



Amorphous calcium silicate hydrates and their possible mechanism for recovering phosphate from wastewater



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ABSTRACT

Amorphous calcium silicate hydrates (A-CSHs) were synthesized using soluble silicates extracted from a natural siliceous shale (M-rite) and $\text{Ca}(\text{OH})_2$. Simultaneous thermogravimetry and differential thermal analysis confirmed that the synthesized A-CSHs contained no detectable amount of free $\text{Ca}(\text{OH})_2$. Their performance on phosphate (P_i) recovery from aqueous solutions was examined using a 3.0-L batch reactor. A-CSHs possessed a greater ability to recover P_i from a synthetic anaerobic sludge digestion liquor than did CaCl_2 and $\text{Ca}(\text{OH})_2$. ^{29}Si magic-angle-spinning NMR analysis suggested that wet A-CSHs consisted of silicate polymers (average chain length of 3.5) that are linked to each other through ion binding with Ca^{2+} . Based on Ca^{2+} release and settleability experiments, it was speculated that Ca- P_i -silicates aggregates were formed by the ionic association of P_i , Ca^{2+} , and negatively charged silicates. This hypothesis could reasonably explain the high settleability of P_i removed by A-CSHs. Powder X-ray diffraction analysis showed that recovered products had an amorphous structure similar to that of A-CSHs. In this study, we suggest that A-CSHs have a unique mechanism for recovering P_i , thereby enabling their high reactivity and settleability.

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1. Introduction

Phosphorus (P) is one of the most critical elements in biological building blocks and plays an essential role in the cellular metabolism of all living organisms [1]. Since no other element can substitute for P in biochemical processes, humans ultimately rely on P availability. On earth virtually all known P exists in the +5 oxidation state (phosphate). Today, phosphate (P_i) is mostly obtained from mined rock P_i [2]. However, natural reserves of high-grade rock P_i are limited and dissipating on a global scale [3]. Hence, increasing attention is paid to P_i recovery for closing the anthropogenic cycle of the P element [4].

To fully realize P_i recycling, it is essential to develop a simple, cost-effective technology for P_i recovery. Previously, we reported

a novel technique for P_i recovery from aqueous solutions using amorphous calcium silicate hydrates (A-CSHs) [5]. A-CSHs were synthesized using infinitely available, inexpensive materials such as siliceous shale and $\text{Ca}(\text{OH})_2$. In small beaker tests, A-CSHs showed a high potential of P_i removal, compared with conventional crystalline CSHs such as autoclaved lightweight concrete particles. P_i removed by A-CSHs exhibited better settleability, filterability, and dewaterability than P_i precipitated with conventional CaCl_2 and $\text{Ca}(\text{OH})_2$. Unlike $\text{Ca}(\text{OH})_2$ and CaCl_2 , no significant carbonate inhibition was observed with P_i removal by A-CSHs. However, no information was available on the chemical structure of A-CSHs and the possible mechanism for P_i recovery from aqueous solutions.

In this study, we carried out P_i recovery experiments using a 3.0-L batch reactor to verify the scalability of P_i recovery by A-CSHs. The chemical structure of A-CSHs and the possible mechanism for P_i recovery from aqueous solutions were investigated using X-ray fluorescence spectroscopy (XRF), simultaneous thermogravimetry (TG) and differential thermal analysis (DTA), ^{29}Si magic-angle-spinning NMR (^{29}Si MAS-NMR) spectroscopy, and powder X-ray diffractometry (P-XRD).

Abbreviations: A-CSHs, amorphous calcium silicate hydrates; DTA, differential thermal analysis; P, phosphorus; P_i , phosphate; P-XRD, powder X-ray diffractometry; Q, silicate tetrahedron; ^{29}Si MAS-NMR, ^{29}Si magic-angle-spinning nuclear magnetic resonance; TG, thermogravimetry; XRF, X-ray fluorescence.

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2. Materials and methods

2.1. P_i recovery experiments

A-CSHs were synthesized in a form of slurry (73 g dry weight/L) using the method described previously [5]. The Ca content of dried A-CSHs was 24%. P_i recovery experiments were performed in a 3.0-L batch reactor having a 2.0-L working volume. The reactor was a 25-cm-high cylindrical vessel made of acrylic resin. It was equipped with an outlet valve to collect precipitates from the reactor bottom. P_i recovery from the synthetic anaerobic digestion liquor, which consisted of 392 mg of KH_2PO_4 , 1.89 g of NH_4Cl , and 3.36 g of NaHCO_3 per liter of deionized water [5], was examined using A-CSHs, $\text{Ca}(\text{OH})_2$, or CaCl_2 at a Ca/P molar ratio of 3.0 (1.45, 0.64, or 0.96 g/L, respectively). Similar experiments were carried out by adding 1.45 g/L A-CSHs (Ca/P = 3.0), $\text{Ca}(\text{OH})_2$ (Ca/P = 6.7), or CaCl_2 (Ca/P = 4.6) to 2.0 L of synthetic anaerobic digestion liquor. The reaction mixture was stirred using an agitator motor (PSH540-001P, Oriental Motor Co., Ltd., Tokyo, Japan) at 200 rpm at room temperature. The mixture pH was continuously monitored using a digital pH meter (DT-1023, Able Co., Tokyo, Japan). Samples were taken at various time intervals and filtered through a 0.22- μm -pore-size Millex-GV filter (Millipore, MA, USA). The filtrate P_i was determined by the molybdenum blue method described by Murphy and Riley [6]. Total P_i was determined as P_i after autoclaving a sample at 121 °C for 30 min.

After 20 min of P_i removal at a Ca/P molar ratio of 3.0, all the reaction mixture was transferred to a 2.0-L graduated cylinder (8.0 cm in diameter) to assess the settleability of the removed P_i . After 10 min of free sedimentation, 1.8 L of the supernatant (90% of the original volume) was gently removed using a siphon. The total P_i concentration in the supernatant was determined as described above. Settleability was evaluated by determining the percentage of total P_i that remained in the cylinder after siphoning the supernatant. Settleability was also evaluated by visual examination. After 20 min of P_i removal from 500-mL P_i solution (392 mg $\text{KH}_2\text{PO}_4/\text{L}$) at pH 9, the slurries were subjected to 5 min of free sedimentation in a 500-mL graduated cylinder (5.5 cm in diameter).

2.2. Structural analysis of A-CSHs

The A-CSHs slurry was filtered through a 0.45- μm -pore-size membrane filter (Millipore). The resulting cake was dried overnight at room temperature under vacuum. The Ca/Si molar ratio of A-CSHs was determined using an XRF spectrometer (ZSX100e, RIGAKU Co., Tokyo, Japan). Free $\text{Ca}(\text{OH})_2$ remaining in A-CSHs was examined using a TG-DTA instrument (model DTG 60/60H, Shimadzu, Kyoto, Japan) as described previously [5]. ^{29}Si MAS-NMR spectra of A-CSHs powders were recorded on an ECA400WB spectrometer (Jeol Resonance Inc., Tokyo, Japan) at a flux density of 9.4 T. The spinning frequency was set at 5.0 kHz. Approximately 1000 scans were accumulated for each sample with a 90-s relaxation delay. ^{29}Si MAS-NMR spectroscopy was also performed with wet A-CSHs. To prepare wet pellets, the A-CSHs slurry was centrifuged at 8000 \times g at room temperature for 30 min. After discarding the supernatant, the wet pellets were analyzed using an AVANCE400 spectrometer (Bruker Biospin Co., Germany) at a flux density of 9.4 T. The spinning frequency was set at 7.0 kHz. Approximately 3750 scans were accumulated with a 60-s relaxation delay. Both ECA400WB and AVANCE400 spectrometers were operated at a frequency of 79.5 MHz at 30 °C using tetramethylsilane as a reference standard.

The standard Q^n nomenclature was used to describe silicate tetrahedron sites [7]. In this nomenclature, Q stands for a given tetrahedron and the superscript (n) refers to the number of

associated bridging oxygens. Bridging oxygens bind to other tetrahedra, while non-bridging ones bind to a low-charge cation such as Ca^{2+} or H^+ . Namely, Q^0 sites are present as monomers. Q^1 sites can be present either in pairs of linked silicate tetrahedra (dimers) or at the ends of silicate chains. Q^2 sites are present in the middle of silicate chains and are further divided into three types by ligand ion: Q^{2P} (H^+ coordination), Q^{2i} (H^+ and Ca^{2+} coordination), and Q^{2Ca} (Ca^{2+} coordination) [8]. Q^3 and Q^4 sites are tetrahedra forming silicate networks. If Q^3 and Q^4 are negligible compared with Q^1 and Q^2 (namely, linear polymers), the average chain length of inorganic silicate residues N can be given as

$$N = 2 \times \sum Q^n / Q^1, \quad (1)$$

where $\sum Q^n = Q^1 + Q^{2i} + Q^{2P} + Q^{2Ca}$ [8].

2.3. Ca^{2+} and silicate release experiments

The release of Ca^{2+} and silicates from A-CSHs was examined in the synthetic anaerobic digestion liquor. When it was necessary to eliminate the effect of carbonate ions, NaHCO_3 was omitted from the synthetic anaerobic digestion liquor. Approximately 10 mL of A-CSHs slurry (0.73 g of A-CSHs) was dispersed in 500 mL of synthetic anaerobic digestion liquor. The suspension was stirred using a magnetic stirrer at 200 rpm at room temperature. Samples were taken at various time intervals and filtered through a 0.22- μm -pore-size membrane filter (Millipore). The concentration of Ca^{2+} in the filtrate was determined using the Metallo Assay Calcium test kit (Metallogenics Co., Ltd., Chiba, Japan) in accordance with the manufacturer's instructions. The concentration of soluble silicates was determined as monosilicate (SiO_4^{4-}) by the method described previously [9]. Similar experiments were also performed using A-CSHs suspended in P_i -free synthetic anaerobic digestion liquor.

2.4. Characterization of recovered P_i

P_i removed by A-CSHs was filtered through a 0.45- μm -pore-size membrane filter (Millipore), dried under vacuum, and subjected to P-XRD analysis. P-XRD analysis was performed using a RINT-2100 diffractometer (Rigaku Co., Tokyo, Japan). XRD patterns were recorded with Ni-filtered Cu $K\alpha$ radiation (step size, 0.02°; scan range, 10–60° 2 θ).

3. Results

3.1. P_i recovery by A-CSHs

In 3.0-L batch reactor experiments, A-CSHs removed 82% P_i from the synthetic anaerobic digestion liquor at a Ca/P molar ratio of 3.0 after 5 min of mixing (Fig. 1a). Thereafter, P_i removal gradually increased to 87% after 20 min. The final pH of the reaction mixture was 8.9 (Fig. 1b). CaCl_2 and $\text{Ca}(\text{OH})_2$ removed 53% and 28% P_i from the synthetic anaerobic digestion liquor after 5 min, respectively. The final pH values after P_i removal by CaCl_2 and $\text{Ca}(\text{OH})_2$ were 7.5 and 8.6, respectively. To further compare P_i removability by A-CSHs with those by CaCl_2 and $\text{Ca}(\text{OH})_2$, P_i removal experiments were carried out using 1.45 g/L A-CSHs (Ca/P = 3.0), $\text{Ca}(\text{OH})_2$ (Ca/P = 6.7), or CaCl_2 (Ca/P = 4.6) in the synthetic anaerobic digestion liquor (Fig. 1c). Despite the relatively low Ca/P molar ratio, A-CSHs showed better P_i removal performance than CaCl_2 and $\text{Ca}(\text{OH})_2$. CaCl_2 and $\text{Ca}(\text{OH})_2$ could remove 65% and 53% P_i after 5 min, respectively, while A-CSHs showed approximately 80% P_i removal.

P_i removed by A-CSHs showed better settleability than P_i precipitated with CaCl_2 and $\text{Ca}(\text{OH})_2$ (Fig. 2a). A-CSHs settled approximately 77% P_i of the synthetic anaerobic digestion liquor after 10 min of free sedimentation. CaCl_2 and $\text{Ca}(\text{OH})_2$ settled

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