Pergamon

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Cement and Concrete Research 33 (2003) 1789–1793

CEMENT AND CONCRETE RESEARCH

Influence of SiO_2 modification on hydrogarnets formation during hydrothermal synthesis

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Received 22 August 2002; accepted 27 May 2003

Abstract

Formation and stability of hydrogarnet and Al-substituted tobermorite were examined at 175 °C temperature in saturated steam environment processing CaO-quartz and CaO-amorphous SiO_2 suspensions. A large quantity of Al_2O_3 was added to the starting mixtures [molar ratio $A/(S+A)=0.10$, duration of hydrothermal synthesis—from 0 to 24 h]. It was determined that hydrogarnets always tend to form more rapidly than 1.13 nm tobermorite. However, later, with extension of synthesis duration, they start to fracture and their quantity reduces almost in half during 24 h. CaO is present in the further reaction with SiO_2 forming hydrated calcium silicates, and released Al^{3+} ions are inserted into Al-substituted tobermorite crystal lattice. Using amorphous $SiO_2 \cdot nH_2O$ as SiO_2 component, starting raw materials react considerably quicker—the total $Ca(OH)_2$ is joined already while increasing the temperature up to 175 °C. Meanwhile, in the mixtures with quartz when their composition is described by the molar ratio $C/(S+A)=1.0$, traces of $Ca(OH)_2$ are found even after 24-h isothermal treatment at 175 °C temperature. Moreover, it depends on SiO_2 modification the hydrogarnets of what type are to be formed. Si-free hydrogrossular forms in the mixtures with quartz and katoite in the mixtures with $SiO_2 \cdot nH_2O$. Si^{4+} ions are inserted into the crystal lattice of the latter compound while the first one remains undisturbed. This is presumably related to the lower solubility of the quartz. It was also noticed that an isomorphic Si^{4+} ions substitution with Al^{3+} ions in the hydrated calcium silicate lattice is considerably quicker when an amorphous SiO_2 is used as SiO_2 component instead of quartz.

Keywords: Hydrogarnet; X-ray diffraction; $Ca(OH)_2$; C-S-H; Tobermorite 1.13 nm

1. Introduction

Among the numerous hydrated calcium silicates occurring in nature as hydrothermal alteration products of calcium carbonate rocks and as vesicle fillings in basalts, particular attention has been given to the family of tobermorite. It can be easy synthesized in hydrothermal conditions too. The interest in the structure and crystal chemistry of the minerals of tobermorite group stemmed from their close relationships with the C-S-H (hydrated calcium silicates) phases formed during the hydration processes of Portland cement [1,2]. Tobermorite also forms during the hydrothermal processes: under the evaporation of silica bricks, aerated concrete, or thermal insulating materials [3,4]. Subsequently, attention has been drawn to the properties of tobermorite as a cationic exchanger and its potential applications in catalysis, in nuclear and hazardous waste disposal [5,6].

Small amounts of inorganic admixtures can affect substantially the kinetics and mechanism of calcium silicate hydrates synthesis as well as the properties of products [7]. They can promote the dissolution of initial lime and silica-bearing compounds and accelerate or hinder the crystallization of products. Some amount of admixture can enter the structure of calcium silicate hydrates. The natural raw materials usually are polluted by aluminium impurities, and therefore the role of aluminium in the stabilization of tobermorite has been widely reported [8–16].

The most widely studied aluminous materials and their effects on various aspects of tobermorite formation include the following: γ-Al_2O_3 [8,9], kaolin [10], fly ash [11], zeolite [12], $Al(OH)_3$ [13,14], and metakaolinite [15,16].

Recently Klimesch and Ray presented the new information about compound formation sequence in the system

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0008-8846/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00200-X

CaO-SiO_2-Al_2O_3-H_2O under hydrothermal conditions. They found that hydrogarnet ($C_3AS_{3-x}H_{2x}$, $x = 0$ to 3) was always among the first phases formed and invariably appeared before 1.13 nm tobermorite [15,16]. Quartz fineness was a deciding factor in the lime–metakaolin reaction, which prevailed over the lime–quartz reaction more in the presence of coarse quartz [17]. The growth of hydrogarnet was inhibited with increasing amounts of quartz, while the formation of Al-substituted tobermorite was accelerated [18]. It was demonstrated too that the reactivity of the aluminous sources also affected the extent of hydrogarnet formation [10,19]. The stability of hydrogarnet decreased with increasing silica content in the bulk composition and with increasing reaction time: hydrogarnet finally disappeared while 1.13 nm tobermorite increased concurrently [15,20].

The findings of Klimesch and Ray show that in the presence of aluminous additives, hydrogarnet formation appears to play a more significant role in relation to 1.13 nm tobermorite formation than it was previously thought.

However, the authors used quartz as SiO_2 component in all their works. Meanwhile, it is already known for a long time that Al admixtures have a more considerable effect on tobermorite formation process when, instead of quartz, an amorphous silica is used as SiO_2 source [21].

The aim of this work is to examine formation and stability of hydrogarnets and Al-substituted tobermorite as well as ion insertion into a tobermorite crystal lattice when both quartz and amorphous silica are used as SiO_2 component.

2. Materials and methods

In this paper, the following reagents were used as starting materials: fine ground $SiO_2 \cdot nH_2O$ (ignition losses 21.43%, specific surface area $S = 1560$ m^2/kg by Blain); fine ground quartz, after grinding washed away from iron impurities by salt acid; amorphous Al_2O_3, which has been obtained after heating up $Al(OH)_3$ for half an hour at 550 °C ($S = 712$ m^2/kg); calcium oxide ($CaO = 97.3\%$; $S = 548$ m^2/kg), which has been obtained by burning calcium carbonate at 1000 °C for 6 h.

The synthesis of hydrated calcium silicates has been carried out in unstirred slurries. The molar ratios of initial mixtures were as follows: $C/(S+A) = 0.83$ or 1.0 and $A/(S+A) = 0.10$, (C-CaO; S-SiO_2; A-Al_2O_3). Dry primary mixtures in the vessels of stainless steel have been mixed with water (water/solid ratio of the suspension W/S = 5.0). Hydrothermal synthesis has been carried out in the medium of saturated steam pressure at the temperature 175 °C (0.8 MPa), the duration of isothermal curing was 0, 1, 2, 4, 8, 16, or 24 h. The products of the synthesis have been filtrated, rinsed with ethyl alcohol to prevent carbonization of the material, dried at the temperature of 105 ± 5 °C, and sieved through sieve No. 008.

The X-ray phase analysis has been conducted using DRON-6 diffractometer (Bragg–Brentano geometry). The investigation has been carried out in the 2θ range from 4° to 60° with Ni-filtered Cu Kα radiation. The compounds lattice parameters calculation was done by using computer program PowderCell [22]. Thermal analyzer Du Pont 990 was applied for differential scanning calorimetry (DSC) studies; the rate of increasing temperature was 10 °C/min. The specific surface area of the raw materials has been determined by Blain's method. The quantity of free CaO in products of the synthesis has been determined by ethylenglicol method.

3. Results and discussions

Analyzing the X-ray diffraction patterns of synthesis products obtained from CaO and quartz mixture [$C/(S+A) = 0.83$, $A/(S+A) = 0.10$], it was determined that formation reactions of new compounds commence very rapidly by additionally increasing temperature in the autoclave. After isothermal, 175 °C temperature is reached; we are able to identify two new compounds—semi crystalline C-S-H(I) type hydrated calcium silicate (main d-spacing = 0.304 nm) and Si-free hydrogrossular—hydrogarnet, the chemical formula of which is $Ca_3Al_2(O_4H_4)_3$ (d-spacing—0.512; 0.443; 0.335; 0.313; 0.280; 0.246; and 0.229 nm). The structural formula of this compound is $3CaO \cdot Al_2O_3(3-x)SiO_2 \cdot 2xH_2O$, where x may vary from 0 to 3. The more accurate stoichiometric composition was determined analyzing PDF-2 data base [23]. From this, the compound lattice parameter dependence versus Si content was drawn (Fig. 1), and the obtained lattice parameter $a = 1.256$ nm showed that SiO_2 is not inserted into the

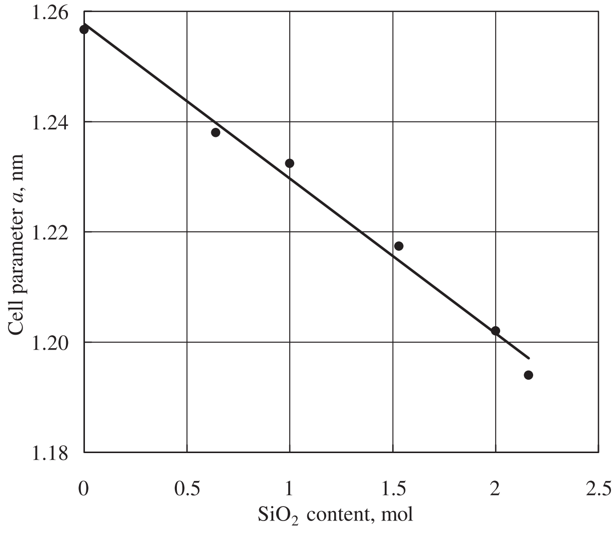

Fig. 1. The lattice parameter of $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ $_{(x=0\text{ to }3)}$ versus SiO_2 content.

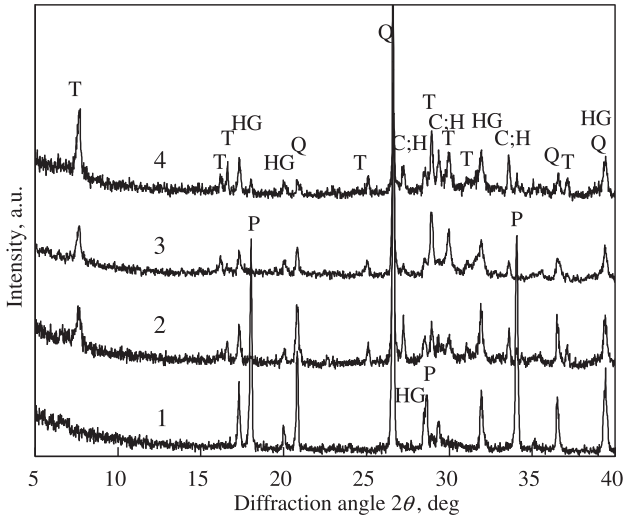

Fig. 2. X-ray diffraction patterns of the products formed during hydrothermal synthesis at 175 °C temperature. SiO_2 component is quartz. Mixture compositions and duration of isothermal treatment: 1 – $C/(S+A)=0.83$; $A/(S+A)=0.10$; $\tau=0$ h, 2 – $C/(S+A)=0.83$; $A/(S+A)=0.10$; $\tau=8$ h, 3 – $C/(S+A)=0.83$; $A/(S+A)=0.10$; $\tau=24$ h, 4 – $C/(S+A)=10$; $A/(S+A)=0.10$; $\tau=16$ h. Indexes: HG—hydrogrossular, P—portlandite $Ca(OH)_2$, Q—quartz, CH—C-S-H(1), T—tobermorite.

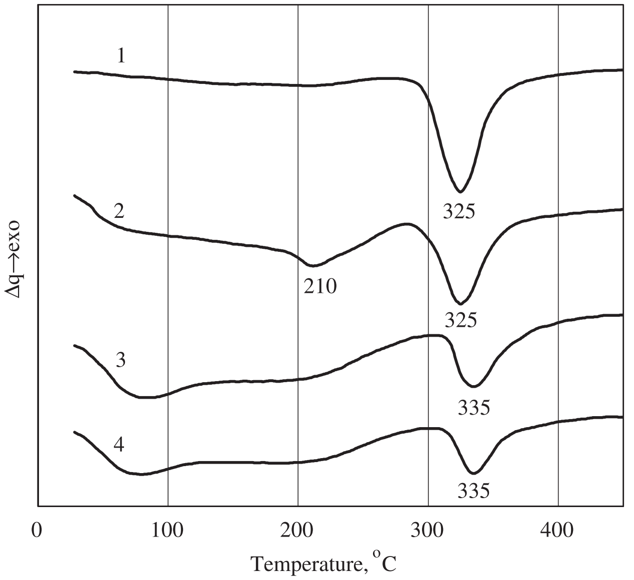

Fig. 3. DSC curves of the products formed during hydrothermal synthesis at 175 °C temperature. Mixture composition: $C/(S+A)=0.83$; $A/(S+A)=0.10$. SiO_2 component and duration of exposure: 1-SiO_2 component—quartz, $\tau=4$ h, 2-SiO_2 component—quartz, $\tau=24$ h, 3-SiO_2 component—$SiO_2 \cdot nH_2O$, $\tau=4$ h, 4-SiO_2 component—$SiO_2 \cdot nH_2O$, $\tau=24$.

formed hydrogrossular crystal lattice in lime–quartz mixtures, in this case $x=3$.

Nonreactant portlandite $Ca(OH)_2$ (d-spacing—0.492; 0.311; and 0.263 nm) and quartz (d-spacing—0.425; 0.334; 0.245; and 0.228 nm) also remain in synthesis products (Fig. 2, curve 1).

The quantity of $Ca(OH)_2$ while expanding duration of reaction is constantly reduced (Table 1), and therefore it becomes impossible to identify after 8-h isothermal treatment at 175 °C temperature. Meanwhile C-S-H(I) recrystallization to 1.13 nm tobermorite is intensively carried out (d-spacing—1.13; 0.548; 0.353; 0.308; 0.297; 0.282; and 0.253 nm) (Fig. 2, curve 2).

In DSC curves (Fig. 3), only endothermic effect is seen at 335 °C temperature after 4-h lime–quartz mixture synthesis when 4.5 molecule of water fractures off the hydrogarnet.

After 24-h isothermal exposure, the area of the peak describing hydrogarnet dehydration process is considerably reduced and the endothermic effect occurs at 210 °C temperature, which is caused by 1.13 nm tobermorite transition to 0.93 nm modification.

As intensity of diffraction reflections shows, the quantity of nonreactant quartz is constantly reduced while extending duration of isothermal treatment.

As it has been already mentioned, Si-free hydrogrossular intensively forms only if the temperature is increased in the autoclave. As the intensity change of its basic reflection (211) (Table 2) shows, the quantity of this compound during the first hour of isothermal treatment at 175 °C temperature increases a bit more and then hydrogrossular gradually commences to fracture. CaO is present in the further reactions with quartz forming hydrated calcium silicates, and Al^{3+} ions are inserted into 1.13 nm tobermorite crystal lattice.

These data well correlate with the quantity of Al^{3+} ions to be inserted into hydrated calcium silicate lattice, which was determined by the method of the DSC. Determination

Table 1
The quantity of nonreactant $Ca(OH)_2$ in synthesis products (%) considering as CaO

Duration of isothermal treatment (h)	Mixture compositions	
	$C/(S+A)=0.83$	$C/(S+A)=1$
0	14.21	15.03
1	11.28	11.99
2	10.14	10.89
4	3.34	4.17
8	–	3.02
16	–	1.87
24	–	traces

SiO_2 component–quartz.

Table 2
Dependence of hydrogrossular (211) diffraction peak intensity change on the synthesis duration at 175 °C temperature

Duration of isothermal treatment (h)	Intensity (arbitrary units)
0	143
1	157
2	141
4	132
8	97
16	89
24	86

technique has been previously described in detail [14]. Comparison of the data presented in Tables 2 and 3 shows that both the hydrogrossular basic reflection and Al_2O_3 quantity present in it are reduced by 1.9 times if the synthesis is extended from 1 to 24 h.

With the increase of CaO quantity in the starting mixture [C/(S + A) = 1.0, A/(S + A) = 0.10], the analogous results have been received. In the beginning of hydrothermal synthesis, Si-free hydrogrossular and C-S-H(1) are formed, the quantity of which constantly decrease in the run of the time. Tobermorite also starts its formation after 8-h isothermal treatment. The only significant difference is that $Ca(OH)_2$ reacts with more difficulties, and therefore its traces can be found even after a 24-h hydrothermal treatment at 175 °C temperature (Table 1).

Hydrothermal reactions are totally different in the mixtures where amorphous $SiO_2 \cdot nH_2O$ was used as SiO_2 component. When mixture composition is described by the molar ratios C/(S + A) = 0.83 and A/(S + A) = 0.10, total $Ca(OH)_2$ already reacts during the temperature increase up to 175 °C (Fig. 4).

Beside C-S-H(1) type hydrated calcium silicates, instead of Si-free hydrogrossular, another compound, calcium aluminium silicate hydrate—katoite, is formed. Its chemical formula, $Ca_3Al_2(SiO_4)_{0,5}(OH)_{10}$, was found from Fig. 1 by $a = 1.244$ nm, (d-spacing—0.505; 0.437; 0.330; 0.309; 0.278; 0.252; 0.242; and 0.226 nm). Thus, differently from the case when quartz has been used as a starting component, the composition of the formed hydrogarnets has SiO_2.

Another difference found is that even in the very beginning of the synthesis, a large semicrystalline C-S-H(I) quantity is formed; however, later it is more severely transferred to tobermorite. This compound forms only after a 16-h hydrothermal synthesis.

Analogous results have been also received in the starting mixture when CaO quantity was increased to the molar ratio C/(S + A) = 1.0. In the beginning of the synthesis, the same new compounds are formed—katoite and C-S-H(I), which in fact starts transferring to 1.13 nm tobermorite already after 8 h of isothermal treatment.

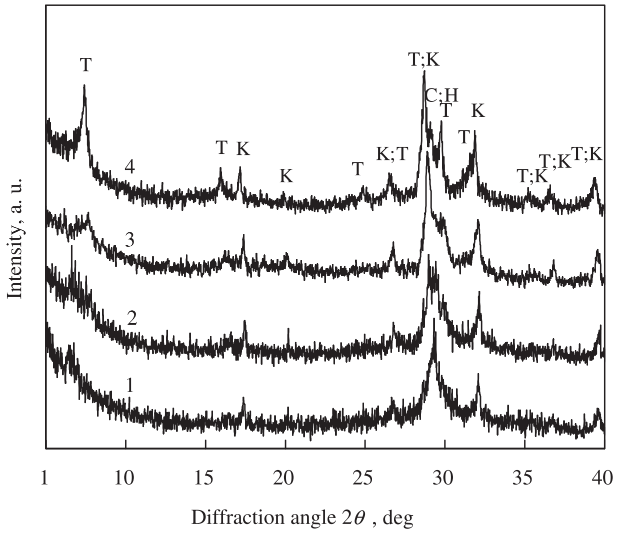

Fig. 4. X-ray diffraction patterns of the products formed during hydrothermal synthesis at 175 °C temperature. SiO_2 component—$SiO_2 \cdot nH_2O$. Mixture compositions and duration of isothermal treatment: 1-C/(S + A) = 0.83; A/(S + A) = 0.10; τ = 0 h, 2-C/(S + A) = 0.83; A/(S + A) = 0.10; τ = 8 h, 3-C/(S + A) = 0.83; A/(S + A) = 0.10; τ = 24 h, 4-C/(S + A) = 1.0; A/(S + A) = 0.10; τ = 24 h. Indexes: K—katoite, CH—C-S-H(I), T—tobermorite.

Totally different results were also received after the analysis of kinetics of Al^{3+} ion insertion into hydrated calcium silicate crystal lattice. Using quartz as SiO_2 component, in the beginning of the reaction, less than one fifth of total Al_2O_3 quantity present in the mixture is inserted into the composition of hydrated calcium silicates (Table 3). In the run of the time, more and more Al^{3+} ions in the tobermorite lattice substitute Si^{4+} ions. Meanwhile, when amorphous $SiO_2 \cdot nH_2O$ is used as SiO_2 component, already

Table 3
Dependence of Al_2O_3 quantity to be inserted into hydrated calcium silicate crystal lattice on the synthesis duration at 175 °C temperature

Modification of SiO_2 component	Synthesis duration (h)	Ignition losses (%)	Al_2O_3 quantity in hydrogarnet (%)	Al_2O_3 quantity in CSH (%)	Degree of Al_2O_3 insertion into CSH (%)
Quartz	0	16.63	7.55	1.66	18.07
	1	16.59	7.48	1.73	18.82
	2	15.51	7.28	1.93	21.02
	4	15.11	6.77	2.44	26.58
	8	14.56	5.46	3.75	40.69
	16	15.60	4.80	4.41	47.90
	24	16.32	4.04	5.17	55.52
$SiO_2 \cdot nH_2O$	0	19.06	4.58	4.63	50.24
	1	18.60	3.99	5.22	56.66
	2	17.91	3.82	5.39	58.54
	4	16.79	3.07	6.14	66.71
	8	16.73	2.68	6.53	70.85
	16	17.53	2.51	6.70	72.70
	24	18.36	2.21	7.0	75.94

Mixture composition: C/(S + A) = 0.83, A/(S + A) = 0.10.

with the temperature increase in the autoclave up to isothermal 175 °C temperature, approximately half of Al_2O_3 quantity present in the mixture is inserted into C-S-H(I) structure.

It has been previously known [14] that the maximum Al^{3+} ion quantity, which may be inserted into the tobermorite crystal lattice when mixture's $C/(S+A)=0.83$, is 7.013% (recalculating into Al_2O_3). This forms one aluminium atom for six silicon atoms and meets the molar ratio $A/(S+A)=0.08$. After comparison of this data with the results presented in Table 3, we see that during 24 h of hydrothermal synthesis when amorphous $SiO_2{\cdot}nH_2O$ is used as SiO_2 component, a maximum possible Al^{3+} ion quantity is inserted into the composition of hydrated calcium silicates. Meanwhile, in the mixtures with quartz, isomorphic substitution of Si^{4+} ions with Al^{3+} ions is considerably slower and reaches only 73.7% of its maximum size during 24 h.

4. Conclusions

Hydrogarnets were always among the first phases formed in the system CaO-SiO_2-Al_2O_3-H_2O under hydrothermal conditions and appeared before 1.13 nm tobermorite.

Using amorphous $SiO_2{\cdot}nH_2O$ as SiO_2 component, the starting raw materials react considerably quicker—total $Ca(OH)_2$ is already joined during the temperature increase up to 175 °C. Using quartz, when mixture composition is described by the molar ratio $C/(S+A)=0.83$, a small nonreactant $Ca(OH)_2$ quantity is found after 8-h and when $C/(S+A)=1.0$—even after 24 h of isothermal treatment at 175 °C temperature.

Using quartz or amorphous $SiO_2{\cdot}nH_2O$ as SiO_2 source, hydrogarnets of different chemical composition—Si-free hydrogrossular or katoite—are formed. Si^{4+} ions are inserted into the crystal lattice of the latter compound but not into the first one. Perhaps this is related to a lower solubility of quartz.

Hydrogarnets formed in the beginning of the reaction, expanding the duration of the synthesis, commence to fracture, and during 24 h their quantity is reduced almost in half. CaO is present in the further reactions with SiO_2, forming hydrated calcium silicates, and released Al^{3+} ions are inserted into 1.13 nm tobermorite crystal lattice.

Isomorphic Si^{4+} ions substitution with Al^{3+} ions in the hydrated calcium silicate crystal lattice is considerably quicker, if amorphous $SiO_2{\cdot}nH_2O$ is used as SiO_2 component. In this case, a maximum possible Al^{3+} ions quantity is inserted during a 24-h hydrothermal synthesis at 175 °C temperature. Meanwhile, using quartz as SiO_2 source, substitution of Si^{4+} ions during the same time does not even reach 75% of its maximum size.

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