Hydrothermal synthesis of calcium silicate hydrates in the presence of 3d-ferromagnetic cations

S A El-Korashy* & E IAI-Wakeel
Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt
and
E A Kishar
University College for Girls, Ain Shams University, Cairo, Egypt
Received 30 August 1996; revised 8 June 1998

The effect of transition metal cations, Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ on the formation of calcium silicate hydrates CaO-SiO$_2$-H$_2$O in the reaction system has been studied. The hydrothermal reaction products have been examined by X-ray diffraction, infrared spectroscopy and atomic absorption spectrophotometric techniques. The results indicate the presence of different shifts in the main interlayer $d$-spacing of calcium silicate hydrate hydrothermal products, especially 11A°-tobemorites: 5CaO·6SiO$_2$·5H$_2$O. Calcium silicate hydrate phases formed are affected by ionic radii, acidic radical, concentration of the concerned cations and the reaction time. The mechanism of the reaction and incorporation (or substitution) of these cations in the crystal lattice of calcium silicate hydrate phases is also discussed.

The chemistry of calcium silicate hydrate is essentially the chemistry of the reaction of Ca(OH)$_2$ with quartz and/or silicates at high temperature steam and higher pressure. The kinetics of phase formation in the reaction system CaO-SiO$_2$-H$_2$O was discussed in extended form in the review of autoclaved calcium silicates given by Taylor$^1$ and Kondo$^2$. The reaction pathway is governed by various parameters influencing the kinetics of the reaction and even the microstructure of the products, such as the presence of foreign ions and their concentrations. Tobermorite is an important constituent of many kinds of autoclaved calcium silicate hydrothermal products. Isomorphous substitution of Al is important since the tobermorite in technical products may incorporate foreign ions such as Al and Fe that could partially substitute Si atoms in its lattice structure$^3$. The effects of this substitution in hydrothermal synthesized tobermorite was systematically investigated by Diamound et al.$^4$, they also confirmed the location of Al in tetrahedral sites in the tobermorite lattice. It has also been reported that some of calcium silicate hydrate compounds may substitute SO$_4^{2-}$-ions in their lattice structure and alter their microstructure$^5$. Tashiro and co-workers$^6$ synthesized xonotlite by hydrothermal reaction of Ca(OH)$_2$, silica gel and coprecipitated SiO$_2$-Cr$_2$O$_3$. They found that 10% or more Cr(III) enters into CSH to form a solid solution, which promote the crystal growth of xonotlite.

Several authors$^7,13$ reported that, calcium silicate hydrate compounds, mainly 11A° tobermorite, 11A°-substituted tobermorites and xonotlite, acted as a cation exchangers for some metal cations with Ca$^{2+}$ or Si$^{4+}$ in their lattice structure and leading to their amorphization$^8$.

The present note reports, the effects of some ferromagnetic cations (Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$) on the hydrothermal synthesis of the main autoclaved calcium silicate hydrates 11A° tobermorite. The ferromagnetic cation chlorides and sulphates were added to clarify the role of the acidic radical on the mechanism of the reactions.

Experimental

CaO was prepared by calcination of CaCO$_3$ (BDH grade) at 1050°C for 3 h. Quartz of purity 99.82% SiO$_2$ with grain size below 45 µm was used. Different fixed amounts of distilled water-containing 1.3 or 10 wt. % ferromagnetic cations Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ as chlorides and sulphates in hydrated forms were added to prepare suspended mixture (1:1 by wt.) with CaO/SiO$_2$ molar ratio of 0.83. The well homogenized mixtures were hydrothermally treated in a high pressure autoclave at 175°C for 1, 7 and 14 days respectively. After autoclaving, the samples were dried at 60°C for 24 h and ground to pass through 0.063 mm standard sieve and then examined using different spectroscopic techniques: X-ray powder diffraction with a Philips diffractometer using Ni-filtered CuK$_\alpha$ radiation, infrared spectrophotometer and atomic-absorption spectrophotometry. AAS was used to deter-
Table 1—The unreacted ferromagnetic cations after hydrothermal reaction, detected by atomic absorption spectrophotometer (AAS)

<table>
<thead>
<tr>
<th>Reaction time/days</th>
<th>Initial cation concentration (wt %)</th>
<th>Fe(^{3+})</th>
<th>Unreacted cations (ppm)</th>
<th>Co(^{2+})</th>
<th>Ni(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cl(^{-})</td>
<td>SO(_4^{2-})</td>
<td>Cl(^{-})</td>
<td>SO(_4^{2-})</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>nil</td>
<td>3</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>nil</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>10</td>
<td>7</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

mine quantitatively the unreacted-cations in the final solid, this was done by stirring a constant weight of milled solid in hot doubly distilled water (at 80°C) for 1 h, then the filtrate was analyzed. In addition, the unreacted Ca(OH)\(_2\) after hydrothermal treatment was measured.

Results and discussion

XRD powder technique showed that 11\(\AA\)-tobermorites were the major calcium silicate hydrate hydrothermal reaction products. The main (002) d-spacing of tobermorites has been found in range 10.90-11.94\(\AA\). The shifts about 11\(\AA\) in normal (unsubstituted) tobermorites occurred clearly in the presence of higher concentrations of ferromagnetic cations. Moreover, calcium silicate hydrate (I) was also detected in specimens containing 1,3% of these cations (sometimes a few specimens contained 10% of these cations). On the other hand, calcium silicate hydrate phases such as: scawatite, nekoite, xenotlitie, gyrolite and hydrogarnet have been detected with variable amounts. The latter of these is detected in specimens containing 3 and 10% of Fe\(^{3+}\) or Co\(^{2+}\) ions, and CaSO\(_4\)·\(\frac{1}{2}\)H\(_2\)O phases are also present in all specimens containing metal cations as sulphates. The unreacted Ca(OH)\(_2\) was determined for the samples hydrothermally treated for 1-day which indicates that the unreacted free lime in the chlorides containing-samples lies in the range 0.1-0.5%, while the samples-containing sulphate revealed percentage of upto 0.25% free lime. It means that Cl\(^{-}\) ions have little negative effect on the rate of Ca(OH)\(_2\) dissolution compared to SO\(_4^{2-}\)ions. In general the unreacted Ca(OH)\(_2\) concentration increase with increase in concentration of metal-cations added to the reaction medium.

The results of the X-ray diffraction patterns of the hydrothermal reactions for CaO/SiO\(_2\) (molar ratio=0.83) system in the presence of different concentrations of ferromagnetic cations show that:

Fe\(^{3+}\)-ions (3\(\alpha\)):

(i) Fe\(^{3+}\)-as Chloride: At lower concentrations (1-3% Fe\(^{3+}\)) the detected phases were 11\(\AA\)-tobermorite, C-S-H, gyrolite Ca\(_4\)(Si\(_6\)O\(_{18}\))\((OH)_2\)·3H\(_2\)O and scawatite Ca\(_7\)(CO\(_3\))(Si\(_6\)O\(_{18}\))·2H\(_2\)O. Increasing the Fe\(^{3+}\) ions to 10% leads to the formation of hydrogarnet C\(_3\)F\(_6\) (3CaO·Fe\(_2\)O\(_3\)·6H\(_2\)O) as the only hydration product during 7-days. Traces of scawatite was observed by increasing hydrothermal treatment to 14-days traces.

(ii) Fe\(^{3+}\)-as Sulphate: The early hydration products (after 1-day) were anhydrous (CaSO\(_4\)), CaSO\(_4\)·\(\frac{1}{2}\)H\(_2\)O, CSH and 11\(\AA\)-tobermorite. The C-S-H was completely recrystallized into 11\(\AA\)-tobermorite after 14-days treatment.

Co\(^{2+}\)-ions (3\(\alpha\)):

The formation of anhydrous CaSO\(_4\) has been detected only in the case of sulphate, in addition to the other common phases. Moreover, the formation of nekoite (CaSi\(_2\)O\(_5\))·2H\(_2\)O, CSH-gel and CaCO\(_3\) took place on using higher concentration of Co\(^{2+}\) as chloride. Presence of 10% Co\(^{2+}\)-ions decrease the amount of the formed tobermorite.

Ni\(^{2+}\)-ions (3\(\alpha\)):

In the presence of 10% Ni\(^{2+}\) ion gyrolite was not formed and the nekoite phase appeared. On the other hand, traces of xenotlitie was detected with 1-3% of Ni\(^{2+}\) ions added as chloride while scawatite phase appeared with 1-3% Ni\(^{2+}\)-ions addition as sulphate. With 10% Ni\(^{2+}\)-ions as sulphate a new
phase nearly with main XRD patterns of the synthetic nickel phlogopite \([\text{K}_2\text{Ni}_6(\text{Al}_2\text{Si}_6)\text{O}_{20}(\text{OH})_4]\) was observed.

The XRD results revealed the following general remarks: (i) The ferromagnetic cations are incorporated in the crystal lattice of calcium silicate hydrates phases, especially in 11A\(^{0}\)-tobermorites which lead to a considerable shift in the (002) d-spacing at 7.8\(^{0}\) (two theta) position of 11A\(^{0}\)-tobermorites. (ii) On addition of these cations as sulphates, \(\text{CaSO}_4\) anhydrous appeared. Its amounts increases with increase in \(M^{n+}\)-ions concentration and reaction time.

The results of ASS shown in Table 1 revealed complete entrance of these cations in the lattice structure of the formed. The recorded 2-9 ppm in some samples, may be attributed to the solubility of these cations in water.

The infrared spectra of reference sample and samples-containing metal sulphates showed similar spectral bands with varying degrees of intensity. These bands were located at, 3481-79, 1665-23, 1486, 1452 (doublet), 1060-976 (appeared as multibroad bands), 939-34, 877, 753-52, 677-69, 519-15 (not found in all samples), 499-89 and 461-45 cm\(^{-1}\). On the other hand, samples containing 10\% metal sulphates possess additional bands located at 1158, 1118 (doublet) and 617-16 cm\(^{-1}\). These bands are due to the presence of \(\text{SO}_4^{2-}\) groups\(^{14,15}\). It was found that, the samples containing 10\% metal-chlorides, showed some differences in their spectrum compared with those containing metal sulphates, revealing some differences in band positions. The spectral bands, found at 3481-79, 1665-23, 1060-976 and 461-45 cm\(^{-1}\), may be due to O-H stretching, O-H bending, Si-O stretching and Si-O-Si bending vibration modes of 11A\(^{0}\)-tobermorite, respectively\(^{15,16}\).

During the hydrothermal reactions between \(\text{SiO}_2\) and \(\text{Ca(OH)}_2\), CSH-phases are formed with different degrees of crystallinity and \(\text{CaO/ SiO}_2\) molar ratios. The \(M^{n+}\) ions are incorporated and/or substituted in the crystal lattice of the formed CSH-phases. On the other hand, the \(\text{CaSO}_4\cdot2\text{H}_2\text{O}\) may enter in the crystal structure of the initially ill-crystalline CSH-phases\(^{18}\) and the excess remains as anhydrous \(\text{CaSO}_4\). By increasing the time of autoclaving some of the \(\text{SO}_4^{2-}\) ions in ill-crystalline CSH-phase are released outside the crystal structure and the amount of the free-\(\text{CaSO}_4\) increases. This was confirmed by the XRD analysis. When \(\text{CaO/ SiO}_2\) mixes with metal chlorides, no evidence for incorporation of \(\text{Cl}^-\) ions in the hydrothermal products is found. However, it is postulated that \(\text{Cl}^-\) ions can be replaced OH\(^-\) groups in the crystal structures CSH\(^{17}\).

The reaction mechanism of \(\text{CaO- SiO}_2-\text{H}_2\text{O}\) in the presence of ferromagnetic cations under hydrothermal conditions can be suggested as shown (Scheme 1).

**I-Atom temperature**

(i) \(\text{CaO+H}_2\text{O}\rightarrow\text{Ca(OH)}_2+\text{heat evolved}

\[\text{M-Cl} \hspace{1cm} \text{M-SO}_4 \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \]

\((x=2 \text{ or } 3) \hspace{1cm} (\text{M}=\text{Fe}^{3+}, \text{Co}^{2+} \text{ or } \text{Ni}^{2+})\)

**II-In autoclave**

(i) In case of \(M-\text{SO}_4\):

\[\begin{align*}
\text{Ca(OH)}_2 \\
\text{SiO}_2 \\
M(\text{OH})_x \\
\text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\end{align*} \rightarrow [M - \text{SO}_4 = \text{CSH}] \rightarrow \text{M - CSH}^+ + \text{CaSO}_4\text{(II) anhyd} \]

(ii) In case of \(M-\text{Cl}\)

\[\begin{align*}
\text{Ca(OH)}_2 \\
\text{SiO}_2 \\
M(\text{OH})_x \\
\text{CaCl}_2 \cdot 6\text{H}_2\text{O}
\end{align*} \rightarrow \text{M - CSH} + \text{C}_2\text{F}_6 \hspace{1cm} (\text{F=Fe}_3\text{O}_3)\]

Scheme (1)

The ionic radii of the transition elements cations, \(\text{Fe}^{3+}, \text{Co}^{2+} \text{and } \text{Ni}^{2+}\) are 0.55, 0.65 and 0.69 \(\text{A}^\circ\) respectively. This is in agreement with the literature that \(\text{Al}^{3+}\)-ions can substitute for \(\text{Si}^{4+}\)-ions in the 11A\(^{0}\)-tobermorite structure. This substitution occur up to 15\% Si in tobermorite lattice structure before hydrogarnet is found\(^{17}\). However, the ionic radii of \(\text{Al}^{3+}\) and \(\text{Fe}^{3+}\) are 0.35 and 0.55 \(\text{A}^\circ\) respectively, theoretically it means that, \(\text{Fe}^{3+}\) may substitute in tetrahedral sites and/or with \(\text{Si}^{4+}\)-ions in the lattice structure of tobermorite rather than \(\text{Co}^{2+}\) and \(\text{Ni}^{2+}\). Copeland et al.\(^{16}\) reported that, in high lime tobermorite gel, \(\text{Fe}\) can be substituted in amounts of 7.1\% and the product has a C/S ratio of 1.52, while \(\text{Al}\) in amount of 5\% substituted in a solid with C/S...
ratio of 1.5. In the crystallization of Fe-tobermorite gel to low-lime gel and then to tobermorite some or all of the Fe$^{3+}$, depending on intensity of autoclaving may be expelled. This explanation do not agree with the present data, because there is no detection of free oxide, geothite (FeO·OH) or even simple chloride salts in the hydrothermal products. The only Fe-bearing phase complex detected at 10% Fe as chloride is the hydrogarnet (3CaO·Fe$_2$O$_3$·6H$_2$O). The hydrogarnet phase appears only in case of Fe-chloride, while on the addition of Fe as SO$_4^{2-}$, it was not formed. This may be due to the uptake of Ca$^{2+}$-ions by the SO$_4^{2-}$-ions to form calcium sulphate during the mixing process. The CaSO$_4$·2H$_2$O formed seemed to be more stable than the hydrogarnet, which needs 3 mole of CaO to be formed.

It was reported that Mg$^{2+}$ ions (0.72 Å) substitute with Ca$^{2+}$ ions in some C–S–H phases, thereby in the present study Co$^{2+}$ and Ni$^{2+}$-ions could be substituted with Ca$^{2+}$ ions in the lattice structure of tobermorite, this may be due to relative matching of their ionic radii with Mg$^{2+}$-ions.

XRD patterns revealed the deviation of the main basal reflection peak at 11.3 Å of the tobermorites especially with higher concentration of metal cations. This supports the substitution of the concerned cations with Ca$^{2+}$ in tobermorites.

References
1 Taylor H F W, “Proceeding of the fifth international symposium on the chemistry of cements” part II “Hydration of cements”, 11 (1968), 1-26, Tokyo.