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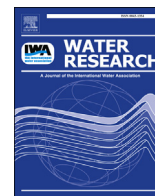
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Sulfide induced phosphate release from iron phosphates and its potential for phosphate recovery

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ABSTRACT

Sulfide is frequently suggested as a tool to release and recover phosphate from iron phosphate rich waste streams, such as sewage sludge, although systematic studies on mechanisms and efficiencies are missing. Batch experiments were conducted with different synthetic iron phosphates (purchased Fe(III)P, Fe(III)P synthesized in the lab and vivianite, Fe(II)₃(PO₄)₂·8H₂O), various sewage sludges (with different molar Fe:P ratios) and sewage sludge ash. When sulfide was added to synthetic iron phosphates (molar Fe:S = 1), phosphate release was completed within 1 h with a maximum release of 92% (vivianite), 60% (purchased Fe(III)P) and 76% (synthesized Fe(III)P). In the latter experiment, rebinding of phosphate to Fe(II) decreased net phosphate release to 56%. Prior to the re-precipitation, phosphate release was very efficient (P released/S input) because it was driven by Fe(III) reduction and not by, more sulfide demanding, FeS_x formation. This was confirmed in low dose sulfide experiments without significant FeS_x formation. Phosphate release from vivianite was very efficient because sulfide reacts directly (1:1) with Fe(II) to form FeS_x, without Fe(III) reduction. At the same time vivianite-Fe(II) is as efficient as Fe(III) in binding phosphate. From digested sewage sludge, sulfide dissolved maximally 30% of all phosphate, from the sludge with the highest iron content which was not as high as suggested in earlier studies. Sludge dewaterability (capillary suction test, 0.13 ± 0.015 g²(s²m⁴)⁻¹) dropped significantly after sulfide addition (0.06 ± 0.004 g²(s²m⁴)⁻¹). Insignificant net phosphate release (1.5%) was observed from sewage sludge ash. Overall, sulfide can be a useful tool to release and recover phosphate bound to iron from sewage sludge. Drawbacks –deterioration of the dewaterability and a net phosphate release that is lower than expected–need to be investigated.

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1. Introduction

Phosphate is essential for all live and without synthetic phosphate fertilizers food production cannot be secured (Cordell et al., 2009). Phosphate is currently used unsustainable with rapid depletion of finite phosphate rock reservoirs – the main source of phosphate to our society (Elser and Bennett, 2011). A circular use of

phosphate is required, that includes its recovery from secondary resources such as sewage sludge or sewage sludge ash (Childers et al., 2011). In many industrial countries with high livestock density excess phosphate is already present in agricultural soils due to manure surpluses (Macdonald et al., 2011; van Dijk et al., 2016). Here, land application of sewage sludge is not an option. Phosphate recovery from sewage sludge should yield a pure product that can be used for the production of a phosphate fertilizer, which can easily be exported to countries with phosphate deficient soils.

The recovery of phosphate from digested sludge liquor in the form of struvite in sewage treatment plants (STPs) that make use of biological phosphate removal has a low recovery efficiency when

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related to the total load of phosphate in sewage. Struvite recovery is only of interest if no iron or alum are used for phosphate removal (Cornel and Schaum, 2009; Korving et al., 2018). However, iron salts are very often used to eliminate phosphate from sewage (WEF, 2011). The iron bound phosphate ends up in the excess sewage sludge. Phosphate recovery from iron phosphate rich sewage sludge is still not economically feasible. This is surprising because it would have benefits such as a high recovery efficiency (Korving et al., 2018) and iron has many properties that are beneficial for modern sewage treatment as it can be used as a coagulant, to prevent sulfide emissions and to efficiently remove phosphate (Wilfert et al., 2015). Only if sludges are anyway incinerated in mono-incinerators, phosphate recovery from ash can be efficient and economic (i.e. economic advantages like selling recovery products compensates for the technology costs and minimized cost for landfilling of the ashes). Phosphate recovery alone will not be enough to make these incinerators economic (Egle et al., 2014, 2015).

Sulfide is an interesting tool that can mobilize phosphate from iron phosphates with potential for subsequent phosphate recovery. The interactions between iron, phosphate and sulfide are very complex and manifold. Efficient application of sulfide for phosphate recovery requires an in-depth understanding of these interactions. In the presence of ferric iron (Fe(III)), sulfide acts as a reducing agent that produces dissolved ferrous iron (Fe(II)) and elemental sulfur (Poulton et al., 2004). Together with ferrous iron, sulfide can form various iron sulfide compounds (FeS_x) that can stay as colloidal material in solution or precipitate (Likosova et al., 2013; Morse et al., 1987; Peiffer et al., 2015; Rickard, 2006). The reactions of sulfide with iron and the type of FeS_x that are formed are inter alia influenced by the type of iron oxide that is initially present (Canfield, 1989), the presence of surface complexing substances such as phosphate (Biber et al., 1994; Stumm et al., 1992) and the experimental/environmental conditions such as the iron to sulfide ratio in the system (Peiffer et al., 2015) or the pH (Rickard, 2006). This shows that it is important to know which iron (phosphate) compounds are present in the sludge, which products are formed upon sulfide addition and how and under which conditions sulfide is added for phosphate recovery. For instance, the formation of soluble colloidal FeS_x can disturb a phosphate recovery process whereas the formation of elemental sulfur can be beneficial (recovery of sulfur).

It was shown that sulfide can effectively mobilize iron bound phosphate from sediment systems (Caraco et al., 1989; Roden and Edmonds, 1997; Smolders et al., 2006). It has also been observed that iron reduction alone, be it chemically or biologically induced, can mobilize phosphate from iron phosphates (e.g. Peretyazhko and Sposito, 2005). However, solid doubts about the general validity of this paradigm have been raised (Borch and Fendorf, 2007; Hupfer and Lewandowski, 2008; Roden and Edmonds, 1997). For example, re-precipitation of phosphate with the produced Fe(II) is likely to occur (Azam and Finneran, 2014). This would not be possible if iron reacts with sulfide to form FeS_x and consequently a more significant phosphate release can be expected (Hupfer and Lewandowski, 2008; Roden and Edmonds, 1997). Using iron reduction to release phosphate from ferric iron phosphate matrices without preventing the rebinding of phosphate is therefore not a promising route. The kinetics and mechanisms of the re-precipitation are unknown.

Sulfide has been used in earlier studies for releasing phosphate to study phosphate recovery from waste streams (Kato et al., 2006; Likosova et al., 2013; Lippens and Vrieze, 2019; Suschka et al., 2001). Likosova et al. (2013) released phosphate from synthetic ferric phosphate and from sludge that originated from a drinking water plant. They suggest that a low pH should be used for the

sulfide induced phosphate extraction to be able to separate the colloidal FeS_x from the liquid phase to obtain a pure phosphate solution. Suschka et al. (2001) used Fe(III) sulfate to remove phosphate from sewage and incubated the ferric phosphate containing sludge under oxygen free conditions. Subsequently, they observed microbial sulfide production and a phosphate release from the sludge that matched the stoichiometric expectations. Kato et al. (2006) used sludge before the anaerobic digestion to study sulfide induced phosphate release. They showed that sulfide can be used as a selective extractant to release iron bound inorganic phosphate, because phosphate was only released from sludge in case significant amounts of iron were present. These studies suggest that sulfide is indeed an interesting option to release phosphate from iron phosphate rich sewage sludge where most of the phosphate is bound to iron. Unfortunately, phosphate release from digested sewage sludge using sulfide has not been studied yet. This is surprising because digested sewage sludge is the most logical point for phosphate recovery with a high recovery potential and a high phosphate concentration.

For a phosphate recovery process digested sludge would be brought to a separate tank, amended with sulfide and dewatered to obtain a phosphate rich solution. The concentrated phosphate in this solution can be precipitated as struvite as is already performed on large scale on reject water from sewage sludge dewatering for STPs applying enhanced biological phosphate removal. Struvite is currently applied as a slow release fertilizer.

Many different iron compounds exist and phosphate can be bound in various ways to these iron phases (Wilfert et al., 2015). The type of iron phosphate will probably affect sulfide induced phosphate release, i.e. the total phosphate release or how much phosphate can be released per mol sulfide and the nature of the formed products and whether they are beneficial or deterring. In STPs ferrous and ferric iron phosphates can occur or a combination of both (Frossard et al., 1997; Thistleton et al., 2001; Wilfert et al., 2016, 2018), but after digestion vivianite is the dominant iron phosphate (Wilfert et al., 2018).

In a set of experiments phosphate release from synthetic ferrous and ferric phosphate precipitates triggered by sulfide was studied to evaluate whether there is a difference between these compounds in phosphate release patterns/efficiency. Furthermore, it was tested if the reduction of ferric iron by sulfide alone could result in more efficient phosphate release compared to experiments in which also FeS_x are formed (higher phosphate release per mol sulfide added). Finally, sulfide was added to several digested sludge samples from full scale STPs to have a comparison with results obtained from the experiments with the synthetic precipitates. This is the first time sulfide induced phosphate release from digested sludges, sewage sludge ash and vivianite was studied. Furthermore, mechanisms of sulfide induced phosphate release from ferric phosphate were studied to examine if targeting on Fe(III) rather than Fe(II) phosphates for phosphate recovery is more efficient. This study will try to clarify whether the mechanisms of sulfide induced phosphate release have the potential to be applied in phosphate recovery technologies. Such technologies would target on iron phosphate rich wastes like sewage sludges.

2. Methods and material

2.1. General procedures

All experiments were carried out in a closed 2 L glass reactor with a nitrogen headspace. The reactor was held at a constant temperature of 25 °C by a temperature controlled bath and a water jacket. The pH was kept constant between 7.0 and 7.5 by adding oxygen free NaOH or HCl respectively using two computer

controlled pumps. During the sludge experiments the reactor was mixed using a magnetically propelled overhead stirrer that allows to maintain oxygen free conditions in the reactor. In experiments with synthetic iron phosphate precipitates a magnetic stirring bar was sufficient to homogenize the suspensions in the reactor. Samples were taken with a nitrogen flushed syringe through a sampling tube. Before sampling some nitrogen was injected into the reactor to flush the tubing and then a sample was withdrawn. Samples were filled in nitrogen flushed plastic centrifuge tubes, centrifuged (10 min, 3600 G) and the supernatant was filtered with nitrogen flushed syringes through nitrogen washed 0.45 μm filters. During the experiments sulfide solutions with different concentrations were dropwise added with a syringe (or a pump in the slow addition experiments) through a septum on top of the reactor. The concentrations of the sulfide solutions varied from experiment to experiment (described in further detail below). All dissolved sulfide concentrations were determined using the methylene blue method after fixation of the samples in 0.5 M ZnAc (APHA, AWWA, WEF, 1998). Dissolved inorganic phosphate was measured using the molybdenum blue method and ion chromatography (Compact IC 761, Metrohm equipped with a Metrohm Metrosep A Supp 4/5 Guard pre-column, a Metrohm Metrosep A Supp 5 (150/4.0 mm) column, and a conductivity detector). The elemental composition of the samples was determined using ICP-AES (ICP-AES, Optima 5300 DV, PerkinElmer). The elemental composition of sludges and sludge ash was determined after a microwave assisted acid digestion (200 °C for 20 min) using concentrated nitric acid or aqua regia followed by ICP-OES (APHA, AWWA, WEF, 1998).

2.2. Experiments with synthetic iron phosphates

2.2.1. Pulse addition

In one set of experiments, sulfide was continuously added dropwise to different iron phosphate precipitates until the desired Fe:S ratio of 1 was reached (Table 1 & Table 2). These experiments were designed to (I) determine how fast phosphate is released from the iron phosphates, (II) how high the total phosphate release is and (III) how efficient the phosphate release is, i.e. how many moles of phosphate can be released per mol of sulfide. The molar ratio of 1 was chosen as it was expected that amorphous FeS with a molar Fe:S of 1 will form. These experiments were done in triplicates. Three different synthetic iron phosphates were used; two amorphous ferric phosphates and one ferrous phosphate precipitate which was identified as vivianite using XRD (Table 1 & Fig. S1). Vivianite and ferric phosphates were chosen for the experiments as both play a significant role during sewage treatment (Wilfert et al., 2018). For one experiment an iron(III) phosphate dihydrate purchased from Sigma Aldrich, labelled as Sigma Fe(III)P in the following was chosen. The ferric and ferrous phosphate precipitates were prepared in nitrogen bubbled oxygen free Milli-Q water by

keeping the pH between 7 and 7.5. The iron salts were slowly added to the phosphate solutions while stirring the reactor (300 rpm) and allowed to react for about 1 h. For the ferric phosphate, phosphate was precipitated using ferric chloride; this precipitate is referred to as Fe(III)P in the following. The circumneutral pH was chosen to mimic conditions that occur in STPs. Under these conditions ferric (oxide) and/or ferric hydroxide phosphate compounds will form (Smith et al., 2008). Vivianite was produced by precipitating phosphate with ferrous sulfate. For more details about the precipitates refer to Table 1. For all experiments a 0.8 M sulfide solution was prepared using Na₂S flocks and oxygen free Milli-Q water. The efficiency of phosphate release, i.e. how many moles of phosphate were released per mole of sulfide removed from solution was determined by using the highest phosphate concentration that was measured during the experiment.

Visual Minteq was used to evaluate which phosphate release we would expect from vivianite after adding sulfide to it. The input for Minteq was equal to the experimental conditions (pH = 7.5; T = 25 °C; iron, phosphate and sulfide concentrations according to Table S1) Mackinawite and vivianite were the only mineral phases that were allowed to form. The software indicated that the only minerals which were supersaturated were iron sulfides more crystalline than mackinawite (such as pyrite).

2.2.2. Slow addition

In these experiments it was tested if the reduction of ferric iron by sulfide could result in more efficient phosphate release compared to experiments where FeS_x are formed. The ferric phosphate precipitates for these experiments were prepared by stepwise adding a ferric iron stock solution (0.25 mol/L) to a phosphate solution (0.06 mol/L) in the reactor while stirring (400 rpm) at pH = 7 until a molar Fe:P ratio of 0.5 was reached. This low Fe:P was selected to prevent overdosing of iron and thus the formation of precipitates with high Fe:P ratio. Precipitates were separated by centrifuging and discarding of the supernatant. Phosphorus and iron levels were measured in the solid and liquid phase. The obtained freshly formed precipitates with a molar Fe:P ratio of 1.07 were dried at 30 °C. This Fe:P ratio is in accordance with earlier studies for very fresh precipitates obtained at low molar Fe:P ratios (Fulazzaky et al., 2014; Smith et al., 2008). For these experiments the sulfide was added in two different ways to evaluate how different experimental conditions (i.e. different supersaturations) affect phosphate release from the precipitates. In experiment I, a 0.5 M sulfide solution was added with a dosing rate of 0.03 mL/min to a solution containing 1.6 mmol/L of the iron phosphate precipitates until a molar ratio S:Fe of 0.2 was reached (at higher ratios FeS_x formation would dominate). In experiment II, an 8 M sulfide solution was added with a dosing rate of 1 mL/min to a solution containing 30 mmol/L iron phosphate precipitates until a molar ratio S:Fe of 0.12 was reached.

Table 1

Characteristics of the iron phosphate precipitates and phosphate release during sulfide addition experiments (Fig. 1). Initial o-P indicates the phosphate levels at the start of the experiment before adding sulfide. Numbers in brackets indicate the standard deviation.

ID	Description	P added (mmol/L)	Fe added (mmol/L)	o-P initial (mmol/L)	Molar Fe:P precipitate	Molar Fe:S reactor	P Release (% of total)	Mol P release vs Mol S ²⁻ consumed
Sigma Fe(III)P	Fe(III)PO ₄ ·x2H ₂ O XRD: Amorphous n = 3	10	10	0.04	1.00	1.00	60 (4.1)	0.60 (0.040)
Vivianite	o-P precipitated using Fe(II)SO ₄ ·7H ₂ O XRD: Vivianite n = 3	10	15	0.20	1.53	1.00	92 (2.3)	0.72 (0.016)
Fe(III)P	o-P precipitated using Fe(III)Cl ₃ ·6H ₂ O XRD: Amorphous n = 3	10	15	0.34	1.55	1.00	75 (2.6)	0.80 (0.053)

Table 2
Results of sulfide addition experiments with various sewage sludges and sewage sludge ash.

	Iron content (mmol/kg sample)	Phosphorus (P) content (mmol/kg sample)	Initial P dissolved (mmol/kg sample)	Molar Fe:P	Molar Fe:S	P release (% of total solid P)	Mol P released vs. Mol S ²⁻ consumed
Digested sludge, STP Amersfoort	18	39	3.4	0.49	0.5	14	0.12
Digested sludge, STP Leeuwarden (Control)	34	67	4.8	0.55	–	–1	–
Digested sludge, STP Leeuwarden (Experiment #1)	31	63	4.1	0.53	2.2	11	0.42
Digested sludge, STP Leeuwarden (Experiment #2)	34	67	4.9	0.55	1.0	18	0.36
Digested sludge, STP Nieuwveer (Experiment #1)	34	50	3.5	0.74	1.0	22	0.28
Digested sludge, STP Nieuwveer (Experiment #2)	40	50	2.7	0.73	0.7	29	0.12
Digested sludge, STP Dokhaven (n = 2)	28	26	2.3	1.18	0.7	31	0.24
Incineration ash from SNB	1302	2692	0.1	0.48	0.5	1.6	n.d.

2.3. Experiments with digested sewage sludge and sewage incineration ash

The digested sludge originated from two plants that rely mainly on enhanced biological phosphate removal (Leeuwarden and Amersfoort) and two A-B plants (Böhnke, 1977) that rely on chemical phosphate removal using ferrous (Nieuwveer) and ferric iron (Dokhaven). Sulfide was added in different quantities to these sludges to evaluate the total phosphate release. Sewage sludge ash was obtained from the mono sewage sludge incinerator SNB in Moerdijk. For the ash experiments, 16 g ash was added to 2 L of oxygen free water. Then sulfide was added to achieve a molar ratio S:Fe of 2. The elemental composition of the sludges and the ash can be found in the SI (Table S4).

During the experiments, the viscosity of all sludge was apparently decreasing. Thus, a capillary suction test (CST) was performed to estimate whether the dewaterability of sludge is changing as a result of sulfide addition (Sanin et al., 2011). Digested sludge from Leeuwarden before and after adding sulfide was used for these experiments (molar Fe:S = 0.5). The measurements were repeated 7 times and the filterability was calculated (Equation (1)).

$$\text{Filterability} = \frac{\Phi(\mu \cdot c)}{\text{CST}} \left[\frac{\text{g}^2}{\text{s}^2 \text{m}^4} \right] \quad (1)$$

$\Phi = 0.794$ (dimensionless constant of the CST apparatus); μ = the viscosity of water at RT (cp); c = dry matter (g/L); CST = capillary suction time (s).

3. Results and discussion

3.1. Synthetic FeP

3.1.1. Pulse addition

In a series of batch experiments, synthetic iron phosphates and sulfide were mixed to evaluate total phosphate release and kinetics of phosphate dissolution. The maximum phosphate release from the synthetic iron phosphate precipitates was reached within 1 h (Fig. 1, respective Fe:S ratios in Table 1). From vivianite about 92% of the phosphate was released after sulfide addition (Table 1). In this experiment enough sulfide was added to bind all iron (assuming the formation of a FeS_x precipitate with a molar Fe:S of 1) and thus to release almost all phosphate. In accordance with the experimental results, thermodynamic modelling using Visual Minteq predicted that 95% of all phosphate can be released from vivianite in our experiments. For the ferric phosphate precipitates, the

phosphate release was lower compared to the experiment with vivianite. For Sigma Fe(III)P, 60% of all phosphate was experimentally released and for Fe(III)P a maximum of 75% (Table 1). However, with Fe(III)P dissolved phosphate levels continuously decreased over the course of the experiment and after 22 h only 56% of all phosphate remained in solution. At this time phosphate release from Fe(III)P and Sigma Fe(III)P were almost identical.

For the preparation of vivianite and of Fe(III)P, o-P was precipitated using Fe(II) or Fe(III) salts respectively. The residual dissolved phosphate concentration after Fe(II) dosing for vivianite was lower compared to the experiment with ferric iron (0.20 vs 0.34 mmol/L, Table 1). The formed iron phosphate in experiments with Fe(II) was vivianite and for Fe(III) amorphous ferric oxide/hydroxide phosphate. Probably, with Fe(III) addition to the phosphate solution, iron oxides or hydroxides form, that can bind the phosphate via adsorption (Smith et al., 2008). The sulfide induced phosphate release was higher for vivianite than for Fe(III)P despite an identical sulfide input. This is because sulfide reacts directly with vivianite to form FeS_x to release phosphate (equation (3)), thus there is no additional investment of sulfide required for reducing Fe(III) to Fe(II). All phosphate should be released from a Fe(III)P precipitate with a molar ratio of 1 when sulfide is added in a molar ratio S:Fe = 1.5 (equation (2)). At the same time Fe(II) (in vivianite) is probably more efficient in phosphate binding compared to ferric iron hydroxides/oxides. In vivianite 1.5 mol of iron are required to bind 1 mol of phosphate. Although the theoretical Fe:P ratio is 1, in sewage it was shown that ferric iron phosphate precipitates have a molar Fe:P ratios of around 2.5, in environmental systems this ratio was estimated to range between 2 and 10 (Gerke, 2010; Luedecke et al., 1989; Schulz and Zabel, 2006). In studies where higher Fe:P ratios were used, mainly iron phosphates with an initial Fe:P ratio close to one formed, such precipitates were found also when phosphate was precipitated from sewage and water using iron salts (see section 2.2.2, Fulazzaky et al., 2014; Smith et al., 2008). During aging the Fe:P ratio in such precipitates increases which results in a net phosphate release. If sulfide is added to systems with a high Fe:P ratio, sulfide will first react with such iron phases that do not bind phosphate (e.g. iron oxides). Hence, the efficiency of phosphate release (mol S added per mol P released) will decrease for systems with precipitates that have a high Fe:P ratio (see discussion below on the molar Fe:P ratio of the ferric precipitate). We were not able (and believe there is no reliable method available) to determine the Fe:P ratio of the actual iron phosphate precipitates in this experiment, but solely Fe and P removal from solution. The latter does not give information whether iron oxides/hydroxides without adsorbed phosphate formed beside iron phosphate precipitates or not.

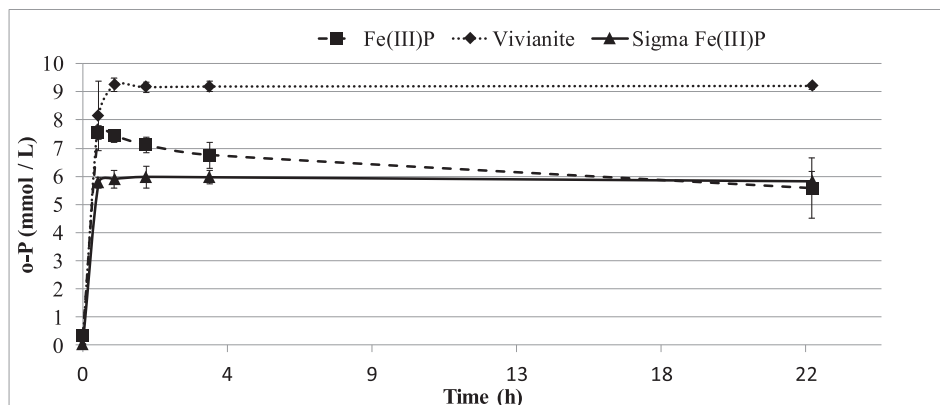
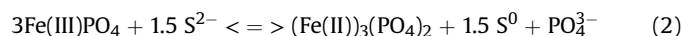


Fig. 1. Patterns of *ortho*-phosphate (o-P) release over time after adding sulfide to different iron phosphate phases. Sulfide in all experiments was added to a final Fe:S ratio of 1. The Fe:P ratios of the initial precipitates ranged between 1 (Sigma Fe(III)P), 1.53 (vivianite) and 1.55 (Fe(III)P). Theoretical maximum phosphate release for vivianite about 100% and for Fe(III)P around 66%.

For ferric phosphates, the reaction with sulfide is more complicated than with vivianite. It is likely that sulfide first reduces Fe(III) to Fe(II), while sulfide is oxidized to elemental sulfur (equation (2), Poulton et al., 2004). Formation of elemental sulfur was accordingly observed as white precipitates in the Fe(III)P experiments. In a second step, Fe(II) or Fe(II)P respectively reacts with remaining sulfide to form FeS (equation (3)).



The formation of FeS_x prevents precipitation of Fe(II)P, as Fe(II) is no longer available. Thus, to form out of 1 mol ferric iron 1 mol of FeS 1.5 mol sulfide would be required. Note, the sulfide input can be higher in case FeS_x with a different stoichiometry, such as pyrite (FeS_2), are formed. In experiments with ferric phosphate the sulfide dose (Fe(III):S = 1) is, according to these assumptions, sufficient to dissolve 66% of all phosphate. However, net phosphate release through the addition of sulfide depends also on the solid molar Fe:P ratio of the ferric precipitate and on the presence of non-phosphate iron compounds (Luedecke et al., 1989). We cannot exclude that also iron precipitates, such as iron oxides or hydroxides formed that do not bind phosphate (i.e. that we overdosed iron during the production of the iron phosphate precipitates). Sulfide should theoretically react preferentially with iron oxides that do not have compounds such as phosphate adsorbed. Because it was shown that adsorbed oxyanions on the surface of iron oxides can inhibit the reaction between sulfide and iron oxides (Biber et al., 1994). For our experiments that would mean that sulfide can be used up without any release of phosphate to the solution.

Phosphate release from Fe(III)P was, at its maximum, higher as stoichiometry would suggest. Initially, about 0.80 instead of 0.66 mol P released per mol S^{2-} consumed and 76% of all phosphate went in solution instead of the expected 66%. Obviously, in the experiments with Fe(III)P, iron reduction played a role and resulted in the phosphate release “bump” in the first hours of the experiment (Fig. 1). Subsequently, phosphate levels started to decrease, probably due to the re-precipitation of phosphate with ferrous iron. Surprisingly, this phenomenon was only visible with the Fe(III)P that we prepared ourselves but not with the Sigma Fe(III)P. Also, only with the Sigma Fe(III)P the solution was black after a 0.4 μm filtration at the end of the experiment as reported earlier (Likosova et al., 2013). High quantities of iron and sulfide were measured in solution in this experiment. Our measurement methods are not

able to distinguish between iron and sulfide that is free and iron and sulfide that is bound in dissolved (complexed/colloidal) FeS_x . But it can be assumed that the black coloration was due to the presence of colloidal FeS_x because the molar Fe:S ratio in solution was approximately 1 (Table S2). To calculate the efficiency of phosphate release in this experiment it was assumed that iron and sulfide occur in a molar ratio of 1 in solution. This means that all added sulfide was used up during this experiment and that no free (dissolved) sulfide was present (Table S1). Only, in the experiment with vivianite significant amounts of sulfide remained in solution after 22 h (0.34 mmol S^{2-} /L; Table S1). Dissolved and precipitated FeS_x can still react with Fe(III) as it can, according to thermodynamics, reduce ferric iron phases (Golterman, 2004). To evaluate whether sulfide can be used as reducing agent to release phosphate more efficiently from ferric phosphate, a slower dosing rate was tested in subsequent experiments. A slower dosing prevents superstition (and thus formation) of FeS_x while the reduction of Fe(III) by sulfide (and thus the formation of Fe(II)) is the dominant reaction pathway.

3.1.2. Slow addition

During the first 1.5 h of experiment I, no black coloration (as an indicator of FeS_x formation) was observed. After this time a gradual darkening was observed and the suspension became completely black after about 4 h. Phosphate release was, with about 1.95 (after 0.5 h) and 1.37 (after 1.5 h) mol of phosphate released per mol sulfide invested, which is more efficient than expected for phosphate release with simultaneous FeS_x formation. In case FeS_x formation would have occurred a release efficiency of 0.67 would be expected (equation (3)). Thus, it can be assumed that chemical iron reduction by sulfide is responsible for the observed phosphate release during the first 1.5 h. After 1.5 h, coinciding with the color change, the extraction efficiency decreased further to about 0.7 mol phosphate/mol sulfide (between 2 and 24 h). Theoretically, 1 mol of sulfide can reduce 2 mol of ferric iron while releasing 2 mol of phosphate (assuming a molar Fe:P of 1 for the ferric phosphate precipitate and assuming that the released phosphate does not re-precipitate with the produced ferrous iron).

In experiment II, where a higher concentrated sulfide solution (8 mol/L) was added to 30 mmol/L iron phosphate, no color change in the reactor was visible in the first 1 h. The suspension turned slightly darker within the next hour and then a clear darkening was observed similar to experiment I. The release efficiency in this experiment was comparable to the one observed after 0.5 h in experiment I, i.e. 1.9 mol of phosphate was released for every mol

of sulfide invested in the first hour. This is close to what can be expected from stoichiometry in case iron reduction is responsible for the release. In both experiments, formation of visible white precipitates (i.e. elemental sulfur) was absent.

The phosphate release induced by chemical reduction of Fe(III) in Fe(III)P is thus more efficient compared to capturing iron in FeS_x. However, released phosphate can precipitate again as Fe(II)P (Azam and Finneran, 2014). Thus, it would be necessary to remove the dissolved phosphate or iron from solution for recovery using e.g. a resin that binds the phosphate or by preventing the precipitation as Fe(II)P by e.g. complexing the Fe(II). Apparently, after some time sulfide was accumulating in the reactor and FeS_x was supersaturated and precipitated.

3.2. Digested sewage sludge and incineration ash

3.2.1. Our observations

After sulfide addition to the ash only about 1.5% of all phosphate was released after about 1 h of reaction time (Table 2). Subsequently, the phosphate in solution decreased continuously until levels below the initial ones at the start of the experiment (24 h, Table S2). In a control experiment, without sulfide addition, phosphate levels also decreased slightly from 0.15 at the beginning of the experiment to 0.10 mmol/L after 24 h (data not shown). The low net phosphate release from the sewage sludge ash indicates that the phosphate compounds in the ash are inert towards sulfide although significant quantities of iron are present (Table S4, Korving et al., 2018). Accordingly, phosphate minerals that have been identified in sludge ash so far do not contain iron as major element. Thus, one would not expect a significant phosphate release from sewage sludge ash (Adam et al., 2009). However, in whitlockite, frequently detected in ash, calcium can be replaced to a certain degree by iron (Anthony et al., 2019) indicating that iron bound phosphate is present and that sulfide could release some phosphate from the ash. For our experiment that could mean initially released phosphate is rebound over time to other compounds in the ash. Thus, higher quantities of phosphate may have been initially released before the first sample was taken after 1 h.

A typical pattern for dissolved phosphate, sulfide and iron concentrations is shown in Fig. 2. For digested sludges a higher iron content resulted in a higher sulfide induced phosphate release (Table 2). In sludge from Amersfoort and Leeuwarden, with molar Fe:P ratios of about 0.5, 14 and 18% of all solid phosphate could be released, respectively. With Leeuwarden sludge the phosphate release was slightly lower compared to Amersfoort although Leeuwarden had, relatively to phosphate, a higher iron concentration in the sludge. Sulfide was added in excess in Amersfoort (S:Fe = 2) and in equimolar ratios in Leeuwarden (S:Fe = 1). In experiments with Leeuwarden sludge no residual sulfide was detected in contrast to the experiments with the Amersfoort sludge where about 5 mmol S²⁻/L were still in solution at the end of the experiment.

In the sludge from Nieuwveer, about 22% of all phosphate could be released when sulfide was added in molar Fe:S ratio of 1. About 1.3 times more phosphate (29%) was released from another digested sludge sample from the same STP at a higher molar S:Fe ratio of 1.5. Accordingly, in an earlier study a higher sulfide dose (S:Fe = 1.5) increased phosphate release from digested sludge sampled in Leeuwarden by a factor of 1.2 (26% of all phosphate) although Fe:P molar ratios were identical in both experiments/sludges (Wilfert et al., 2016).

It was assumed that adding sulfide in a molar ratio of 1 is enough to release all phosphate from iron phosphate in the sludge because: (I) iron is present in its reduced form in the digested sludge (Wilfert et al., 2018), (II) part of the iron was anyway already present as iron sulfide (Wilfert et al., 2018) and (III) freshly amorphous iron sulfide compounds form with a molar Fe:S ratio equal or slightly above 1 (Rickard, 2006). In earlier studies at pH = 4 an increase in the sulfide dosing (up to S:Fe ratios of 2.5) resulted in higher extraction efficiency of phosphate from Sigma Fe(III)P and drinking water sludge (Likosova et al., 2013). Kato et al. (2006) reported that phosphate release already levelled off at S:Fe ratios between 1 and 2 in surplus sewage sludge sampled. It is possible that different FeS_x with different molar Fe:S ratios form and varying sulfide input is required to release the phosphate.

From Dokhaven sludge about 30% of all phosphate could be

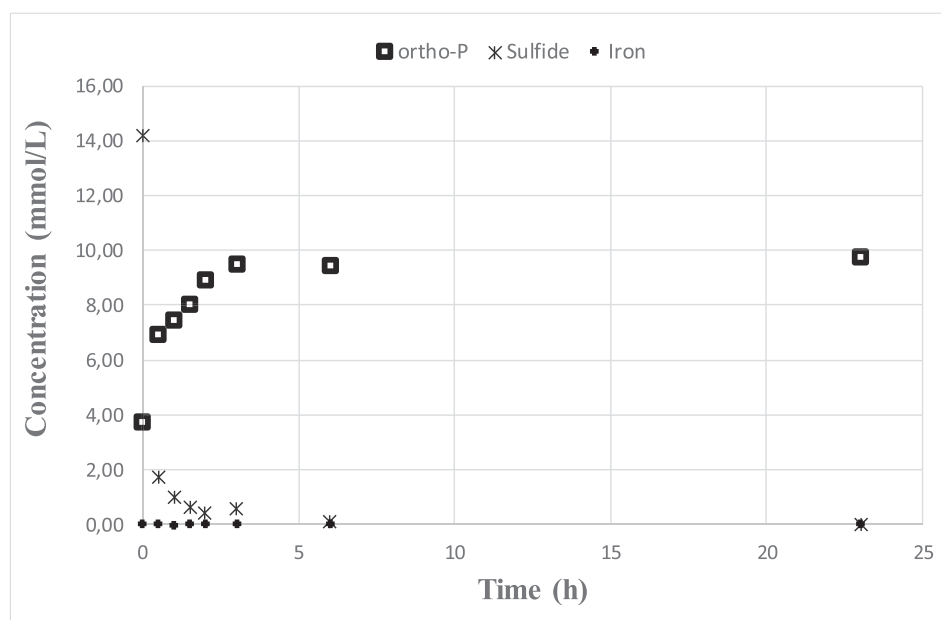


Fig. 2. Patterns of dissolved o-P, sulfide and iron over time after a pulse dose of sulfide to digested sewage sludge sampled from the STP Leeuwarden (Fe:S = 2.2, see Tables 2 and S2 for further information).

released. This is surprising because the sludge from Dokhaven showed a much higher Fe:P molar ratio and thus a higher phosphate release was expected. An earlier study indicates that iron bound phosphate (as vivianite) in Leeuwarden accounts for around 20–30%, in Nieuwveer around 40% and in Dokhaven for about 65% of all phosphate (Wilfert et al., 2016, 2018). Only in Leeuwarden the sulfide induced phosphate release (18%) comes close to values one would expect based on iron phosphate quantification by Mössbauer spectroscopy and XRD. In the other sludges the phosphate release is only about the half of the expected release. This raises the question why phosphate release was lower than expected. Earlier measurements in these studies showed some inconsistencies (Wilfert et al., 2016, 2018). And perhaps iron bound phosphate was overestimated. It is also possible that part of the released phosphate precipitates with other substances that are in solution, such as calcium or magnesium, or that the released phosphate adsorbs to other phases in the sludge matrix. Similar observations were made for sediment systems (Roden and Edmonds, 1997). Additionally, as discussed above, some of the released phosphate could precipitate with iron when the sulfide input is not enough to fulfil the stoichiometry of the formed FeS_x . This would imply that with a higher S:Fe ratio a higher phosphate release would be expected. However, in all sludge experiments, except of the one from Leeuwarden, significant quantities of dissolved sulfide were still present at the end of the experiment (Tables S2 and S3).

The efficiency of phosphate release was expressed as the sulfide that was used up (i.e. removed from solution) versus the phosphate that was released to the solution by the time that the highest phosphate release was measured. The efficiency was highest in the experiment where the lowest S:Fe was dosed (Leeuwarden #1) and was lowest in the sludge of Amersfoort (S:Fe = 2) and Nieuwveer (S:Fe = 1.5). Overall the efficiency for the real sludges was much lower (between 0.1 and 0.4 mol phosphate released per sulfide reacted) compared to synthetic iron phosphates where the efficiency was between 0.7 (vivianite) and 0.8 (Fe(III)P). This can be due to various reasons. First, the measurement of dissolved sulfide concentrations is not free of doubts since free sulfide is actually not free but bound to iron as colloidal material. This is usually visible by a black coloration of the filtrate and would result in an overestimation of the efficiency. This black coloration was only noted in the experiment with Sigma Fe(III)P and accordingly corrected for. An underestimation of the phosphate release efficiency can be derived from the fact that some of the sulfide that was removed from solution was actually not used up during the reaction with iron. This could happen when e.g. H_2S gases out of solution or if sulfide precipitates in other forms, e.g. as polysulfides (Wan et al., 2014). Care was taken to fix sulfide with ZnAc and additionally outgassing of sulfide at circumneutral pH should not be very significant. However, it cannot be excluded that some of the sulfide emitted as H_2S from solution. Polysulfides were not quantified during the experiments.

During the experiment with sludge a strong decrease in the viscosity was observed visually. To check if sulfide could also influence the dewaterability of the sludge CST measurements were carried out. The filterability of digested sludge ($0.13 \pm 0.015 \text{ g}^2(\text{s}^2\text{m}^4)^{-1}$) was clearly higher compared to the same sludge after sulfide addition ($0.06 \pm 0.004 \text{ g}^2(\text{s}^2\text{m}^4)^{-1}$) indicating the formation of small particles in sulfide amended sludge. This strongly suggests that sulfide addition to sewage sludge will result in a much lower dewaterability and probably in higher sludge disposal costs. Disposal of sewage sludge is a big cost factor in municipal STPs (Mikkelsen, 2002). Similar to our findings, earlier research showed that the addition of sulfide and the reduction of Fe(III) to Fe(II) in Fe(III) containing activated sludge results in disintegration of the flocs and a decrease of the sludge

dewaterability (Caccavo et al., 1996; Nielsen and Keiding, 1998). However, for struvite precipitation sometimes (e.g. in the Airprex process) magnesium is added to the sewage sludge which could mitigate and perhaps even neutralize the diminishing effect of sulfide on the filterability. Bivalent cations such as magnesium improve dewaterability of sludges by neutralizing electrical charges of sludge flocs (Sobeck and Higgins, 2002).

In digested sludge it can be assumed that most of the iron is present as Fe(II) due to chemical or biological iron reduction during the anaerobic digestion (Ivanov et al., 2003) and therefore the reason for the decreasing dewaterability in our experiments could be the formation of FeS_x . Earlier studies showed that indeed almost all iron in digested sludge from Leeuwarden and Nieuwveer was present as Fe(II) and more precise as vivianite and to a lower extent as FeS_x (Wilfert et al., 2016). If this information is correct then most iron is not available as a coagulant. Part of the iron in the sludge could however act as a stabilizer in EPS or be bound in Proteins (Li et al., 2012; Oikonomidis et al., 2010). When this iron reacts with sulfide it can modify these structures which would then results in the deterioration of the sludge dewaterability (Liu and Fang, 2003). The mechanism of the decrease in viscosity and filterability remains unclear.

It is possible to release significant amounts of phosphate from activated sludge and digested sewage sludge through the addition of sulfide. In activated sludge most iron probably is present as Fe(III) (Nielsen et al., 1997; Rasmussen and Nielsen, 1996; Thistleton et al., 2001), although in surplus sludge also significant amounts of Fe(II) were found (Frossard et al., 1997; Wilfert et al., 2018). In digested sludge most iron is present as Fe(II) (Frossard et al., 1997; Wilfert et al., 2018). From both, ferrous and ferric iron bound phosphate, phosphate can be released by adding sulfide. Ours and earlier studies (Azam and Finneran, 2014; Ghassemi and Recht, 1971; Luedecke et al., 1989) show that Fe(II) , i.e. vivianite, can bind as much or even more phosphate compared to Fe(III) compounds such as iron oxides or hydroxides. Sulfide induced phosphate release is thus more efficient from Fe(II) in case FeS_x are formed because additional sulfide/electron investment for Fe(III) reduction is not necessary. In case sulfide acts as a reducing agent to release phosphate from ferric phosphates, phosphate release can be even more efficient. The risk about the latter route is, however, that the released phosphate precipitates with the produced Fe(II) which results in a lower net phosphate release. Capturing phosphate before its re-precipitation is an interesting perspective for efficient phosphate release and recovery from ferric phosphate containing waste matrices.

In the framework of sewage treatment, sulfide forms mainly in sewer systems (Hvitved-Jacobsen et al., 2013; Nielsen et al., 1992) and during the anaerobic digestion process (Chen et al., 2008). During anaerobic digestion the sulfide production is limited by the supply of sulfate in the sludge and by sulfur that is bound in organic compounds. If substantial amounts of sulfide were formed during anaerobic digestion, iron bound phosphate would dissolve and remain in solution because sulfide and phosphate would compete for the iron (Nriagu, 1972). After the digestion process, the sludge is dewatered and the sludge filtrate is recirculated to the treatment line. Thus, successful phosphate removal in STPs requires that most phosphate remains in the sludge solids. High phosphate levels in the filtrate would prevent efficient phosphate removal in the STP. The limited amount of sulfide formed during digestion is an explanation why iron addition can be used for efficient phosphate removal even in plants with anaerobic digesters (Thomas, 1965). If however excess sulfide is added to the sludge, phosphate recovery should be very efficient since most of the phosphate is bound to iron in STPs with iron based phosphate removal (Wilfert et al., 2018). Sulfide is readily available and cheap since it is produced

Table 3
Results of sulfide addition to synthetic iron phosphates and sludges, earlier studies.

Medium	pH	Total molar Fe:P	Molar Fe:S	P Release (% of total solid)	Study
Sludge (Drinking water plant)	4	8.4	0.59	75	Likosova et al. (2013)
Pre-coagulated sludge	5.3–7.0	4.1	0.50	43	Kato et al. (2006)
Sigma Fe(III)P	4	1	0.67	70 (± 6)	Likosova et al. (2013)
Sigma Fe(III)P	4	1	0.40	90 (± 6)	Likosova et al. (2013)
Synthetic Fe(III)P	5.3–7.0	1	0.50	93	Kato et al. (2006)

in installations for biogas cleaning and sulfur is a waste product of the oil industry (Graaff et al., 2012; STOWA, 2011). A recovery technology for phosphate using sulfide would have a low ecological footprint (e.g. sulfide is a waste product from industry), high recovery efficiency (high percentage of phosphate is bound to iron in sewage sludge) and could be realized with low technological complexity. It could also be used to enhance the recovery potential of existing struvite recovery plants that are limited in their recovery because part of the phosphate is bound to iron and therefore not available for recovery. This is especially important for instance in Germany where new legislation requires 50% recovery which is currently not possible via conventional struvite precipitation technology.

The total phosphate release from the digested sludges was not as high as expected, because earlier quantification of iron bound phosphate in the digested sludges suggested that more phosphate could be released from iron using sulfide (Wilfert et al., 2018). Also, a much higher release of phosphate from drinking water sludge was measured by Likosova et al. (2013) (Table 3). This could be due to the fact that drinking water sludge probably consists mainly of iron (molar Fe:P ratio of this sludge was 8.4); implying that the risk of phosphate binding to other cations in this type of sludge is lower compared to the complex matrix that sewage sludge is composed of. Kato et al. (2006) also achieved higher phosphate dissolution compared to our study with activated sludge that contained more iron and by using a higher sulfide input (relative to the iron in the sludge). Thus, it cannot be excluded that higher sulfide/iron dosing would indeed have resulted in higher phosphate mobilization from our sludges. In their (Kato et al., 2006) activated sludge, probably more phosphate was bound in organic matter, compared to digested sludge, which is not solubilized by sulfide, which would thus negatively affect the release efficiency. The sulfide investment is also dependent on the presence of iron phases that are not iron phosphates such as ferric iron oxides/hydroxides. Probably, sulfide reacts first with these iron compounds because it was shown that the reductive dissolution of iron oxides is inhibited in the presence of adsorbed phosphate (Biber et al., 1994). For both activated and digested sludges a deterioration of the dewaterability due to sulfide addition can be expected which would result in high costs for sludge disposal (Nielsen and Keiding, 1998).

Sulfide extracts specifically iron bound phosphate (Kato et al., 2006). For the sludge sampled in Amersfoort, where an Ostara process is implemented for phosphate recovery via struvite, our sulfide extraction showed that this recovery route is indeed limited by the phosphate that is bound to iron. The dissolved phosphate in the sludge increased due to sulfide addition from 3.4 to 7.4 mmol/L. During struvite recovery only dissolved phosphate in the digested sludge can be recovered. Thus, sulfide could increase the recovery potential by a factor of two in this plant.

It seems concerns (Likosova et al., 2013) about the formation of dissolved colloidal FeS_x is not an issue for sewage sludges and also not for the synthetic iron phosphate precipitates, except for the Fe(III)P from Sigma. In centrifuged samples (without filtration) only little iron sulfide was present in the supernatant (visible by a slightly black color of the supernatant). Likosova et al. (2013) made

their experiments at pH = 4 to minimize the formation of colloidal FeS_x . Going to this pH might not be necessary in case real sewage sludge is used. Their observed total phosphate release from synthetic iron phosphates and the one from Kato et al. (2006), at a high sulfide overdose, were very similar despite differences in pH during the experiments (Table 3).

4. Conclusion

Overall, sulfide efficiently released phosphate from synthetic iron phosphates and sewage sludge. Mechanisms and efficiencies for phosphate release depend also on the type of iron phosphates. Sulfide has the potential to be a useful tool for phosphate recovery. For instance, to increase phosphate release in plants where struvite recovery is limited by the phosphate that is bound to iron or in plants with chemical phosphate removal using large quantities of iron salts that lead to a large pool of iron bound phosphate in the sludge. But the decrease in sludge dewaterability and the limited net phosphate dissolution from the iron phosphate rich sewage sludge are constraints. Understanding the mechanisms for both of these phenomena will certainly help to use sulfide in a more effective way for recovering phosphate from iron phosphate containing sludge in efficient manner. A microscopic observation of the sludge flocs could e.g. help to evaluate the mechanism of the decrease in filterability of the digested sewage sludge in response to sulfide addition. The limitation in phosphate release in response to sulfide addition (be it sulfide acting as a reducing agent or as a building block to form FeS_x) is, in our opinion, due to rebinding of phosphate in the solid matrix. It should be evaluated if there is a chance to capture phosphate before its re-precipitation or re-sorption. Future in depth studies, should investigate the speciation of iron and sulfide more detailed and establish mechanistic models to back up the hypothesis raised in the context of this research.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at

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