



Phosphorous recovery from sewage sludge using calcium silicate hydrates

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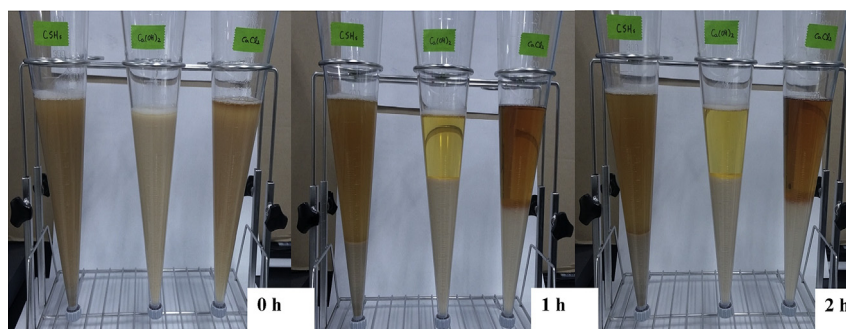
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HIGHLIGHTS

- Phosphorous eluted from sewage sludge can be effectively recovered by CSH.
- 55% of the phosphorus in the sludge (123 g-P/kg) was released into 0.1 M H₂SO₄.
- 15 g/L of CSH recovered 89.6% of the eluted phosphorus without further treatment.
- The resulting calcium phosphate product from CSH exhibited superior settleability.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphorous is an essential limiting nutrient for which there is no substitute. Its efficient recovery from sewage treatment plants is important to mitigate both dependence on limited reserves of exploitable phosphate rock and eutrophication of surface waters. Here, we evaluate the use of calcium silicate hydrates (CSH) to recover phosphorous eluted from sewage sludge. Phosphorous elution experiments were conducted with acid and base leaching solutions. The phosphorous recovery efficiency with CSH was compared to that with other calcium compounds, and the final product was analyzed to assess its potential value as fertilizer. Dried sewage sludge from the West Lake Ecological Water Resource Center, South Korea, having 123 g-P kg⁻¹, was used for these tests. About 55% of the phosphorus in the sludge was released with an elution solution of 0.1 M H₂SO₄. A dose of 15 g L⁻¹ of CSH recovered 89.6% of the eluted phosphorous without the need for additional pre-treatment, and the resulting calcium phosphate product (in brushite form, based on XRD analysis) exhibited superior settleability than that resulting from Ca(OH)₂- and CaCl₂-induced precipitation. XRD peaks of the calcium sulfate hydrate (in gypsum form) and residual CSH were also observed. The final product contained a relatively high content of the

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total P_2O_5 eluted in a 2% citric acid solution (43.1%), which suggests that it might be readily used to fertilize crops.

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1. Introduction

Phosphorous is an essential nutrient for crop growth, and the demand for phosphorous as fertilizer has rapidly grown due to an increase in population and livestock production. To date, phosphorous production through mining was able to meet the demands of the developing fertilizer industry, but this system is not practical as the natural inorganic phosphorous cycle (i.e., erosion, sedimentation, tectonic alteration and uplift) takes several million years (Cornel and Schaum, 2009). According to a UK Soil Association report (Soil Association, 2010), the supply of phosphorous from mined phosphate rock could peak as early as 2033. After this peak, phosphorous is expected to get more expensive and scarce, jeopardizing food security (Cordell et al., 2009). Therefore, there is growing interest in phosphorous recovery from the anthropogenic organic phosphorous cycle (i.e., soil – plants – humans/animals – organic waste – soil) for preservation of phosphorous resources and the prosperity of human beings (Cordell et al., 2009; Cordell and White, 2013). Enhanced phosphorus recovery also helps mitigate its discharge to surface waters and associated eutrophication (Mayer et al., 2016).

Sewage sludge is an anthropogenic organic waste with high potential for phosphorous recovery. Annually, 7.2 million tons of dry sewage sludge are produced in the US. Assuming a phosphorous content of 2.3%, this could produce 165,600 tons of phosphorous, which represents approximately 10% of the total phosphorus used annually in the US as fertilizer (1.71 million tons/year) (Peccia and Westerhoff, 2015). A similar trend exists in South Korea, with 13 thousand tons of phosphorous from sludge annually, approximately 8% of the total phosphorus used as fertilizer (Jeong et al., 2009). Traditionally, sewage sludge is widely used in agriculture due to its high nutrient content and its potential to improve soil properties (pH, organic matter, porosity, cation exchange capacity, water contents, etc.) (Lederer and Rechberger, 2010; Vadenbo et al., 2014). However, various contaminants can accumulate in sewage sludge and several countries in Europe, such as Austria and Denmark, were reducing its agricultural use (Mattenberger et al., 2008; Ottosen et al., 2013). Therefore, many studies have been conducted to recover phosphorous from sewage sludge using thermal and/or chemical treatment, usually wet chemical treatment by the addition of an acid or base solution with heat, if necessary (Stark et al., 2006; Wang et al., 2010; Bi et al., 2014; Shiba and Ntuli, 2017).

Precipitation/crystallization methods with magnesium or calcium are generally used to recover phosphorous from phosphorous-rich solutions. The recovered phosphorous is commonly in the form of magnesium ammonium phosphate (MAP method; e.g., struvite, $MgNH_4PO_4 \cdot 6H_2O$) or calcium phosphate (HAP method; e.g., hydroxyapatite, $Ca_5(PO_4)_3OH$). The MAP method also recovers nitrogen from the solution, but the ratio of nitrogen to phosphorous is not optimal to fertilize plants (Mayer et al., 2016). The calcium phosphate product from the HAP method has similar composition to phosphate rock, and can be used as a raw material for industry or applied directly as a fertilizer in agriculture. These valuable products can be synthesized using various calcium compounds including natural minerals and regenerated materials such as calcite and crushed concrete (Berg et al., 2005; Okano et al., 2013; Hermassi et al., 2015).

Calcium silicate hydrates (CSH) are one of the calcium compounds and main components of Portland cements. It can be synthesized by double precipitation of calcium oxide (CaO) and silicon dioxide (SiO_2). Depending on the Ca/Si ratio, there are also different mineral structures and natural rocks present, such as Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$, Ca/Si = 0.83), Foshagite ($Ca_4(Si_3O_9)(OH)_2$, Ca/Si = 1.33), and Jennite ($Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$, Ca/Si = 1.50) (Richardson, 2008). A portion of the CSH can dissociate into calcium and silicate in water, and either aggregates with phosphate or remove phosphate by growing hydroxyapatite crystals on their surface (Guan et al., 2013a; Okano et al., 2015). There are several advantages of using CSH for phosphorous crystallization in a phosphorous-rich solution (Jiang and Wu, 2012; Yamashita et al., 2013; Okano et al., 2015): (1) it requires no CO_2 degassing and pH adjustment as a pretreatment, (2) it exhibits better settleability than using conventional calcium compounds, (3) it has high capacity of soluble phosphate that can be used directly as fertilizer, and (4) it offers the potential for effective inactivation of harmful microorganisms. Chen et al. (2009) used another type of CSH, Xonotlite, for phosphate removal and recovery from an aqueous solution. Guan et al. (2013a) synthesized porous CSHs with different Ca/Si ratios for phosphorus recovery from wastewater. Although previous studies have evaluated the use of CSH for phosphorous recovery from synthetic wastewater (Chen et al., 2009; Jiang and Wu, 2012; Guan et al., 2013a, 2013b; Okano et al., 2015; Zeggel et al., 2017), no previous publication considered its direct use (without pre-treatment such as pH adjustment) to recover phosphorous from solutions eluted from real sewage sludge.

In this study, phosphorous elution tests from a specific site sewage sludge were performed by a wet chemical treatment method, and the extraction efficiency of acid and base was evaluated. To reduce treatment process, CSH was directly used to recover phosphorous from the eluted solution, and the settleability was compared with those of common calcium compounds. The characteristics of the final product and its available phosphorous contents were also determined to assess its potential value as fertilizer.

2. Materials and methods

2.1. Chemicals and sewage sludge preparation

Dewatered sludge cake was collected from the sewage treatment plant located in the West Lake Ecological Water Resources Center (Suwon, Korea), which treats an average of $39,193 \text{ m}^3 \text{ d}^{-1}$ of domestic sewage using a biological nutrition removal (4 stage-BNR) process and an average of $32 \text{ m}^3 \text{ d}^{-1}$ of dewatered sludge is generated following gravity thickening with polyaluminum chloride (PAC) and mechanical dewatering, and finally disposed of as directed. Prior to use, the sludge cake was oven dried at 105°C for 18 h to remove excess water and then pulverized in a ball mill to homogenize the sample. The chemical composition of the dried sewage sludge was determined using an X-ray fluorescence spectrometer (XRF, ZSX Primus II, Rigaku, Japan), and the data are shown in Table 1.

Calcium silicate hydrate (Extra pure, Junsei Chemical, Saitama, Japan) was used for the recovery of phosphorus from the sewage

Table 1
Chemical composition of dried sewage sludge.

Components	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	etc.	Total
Contents (mass %)	1.72	26.1	13.0	28.2	8.70	3.04	10.5	6.50	2.24	100

sludge elution solution. The chemical formula of the calcium silicate hydrate was $\text{CaO}_3\text{Si} \cdot n\text{H}_2\text{O}$ and contained a minimum of 25% of CaO and 30% of SiO_2 . The Ca/Si ratio was approximately 1.00, which is larger than tobermorite (Ca/Si = 0.83) but smaller than foshagite (Ca/Si = 1.33) and jennite (Ca/Si = 1.50) (Richardson, 2008). To compare the effect of calcium compounds, $\text{Ca}(\text{OH})_2$ (Extra pure, Showa Chemical, Tokyo, Japan) and CaCl_2 (Extra pure, Showa Chemical, Tokyo, Japan) were used for the phosphorus recovery tests. A reagent grade of HCl, H_2SO_4 , and NaOH was used for phosphorus release experiments.

2.2. Phosphorous release experiments

Phosphorous release from the dried sewage sludge was conducted using acid and base leaching solutions. Different molar concentrations (0.1, 0.5, and 1.0 M) of HCl and H_2SO_4 were used as acid leaching solutions, while NaOH was used for the base leaching solution. To 40 mL of each leaching solution, 0.8 g of dried sewage sludge was added. The solution was mixed using a rotary shaker at 20 rpm for 2 h. After the reaction, the suspension was centrifuged at 4100 rpm for 20 min (VS-400, Vision Scientific Co. LTD, Daejeon, Korea) and the supernatant was collected for the phosphorus recovery test. The phosphorus and other component concentration released from the dried sewage sludge to the leaching solution was then measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Prodigy ICP, Teledyne Leeman Labs, Hudson, USA).

2.3. Phosphorous recovery with different Ca compounds

Phosphorous in the leaching solution was directly recovered using various Ca compounds such as CSH, $\text{Ca}(\text{OH})_2$, and CaCl_2 . Different doses (10, 15, and 20 g L^{-1}) of CSH were mixed with 40 mL of leaching solution for 2 h and the suspension was separated. The resulting suspension from the different CSH doses (15 g L^{-1}) was compared across the Ca compounds used.

For the settleability test, 3.0 g of each Ca compound was added to 200 mL of leaching solution and shaken for 2 h. The suspension was then poured into a 1000 mL Imhoff cone and the volume occupied by sludge was recorded with time. After 2 h of settlement the supernatant was gently removed using a siphon method and the remained sludge was filtered through a GF/C filter. An amount of 1.5 g of filtered cake was placed on a glass desiccator containing silica gel at room temperature and the dewaterability was evaluated by the weight change. The other 1.5 g of filtered cake was dried using a convection oven (CO-150, Han Yang Scientific Equipment Co. Ltd, Korea) at 105 °C for 18 h to determine the water content.

2.4. Analysis of CSH after phosphorous recovery

The water in the CSH precipitate after phosphorous recovery (P-CSH) was removed using a convection oven at 60 °C for 18 h. After drying the crystalline structure and chemical composition of the P-CSH was analyzed using an X-ray diffractometer (XRD, D-max 2500/PC, Rigaku, Japan) and X-ray fluorescence spectrometer (XRF, ZSX Primus II, Rigaku, Japan), respectively. In order to assess the potential value of the final product as a fertilizer, the available phosphorous recovered with CSH (i.e., phosphorus pentoxide,

P_2O_5) was determined as the total soluble phosphorus concentration subsequently eluted with water or 2% citric acid solution (standard method of Korea Rural Development Administration) (Shaver, 2008). In addition, the other components eluted from the P-CSH were also measured by ICP-OES.

2.5. Statistical analysis

Phosphorous release and recovery experiments were performed in triplicate, and the data are presented as the average value with standard error using error bars. Whether differences between treatments were statistically significant was determined using Student's t-test at the 95% confidence level.

3. Results and discussion

3.1. Phosphorus release properties of prepared sewage sludge

The dried sewage sludge from the West Lake Ecological Water Resource Center had high contents of P_2O_5 (28.2 mass %) as well as Al_2O_3 , SiO_2 , CaO, and others (Table 1). The concentration of P_2O_5 was approximately 123 g-P kg^{-1} , which is as high as that in currently mined phosphate rock (110–160 g-P kg^{-1}) (Ottosen et al., 2016) and exceeds the range reported for sewage sludge (32–123 g-P kg^{-1}) (Del Mundo Dacera et al., 2009; Ottosen et al., 2014; Ebberts et al., 2015). The content of Al_2O_3 (26.1 mass %) was a result of the use alum as a coagulant and can be separated by a heat treatment method (Adam et al., 2009; Cornel and Schaum, 2009; Petzet et al., 2012), but it was not considered in this study.

Two kinds of acid solution (H_2SO_4 , HCl) and one base solution (NaOH) were used as eluents to release phosphorous from the sewage sludge. As shown in Fig. 1, phosphorous release from sludge increased with the acid or base concentration increased from 0.1 M to 1.0 M. The phosphorous release from the Al-rich sewage sludge using acid and base solutions was represented as follows (Petzet et al., 2012):

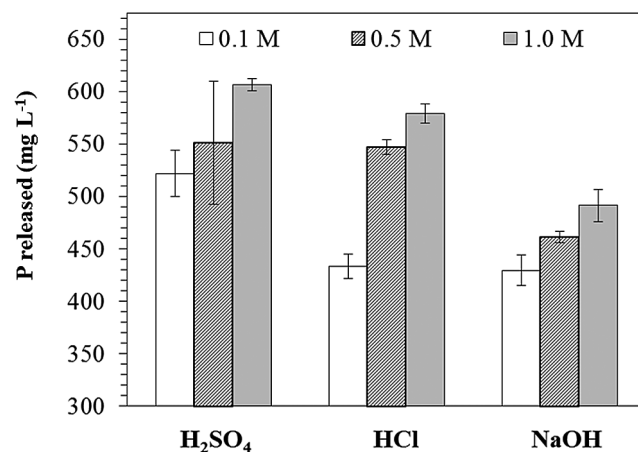
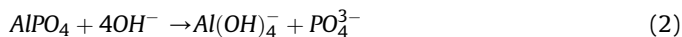


Fig. 1. Phosphorus release from dried sewage sludge eluted with HCl, H_2SO_4 , or NaOH (0.1, 0.5, and 1.0 M).



Accordingly, phosphorous release was enhanced following the increase of acid ($[\text{H}^+]$) or base ($[\text{OH}^-]$) concentrations. The acid solution was more effective than the base solution in releasing phosphorous. At the same molar concentration, sulfuric acid (H_2SO_4) was most effective from a stoichiometric perspective. The use of sulfuric acid is practical for phosphorous recovery as it is relatively inexpensive and easily obtained in large quantities (Ottosen et al., 2013; Ye et al., 2017). However, phosphorous release from the sewage sludge did not match the theoretical stoichiometric ratio due to the presence of other acid-soluble constituents such as MgO , K_2O , CaO , and Fe_2O_3 that titrate some of the acid that would otherwise be available to extract phosphorus (Petzet et al., 2012). While the concentration of sulfuric acid was increased 10-fold, the elution concentration of phosphorus was only increased by 16%. Therefore, 0.1 M sulfuric acid (H_2SO_4) was selected for further phosphorous release experiments.

In addition to Al, Si, P, Ca, and Fe, which are commonly found in sewage as a major element (Donatello et al., 2010), large amounts of Mg and K were also contained in this sludge (Table 1) and were eluted with 0.1 M H_2SO_4 (Fig. 2). Total Al, Si, Ca, Fe, Mg and K were approximately 41.85, 18.38, 22.74, 13.77, 3.14 and 7.65 mg g^{-1} , respectively, from XRF measurements (w/o normal data), and 84.0%, 6.4%, 47.2%, 24.8%, 100%, 24.5% of each elements were dissolved as a side reaction, while 55% of P was released. Potentially toxic metals such as Mn, Cu, and Zn were also found in the elution solution with concentrations of 2.07, 13.59, and 8.64 mg L^{-1} , respectively.

3.2. Effect of Ca compounds on phosphorus recovery

The dose test was conducted to determine the amount of CSH that could recover phosphorous from the acid elution solution (0.1 M H_2SO_4) without any additional pre-treatment such as pH adjustment. The phosphorous removal efficiency was evaluated by increasing the injection amount by increments of 5 g L^{-1} of CSH (Fig. 3 (a)). The removal efficiency was negligible (1.2%) up to a dose of 10 g L^{-1} of CSH, but then sharply increased to 89.6% when using 15 g L^{-1} of CSH for phosphorous recovery from the acid elution

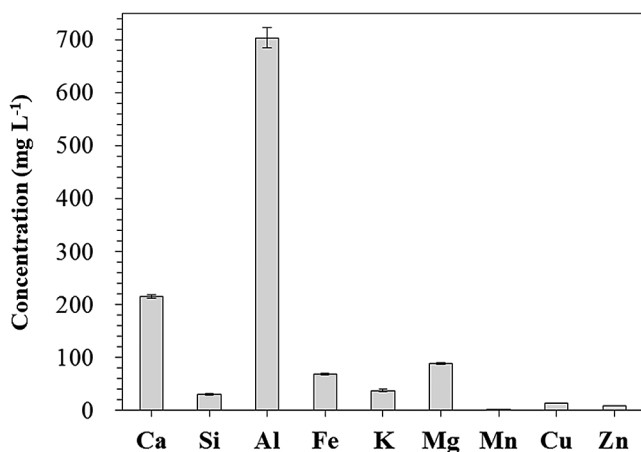


Fig. 2. Elution of other components from dried sewage sludge by 0.1 M H_2SO_4 .

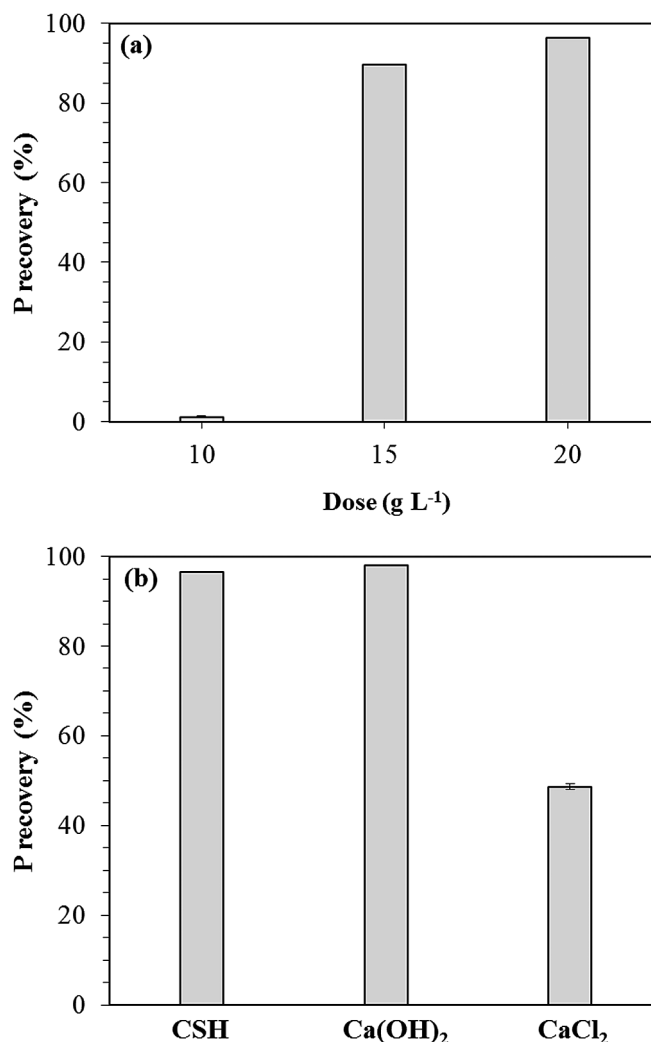


Fig. 3. Effect of (a) CSH dosage and (b) different Ca compounds on phosphorus recovery.

solution. The removal efficiency continued to increase and reached 96.3% at 20 g L^{-1} of CSH. Jiang and Wu (2012) reported 90.5% phosphate removal achieved with 5 g L^{-1} of CSH (tobermorite) in model water (30 $\text{mg-PO}_4^{3-} \text{L}^{-1}$). Guan et al. (2013a) also showed 5 g L^{-1} of porous CSH (jennite) decreased the phosphorus concentration from 100 to 8.05 mg L^{-1} (approximately 91.9%). However, those experiments were carried out at near-neutral pH conditions, not in acidic solutions as in our experiments. Therefore, the remaining experiments were conducted using a dose of 15 g L^{-1} of CSH, which resulted in approximately 90% phosphorous recovery from the solution. Notably, the actual dose injected could be reduced through reuse of used CSH and increase the phosphorous content in the final product (Le Corre et al., 2009; Song et al., 2006).

Further experiments were carried out with commonly used calcium compounds, calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium chloride (CaCl_2), to benchmark phosphorous recovery and slurry properties using CSH. The phosphorous removal efficiency of each calcium compound at the fixed dose (15 g L^{-1}) is shown in Fig. 3 (b). The removal efficiency reached with CSH was 96.6% which was comparable to $\text{Ca}(\text{OH})_2$ (98.0%) but significantly greater compared to CaCl_2 (48.7%). Despite its high solubility, CaCl_2 was not effective in increasing the pH of the solution and was therefore not selected for phosphorus recovery (Okano et al., 2015).

The settleability of each calcium compound containing phosphorous (Ca-P sludge) was tested in an Imhoff cone (Fig. 4), and the settling efficiency was assessed by the sludge volume (V_s) occupied in the total volume (V_T) over time as shown in Fig. 5 (a). The CSH and CaCl_2 were effectively settled down and the relative volume (V_s/V_T) decreased to 0.09 and 0.20 within 30 min, respectively, and remained constant through until the last measurement at 120 min. However, the settling of Ca(OH)_2 was relatively slow and the relative volume (V_s/V_T) reached 0.40 at 30 min and decreased to 0.32 by 120 min. This reflects faster settling of the CSH slurry and easier decanting of the supernatant due to a lower relative settled volume (0.09). This superior settling property is related to the silicate (SiO_2) contained in the CSH. Apparently, settling efficiency of CSH was enhanced by released calcium ions (Ca^{2+}) that aggregate with SiO_2 , increasing the settling velocity (Guan et al., 2013a; Okano et al., 2015).

The dewaterability of filtered Ca-P sludge was determined by the weight change using a desiccator (Fig. 5 (b)). The decreasing trend of the CSH was similar to Ca(OH)_2 , where approximately 22% and 28% weight of the CSH and CaCl_2 , respectively was removed during 24 h. The higher content of phosphorus in Ca-P sludge can cause lower dewaterability (Petzet and Cornel, 2012; Zhang and Chen, 2009). The water content of Ca-P sludge was measured using a convection oven. As shown in Fig. 5 (c), CSH contained 41.50% of water in their filtered slurry, while Ca(OH)_2 and CaCl_2 had 61.81% and 35.84%, respectively. The higher water content of Ca(OH)_2 are consistent with its slower settling (Fig. 4). From these results, and considering recovery efficiency and sludge handling, CSH is the better calcium compound for phosphorous recovery from an acid solution.

3.3. Characteristics of final product

After lightly drying the CSH slurry containing phosphorous (P-CSH), the characteristics of the final product were analyzed using the X-ray methods XRF and XRD (Table 2). P-CSH contained significant amounts (in decreasing order) of SO_3 , SiO_2 , CaO , Al_2O_3 . The SO_3 originated from the acid elution solution (H_2SO_4), while SiO_2 and CaO were the result of injected CSH for phosphorous recovery. Al_2O_3 and P_2O_5 originated from sewage sludge that was eluted in the acid elution solution and recovered by CSH. The higher content of SiO_2 and CaO compared to P_2O_5 suggests that the final product can be reused for phosphorous recovery as a seed material (Song et al., 2006).

XRD patterns of the final product was shown in Fig. 6. Phosphorous can form various calcium-associated compounds such as amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$), dicalcium phosphate dehydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), β -whitlockite ($\beta\text{-Ca}_3(\text{PO}_4)_2$),

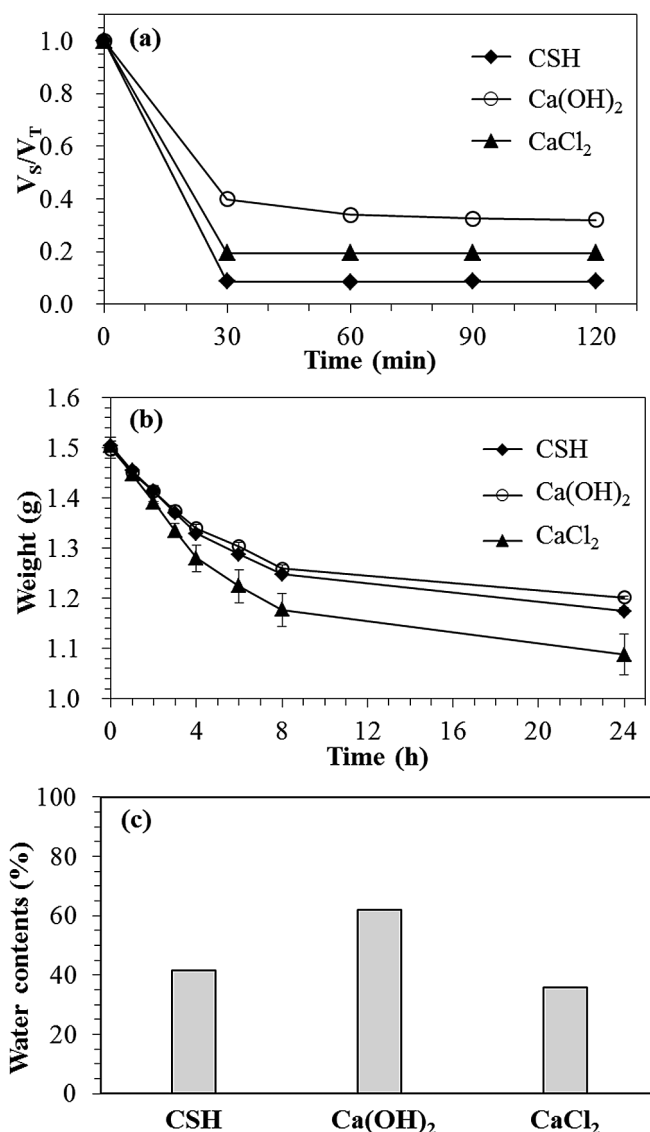


Fig. 5. Properties of Ca-P sludge obtained using CSH, CaCl_2 , and Ca(OH)_2 : (a) settleability, (b) dewaterability, and (c) water contents.

octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), when using HAP methods for phosphorous recovery (Petzet et al., 2012; Hermassi et al., 2015). Specifically, the calcium hydrogen phosphate hydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Brushite, JCPSD:

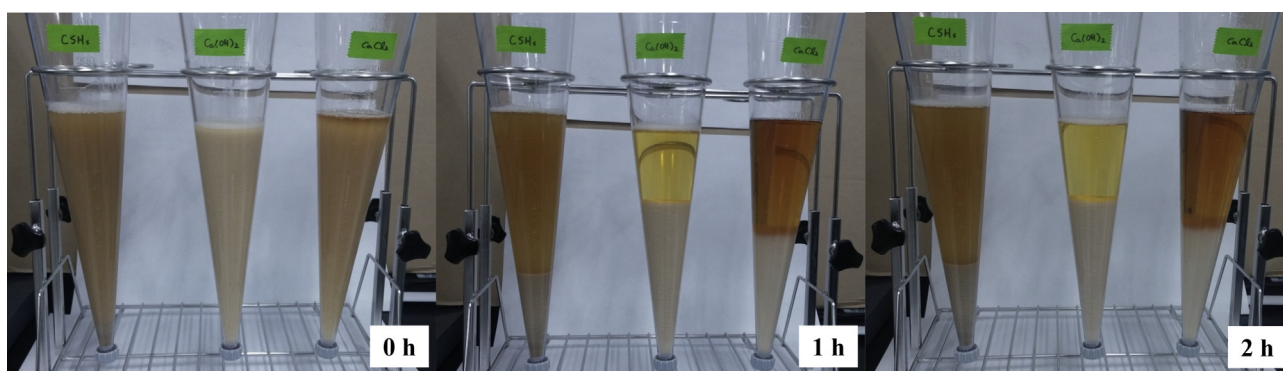


Fig. 4. Visualization of Ca-P sludge volume change in an Imhoff cone during settling time.

Table 2
Chemical composition of CSH after phosphorus recovery.

Components	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	etc.	Total
Contents (mass %)	0.28	8.17	28.7	6.13	31.0	0.09	25.1	0.42	0.11	100

11–293) peaks correspond to 2θ data at 11.604° and 23.391° . Therefore, the calcium phosphate compound contained in our final product was likely brushite (Hermassi et al., 2015; Okano et al., 2015), and the crystal size (estimated by the Scherrer equation (Wang et al., 2017)) was about 54 nm. The peaks of silicon oxide (SiO₂, Quartz), calcium carbonate (CaCO₃, calcite), and calcium hydroxide (Ca(OH)₂) were not clearly found under our experimental conditions (Berg et al., 2005; Jiang and Wu, 2012; Guan et al., 2013b; Yamashita et al., 2013). The calcium sulfate hydrate (CaSO₄·2H₂O, Gypsum, JCPDS: 33–311) peaks were observed at 11.589° , 20.722° , 29.111° , 31.104° , 33.344° , 40.625° , 43.341° , and so on. However, the peaks of calcium oxide (CaO, Lime) and aluminum oxide (α -Al₂O₃) were not detected in the XRD data. Similar to the results reported by Ottosen (Ottosen et al., 2013), significant formation of gypsum crystals instead of CaO occurred when extracting phosphorous from incinerated sewage sludge ash using H₂SO₄. Despite of the high content of aluminum in the final product, aluminum containing minerals were not identified under our experimental conditions, suggesting that it was present in amorphous phases (Ottosen et al., 2014). Calcium silicate hydrate (CaOSiO₂·H₂O, JCPDS: 34–2) peaks also remained in the final product at 29.063° and 31.937° , corroborating the XRF results and showing significant residual calcium that might be reused for phosphorous recovery.

Table 3

Elution concentration of other components from P–CSH precipitate by water and 2% citric acid.

Components	Water (mg L ⁻¹)	2% citric acid (mg L ⁻¹)
Ca	579.72 ± 1.08	738.24 ± 11.72
Si	6.92 ± 0.21	57.93 ± 1.22
Al	ND ^a	555.39 ± 8.69
Fe	0.42 ± 0.01	30.04 ± 0.14
K	8.05 ± 0.12	23.53 ± 0.13
Mg	10.99 ± 0.88	22.54 ± 0.55
Mn	ND ^a	ND ^a
Cu	ND ^a	ND ^a
Zn	0.26 ± 0.01	0.98 ± 0.03

^a ND: not detectable.

As with Quinoline gravimetric analysis (Shaver, 2008), the phosphorous concentration eluted from the P–CSH in water and 2% citric acid solution were evaluated and calculated as P₂O₅ content to check for potential agronomical value as a fertilizer. The total P₂O₅ content in P–CSH was determined by chemical analysis was 6.13% based on XRF results (Table 2), and the concentration of dissolved P₂O₅ in the water and citric acid were 0.21% and 2.64%, respectively. The calculation from the dissolved concentration for the total content suggests that 43.1% of the total P₂O₅ will be used for crops (i.e., 2% citric acid soluble), while only 3.4% would be percolate through soil (i.e., water soluble). This result is in good agreement with calcium phosphate mineralogy, inferring that the brushite form is more suitable for crop fertilization than hydroxyapatite due to its higher solubility (Hermassi et al., 2015).

The concentration of the other elements in the P–CSH eluted by water or 2% citric acid solution was also measured (Table 3). The concentration of calcium dissolved in the water was $579.72 \pm 1.08 \text{ mg L}^{-1}$, and it could be reused as calcium seed materials for phosphorous recovery due to its relatively high concentration. A small amount of silicon ($6.92 \pm 0.21 \text{ mg L}^{-1}$), potassium ($8.05 \pm 0.12 \text{ mg L}^{-1}$), and magnesium ($10.99 \pm 0.88 \text{ mg L}^{-1}$) were also present in the water. The concentrations of these components, along with aluminum and iron, increased in the 2% citric acid solution. Due to the high concentration of aluminum in the citric acid solution, pre-treatment to remove it should be required prior to application as a crop fertilizer (Adam et al., 2009; Petzet et al., 2012). Alternatively, the recovered product might be used in the electrothermal phosphate industry (Cornel and Schaum, 2009). The concentrations of potentially toxic heavy metals such as Mn, Cu, and Zn were negligible in both of water and 2% citric acid solution.

4. Conclusions

CSH was used for phosphorous recovery from sewage sludge subjected to leaching from an acid solution. The sewage sludge used in this experiment contained large amounts of phosphorous and aluminum and showed high release characteristics when sulfuric acid was used as eluent. The phosphorous dissolved in the acid leaching solution was recovered by CSH without an additional preprocess; and the settleability was better than with other calcium compounds such as CaCl₂ and Ca(OH)₂. The calcium phosphate in the final product was brushite, and it contained 43.1% of available phosphate as a crop fertilizer. Overall, sewage sludge could be used

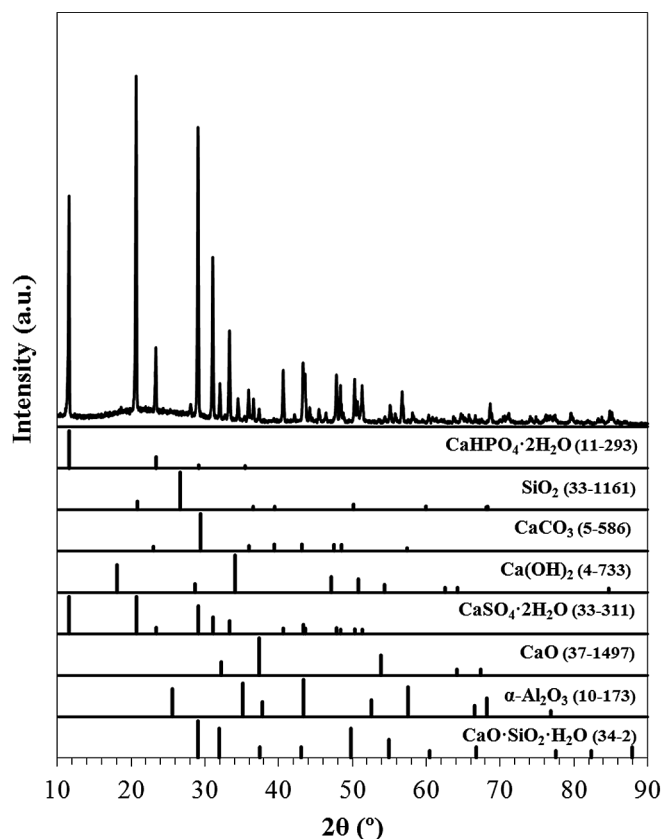


Fig. 6. XRD patterns of CSH after phosphorus recovery.

as an alternative phosphorous source to minimize dependence on phosphate rock. Due to superior settleability and high phosphorous recovery efficiency, CSH is expected to be a practical alternative for phosphorous recovery from various aqueous solutions.

Authors' contributions

Chang-Gu Lee and Hee-Gon Kim carried out the whole experiments, participated in the reference research and drafted the manuscript. Seongpil Jeong and Seunghak Lee carried out the analysis of CSH. Pedro J.J. Alvarez, Ki Bong Lee, Sang-Hyup Lee and Jae-Woo Choi helped to review and to edit the manuscript. In addition, Jae-Woo Choi conceived of the study, participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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