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Communication

Improvement of acid resistance of calcium silicate hydrate by thermal treatment

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Abstract

The following conclusions were obtained from the examinations of the acid resistance of calcium silicate hydrate.

(1) The 1.1-nm tobermorite was formed from the batch mixture with a Ca/Si molar ratio of 0.6. Xonotlite was formed from the batch mixture with a Ca/Si molar ratio of 1.0.

(2) For the sample prepared from a Ca/Si molar ratio of 1.0 in a batch mixture, β-wollastonite was formed by thermal treatment as the transition phase, and it was significantly dissolved in a hydrochloric acid solution.

(3) For the sample prepared from a Ca/Si molar ratio of 0.6 in a batch mixture, β-wollastonite was formed by thermal treatment above 1000 °C, but the dissolved amount of this sample by acid treatment was small and left the original morphology. It was suggested that excess silica content was deposited on surface during the thermal transition from the 1.1-nm tobermorite to β-wollastonite. The deposited silica content significantly improved the acid resistance of β-wollastonite due to the surface coating with a silica layer.

Keywords: Thermal treatment; Calcium silicate hydrate; Acid resistance

1. Introduction

Calcium silicate hydrate is prepared by reacting silica and calcium oxide under hydrothermal conditions. It is known that calcium silicate hydrate has good properties as filter aid material due to its porous structure [1]. However, calcium silicate hydrate powder is easily decomposed by an acidic aqueous solution. Therefore, it is necessary to improve the acid resistance of calcium silicate hydrate for use as a filter aid material. Some studies on the acid resistance of cement mortar and its composite have been made [2,3], but the acid resistance and their improvement were rarely studied among the calcium silicate hydrate powders.

Several kinds of calcium silicate hydrates were prepared by varying the Ca/Si molar ratio and calcining temperature at 800–1000 °C. Its acid resistance properties were then studied. This study was performed to produce a high-performance filter aid material from calcium silicate hydrate, which has a porous structure with secondary particle aggregates.

2. Experiment

The silica source was α-quartz powder with a diameter of ~6.7 μm, and the CaO source was prepared by calcining reagent-grade calcium carbonate at 1000 °C for 4 h. Distilled water was used in all experiments. Batch mixtures were prepared from a Ca/Si molar ratio of 0.6 or 1.0 with a water/solid ratio of 40. Calcium silicate hydrates were synthesized under hydrothermal conditions using a stainless autoclave equipped with a magnetic stirrer for 8 h at 180–190 °C. The synthesized calcium silicate hydrates were then thermally treated at 800–1100 °C for 1 h using an electric furnace. The solubility of the calcium silicate hydrate in acidic solution was measured as follows: 0.15 g of sample were treated for 1 h in a 200-ml acidic solution, the pH of which was adjusted to 2 by pH controlling equipment with hydrochloric acid solution, and the amounts of the dissolved Si and Ca were determined by molybde-

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num colorimetry and an atomic absorption method, respectively. The Ca/Si molar ratio of the synthesized calcium silicate hydrate was determined according the method of Kondo [4].

3. Results and discussion

X-ray diffraction patterns of the calcium silicate hydrate and thermally treated samples are shown in Figs. 1 and 2. The sample shown in Fig. 1 was synthesized from the batch mixture with a Ca/Si molar ratio of 0.6 and it was 1.1-nm tobermorite with a Ca/Si molar ratio of 0.74. A large amount of tobermorite decomposed into an amorphous phase by thermal treatment at 800 °C, as indicated by the X-ray diffraction pattern showing the broad hallow peak near 25°, and thoroughly underwent a phase transition to β-wollastonite at 1000 °C. Xonotlite with a Ca/Si molar ratio of 1.03 was formed from the batch mixture with a Ca/Si molar ratio of 1.0, as mislabeled in Fig. 2. Xonotlite underwent a phase transition to β-wollastonite at 800 °C without a transition to the amorphous phase. The dissolution behavior of the calcined calcium silicate hydrate treated with pH 2 solution is shown in Fig. 3. For the Ca/Si molar ratio of 0.6 in the batch mixture, the dissolution amount of CaO content increased after heat treatment at 800 °C, but its dissolution amount remarkably decreased after heat treat-

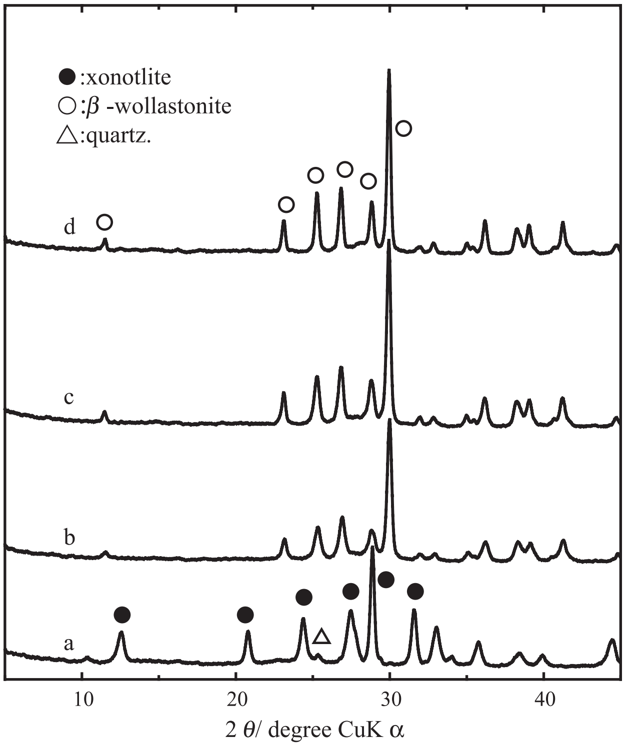

Fig. 2. X-ray diffraction patterns of heat-treated calcium silicate hydrates. CaO/SiO_2 molar ratio in a batch mixture: 1.0. Heating temperature: (a) original, (b) 800 °C, (c) 1000 °C and (d) 1100 °C.

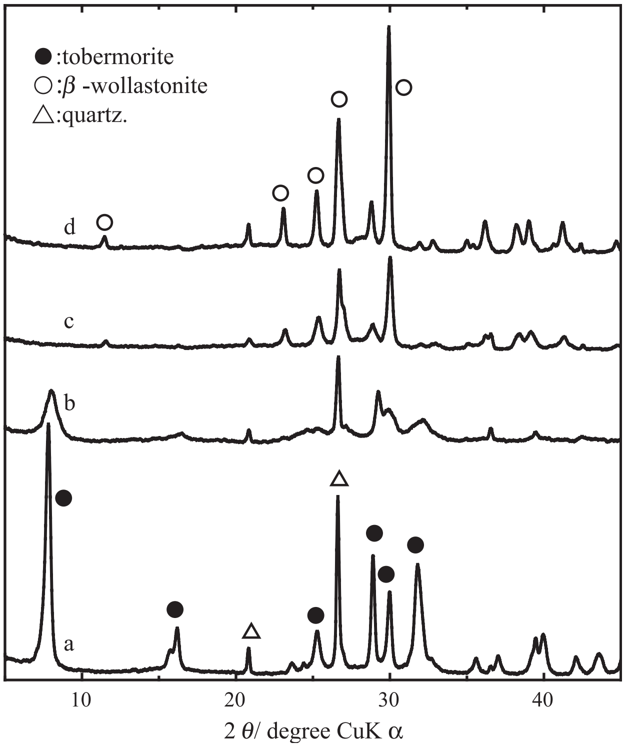

Fig. 1. X-ray diffraction patterns of heat-treated calcium silicate hydrates. CaO/SiO_2 molar ratio in a batch mixture: 0.6. Heating temperature: (a) original, (b) 800 °C, (c) 1000 °C and (d) 1100 °C.

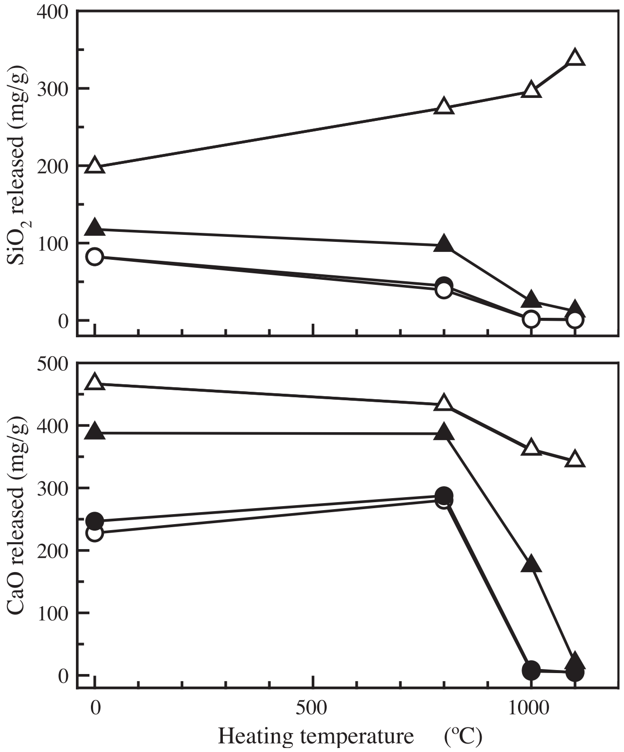

Fig. 3. Dissolution amounts of CaO and SiO_2 from heat-treated calcium silicate hydrates when treated with pH2 solution for 1 h. CaO/SiO_2 molar ratio in a batch mixture: ● 0.4, ○ 0.6, ▲ 0.8, △ 1.0.

ment at temperatures above 1000 °C. On the other hand, the dissolution amount of the SiO_2 content gradually decreased with an increase in the treatment temperature and its value remarkably decreased at temperatures above 1000 °C. For the Ca/Si molar ratio of 1.0 in the batch mixture, the dissolution amount of the CaO content gradually decreased with an increase in the treatment temperature. The dissolution amount of the SiO_2 content increased with an increase in the treatment temperature in contrast to that of the Ca/Si molar ratio of 0.6. It is known that calcium silicate hydrate transform into silica gel and calcium carbonate mixture when treated with a weak acid such as carbonic acid, leaving the original morphology of the sample, but it was completely dissolved out when treated with a strong acid such as hydrochloric acid [5]. In this study, hydrochloric acid was used as the acidic solution, and a large part of sample was dissolved in the acid solution when not thermally treated. SEM observations of acid-treated samples indicated that its crystal structure was destroyed, and the morphology change was greater for the Ca/Si molar ratio of 1.0 in a batch mixture. The sample was amorphous for the Ca/Si molar ratio of 0.6 in a batch mixture after heat treatment at 800 °C, but it probably had rather rigid structure due to the high silica content and silica network, so it was suggested that the Ca content was selectively dissolved out, but silica skeleton was maintained when treated with hydrochloric acid. For the sample prepared from the Ca/Si molar ratio of 1.0 in a batch mixture, the Ca/Si molar ratios of the hydrochloric acid-treated solution were as follows: 1.69, 1.31 and 1.08 for the heated samples at 800, 1000 and 1100 °C, respectively. The Ca/Si molar ratios in the hydrochloric acid-treated solution remarkably decreased when treated at 1100 °C, and β-wollastonite was formed as the thermal transformation product at 1100 °C. In this case, almost all the contents of the Ca and Si were transformed to β-wollastonite, and the Ca/Si molar ratio of hydrochloric acid-treated solution was 1.08, which was almost the same as that of β-wollastonite. Therefore, it is obvious that β-wollastonite formed by the thermal treatment was significantly dissolved in the hydrochloric acid solution. For the sample prepared from the Ca/Si molar ratio of 0.6 in the batch mixture, β-wollastonite was formed by the thermal treatment above 1000 °C, but the dissolved amount of this sample by acid treatment was small in contrast to the above sample and left the original morphology of tobermorite aggregate particles. The molded sample prepared from the Ca/Si molar ratio of 0.6 in a batch mixture was thermally treated for 1 h at 1000 °C and analyzed by XPS to measure surface chemical composition. As shown in Fig. 4, the surface layer was composed with major SiO_2 and minor CaO contents and the inner content was homogenous. The chemical composition of calcium silicate hydrate prepared from the Ca/Si molar ratio of 0.6 in a batch mixture was 0.74 Ca/Si, which was quite different from that of β-wollastonite. Therefore, it was first transformed to amorphous phase by thermal treatment due to the large difference in composition; finally, β-wollastonite was formed as the transition product with excess silica content. Therefore, excess silica content was deposited on surface. It was suggested that the deposited silica content on the surface significantly improved the acid resistance of this sample.

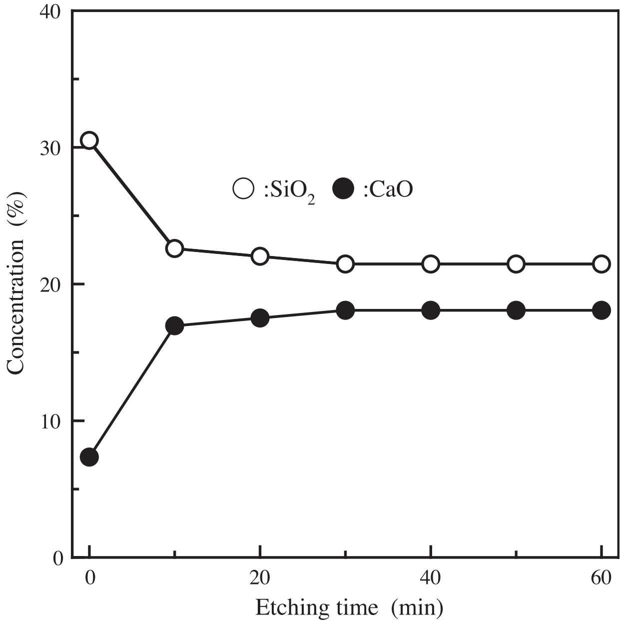

Fig. 4. XPS analysis of surface composition of heat-treated calcium silicate hydrates after being molded. CaO/SiO_2 molar ratio in a batch mixture: 0.6. Heating temperature: 1000 °C.

4. Conclusions

The 1.1-nm tobermorite was formed from the batch mixture with a Ca/Si molar ratio of 0.6, and xonotlite was formed from the batch mixture with a Ca/Si molar ratio of 1.0. For both samples, β-wollastonite was formed by thermal treatment as the transition phase. For xonotlite, β-wollastonite was significantly dissolved in hydrochloric acid solution. In contrast, for 1.1-nm tobermorite, the dissolved amount of β-wollastonite by acid treatment was small and left the original morphology. It was suggested that excess silica content was deposited on surface during the thermal transition from the 1.1-nm tobermorite to β-wollastonite. The deposited silica content significantly improved the acid resistance of β-wollastonite due to the surface coating with a silica layer.

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