

FIXATION OF CHLORIDES BY CALCIUM SILICATE HYDRATES

Koshiro Koizumi, Yasuhiro Umemura*, Tetsuya Yoneda, and Naomitsu Tsuyuki

Department of Chemistry, College of Science and Technology, Nihon University, 7-24-1, Narashinodai, Funabashi, Chiba 274-8501, Japan.

*Department of Civil Engineering, College of Science and Technology, Nihon University, 1-8-14, Kanda surugadai, Chiyoda-ku, Tokyo 101-8308, Japan.

Introduction

It is well known that the chloride ion, which causes salt damage, is fixed in the materials formed by hydration of cement. "Friedel Salt" is researched in detail and known as a stable cement material which contains chloride ions.^{1,2} Tsuyuki and others have reported that they are trying to fix chloride ions into concrete by use of barium salt.³ However, the reports above are the case of the reaction in cement paste or concrete at the normal (room) temperature. And, moreover, it is known that calcium silicate compounds and calcium chloride, when burned at the temperature between 800 and 1000°C, generate stable minerals, such as $\text{CaO}\cdot\text{SiO}_2\cdot\text{CaCl}_2$,⁴ $2\text{CaO}\cdot\text{SiO}_2\cdot\text{CaCl}_2$ ⁵ and $9\text{CaO}\cdot 6\text{SiO}_2\cdot\text{CaCl}_2$ ⁶ and so on. We have focused on the wastes of the Autoclaved Lightweight Concrete (ALC) which have the calcium silicate hydrates (C-S-H) as the principle ingredients, and have studied the feasibility of C-S-H as chloride fixation material at the high temperature. This paper clearly shows how the mechanism of the fixation of chloride ions is made at the high temperature, using the hydrothermally synthesized pure C-S-H. Depending on the result of these experiments, we could expect the C-S-H to work as a reducible material against toxic substances comprised of chlorines, such as polychlorinated dibenzo-dioxins which origin is inorganic chlorides from food residue at a waste incineration process.⁷ Furthermore, it is expected that we could make use of the waste of ALC effectively in the near future. Two types of C-S-H having different CaO/SiO₂ molar ratio were synthesized and burned with calcium chloride to compare the difference in chloride fixation capability. Changes in the chain length of silicate anions associated with burning and fixation of the chloride were studied in terms of chloride fixation capability using trimethylsililation technique.⁸

Materials and methods:

Synthesis of C-S-H

The two types of C-S-H those with CaO/SiO₂ ratio of 1.0 and 1.5 were synthesized hydrothermally to clear that the difference in chloride fixation capability according to CaO/SiO₂ molar ratio. The lime was a guaranteed commercial reagent burned at 1000°C and the silica was a commercial quartz powder with a mean diameter of 3.5 micrometers. The lime and the quartz were mixed with a distilled water with mass ratios of 19.4 : 20.6 : 60 for CaO/SiO₂ ratio of 1.0 (CSH_{1.0}), and 23.4 : 16.6 : 60 for CaO/SiO₂ ratio of 1.5 (CSH_{1.5}) respectively. Autoclave curing was made for 3 hours at a temperature of 180°C and the subsequent annealing was made in a desiccator. The resulting samples were subjected to powder X-ray diffraction analysis.

Burning method

The synthesized C-S-H and the chloride compounds were burned in the following conditions. The C-S-H and a guaranteed commercial reagent CaCl₂ were mixed with a mass ratio of 2:1 in a methanol solution. After drying at a room temperature, the samples were burned in an electric furnace for an hour. The burning temperature was varied in units of 100°C from 600°C to 1000°C. The resulting minerals were identified by X-ray diffraction analysis.

Trimethylsililation

The chain length distribution of silicate anions in the C-S-H and burned calcium silicate (dehydrated C-S-H ; C-S) were approached by the trimethylsililation (TMS) technique to know the C-S-H structure associated with the fixed chlorides. Silicate derivatives were obtained according to the method proposed by Sugihara and others⁹⁻¹¹. Trimethylchlorosilane and Hexamethyldisiloxane were mixed with a solvent methanol at a volumetric ratio of 1 : 3 : 2. 18 mL of the solution was added to 200 mg of the synthesized C-S-H or C-S and stirred for 60 minutes at a room temperature. After the full reaction, 20 mL of water was added to the solution, which was then

applied to a separating funnel and shaken to complete the liquid-liquid extraction. Water soluble lower layer was removed and the residual upper layer was further rinsed out for several times to remove water soluble components from the upper organic solvent layer. 2.0g of non-ionic ionexchange resin (AMBERLYST-15, Rohm and Haas Company) were added to avoid isomerization and the solvent was kept for 24 hours. Then the solvent was thickened less than 1 milliliter under the nitrogen atmosphere and subjected to gas chromatography (GLC) analysis. Identification of the GLC intensity peaks are referred to the literature 9 and the integrated peak areas drawn by the indicator (CR-6A, Shimadzu) were substituted for the relative composition of the components because the reference material for the determination was not available.

Elution test

Chloride ion eluted from the burned C-S-CaCl₂ was tested to confirm the stability in fixation. 1.0g of the burned C-S-CaCl₂ was stirred and dispersed in 200 mL of distilled water. The solution was sampled at a regular interval and the Cl⁻ concentration was determined by ion chromatography (LC-10A, Shimadzu).

Results and Discussion:

Properties of synthesized C-S-H and effects of burning temperature upon fixation

Mineral compositions of the two synthesized C-S-H (CSH_{1.0} and CSH_{1.5}) were determined by X-ray diffraction analysis. In addition to the common peak of unreacted silica, poorly crystallized tobermorite was identified in the CSH_{1.0}, while poorly crystallized C-S-H was observed in the CSH_{1.5}. It was confirmed that the synthesized C-S-H is almost equivalent to C-S-H which is the main ingredient of ALC. Each C-S-H showed a characteristic thermal behavior by TG-DTA analysis. A large exothermal peak around 850°C was observed corresponding to the formation of Wollastonite (CaO·SiO₂) (indicated as CSH_{1.0} and CSH_{1.5} in Fig.2), which indicated that chloride ions may be fixed as CS·CaCl₂ mineral. The chain length distributions of silicate anions in the synthesized C-S-H were determined from the results of trimethylsilylation (indicated as CSH_{1.0} and CSH_{1.5} in Fig.3). The synthesized C-S-H was mixed with a half mass of CaCl₂, at mass ratio of 2:1, in a methanol solution. After drying at a room temperature, specimens were subjected to burning in an electric furnace under variable burning temperatures. Changes in X-ray diffraction peaks according to burning temperature are as follows: It was confirmed that CaO·SiO₂·CaCl₂ formed in the CSH_{1.0} when burned at 700°C, and in CSH_{1.5} when burned at 600°C, showing the fixation of chloride ions even at low temperatures. When the burning temperature increased, a chloride containing mineral 9CaO·6SiO₂·CaCl₂ became dominant in either C-S-H. X-ray diffraction peak intensities of d=0.2744 nm and d=0.3002 nm, corresponding to the CaO·SiO₂·CaCl₂ in samples of CSH_{1.0} and CSH_{1.5} respectively, were compared in Fig.1, where maximum diffraction was observed at a temperature range from 800 to 900°C. Thermal analysis of the burned mixture of C-S-H and CaCl₂ is shown in Fig.2, where it is shown that the exothermal peak due to the formation of Wollastonite is significantly lowered around 740°C while that of C-S-H alone was around 850°C. Thus the results of the X-ray diffraction and the thermal analysis may result in a possibility that chloride ions can be fixed in a stable mineral when burned at 800°C.

Changes in silica skeleton due to burning

C-S contains silicate ion whose structure may be modified during burning. Thus the changes in silica structure associated with burning were traced with the help of TMS technique. It was supposed from the thermal analysis that two types of C-S-H used in this experiment may show a considerable change in their crystal structures at a temperature between 800 and 850°C. In order to compare the silicate anion structure of C-S-H with that of burned C-S, 3 specimens were sampled at different temperatures and subjected to TMS analysis. The first one was at 400°C, much lower temperature than the transition to Wollastonite, and the other two were at 800°C and at 900°C, before and after transition. Results are shown in Fig.3. Dimer was dominant before burning and the chain length distribution exhibited a tendency of becoming uniform associated with a relatively low temperature burning of 400°C. While at higher temperatures of 800 and 900°C, it seemed that silica chains were extensively broken and existing as monomers. The most distinctive feature unlike those unburned or burned at a low temperature was the presence of underived C-S of nearly 50% after TMS derivative reactions though the composition varied according to the type of C-S. The reason of the partial TMS derivation of the high temperature treated C-S may be attributed to a transition of silica chains to a glassy, disordered polymeric structure, while the rest short-chain components may be selectively trimethylsilylated. Another C-S sample

burned with CaCl_2 at 800°C , which has been proven to be an appropriate burning temperature for chloride fixation, was also subjected to TMS analysis. Results are shown in Fig.4, where it is observed that monomer is dominant in each type of C-S compared to C-S alone. Thus silica in C-S may form a partially glassy polymer chain at a high temperature treatment regardless of the presence of chlorides.

Elution of chlorides from the burned C-S

Elution of chlorides from the burned C-S- CaCl_2 mixture was tested. Results are shown in Fig.5. It was shown that the elution of chloride ion occurred rapidly within the first 2 to 4 hours in either C-S leading to a subsequent stable low elution. The elution rate used in the figure was defined as a ratio of released Cl^- concentration to the total chloride in the burned C-S- CaCl_2 mixture. Elution rate of C-S with a $\text{CSH}_{1.5}$ burned with CaCl_2 was slightly smaller than that of the other and the amount was less than 15 percent. Therefore in each C-S, about 80 percent of chloride at least can be fixed in a stable manner. After the elution test, the powder sample was recovered and reexamined the stability to concentrated acid. Because no elution was observed under any types of concentrated acid, chlorides may be fixed as a solid solution in a glassy C-S.

Changes in silica skeleton of burned C-S-H with NaCl

When we assume that these synthesized C-S-H were used in the incinerator for fixation of chloride ions of which origin is municipal waste, it is more realistic to use NaCl as chloride. Then, the silicate anion structures of the synthesized materials, which consisted of C-S-H and NaCl burned at 800°C , were analyzed as well as the case of CaCl_2 . However, the detective substances of silicate anions (monomer to hexamer types silicate chains) were not detected by use of TMS technique. These results suggest that the longer chain silicate anions like three-dimensional random networks formed by promoting vitrification. The DTA curves of mixtures of synthesized C-S-H and NaCl in different mixing were described in Fig.6. The phase transition temperature that C-S-H makes Wollastonite has decreased, as well as the case of mixing with CaCl_2 . In accordance with increasing of the addition of NaCl, the phase transition temperature has declined to 700°C . As mention above, it is thought that a lot of chlorides can be fixed as molten state by mixing and burning with synthesized C-S-H or ALC waste powders in incinerator.

References:

1. J.K.Solem-Tidhmack and G.J.McCarthy, *Cem. Concr. Res.*, 25 [3] 658-70 (1995)
2. U.A.Birnin-Yauri and F.P.Glasser, *Cem. Concr. Res.*, 28 [12] 1713-23 (1998)
3. N.Tsuyuki, R.Watanabe, K.Koizumi Y.Umemura and O.Machinaga, *Cem. Concr. Res.*, 30 [9] 1435-42 (2000)
4. P.Stemmermann and H.Pollmann, *Neues Jahrb. Mineral., Monatsh.*, [9] 409-31 (1992)
5. R.Czaya, *Z. anorg. Allgem. Chem.*, 375 124-7 (1970)
6. B.Hermoneit, B.Ziemer and G.Malewski, *J. Cryst. Growth*, 52 660-4 (1981)
7. T.Hatanaka, T.Imagawa and M.Takeuchi, *Organohalogen Compounds*, 41 161-4 (1999)
8. T.Yasue and Y.Arai, *Gypsum and Lime*, [211] 385-395 (1987)
9. H.Okusu, G.Masuda, M.Wakita and Y.Suginohara, *J. Japan Inst. Metals*, 45 [9] 915-22 (1981)
10. H.Okusu, H.Takeshita, K.Mizoguchi and Y.Suginohara, *J. Japan Inst. Metals*, 47 [11] 956-63 (1983)
11. N.Tsuyuki and K.Koizumi, *J. Am. Ceram. Soc.*, 82 [8] 2188-92 (1999)
12. H.Vogg and L.Stieglitz, *Chemosphere*, 15 [2] 1373-8 (1986)

Figure 1. Difference in X-ray diffraction peak intensities of $\text{CaO}\cdot\text{SiO}_2\cdot\text{CaCl}_2$ according to CaO/SiO_2 molar ratio

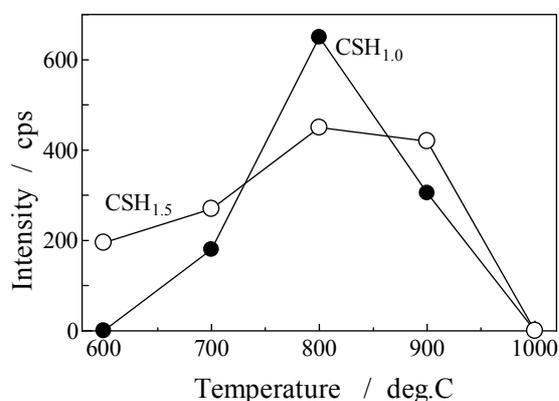


Figure 2. Differential thermal analysis of the burned mixture of C-S-H and CaCl_2

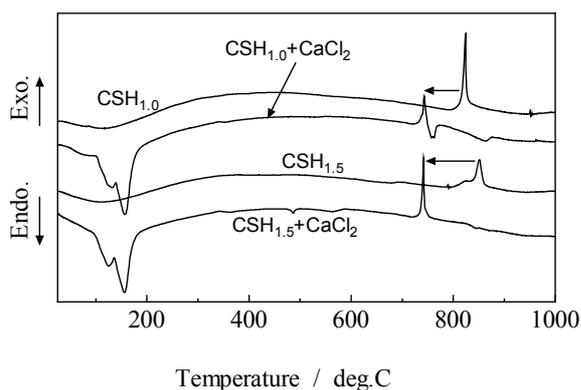


Figure 3. Chain length distribution of silicate anions in the synthesized C-S-H and burned C-S

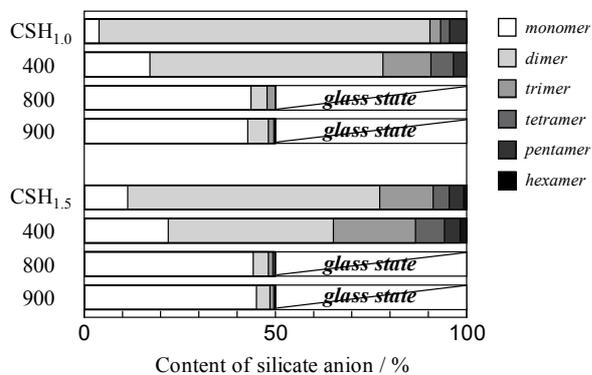


Figure 4. Chain length distribution of silicate anions in the C-S burned with CaCl_2

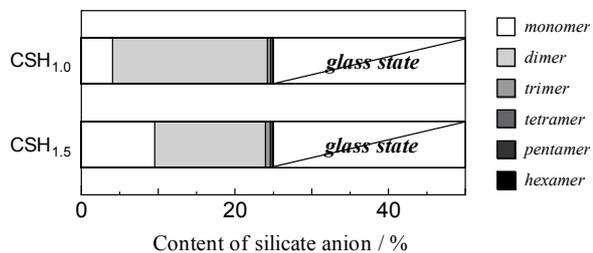


Figure 5. Elution of chlorides from the burned C-S- CaCl_2 mixtures

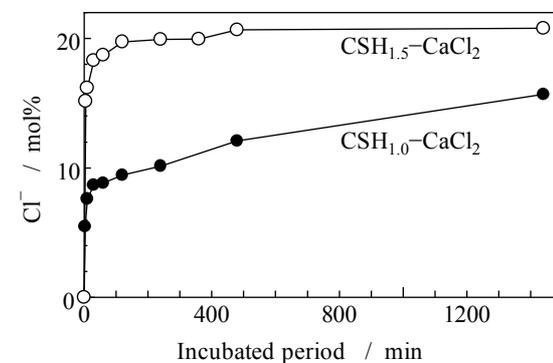


Figure 6. Differential thermal analysis of the burned mixture of C-S-H and NaCl

