Analyses of decalcification process of calcium silicate hydrate (C-S-H) phase

Can Sun¹, Lin Liu ²,*, Yuanbo Du³

¹College of Civil and Transportation Engineering, Hohai University, Nanjing 210098, China
²Jiangsu Research Institute of Building Science Co., LTD., Nanjing 210008, China
³School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, China

*Corresponding author e-mail: liulin@hhu.edu.cn

Abstract. To comprehensively learn the dynamic decalcification process of C-S-H, changes of calcium-to-silicon molar ratio (Ca/Si ratio) of C-S-H powders with NH₄NO₃ solution concentration and with decalcification time as well as decalcification homogeneity are investigated. C-S-H particles are decalcified by NH₄NO₃ solution of different concentration at different time. Ca/Si ratios on the outer surface and inside the C-S-H particles were measured by Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). X-ray diffraction (XRD) tests were conducted to study the crystalline structure of C-S-H. It is found that the calcium at the edge of C-S-H particles is preferentially removed, and the decalcification gradually progress inside as the leaching period is extended. Instead of immersing C-S-H powders in the standard 6 mol/L NH₄NO₃ solution for a predetermined time, it is recommended that C-S-H powders are immersed in NH₄NO₃ solution of different concentration for extended time periods to obtain homogeneously decalcified C-S-H particles.

1. Introduction

C-S-H, as the main hydration product of Portland cement [1-3], whose decalcification phenomenon is a key issue for the durability of concrete structures. When concrete structures are in contact with soft water or corrosive chemical solutions, calcium leaching occurs. In recent years, the calcium leaching of cement paste and the decalcification of C-S-H have been intensively studied. A lot of studies have focuses on the microstructure of C-S-H [4-5], the mechanical properties of cement paste [6] and C-S-H [7-8] and the crystalline phases in cement paste [9], etc. In addition, effects of decalcification on the microstructure [1, 3, 10-13], on the specimens’ deformation [3] and the changes in mechanical properties [14-16], etc, has been studied intensively. Rarely do studies focus on the dynamic process of C-S-H decalcification, especially the decalcification homogeneity.

In nature, the decalcification of C-S-H takes a long time, which happens after the dissolution and loss of portlandite (CH) [3, 17]. To speed up the calcium leaching process of Portland cement, ammonium nitrate (NH₄NO₃) solution of 6 mol/L is typically used in experimental studies to speed up the decalcification process[10, 12-13, 18-20]. It has been indicated that 6 mol/L NH₄NO₃ solution can accelerate the leaching speed up to 130 times [21], and the microstructure of the Portland cement based material is left largely intact [3]. For cement paste or concrete, the specimens were normally
immersed into NH4NO3 solution of 6 mol/L for a certain time for decalcification [3, 10-13]. However, for pure C-S-H powder samples, this approach is too aggressive. If the decalcification time is short, there might be a non-uniform Ca/Si ratio distribution inside the particles. On the other hand, if the decalcification time is too long, the samples might be overly decalcified leading to the breakdown and loss of the microstructure.

In order to get decalcified C-S-H with a given Ca/Si ratio, alternative methods have been tried. He and his co-workers conducted decalcification experiments by dropping NH4NO3 solutions directly onto cement paste powders [12]. Nevertheless, the decalcification homogeneity is not clear. Swanton and his co-workers replaced demineralised water in the C-S-H slurry cyclically for calcium leaching, which was very time consuming [22]. So far, comprehensive understandings about the dynamic decalcification process of C-S-H powders have not been reported. Influences of NH4NO3 concentration, decalcification time and particle size on the decalcification homogeneity of specimens have not been addressed.

In order to acknowledge the dynamic decalcification process of C-S-H, relationship between Ca/Si ratio and decalcification time, decalcification ability of NH4NO3 solution with different concentrations and C-S-H homogeneity are investigated. C-S-H powders are synthesized and immersed in NH4NO3 solution of different concentration with different times for decalcification. To make the calcium leaching process clear, Ca/Si ratio on the surface and inside C-S-H particles were tested by SEM-EDX. Distributions of Ca/Si ratio along surface to center inside C-S-H particles were illustrated. The particle size effect on C-S-H decalcification is discussed.

2. Experimental procedure

2.1. C-S-H preparation

C-S-H is usually synthesized by the reaction of SiO2 and CaO [23, 24] or the reaction of Ca-salt and alkali silicate in aqueous solution [25]. In this research, we mixed SiO2 and CaO in a glove box filled with N2. The initial bulk Ca/Si ratio was 1.4 and the water/solid ratio is 45. The mixtures were put in Teflon bottles and cured at 80°C for 75 days. The mixtures were filtered with 0.45 μm nylon filters paper in a glove box filled with N2, and then the C-S-H solids were dried in vacuum desiccators which was placed with saturated CaCl2 solutions corresponding to a relative humidity of 29% at 25°C.

2.2. C-S-H decalcification

Two series of decalcification tests were performed. The first, designated S1, used C-S-H powders immersed in 1.16 M NH4NO3 solution for 0.5-15 minutes. The second, designated S2, used C-S-H powders immersed in 6 M NH4NO3 for 2-10 minutes. In both S1 and S2, 1.5 g of C-S-H powders were immersed in 45 ml of NH4NO3 solution. Detailed preparing procedures are as follows: C-S-H powders of 1.5 gram were immersed in 45 mL NH4NO3 solution of 1.16 mol/L or 6 mol/L. After shaking for the predetermined times, the mixtures were filtered with 0.45 μm nylon filter paper and rinsed repeatedly with deionized water and ethanol. All of the above operations were performed in a glove box filled with N2. All the filtered solids were dried in vacuum desiccators which was placed with saturated CaCl2 solutions. Hereby, decalcified C-S-H powders in S1 and S2 with a given decalcification time were obtained, see Table 1.

2.3. Measurement of Ca/Si ratio

The Ca/Si ratio of decalcified C-S-H powders were measured by SEM-EDX. Ca/Si ratios on the outer surface of the C-S-H particles and inside the C-S-H particles were respectively examined. The former was obtained by directly placing some samples into the SEM chamber. The latter needs a pre-treatment procedure. Some powders were placed in a mold and casted in resin. After hardening, they were cut and polished. Then, the morphology of the C-S-H particles and the Ca/Si ratios at different positions from the outer surface to the center of the particles could then be measured.
2.4. X-ray diffraction (XRD) analysis
Several studies have reported different properties for C-S-H aged at different temperatures [26], and C-S-H are converted into tobermorite at high temperature [27]. In order to study the microstructure of our C-S-H, which were aged at 80°C, XRD tests were conducted. Some C-S-H powders were immersed in NH₄NO₃ solution of different concentration for 18 hours to get C-S-H powders with Ca/Si ratios from 0.56 to 1.10. XRD tests were performed on reference samples and these C-S-H powders after decalcification. The measured 2 theta range is 2 to 70 degree. The step size is 0.0084 degree, and acquisition time at each step is 40.01.

3. Results and Discussion
Surface Ca/Si ratio of S1 and S2 were first analyzed to show the relationship between Ca/Si ratio and decalcification time as well as influence of NH₄NO₃ concentration on decalcification. Then, to reveal the decalcification homogeneity in C-S-H particles during calcium leaching, distribution of Ca/Si ratio from the outer surface to the center of the particles was illustrated. Next, effect of particle size on the decalcification process was further discussed where particles of sizes from 10 µm to 300 µm were analyzed.

3.1. Relationship between surface Ca/Si ratio and decalcification time
Changes of the surface Ca/Si ratio with the decalcification time are given in Fig. 1. The Ca/Si ratio of the outer surface decreases rapidly within the first few minutes, 1 min for S1 and 2 min for S2, before remaining near constant for the remaining experiment runtime. This indicates that the removal of calcium from C-S-H is fast at the beginning, then the reaction slows and approaches a steady state. Comparing S1 with S2, it is found that at the same decalcification time, the average Ca/Si ratio of S2 drops to lower values than in S1. After decalcification for 15 min, the initial Ca/Si ratio = 1.33 decreases to 0.74 and 0.41 in S1 and S2, respectively. It is clear that the decalcification ability of NH₄NO₃ solution with a higher concentration is stronger than the lower one.

![Fig 1. Changes of surface Ca/Si ratio with decalcification time](image)

3.2. Decalcification homogeneity
Homogeneity of calcium leaching from C-S-H particles is a key point related to the dynamic process of C-S-H decalcification. Distribution of Ca/Si ratio from the surface to the center of each C-S-H particle were analyzed. C-S-H particles of S1 with decalcification time 0.5 min, 2 min and 15 min (i.e., S1D0.5, S1D2, and S1D15), and of S2 with decalcification time 2 min and 9 min (i.e., S2D2, S2D9) as well as reference sample without decalcification are shown in Fig.2. To eliminate the influence of particle size, particles of similar size (about 30µm×40µm) were chosen for comparison.
Fig. 2. Ca/Si ratio from the outer surface to the center inside individual C-S-H particles

Most of the points measured in non-decalcified samples shows that the Ca/Si ratio is about 1.0 (Fig. 2a), while some points are measured at very high Ca/Si ratio, i.e. 4.44. These Ca/Si ratios correspond to C-S-H and a mixture of C-S-H and CH, respectively. It is been indicated that the initial bulk Ca/Si ratio = 1.4 of the non-decalcified C-S-H was therefore heterogeneous and contained a mixture of C-S-H and CH.

Fig. 2(b) shows the Ca/Si ratio distribution in samples decalcified in 1.16mol/L NH₄NO₃ solution for 0.5 min. The disappearance of very high Ca/Si ratio confirmed that CH dissolves first. Obvious distinctions of Ca/Si ratio at different positions inside the particles were observed. The Ca/Si ratio in the middle part remains at 1.10, while the Ca/Si ratio at the edge decreases to 0.75. There is a trend that the Ca/Si ratio gradually decreases from the middle to the edge, indicating that the calcium at the edge of the particles is preferentially removed. The Ca/Si ratio distribution in samples decalcified for 2 minutes shows a similar trend. Nevertheless, the difference between maximum Ca/Si and minimum Ca/Si in one particle is reduced from 0.35 to 0.13, indicating that the decalcification...
progress from the outer surface to the middle of the particles. The Ca/Si ratio distribution in samples decalcified for 15 min suggests that Ca/Si ratio of the whole particles reaches equilibrium, where the difference between maximum Ca/Si and minimum Ca/Si is further reduced to 0.04, and the Ca/Si ratio at the outer surface and center of the particle are almost the same. Samples decalcified in 6mol/L NH$_4$NO$_3$ solution for 2 min and 9 min show the similar features (see Fig. 2(e) and (f)).

Ca/Si ratio distribution inside C-S-H particles reflects the decalcification process in detail and can provide convincing proof for determining decalcification time when the equilibrium state inside C-S-H has been achieved. For S1, the averaged Ca/Si ratio on the surface of C-S-H particles becomes almost constant after the samples being immersed for 1 min (see Fig. 1), while the discrepancy of Ca/Si ratios at different positions inside the C-S-H particles decalcified for 2 minutes is still significant as shown in Fig.2(c). This means that although Ca/Si ratio on the surface of C-S-H particles tends to be stable after a short decalcification time (i.e., 1 min), the decalcification reaction inside particles is still in progress. After decalcification for 15 min, the Ca/Si ratio at different positions inside the particles becomes uniform (see Fig. 2(d)), and the steady state has been achieved.

Comparison of S1D2 with S2D2, it is found that after decalcification 2 minutes, the difference in Ca/Si ratios inside the C-S-H particles immersed in 6mol/L NH$_4$NO$_3$ solution is greater than that in 1.16mol/L NH$_4$NO$_3$ solution, see Fig. 2(c) and (e). This indicates that the higher the concentration of NH$_4$NO$_3$ solution, actually takes longer for decalcification to reach steady state.

### 3.3. Comparison of average surface Ca/Si ratio and average particle Ca/Si ratio

Fig. 3 compares average surface Ca/Si ratio and average particle Ca/Si ratio. Results show that, average surface Ca/Si ratio (1.33) is much higher than average particle Ca/Si ratio (1.04) before decalcification. When measuring surface Ca/Si ratio, C-S-H and CH could not be distinguished, so the existence of CH before decalcification led to a higher Ca/Si ratio. When measuring particle Ca/Si ratio, CH could be recognized by morphology on SEM-EDX pictures, and the points measured at very high Ca/Si ratio (e.g. 4.44 in Fig. 2(a)) were excluded when calculating average particle Ca/Si ratio. The average particle Ca/Si ratio is closer to the real Ca/Si ratio, because it eliminates the interference of CH. Difference between average surface Ca/Si ratio and average particle Ca/Si ratio decreases with the increasing decalcification time, because CH dissolved and the decalcification reaction gradually approached steady state.

![Fig 3. comparison of average surface Ca/Si ratio and average particle Ca/Si ratio.](image)

### 3.4. Particle size effect on decalcification homogeneity

In order to investigate the particle size effect on C-S-H decalcification, for case S1D0.5, S1D2, S1D15, the average Ca/Si ratio of particles of size from 10 µm to 300 µm were analyzed. The average Ca/Si ratio, standard deviation and range of particles of different sizes are shown in Table 1. For S1D0.5, it is found that the range and the standard deviation of Ca/Si ratio in the particle increases...
with its increasing size. This indicates that smaller particles take less time to reach steady state than larger articles. Smaller size particles are therefore more readily decalcified homogeneously. S1D2 shows the same trend as S1D0.5. For S1D15, the range and standard deviation of Ca/Si ratio do not show special trend for all particles of different sizes. Nevertheless, comparing to S1D0.5 and S1D2, those are getting much smaller, which confirms that the decalcification reaction reaches steady state after decalcification for 15 min. Therefore, after a prolonged decalcification time, the particle size does not affect the decalcification homogeneity.

### Table 1. Ca/Si ratio, standard deviation and range of samples of different sizes

| Sample  | Particle size (µm) | Number of test points | Average Ca/Si ratio | Standard deviation | Range |
|---------|--------------------|-----------------------|----------------------|--------------------|-------|
| S1D0.5  | 200×200            | 7                     | 0.93                 | 0.15               | 0.44  |
|         | 20×30              | 8                     | 0.96                 | 0.13               | 0.35  |
|         | 10×10              | 8                     | 1.00                 | 0.09               | 0.26  |
| S1D2    | 120×90             | 9                     | 0.73                 | 0.13               | 0.42  |
|         | 60×50              | 9                     | 0.74                 | 0.04               | 0.13  |
|         | 15×20              | 9                     | 0.70                 | 0.05               | 0.15  |
|         | 100×300            | 9                     | 0.78                 | 0.04               | 0.13  |
| S1D15   | 45×45              | 8                     | 0.74                 | 0.03               | 0.11  |
|         | 35×45              | 9                     | 0.81                 | 0.04               | 0.12  |
|         | 10×10              | 7                     | 0.84                 | 0.06               | 0.19  |

3.5. **XRD result**

Some C-S-H powders were immersed in NH₄NO₃ solution of different concentration for 18 hours to get uniformly decalcified C-S-H of different Ca/Si ratio. Ca/Si ratios on the outer surface of the C-S-H powders were measured by SEM-EDX. Since decalcification time is much longer than 15 minutes, the reaction has reached the steady state, and the outer surface Ca/Si ratio is close to average particle Ca/Si ratio. XRD tests were performed on the reference sample and C–S–H powders after decalcification. As shown in Fig.4, all samples show similar features in their diffraction patterns, and present peaks of C-S-H, indicating that the samples prepared by the reaction of CaO and SiO₂ and after decalcification are C-S-H.

![X-ray diffraction patterns of C-S-H powders using Co as target material.](image)

**Fig 4.** X-ray diffraction patterns of C-S-H powders using Co as target material.

4. **Conclusion**

In order to acknowledge the dynamic decalcification process and decalcification homogeneity of C-S-H, C-S-H powders relatively strongly crystalline were decalcified by NH₄NO₃ solution of different concentration with different time for decalcification. Ca/Si ratios on the surface and inside C-S-H particles were measured by SEM-EDX. This paper draws the following conclusions:
(1) The decalcification ability of NH₄NO₃ solution with a higher concentration is stronger than the lower one.

(2) Decalcification is initially rapid, but slows after several minutes to reach a steady state. Using more concentrated NH₄NO₃ solutions requires longer times to reach the steady state.

(3) Decalcification starts on the outer surface of the C-S-H particles before progressing towards the center. Homogeneously decalcified C-S-H particle can be obtained by prolonging the decalcification time. Compared to put C-S-H particles into NH₄NO₃ solution with a given concentration for different time, it is more reasonable to put C-S-H particles into NH₄NO₃ solution of different concentration for a prolonged time to get uniformly decalcified C-S-H of different Ca/Si ratio.

(4) The particle size does not affect the final Ca/Si ratio but smaller particles are more homogeneously decalcified and require shorter times to reach the steady state.

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