



Cement Chemisrty: The Hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ Compound

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ABSTRACT

Dicalcium silicate (Ca_2SiO_4) is an important component of cement. The compound of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ can be formed if the Sr-containing precursors are used to synthesize the cement. The presence of Sr may alter the hydration of the products. The hydration chemistry of the $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound is reported. The hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ was conducted under a nitrogen atmosphere for about 6 months. The dry samples were characterized using XRD, FTIR, TGA-DSC, and SEM-EDX methods. It is confirmed that the hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ produces mainly $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$. Furthermore, the Sr doped $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ are possibly formed. The compound of CaCO_3 , as the result of interactions between $\text{Ca}(\text{OH})_2$ and atmospheric CO_2 gas during the sample handling, is also observed. Dicalcium silicate (Ca_2SiO_4) is an important component of cement. The compound of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ can be formed if the Sr-containing precursors are used to synthesize the cement. The presence of Sr may alter the hydration of the products. The hydration chemistry of the $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound is reported. The hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ was conducted under a nitrogen atmosphere for about 6 months. The dry samples were characterized using XRD, FTIR, TGA-DSC, and SEM-EDX methods. It is confirmed that the hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ produces mainly $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$. Furthermore, the Sr doped $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ are possibly formed. The compound of CaCO_3 , as the result of interactions between $\text{Ca}(\text{OH})_2$ and atmospheric CO_2 gas during the sample handling, is also observed.

Keywords: Cement, Dicalcium silicate, Hydration, $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$, $\text{Ca}(\text{OH})_2$.

INTRODUCTION

Cement is a hydraulic compound which able to bind other solid materials, forming a hard and insoluble solid mass unit. In practice, the cement is applied to agregate stones, bricks, concrete blocks, ceramics or more other building materials. Active compounds in Portland cement include calcium

silicate. If lime and silica are mixed thoroughly and heated, four different calcium silicate compounds will be formed, one of which is dicalcium silicate (Ca_2SiO_4), which has five forms of polymorphism, namely α , α' , α'' , β and γ .¹

Portland cement is made of a mixture of minerals containing various elements including Mg,



Ca, Si, and Al. However, a trace of Sr may exist in the minerals. So there is a possibility that the element of Sr is doped in the Ca_2SiO_4 producing $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound. This is supported by Bickle (1994) stated that the compound of Sr doped in β - or α 'L- Ca_2SiO_4 can be formed in the cement if Sr exists in the cement raw materials.²

In use, the cement is generally mixed with water, so that it forms hardened cement hydrate. The hydration of dicalcium silicate can only be studied if the hydrate form is stable as a solid solution. The hydration rate of dicalcium silicate is varied. Very slow rate of hydration of γ - Ca_2SiO_4 relative to other Ca_2SiO_4 polymorphs is caused by the position and arrangement of oxygen atoms around Ca^{2+} ions in γ - Ca_2SiO_4 which is irregular compared to other polymorphs.³ This indicates that the Ca_2SiO_4 hydrolysis depends on the thermodynamic factors, especially the lattice energy and hydration heat. The hydration products of β - Ca_2SiO_4 are $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and portlandite ($\text{Ca}(\text{OH})_2$).^{4,5} In the air, $\text{Ca}(\text{OH})_2$ may interact with CO_2 and H_2O . It is well known that the compound of calcium hydroxide is not very stable in the concrete, and will usually react with other components to form a more stable structure.⁶⁻⁸

Elements that are doped in the compounds may alter the nature and the activity of other compounds, such as calcium silicate hydration. The hydration reaction of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compounds has not been studied. The hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ under a nitrogen gas environment will be studied.

EXPERIMENTAL

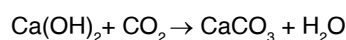
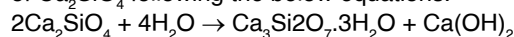
This research was conducted to examine the hydration reaction of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ ($x = 0, 0.01, 0.025$ and 0.05) compound. The hydration process was carried out by adding distilled water to the $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound, with weight ratio of 100:1, in the sample bottle. The mixture was stirred and bubbled with nitrogen gas to remove CO_2 from the mixture. After the free CO_2 mixture was obtained, the sample bottle was immediately tightly closed so that the mixture of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ was isolated from the air. Then the mixture was allowed to stand for 6 months, and followed by drying at 110°C to evaporate the water to obtain dry $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ hydrated. The characterization of the hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ was undertaken by using

powder X-Ray Diffraction (XRD *Bruker D2 Phaser*), SEM-EDX (JEOL IT300), FTIR (Thermo Nicolet IS 10) and TGA-DSC (Linseis) methods.

RESULT AND DISCUSSIONS

The X-Ray Diffraction Spectroscopy (XRD) method has been applied to determine the qualitative aspects of components in the hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ ($x = 0, 0.01, 0.025$ and 0.05) compound. The X-ray diffraction patterns of the samples are depicted in Figures 1 and 2.

The XRD diffraction patterns of hydrated samples (Fig. 1 and 2) indicate that the hydration reaction is expected to occur in $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$. The hydration reactions take place similar to the hydration of Ca_2SiO_4 following the below equations.



The hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound produces $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$, and it is also believed that the isomorphous of $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ that is $\text{Ca}_{3-x}\text{Sr}_x\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ exists. The XRD spectra also indicates the presence of CaCO_3 compound. This is possible because of the samples are not always isolated under the nitrogen gas. Calcium hydroxide is relatively unstable in the open air, and so it reacts easily with other compounds in the air, one of which is CO_2 and forms calcium carbonate. In addition, unreacted $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound is also observed. This is possible because the hydration of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound is very slow and taken place from the outer to inner layer, leaving the inner part of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ unreacted.

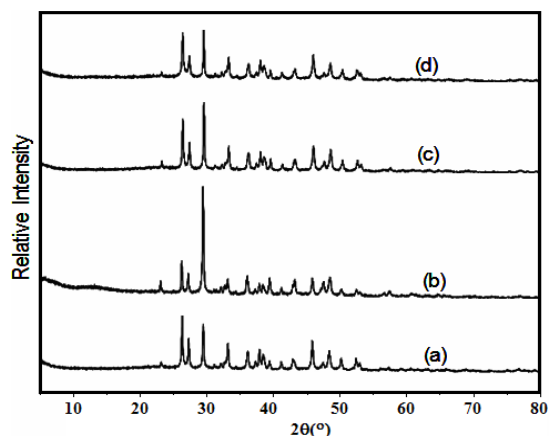


Fig. 1. The X-ray diffraction patterns of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compounds with $x = 0$ (a), 0.01 (b), 0.025 (c), dan 0.05 (d)

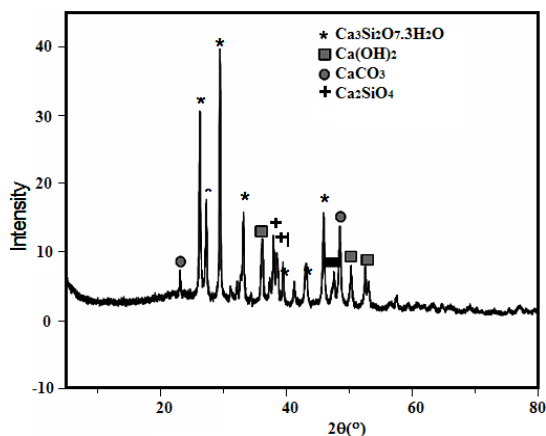


Fig. 2. The X-ray diffraction patterns of hydrated $\text{Ca}_{1.975}\text{Sr}_{0.025}\text{SiO}_4$

The IR spectra of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compounds are depicted in Fig. 3 and 4. The Si-O stretching vibrations is observed in the low and narrow band located at $\sim 800\text{ cm}^{-1}$. This is in agreement with the finding of Ping *et al.*, stated that the vibration of Si-O stretching appears in the region of $795\text{-}800\text{ cm}^{-1}$, and the Si-O stretching from SiO_4 tetrahedron is located in the region of $800\text{-}1000\text{ cm}^{-1}$.^{9,10} The band position may shift to higher or lower wave number according to the ratio of calcium/silica.

The Si-O-Si asymmetric stretching of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound with different variations of x are observed at peak of $\sim 1000\text{ cm}^{-1}$ with height and width shaped bands. The intensity can be related to the progress of hydration.^{11,12}

The O-H stretchings in free water appears with low and wide band at wave number $\sim 3400\text{ cm}^{-1}$.^{13,14} Absorption at $\sim 3640\text{ cm}^{-1}$ represents O-H stretching of $\text{Ca/Sr}(\text{OH})_2$ compound. This weak and wide peak is overlapped with OH's stretching band of free water. The weak and narrow band at $\sim 874\text{ cm}^{-1}$ represents Ca/Sr-O bond.¹⁵

The bands at $1400\text{-}1600\text{ cm}^{-1}$ indicate the presence of CaCO_3 . The formation of CaCO_3 is a complex process involving reactions on the $\text{Ca}(\text{OH})_2$ particle surfaces. The mechanism of this reaction is not yet fully understood. In the early stages the carbonate formed could be considered amorphous, which then is developed to crystalline phase. The C-O bending molecular vibration is observed as sharp and high band at $\sim 1480\text{ cm}^{-1}$, while the band in the region of 1483 cm^{-1} belongs to the CO_3^{2-} group. Vibration of the C-O bending is observed at $\sim 850\text{ cm}^{-1}$, which is the region of the bending vibration of the carbonate

group.¹⁶ A very small band at 2927 cm^{-1} can be associated with calcite vibrations of C-O.¹⁷

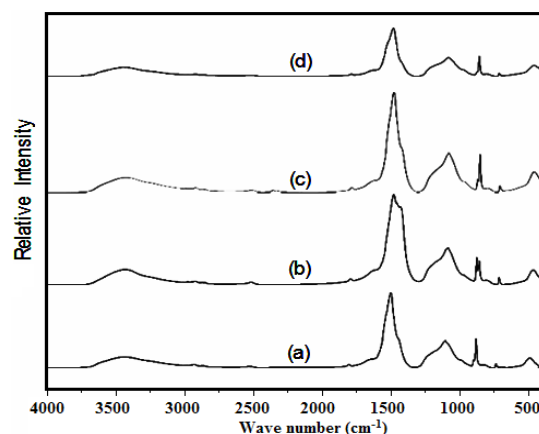


Fig. 3. The IR spectra of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compounds with $x = 0$ (a), 0.01 (b), 0.025 (c), dan 0.05 (d)

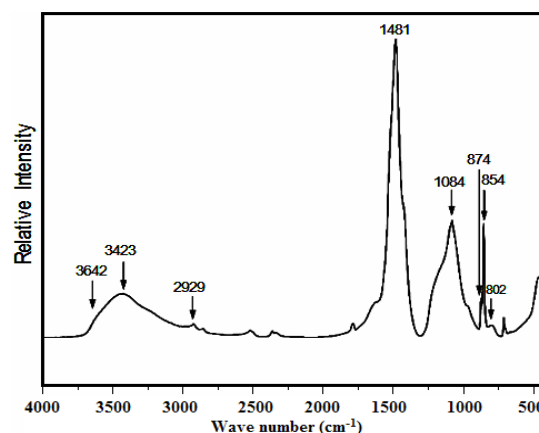
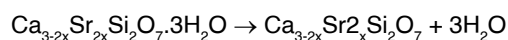


Fig. 4. The IR spectra of hydrated $\text{Ca}_{1.975}\text{Sr}_{0.025}\text{SiO}_4$ compound

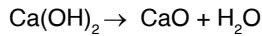
The thermogravimetric analysis (TGA) is undertaken on about 22 mg of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ sample. TGA measurement shows that the typical thermal decomposition of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound occurs in several steps as shown in Figure 5.

The thermal decomposition of the all hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compounds occurs at similar temperature. The compounds are estimated to undergo water releasing in the $\text{Ca}_{3-2x}\text{Sr}_{2x}\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ at $100\text{-}165^\circ\text{C}$, to form $\text{Ca}_{3-2x}\text{Sr}_{2x}\text{Si}_2\text{O}_7$ and free H_2O . The reaction is as follows.



Decomposition continues to a temperature of $\sim 600^\circ\text{C}$ in which the estimated loss of water in the $\text{Ca}(\text{OH})_2$ producing CaO . In theory, the

decomposition of Ca(OH)_2 occurs at 240-550°C. The decomposition of Ca(OH)_2 compound is less in accordance with the theory, presumably because the water in Ca(OH)_2 compounds is very crystalline so it requires longer time and higher temperature to release. The Ca(OH)_2 decomposition can be described as follows.



The presence of CaCO_3 compounds in the sample can be made possible because Ca(OH)_2 is a reactive compound and is not always in an open CO_2 -free condition. The decomposition of the carbonate occurs at a temperature of 750-780°C which is the loss of CO_2 from the CaCO_3 compound. The reactions are:

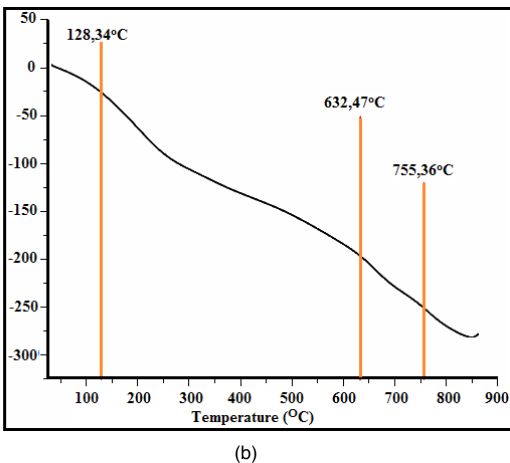
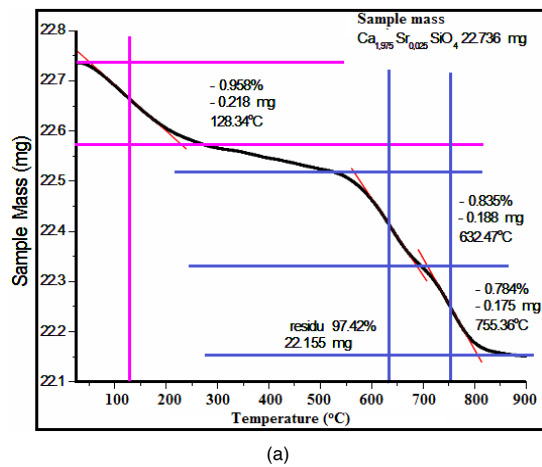
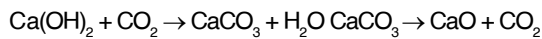


Fig. 5. The typical TGA (a) and DSC (b) curves of the hydrated $\text{Ca}_{1.975}\text{Sr}_{0.025}\text{SiO}_4$ compound

The Scanning Electron Microscopy Electron-Dispersive X-Ray Analyzer (SEM-EDX) is used to determine the surface morphology and composition of the samples of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ with $x = 0, 0.01, 0.025$ and 0.05 .

The SEM image (Fig. 6) indicates that the hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound having an irregular shape, with the size at about $0.3 \mu\text{m}$ to $0.67 \mu\text{m}$ in diameter based on the EDX analysis, the quantity of Ca, Sr and Si atoms in the sample is obtained. However, the EDX analysis cannot be used as a basis for determining the number of atoms in the sample, because in general the EDX analysis is only undertaken on the surface of the sample.

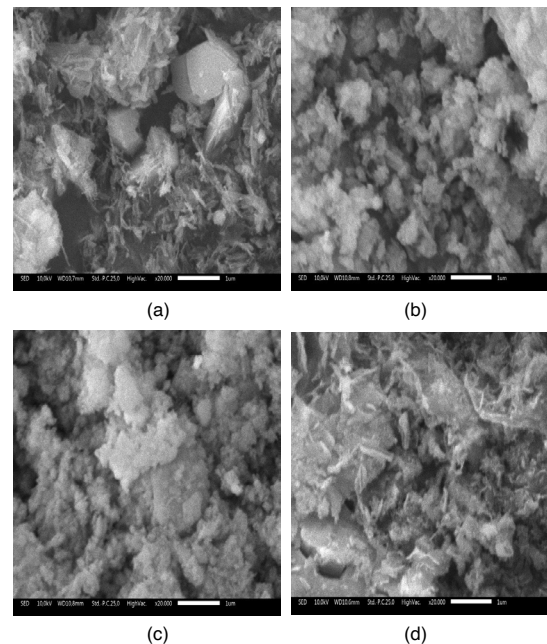


Fig. 6. The SEM images of the hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ compound with $x = 0$ (a), 0.01 (b), 0.025 (c) and 0.05 (d)

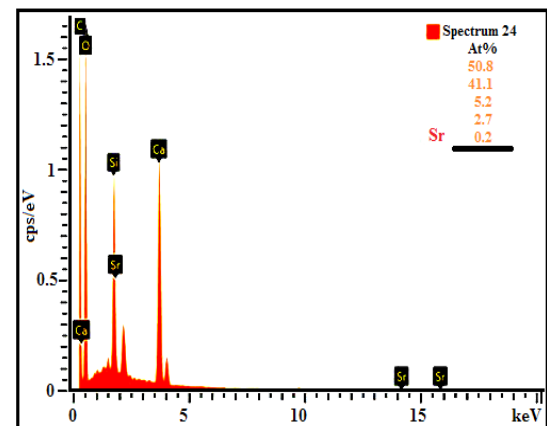


Fig. 7. EDX Spectra of hydrated $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ with $x = 0.025$

CONCLUSION

The compound of $\text{Ca}_{2-x}\text{Sr}_x\text{SiO}_4$ has been hydrated producing at least two major products, that are $\text{Ca}_{3-2x}\text{Sr}_{2x}\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ dan $\text{Ca}(\text{OH})_2$. The $\text{Ca}(\text{OH})_2$ is partly carbonated to CaCO_3 . The products have been confirmed by existences of Si-O stretching, O-Si-O stretching, O-H stretching, Ca-O stretching dan C-O bending dan stretching bands. The molecules of water of $\text{Ca}_{3-2x}\text{Sr}_{2x}\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ are released during heating at 100-165°C, while heating at 600-650°C causes the decomposition of $\text{Ca}(\text{OH})_2$

producing CaO. The CO_2 gas is produced by the heating CaCO_3 at 750-780°C.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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