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## Precipitation and recovery of phosphorus from the wastewater hydrolysis tank



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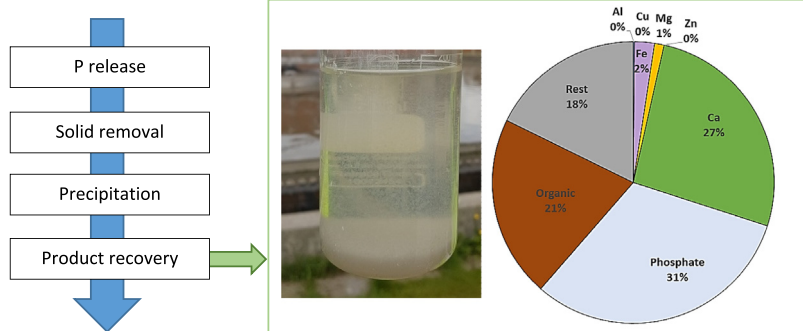
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### HIGHLIGHTS

- The lamellar separator removed >95% of organic materials from the hydrolysis tank sludge.
- Over 90% of the phosphate was precipitated by adding calcium salts at pH 8.5.
- Phosphate precipitates mainly as amorphous calcium phosphate.
- The precipitate contains 20% organic materials
- Less than 2% of the final product was iron

### GRAPHICAL ABSTRACT



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### ABSTRACT

Phosphorus, a limited resource, is also an environmental pollutant that should be removed from wastewater and ideally reused. A pilot-scale facility was set up and used to precipitate and recover phosphorus from wastewater. The return activated sludge in a hydrolysis tank was flocculated and separated and the solid material returned to the hydrolysis tank; the flocculation process did not harm the microorganisms. Phosphate in the reject water was precipitated with different calcium salts and the phosphorus-containing precipitate recovered. The precipitate consisted mainly of phosphate and calcium, and under 5% of the final product consisted of iron and aluminum. Around 20% of the precipitate was organic material. The pilot-scale test was supplemented with bench-scale tests using calcium salt, magnesium salt, and NaOH/KOH. Without the addition of calcium ions, phosphate could be precipitated by increasing pH to 9.5, resulting in a concentration of phosphorus in the reject water of under 2 mg/L. If calcium salt was added (Ca:P ratio of 2:1), it was possible to remove phosphate at pH 9 (<1 mg/L). In general, the concentration of dissolved phosphate was 8–10 mg/L lower after precipitation when calcium salt was used compared with all other tested salts. This difference increased if additional phosphate was added to the sludge. The bench- and pilot-scale experiments yielded comparable data. At the pilot-scale facility, it was possible to remove 90% of the phosphate by adding calcium salt and regulating the pH to 8.5.

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## 1. Introduction

Phosphorus is an essential nutrient required to ensure feed and food production for the world's growing population. Most phosphorus

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fertilizers come from mining phosphate-rich rocks, a limited resource estimated to be depleted by the end of this century (Shu et al., 2006; Cordell et al., 2009). It is therefore necessary to recycle phosphorus to ensure food security for future generations. Recovering phosphorus from wastewater is one method to overcome potential phosphorus scarcity. Today, phosphorus losses to natural water bodies account for approximately 10% of fertilizers applied (Melia et al., 2017), so the potential is great. For example, the Danish Environmental Protection Agency has estimated that reuse of phosphorus from wastewater could cover around 20% of the total phosphorus imported in Denmark, and the Agency has the ambition of increasing phosphorus recycling from sewage sludge from 50 to 55% to 80% (Government, 2013). Phosphorus is also a potential environmental pollutant causing eutrophication (Mayer et al., 2016; Daneshgar et al., 2018; Reitzel et al., 2019). Municipal wastewater that is insufficiently treated plays a key role in accelerating eutrophication (Preisner et al., 2020). Efforts to recover phosphorus serve both to protect the environment and conserve a limited resource (Reitzel et al., 2019).

Phosphorus can be removed from wastewater chemically and biologically. Iron or aluminum salts are often used to precipitate phosphate and remove phosphorus chemically. Phosphate can be removed biologically by polyphosphate-accumulating organisms (PAOs). If biological phosphorus removal is facilitated, the process is called enhanced biological phosphorus removal (EBPR) (Larsen et al., 2006; Venkiteswaran et al., 2018). Phosphorus ends up in sewage sludge, which can be used directly as a fertilizer. Land spreading of sludge is a simple and cheap method to reuse phosphorus. Sludge from enhanced membrane bioreactor (EMBR) plants has higher plant availability than non-EMBR sludge (Glæsner et al., 2016). However, the use of sludge in agriculture is increasingly restricted because sludge may contain microplastics, heavy metals, pathogens, and toxic organic compounds (Tarayre et al., 2016; Vardanyan et al., 2018). In several European countries (including Germany, Italy, and France) less than 50% of the produced sludge is used on agricultural fields, whereby a large portion of the phosphorus resource is lost or has to be recovered from the sludge (Mininni et al., 2015). Dewatered sludge can be incinerated and phosphorus recovered from the ash. This is an expensive method and it has been questioned whether the technology is sustainable (Vaneckhaute et al., 2017; Limmeng et al., 2017). Alternatively phosphorus can be recovered from the liquid phase after dewatering. In the case of EMBR facilities, phosphate is taken up under aerobic conditions and released again under anoxic conditions, with a high concentration of dissolved phosphate being obtained after anaerobic digestion or in the fermented return activated sludge. Higher concentrations can be obtained in the return activated sludge tank by adding acetate, as in the Phostrip process (Van Loosdrecht et al., 1997; Salehi et al., 2018). It is thereby possible to precipitate phosphorus from the liquid phase as, for example, struvite (Amann et al., 2018). Phosphate can also be extracted from the sludge phase by acidification, after which solid materials are removed by flocculation and separation. The phosphate is then recovered from the liquid phase by precipitation (Quist-Jensen et al., 2018). Thus, if sludge cannot be used directly as a fertilizer, three commercial alternatives for phosphorus recovery exist: recovery from the sludge, recovery from the liquid phase after dewatering of activated or digested sludge, and recovery from the ash after incineration (Egle et al., 2016; Daneshgar et al., 2018). These methods vary in the amount of phosphorus that can be recovered and the need for added chemicals (Amann et al., 2018).

In the case of EMBR plants, recovery of phosphorus from the liquid phase is a promising method, both for phosphorus recovery and for avoiding operational problems. Unintentional phosphate precipitation causes scaling in pipes, pumps, etc., at wastewater treatment plants (WWTPs), which increases operational costs. This problem is more pronounced in EBPR plants, because phosphate is released to the liquid phase under anaerobic conditions (Law and Pagilla, 2018). Approximately 85% of phosphorus can potentially be removed by the EBPR process (Melia et al., 2017).

Phosphorus can be recovered from the liquid phase in the return activated sludge or after digestion. Most current research focuses on the filtrate after anaerobic digestion (Law and Pagilla, 2018). After digestion, the phosphorus concentration is usually 50–500 mg phosphorus/L and the ammonium concentration is approximately five times higher (Mehta et al., 2015). Many studies focus on struvite precipitation, because it is possible to simultaneously remove phosphorus and nitrogen (Daneshgar et al., 2018). Furthermore, struvite is a slow-release fertilizer (Melia et al., 2017).

Phosphorus can also be recovered from the side-stream before anaerobic digestion (i.e., in the hydrolysis tank) or perhaps in combination with phosphorus recovery from the digester filtrate. If return activated sludge is stored and degraded anaerobically before it is recycled to the biological tank, phosphate is released and can be recovered (Mehta et al., 2015). Volatile fatty acids can be added to enhance phosphorus release as in the Phostrip process (Van Loosdrecht et al., 1997; Salehi et al., 2018). Phosphorus recovery from the side-stream of undigested sludge could prevent its release and precipitation in the digester (Shaddel et al., 2019). Furthermore, precipitation of phosphorus from the hydrolysis tank instead of phosphorus recovery from the digester filtrate reduces the risk of ammonia emission during phosphorus recovery (Magrí et al., 2020). The liquid from the hydrolysis tank contains a high concentration of phosphate but a low concentration of ammonium compared with the filtrate from sludge after anaerobic digestion (Shaddel et al., 2019). Thus, calcium phosphate precipitation may be a better solution than struvite precipitation.

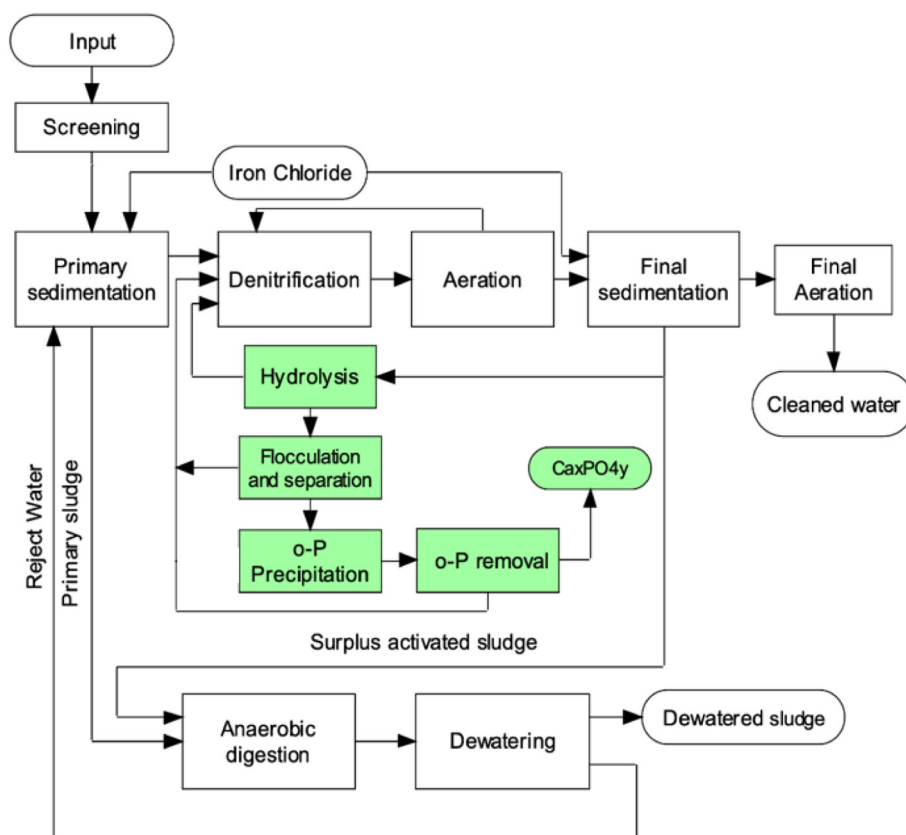
In this study, we explore the potential to recover phosphorus from the hydrolysis tank of an EBPR WWTP, i.e., the side-stream before digestion. Biological phosphorus removal was optimized to increase the level of phosphate in the hydrolysis tank. A pilot-scale facility was set up where sludge was flocculated and removed using a lamella separator. Phosphorus was precipitated from the effluent and collected in a drum filter. Sludge from the lamella separator and filtrate from the drum filter were recycled to the hydrolysis tank. No external carbon was added to the process. The study was done to test the potential for recovering phosphate from the hydrolysis tank, as a simple method to remove and recover phosphorus and avoid potential scaling in the WWTP.

## 2. Materials and methods

### 2.1. Wastewater treatment plant

Randers WWTP is a two-step activated sludge plant treating domestic wastewater with a yearly intake of 9.3 million m<sup>3</sup> wastewater or 25,500 m<sup>3</sup> per day. Phosphorus is removed by adding iron chloride and to a lesser extent by biological phosphorus removal. The consumption of iron chloride is 800 L/day, but reduced to 400 L/day to increase biological phosphorus removal. The plant was designed for 160,000 population equivalent (PE) but, at the time of study, was loaded with 100,000 PE. Activated sludge from the biological tank is pumped into a 1425 m<sup>3</sup> hydrolysis tank with a retention time of 24 h. A schematic of the plant is given in Fig. 1, with the green boxes showing the pilot-scale setup.

Initial tests were done to reduce the iron chloride used and increase the biological phosphorus removal. The concentration of orthophosphate in the effluent and in the hydrolysis tank was measured. After optimization of the biological phosphorus removal and the orthophosphate release in the hydrolysis tank, samples were taken from the hydrolysis tank, analyzed, and used for flocculation, microbial activity, and precipitation tests at bench scale. Based on these experiments, a pilot-scale setup was established, in which sludge from the hydrolysis tank was flocculated, solid materials removed, and phosphorus in the reject wastewater precipitated and recovered in a drum filter (Fig. 1). All streams aside from the phosphorus precipitate were returned to the biological tank. This includes flocculated sludge and the reject water after precipitation of phosphate.



**Fig. 1.** Phosphorus removal from hydrolysis tank. A sketch of the plant at Randers WWTP. The green boxes shows the hydrolysis tank and pilot-scale setup for precipitation and recovery of phosphorus.

## 2.2. Flocculation test

BoFlocc P 6267 M, which is a cationic polymer, was used to flocculate sludge from the hydrolysis tank. The raw polymer (50% active polymer) was diluted 250 times with tap water to an active polymer concentration of 0.2%. Five experiments were done by adding 2, 3, 4, or 5 mL of 0.2% polymer solution to 300 mL of sludge from the hydrolysis tank in a 2-L beaker and gently mixed. The experiments with 5 mL of polymer were done twice. The added concentration of polymer varied between 6.7 and 16.7 mL/L sludge. The formed flocs were unstable and easily broke down into smaller flocs at higher shear. The flocculated sample was filtered through a 600- $\mu\text{m}$  filter. For the sample with only 2-mL of polymer, flocs were small and a 100- $\mu\text{m}$  filter was used instead. The relative amount of filtrate was measured (filtrate/feed volume). The filtrate after flocculation and the sludge from the hydrolysis tank were analyzed by measuring the orthophosphate concentration, pH, and conductivity.

## 2.3. Activity of polyphosphate-accumulating organisms

Samples were taken from the hydrolysis tank and divided into two: 1) samples without further treatment, and 2) samples flocculated with 10, 13.3, and 16.7 mL of 0.2% BoFlocc P 6227 M polymer per L of sludge. The PAO activity was measured under aerobic conditions (phosphate accumulating) and anaerobic conditions (phosphate release). The test was done using 1 L of sludge, which was aerated for 50 min, after which the experiment was performed under anaerobic conditions. After 80 min, 20 mg of acetic acid was added. Samples were taken every 10 min, filtered, and analyzed to measure the concentration of phosphate. All tests were conducted in triplicate.

## 2.4. Bench-scale precipitation of phosphate

Sludge was taken from the hydrolysis tank and the solid material removed using different separation techniques, ending up with four liquid samples with varying organic matter contents.

Liquid sample 1 (GEO): 15 mL of 0.2% BoFlocc P 6267 NM were added per L of sludge, after which the sample was gently mixed and filtered through a GeoTube membrane (TenCate, Nijverdal, Netherlands).

Liquid sample 2 (FILT): 15 mL of 0.2% BoFlocc P 6267 NM were added per L of sludge, after which the sample was gently mixed and filtered through a GeoTube membrane. The liquid was then filtered through a 100- $\mu\text{m}$  paper filter.

Liquid sample 3 (SED): Sludge from the hydrolysis tank was stored at 5 °C for 24 h, after which the liquid was decanted.

Liquid sample 4 (MIX): A mixture containing 1.2 kg of liquid sample 2 (FILT) and 0.8 kg of liquid sample 3 (SED).

The orthophosphate concentration, total phosphorus, COD, pH, and conductivity were measured after removal of solid materials. Precipitation experiments were performed by adding calcium salt (2 mol Ca per mole P), magnesium salt (2 mol Mg per mole P), or NaOH/KOH to regulate pH. The following salts were used:  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaO}$ , NaOH, KOH,  $\text{MgCl}_2$ , or a combination of these. For two of the experiments,  $\text{KH}_2\text{PO}_4$  was added to increase the concentration of orthophosphate. Both calcium and magnesium salt were dosed based on the concentration of orthophosphate in the liquid sample. An overview of the experiments is given in Appendix.

The salt was added, mixed strongly (250 rpm) for 2–3 min and then slowly (120 rpm) for 10 min. The mixture was allowed to stand for approximately 20 min after which the clear liquid was decanted. The precipitate was collected by filtering the remainder of the mixture through a 15- $\mu\text{m}$  filter paper (AGF 118, Munktell 3 W, grade 118). The filtrate

was analyzed by measuring the orthophosphate concentration, pH, and conductivity. The precipitate was analyzed by measuring the dry weight and cations using inductively coupled plasma spectrometer (ICP) analysis.

## 2.5. Pilot-scale setup and experiments

A pilot-scale setup was established at Randers WWTP (Fig. 2). During testing, 1 m<sup>3</sup>/h of sludge from the hydrolysis plant was pumped into the system and flocculated with 21 mL/L of 0.2% BoFloc P 6267 M. The flocculated sludge was mixed gently in a mixing tank (hydraulic residence time, 1 h) and continuously added to a lamella separator, where 60% of the flow ended up as reject water. Reject water was transferred to a 1-m<sup>3</sup> tank for precipitation testing or back to the hydrolysis tank. For each precipitation experiment, 470–800 L of reject water was used. After precipitation, a 42- $\mu$ m drum filter was used to separate the precipitate and liquid with only passive filtration, i.e., there was no rotation of the drum filter. Samples of the sludge from the hydrolysis tank, bottom sludge from the lamella separator, reject water from the lamella separator, and filtrate from the drum filter were taken and analyzed for dry matter, ignition loss, pH, conductivity, orthophosphate concentration, total phosphate, COD, and ammonia. The cations in some of the samples were analyzed using ICP.

Nine experiments were conducted in which Ca(OH)<sub>2</sub> or Ca(Cl)<sub>2</sub> was added. Both hydrated lime (Vejle Kalk, Vejle, Denmark) with 58% Ca

(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> powder (Faxe hydratkalk, Danmark) were used. An overview of the experiment are shown in Appendix. The Ca(OH)<sub>2</sub> powder was suspended in water before use, but not all Ca(OH)<sub>2</sub> powder was dissolved before addition and within the precipitation tank, so the Ca(OH)<sub>2</sub> powder was tested only once; instead, hydrated lime was used. Ca(Cl)<sub>2</sub> powder (Brenntag Nordic, Vejle, Denmark) was mixed with water and added to the precipitation tank. The Ca(Cl)<sub>2</sub> did not affect the pH, so to increase the pH, NaOH was added slowly. In two experiments, 3 M NaOH was added gradually, and the product was tested at pH values ranging from 7 to 9.6.

Samples were taken and filtered through a 0.45- $\mu$ m filter, after which dry matter, ignition loss, pH, conductivity, ammonia, calcium concentration, and orthophosphate concentration were measured. For some samples, ICP analysis was used to determine the content of cations.

The precipitates were sampled after the drum filter and were used to measure dry matter content, ignition loss, and concentration of cations and phosphorus by means of ICP analysis.

## 2.6. Chemical analysis

The dry matter content of the samples was estimated by leaving approximately 15 g of the precipitate in a drying oven at 105 °C for 24 h. Afterwards, the dry matter was incinerated at 550 °C for 2 h to determine the ignition loss. The pH and conductivity were measured using

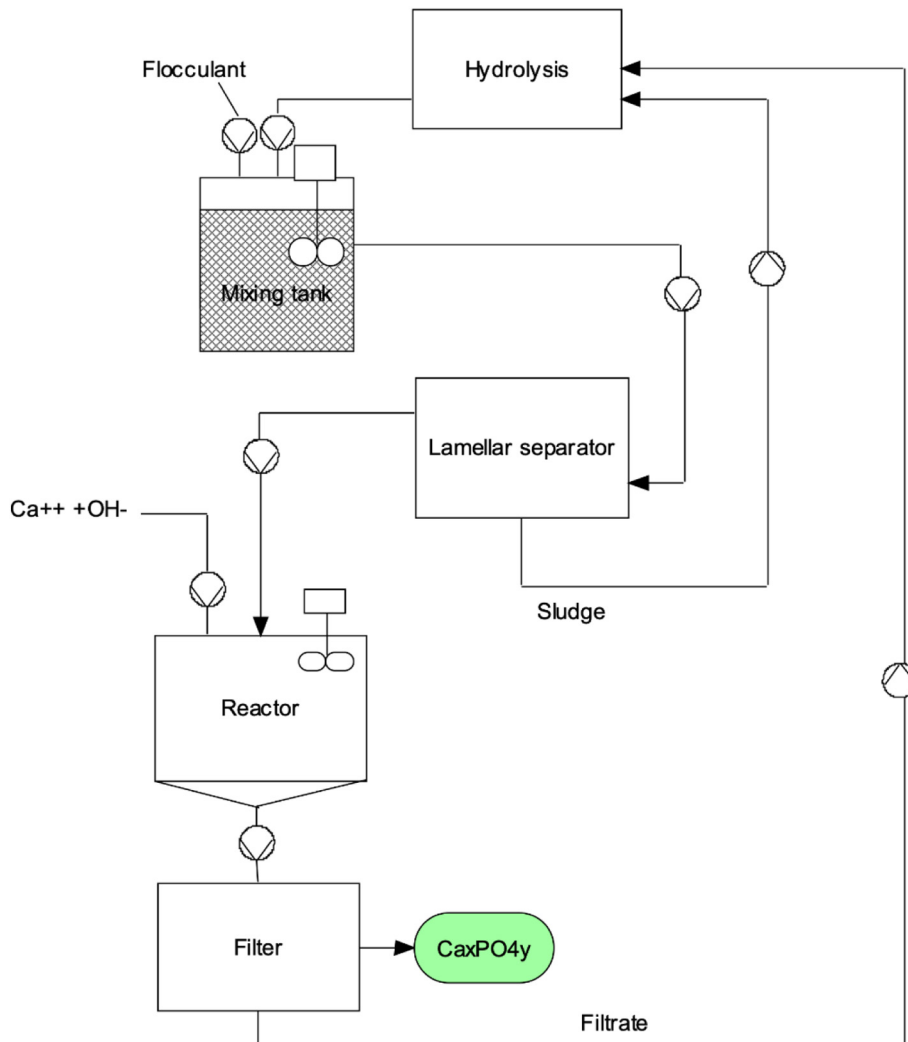


Fig. 2. Experimental setup of pilot plant.



a SevenMulti meter (Mettler Toledo, Columbus, OH, USA) with a BlueLine 17 pH electrode (SI Analytics, Mainz, Germany) and an Inlab 731 conductivity electrode (Mettler Toledo). The ammonium concentration was measured using the Berthelot method in which salicylate was used as a substitute for phenol (Danish Standard, 1975; Searle, 1984).

The concentration of cations in the raw sludge was measured using an iCap 6300 DUO inductively coupled plasma spectrometer (ICP) (Thermo Scientific, Waltham, MA, USA). First, the cations were extracted from the sludge with concentrated HNO<sub>3</sub> and then the samples were filtered through a 0.45- $\mu$ m filter. The concentrations of Fe, Ca, Cr, Cu, Fe, Mg, Pb, P, and Zn were then quantified using ICP; the samples were measured in radial view.

The orthophosphate (o-P) and total-phosphate (t-P) were measured at each pH value according to the procedure given in Danish Standards (Danish Standard, 1985b; Danish Standard, 1985a). The soluble COD was measured using test kits from Hach-Lange (Loveland, CO, USA). The calcium concentration was measured by filtering the samples through a 0.45- $\mu$ m filter and analyzing them using a PinAAcle 900F atom adsorption spectrometer (Perkin Elmer, Waltham, MA, USA).

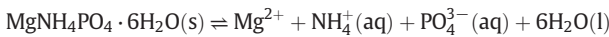
## 2.7. Microscope

Crystal images were obtained using an Axiolab 5 optical microscope equipped with an Axiocam 208 colour camera (ZEISS, Oberkochen, Germany). Approximately 1 mL of solution containing the crystals in the mother liquid was spread on a glass slide and several images were captured (10 $\times$  magnification).

## 2.8. Chemical equilibrium simulation

The solubility of struvite was calculated as function of pH and compared with experimental determined concentrations of magnesium, ammonium and phosphate ions.

The reaction for struvite is



The conditional solubility product for struvite was calculated as

$$K_s^* = \frac{K_s}{\alpha_{\text{PO}_4^{3-}} \cdot \alpha_{\text{NH}_4^+} \cdot \alpha_{\text{Mg}^{2+}}} \quad (1)$$

where  $K_s$  is the solubility product given in Table 1 and  $\alpha$  is the fraction of the species in the required form (Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> or PO<sub>4</sub><sup>3-</sup>) in relation to the total concentration of the component. It has been assumed that all dissolved magnesium exist as Mg<sup>2+</sup>, whereby  $\alpha_{\text{Mg}^{2+}}$  is equal to 1. More struvite can be dissolved than calculated from the solubility formula due to the acid-base reactions, which involve both ammonium and phosphate.

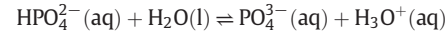
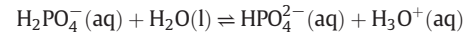
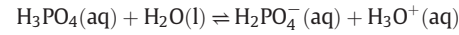
Ammonium is an acid and will react with water forming ammonia at high pH  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ . The equilibrium constant for the reaction  $-\log(K_N) = 9.1$ , and

**Table 1**  
Thermodynamic data.

Mineral	Formula	$-\log(K_s)$
Hydroxyapatite (HAP)	Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	44.33
Brushite	CaHPO <sub>4</sub>	19.275
$\alpha$ 1-tricalcium phosphate (ALFA1 TCP)	$\alpha$ 1-Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	25.5
$\alpha$ 2-tricalcium phosphate (ALFA2 TCP)	$\alpha$ 2-Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	28.25
$\beta$ -tricalcium phosphate (BETA TCP)	$\beta$ -Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	28.92
Struvite	MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	12.6

$$\alpha_{\text{NH}_4^+} = \frac{1}{1 + K_{N1}/[\text{H}^+]} \quad (2)$$

Phosphoric acid is a triprotic acid



with the following three equilibrium constants  $-\log(K_{P1}) = 2.1$ ,  $-\log(K_{P2}) = 7.2$ , and  $-\log(K_{P3}) = 12.3$

$$\alpha_{\text{PO}_4^{3-}} = \frac{K_{P1}K_{P2}K_{P3}}{[\text{H}^+]^3 + [\text{H}^+]^2K_{P1} + [\text{H}^+]K_{P1}K_{P2} + K_{P1}K_{P2}K_{P3}} \quad (3)$$

A similar procedure was used for calcium phosphate products, where

$$K_s^* = \frac{K_s}{(\alpha_{\text{PO}_4^{3-}})^n \cdot (\alpha_{\text{Ca}^{2+}})^m} \quad (4)$$

and  $n$  is the stoichiometric coefficient for phosphate and  $m$  is the stoichiometric coefficient for calcium. It has been assumed that all dissolved calcium exist as Ca<sup>2+</sup>, whereby  $\alpha_{\text{Ca}^{2+}}$  is equal to 1. The solubility products ( $K_s$ ) of the calcium phosphate are given in Table 1

For brushite

$$K_s^* = \frac{K_s}{\alpha_{\text{HPO}_4^{2-}} \cdot \alpha_{\text{Ca}^{2+}}} \quad (5)$$

where

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{H}^+]K_{P1}K_{P2}}{[\text{H}^+]^3 + [\text{H}^+]^2K_{P1} + [\text{H}^+]K_{P1}K_{P2} + K_{P1}K_{P2}K_{P3}} \quad (6)$$

A freeware chemical equilibrium visualization program (Visual MINTEQ version 3.1; KTH, Stockholm, Sweden) was used to do the calculations for calcium phosphate minerals e.g. to calculate the concentration of dissolved calcium and phosphorus in equilibrium with HAP, brushite,  $\alpha$ 1-tricalcium phosphate,  $\alpha$ 2-tricalcium phosphate, and  $\beta$ -tricalcium phosphate (Jon Petter Gustafsson, 2013). Visual MINTEQ has a wide thermodynamic database and model default values were used for all equilibrium constants; calculation were conducted at 25 °C. The Davies method was used for activity corrections during simulations.

## 3. Results

### 3.1. Biological phosphorus removal

Full-scale tests were done at Randers WWTP, where the dosage of iron chloride was gradually reduced to increase biological phosphorus removal. Consequently, more biological phosphorus was released in the hydrolysis tank. By reducing the iron chloride dosage, it was possible to increase the concentration of phosphate in the hydrolysis tank from 10 to 15 mg/L (spring 2020) up to 40–60 mg/L (after 1 August 2020).

### 3.2. Flocculation test

Sludge from the hydrolysis tank was sampled after reducing the iron dosage and improving the phosphate release. The samples were flocculated by adding 6.7–16.7 mL of 0.2% polymer per L of sludge. After polymer addition, the pH was raised by 0.5–1 pH units. The flocculated sludge was then filtered and the filtrate volume determined. It was found that the final filtrate volume increased with polymer dosage.

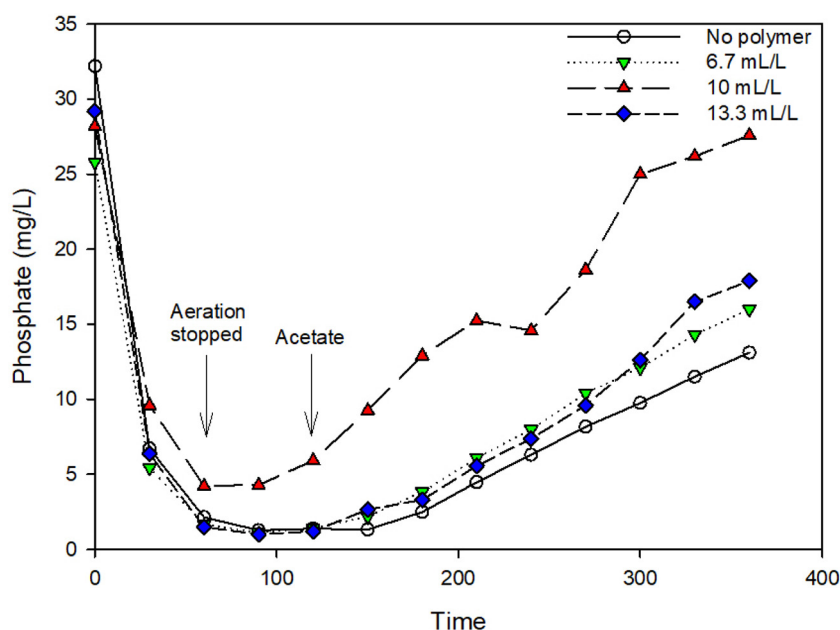


Fig. 3. Activity test of phosphorus-accumulating microorganisms.

The size of the flocs was directly correlated with the polymer dosage. At the lowest dosage, the flocs passed through the 600- $\mu\text{m}$  filter but could be retained by the 100- $\mu\text{m}$  filter. At the highest polymer dosage, the flocs were retained by the 600- $\mu\text{m}$  filter. The concentration of phosphate was measured to be 65 mg/L in untreated sludge and dropped to 50–58 mg/L after flocculation. The concentration of phosphate in the reject water was not correlated with the polymer dosage, so the polymer did not bind phosphate. The lower concentration of phosphate in the filtrate was probably a result of a higher pH after flocculation, during which part of the phosphate precipitated.

To test whether the polymer affected the bacterial activity, the activity of phosphorus-accumulating microorganisms was measured in flocculated sludge and compared with the activity in untreated sludge taken directly from the hydrolysis tank. During the first hour, the sample was aerated and the phosphate level declined as the phosphate accumulated in the bacteria (Fig. 3). After 60 min, aeration was stopped. Acetic acid was then added after 120 min, causing the phosphate to be released again. No significant difference was observed between flocculated and untreated sludge.

### 3.3. Bench-scale flocculation, separation, and precipitation of phosphorus

New sludge samples were taken from the hydrolysis tank and the solid material was removed by sedimentation or by flocculation and filtration. Sedimentation removed the large particles, but the organic content of the supernatant remained high (COD >2000 mg/L). Flocculation and filtration were more effective for removal of organic materials when the sludge was filtered through both the GeoTube (TenCate) filter and the paper filter (COD = 20–25 mg/L). The concentration of phosphate was higher after sedimentation than after flocculation and

filtration, due to the polymer addition as already discussed (Table 2). The total concentration of phosphorus in sludge from the hydrolysis tank was 202.5 mg/L. After sedimentation, 22% of the orthophosphate ended up in the supernatant. After flocculation and filtration, 19% of the phosphorus ended up in the filtrate. The concentration of phosphate depended on the biological process and the activity of the phosphorus-accumulating microorganisms.

The supernatant from the sediment was used for precipitation experiments in which different calcium salts were tested. Both  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$  were used and it was possible to precipitate >95% of the phosphorus. Small amounts of phosphate were released when the samples were stored for 4–24 h (experiments 1 and 2).  $\text{CaCO}_3$  was only partly dissolved after addition and only 20–30% of the phosphate was precipitated (Fig. 4).

Three tests were done to study how organic materials affect the precipitation process. Sludge liquids with varying contents of organic materials (COD from 20 mg/L to <2000 mg/L) were used.  $\text{Ca}(\text{OH})_2$ ,  $\text{NaOH}$ , or  $\text{CaCl}_2$  was added (experiments 4–12). The pH value of the liquid was 7.1–7.4 and was not changed by adding  $\text{CaCl}_2$ . For the experiment in which  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  were used, the final pH was measured to be 9.2. Approximately 80% of the orthophosphate was removed and precipitated by increasing the pH. If a calcium salt was used, 90–97% of the orthophosphate was removed; if  $\text{CaCl}_2$  was added, only 5–10% of the orthophosphate was removed.

Organic materials were co-precipitated with the phosphate and a relatively large difference in the amount of precipitate was observed for the liquid sample with a low content of COD compared with the two other samples (Fig. 5).

Several different salts were used, pH was measured after precipitation, and the concentration of phosphate was plotted as a function of

Table 2  
Flocculation test.

0.2% Bofloc P 6227 M (mL/L)	Orthophosphate (mg/L)	Filtrate (% total)	pH	Conductivity ( $\mu\text{S}/\text{cm}$ )	Flocs
0	65		6.7	944	
6.7 <sup>a</sup>	49.5	67	7.6	908	Small flocs (retained by 100- $\mu\text{m}$ but not 600- $\mu\text{m}$ filter)
10	58.8	75	7.4	899	Small flocs (retained by 600- $\mu\text{m}$ filter)
13.3	53.8	87	7	896	Medium flocs
16.7	54.9	92	7.34	902	Large flocs that easily break down
16.7	54.4	92	7.5	761	Large flocs that easily break down

<sup>a</sup> 100- $\mu\text{m}$  filter used.

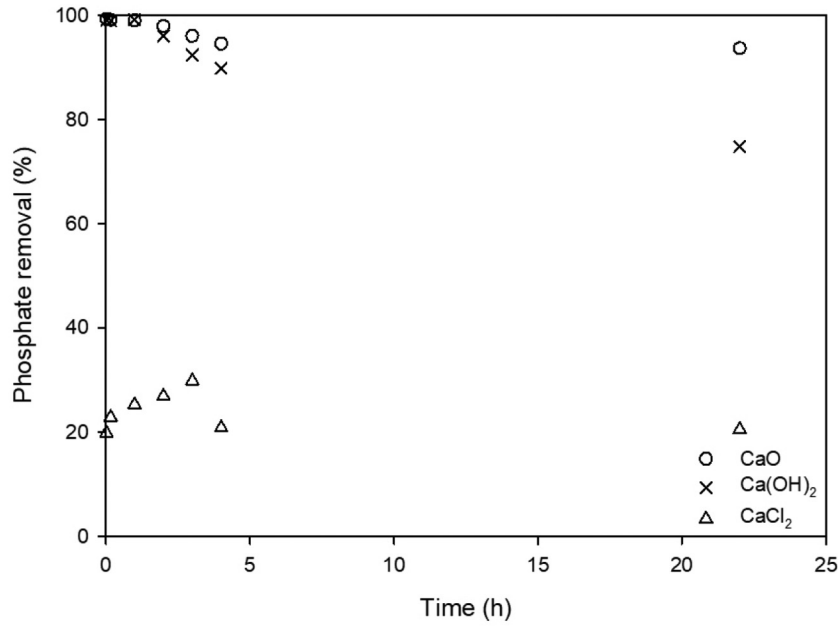


Fig. 4. Precipitation with calcium salt; removal of phosphate in solution after filtration measured as a function of precipitation time.

pH (Fig. 6). There were two groups of experiments: the first consisted of all experiments in which calcium salts were used (open circles) and the second of all other experiments (closed triangles). In two experiments, extra orthophosphate was added before precipitation, in one before precipitation with calcium salt (green circle) and in the other before precipitation with magnesium salt (green triangle). The concentration of orthophosphate in the liquid after removing the precipitate decreased almost linearly with pH, and was below 5 ppm at pH 9 for calcium salts and at pH 9.5 for other salts.

In general, the concentration of phosphate in the liquid was approximately 8–10 mg/L lower after using calcium salts than other salts at all pH values. Furthermore, if 40 mg/L of extra phosphate was added (experiments 26 and 27), calcium salts were more efficient in removing the extra phosphate than were magnesium salts at the same pH (Fig. 6). If calcium salts were used, the same phosphate concentration was obtained regardless of whether or not extra phosphate was added. If magnesium salts were used, the equilibrium concentration of

phosphate increased by approximately 40 mg/L when extra phosphate was added, i.e., the extra phosphate was not precipitated. This was as expected, because the reaction between calcium and phosphate determines the phosphorus concentration, and the drop in phosphate concentration with pH can be explained as a reaction between existing calcium and phosphate. The amount of precipitate increased when extra phosphate was added to the sample before the addition of calcium salts. If all the extra 40 mg/L of phosphate precipitated as Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, this would result in 200 mg of extra precipitated dry material per L of sample. This is in agreement with the experimental data, according to which the dry weight of the precipitate was 200–250 mg/L higher for the sample with extra orthophosphate. When the magnesium salts were used, the amount of precipitate was independent of whether or not extra phosphate was added. In general, the amount of precipitated material increased with pH.

The composition of the precipitate was determined, showing that 40–60% of the precipitate contains calcium and phosphate, even in

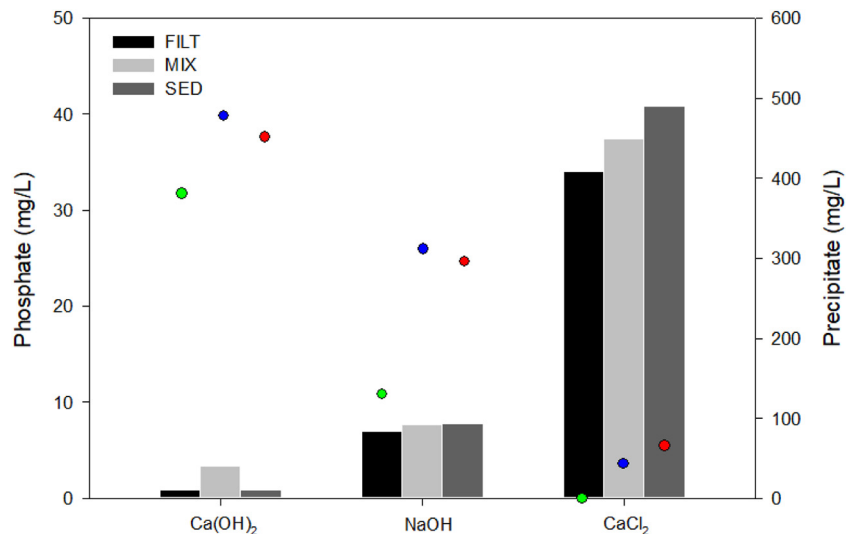


Fig. 5. Orthophosphate in the liquid phase after precipitation (bar) and mass of precipitate after addition of salt, measured as precipitated dry content per L of sample (circles).



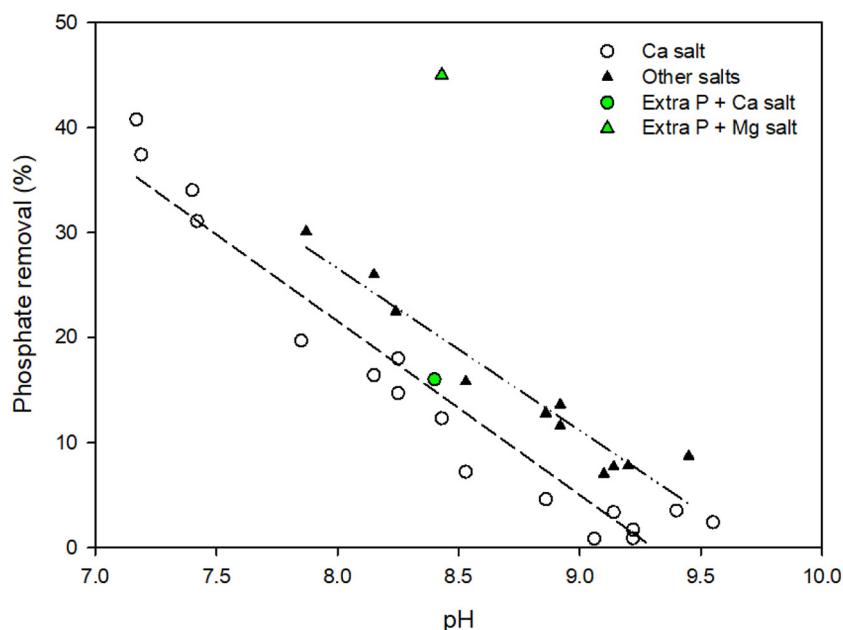


Fig. 6. Phosphate concentration after precipitation (experiments 4–21).

samples without added calcium salt (Fig. 7A). Only minor amounts of iron and magnesium co-precipitated with the calcium phosphate, even when magnesium salts were added.

The ratio between calcium and phosphate in the precipitate was measured to be 1.2–2 calcium ions per phosphate ion (Fig. 7B). The ratio between magnesium and orthophosphate and between iron and orthophosphate was below 0.5. The ratio between magnesium and phosphate increased when magnesium salts were added, but was still below 0.5.

### 3.4. Pilot-scale flocculation, separation, and precipitation of phosphorus

A pilot-scale setup was installed at Randers WWTP. Polymer was added using 21 L of 0.2% polymer/h to 1 m<sup>3</sup> of sludge/h. In the lamella separator, approximately 60% of the volume ended up as reject water and was used for phosphate precipitation. The rest (40%) ended up as bottom sludge and was returned to the hydrolysis tank. The flow of sludge from the hydrolysis tank could be increased to 1.5 m<sup>3</sup> of sludge/h by using 36 L of 0.2% polymer/h, without particles and flocs in the reject water. It was thereby possible to increase the relative volume of the reject water to 70–75%. All experiments were done with an inlet flow of 1 m<sup>3</sup> of sludge/h.

The dry matter in the sludge from the hydrolysis tank was around 1% and twice as high in the bottom sludge (Table 3). No significant change in pH or conductivity was observed. The phosphate concentration was lower in the filtrate than in the sludge from the hydrolysis tank, as observed in the bench-scale experiments.

The composition of the sludge from the hydrolysis tank and of the reject water was analyzed (Table 4). Almost 98% of the ions were removed from the filtered water, resulting in an iron concentration below 10 mg/L. Approximately half of the magnesium was removed and 70% of the calcium was precipitated, leaving 78 mg/L of calcium in the reject water, so more calcium than phosphorus was left in the reject water. The concentration of phosphate was around 50 mg/L (or 20% of the total phosphorus content in the sludge from the hydrolysis tank). The reject water was measured to have a COD content of 80 mg/L, which was higher than the COD measured in the bench-scale experiments after flocculation and filtration, but significantly lower than in the supernatant from samples settled without addition of polymers.

Most of the organic materials (>96%) were removed from the reject water after flocculation and separation, whereas 20–30% of the inorganic materials including ions, were left in the reject water.

Different calcium salts were added to the reject water to precipitate the orthophosphate, in a rapid process. The phosphate concentration was reduced considerably within the first 3 min and then only slightly over the next 40 min. This agrees well with the results obtained in the bench-scale experiments.

The concentration of dissolved phosphate strongly depends on pH (Fig. 8). At pH values above 8.7, almost all phosphate was removed, and more than 95% was removed at pH 8.5.

Most of the orthophosphate is expected to precipitate as calcium phosphate. The equilibrium curve for five calcium phosphate minerals is shown in Fig. 9, i.e., HAp, Brushite,  $\alpha$ 1-,  $\alpha$ 2-, and  $\beta$ -tricalcium phosphate (TCP). The y-axis shows the calcium ion concentration times the dissolved phosphate concentration at equilibrium. The circles represent the ion concentration products of the experiments, i.e., the measured calcium ion concentration times the measured dissolved phosphate concentration. More phosphate and calcium were dissolved than expected at equilibrium, for example, for HAp, so the samples were oversaturated with calcium and phosphate. The data agree well with literature findings showing that intermediate phases are obtained during the precipitation of calcium phosphate (Johnsson and Nancollas, 1992; Wang and Nancollas, 2008; Cichy et al., 2019; Magri et al., 2020).

The formed precipitated particles were small (around 10  $\mu$ m) and co-precipitated with some of the organic materials (Fig. 10). Most of the precipitate passed through the drum filter at the beginning of the filtration, but after 10–20 min, a filter cake was formed and most precipitate was retained by the filter.

The amount of base required to raise the pH was measured (Fig. 11). Raising the pH to 8.5 required approximately 2–4 mmol of hydroxide ions per L of reject water. This figure is based on data from both bench- and pilot-scale experiments.

The composition of the precipitate was analyzed, showing that almost 60% of the precipitate consisted of calcium and phosphate (Fig. 12). This agrees with the data from the bench-scale experiments. The precipitate contained only minor amounts of iron (2%), magnesium (1%), aluminum, and copper (Table 5); approximately 20% of the precipitate consisted of organic materials.

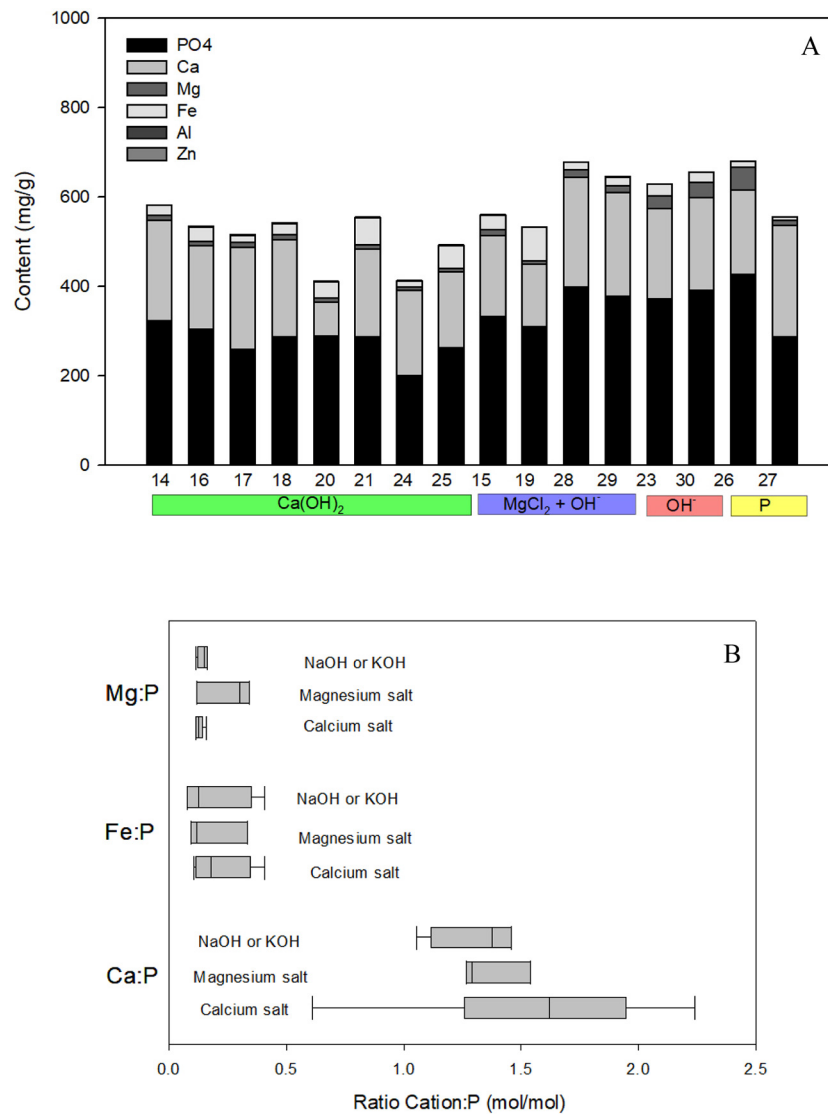


Fig. 7. Analysis of the precipitate after the addition of salts and filtration (A) and ratio between phosphate and calcium in the precipitate (B).

Struvite is one of the products often precipitated and used to recover phosphorus from wastewater. This is an attractive approach for reject water from the digester, in which the ammonium concentration is more than 10 times higher than the phosphate concentration. The concentration of ammonium was almost the same as that of dissolved phosphate in sludge from the hydrolysis tank, so this material was less appropriate for struvite precipitation. A small amount of struvite may have been formed during the precipitation process, but only a minor amount of magnesium was found in the precipitate.

The phase diagram for struvite (Fig. 13) shows that some struvite could potentially be precipitated by increasing the pH; however, the amount of struvite that can thus be precipitated is low, and considerable magnesium must be added to produce it.

#### 4. Discussion

Flocculation and separation of sludge in a lamella separator yielded reject water with a low COD content and high concentrations of calcium and phosphate. The concentration of dissolved phosphate was approximately 15% lower after addition of polymers, probably due to the increase in pH by 0.5–0.9 pH units after flocculation. The pH increase may be a result of CO<sub>2</sub> stripping during mixing. Polymers are expensive and sedimentation without flocculation may be used as an alternative, resulting in more organic materials in the reject water (>100 times higher COD) and more precipitate after phosphorus precipitation. This lowers the quality of the product. Polymer addition did not harm the microorganisms, i.e., the same phosphate removal

Table 3  
Inlet and outlet from flocculation and lamella separator.

	Dry matter	Inorganic content	pH	Conductivity	Orthophosphate
Hydrolysis sludge	1.0–1.3%	28–30%	6.9–7.0	960–1340 $\mu\text{S}/\text{cm}$	67–83 mg/L
Reject	0.09–0.12%	77–83%	6.9–7.5	916–1370 $\mu\text{S}/\text{cm}$	43–46 mg/L
Bottom sludge	2.0–2.4%	28–29%	6.7–6.9	1250–1470 $\mu\text{S}/\text{cm}$	

**Table 4**  
Ions in the inlet and outlet from flocculation and lamella separator (all concentrations in mg/L).

	Al	Cu	Fe	Mg	Zn	P	Ca	NH <sub>4</sub> -N	COD
Hydrolysis sludge	22–26	9–11	340–350	48–50	4.8	270–280	260–279	26	
Reject	–	–	5.4–6.4	24–25	–	48–49	78.3–78.9	12–19	70–80

and release activity was measured in flocculated sludge and in raw sludge from the hydrolysis tank. Thus, the flocculated and concentrated flocs can be returned to the biological process to ensure a long sludge age and effective treatment process.

Precipitation of phosphate was a fast process, as observed elsewhere (Vasenko and Qu, 2018). The solubility of the phosphate was well above

that of HAp, indicating that intermediate forms of calcium phosphate are formed, as expected based on previous literature findings (Johnsson and Nancollas, 1992; Wang and Nancollas, 2008). They found, that at high pH and in equilibrium, calcium phosphate will precipitate as hydroxyapatite (HAp), but the process is slow and intermediate phases such as amorphous calcium phosphate (Ca:P molar ratio

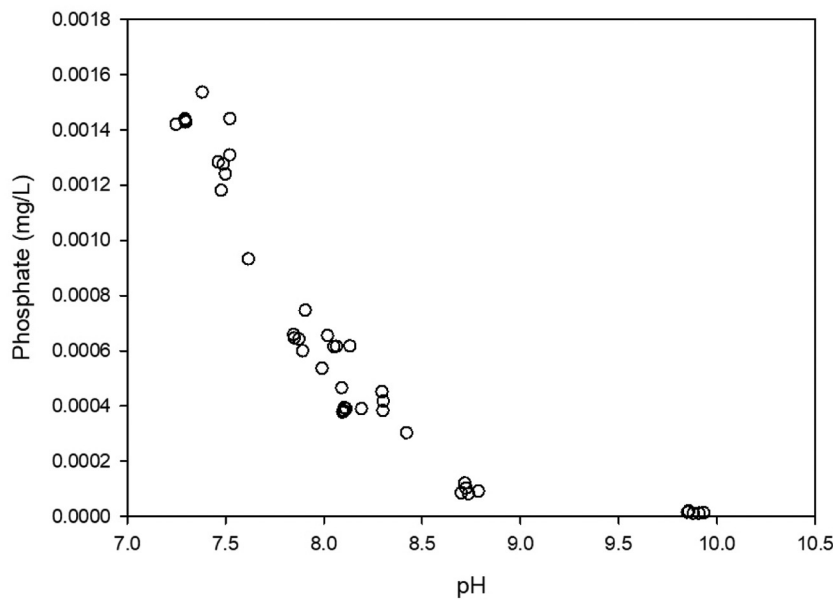


Fig. 8. Concentration of phosphate as a function of pH; data from pilot-scale setup.

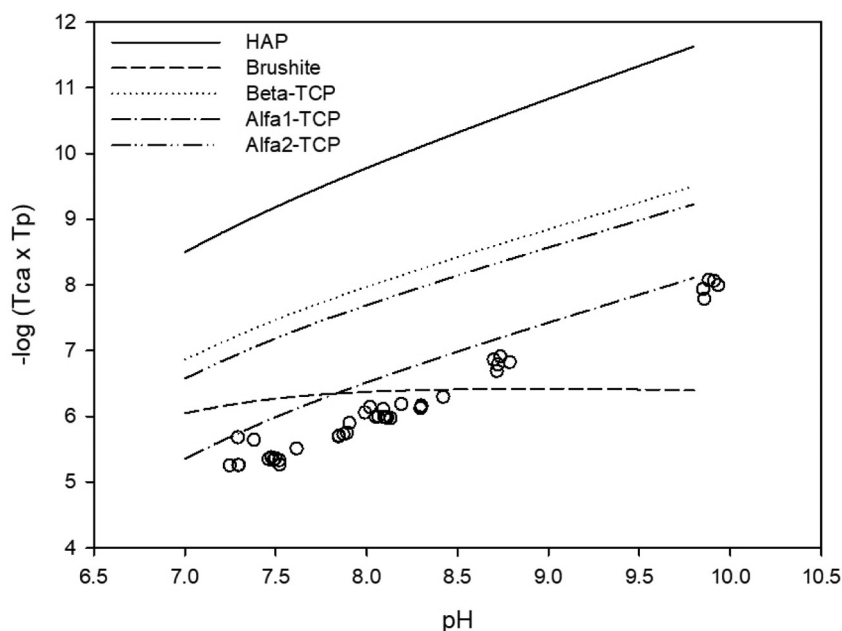


Fig. 9. Concentration of phosphate in solution after precipitation.

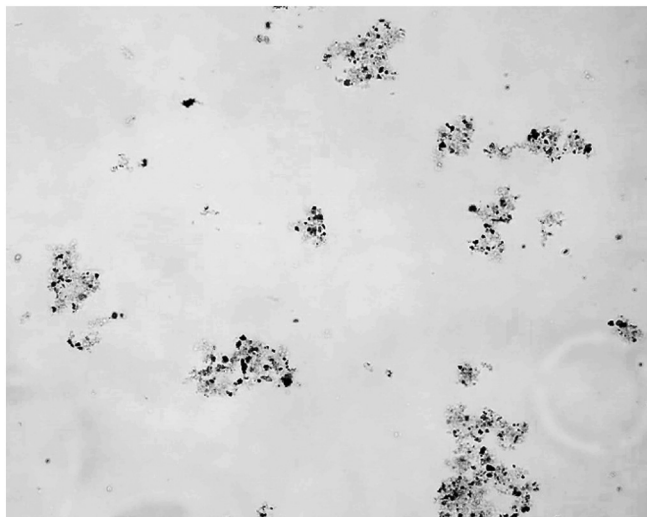


Fig. 10. Precipitate after 30 min (pilot-scale experiment 3).

1.2–2.2), octacalcium phosphate (Ca:P = 1.33), tricalcium phosphate (Ca:P = 1.5), and brucite (Ca:P = 1) are usually formed and later transformed into HAp (1.67) (Johnsson and Nancollas, 1992; Wang and Nancollas, 2008; Cichy et al., 2019; Magrí et al., 2020). The calcium phosphate ratio (Ca:P) was measured to be 1.2–2, similar to that of amorphous calcium phosphate. The concentration of calcium was higher than that of phosphate, i.e., approximately 20% based on molar concentration, but not with a Ca:P ratio of 1.5:1 as in tricalcium phosphate or of 1.67:1 as in Hap. The ratio may be difficult to interpret, as calcium may bind and precipitate with carbonate and organic materials, and phosphate may bind and precipitate with iron, aluminum, and magnesium. However, in a previous study it has been found that fast precipitation in digested and filtered sludge results in amorphous calcium phosphate products (Vasenko and Qu, 2018; Cichy et al., 2019).

More than 90% of the phosphorus is removed at pH 8.5. In synthetic wastewater, Shaddel et al. (2019) found that the optimum pH for phosphorus precipitation was 8.5, whereas Cichy et al. (2019) found the optimum pH to be 9–11. Data from this study shows a higher removal of

phosphate at pH 9–10 than at pH 8.5, confirming the data from Cichy et al. (2019) and equilibrium calculations from Fig. 9.

Most iron and aluminum was removed with the sludge during solid–liquid separation, which reduced the concentrations of both iron and aluminum in the phosphate product. High concentration of iron or aluminum may be a problem if phosphorus is extracted from acidified sludge (Quist-Jensen et al., 2018) as iron or aluminum phosphate lower phosphate uptake. A relatively high concentration of magnesium was found in the reject water, but not in the precipitate. If magnesium salts were added, the amount of magnesium in the precipitate increased (i.e., the Mg:P ratio increased), but the amount of magnesium was small at around 1%. The precipitation of struvite was unlikely due to the low concentration of ammonia.

The precipitate consisted of crystals that were easy to detect under the microscope. Organic materials formed fluffy particles comprising both individual particles and particles with embedded crystals. Vasenko et al. (2020) added calcium salt to filtrate after anaerobic digestion for the precipitation of phosphorus, and showed that organic material is co-precipitated (Vasenko et al., 2020). Calcium was expected to form complexes with carboxylic groups on the organic materials, such as humic-like substances (Ouattmane et al., 1999), and thereby form organic gel particles. Organic material, such as humic substances, can inhibit the growth of dicalcium phosphate dihydrate (DCPD) and HAp crystals (Amjad, 1989; Freche and Lacout, 1992; Yong-hui et al., 2006; Vasenko and Qu, 2018). This may be due to the adsorption caused by interaction between calcium ions and functional groups or organic materials (i.e., carboxylic acid and phosphate) (Freche and Lacout, 1992). The organic materials in the precipitate were not analyzed in this study but were expected to be dominated by extracellular polymeric substances such as humic-like substances and polysaccharides based on the previously mentioned studies.

The formed particles are small which may be problematic for the further handling. Vasenko and Qu (2017) found that the growth rate of the crystals is faster at a low N:P ratio (i.e., N:P 10), but a low N:P ratio also results in small-mean-sized crystals. This has been observed in synthetic solutions. Thus, the low concentration of ammonium in the liquid may reduce the size. Larger particles could be formed by adding calcium chloride and then increasing the pH slowly by adding NaOH, and the precipitation process may be further optimized to obtain larger particles. The formed particles could partly be retained by the drum filter,

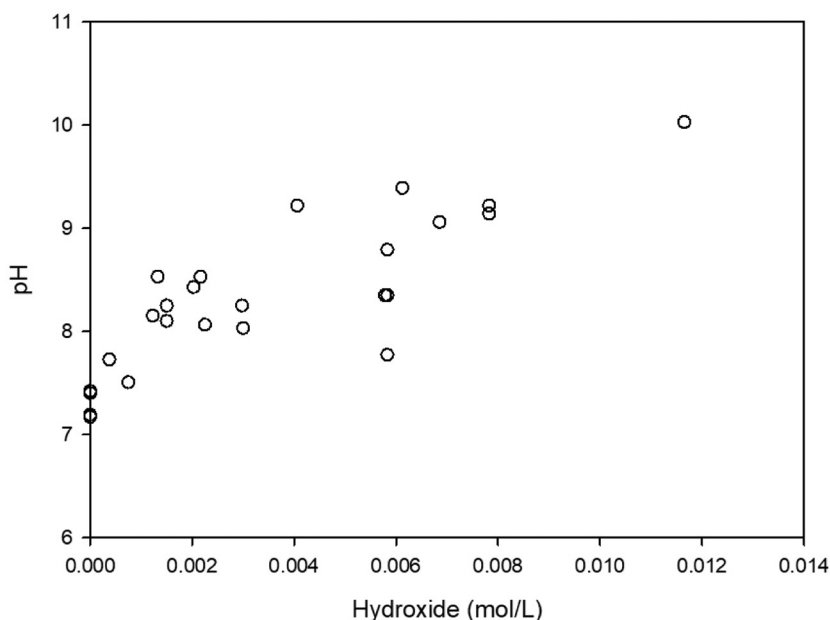


Fig. 11. Consumption of hydroxide ions to raise the pH (i.e., titration curve).

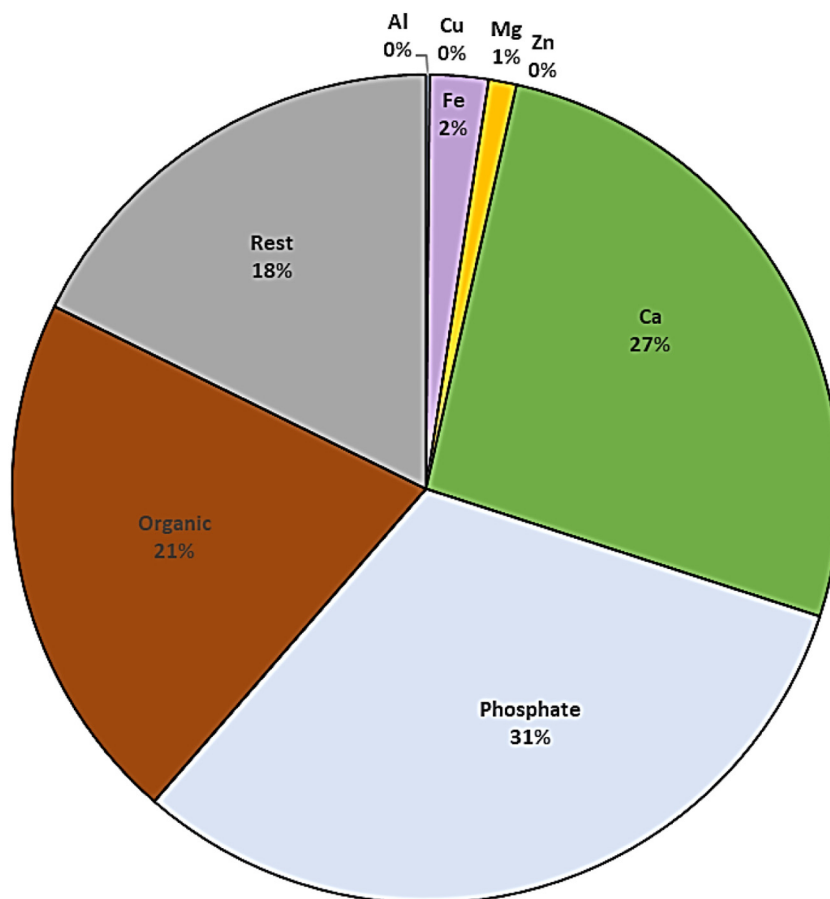


Fig. 12. Composition of precipitate; average from experiments 6–9.

building up a filter cake that collected the particles. An alternative was to use a filter with a smaller pore size, which reduced the capacity of the drum filter, or possibly even a lamella separator.

It was possible to remove approximately 90% of the phosphorus from the reject water, which contains 20% of the phosphorus from the hydrolysis sludge, while the rest of the phosphorus was solid-bound phosphorus. The reject water after phosphate precipitation and separation was returned to the main waste stream before the activated sludge process. The reject water was thereby diluted by a factor 1:10. Because of the dilution, the changes in pH are expected to be minor and it is not expected to affect the activated sludge process. The reject water contained calcium. High concentration of calcium gives large, compact sludge flocs and are beneficial for the wastewater treatment process (Biggs et al., 2001; Higgins et al., 2004; Christensen et al., 2015). Phosphorus is removed and the phosphorus removal is expected to influence the biological phosphorus removal in the activated sludge process (Zu et al., 2020), but this has not yet been studied.

The final product is calcium phosphate with 20% organic materials and around 2% iron. Simple cost estimation indicated that polymer flocculation is the most expensive part of the phosphorus recovery process. Calcium phosphate precipitation may be an attractive alternative to

struvite production, which is costly (Hao et al., 2013). Both magnesium salt and bases are required for struvite precipitation, and up to 75% of the cost of struvite formation comes from the required magnesium salt (Melia et al., 2017). Calcium salts are cheaper than magnesium salts and, according to Law and Pagilla (2018), recovery of phosphorus as calcium phosphate has a promising future for technical and economic reasons. Calcium phosphate can be used as a fertilizer or stored as a phosphorus reserve (Law and Pagilla, 2018). Struvite and other magnesium phosphates are better fertilizers than calcium phosphate, whereas calcium phosphate is a better raw material for the production of fertilizers (Magrí et al., 2020). Calcium phosphate can be used as an electro-thermal raw material as opposed to struvite (Shaddel et al., 2019). Previous studies show that HAp has lower fertilizer efficiency than recovered calcium phosphate, which has up to 85–95% of the efficiency of triple super phosphate versus 22% for HAp, possibly due to poor crystallization (Bauer et al., 2007; Achat et al., 2014). The higher plant availability may be due to the organic content, which stimulates soil microbial activity (Achat et al., 2014). Others have found that the calcium phosphate recovered from wastewater was only efficient in acid soil (Cabeza et al., 2011). The high organic content may potentially be a problem for further handling, but the organic material can be removed using a two-step procedure in which ozonation is done before the second precipitation step (Vasenko et al., 2020).

## 5. Conclusions

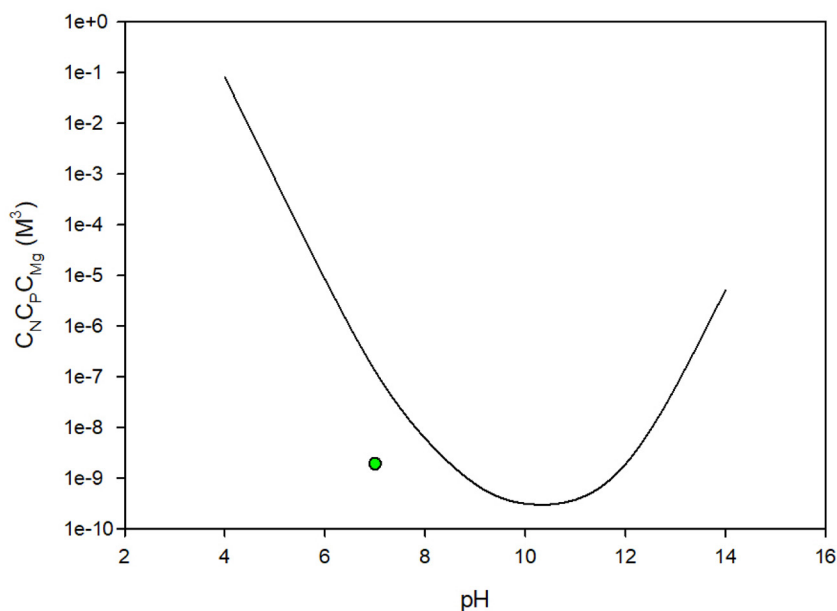
A pilot-scale facility was used to precipitate and recover phosphorus from return activated sludge in a hydrolysis tank. Sludge was flocculated and transferred to a lamella clarifier. Phosphate in the reject from the clarifier was precipitated with calcium salt and collected in a drum filter. The flocculation process did not harm the microorganisms

Table 5

Composition of precipitate (all data in mg/g dry material); OP is orthophosphate. The number of the experiment refers to the number given in Table A2 in appendix.

Experiment	Al	Fe	Mg	Zn	OP	Ca
6.7	1.58	33.53	12.78	0.108	103.9	262.90
7	1.38	27.45	10.9	0.041	110.4	282.4
8	1.43	23.72	12.18	0.049	92.28	268.1
9	1.33	7.97	7.97	0.03	108.4	259





**Fig. 13.** Phase diagram for struvite precipitation and the ion product. The green dot indicate the actual ion product in the effluent after flocculation and settling.

responsible for the biological phosphorus removal, and the lamella clarifier removed >95% of the organic materials. The measured concentration of orthophosphate in the reject water was 15% lower after flocculation than without flocculation, probably due to an increase in pH (0.5–0.9 pH unit), which may reduce the solubility of phosphate. There was no correlation between polymer dosage and dissolved phosphate in the reject water. Additional precipitation tests were done at bench scale using calcium salts, magnesium salts, and NaOH or KOH. Without addition of calcium, phosphate could be precipitated by increasing the pH to 9.5, resulting in a concentration of phosphorus in the reject water that was below 2 mg/L. If calcium salts were added (Ca:P ratio 2:1), it was possible to remove phosphate at pH 9 (<1 mg/L). In general, the concentration of dissolved phosphate was 8–10 mg/L lower after precipitation with calcium salts than with precipitation with other salts in the pH interval of 7–9. This difference increased if extra phosphate was added to the sludge. The precipitation reaction was fast (<10 min). The precipitate consisted mainly of phosphate and calcium and less than 5% of the final product consisted of iron and aluminum. Around 20% of the precipitate was organic materials. The precipitated particles were small at around 10  $\mu\text{m}$ . The bench- and pilot-scale experiments yielded comparable data. At the pilot-scale facility, it was possible to remove 90% of the phosphate by adding calcium salt and regulating the pH to 8.5.

#### CRediT authorship contribution statement

Morten Lykkegaard Christensen did most of the paper writing, conceive the presented idea, developed the theory together with CAQJ and BMH, and supervised the project

#### Appendix A

A short overview of the bench precipitation experiments are shown in Table A1

**Table A1**

Bench precipitation experiments; the last four columns show whether calcium salt (Ca), magnesium salt (Mg), extra orthophosphate (P), and/or KOH/NaOH (OH) were added.

Exp.	Sample	Added salt	Ca	Mg	P	OH
1	300 mL SED, 3	76.8 mL 1.50 g/L Ca(OH) <sub>2</sub>	x			
2	300 mL SED, 3	76.8 mL 1.14 g/L CaO	x			

(continued on next page)

Cristina Cvitanich carried out the laboratory experiments, did the data analysis and contributed to the final manuscript with ideas and critical feed-back

Cejna Anna Quist-Jensen developed the theory together with MLC and BMH, did the microscope analysis and data analysis, and provided critical feed-back of the paper

Martin Thau did the pilot-scale experiment together with BMH, contribute to the results section, and contributed with his knowledge on wastewater treatment

Bjørn Malmgren-Hansen planned the pilot-scale experiment. He performed the pilot-scale experiments together with MT, he developed the theory together with MLC, discussed the results and contributed to the final manuscript

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table A1 (continued)

Exp.	Sample	Added salt	Ca	Mg	P	OH
3	300 mL SED, 3	76.8 mL 2.00 g/L CaCO <sub>3</sub>	x			
4	300 mL FILT, 2	62 mL 20 mM Ca(OH) <sub>2</sub>	x			
5	300 mL SED, 3	73 mL 20 mM Ca(OH) <sub>2</sub>	x			
6	300 mL MIX, 4	73 mL 20 mM Ca(OH) <sub>2</sub>	x			
7	300 mL FILT, 2	62 mL 20 mM CaCl <sub>2</sub>	x			
8	300 mL SED, 3	73 mL 20 mM CaCl <sub>2</sub>	x			
9	300 mL MIX, 4	73 mL 20 mM CaCl <sub>2</sub>	x			
10	300 mL FILT, 2	0.2 M NaOH to pH 9.2				x
11	300 mL SED, 3	0.2 M NaOH to pH 9.2				x
12	300 mL MIX, 4	0.2 M NaOH to pH 9.2				x
13	1.8 L GEO, 1	103 mL 20 mM CaCl <sub>2</sub>	x			
14	1.8 L GEO, 1	103 mL 20 mM Ca(OH) <sub>2</sub>	x			
15	1.8 L GEO, 1	12 mL 0.2 M NaOH				x
16	1.8 L GEO, 1	57 mL 20 mM Ca(OH) <sub>2</sub>	x			
17	1.8 L GEO, 1	0.2708 g Ca(OH) <sub>2</sub>	x			
18	1.8 L GEO, 1	0.1354 g Ca(OH) <sub>2</sub>	x			
19	1.8 L GEO, 1	0.2 M NaOH to pH 8.15				x
20	1.8 L GEO, 1	0.100 g Ca(OH) <sub>2</sub>	x			
21	1.8 L GEO, 1	0.1988 g Ca(OH) <sub>2</sub>	x			
22	1.8 L GEO, 1	0.2 mM NaOH to pH 8.25				x
23	1.8 L GEO, 1	0.83 g MgCl <sub>2</sub> ·6H <sub>2</sub> O, NaOH to pH 8.86		x		x
24	1.8 L GEO, 1	0.28 g Ca(OH) <sub>2</sub>	x			
25	1.8 L GEO, 1	0.11 g Ca(OH) <sub>2</sub>	x			
26	1.8 L GEO, 1	1.65 g MgCl <sub>2</sub> ·6H <sub>2</sub> O, 0.31 g KH <sub>2</sub> PO <sub>4</sub> , KOH to pH 8.4		x	x	x
27	1.8 L GEO, 1	0.44 g Ca(OH) <sub>2</sub> , 0.31 g KH <sub>2</sub> PO <sub>4</sub>	x		x	
28	1.8 L GEO, 1	KOH to pH 8.9				x
29	1.8 L GEO, 1	0.2 M NaOH to pH 8.9				x
30	1.8 L GEO, 1	0.82 MgCl <sub>2</sub> ·6H <sub>2</sub> O, KOH to pH 8.9		x		x
31	1.8 L GEO, 1	0.82 MgCl <sub>2</sub> ·6H <sub>2</sub> O, 0.2 M NaOH to pH 7.8		x		x

A short overview of the bench precipitation experiments are shown in Table A1

Table A2

Pilot-scale plant experiment.

Experiment	Precipitation salt	Volume (L)	Calcium salt (g)	NaOH (mL)
1	Hydrated lime Ca(OH) <sub>2</sub>	500	308	
2	Powder Ca(OH) <sub>2</sub>	500	110	
3	Hydrated lime Ca(OH) <sub>2</sub>	500	616	
4	Hydrated lime Ca(OH) <sub>2</sub>	500	308	
5	Hydrated lime Ca(OH) <sub>2</sub>	500	308	
6.1	Powder Ca(Cl) <sub>2</sub>	500	215.5	
6.2	Powder Ca(Cl) <sub>2</sub>	500	215.5	63
6.3	Powder Ca(Cl) <sub>2</sub>	500	215.5	125
6.4	Powder Ca(Cl) <sub>2</sub>	500	215.5	250
6.5	Powder Ca(Cl) <sub>2</sub>	500	215.5	375
6.6	Powder Ca(Cl) <sub>2</sub>	500	215.5	500
6.7	Powder Ca(Cl) <sub>2</sub>	510	215.5	1020
7	Hydrated lime Ca(OH) <sub>2</sub>	500	408	
8	Hydrated lime Ca(OH) <sub>2</sub>	470	300	
9	Powder Ca(Cl) <sub>2</sub>	800	339	1400

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