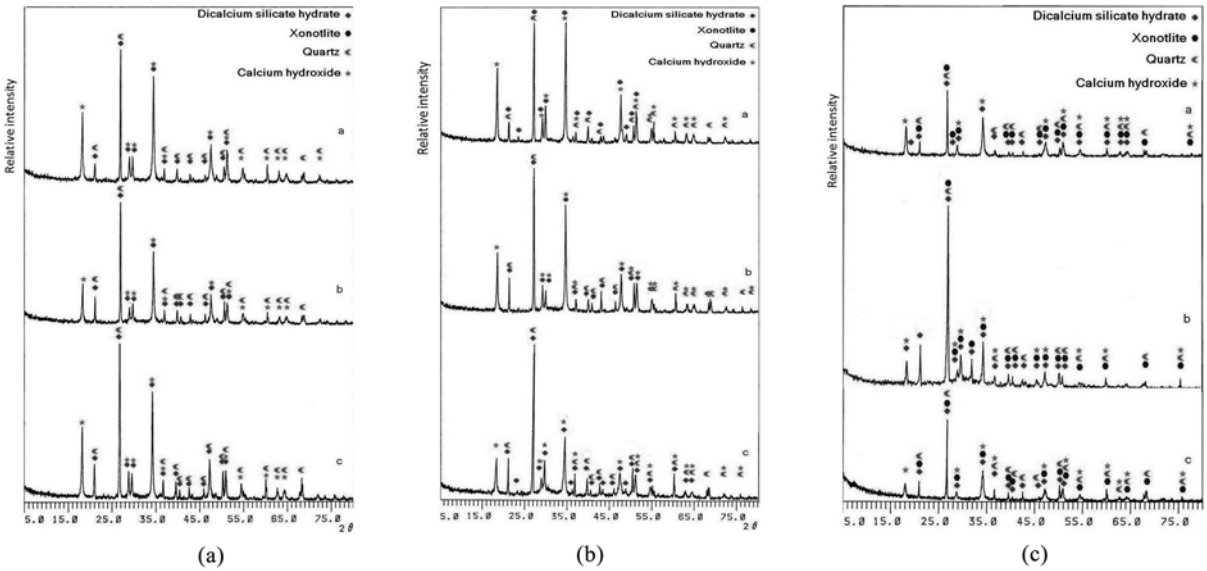


Fig. 1. XRD patterns of samples made of silica and hydrothermally treated at different pressures. a) SiO_2/CaO molar ratio of 0.54, b) SiO_2/CaO molar ratio of 0.8, c) SiO_2/CaO molar ratio of 1.

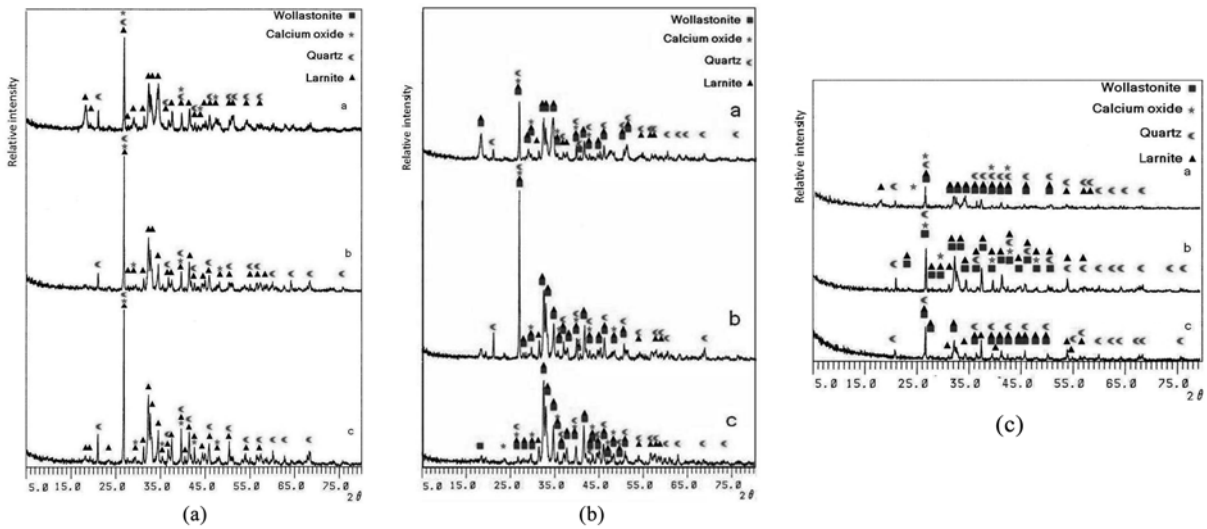


Fig. 2. XRD patterns of hydrothermally treated samples at different pressures, after calcination at 1000 °C for 5 h. a) SiO_2/CaO molar ratio of 0.54, b) SiO_2/CaO molar ratio of 0.8, c) SiO_2/CaO molar ratio of 1.

has a compositon very close to wollastonite and is mainly produced from the calcination of dicalcium silicate hydrate ($Ca_2SiO_4.H_2O$). At a SiO_2/CaO molar ratio of 0.8, wollastonite gave the maximum value. This is completely compatible with the suggested mechanism for synthesizing of wollastonite by other researchers [12].

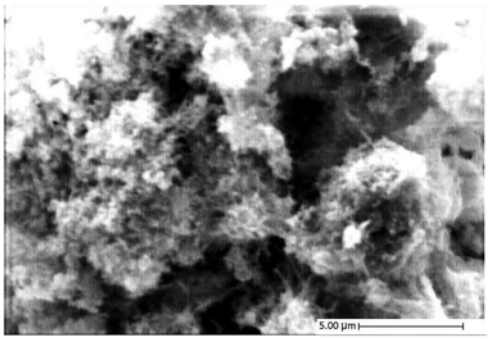
SEM images of the sample prepared from silica with a SiO_2/CaO molar ratio of 0.8, hydrothermal treated at a pressure of 7 atm (H8S7) and calcined at 1000 °C for 5 h (HF8S7) are shown in Figs. 3, 4 respectively. Fig. 3 shows very fine needle like xonotlite crystals.

Fig. 4 shows the wollastonite particles with fine acicular shapes and larnite with sub-spherical grains. It is also seen that the amount of wollastonite in comparison with larnite is not significant. It can be said that using coarse silica, even at a high hydrothermal pressure, larnite is the dominant formed phase. Perhaps applying a higher pressure or a longer time could help the formation of wollastonite.

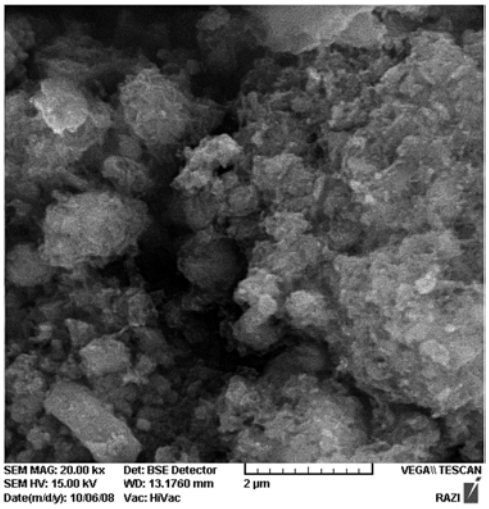
Samples with nano silica

XRD patterns of the hydrothermal treated samples at pressures of 3, 5 and 7 atm are shown in Fig. 5(A, B, C) respectively. Also XRD patterns of the samples, after calcination at 1000 °C are shown in Fig. 6(A, B, C) respectively.

It is seen that due to high activity of nano silica, in comparison with using silica, xonotlite is formed at all pressures and SiO_2/CaO molar ratios with a greater quantity, but similarly to the previous results at all pressures xonotlite had a maximum value at a SiO_2/CaO molar



(a)



(b)

Fig. 3. SEM images of hydrothermally treated sample at a pressure of 7 atm (H8S7). a) overview, b) higher magnification.

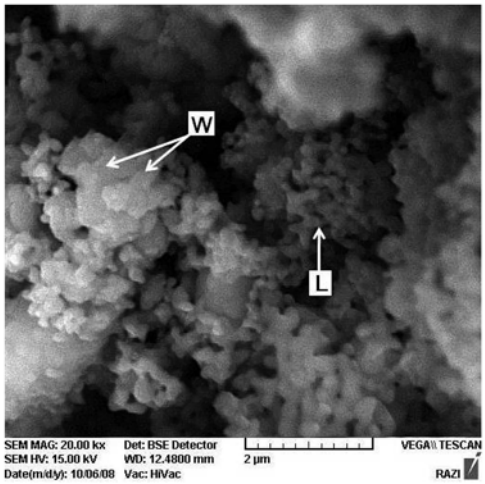
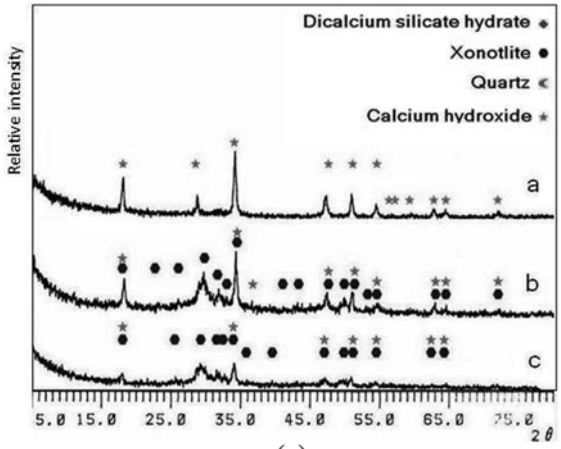
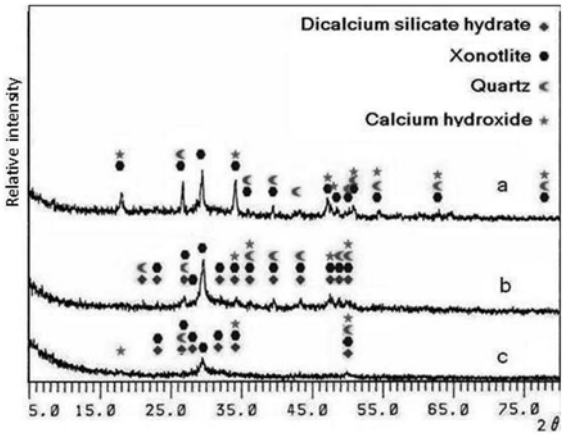


Fig. 4. SEM image of sample calcined at 1000 °C for 5 h (HF8S7) (W = Wollastonite, L = Larnite).



(a)



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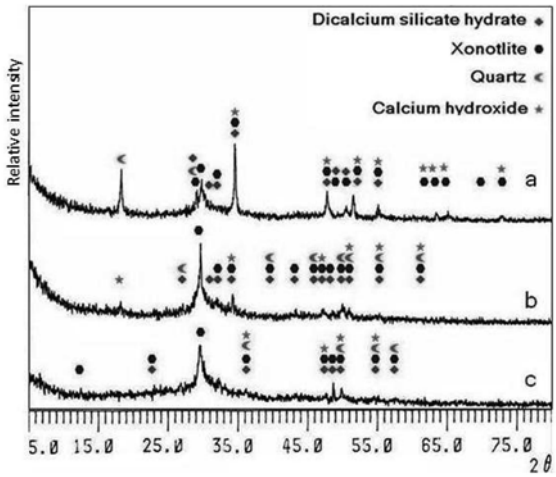
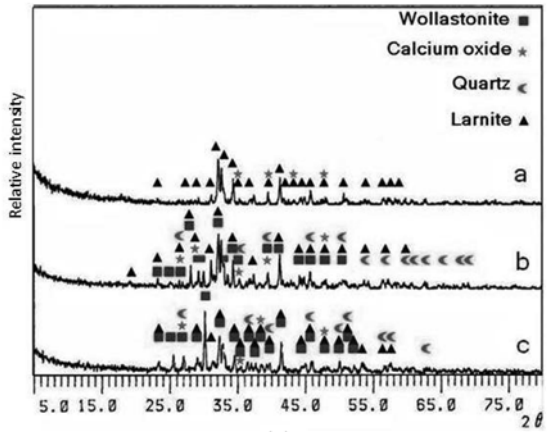


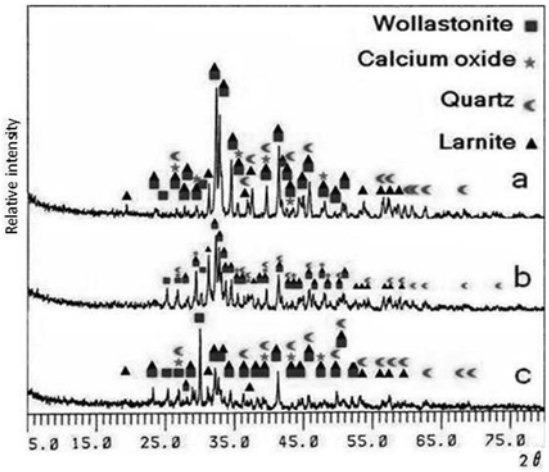
(c)

Fig. 5. XRD patterns of samples made of nano silica and hydrothermally treated at different pressures. 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.

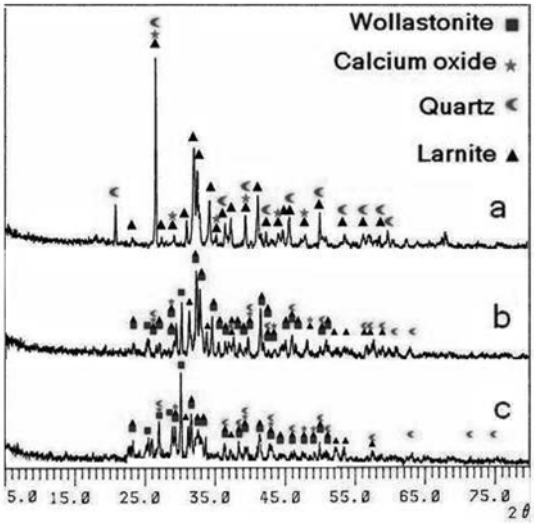
ratio of 0.8. It also seems that with an increase in the pressure, the amount of formed xonotlite increases. In comparison with the case of using silica, there are some differences such as that the tall and sharp peaks from mainly raw materials are replaced by short and wide peaks of the product phases. Also the amount of unreacted materials has decreased significantly. Another difference is a peak widening phenomenon which is due to the fineness of the product particles and also the existence of unreacted nano silica that can act as an amorphous phase.



(a)



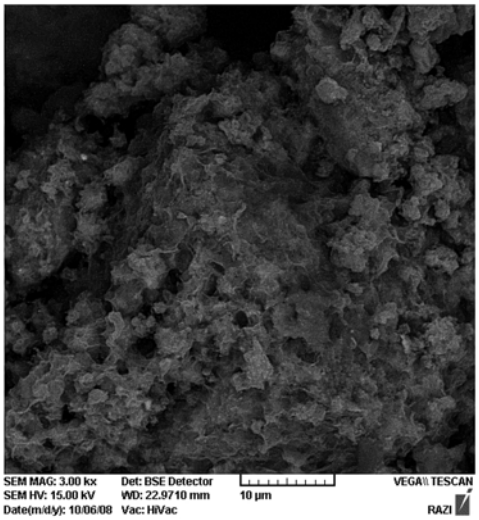
(b)



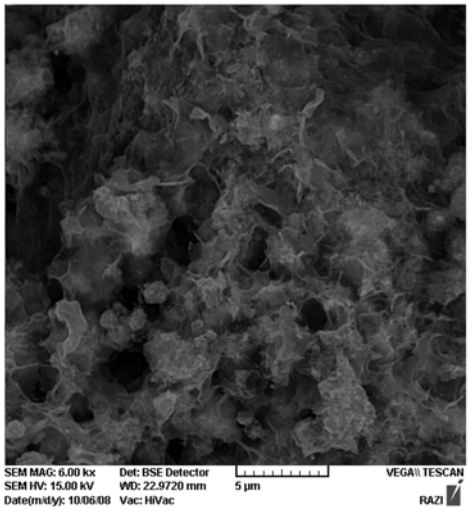
(c)

Fig. 6. XRD patterns of hydrothermally treated samples at different pressures, after calcination at 1000 ºC for 5 h. 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.

After calcination, wollastonite and larnite were the main phases. As was mentioned for the hydrothermally treated samples, by increasing the pressure, the amount of formed phases especially xonotlite increased, so it is expected that by increasing the pressure, similar to the case of using silica, the amount of wollastonite increased. This is compatible with XRD patterns of calcined samples. It can be seen that the intensity of both wollastonite and larnite have increased, but the increase in the amount of wollastonite is more noticeable. This is evidence that at all pressures wollastonite had a maximum value at a SiO_2/CaO molar ratio of 1, while in all samples with this molar ratio wollastonite was the main phase.



(A)



(B)

Fig. 7. SEM images of hydrothermal treated samples at pressure of 7 atm (H1N7). a) overview, b) higher magnification.

SEM images of the samples, prepared from nano silica with a SiO_2/CaO molar ratio of 1, hydrothermally treated at a pressure of 7 atm (H1N7) and calcined at 1000 ºC for 5 h (HF1N7) are shown in Figs. 7 and 8, respectively.

Fine and needle like crystals of xonotlite are obviously seen in Fig 7. Also Fig. 8 shows the wollastonite grains with acicular shapes of the sample calcined at 1000 ºC.

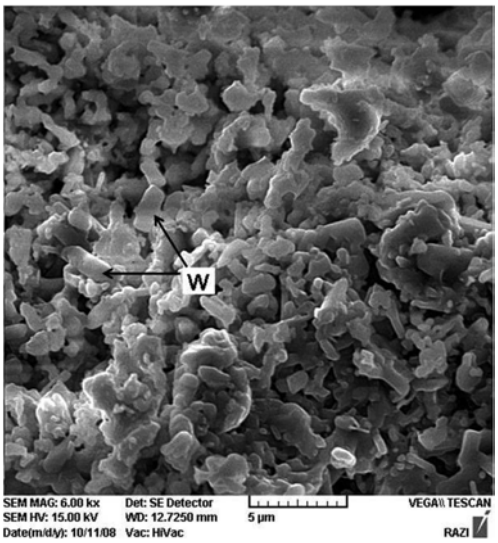


Fig. 8. SEM image of sample calcined at 1000 °C for 5 h (HF1N7) (W = Wollastonite).

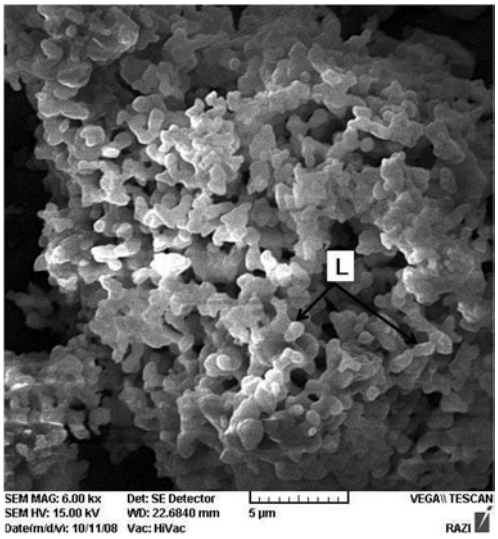


Fig. 9. SEM image of sample calcined at 1000 °C for 5 h (HF8N3) (L = Larnite).

As is shown in the XRD curves and also in the SEM images, wollastonite with an acicular shape and submicrometer size is the dominant phase. Also energy dispersive spectroscopy (EDS) elemental analysis of wollastonite particles showed that Si and Ca are the only elements detected.

An SEM image of a sample, prepared from nano silica with a SiO_2/CaO molar ratio of 0.8, hydrothermally treated at a pressure of 3 atm and calcined at 1000 °C for 5 h (HF8N3) is shown in Fig. 9. Groups of larnite with sub-spherical grains are easily seen in this figure. EDS elemental analysis of the larnite particles showed that Si and Ca are the only elements detected with a different ratio in comparison with EDS analyses of wollastonite (Fig. 8).

Conclusions

1. By using silica and nano silica, increasing the pressure had a significant effect on the reaction efficiency of hydrothermal and calcination processes.
2. Using silica, a SiO_2/CaO molar ratio of 0.8 was the optimum ratio for producing the maximum value of wollastonite but by using nano silica, a SiO_2/CaO molar ratio of 1 was the optimum ratio.
3. Using silica, even at high hydrothermal treatment pressures, the amount of xonotlite was not significant and consequently micrometer larnite was formed as the main phase after calcination.
4. Using nano silica, after the hydrothermal treatment, xonotlite was formed in a noticeable quantity, so submicrometer wollastonite with an acicular shape was achieved.

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