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Phosphate Recovery From Sewage Sludge Containing Iron Phosphate

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Phosphate Recovery From Sewage Sludge Containing Iron Phosphate

Proefschrift

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aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. dr. ir. T.H.J.J. van der Hagen
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geboren te Stuttgart, Duitsland

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Wetenschap is heel simpel, maar het moeilijkste wat er is is simpel wetenschap bedrijven.

Vrij naar Johan Cruyff

For my family

CHAPTER 1: INTRODUCTION

1.1 PHOSPHORUS AND PHOSPHATE 1
1.2 HARMS AND BENEFITS RELATED TO PHOSPHATE 2
1.3 PHOSPHATE RECOVERY 3
1.4 THESIS OUTLINE 5
1.5 REFERENCES 6

CHAPTER 2: THE RELEVANCE OF PHOSPHORUS AND IRON CHEMISTRY TO THE RECOVERY OF PHOSPHORUS FROM WASTEWATER

2.1 INTRODUCTION 9
2.2 IRON AS A KEY ELEMENT IN WASTEWATER TREATMENT PLANTS OF THE FUTURE 11
2.3 IRON AND PHOSPHORUS INTERACTIONS 13
2.4 TRANSFORMING IRON–PHOSPHORUS COMPOUNDS 19
2.5 APPROACHES TO RECOVER PHOSPHORUS FROM IRON 25
2.6 REFERENCES 27

CHAPTER 3: EFFECT OF IRON ON PHOSPHATE RECOVERY FROM SEWAGE SLUDGE

3.1 THE ROLE OF IRON IN SEWAGE TREATMENT PLANTS 47
3.2 CHEMICAL PHOSPHATE REMOVAL USING IRON SALTS 50
3.3 IMPACT OF IRON ON SELECTED PHOSPHATE RECOVERY TECHNOLOGIES 53
3.4 SUMMARY AND OUTLOOK 60
3.5 REFERENCES 61

CHAPTER 4: VIVIANITE AS AN IMPORTANT IRON PHOSPHATE PRECIPITATE IN SEWAGE TREATMENT PLANTS

4.1 INTRODUCTION 71
4.2 MATERIAL AND METHODS 72
4.3 RESULTS 76
4.4 DISCUSSION 85
4.5 CONCLUSION 90
4.6 REFERENCES 90

CHAPTER 5: VIVIANITE AS A KEY MINERAL IN SEWAGE TREATMENT PLANTS AND ITS POTENTIAL ROLE FOR PHOSPHATE RECOVERY

5.1 INTRODUCTION 107
5.2 MATERIAL AND METHODS 108
5.3 RESULTS 110
5.4 DISCUSSION 115

5.5 Conclusion 120
5.6 References 120

CHAPTER 6: FE(III) REDUCTION AND VIVIANITE FORMATION IN ACTIVATED SLUDGE

6.1 Introduction 141
6.2 Material and Methods 142
6.3 Results 145
6.4 Discussion 151
6.5 Conclusion 158
6.6 References 159

CHAPTER 7: SULPHIDE INDUCED PHOSPHATE RELEASE FROM IRON PHOSPHATE

7.1 Introduction 173
7.2 Material and Methods 175
7.3 Results and Discussion 177
7.4 Conclusion 185
7.5 References 186

CHAPTER 8: PHOSPHATE RECOVERY VIA MAGNETIC SEPARATION OF VIVIANITE FROM DIGESTED SEWAGE SLUDGE

8.1 Introduction 195
8.2 Material and Methods 195
8.3 Results 197
8.4 Discussion 201
8.5 References 204

CHAPTER 9: BIOGENIC IRON OXIDES FOR PHOSPHATE REMOVAL

9.1 Introduction 209
9.2 Material and Methods 209
9.3 Results and Discussion 211
9.4 References 214

CHAPTER 10: THESIS CONCLUSION & OUTLOOK

10.1 Conclusion 223
10.2 Outlook 227

CHAPTER 11: KIDS' SUMMARIES OF THESIS CHAPTERS

11.1 INTRODUCTION 233
11.2 MATERIAL AND METHODS 233
11.3 RESULTS 235
11.4 DISCUSSION 241

SUMMARY *242*

SAMENVATTING *248*

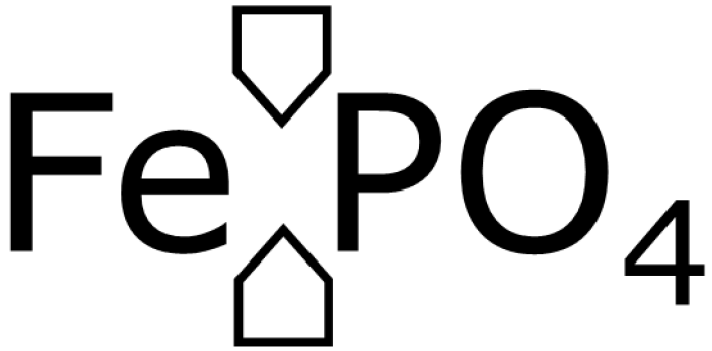
ACKNOWLEDGEMENTS *254*

CURRICULUM VITAE *257*

LIST OF PUBLICATIONS *258*

ATTRIBUTION OF IMAGES *259*

Chapter 1: Introduction



1.1 Phosphorus and phosphate

It probably all started with a big bang about 14 billion years ago (Silk, 1980). Neutrons, protons and electrons started to form helium and deuterium which were the building blocks for other light elements (Alpher et al., 1948). During stellar nucleosynthesis phosphorus was formed from these elements (Cescutti et al., 2012). Phosphorus made it to the 17th most abundant element in universe (Kwok, 2012). In the earth crust it is the 11th most abundant element and about 200 phosphorus minerals are known (Greenwood and Earnshaw, 1990).

Sometime after the stellar synthesis elemental phosphorus was discovered by humans namely by the German alchemist Henning Brand in 1669. Lasting for several days he used hundreds of litres of urine to produce white phosphorus by applying various cooling and heating steps (Overway, 2017). When this material was exposed to oxygen it started to glow, explaining why phosphorus is called phosphorus (Greek for light-bearer). Phosphorus was, probably unique for all elements, first extracted from excreta. This shows that human excreta (i.e. urine) contains substantial quantities of phosphorus, the phosphorus that is in the urine is water soluble and that elemental phosphorus is very reactive.

Elemental phosphorus occurs in different forms but mainly as white and red phosphorus. These forms, especially the white one, are very reactive. For this reason white phosphorus is –still- used to produce horrible weapons. Red phosphorus is, despite its reactivity, often used to produce, together with other materials such as polyamides, effective flame retardant.

Phosphorus occurs in gaseous forms too, e.g. as phosphine. It was hypothesized that phosphine can occur in significant quantities in some environments with excess phosphate supply, such as in sewage treatment plants (Devai et al., 1999; Dévai et al., 1988). However, in these studies very large phosphorus imbalances between 30-40% are stated. It is possible that rather measurement errors than phosphine production are the reason for this gap. The role metals and microorganisms play in the formation of this gaseous and reduced phosphorus species and its significance in sewage treatments plants is not fully understood yet (Roels and Verstraete, 2001). More reliable indications for phosphine formation were shown for sediments (e.g. Geng et al., 2005). The Earth has an oxygen atmosphere and hence phosphorus occurs, most likely, mainly as various types of phosphates because of the instability of elemental phosphorus and other more reduced phosphorus compounds (such as phosphite, phosphine etc.). Phosphates are the fully oxidized form (oxidation number +5) of phosphorus. Phosphorus can also exist in several reduced forms (down to an oxidation number of -3) and the role of such reduced phosphorus compounds is often underestimated (Pasek et al., 2014).

Phosphate is essential for all living organisms on earth. It is a building block for molecules that are involved in reproduction (DNA) and energy transfer (ATP) or in molecules that are part of cell membranes (phospholipids). Phosphate is so crucial because it acts as a sophisticated glue in such molecules (Westheimer, 1987). For instance, phosphoric acid in DNA can link nucleotides, at the same time keeping a negative charge that protects the molecule from hydrolysis and keeping the molecule within lipid membranes. Furthermore, phosphate is, in the

form of various calcium phosphate minerals, part of skeletal structures or of teeth in many organisms (Bentov et al., 2016; Glimcher, 2006). This shows another characteristic of phosphate: it has a high affinity for metals.

Phosphate can be part of organic molecules, polyphosphates or it can be bound to metals. In these forms phosphate can be soluble (usually defined as passing a 0.2 or 0.45 µm filter) or insoluble; i.e. particulate (Golterman, 2004; Weir and Soper, 1963). Free dissolved inorganic phosphate is called ortho-phosphate (o-P). The speciation of the o-P in solution depends on the pH of the solution (Figure 1-1).

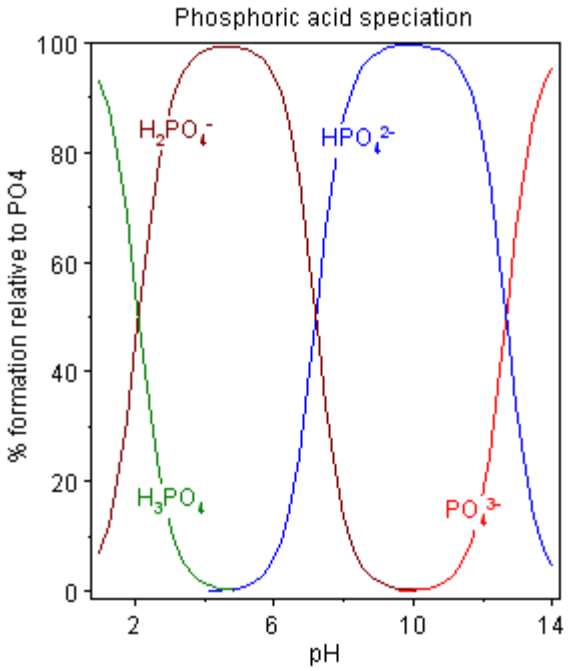


Figure 1-1: Ortho- phosphate speciation at different pH (wikimedia.org).

1.2 Harms and benefits related to phosphate

Fertilization is an essential part of modern agriculture due to the significance of phosphate for biology. Accordingly, of all mined phosphate that we use today about 80% is used in agriculture (van Vuuren et al., 2010). Higher grade phosphate (e.g. phosphoric acid) is used in food industry and for other purposes (e.g. as detergent, for the production of lithium iron phosphate batteries etc.). World population growth, an increasing demand of biofuels and changes in dietary behaviours of humans have resulted in a higher demand for phosphate, especially for phosphate fertilizer (Childers et al., 2011). Phosphate is a non-replaceable resource. Depleted oil or gas supplies can be substituted by alternative energies but depleted phosphate reserves cannot. From this perspective phosphate is very crucial and beneficial to humans.

Phosphate was and is still not used in a sustainable way (Ulrich and Frossard, 2014). For instance, an imbalance exists between places where phosphate accumulates, due to cattle farming, and places where phosphate is required for growing crop (Macdonald et al., 2011). Also because of these phosphate surpluses in some parts of the world, phosphate reaches surface

waters where it causes ecological and subsequently economical damage (Carpenter, 2008). Just in the USA, costs related to freshwater eutrophication were estimated to be about 2.2 billion US Dollars (Dodds et al., 2008). Furthermore, most of the currently used phosphate is mined from finite phosphate rock reservoirs that were formed on geological time scales. These reservoirs are mainly located in a few countries (Reijnders, 2014). Hence, there is a geopolitical dependency on these countries (De Ridder et al., 2012). During phosphate rock mining large amounts of waste are produced (Tayibi et al., 2009) and large areas of land are destroyed during the surface mining. Phosphate rock contains pollutants, such as cadmium that can eventually end up and accumulate in the agricultural soils of the phosphate importing countries (Schröder et al., 2010). Additionally, it is currently debated how long these reservoirs will last (Scholz and Wellmer, 2016). Regardless of the discussions related to the finite supply of phosphate rock also the other named aspects (regarding environmental and economic issues and geopolitics) speak in favour for a more sustainable use of phosphate. A more responsible use of phosphate comprises a more efficient use of phosphate in agriculture (Lun et al., 2017; Schröder et al., 2011) and phosphate recovery from secondary resources such as manure or sewage sludge (Carpenter and Bennett, 2011).

1.3 Phosphate recovery

Despite the outlined issues related to phosphate, we still use phosphate as a disposable good without significant recycling routes. It ends up in surface waters, landfills or in the lithosphere and accumulates in agricultural soil (van Dijk et al., 2016). Phosphate in wastestreams and soils is not present in readily usable forms but bound to other metals or is present in complex waste matrices such as manure or sewage sludge. Sludge from wastewater treatment can often not directly be spread on land as phosphate fertilizer. There are concerns related to the phosphate availability (Kidd et al., 2007; Prochnow et al., 2008; Römer, 2006), contaminants (Clarke and Smith, 2011), there is a trend towards equilibrium fertilisation (Neeteson et al., 2006) and because the proportion of nutrients in these wastes does not meet crop requirements (Lu et al., 2012). Additionally, as mentioned above, phosphate currently accumulates in highly populated countries with intense cattle farming. On the other hand, countries, from where phosphate is exported via the crop, suffer from a phosphate deficit in their soils (Macdonald et al., 2011). These problems show that applying sewage sludge on agricultural land is, for most industrial countries, not an option. Phosphate recovery technologies should produce a pure product that enables transportation and that can be exported from regions with phosphate surpluses to regions with phosphate deficits. Policy makers, companies and research institutes are currently looking for efficient and cheap technologies to recover phosphate from secondary phosphate streams (Der Schweizerische Bundesrat, 2015; Deutscher Bundestag, 2017; Egle et al., 2014). Recovering phosphate from these secondary resources would reduce the needs for phosphate imports. The task of phosphate recovery seems simple, phosphate has to be separated/selectively released from complex wastestreams. Then fertilizer can be produced from this concentrated phosphate stream. However, to achieve this often a lot of energy or plenty of chemicals have to be used. Sometimes only low recovery efficiencies are achieved.

Next to manure, sewage sludge is the most important secondary phosphate source in Europe (van Dijk et al., 2016). Phosphate recovery is an important part of the future vision to transform sewage treatment plants into nutrient and energy factories. For Europe, van Dijk et al., 2016 estimated that about 15% of all imported phosphate (including phosphate that is imported via crop) ends up in sewage sludge. This thesis focusses on phosphate recovery from sewage sludge as an important secondary source for phosphate.

Why did this study focus on iron phosphate rich sewage sludge? Currently, iron plays a crucial role for sewage treatment (e.g. for phosphate removal, as a coagulant, for preventing hydrogen sulphide emissions) and it can play an even more important role in future. The only disadvantage related to the application of iron is the lack of an efficient and economic technology to recover phosphate from iron phosphate which is contained in sewage sludge.

Iron and phosphate are really an odd couple. In agricultural, environmental and sewage systems their interactions are still not fully understand. In agriculture there is a debate whether phosphate bound to iron is crop available or not (Krogstad et al., 2005; Nanzer et al., 2014; Prochnow et al., 2008; Römer, 2006). In sewage treatment systems the presence of iron has often been considered as a disadvantage for phosphate recovery (ACHS, 2009; Egle et al., 2014). On the other hand in aquatic ecosystems, efforts to immobilize phosphate in the sediment by using iron often end in vain (Wang and Jiang, 2016). These controversies show how complex the interactions between iron and phosphate are. Yet, it also shows that many options exist to manipulate these interactions which could be useful to develop phosphate recovery technologies.

1.4 Thesis outline

In the ***second chapter*** of this thesis the role of iron phosphate compounds for sewage treatment is discussed. It is explained that actually iron and phosphate interactions are not odd, rather odd is the limited knowledge about the iron and phosphate biogeochemistry. More knowledge would possibly explain some of the controversial observations and ongoing discussions in research related to iron and phosphate. This chapter suggests to study interactions between iron and phosphate during sewage treatment to be able to develop elegant phosphate recovery technologies from sewage sludge. This knowledge can also create a lot of spin-of knowledge for other research disciplines.

In the ***third chapter*** it is described how iron can affect current phosphate recovery technologies from sewage sludge. It comprises low tech options such as land application of sewage sludge but also recovery methods from sewage sludge ash and technologies that produce struvite from digested sludge liquor. Phosphate recovery via vivianite ($Fe(II)_3[PO_4]_2 \bullet 8H_2O$) is discussed for the first time.

In the ***fourth chapter*** Mössbauer spectroscopy and XRD were used to show that vivianite is an important phosphate precipitate in two Dutch sewage treatment plants before and after anaerobic digestion of sludge.

In ***chapter five*** a similar methodology as in chapter four was chosen to analyse surplus and digested sewage sludge from various sewage treatment plants in Germany, Netherlands and Finland. The relevance of vivianite in these sludges was studied.

In ***chapter six*** kinetics of vivianite formation in activated sludge that was stored under anaerobic conditions was studied along with the microbial population. The sludge for the experiments was sampled in one sewage treatment plant with high and in one plant with low iron dosing.

In ***chapter seven*** sulphide induced phosphate release from different synthetic iron phosphate compounds and from digested sewage sludge was studied.

In ***chapter eight*** first experiences on vivianites' magnetic separation from digested sewage sludge are reported. Additionally, a concept for vivianite based recovery routes is suggested.

And now for something completely different, in ***chapter nine*** the retention of phosphate by microbially produced iron oxides is studied. This study explores why it was reported earlier that these structures have a much higher phosphate binding capacity and affinity compared to their chemical equivalents.

Chapter ten summarizes the main outcomes of this thesis and gives an outlook on which pathways phosphate recovery from sewage sludge containing iron phosphate could take.

Chapter eleven contains summaries written by kids on most of the research topics in this thesis.

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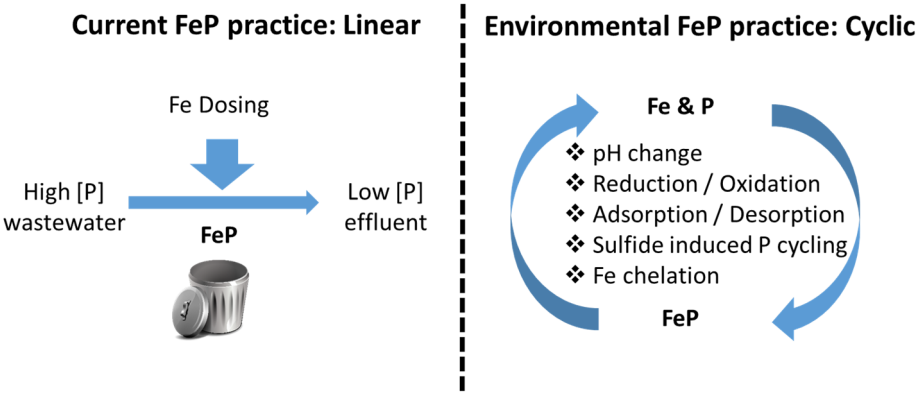
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Chapter 2: The relevance of phosphorus and iron chemistry to the recovery of phosphorus from wastewater



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2.1 Introduction

2.1.1 Background

Phosphorus is an essential nutrient and is very important for global food production. In 2000, 19.7 Mt of phosphorus was mined as phosphate rock. The major part, 15.3 Mt phosphorus, was used to produce fertilizers (van Vuuren et al., 2010). The demand for phosphorus will further increase in future due to a growing global population, dietary changes and a rising share of biofuels (Cordell et al., 2009). Apart from partial recycling of phosphorus by applying manure to agricultural land, the usage of phosphorus around the world is linear, with very few recycling routes and huge inefficiencies in its production and use (Cordell et al., 2009; Reijnders, 2014; van Vuuren et al., 2010). Ecological, geopolitical and economic concerns demand phosphorus recovery (Cooper et al., 2011; Cordell et al., 2009; De Ridder et al., 2012; Reijnders, 2014; van Vuuren et al., 2010). Hence, a cyclic use of phosphorus and thus development of technologies that allow the recovery of phosphorus from secondary sources is required. Globally, about 1.3 Mt phosphorus/year is treated in sewage treatment plants (STPs) (van Vuuren et al., 2010). We focus in this review on municipal wastewater as a major secondary source of phosphorus. The implications of the interactions described for phosphorus and iron are also relevant to other wastewaters and even surface water.

Phosphorus is removed from wastewater to prevent eutrophication in effluent receiving surface waters (Conley et al., 2009; Jarvie et al., 2006). The most popular phosphorus removal techniques are enhanced biological phosphorus removal (EBPR) and the more widely used chemical phosphorus removal (CPR) using iron or aluminium salts (Table S 2-1 in supporting information) (Carliell-Marquet and Cooper, 2014; De-Bashan and Bashan, 2004; DWA, 2005; Korving, 2012; Morse et al., 1998; Paul et al., 2001). Iron salts are usually preferred. They are cheaper than aluminium salts (Geraarts et al., 2007; Paul et al., 2001). Also in EBPR plants, iron is often dosed to support phosphorus removal (Table S 2-1 in supporting information). Apart from phosphorus removal, iron plays an important role in modern wastewater treatment in general. It is used to prevent hydrogen sulphide emissions during anaerobic digestion and acts as a coagulant to improve sludge dewatering (Charles et al., 2006; Ge et al., 2013; Higgins and Murthy, 2006). Wastewater pumping stations dose iron to control odours and corrosion (Nielsen et al., 2005) and this practice may even aid the removal of phosphorus in STPs (Gutierrez et al., 2010). Furthermore, significant amounts of iron (typically: 0.5–1.5 mg Fe/L, Hvitved-Jacobsen et al., 2013) can already be present in the influent of STPs. For instance, data from 19 STPs in the Waterschap Vechtstromen in The Netherlands showed influent iron concentrations between 1 and 10 mg/L resulting in an average Fe/P molar ratio of about 0.26 (unpublished data). These examples illustrate that iron is omnipresent in modern STPs (Table S2-2 in supporting information) and thus, that significant amounts of phosphorus can be iron bound, also in STPs that do not rely on iron based CPR.

The presence of iron is often perceived as negative when evaluating phosphorus recovery options (ACHS, 2009; Egle et al., 2014; Morse et al., 1998; Römer, 2006; Samie and Römer, 2001; Schipper et al., 2001; Schipper and Korving, 2009). However, we will show that

phosphorus is efficiently mobilized from various iron–phosphorus compounds (FePs) in environmental systems. This apparent mismatch can be explained by the current lack of understanding of the iron and phosphorus chemistry. We will evaluate the literature that we believe is important to help understanding iron and phosphorus interactions in STPs. We will also present possible directions that research and technology related to phosphorus recycling from wastewater could take, as inspired by the science of environmental mobilization mechanisms.

2.1.2 Critical evaluation of current phosphorus recovery options

Currently, phosphorus recovery methods from wastewater, applied on practical scales, include agricultural use of sludge, production of struvite in EBPR plants and recovery of phosphorus from sludge ash. After hygienisation, sludge (often termed biosolids) can be applied to agricultural land. This practice is a widespread, low cost option for phosphorus recycling. About 50% of all sludge in the USA (Moss et al., 2013) and about 40% of all sludge in the 27 EU countries (Kelessidis and Stasinakis, 2012) was applied in agriculture in 2004 and 2005 respectively. Public concerns about pathogens, heavy metals, and organic micro-pollutants in biosolids are widespread (Aubain et al., 2002; Beecher and Harrison, 2005; Langenkamp et al., 2001; Robinson et al., 2012). But several studies showed that associated risks are low (Lu et al., 2012; Smith, 2009). Increasing regulations may further reduce concentrations of certain compounds (Oliver et al., 2005; Olofsson et al., 2012), at the same time emerging contaminants create new concerns (Clarke and Smith, 2011). The presence of iron in biosolids lowers the water soluble phosphorus fraction (Brandt et al., 2004; Krogstad et al., 2005; Miller and O'Connor, 2009; O'Connor et al., 2004). This can be considered positive, because it may prevent phosphorus loss by surface runoff (Elliott and O'Connor, 2007; Lu et al., 2012). Some authors perceive the presence of iron in biosolids as negative as it resulted in a reduced plant availability of phosphorus (Kidd et al., 2007; Krogstad et al., 2005; Römer, 2006; Samie and Römer, 2001). However, other studies show iron bound phosphorus can still be plant available (Kahiluoto et al., 2015; Nanzer et al., 2014; Prochnow et al., 2008). The biggest problem of biosolid application is perhaps the fact that there are areas with surpluses of phosphorus on agricultural land due to manure surpluses (Macdonald et al., 2011; Schröder et al., 2011). Transporting sludge from such areas to areas with phosphorus deficits is problematic because of the transport costs and logistics involved. Thus, a pure and high value phosphorus recovery product is preferred over a complex product like sludge.

Several options exist for phosphorus recovery to produce high value products (Cornel and Schaum, 2009; Desmidt et al., 2015; Hermann, 2009; Morse et al., 1998; Petzet and Cornel, 2011). Currently, struvite precipitation is attracting the most interest despite of a limited phosphorus recovery potential. This technique requires a combination of EBPR and sludge digestion, ideally in combination with a phosphorus stripping process (Cullen et al., 2013). But in many countries iron based CPR plants dominate (Table S 2-1 in supporting information). Furthermore, the efficiency to recover phosphorus as struvite is typically only 10–50% of the total influent phosphorus load (Cornel and Schaum, 2009; Hermann, 2009; Lodder et al., 2011).

This is due to the presence of phosphorus fractions that are not extracted during anaerobic digestion (phosphorus fixed in biomass or bound to metals like iron).

In a few countries, a significant proportion of the sludge is incinerated in mono-incinerators (Kelessidis and Stasinakis, 2012). Recovery of phosphorus from sludge ash has advantages: (1) economies of scale due to centralized incinerators, (2) nearly all phosphorus removed can be recovered, (3) destruction of unwanted compounds and (4) phosphorus is present in a concentrated form. Various promising thermo- and wet-chemical technologies have been developed to recover phosphorus from sludge ash (Adam et al., 2009; Cornel and Schaum, 2009; Desmidt et al., 2015; Donatello and Cheeseman, 2013; Hermann, 2009, 2014; Langeveld and Wolde, 2013a; Schipper et al., 2001). For these technologies iron plays a role too. It is influencing the extractability of phosphorus (Langeveld and Wolde, 2013a) or the water solubility of phosphorus in the final product (Adam et al., 2009). These techniques depend on expensive infrastructure for incineration. Phosphorus recovery alone will not be a sufficient reason to build sludge incinerators.

2.2 Iron as a key element in wastewater treatment plants of the future

2.2.1 A future treatment plant

The presence of iron is important in wastewater treatment already today. In future, iron could play an even more important role in STPs (Figure 2-1). Adding iron is a key step in upcoming STPs as energy and phosphorus factories. Energy-producing STPs already exist (Nowak et al., 2011). Such plants often apply the A-B process, using a very high loaded biological treatment (adsorption or A-stage) followed by a bio-oxidation process or B-stage to remove nitrogen (Böhnke et al., 1997). During the A-stage, soluble chemical oxygen demand (COD) in the wastewater is used for microbial growth and (bio)flocculation removes the biomass, and colloidal and particulate COD from the wastewater. Iron addition is the cheapest option for the required coagulation and flocculation of the COD and for phosphorus elimination in the A-stage (Böhnke et al., 1997, 1997; Li, 2005). Anaerobic digestion of A-stage sludge produces a large amount of biogas (Böhnke et al., 1997). Meanwhile, the A-B process has been further improved by using anaerobic ammonium oxidation (anammox) to remove nitrogen in the side streams of several STPs at elevated temperatures (25–40 °C) (Abma et al., 2007; Jetten et al., 1997; Lackner et al., 2014; Nowak et al., 2015). The anammox process does not need COD for nitrogen removal, while reducing the energy demand simultaneously. The use of anammox at lower temperatures of 10-20 °C (cold anammox) in the main treatment lines of STPs is being researched (Lotti et al., 2014). Using anammox in the main line could potentially allow a STP to produce energy at a net rate of 86 J/(person d). A typical STP, using a classical activated sludge process, consumes 158 J/(person d) (Kartal et al., 2010).

In the future STP (Figure 2-1), phosphorus and COD removal can be achieved by adding iron in the A-stage. Nitrogen is removed using cold anammox. The settled sludge would be digested to produce biogas and subsequently, phosphorus could be recovered from the digested sludge. Phosphorus recovery could be done by selectively bringing iron-bound phosphorus into

solution using a chemical or biotechnological phosphorus recovery process that is yet to be developed. The sludge would then be dewatered and the phosphorus precipitated and recovered as struvite or apatite.

Alternatively, phosphorus could be removed using an adsorption stage after the cold anammox. Owing to environmental concerns like eutrophication, more stringent regulations on phosphorus discharge limits (Oleszkiewicz and James, 2006; UK technical advisory group, 2008) may anyway require phosphorus polishing of the effluent. To achieve low phosphorus concentrations in the effluent, iron based adsorbents have already been used (Pratt et al., 2012; Ragsdale, 2007) due to the high affinity of iron oxides for ortho-phosphate (o-P) (Blaney et al., 2007; Genz et al., 2004; Martin et al., 2009). Adsorption also offers the possibility of phosphorus recovery and the re-use of the adsorbents (Loganathan et al., 2014).

Most of the wastewater treatment techniques described above are already being used or tested at the pilot scale. Currently, the only missing process (as in current treatment processes) is economically feasible phosphorus recovery from sludge containing FePs. We envisage to develop a phosphorus recovery process which is inspired by environmental mechanisms.

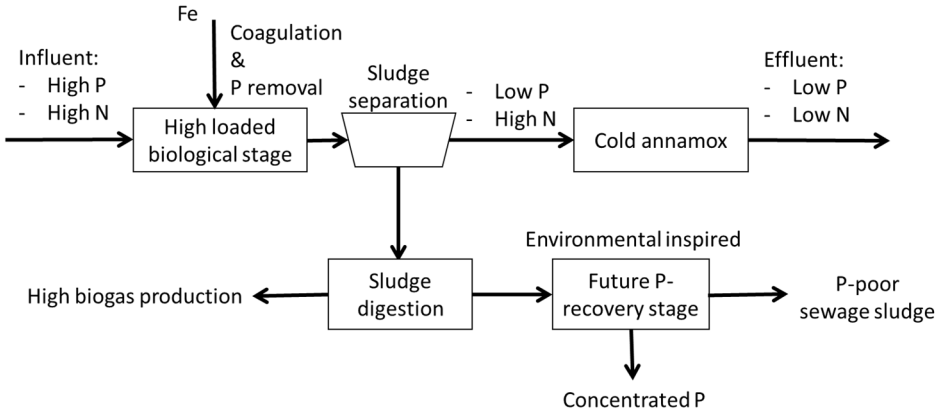


Figure 2-1: Proposed processes for an energy-producing wastewater treatment plant in which phosphorus is recovered.

2.2.2 Environmental cycling: inspiration for recovering phosphorus?

A combination of iron and phosphorus is often considered to have a negative impact when evaluating the potential for using sludge in agriculture (Römer, 2006; Samie and Römer, 2001) or phosphorus recovery (ACHS, 2009; Egle et al., 2014; Morse et al., 1998; Schipper et al., 2001; Schröder et al., 2010). Current processes for recovering phosphorus from FePs-containing sludge and ash require large changes in pH, pressure, or temperature, e.g., the Krepro, Seaborne, Mephrec, Ashdec, and Ecophos processes (Adam et al., 2009; Hermann, 2009, 2014; Langeveld and Wolde, 2013a; Levlin et al., 2002; Schipper and Korving, 2009). Usually, it is not economically feasible to use these processes. In contrast, phosphorus is mobilized very efficiently from FePs in aquatic and terrestrial ecosystems (Bolan et al., 1987; Chacon et al., 2006; Hinsinger, 2001; Roden and Edmonds, 1997). A biomimetic process could therefore be a more attractive alternative.

Fungi, bacteria, and plants are able to mobilize iron bound phosphorus and allow phosphorus cycling. The mobilization of phosphorus can be so efficient that it results in environmental damage by causing eutrophication in freshwater systems (Smolders et al., 2006). Phosphorus can be released from FePs by iron-reducing (Chacon et al., 2006; Roden and Edmonds, 1997) or sulphate reducing bacteria (Chacon et al., 2006; Roden and Edmonds, 1997; Smolders et al., 2006). Plants and fungi have developed a wide variety of strategies to access iron and phosphorus in FePs (Cardoso and Kuyper, 2006; Hinsinger, 2001). For example, excretion of carboxylate anions (such as oxalate or citrate) that chelate iron and release phosphorus (Geelhoed et al., 1999; Gerke et al., 2000), exudations of anions (e.g., bicarbonate or hydroxide) to desorb phosphorus from iron oxides (Dakora and Phillips, 2002; Gahoonia et al., 1992) or reduction of FePs (Gardner et al., 1983) and inducing pH changes to release phosphorus from FePs (Hinsinger, 2001). Mechanisms presumed to be predominantly related to the mobilization of iron (e.g. excretion of siderophores or iron reduction, Altomare et al., 1999) may also play a role in mobilizing phosphorus (Gardner et al., 1983; Reid et al., 1985). Dissolved organic matter can assist in the mobilization of phosphorus from FePs by chelating iron (Lobartini et al., 1998) or by facilitating the microbial reduction of iron (Lovley et al., 1996; Lovley et al., 1998; Peretyazhko and Sposito, 2005).

Iron plays an important role in controlling the mobilization of phosphorus in soil and sediment systems. Therefore, a great deal of research has been performed on the role of iron in the phosphorus cycle. The results, show that iron and phosphorus cycling is possible, and this implies that recovering phosphorus from FePs is achievable as well. Insufficient understanding of the iron and phosphorus chemistry in STPs has prevented the environmental mechanisms responsible for mobilizing phosphorus from being transferred to industrial processes.

In section 2.3, we highlight the need for distinguishing between the different kinds of FePs to better understand the binding and release of phosphorus. In section 2.4, we will show that various FePs are formed and transformed during wastewater treatment processes but that little information is available on the occurrence and behaviour of these FePs. In section 2.5, we will describe the findings on the mobilization of phosphorus from FePs that could offer inspiration for the development of new phosphorus recovery technologies.

2.3 Iron and phosphorus interactions

2.3.1 Diversity of iron–phosphorus compounds

2.3.1.1 Introduction to iron–phosphorus compounds

Iron is a transition metal and its chemistry is very diverse (Cornell and Schwertmann, 2003b). It can exist in several oxidation states varying between -2 to +6 although +2 (ferrous) and +3 (ferric) are the most common oxidation states encountered. The solubility of ferrous and ferric ions vary with pH and oxidation reduction potential (ORP) (Figure 2-2). Depending on the pH, the ferrous and ferric ions can form various insoluble oxides, oxyhydroxides and hydroxides, collectively termed iron oxides (Cornell and Schwertmann, 2003b).

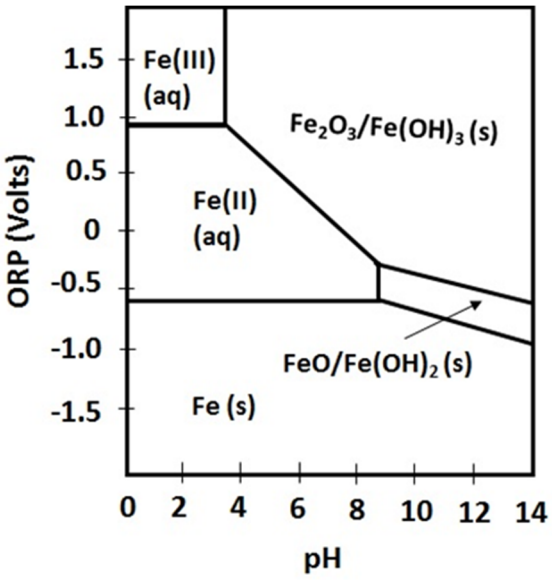


Figure 2-2: Simplified Pourbaix diagram showing the stable iron species under different conditions (modified from Tilley, 2005).

The FePs found in STPs can be either iron phosphate minerals or adsorption complexes which involve adsorption of o-P to iron oxides (Frossard et al., 1997; Huang and Shenker, 2004; Luedecke et al., 1989; Smith et al., 2008) (different methods to characterize FeP interactions are listed in Table S 2-3). These FePs have often not been well described. This has led to publications on the removal of phosphorus using iron or on the recovery of phosphorus from FePs often containing unspecific expressions such as "insoluble iron phosphates", "metal phosphates", and "iron III phosphates". We will give examples which illustrate that phosphorus can be bound to iron in various ways and that the amount and strength of phosphorus bound to iron differ. This suggests that there is a range of mechanisms through which FePs can be altered resulting in phosphorus release, underlining the importance to differentiate between various FeP.

2.3.1.2 Iron oxides and their interaction with o-P

At least 16 iron oxides exist (Cornell and Schwertmann, 2003b). Prominent examples of ferric iron oxides are goethite, ferrihydrite, lepidocrocite, akaganeite, and hematite. Green rust iron oxides and magnetite are examples of iron oxides that contain both ferrous and ferric iron. The different iron oxides have different crystalline structures or are amorphous, and these structures largely determine properties such as porosity, specific surface area, the number of exposed surface sites, solubility, and reducibility. These properties in turn affect the o-P binding properties of the iron oxides and the bioavailability of adsorbed o-P (Barron et al., 1988; Guzman et al., 1994; McLaughlin et al., 1981; Parfitt et al., 1975; Wang et al., 2013). The surface area of the iron oxide usually correlates with its capacity to adsorb o-P (Figure S 2-1 in supporting information). Amorphous or less crystalline iron oxides have higher o-P adsorption capacities than more crystalline iron oxides, and this is attributed to amorphous iron oxides having higher surface areas (Borggaard, 1983; Parfitt et al., 1975; Wang et al., 2013). o-P

adsorption to iron oxides can also differ due to the type and density of surface hydroxyl groups present on the crystal faces, which are the functional groups where o-P adsorption occurs (Cornell and Schwertmann, 2003b). Hematites showed o-P adsorption capacities varying from 0.19 to 3.33 µmol/m^2 due to the differences in their crystal faces (Barron et al., 1988). In contrast, goethites showed a narrower range of o-P adsorption capacities between 2.16 to 2.83 µmol/m^2 owing to their relatively constant crystal face distribution (Torrent et al., 1990). Figure 2-3 shows the o-P adsorption capacities in different iron oxides. The o-P adsorption capacity varies within the same type of iron oxides based on the conditions under which they are synthesized and used (Barron et al., 1988; Cabrera et al., 1981; Guzman et al., 1994).

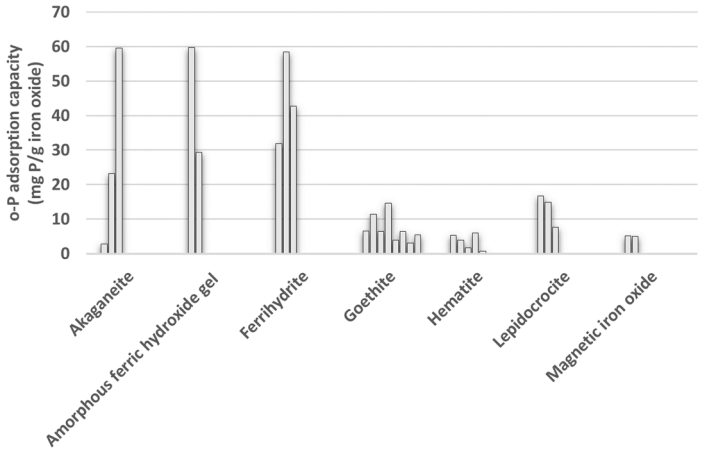


Figure 2-3: o-P adsorption capacities of different iron oxides. Details of conditions used for adsorption are presented in Table S 2-4 in supporting information.

o-P adsorption onto iron oxides occurs since the iron beneath the surface hydroxyl acts as a Lewis acid and exchanges the surface OH groups for other ligands (Cornell and Schwertmann, 2003b). When o-P is bound directly to an iron oxide surface through a ligand exchange mechanism, without any water molecules between the o-P and the surface, (Figure 2-4 a,b,c) the resulting complex is called an innersphere complex (Goldberg and Sposito, 1985). An innersphere complex can comprise of a single o-P molecule attached through one or two oxygen bonds (mono or bidentate respectively) with either one or two iron atoms (mono or binuclear, respectively, Sparks, 2003). The type of complex formed determines the relative strength at which the o-P is bound. Bidentate complexes have more stable structures than monodentate complexes, which implies that it could be easier to release o-P from monodentate than from bidentate complexes (Abdala et al., 2015). The types of innersphere complexes differ based on the type of iron oxides and the conditions such as the pH and the initial o-P concentration (Abdala et al., 2015; Arai and Sparks, 2001; Goldberg and Sposito, 1985). Thus, o-P adsorption and desorption properties vary for different iron oxides and for the conditions where the iron oxides are produced and used. This make adsorption a very versatile process and offers the possibility of engineering specific adsorbents based on iron oxides.

Adsorption is not the only interaction that occurs between o-P and iron oxides. It is possible to have surface precipitation (Figure 2-4 e), which is the formation of three-dimensional entities as opposed to the two-dimensional monolayer coverage during adsorption (Davis and Hayes, 1987; Sparks, 2003). Surface precipitation can lead to the formation of a solid phase from which phosphorus is less readily desorbed because the phosphorus buried in the surface precipitate is no longer in equilibrium with the solution (Li and Stanforth, 2000a). The dissolution of iron from the iron oxide contributes to the formation of the surface precipitate (Jonasson et al., 1988; Li and Stanforth, 2000a). For instance, nano zero-valent iron (nZVI) particles were shown to have very high o-P adsorption capacities (245 mg P/g) even though their surface area (27.6 m^2/g) was not very high (Wen et al., 2014). This high capacity to remove o-P was explained as being partly caused by the occurrence of precipitation, which was facilitated by the dissolution of iron from the nZVI particles. The initial o-P concentration in the solution influences the type of binding with iron oxide by determining the surface coverage of o-P. Surface complexation tends to dominate at low surface coverages, and surface precipitation becomes dominant as the surface loading increases (Li and Stanforth, 2000a; Sparks, 2003). At a high surface coverage with o-P, goethite and strengite (an iron phosphate mineral) have similar points of zero charge (PZC), suggesting that surface precipitation occurred on goethite (Li and Stanforth, 2000a).

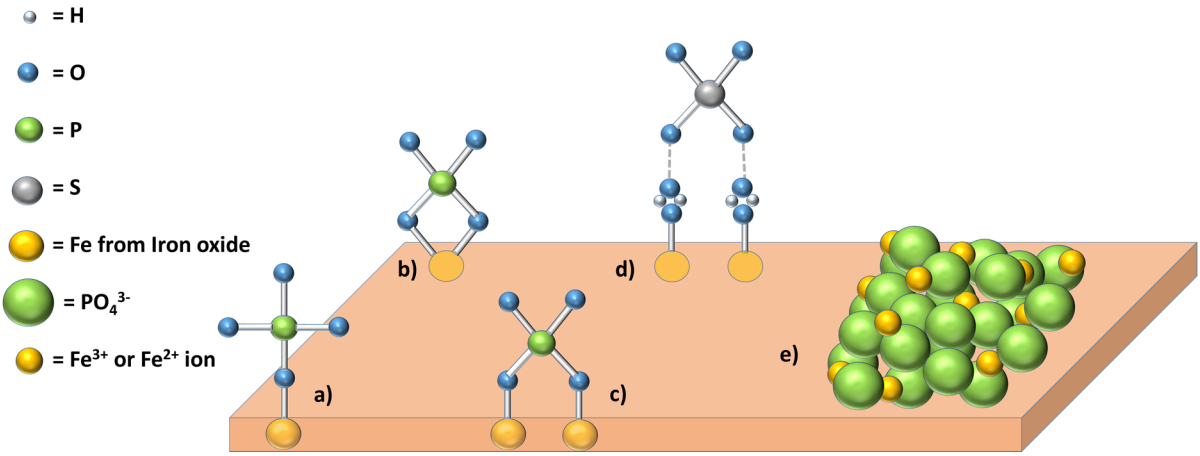


Figure 2-4: Anion binding onto iron oxides. o-P adsorbed as innersphere complexes (Abdala et al., 2015; Arai and Sparks, 2001; Parfitt and Atkinson, 1976): a) mononuclear monodentate b) mononuclear bidentate c) binuclear bidentate. Sulphate adsorption is shown as an example for d) outersphere complex in which water molecules are present between the iron oxide surface and the sulphate (Peak et al., 1999) e) example of surface precipitation in which dissolved iron from the iron oxide surface contributes to the formation of multiple layers of FeP precipitates (Li and Stanforth, 2000a) on the surface of the iron oxide.

2.3.1.3 Iron phosphate minerals

Iron phosphate minerals are polyatomic complexes of iron and phosphate (Moore, 1969, 1970; Stoch et al., 2014). Unlike adsorption complexes where o-P is removed from solution by binding on the surface of a solid (e.g. iron oxide, Sparks, 2003), iron phosphate minerals are usually formed in the presence of o-P and dissolved iron (Bache, 1964; Ming et al., 2011; Roldan et al., 2002). However, the exact mechanisms involved in formation of iron phosphate

precipitates can be complex (Lente et al., 2000; Luedecke et al., 1989). Vivianite ($Fe(II)_3[PO_4]_2 \cdot 8H_2O$) and strengite ($Fe(III)[PO_4] \cdot 2H_2O$) are the common examples of iron phosphate minerals, although there exist several others like lipscombite ($(Fe(II)(Fe(III))_2(PO_4)_2(OH)_2$), beraunite ($(Fe(II)(Fe(III))_5[(PO_4)_4|(OH)_5] \cdot 6H_2O$) and rockbridgeite ($Fe(II)(Fe(III))_4(PO_4)_3(OH)_5$ (Moore, 1970). The stability of different iron phosphate minerals vary in terms of their formation and solubility with respect to pH and redox conditions (Nriagu and Dell, 1974) which in turn might have implications on the phosphorus release from these compounds. Vivianite has been found in STPs and its formation and role in recovering phosphorus from wastewater will be discussed in detail in later sections.

2.3.2 Iron–Phosphorus compounds in sewage treatment processes

2.3.2.1 Introduction to chemical phosphorus removal using iron salts

Among other reasons, iron salts are added to wastewater to remove phosphorus (Thomas, 1965; WEF, 2011). The efficiency at which phosphorus is removed in a STP by adding iron is influenced by the oxygen concentration (for ferrous salts), the concentrations of competing ions, the presence of organic matter, the pH, the alkalinity, mixing, the age of the iron or iron oxide flocs, the type of phosphorus present, and whether ferric or ferrous iron salts are used (WEF, 2011). FePs are exposed to dramatic changes in ORP and temperature over a period of about one month in a STP with an anaerobic digestion process. The following examples will show that adsorption, mineral formation, and recrystallization may occur at different stages in a STP (Figure 2-5).

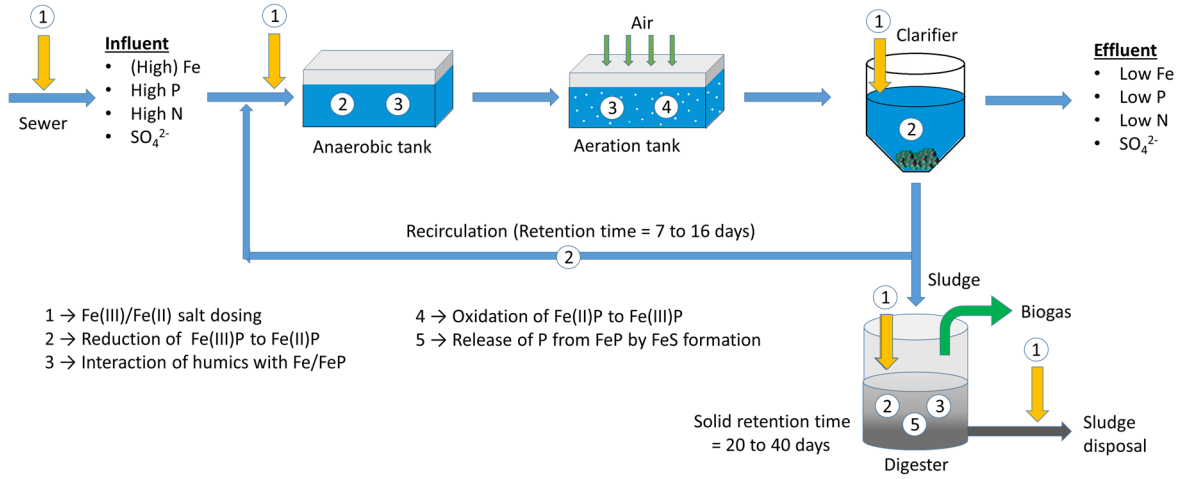


Figure 2-5: STP schematic highlighting possible iron and phosphorus interactions at different stages. Iron can be dosed at various stages for reasons like sulphide removal, phosphorus removal, flocculation and to facilitate dewatering of sludge.

2.3.2.2 Dosing ferric versus ferrous iron salts

The exact mechanisms through which ferric or ferrous iron salts initially remove phosphorus are not yet understood. The hydrolysis of ferric iron in an aqueous solution is usually very rapid (Wendt von, 1973). It has been suggested that the adsorption of o-P onto iron oxides is an important (Luedecke et al., 1989; Recht and Ghassemi, 1970a) or even the major mechanism

(Smith et al., 2008; Szabo et al., 2008) involved in the removal of o-P from wastewater when ferric iron salts are dosed.

The situation is even more complex when ferrous iron is added because this can be partly or fully oxidized to ferric iron. The ferrous salts are usually added to aerated stages of the STP to allow oxidation to ferric iron. The kinetics of ferrous iron oxidation strongly depend on the oxygen concentration and particularly on the pH (Stumm and Morgan, 1996). Half of the ferrous iron in water containing 5 mg/L dissolved oxygen has been found to be oxidized to ferric iron within 45 minutes at pH 7 and within 0.5 minutes at pH 8 (Ghassemi and Recht, 1971; Singer and Stumm, 1969). The presence of other ions (e.g., sulphate or o-P) or dissolved organic matter can considerably influence the oxidation kinetics (Pham et al., 2004; Stumm and Morgan, 1996; Theis and Singer, 1974). The kinetics of ferrous iron oxidation and hydrolysis in wastewater are not well established. In a STP, about 40% of the ferrous iron that was added was found to be rapidly oxidized to ferric iron (at relatively high pH 8.2 and dissolved oxygen concentration of 4.6 mg/L, Thistleton et al., 2001). Similarly, half of the ferrous iron in activated sludge could be oxidized within minutes but about 10% of the ferrous iron fraction was not oxidized even after 6 days of aeration (Nielsen, 1996). Measurements on sludge taken from the aeration tank of a STP in which ferrous iron was used to remove phosphorus suggest that most of the iron in the sludge was ferric iron (Rasmussen and Nielsen, 1996). In contrast, 43% of the total iron in activated sludge before anaerobic digestion was found in the form of the ferrous iron phosphate mineral vivianite (Frossard et al., 1997). This data indicates either extensive reduction of ferric iron during wastewater treatment or incomplete oxidation of the ferrous iron that has been added to the aerated tanks. However, also in the absence of oxygen, o-P could be removed with a ferrous Fe:P molar ratio of 1.5 in batch tests using secondary effluents, a maximum o-P removal efficiency (98%) was found at pH 8 (Ghassemi and Recht, 1971). It has been suggested that the removal of phosphorus can be made more efficient if ferrous iron is slowly oxidized in situ (Ghassemi and Recht, 1971; Leckie and Stumm, 1970; Svanks, 1971).

2.3.2.3 Vivianite formation in wastewater treatment plants

During wastewater treatment, initially formed FePs may change because of exposure to different ORPs and, therefore, to different microbial and chemical processes (Frossard et al., 1997; Nielsen, 1996; Nielsen et al., 2005; Rasmussen et al., 1994; Rasmussen and Nielsen, 1996). Vivianite can be formed when ferrous iron is added to remove phosphorus (Frossard et al., 1997; Ghassemi and Recht, 1971; Singer, 1972). Mössbauer spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) analyses, showed that 43% of the iron in activated sludge from a STP in which ferrous sulphate was used to remove phosphorus, and 60–67% of the iron in the digested sludge was bound in vivianite (Frossard et al., 1997). Vivianite is sparingly soluble in water ($K_{sp} = 10^{-36}$), and it is stable in the absence of oxygen, at pH 6–9, under non-sulphidic conditions, and in the presence of high ferrous iron and o-P concentrations (Nriagu, 1972). In STPs in which ferric salts are used to remove phosphorus or in STPs which apply different treatment strategies (e.g., the A-B process), it is not known whether vivianite forms or not and if so to what degree. The microbial reduction of ferric iron

in anaerobic treatment stages could initially lead to phosphorus release from FePs (Nielsen, 1996; Rasmussen and Nielsen, 1996). However, the reduced iron could ultimately act as a phosphorus sink by forming vivianite, which has a higher phosphorus content (Fe:P molar ratio of 1.5) than ferric FeP precipitates found in experiments with wastewater (Fe:P molar ratio of 2.5, Luedecke et al., 1989). The formation of ferric phosphate minerals like strengite (Fe:P molar ratio of 1) does not seem to play a significant role in STPs. In STPs strengite and lipscombite in iron stabilized digested sludge were found after high iron dosing (Fe:P of 6.15) only (Huang and Shenker, 2004). Hence, the formation of vivianite could be the final mechanism for the retention of phosphorus in STPs.

2.4 Transforming iron–phosphorus compounds

2.4.1 Oxidizing and reducing conditions

2.4.1.1 Introduction

Iron plays an important role in retaining phosphorus in soil and sediments because of the formation of FePs (Figure 2-6, Cornell and Schwertmann, 2003b; Froelich, 1988; Schulz and Zabel, 2006; Sundareshwar and Morris, 1999). The mobilization and retention of phosphorus from FePs in these systems, in response to changes of ORPs, is well documented (Caraco et al., 1989; Roden and Edmonds, 1997; Smolders et al., 2006). Similar processes could also occur in STPs.

STPs require a large range of ORPs to allow different microbial processes to take place. The ORPs in a STP will range from less than −300 mV, during anaerobic digestion or the anaerobic period of an EBPR process, to more than +200 mV during the nitrification process. Here, microbial and chemical processes can take place that alter FePs by oxidizing or reducing the iron or by replacing the phosphorus with sulphide or other ions. These modifications can affect the phosphorus removal performance and other parameters, such as the dewaterability of the sludge (Nielsen, 1996). Nevertheless, iron speciation in response to varying ORPs in STPs has not received much attention. In a potential phosphorus recovery process, exposing FePs to ORPs that anyway occur in STP, could assist in phosphorus mobilization. For instance, at low ORPs iron reducing or sulphate reducing bacteria could mobilize iron bound phosphorus. On the other hand, oxidation can mobilize phosphorus bound in vivianite. The chemical or biological processes that could mobilize phosphorus from FePs could be facilitated by the presence of dissolved organic matter. In this section, we give a short overview on how ORPs can influence phosphorus binding to iron. We will show that changes in the ORPs in both, positive and negative ranges and subsequent changes in microbial processes can assist in either retaining or mobilizing phosphorus from FePs.

2.4.1.2 Iron reduction and iron oxidation

The chemical or biological reductive dissolution of ferric iron can cause iron-bound phosphorus to be released. In general, dissimilatory iron-reducing bacteria are widespread in soil and sediment systems (Lovley et al., 1991a; Lovley, 1997; Weber et al., 2006). These organisms reduce ferric iron in iron oxides or iron phosphate minerals, thereby mobilizing phosphorus

(Heiberg et al., 2012; Patrick et al., 1973; Peretyazhko and Sposito, 2005). However, in the absence of sulphate, ferrous iron compounds were formed that bound most of the released phosphorus (Borch and Fendorf, 2007; Roden and Edmonds, 1997). The reducibility of an iron oxide depends on its crystal structure, solubility, and surface area (Bonneville et al., 2009; Larsen and Postma, 2001). Crystalline iron oxides with low surface area (e.g., goethite and hematite) and low solubility are usually less accessible to iron-reducing organisms than amorphous iron oxides, e.g., lepidocrocite and ferrihydrite (Bonneville et al., 2009; Cheng et al., 2015; Munch and Ottow; 1983).

Once formed, ferrous iron can precipitate as secondary iron oxides (e.g., magnetite or green rust) or as ferrous iron phosphate minerals (e.g., vivianite, Weber et al., 2006). In the presence of electron acceptors (e.g., oxygen or nitrate), dissolved or solid ferrous iron compounds may be oxidized. Biogenic iron oxides that can be formed in the presence of iron-oxidizing bacteria include goethite, magnetite, ferrihydrite, and green rust (Weber et al., 2006). Biogenic iron oxides are often amorphous and nanocrystalline (Fortin and Langley, 2005) and thus showed high o-P binding capacities (Rentz et al., 2009). Biologically formed iron oxides can contain organic matter, which disrupts the crystallization process (Cornell and Schwertmann, 2003b; Posth et al., 2014) and makes the iron more accessible and therefore more easily reduced. This reduction process might be assisted by humic substances (Piepenbrock et al., 2014a; Piepenbrock et al., 2014b).

It has been shown that iron-reducing and iron-oxidizing bacteria are very active in STPs (Nielsen, 1996; Rasmussen et al., 1994; Rasmussen and Nielsen, 1996). Reduction (presumably enzymatic) of iron has been measured in activated sludge immediately after storage under anaerobic conditions. The ferrous iron produced stayed mainly within the organic matrix of the sludge despite of humic substances showing lower affinity to ferrous than ferric iron (Rasmussen and Nielsen, 1996; Stevenson, 1994). The authors hypothesized that the reduction of iron can cause significant phosphorus release from sludge under anaerobic conditions in STPs. However, the formation of secondary ferrous iron oxides or vivianite that can bind phosphorus was not taken into account. It has also been shown that the microbial oxidation of ferrous iron in activated sludge using nitrate as an electron acceptor plays a significant role in the denitrification stage in STPs (Nielsen, 1996). The authors hypothesized that this anoxic oxidation of ferrous iron could improve sludge dewatering and phosphorus retention. The kinetics of iron oxidation and reduction and the transformation of iron, that is cycled through treatment stages with high and low ORPs, have not been determined yet. Thus, it is not known whether ferrous or ferric, crystalline or amorphous, biogenic or chemogenic iron compounds dominate at different stages of a STP. Humic substances also play a role in the redox chemistry of iron. This will be discussed in section 2.4.2.

2.4.1.3 Sulphide and iron–phosphorus compounds

Sulphide can reduce ferric iron compounds (Poulton et al., 2004) and can further react to form various iron sulphide compounds (FeSs, Morse et al., 1987). It has been hypothesized that this could be the main mechanism through which iron bound phosphorus is released from sediments

(Caraco et al., 1989; Roden and Edmonds, 1997; Smolders et al., 2006). The reactivity of an iron oxide toward sulphide (as for iron-reducing bacteria) depends on the crystallinity of the iron oxide. Reaction times have been found to range from minutes for poorly crystalline iron oxides (e.g., hydrous ferric oxide, ferrihydrite, and lepidocrocite) to days or years for more crystalline iron oxides (e.g., hematite and goethite) (Canfield, 1989; Poulton et al., 2004). The presence of o-P can decrease the reductive dissolution of different iron oxides by sulphide via formation of binculear innersphere complexes (Biber et al., 1994; Stumm, 1997; Yao and Millero, 1996).

Sulphide has already been used to solubilize phosphorus selectively from FePs containing sludge for phosphorus recovery. Sulphide released 75% of the solid phosphorus into solution at pH 4 from sludge collected at a water production plant (Likosova et al., 2013). Similarly, 43% of the total solid phosphorus was found to be released from sludge pre-coagulated with iron by adding sulphide (Kato et al., 2006). In another study, iron sulphate was added to precipitate phosphorus in sludge liquor and the microbial reduction of the added sulphate produced sulphide (Suschka et al., 2001). Subsequently, phosphorus was released (1.5 moles of sulphide released about one mol o-P) over a timescale of days, without gaseous hydrogen sulphide formation.

To our knowledge, it is not known if sulphide induced phosphorus release is influenced by the type of FeP. However, analogous to the difference in reactivity of sulphide to iron oxides, it is likely that the amount of sulphide required to release phosphorus from FePs with different crystal structure varies.

2.4.1.4 Transforming vivianite

Vivianite could be an important ferrous iron phosphate compound in STPs (section 2.3.2.3). Transformation of vivianite by oxidation or by exposing it to sulphide can induce phosphorus release. Chemically, about 5–10% of the ferrous iron in freshly synthesized vivianite has been found to oxidize within minutes when exposed to air and about two thirds of the ferrous iron was oxidized after air bubbling for 53 days (Roldan et al., 2002). In this study, oxidation occurred in the presence of a phosphorus sink (an anion exchange membrane). The initial Fe:P ratio (determined by energy dispersive X-ray spectrometry (EDX)) was 1.4 and the final Fe:P ratio was around 6.2. The complete oxidation of vivianite and the formation of an amorphous iron phosphorus compound was much faster (16 days) when the oxidation was microbially induced (Miot et al., 2009). No phosphorus sink was present, but the Fe:P ratio (determined by EDX) decreased from 1.3 (vivianite) to 2.8. Due to these properties vivianite has been used as a slow release iron and phosphorus fertilizer (Diaz et al., 2009; Eynard et al., 1992; Roldan et al., 2002). Accordingly, vivianite may recrystallize when sludge is exposed to air resulting in phosphorus release.

During anaerobic digestion, substantial sulphide formation by sulphate reducing bacteria would most likely result in the release of significant amounts of iron-bound phosphorus, as reported for anoxic sediments (Smolders et al., 2006). The formation of vivianite during anaerobic

digestion is not hampered by FeSs formation since the supply of sulphate is limited in digesters (Chen et al., 2008; van den Brand et al., 2014). When considering the recovery of phosphorus from sludge by sulphide, the crystallinity of vivianite should be taken into account. Vivianite could be rather insensitive to sulphide, similar to more crystalline iron oxides (Canfield, 1989; Poulton et al., 2004).

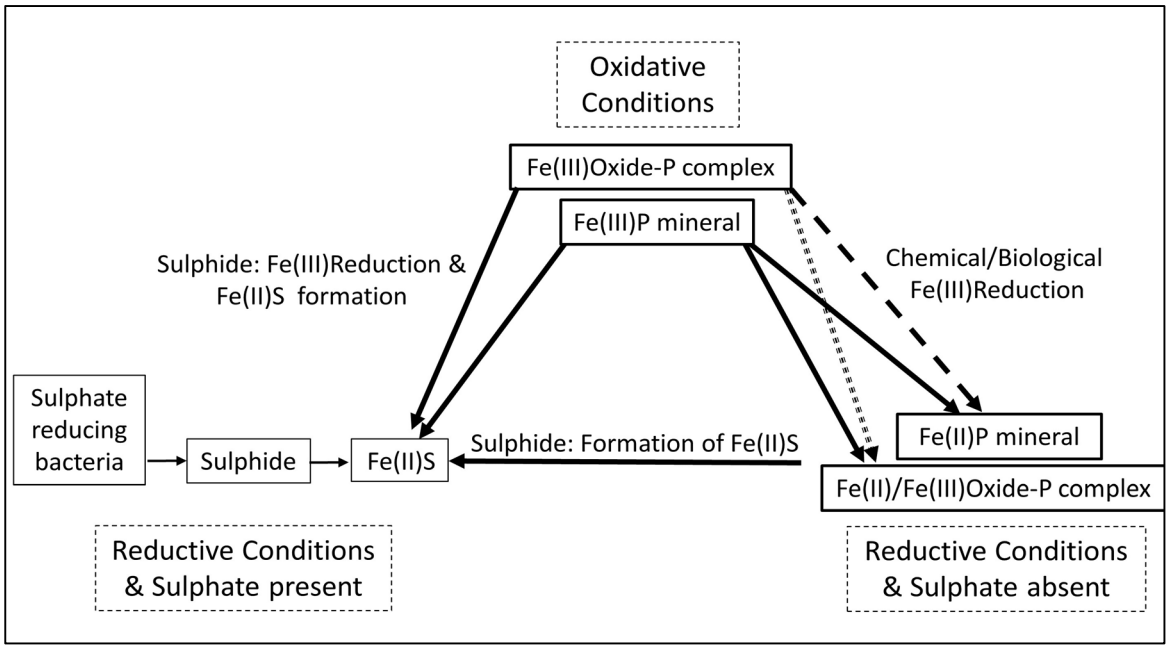


Figure 2-6: Redox processes and the cycling of phosphorus. The arrow keys represent the effect on soluble phosphorus: ⟶ implies phosphorus release, — ⟶ implies phosphorus sink, ⋯⟶ implies not clear.

2.4.2 Humic substances

2.4.2.1 Introduction

Organic matter contributes 40–80 wt. % of the total solids in sludge.(Tchobanoglous et al., 2013) Organic matter, like humic substances, plays an important role in iron and phosphorus cycling in soil and aquatic systems. Humic substances have received attention because of their omnipresence and relevance to iron and phosphorus chemistry. Humic substances include humic acids, fulvic acids, and humins (Stevenson, 1994). These are relatively large, refractory and complex molecules that are products of organic matter degradation. Humic substances lack well-defined compositions but usually contain large numbers of oxygen-containing functional groups, such as carboxyl and hydroxyl groups (Stevenson, 1994). This characteristic explains some of their interactions with iron and phosphorus. Humic substances contributed about 20% of the total dissolved organic carbon in secondary effluent (Frimmel, 1999) and 10–20% of the total organic carbon in sludge dry matter (Riffaldi et al., 1982). It has been estimated that 22% of the iron in activated sludge could be bound to organic matter (Rasmussen and Nielsen, 1996). Accordingly, pyrophosphate extractions showed that approximately 30% of iron in digested sludge could be bound to organic matter (Carliell-Marquet et al., 2009; Ito et al., 2000) Since humic substances are present in abundance in STPs, they can considerably effect iron and phosphorus speciation. Their effects need to be considered during research on phosphorus

recovery processes from wastewater. Especially, since the effect of humic substances on FePs has shown controversial results (Figure 2-7). In the next section, we will briefly discuss how humic substances interact with iron and the various ways in which they can affect iron and phosphorus interaction.

2.4.2.2 Humic substances interaction with iron and phosphorus

The bond between iron and humic molecules is relatively strong and can prevent the hydrolysis and polymerization of iron (Karlsson and Persson, 2012). Mössbauer spectroscopy (Schwertmann et al., 2005) and synchrotron-based spectroscopy (Karlsson and Persson, 2012) have indicated that ferric iron can occur as oxides and non-oxides together with organic matter. It has also been shown that different bonds between iron and humic substances have different strengths (Senesi et al., 1989) and that mononuclear and polymeric iron humic complexes occur (Karlsson and Persson, 2010, 2012; Morris and Hesterberg, 2012). The type of complex formed influences iron speciation, and the processes that lead to the different species being formed include iron hydrolysis, polymerization, and the binding of arsenate, which has similar structure and reactivity as o-P (Karlsson and Persson, 2012; Mikutta and Kretzschmar, 2011; Puccia et al., 2009; Sjöstedt et al., 2013).

The presence of humic substances decreased the o-P adsorption capacity of goethite (Antelo et al., 2007; Fu et al., 2013; Sibanda and Young, 1986). It has also been suggested that humic substances have either limited or positive effects on the binding of o-P to iron (Borggaard et al., 2005; Gerke, 2010b; Gerke and Hermann, 1992). It has been hypothesized that the o-P adsorption capacity of iron could increase because of the formation of iron–humic–phosphorus complexes (Gerke, 2010b; Weir and Soper, 1963). Such complexes have been found to have about eight times higher o-P adsorption capacities than pure iron oxide phases (Gerke and Hermann, 1992). This could be due to the iron being finely distributed on the organic surfaces (Gerke and Hermann, 1992). In studies using Mössbauer spectroscopy, it has been confirmed that iron oxides can be evenly distributed over the surfaces of humic compounds (Sorkina et al., 2014). Yet, to the best of our knowledge, there is no direct proof for the existence of such iron–humic–phosphorus complexes. However, the binding of arsenic by humic–iron compounds has been proven using extended X-ray absorption fine structure analyses (Mikutta and Kretzschmar, 2011).

The presence of humic substances could increase the o-P adsorption capacity of iron oxides by preventing crystallization of amorphous iron oxides (Gerke, 1993; Schwertmann, 1966, 1970; Schwertmann et al., 2005). However, it has also been shown that organic matter does not have a significant influence on the crystallization of iron oxides and does not affect the adsorption of phosphorus (Borggaard et al., 1990). Ferrous iron can be bound by humic substances, influencing oxidation properties of ferrous iron, the crystallization of iron oxides, and the bioavailability of ferrous iron (Catrouillet et al., 2014; Pédrot et al., 2011). It has been found that humic substances can dissolve phosphorus by chelating iron from ferric FePs (Lobartini et al., 1998). Ferric iron can be kept in solution when it has been complexed with humic acids and may, in that state, bind o-P (Gerke, 2010b; Karlsson and Persson, 2012; Weir and Soper, 1963)

Iron-reducing bacteria can use humic substances as electron acceptors during the oxidation of organic compounds (Lovley et al., 1996). The rate at which iron is reduced may be increased by the presence of humic substances and usually inaccessible iron oxides may be made available (Lovley et al., 1998). The ability of humic substances to transfer or shuttle electrons to ferric iron has led to the hypothesis that even fermenting bacteria, sulphate-reducing bacteria, or methanogens could reduce ferric iron (Kappler et al., 2004; Piepenbrock et al., 2014a; Piepenbrock et al., 2014b). When humic substances act as electron acceptors, they can be restored after exposure to oxygen (Klüpfel et al., 2014). Figure 2-7 summarizes the possible effect of humics on iron and phosphorus interactions.

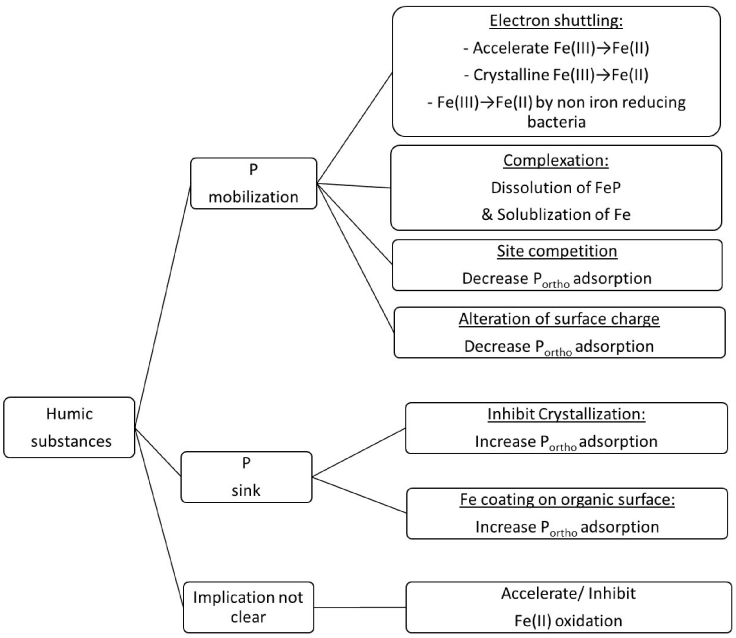


Figure 2-7: Effect of humic substances on iron and phosphorus interaction.

2.4.3 The effect of pH

2.4.3.1 Introduction

The pH can have a considerable effect on iron and phosphorus interactions since it affects several factors like the speciation of o-P, the surface charge of iron oxides and the solubility of iron oxides and iron phosphate minerals. We will discuss the effect of pH on iron and phosphorus interactions in two contexts. Firstly, the effect of pH on adsorption of o-P on and desorption of o-P from iron oxides respectively. This will be followed by a short discussion on existing techniques to recover phosphorus from FePs in sludge to show controversial experiences that have been made in these studies.

2.4.3.2 Desorption of o-P from iron oxides

The surface potential of the adsorbent as well as the o-P becomes more negative as the pH increases (Stumm et al., 1992). Beyond the PZC of the iron oxide, electrostatic repulsion leads

to a decrease in o-P adsorption (Yoon et al., 2014). Furthermore, an increase in pH increases the hydroxide ion concentration, which results in o-P desorption. The hydroxide ion is the hardest Lewis base among the common inorganic ions, so it is an effective reagent for desorption (Awual et al., 2011). Desorption of o-P from iron oxides has been studied somewhat less than adsorption. Not all of the adsorbed o-P is easily released by competing ions (Cabrera et al., 1981; Torrent et al., 1990). The proportion of the adsorbate ion that is not easily desorbed could be explained by the formation of surface precipitates, the slow restructuring of the solid, or diffusion limitations related to the porosities of the iron oxides (Cabrera et al., 1981; Chitrakar et al., 2006; Davis and Hayes, 1987; Li and Stanforth, 2000a). XRD measurements have shown that the crystallinity of goethite increased after one adsorption-desorption cycle (with NaOH), and this affected o-P adsorption negatively (Chitrakar et al., 2006). However, no change in crystallinity and reusability (after 10 cycles) was observed after desorption using akaganeite (Chitrakar et al., 2006).

2.4.3.3 Inducing pH changes to recover phosphorus

Wastewater and sludge is usually at pH 6–8 in STPs (Tchobanoglous et al., 2013) but much higher or lower pH are applied in some processes to recover phosphorus. It has been suggested that at pH 13, phosphorus may be released from FePs containing sludge using a microbial electrolysis cell (Fischer et al., 2011; Fischer et al., 2015). Phosphorus extraction from FePs containing sludge, taken from a STP using iron electrolysis for phosphorus removal, was more selective and greater in alkaline compared to acidic conditions (92 compared to 70% of total phosphorus extracted, Sano et al., 2012). In other studies, relatively little phosphorus was released under alkaline extraction conditions from FePs containing sludge (13% extracted at pH 13, Maier et al., 2005) and iron-rich sludge ash (3–28% extracted using 1 M NaOH, Cornel et al., 2004). These contradictory results further underline the importance of characterizing FePs. The re-precipitation of released phosphorus (as calcium or magnesium phosphorus compounds) could influence its net release. Strong acidification will dissolve and release phosphorus from iron oxides and iron phosphate minerals thereby mobilizing most of the phosphorus in sludge and ash samples (Atienza–Martínez et al., 2014; Biswas et al., 2009; Maier et al., 2005; Petzet et al., 2012; Pinnekamp et al., 2011). Acidification is part of current phosphorus recovery techniques (such as Ecophos, ICL, PHONAX, Seaborne, and Recophos) but can also bring heavy metals and other metals into solution.

2.5 Approaches to recover phosphorus from iron

Future energy producing STPs will rely on the removal of phosphorus and COD by iron addition. An economically feasible process for recovering phosphorus from FePs does not yet exist. Many different FePs may be formed in STPs because of the wide range of microbial and chemical processes that occur. The development of processes for recovering phosphorus from FePs demands more research, especially on iron and phosphorus interactions in STPs. The generated knowledge will help to identify the best stages for introducing phosphorus recovery processes and will prepare a base for additional focused research. Furthermore, this research will help to better understand and to improve sewage treatment processes, in general. For

instance, it may be possible to induce formation of a specific FeP from which phosphorus is easily extractable. A wide range of processes for releasing phosphorus from FePs in nature exist, these processes depend also on the types of FePs present. The most relevant mechanisms are summarized below:

- The reduction of iron may trigger initial phosphorus release from ferric FePs, but the vivianite subsequently formed can act as a net phosphorus sink. In contrast, the oxidation of iron may cause net release of phosphorus bound in vivianite. Biological and chemical oxidation and reduction of FePs occur in STPs. The use of these processes to develop a phosphorus recovery process remains to be addressed.

- Microbial reduction and oxidation of iron plays an important role in the binding and release of phosphorus. Different iron compounds have different availabilities to the microbes that are responsible for the oxidation or reduction of the iron. These processes may be facilitated (e.g., by the presence of humic substances) or hampered (e.g., by the crystal structure of the ferric FePs) by other parameters.

- Sulphide selectively releases phosphorus bound to ferric and ferrous FePs. Sulphide is formed to a limited extent during anaerobic digestion of sludge. However, further stimulation of sulphate reducing activity (e.g. after anaerobic digestion) would require COD input and would reduce the net energy yield of the STP. Additionally, sulphide is corrosive and toxic. Therefore, although sulphide addition could be useful to recover phosphorus, the dosing of sulphide needs to be optimized and economic feasibility needs to be considered as well. The reaction mechanisms between sulphide and FePs and the type of FeP in STPs have to be investigated in detail to evaluate the potential of sulphide for phosphorus recovery from FePs.

- Under very alkaline or acidic conditions phosphorus is released from most FePs. However, contradictory results have been found under alkaline conditions, suggesting that the release depends on the types of FePs that are present in sludge.

- The presence of high concentrations of organic matter in STPs complicates the iron and phosphorus chemistry involved. The role of organic matter in the iron and phosphorus biogeochemistry is not clear. It can, however, be assumed that it significantly influence iron and phosphorus speciation in STPs. Thus, organic matter should be included in future research on the development of a biomimetic process to recover phosphorus from FePs.

Another approach for recovering phosphorus is to simplify the complex FePs interactions by engineering iron-based adsorbents. Iron-based adsorbents are already used to remove phosphorus from STPs effluents. The regeneration of these adsorbents could be an effective approach for phosphorus recovery. Currently, this aspect receives insufficient attention. The diversity of FePs chemistry can be used to influence the binding and release characteristics of

phosphorus, for example, by varying the crystallinity, pore size distribution or surface area of the iron oxide based adsorbent.

We believe that a process for recovering phosphorus using iron should be developed in two steps. First, suitable FePs should be identified and characterized. Second, specific tools for mobilizing phosphorus from these compounds should be identified. Developing a biomimetic process to recover phosphorus from FePs would be an important step towards STPs acting as energy and nutrient factories.

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Supplementary Information

Table S 2-1: Enhanced phosphorus removal methods used in some northern European countries (EBPR = enhanced biological phosphorus removal, CPR = chemical phosphorus removal).

Country	Type of weighting	No tertiary treatment	Mostly EBPR	EBPR with CPR support	CPR	Reference
Germany	People equivalents	2%	6%	31%	61%	DWA, 2005
	No. of plants	20%	16%	21%	43%	DWA, 2005
Netherlands	Sludge production	4%	13%	51%	32%	Korving, 2012
United Kingdom	People equivalents	no data	5%	no data	95%	Carliell-Marquet, 2014
	No. of plants	no data	23%	no data	77%	Carliell-Marquet, 2014
France	No. of plants	no data	17%	36%	47%	Paul et al., 2001

Table S 2-2: Iron concentrations that have been found in sewage sludge (in g/kg on a total solids basis).

Country	Lowest Fe concentration	Highest Fe concentration	Average Fe concentration	Comments and reference
Germany	-	-	50	Average of 202 sludge samples (DWA, 2005)
Sweden	4.4	150	49	Based on 47 sludge samples (Eriksson, 2001)
Netherlands	-	-	31	Average of 28% of Dutch sewage sludge (Schipper and Korving, 2009)
United States	1.6	299	-	Based on 84 biosolid samples (USEPA, 2009)
United States	3.8	84	-	Based on 41 biosolid samples (Brandt et al., 2004)

Table S 2-3: Methods used for characterizing iron oxides and FeP interactions.

Qualitative	Quantitative
Infra Red (IR)/Fourier Transform Infra Red spectroscopy (FTIR) - IR studies were used to show the functional groups involved in the o-P binding to iron oxides and to find the type of innersphere complex formed by o-P with the iron oxide surface (Arai and Sparks, 2001; Elzinga and Sparks, 2007; Parfitt and Atkinson, 1976; Persson et al., 1996; Russel et al., 1974).	**N_2 adsorption-desorption experiments** were used to estimate specific surface area and pore size distribution of iron oxides (Cabrera et al., 1981; Colombo et al., 1994; Torrent et al., 1990; Wang et al., 2013). **Water vapor sorption experiments** were also used for estimating specific surface area of iron oxides (Colombo et al., 1994; Torrent et al., 1990).
X-ray Diffraction (XRD) was used to identify different iron oxides, to identify the crystallinity of iron oxides before and after o-P binding and iron phosphorus minerals (Chitrakar et al., 2006; Colombo et al., 1994; Daou et al., 2007; Frossard et al., 1997; Gálvez, 1999; Patrick et al., 1973; Wang et al., 2013).	**Thermal gravimetric analysis (TGA)** was used to investigate the amounts of physically adsorbed H_2O and OH content in the iron oxide structure (Wang et al 2013; Chitrakar et al. 2006).
X-ray photoelectron spectroscopy (XPS) was used to investigate composition and chemical state before and after phosphonation of nZVI and magnetite by evaluating the binding energies of the surface species (Daou et al., 2007; Wen et al., 2014)	**Electrophoresis measurements and potentiometric titration experiments** were done to determine the zeta potential and PZC of different iron oxides (Antelo et al., 2007; Li and Stanforth, 2000; Parfitt and Atkinson, 1976).

Qualitative	Quantitative
Mössbauer spectroscopy was used for identification of iron oxides (Daou et al., 2007), vivianite in sludge (Frossard et al., 1997), and to show the interaction between organic matter and iron oxide (Schwertmann et al., 2005).	
X-ray adsorption spectroscopy (XAS) which includes Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Adsorption Near Edge Structure (XANES) studies were used to determine the surface complex by providing information on the local molecular bonding environment / the bonding configuration of the surface species formed by o-P binding to iron oxide surfaces (Abdala et al., 2015; Khare et al., 2007).	
Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), were used to determine the morphology and particle size of iron oxides (Cabrera et al., 1981; Gálvez, 1999; Martin et al., 1988; Torrent et al., 1990; Yoon et al., 2014). **Energy dispersive X-ray spectrometry (EDX)** was used to determines Fe:P molar rations in vivianite (Miot et al., 2009; Roldan et al., 2002).	

Table S 2-4: Conditions used for o-P adsorption on different iron oxides.

Type of iron oxide	Surface area (m^2/g)	Adsorption capacity (mg P/ g iron oxide)	Initial o-P (mg P/L)	Iron oxide (g/L)	Initial pH	Electrolyte	Time	T (°C)
Goethite (Parfitt et al., 1975)	80	6.5			3.5	0.1 M KCl		
Lepidocrocite (Parfitt et al., 1975)	108	16.72			3.5	0.1 M KCl		
Hematite (Parfitt et al., 1975)	22	5.26			3.5	0.1 M KCl		
Ferric hydroxide gel (Parfitt et al., 1975)	257	29.42			3.5	0.1 M KCl		
Lepidocrocite-1 (Cabrera et al., 1981)	128	14.83	80.52	4.00	3.4	0.1 M NaCl	6 d	25
Lepidocrocite-2 (Cabrera et al., 1981)	85.7	7.71		4.00	3.2	0.1 M NaCl	6 d	25
Goethite-1 (Cabrera et al., 1981)	87.4	11.4	96.01	4.00	3.1	0.1 M NaCl	6 d	25
Goethite-2 (Cabrera et al., 1981)	54.4	6.38		4.00	3	0.1 M NaCl	6 d	25
Fe-Gel (McLaughlin et al., 1981)	280	59.77		1.88	6	0.1 M $NaClO_4$	7 d	23
Hematite (McLaughlin et al., 1981)	18	3.87		1.88	6	0.1 M $NaClO_4$	7 d	23
Goethite (McLaughlin et al., 1981)	17	3.19		1.88	6	0.1 M $NaClO_4$	7 d	23
Akaganeite (McLaughlin et al., 1981)	29.4	2.82		1.88	6	0.1 M $NaClO_4$	7 d	23
Ferrihydrite (Guzman et al., 1994)	266	58.49					16 d	
Hematite-H1 (Guzman et al., 1994)	72	6.02					16 d	
Hematite-H2 (Guzman et al., 1994)	15	0.74					16 d	
Goethite-G1 (Guzman et al., 1994)	169	14.66					16 d	
Goethite-G2 (Guzman et al., 1994)	48	3.87					16 d	
Akaganeite (Genz et al., 2004)	280	23.3			5.5		96 h	20
Ferrihydrite (Borggaard et al., 2005)	264	42.74	49.55	1.00	5	0.2 M NaCl	28 d	22
Goethite (Borggaard et al., 2005)	76	6.41	49.55	2.00	5	0.2 M NaCl	28 d	22
Akaganeite (Deliyanni et al., 2007)	330	59.62	300	0.50	7		24 h	25
Magnetite nanoparticles (Daou et al., 2007)	31	5.2		1.00	3		24 h	
Ferrihydrite (Wang et al., 2013)	348	31.9	250	0.30	4.5	0.01 M KCl	24 h	25
Goethite (Wang et al., 2013)	45	3.13	250	2.35	4.5	0.01 M KCl	24 h	25
Hematite (Wang et al., 2013)	31	1.73	250	3.33	4.5	0.01 M KCl	24 h	25
Goethite (Fu et al., 2013)	30.32	5.48	20	2.00	4.5	0.01 M KNO_3	50 h	22
Magnetic iron oxide nanoparticles (Yoon et al., 2014)	82.2	5.03	20	0.60			24 h	30

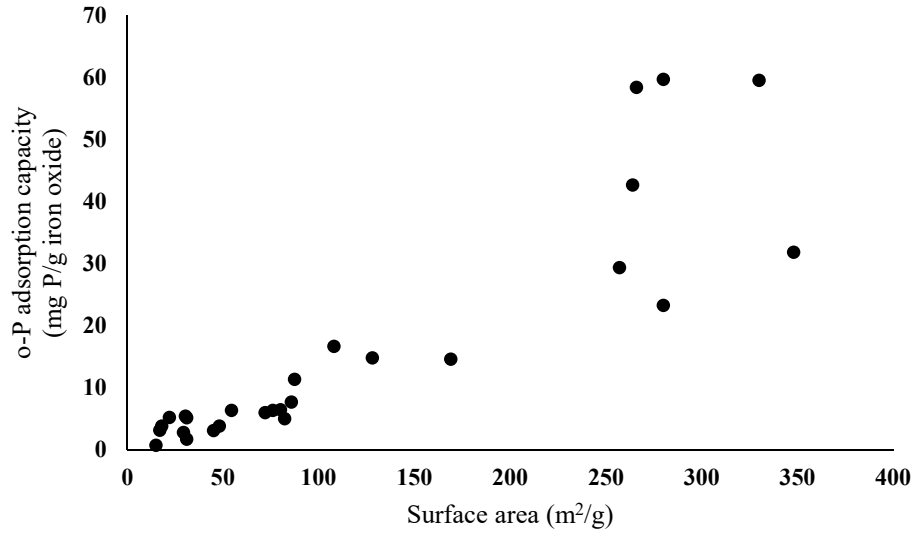


Figure S 2-1: o-P adsorption capacity as a function of surface area of different iron oxides.

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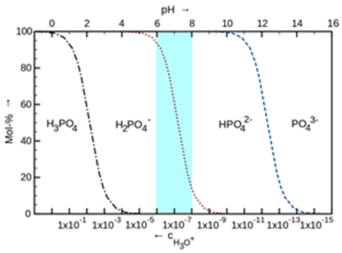
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Chapter 3: Effect of iron on phosphate recovery from sewage sludge











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3.1 The role of iron in sewage treatment plants

3.1.1 Today

Currently, phosphate is removed from sewage with the intention to prevent the eutrophication of surface waters rather than with the objective to recover phosphate. Surface water quality regulations to protect the environment, and as a consequence stricter sewage discharge limits, have led to the introduction of advanced phosphate removal techniques. Implementation of such advanced (also known as tertiary) treatment may vary per region, country and continent (Oleszkiewicz et al., 2015). In the European Union sewage from 286 million people equivalent (p.e.) receives advanced treatment whereas for 39 million p.e. tertiary treatment should still be implemented (European Commission, 2016). Compliance varies strongly per country: some countries comply for 100% while new entrants to the European Union show lower compliance rates (European Commission, 2016). Only few countries start to implement regulations for phosphate recovery from sewage now (Der Schweizerische Bundesrat, 2015; Deutscher Bundestag, 2017). The most popular advanced phosphate removal technologies are chemical phosphate removal (CPR) using iron or aluminium salts and enhanced biological phosphate removal (EBPR).

To meet effluent phosphate limits EBPR is often supported by CPR. For north-west European countries, for which we could find data, CPR dominates but it is often combined with EBPR (Table 3-1). The relative use of CPR versus EBPR may differ from country to country. For instance West Canada predominantly applies EBPR, whereas in East Canada CPR dominates (Oleszkiewicz, 2014). In Japan, approximately 25% of the plants use CPR and 4% use EBPR (personal communication H. Ohtake, 2017).

Table 3-1: Enhanced phosphate removal methods used in some north-western European countries (EBPR = enhanced biological phosphate removal, CPR = chemical phosphate removal).

Country	Type of weighting	No tertiary treatment	Mostly EBPR	EBPR with CPR support	CPR	Reference
Germany	People equivalents	2%	6%	31%	61%	DWA, 2005
	No. of plants	20%	16%	21%	43%	DWA, 2005
Netherlands	Sludge production	4%	13%	51%	32%	Korving, 2012
United Kingdom	People equivalents	0.01%	4.7%	18.3%	77.0%	Cooper, 2014
	No. of plants	0.4%	1.3%	3.8%	94.5%	Cooper, 2014
Sweden	Water volume	0%	0.2%	3%	97%	SCB, 2016, personal communication B. Hansen, 2017
France	No. of plants	no data	17%	36%	47%	Paul et al., 2001

Iron salts are usually preferred because they are cheaper. For instance, 77% of German (DWA, 2005) and 88% of French (Paul et al., 2001) sewage treatment plants (STPs) use iron for CPR.

In the United Kingdom 88% of all STPs use iron salts, here the preference for iron is not only because of lower costs but also because discharge limits are more stringent when aluminium salts are used because of concerns related to the toxicity of aluminium (Cooper, 2014; Ofwat, 2005). In Japan aluminium salts are dominantly used for CPR (personal communication H. Ohtake, 2017).

Dosing higher quantities of iron can reduce effluent phosphate levels to very low levels (Fytianos et al., 1998; Takacs et al., 2006). Besides for phosphate removal, iron is often added to sludge digesters to prevent hydrogen sulphide being emitted in the biogas. Iron salts are also used to act as a coagulant to improve the effectiveness of the sludge dewatering process. It has also been suggested to add iron salts to prevent struvite formation in digesters (Mamais et al., 1994).

There are several other sources of iron in sewage, these explain why iron is present even when no iron salts are applied in STPs. According to Hvitved-Jacobsen et al., 2013 iron is normally present in the raw sewage at 0.5–1.5 mg Fe/L, and dissolved inorganic phosphate (o-P) is 3–10 mg P/L, which would result in Fe/P molar ratios between 0.07 and 0.09. However, iron concentrations can be much higher because, for example, iron is added in sewage pumping stations to control odours and corrosion, and this practice may even aid the removal of phosphate in STPs (Gutierrez et al., 2010). Also intrusion of iron rich groundwater can be a reason for elevated iron levels in raw sewage. Between 10 – 50% but also up to 100% of the water that is treated in STPs can be extraneous water with groundwater infiltration as main source (Franz, 2006). In the Netherlands iron has been found at concentrations between 1 and 10 mg/L in the influents of 19 STPs operated by the Waterschap Vechtstromen. The average Fe/P molar ratio was found to be 0.26 (unpublished data, Figure 3-1). The iron concentrations in the effluents from those STPs were 0.1–0.3 mg/L showing that most influent iron is removed via the surplus sludge.

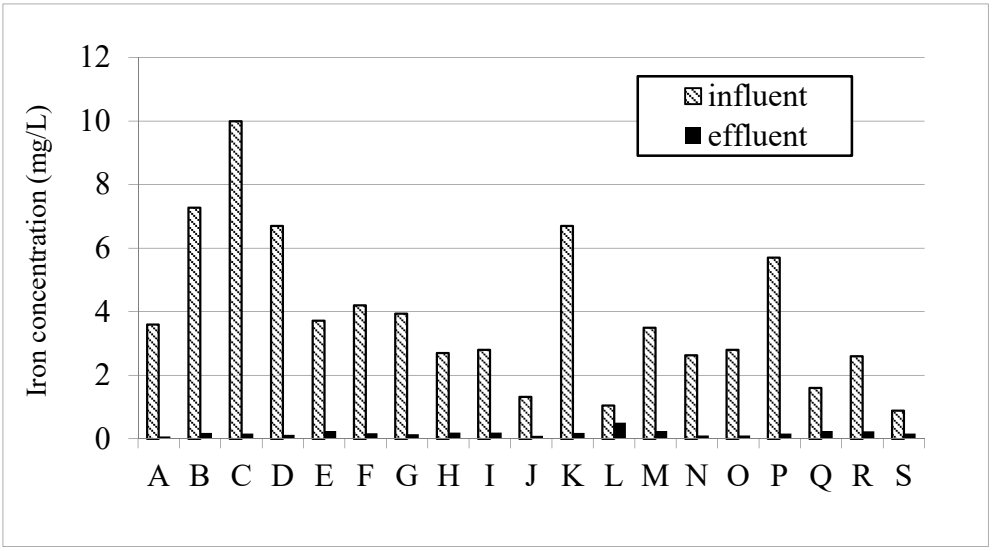


Figure 3-1: Iron concentrations in the influent and effluent of 19 STPs of Waterschap Regge & Dinkel (now: Waterschap Vechtstromen). Data from 2008 with 2-5 samples per STP.

The different sources of iron used and, most importantly, the different methods to remove phosphate explain the wide ranges of iron concentrations that are encountered in sewage sludge (Table 3-2) and sewage sludge incineration ash (Table 3-4). Overall it seems that iron is omnipresent in sewage / STPs and thus that part of the phosphate is bound to iron even in plants where no iron is dosed for phosphate removal. Thus, for all phosphate recovery technologies iron is an element that has to be dealt with. We will explain / show later how the presence of iron can also limit the recovery efficiency for struvite in EBPR plants.

Table 3-2: Iron concentrations that have been found in sewage sludge (in g/kg on a total solids basis).

Country	Lowest iron concentration	Highest iron concentration	Average iron concentration	Comments and reference
Germany	-	-	50	Average of 202 sludge samples (DWA 2005)
Sweden	4.4	150	49	Based on 47 sludge samples (Eriksson, 2001)
Netherlands	-	-	31	Average of 28% of Dutch sewage sludge (Schipper and Korving, 2009)
United States	1.6	299	-	Based on 84 biosolid samples (USEPA, 2009)
United States	3.8	84	-	Based on 41 biosolid samples (Brandt et al., 2004)
New Zealand	-	-	3-25	Median values of 4 sludge types (raw, aerobic, anaerobic, pond sediment) determined in 66 samples (Ogilvie, 1998)
Egypt	7	12	9.3	Based on 5 STPs (Lasheen and Ammar, 2009)

3.1.2 Tomorrow

The presence of iron is already today very important for sewage treatment, but iron could play an even more important role in future STPs that act as energy and phosphate factories (Jetten et al., 1997; Wilfert et al., 2015a). Iron is already widely used in energy producing STPs for combined COD and phosphate removal (Böhnke, 1977; Li, 2005; Nowak et al., 2011). Implementing anaerobic ammonium oxidation (anammox) in the main and sidestream can further increase the energy yield in such plants. Most of the sewage treatment techniques described above are already being used or tested at the pilot scale. At the moment, the only missing process (as in other conventional treatment processes) is the economic feasible recovery of phosphate and iron from sewage sludge containing iron phosphate (FeP) without incinerating the sludge. In the following section we will introduce how iron affects current and future phosphate recovery technologies. Along these effects, basic biological, geological and chemical concepts will be explained that are relevant to understand the role of iron in these processes. A combination of iron and phosphate is often considered to have a negative impact when evaluating the potential of phosphate recovery from sludge (ACHS, 2009; Egle et al., 2014; Morse et al., 1998; Römer, 2006; Samie and Römer, 2001; Schipper and Korving, 2009; Schröder et al., 2010).

3.2 Chemical phosphate removal using iron salts

3.2.1 Basic knowledge

The chemistry of iron is very diverse (Faivre, 2016; Schwertmann and Cornell, 2000b) and so are the possible reactions of iron compounds with phosphate during CPR (Smith et al., 2008). This has led to publications, related to the removal of phosphate using iron or on the recovery of phosphate from FePs, that contain unspecific expressions such as “insoluble iron phosphate”, “metal phosphates”, or “iron III phosphates precipitates”.

For CPR mainly ferrous, Fe(II) or ferric, Fe(III) iron is used. Ferric iron is usually soluble at low pH (pH < 2) only. Dissolved ferric iron rapidly forms insoluble iron oxides, oxyhydroxides, and hydroxides (collectively termed iron oxides in the following according to Schwertmann and Cornell, 2000b) as the pH increases (Figure 2-2). Dissolved Fe(II) is usually only stable at low redox potential in the absence of oxygen, its solubility is pH dependent. In the absence of oxygen, Fe(II) is more soluble over a broader pH range than Fe(III) (Figure 2-2).

Iron is usually added to sewage in STPs by dosing iron salts or iron coagulants but also via electrocoagulation (Mishima and Nakajima, 2011; WEF, 2011). The exact mechanisms through which o-P is initially removed after adding the Fe(II)/Fe(III) are not fully understood. The hydrolysis of Fe(III) in an aqueous solution is usually very rapid (Wendt von, 1973). It has been suggested that the adsorption of o-P onto iron oxides is an important or even the major mechanism involved in the removal of o-P from sewage when Fe(III) salts are used (Lu et al., 2016; Mao et al., 2016; Smith et al., 2008). The situation is even more complex when Fe(II) is added because it can be partly or fully oxidized to Fe(III). Ferrous iron is usually added to aerated stages of the STP to allow its oxidation to Fe(III). To the best of our knowledge it is not known to which degree the Fe(II) is oxidized during this process. The kinetics of Fe(II) oxidation strongly depend on the oxygen concentration and particularly on the pH (Stumm and Morgan, 1996). Half of the Fe(II) (total Fe was about 30 mg/L) in bicarbonate buffered water containing dissolved oxygen at 5 mg/L has been found to be oxidized to Fe(III) within 45 minutes at pH 7 and within 0.5 minutes at pH 8 (Ghassemi and Recht, 1971; Stumm and Morgan, 1996). The presence of other ions (e.g., sulphate or o-P), catalysts or dissolved organic matter can considerably influence the oxidation kinetics (Pham et al., 2004; Stumm and Morgan, 1996; Theis and Singer, 1974; van der Grift et al., 2016). In a full-scale STP, about 40% of the Fe(II) that was added was found to be rapidly oxidized to Fe(III) at a relatively high pH of 8.2 and high dissolved oxygen concentration of 4.6 mg/L (Thistleton et al., 2001). Accordingly, measurements on sewage sludge taken from STPs in which also Fe(II) was used to remove phosphate suggest that most of the iron in the sludge was Fe(III) (Nielsen, 1996; Rasmussen and Nielsen, 1996). In contrast, others found that a large fraction of the iron in surplus sewage sludge was present as Fe(II), in the form of the ferrous iron phosphate mineral vivianite, $Fe(II)_3[PO_4]_2 \bullet 8H_2O$ (Frossard et al., 1997; Wilfert et al., 2016).

Although often perceived differently, Fe(II) can very efficiently remove o-P. In batch tests experiments using secondary effluents Fe(II dosing to a Fe(II):P molar ratio of 1.5 showed

almost complete o-P removal (98%) at pH 8 and initial o-P concentrations of 12 mg P/L (Ghassemi and Recht, 1971). Vivianite was formed in these experiments. It seems that the efficiency at which phosphate is initially removed in an STP by adding iron is influenced by the oxygen concentration (for ferrous salts), the concentrations of competing ions, the presence of organic matter, the pH, the alkalinity, mixing intensity, the age of the iron oxide flocs, the type of phosphate present, and whether Fe(III) or Fe(II) salts are used (WEF, 2011).

Different FePs as well as iron oxides may form when an iron-based phosphate removal process is applied. Ferrous or ferric phosphate minerals, e.g., vivianite and strengite ($Fe(III)[PO_4]•2H_2O$), are examples of solid FePs that could theoretically form during CPR. However, in literature we could not find any indications for strengite formation during sewage treatment. It is also possible that FePs with impurities form. The impurities can be organic matter inclusions or originate from the co-precipitation of iron or phosphate with other elements (calcium, potassium, magnesium etc.). The initially formed FeP precipitates may alter during further sewage treatment, because of exposure to different oxidation reduction potentials (ORPs) and, therefore, to different microbial and chemical processes (Nielsen, 1996; Nielsen et al., 2005). Thus, the iron in the iron oxides or in the minerals may be oxidized or reduced and iron oxides may age, forming a more crystalline phase over time, which might lead to an increase or decrease in the strength and capacity of phosphate binding (Lu et al., 2016; Mao et al., 2016; Smith et al., 2008).

These examples show that adsorption, mineral formation, and recrystallization may occur at different stages in and on the time scale of an STP. FePs are exposed to dramatic changes in ORP but also in changes of temperature over a period of about one month in an STP with an anaerobic digestion process. Little information is available on the speciation of iron and phosphate in STP after iron has been added. These examples illustrate that phosphate can be bound to iron in a range of ways and that the amount of phosphate bound to the iron and the strength of the bonds differ significantly for different types of FeP. To determine the type of FeP as a major phosphate phase in sewage sludge is of interest as it (I) influences the bioavailability of the phosphate when sludge is used in agriculture, (II) yields thermodynamic data on FeP to allow modelling e.g. the struvite content in sewage sludge (up to now often unspecific thermodynamic data of FeP is used, Flores-Alsina et al., 2016) and (III) affects the efficiency of phosphate release from sewage sludge upon pH changes (section 3.3.4.1). Getting more insight into the types of FePs could, on the one hand, improve phosphate removal but could also lead to ideas on how to separate FePs and recover phosphate from sewage in efficient ways.

3.2.2 Vivianite as an important iron phosphate compound

Several studies showed that vivianite is present in environmental systems (Rothe et al., 2016) but also in wastewater treatment systems it can be a very important FeP (Azam and Finneran, 2014; Frossard et al., 1997; Nriagu and Moore, 1984; Singer, 1972; Wilfert et al., 2016; Zhang, 2012). Vivianite forms in the absence of oxygen in non-sulphidic systems and is very stable

over a broad pH ranges (Nriagu, 1972). It seems that vivianite is, under these conditions, more stable than most other phosphate minerals (Nriagu and Dell, 1974).

Once vivianite is formed, the complete oxidation of the vivianite Fe(II) is relatively slow (Miot et al., 2009; Roldan et al., 2002). However, limited information is available on how fast vivianite actually forms and how fast it oxidizes once it is formed in sewage systems. Due to its low solubility, quick formation and slow degradation (i.e. oxidation) it seems logically that significant amounts of phosphate are bound in vivianite in waste streams where Fe(II), phosphate, oxygen free conditions and relatively low concentrations of sulphide occur. Vivianite could form directly upon Fe(II) dosing or indirectly when Fe(III) is chemically / biologically reduced to Fe(II).

Iron reduction and thus vivianite can occur in activated sludge systems before the anaerobic digestion process (Frossard et al., 1997; Nielsen, 1996; Wilfert et al., 2016). It is hard to predict whether vivianite dominates or not in activated sludge due to manifold treatment designs and varying redox conditions. However, we believe that during anaerobic digestion, all Fe(III) is transformed to Fe(II) and that vivianite can form. When sufficient iron is dosed, the formation of vivianite during anaerobic digestion is not hampered by the formation of insoluble iron sulphide compounds (FeS_x), induced by sulphate reducing bacteria, since the supply of sulphate is limited in digesters (Chen et al., 2008; Nriagu, 1972; van den Brand et al., 2015). In digesters optimal conditions for vivianite formation / crystallization occur.

We suggest that further research should focus on quantification and characterization (e.g. size of crystals/particles, growth rates) of vivianite in STPs. It has to be evaluated how pure the vivianite in the sludge is, because vivianite is notorious to contain also impurities like heavy metals (Rothe et al., 2016; Taylor et al., 2008). Similar to struvite, also vivianite can cause problems for operators by pipe clogging especially at elevated temperatures (Marx et al., 2001; Reusser, 2009). Why not use current approaches to recover phosphate from sewage sludge in the form of struvite as an inspiration to recover phosphate in the form of vivianite from waste streams? It could be separated from waste streams or its formation could be induced by e.g. seeding. To selectively separate vivianite from waste streams technologies based on density or magnetism could be used. This route seems attractive because vivianite could result in higher phosphate recovery efficiencies than routes based on struvite formation due to a lower solubility of vivianite (section 3.3.3). Additionally, the vivianite formation obviously takes anyway place in STPs. For full recovery, the separated vivianite can be dissolved in alkaline solutions, the phosphate goes in solution whereas the Fe(II) remains in the precipitate and forms iron oxides. Other applications are also thinkable, e.g. vivianite has been used as a slow phosphate release fertilizer (Roldan et al., 2002), as a pigment (Čermáková et al., 2015), for anti-corrosion measures (Da Silva et al., 2004) and it also plays a role during the production of lithium iron phosphate batteries (Chen et al., 2011).

For recovery, processes relying on sludge incineration vivianite is not of relevance because it starts to decompose already at temperatures as low as 100 °C (Čermáková et al., 2015; Poffet,

2007) into various iron and iron phosphate phases (Čermáková et al., 2015; Rodgers and Henderson, 1986; Waerenborgh and Figueiredo, 1986). Indeed, no reports on the presence of vivianite in ash have been found.

3.3 Impact of iron on selected phosphate recovery technologies

3.3.1 Introduction

A large number of phosphate-recovery technologies have been developed (Desmidt et al., 2015; Egle et al., 2014) but only few technologies have been realized at practical scale. Iron present in sewage sludge often has an impact on phosphate recovery technologies. The impact may depend on the principle of the phosphate-recovery technology and as an example the effect on three important phosphate-recovery technologies is discussed: agricultural use of sludge, recovery as struvite from sewage sludge and recovery from sewage sludge ash.

3.3.2 Agricultural use of sewage sludge

The use of sewage sludge in agriculture is a low cost option for recycling phosphate. Sewage sludge usually needs to be hygienized before it is applied to land, and it is then often referred to as biosolids.

In 2005, 41% of all of the sewage sludge produced in the 27 EU countries was used in agriculture, 17% was composted, 19% was incinerated, 17% was landfilled, and 12% was treated in other ways (Kelessidis and Stasinakis, 2012). There is currently a trend away from landfilling and toward either incineration or applying it to agricultural land in these countries (Kelessidis and Stasinakis, 2012). Some countries, such as the Netherlands and Switzerland, chose to incinerate most of the sewage sludge, but others, including the United Kingdom and France, mainly rely on applying sewage sludge to agricultural land (Kelessidis and Stasinakis, 2012). In the US 55% of all generated biosolids were applied to soils, of which 74% was used for agricultural purposes. The remaining 45% was landfilled or incinerated (Beecher et al., 2007). In Japan, sewage sludge is not applied on agricultural land (Ohtake and Okano, 2015). These contrasts show that agricultural use of sewage sludge is very dependent on local policies.

The presence of iron in sewage sludge lowers the water solubility of phosphate in biosolids (Brandt et al., 2004; Krogstad et al., 2005; Miller and O'Connor, 2009; O'Connor et al., 2004). This is considered to be a positive effect in some cases because it may prevent the phosphate being lost in surface runoff (Elliott and O'Connor, 2007; Lu et al., 2012). However, it can also be considered a negative effect because it may limit the amount of phosphate that can directly be taken up by the plants (Kidd et al., 2007; Krogstad et al., 2005; Römer, 2006; Samie and Römer, 2001) although some of these studies used biosolids with high Fe/P ratios. Also, the relation between water solubility and bioavailability is debated and other studies show that iron bound phosphate is available to plants (Kahiluoto et al., 2015; Nanzer et al., 2014; Prochnow et al., 2008).

Regional surpluses of phosphate on agricultural lands (Macdonald et al., 2011; Schröder et al., 2011) are probably the biggest problem for practical application of biosolids. For effective use of the phosphate the biosolids should be applied in balance with the uptake of phosphate by the

crops. Manure has similar N:P ratios to sludge and is often in competition with sludge, especially in regions with animal farming. In these areas costs related to transportation of sludge to other regions with phosphate deficit are an obstacle for sludge application.

3.3.3 Direct struvite precipitation

A large number of struvite precipitation techniques are available and these techniques are often assumed to be the optimum method for recovering phosphate. Struvite precipitation is possible from sludge or water streams containing high concentrations of soluble phosphate. These are typically found when a STP combines EBPR and sludge digestion. Struvite can then be precipitated and recovered via a combination of pH increase and magnesium-addition, either directly in the sludge or in the reject water after sewage sludge dewatering.

However the market share taken by such techniques is limited because they can only be used in combination with EBPR (Table 3-1). It is often argued that CPR should be replaced by EBPR, but CPR is still widely used. The reasons for a dominance of CPR methods may be different in different countries. The investment costs are lower for CPR than for EBPR methods, and CPR processes are easier to control (Kang et al., 2008). The energy requirements are slightly higher for EBPR because it requires more pumping for internal recirculation, but life-cycle assessment studies have shown that the higher energy costs can be compensated for by the smaller amounts of chemicals used (Coats et al., 2011). It is more difficult to dewater sewage sludge produced by EBPR (Shimp et al., 2013), and dewatering requires more flocculants (Korving, 2012).

In addition to the restricted application of EBPR, recovery efficiencies for struvite are relatively low, 10-40% of the influent phosphate load (Cornel and Schaum, 2009; Egle et al., 2015; Ewert et al., 2014). For example, full-scale installations for struvite crystallization in digested sludge liquor with the Airprex system show recoveries efficiencies of 5-10% of the influent phosphate load (Ewert et al., 2014). Recovery efficiencies are slightly higher for struvite crystallization from the rejection liquid after sludge dewatering using for example Pearl, Nuresys, Phospaq, Phosphogreen or Struvia technologies. For instance, Marchi et al., 2015 report 15% recovery of the total influent phosphate in a full scale struvite recovery installation at the Nuresys plant in Leuven in Belgium. Delahaye, 2017 reports 15% recovery for a STP in Denmark using Suez' Phosphogreen technology. Higher recovery efficiencies are possible if phosphate is stripped from the activated sludge before digestion, for instance via the WASSTRIP process. Using this approach phosphate-recovery could be increased from 10% to 17% at the Durham Advanced STP in Tigard, Oregon (Cullen et al., 2013) and by Suez from 15% to 35% at the Åby STP in Denmark (Delahaye, 2017). At the STP Amersfoort the WASSTRIP approach is combined with thermal hydrolysis of the sludge before the digestion to maximize phosphate recovery via struvite precipitation. This plant intends to recover up to 40 % of all the phosphate entering the plant via the influent and external sludges digested at this central digestion facility (Lycke et al., 2017).

Background concentrations of iron and aluminium can partly explain the low recovery efficiency via struvite precipitation. Iron has a higher affinity for phosphate than magnesium

and is therefore often use to prevent struvite scaling in STPs (Baker et al., 2006; Doyle and Parsons, 2002; Mamais et al., 1994; Neethling and Benisch, 2004). Similarly, iron present in the sludge that can bind phosphate will make phosphate unavailable for recovery via struvite precipitation. Also aluminium salts have been used to prevent struvite formation (Baker et al., 2006).

Figure 3-1 illustrates the presence of iron in the influent of STPs. The majority of these plants rely on EBPR, sometimes assisted with supplemental dosage of iron salts. As discussed (section 3.1.1) the iron in the influent is concentrated in the sewage sludge and is significant in relation to influent phosphate loads. The relevance of background concentrations of iron in the influent is further illustrated by a study on the EBPR plant in Derby where vivianite scaling in an acid phase digester was related to iron concentrations of 12 mg/L in the influent of this plant (Bjorn, 2010). Also other STPs of this utility showed significant iron concentrations (3.7±0.2 mg/L) in the influent.

3.3.4 Crystallization after solubilizing phosphate from the sludge

3.3.4.1 Inducing pH changes

3.3.4.1.1 General remarks

Sewage and sewage sludge is usually at pH 6–8 (Tchobanoglous et al., 2013). At very high (>12) and low pH (<2), bulk phosphate should be solubilized from most FePs, i.e. irrespective if phosphate is adsorbed to iron oxides or if it is present in a mineral form. It seems logical that the amount of base or acid that needs to be invested to release all phosphate from iron also depends on the type of FeP. Usually, in literature pH equal or above 12 are used for desorption of adsorbed o-P. However, varying levels of o-P desorption are achieved. It seems that the presence of other elements (e.g. calcium, aluminium, magnesium) can affect the net phosphate release from the sewage sludge at certain pH levels due to re-precipitation of the phosphate. In case phosphate is adsorbed to iron oxides, the pH affects o-P adsorption by affecting the charge on the adsorbent as well as the o-P ion (Stumm et al., 1992). As the pH increases beyond the PZC of the iron oxide, electrostatic repulsion leads to a decrease in o-P adsorption. Additionally, ligand exchange (by OH) is a mechanism to release adsorbed o-P (Yoon et al., 2014). If vivianite is present, a pH of around 12 should theoretically dissolve most phosphate from vivianite. At this pH, where o-P tends to desorb from adsorbents, iron oxides are formed (Nriagu, 1972).

3.3.4.1.2 Acidification

Strong acidification will dissolve and release phosphate and Fe(III) from iron oxides and iron phosphate minerals thereby mobilizing most of the solid phosphate in sludge and ash samples. But at low pH also heavy metals and other metals can go in solution. Several approaches have been used to leach phosphate from the sludge and thus make more of the phosphate available for recovery. The Seaborne and Stuttgart and processes are examples of a strategy where the sludge is acidified to leach the phosphate from the sludge to be able to recover phosphate as struvite. The Seaborne process was operated at demonstration scale for several years at the STP

Gifhorn, Germany (Hermanussen et al., 2012). The initial intention was to acidify the sludge to pH=2 to release phosphate and heavy metals from the sludge. After dewatering the pH of the water phase was increased, followed by a heavy metals removal step using sulphide and a phosphate recovery step yielding struvite. During the operation of the plant the pH of the leaching phase was first increased to 3 and later to between 5 and 5.5 to minimize acid consumption and to reduce the amount of flocculation chemicals during the dewatering phase. The Seaborne plant treated sewage sludge from the STP Gifhorn where iron salts were used to support EBPR. Table 3-3 shows that most of the phosphate could be released if the sludge was acidified to a pH of 2 or 3. Also most of iron was solubilized.

Table 3-3: Release of phosphate, iron and aluminium as a function of pH for sludge from the STP Gifhorn (Hermanussen et al., 2012).

pH	Solubilisation (% of total)		
	Phosphate	Iron	Aluminium
4	55	40	0
3	70	70	25
2	90	95	85

A subsequent pH increase to recover phosphate as struvite after magnesium addition would then also lead to re-precipitation of FePs (at pH 6). The recovered struvite therefore contained significant amounts of iron (iron concentration was 63 g/kg TS whereas the magnesium concentration was 19 g/kg). Therefore, an alternative approach was tested where the iron was first precipitated with sulphides. Experiments showed that the iron could be precipitated with sulphide at pH 5.5 with a sulphide dosage of 0.8-1.2 mol sulphide per mol iron. Overall 52-74% of all the phosphate could be recovered in this process combining acidification followed by iron removal using sulphide (Hermanussen et al., 2012).

Also in the Stuttgart process digested sludge is acidified to release phosphate. This process was tested on a pilot scale at the STP Offenburg, Germany. This STP uses iron salts to remove phosphate. Acidification to pH 4-5 solubilized about 60-70% of all phosphate with solubilisation efficiencies varying between 38-84% between batches (Antakyali et al., 2013). After a solid-liquid separation, citrate is added to complex iron and other metals salts (ratio 1-1.5 mol/mol) in solution and struvite is then precipitated at pH 8.5.

The Krepro process was operated at full scale at the Helsingborg STP in Sweden (Karlsson, 2001; Odegaard et al., 2002). In this process dewatered iron containing sewage sludge was acidified to a pH between 1-3 to leach phosphate, heavy metals and iron into the water phase. This step was followed by a thermal hydrolysis to release organic bound phosphate and to improve the dewaterability of the sludge. The acidified and hydrolysed sludge was then dewatered producing a relatively dry dewatered sludge cake (ca. 35% dry matter) with low concentrations of heavy metals, iron and phosphate. A ferric phosphate precipitate containing about 75% of all phosphate from the feed material was recovered from the liquid phase through a pH-increase. Heavy metals could subsequently be removed from the liquid phase through precipitation with sulphides or as hydroxides after further pH-increase. The remaining soluble

iron could be returned to the STP for precipitation of phosphate or could be recovered as iron oxides through further pH adjustment. Pot and field trials were performed with the recovered FeP. Although the phosphate was not water-soluble growth yields were only slightly lower (4-5%) compared to application of mineral fertilizer.

3.3.4.1.3 Alkaline treatment

Alkaline treatment of sludge is another approach to release phosphate from iron containing sludge. An alkaline treatment has the advantage over an acidic treatment that less metals will dissolve. After solid liquid separation phosphate can be precipitated from the liquid phase to produce calcium phosphate as a valuable recovery product that can be directly used in the fertilizer industry. However, controversies about the solubility of FeP at alkaline pH and its efficiency to release phosphate from sewage sludge exist. Sano et al., 2012 describe phosphate recovery from FeP containing sewage sludge. The phosphate in this sludge was precipitated by slowly bringing Fe(II) into solution using electrolysis. An alkaline pH (between 13 and 14) resulted in the extraction of 92% of all phosphate compared to 70% trials in which an acid was used. A more recent study of Xu et al., 2015 investigated the release of phosphate from iron phosphate under alkaline conditions. The waste activated sludge was taken from a sewage treatment process with EBPR. The authors state that phosphate was liberated from the FeOOH-P by ion exchange mechanisms at pH 11, the iron content of the sludge was not reported. Fischer et al., 2015 used dewatered FeP containing digested sludge. They used a microbial electrolysis cell to increase the pH of the sludge to 12.7. At this pH they reported a release of 66.7% of the phosphate, but also yields up to 95% were observed. At pH higher than 12.7 a drop in phosphate release was detected. Maier et al., 2005 studied phosphate release from FeP rich digested sludge at alkaline and acidic pH to produce struvite. Tests with iron containing sludge showed that under acidic conditions at pH 2 the total phosphate release was higher than 85% but in alkaline conditions at pH 13 only 13% of total phosphate could be released. Also Cornel et al., 2004 could only release up to 28% of the phosphate in iron containing sludge with 1M NaOH at unknown pH. In general, it appears that under acidic conditions more phosphate is released from iron containing sludge compared to alkaline conditions. Whereas more phosphate was released under alkaline conditions from aluminium-rich sludge (46–56% extracted at pH 13, Maier et al., 2005) and ash (27–54% extracted using 1 M NaOH; Cornel et al., 2004).

3.3.4.2 Iron reduction and sulphide induced phosphate release

Iron reducing bacteria are present and active in activated sludge systems (Nielsen, 1996). They can reduce Fe(III) in iron oxides or iron phosphate minerals, thereby mobilizing phosphate (Heiberg et al., 2012; Patrick et al., 1973; Peretyazhko and Sposito, 2005). However, it was also shown that Fe(II) compounds that are formed could, in the absence of sulphate, bind most of the released phosphate (Azam and Finneran, 2014; Borch and Fendorf, 2007; Cheng et al., 2015; Emerson et al., 2012). Vivianite can precipitate relatively quick, relative to SRTs in STPs (Azam and Finneran, 2014; Roldan et al., 2002). Thus, the microbial reduction of Fe(III) in anaerobic treatment stages could lead to the initial release of phosphate from FeP. Ultimately, the reduction of Fe(III) could even act as a phosphate sink, which is suggested by the higher

phosphate content (relative to iron) in vivianite (Fe:P molar ratio of 1.5) compared to ferric oxide phosphate precipitates in STPs which has been reported as high as 2.5 (Luedecke et al., 1989). At pH values that are encountered in STPs, even freshly formed precipitates showed molar Fe:P ratios greater than 1 (Fulazzaky et al., 2014; Smith et al., 2008).

Fe(III) reduction is not necessarily a reason for phosphate release from iron. In the presence of sulphide, iron is not able to bind phosphate any longer. Sulphide is not only capable of reducing iron, it can also form rather insoluble FeS_x. It has been shown that this could be the main mechanism through which iron-bound phosphate is released from sediments (Caraco et al., 1989; Roden and Edmonds, 1997; Smolders et al., 2006). Consequently, sulphide has been proposed to solubilize phosphate from FeP sludge. Sulphide was found to release 75% of the phosphate into solution at pH 4 from sludge collected at a water production plant (Likosova et al., 2013). Similarly, 43% of the total phosphate was found to be released from sewage sludge pre-coagulated with iron by adding sulphide (Kato et al., 2006). In another study, phosphate in sludge liquor was precipitated using iron sulphate salts. The sludge was incubated under anaerobic conditions to allow microbial sulphate reduction (Suschka et al., 2001). Subsequently, phosphate was released stoichiometrically (1.5 moles of phosphate released per mole of sulphide) over a timescale of days, without gaseous hydrogen sulphide being formed. The efficiency of the total phosphate release by sulphide was not mentioned.

When phosphate is solubilized from sewage sludge it could also remain part of the precipitate when it is e.g. adsorbed by other phases, precipitates with dissolved elements that occur in the sludge liquor or when it re-precipitates with other metals from the sludge solids. Thus, it is possible that the mobilized phosphate cascades from one solid phosphate phase to the next while the order of formed phases is determined by the solubility and the kinetics of precipitation. Similar observations were made for sediments when released phosphate was adsorbed to calcium, silicon or aluminium phases (Boström and Pettersson, 1982; Richardson, 1985; Roden and Edmonds, 1997). In other study on sediments a huge excess supply of sulphide was necessary to release substantial amounts of phosphate from sediments (Golterman, 1995).

3.3.5 Recovery from sewage sludge ash

A significant proportion of the sewage sludge produced in countries like The Netherlands, Switzerland and Germany is incinerated in dedicated sewage sludge incinerators. These mono-incinerators produce a phosphate-rich ash from which phosphate can be recovered. Thermo-chemical and wet-chemical technologies have been developed to recover phosphate from this ash (Cornel and Schaum, 2009; Desmidt et al., 2015; Donatello and Cheeseman, 2013).

Table 3-4 shows that most ashes contain a significant amount of iron in relation to the phosphate content, ranging from 0.2 – 0.7 mol Fe/mol P. This illustrates the fact that iron is omnipresent in sewage sludge as discussed in section 3.1. The ash is a complex mixture of amorphous (40-70%) and crystalline components (Cyr et al., 2007). Most researchers report whitlocktite as the most common phosphate phase in the ash (Adam et al., 2009; Cyr et al., 2007; Guedes et al., 2016; Magdziarz et al., 2016; Petzet et al., 2012). Whitlocktite is a complex phosphate

containing mineral that can contain calcium, magnesium and iron in varying ratios in the crystal lattice. Next to this mineral, aluminium phosphates are the second most reported phosphate bearing phase (Biswas et al., 2009; Petzet et al., 2012). Iron may also be present as hematite or even magnetite (Adam et al., 2009; Biswas et al., 2009; Cyr et al., 2007; Guedes et al., 2016; Magdziarz et al., 2016).

Table 3-4: Typical content for iron, phosphate, aluminium and calcium in various ashes.

Reference	Remark	Country	Fe (g/ kg ds)	Al (g/ kg ds)	Ca (g/ kg ds)	P (g /kg ds)	Fe/P (mol)	Al/P (mol)	Ca/P (mol)
Cyr et al. 2007		France	33	67	147	65	0.28	1.2	1.8
Cyr et al. 2007	> 20 ashes	Various	64	14	106	51	0.70	0,3	1,6
Geraarts et al. 2007	Ash from 25% of Dutch sewage sludge	NL	88	55	152	84	0.58	1.0	1.4
	Low-iron ash	NL	40	63	136	92	0.24	1.1	1.1
Adam et al. 2009	7 ashes	Ger / NL	91	13	108	92	0.55	0.2	0.9
Biswas et al. 2009	1 ash	Jap	52	60	57	88	0.33	1.1	0.5
Petzet et al. 2012	4 ashes	Ger	66	68	127	88	0.40	1.2	1.1
Ottosen et al. 2013	Al-rich ash	DK	70	67		70	0.12	1.2	
	Iron-rich ash	DK	98	20		98	0.33	0.4	
Magdiarz et al. 2016	4 ashes	Pol	91	41	177	104	0.49	0.7	1.3

Wet-chemical approaches (Ecophos, Leachphos, Tetraphos, Easymining) leach phosphate from the ash through acidic dissolution (Egle et al., 2015). Typically phosphate starts being released from pH 3-4 on to reach nearly 90% release at pH 2 (Guedes et al., 2016; Ottosen et al., 2013; Petzet et al., 2012). Down to pH 2 leaching of iron from the ash is still minimal. Aluminium is released in a similar pH range as phosphate. Biswas et al., 2009 report up to 40% leaching of iron from the ash in 1 M sulphuric acid (pH not reported) but used relatively high solid to liquid ratios. Both Cornel et al., 2004 and Ottosen et al., 2013 report a lower acid consumption for high iron containing ashes compared to ashes with a relatively high aluminium content (ca. 30-40% less based on Cornel et al., 2004). The dissolution of aluminium is a problem for the subsequent recovery of phosphate from the solution, as the aluminium will re-precipitate back to aluminium phosphate when the pH is increased. In this approach aluminium should therefore first be removed from the eluate to be able to get a pure calcium phosphate product. Petzet et

al., 2012 proposed an alternative acid-alkaline approach. Heavy metals may leach easier from ashes with higher iron content (Ottosen et al., 2013).

Phosphate in sewage sludge ash can also be made water soluble via dry acidulation of the ash (Langeveld and Wolde, 2013b; Weigand et al., 2011). Langeveld and Wolde, 2013b report that ashes have a negative effect on the solubilisation of phosphate when added as an additional raw material to their regular triple superphosphate production from phosphate rock. Higher iron concentrations gave a bigger negative effect.

Significant amounts of phosphate have been recycled from ash with a low iron content using a thermal process used to produce white phosphorus (Schipper and Korving, 2009). To be suitable for this process the ash had to have a Fe/P molar ratio of less than 0.2 to minimize the amount of ferroP by-products produced (Geraarts et al., 2007; Schipper and Korving, 2009). The only European company producing white phosphorus closed down in 2012 and therefore is process cannot be used anymore. In the European Recophos project a new concept has been developed based on this process that can also treat high iron containing ashes. Through a novel furnace design the gaseous phosphorus can exit the furnace quicker, which should result in a lower formation of ferroP by-products (Rapf et al., 2012).

Furthermore, thermochemical treatment of sewage sludge ash can remove heavy metals and increase the bioavailability of the phosphate in the ash (Adam et al., 2009), and a pilot plant using this process was operated in Leoben, Austria (Hermann, 2011). The phosphate in the treated ash treated was bioavailable in acidic and neutral soils even though the ash contained significant concentrations of iron (Nanzer et al., 2014).

3.4 Summary and outlook

Iron is an element that is omnipresent in STPs. It has many useful properties that can be used during sewage management and thus iron is very often required for modern and successful sewage treatment. Even without iron dosing in STPs, iron can enter STPs in substantial amounts due to external iron sources that are outside of its boundaries. Iron is relatively insoluble and has a high affinity towards phosphate. Thus, the iron mainly ends up in the sewage sludge where it can bind a significant part of the total phosphate. This suggests that all phosphate recovery technologies have to deal with iron bound phosphate. This chapter shows that the presence of iron for phosphate recovery technologies has positive, negative and sometimes indistinct effects. For instance, recovery technologies that make use of a wet digestion to recover phosphate from ash showed lower acid consumptions for iron rich than for aluminium rich ash. Additionally, recovery technologies related to vivianite offer, theoretically, high efficient phosphate recovery. Vivianite based recovery routes deserve more attention than they have had until now. The presence of iron can reduce the efficiency of phosphate recovery technologies, e.g. when recovery of struvite is intended in EBPR plants and background iron will take away phosphate from the proposed recovery product struvite because of the higher affinity of iron for phosphate. Also some technologies for recovery of phosphate from ash show a lower performance in the presence of iron, like in the case of dry acidulation or when ash is used as

raw material for white phosphate production. In some instances the role of iron on phosphate recovery is indifferent, for example, thermochemical treatment of sewage sludge ash allows high amounts of iron and the process is insensitive to the iron concentration in the ash. The role of iron is often also inconclusive. For instance, the lower solubility of phosphate bound to iron in sludge that is applied on agricultural land is sometimes considered as positive and sometimes as negative. Due to the omnipresence of iron in sewage related waste streams and due to the inconsistent role of iron for individual phosphate recovery technologies we suggest that the role of iron in a waste stream should be evaluated before a phosphate recovery technology is implemented. If necessary, the treatment strategies for the waste stream can be adjusted to improve phosphate recovery. In any case developers should be aware of the potential and obstacles the iron and phosphate chemistry offers in relation to phosphate recovery.

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Chapter 4: Vivianite as an important iron phosphate precipitate in sewage treatment plants



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4.1 Introduction

Phosphorus is an essential element for all life. It is often a limiting nutrient for crops and thus a crucial part of fertilizers. Currently, the use of phosphorus is not sustainable and its supply is not guaranteed in the future: (I) Phosphate rock reservoirs, the main source of phosphorus for fertilizers, are depleting (Scholz and Wellmer, 2016; Walan et al., 2014), (II) these reservoirs are located in a few countries (De Ridder et al., 2012), (III) for current phosphorus applications and depletions regional imbalances exist (Macdonald et al., 2011; van Dijk et al., 2016) and (IV) phosphorus surpluses cause eutrophication in surface waters (Carpenter, 2008). The recovery of phosphorus from secondary resources would help to make its use in our society circular and more sustainable (Carpenter and Bennett, 2011; Childers et al., 2011).

Sewage is an important secondary source for phosphorus (van Dijk et al., 2016). In sewage treatment plants (STPs), phosphorus is typically removed to diminish eutrophication in surface waters by chemical phosphorus removal (CPR) or enhanced biological phosphorus removal (EPBR). In both cases, phosphorus is concentrated in the sewage sludge. Iron dosing for CPR is efficient, simple and cheap (Geraarts et al., 2007; Paul et al., 2001; Thomas, 1965; WEF, 2011). Future energy producing STPs rely on chemical phosphorus and chemical oxygen demand (COD) removal (Böhnke, 1977; Wilfert et al., 2015a). Additionally, iron is commonly applied in modern sewage treatment also for other reasons than CPR. Ferric, Fe(III) and ferrous, Fe(II) iron salts are dosed as flocculants to remove COD (Li, 2005), to prevent the emission of hydrogen sulphide (H_2S) in sewer systems and digesters (Hvitved-Jacobsen et al., 2013; Nielsen et al., 2005) and to improve sludge dewatering (Higgins and Murthy, 2006). Additionally, iron may originate from groundwater intrusion into the sewer systems (Hvitved-Jacobsen et al., 2013; Kracht et al., 2007). Thus, in most STPs, part of the phosphorus will be bound to iron. An economic feasible recovery of phosphorus from sewage sludge containing iron phosphorus compounds (FeP), without sludge incineration, is a technological challenge that remains unsolved, also due to scarce information on FeP mineralogy in STPs (Wilfert et al. 2015).

The initial reactions, after Fe(III) or Fe(II) addition to sewage and the subsequent removal of phosphorus are complex (El Samrani et al., 2004; Luedecke et al., 1989; Smith et al., 2008; Takacs et al., 2006). These reactions are important as they drive primary phosphorus removal from sewage by bringing phosphorus from the liquid to the solid phase. In STPs, the solid retention time (SRT) can be a few hours, as in the A-stage of AB-processes (Böhnke, 1977; Böhnke et al., 1997), but it is usually on the time scale of 5-20 days when the conventional activated sludge process is applied (Tchobanoglous et al., 2013). In those processes, alternating redox conditions are applied to achieve COD and nitrogen removal. Hence, once formed the initial FeP may change due to oxidation of Fe(II) or reduction of Fe(III) respectively (Nielsen, 1996; Nielsen et al., 2005; Nielsen and Nielsen, 1998; Rasmussen and Nielsen, 1996) or due to aging effects (Recht and Ghassemi, 1970b; Szabo et al., 2008). Most likely, the FeP, that end up in the surplus sludge and that determine the phosphorus removal efficiency of STPs, differ from the initial precipitates.

Several researchers reported the ferrous iron phosphate mineral vivianite ($Fe(II)_3[PO_4]_2 \cdot 8H_2O$) in surplus sludge and anaerobically digested sludge (Frossard et al., 1997; Ghassemi and Recht, 1971; Seitz et al., 1973; Singer, 1972). Frossard et al., 1997 were able to quantify vivianite in sewage sludge using Mössbauer spectroscopy even though the sludge samples in this study were exposed to air. This could have resulted in full/partial oxidation of Fe(II) compounds and partial transformation of vivianite to amorphous FeP (Roldan et al., 2002) or to other changes of the phosphorus fractions (Kraal et al., 2009). Additionally, all Mössbauer measurements were done at room temperature (300 K). Complex samples should ideally be measured at lower temperatures (e.g. 4 K) as well, to reveal unambiguously the spectral contributions and magnetic properties of the iron phases. (Murad and Cashion, 2004).

We have investigated two STPs, with different treatment strategies to determine the fate of iron and FeP during treatment. The STP Leeuwarden applies EBPR, additionally respectively Fe(II) or Fe(III) are dosed in two different treatment lines. The STP Nieuwveer uses the AB technology (Böhnke et al., 1997; De Graaff et al., 2015), here Fe(II) is dosed. AB-plants in combination with cold anammox have the potential to be energy factories (Jetten et al., 1997; Siegrist et al., 2008).

The fate of iron and FeP was evaluated by various measurements on the liquid and solid fractions of the sewage (sludge) at different locations in the treatment line. Mössbauer spectroscopy (qualitative and quantitative analyses of iron compounds), XRD (semi-quantitative analyses of all crystalline material) and SEM-EDX (particle morphology and elemental composition) were used to characterize the solid fractions. Mass balances for phosphorus and iron helped to identify the significance of different sources (influent, external sludge, iron dosing) and sinks (effluent, sludge disposal) for these elements. Mössbauer spectroscopy and XRD were used to estimate phosphorus bound in vivianite and sulphide extraction was used to quantify phosphorus bound to iron. Thereby, the phosphorus recovery potential of a technology that targets specifically on FeP was determined.

Identifying the forms of FeP in activated sludge would help to obtain thermodynamic (e.g. equilibrium concentrations) and stoichiometric (molar Fe:P ratios) information that is necessary to develop technologies to recover phosphorus from FeP. Although, in literature, some indications for vivianite formation as major phosphorus compound during sewage treatment can be found, the role of vivianite and its importance has been neglected, the reason why this study was carried out.

4.2 Material and Methods

4.2.1 STPs and sampling

In the AB plant Nieuwveer (influent: 75706 m^3 d^{-1} in 2014), Fe(II) is added in the aerated (≈0.3 mg dissolved oxygen (DO) L^{-1}) A-stage for phosphorus and COD removal. SRTs are 15 hours in the A-stage, 16 days in the B-stage (DO in aerated sections ≈1.8 mg DO L^{-1}) and 25 days during anaerobic digestion. In the EBPR plant Leeuwarden (38,000 m^3 d^{-1} in 2014), the influent is split in two treatment lines (60% of the sewage goes to Line 1). Besides for CPR,

iron is dosed to prevent H_2S emissions into the biogas during anaerobic digestion. In Line 1, Fe(III) is dosed and in Line 2 Fe(II) is dosed in the nitrification zone (≈1.5 mg DO L^{-1}). SRTs before digestion are around 15 days (50% in the aerated zone) and during anaerobic digestion around 42 days. The digesters of both STPs, receive external sludge which accounts for about 30% (Nieuwveer) and about 25% (Leeuwarden) of the total digested sludge. At both locations, samples were taken to analyse the composition of the sewage (sludge). From these measurements (Table S 4-2 & Table S 4-3) iron and phosphorus mass balances were calculated. To calculate iron and phosphorus loads, average daily flow rates of the sampling days were used. Samples were taken between December 2014 and March 2015, after a period of 48 h without precipitation. The STP Leeuwarden was sampled three times. Results reported in Table S 4-2 and for the mass balances are average values of the triplicate measurements and of the daily loads of these samplings. The STP Nieuwveer was sampled once in March 2015.

Samples were stored and transported in cooling boxes on ice to reduce microbial activity. Sample processing started 1 h (Leeuwarden) and 3 h (Nieuwveer) after sampling. Sample drying started latest 8 h after sampling and was completed within 24 h. Sampling and sample processing were done under anaerobic conditions to prevent oxidation and degassing of samples. Sewage was collected; using syringes with attached tubing that were washed several times with sewage. Sewage sludge was taken from valves using a funnel with attached tubing. Samples were then filled in serum bottles. To rinse bottles, about three times their volume was flowed through the bottle by inserting the end of the tubing to the bottom of the bottle. Then the bottles were sealed with butyl rubber stoppers (referred to as anaerobic samples hereafter). With these samples the composition of the liquid phase was determined and material for solid analyses was obtained. For total solids (TS), volatile solids (VS) and to determine the total elemental composition of the sewage (sludge), separate samples, without special pre-cautions to prevent sample oxidation, were taken (hereafter, referred to as mass balance (MB) samples). Separate sampling was considered to be necessary as the TS content of the anaerobic samples could change due to rinsing of serum bottles.

In Nieuwveer, the influent sample was a mixture of raw influent and recirculated effluent (40% of the effluent is recirculated). For the mass balances, the iron and phosphorus concentrations of the raw effluent were calculated. The external sludge sample was taken from a pre-storage tank, and contained an unknown mixture of external sludge. In Leeuwarden, phosphorus loads from external sludge were below the detection limit and had to be calculated from the difference in phosphorus loads before and after digestion.

4.2.2 Analyses

Oxidation-Reduction Potential (ORP), pH and conductivity were measured potentiometrically in the plants. Total elemental composition of MB samples were determined after microwave assisted acid digestion (HNO_3=69%, 15 min, 180 °C) followed by ICP-OES. Total solids and VS were measured according to standard methods (APHA, AWWA, WEF, 1998). For total alkalinity measurements, 10 mL MB sample was titrated to pH=4.5 with 0.1 N HCl (APHA, AWWA, WEF, 1998).

The anaerobic samples were transferred into plastic centrifuge tubes inside an anaerobic glovebox (95% N_2/5 % H_2, O_2<10 ppm) and centrifuged (15 min, 3200 G). Dissolved elemental compositions (ICP-OES), dissolved anions (IC) and dissolved organic carbon, DOC (LC-OCD) were determined after filtration of the supernatant (0.45 µm) inside the glovebox. Dissolved Fe(II)/Fe(III) was determined in the filtrate using the ferrozine method according to Viollier et al., 2000. In short, an appropriate sample volume was added to 100 µL ferrozine reagent and made up to a total volume of 1100 µL using Milli-Q water. After 15 minutes the absorbance of the ferrozine-Fe(II) complex was recorded. Subsequently, to reduce all Fe(III) to Fe(II), 150 µL of a 1.4 mol L^{-1} hydroxylamine solution was added to 800 µL of this solution. The reduction time was 12 h (30 ºC) to make sure that organic complexed Fe(III) was completely reduced (Rasmussen and Nielsen, 1996; Verschoor and Molot, 2013). Eventually, 50 µL of a 10 mol L^{-1} ammonium acetate buffer solution was added and the absorbance was again measured. With these information the Fe(II) and Fe(III) concentration can be calculated. All ferrozine measurements were confirmed by measuring total iron by ICP-OES. Additionally, Fe(II)/Fe(III) stock solutions were added to filtrates to test the reliability of the photometric measurements (Table 4-1). For sulphide (S^{2-}) measurements, samples were filtered inside the glovebox into a zinc acetate solution (0.8 M), stored in the dark and measured after 24 h by the methylene blue method (Cline, 1969).

Solid material was derived from centrifuge pellets of the anaerobic samples. Inside the glovebox, pellets were finely spread on glass plates, dried (25 °C, 24 h, in the dark) and grinded using a mortar and pestle. Vivianite can be found when samples are dried at room temperature, even in the presence of oxygen. Higher temperatures for sample drying should be avoided. Above 70 °C, in the presence oxygen, vivianite is transformed within hours into an amorphous iron phosphate compound (Čermáková et al., 2015). Thus, in such sludge samples, vivianite disappears (Poffet, 2007).

Samples for XRD analyses were filled in glass capillaries and sealed first with modelling clay and then superglue. Right before analyses, glass capillaries were sealed using a burner. The measurements were done on a PANalytical X´Pert PRO diffractometer with Cu-Ka radiation (5-80 º2θ, step size 0.008º). The results from XRD analyses were made semi-quantitative by determining the amorphous and crystalline peak area of the spectra (Origin Pro 9). This allows the determination of the degree of crystallinity and thus of the total mineral share of the sample. All samples that were analysed by Mössbauer spectroscopy were also analysed by XRD. In addition, two samples that were sampled in the aerated treatment lines (referred to as A-stage and Line 2 activated sludge samples) were analysed using XRD.

For Mössbauer analyses, samples were filled in plastic rings, sealed with Kapton tape and super glue and then wrapped in parafilm. It was expected that considerable amounts of phosphorus are bound in vivianite, thus a vivianite standard was prepared according to Roldan et al., 2002. Transmission ^{57}Fe Mössbauer spectra were collected at 4 and 300 K with conventional constant-acceleration and sinusoidal velocity spectrometers using a ^{57}Co(Rh) source. Velocity calibration was carried out using an α-Fe foil. The Mössbauer spectra were fitted using

Mosswinn 4.0 (Klencsár, 1997). Morphology and elemental compositions of sludge particles in the grinded solids was also analysed by SEM-EDX. Samples for SEM-EDX were exposed to air during measurements.

Extractability of iron in digested sludge was investigated using water, to extract water soluble iron (pH=7, Wolf et al., 2009). Na-pyrophosphate solution (0.1 mol L^{-1}, pH=9.5) was used to extract and quantify organic bound iron. Pyrophosphate was used to extract organic bound iron and iron minerals mainly in soil but also from sewage sludge, vivianite was partially dissolved with this extract (Carliell-Marquet et al., 2009; McKeague, 1967; van Hullebusch et al., 2005). With pyrophosphate extraction no distinction between Fe(II)/Fe(III) could be made. Ammonium oxalate (0.2 mol L^{-1} NH_4-oxalate, pH=3) extracts poorly crystalline iron, it was used to determine Fe(II)/Fe(III) in activated sludge before (Rasmussen and Nielsen, 1996). Each extraction was done in separate butyl rubber stoppered serum bottles, the extracts were added to wet sludge (n=3). Oxygen in the extracts was removed using headspace gas exchange equipment with a gas mixture containing 70% N_2 and 30% CO_2 in 5 cycles. The extract:TS ratios were 100:1 for H_2O and pyrophosphate and 1000:1 for oxalate. All samples were shaken in the dark (16 h, 30 °C, 100 rpm) before analysing iron in the filtered (0.45 µm) but not centrifuged extracts.

4.2.3 Estimate phosphorus bound to iron

Phosphorus bound in vivianite was calculated from results of semi-quantitative XRD and Mössbauer spectroscopy. Additionally, to determine sulphide extractable phosphorus, 0.5 molar Na_2S solution was added to 2 L digested sludge (molar Fe:P=0.55) and surplus sludge from Line 1 (molar Fe:P=0.25) from Leeuwarden and to digested sludge from Nieuwveer (molar Fe:P =0.73) in molar ratios S^{2-}:Fe of 1.5. These samples were taken several months before/after the other samples. For Leeuwarden, molar Fe:P were very similar to the sludge used for other analyses, digested sludge showed a Fe:P=0.56 and Line 1 a Fe:P=0.28 but for Nieuwveer the sludge for the sulphide experiments had a lower Fe:P (0.73 vs 0.89). It was assumed that sulphide extracts specifically phosphorus bound to FeP (Kato et al., 2006). The experiments were done in a gastight reactor with pH control (pH=7.5) with a reaction time of at least 24 h. Samples from the reactor were taken using N_2 flushed syringes, filled in N_2 rinsed plastic centrifuge tubes under a stream of N_2 and centrifuged (15 min, 3200 G). Subsequently, sulphide, o-P and the elemental composition were determined in samples that were filtered using N_2 flushed syringes and filters (0.45 µm). At the end of these experiments at least 1 mmol sulphide L^{-1} was still in solution indicating that the extraction was not sulphide limited. The maximum amounts of phosphorus that could be bound to iron, magnesium and aluminium were quantified by using the elemental composition of the TS (Table S 4-2 & Table S 4-3). For these calculations it was assumed that all solid magnesium is present as struvite (molar Mg:P =1), all iron as vivianite (molar Fe:P=1.5) and aluminium as a precipitate with a molar Al:P of 1.5 (Hsu, 1976).

4.3 Results

4.3.1 Mass balances

In the STP Leeuwarden, mass balances showed, that the influent iron load equals approximately the dosed iron (Figure 4-1A). The effluent load was approximately 15% of the influent iron and 10% of the influent phosphorus. The solid molar Fe:P ratio almost doubles from 0.33 before to 0.57 after anaerobic digestion due to digestion of external sludge with a high iron (8.4 g Fe kg^{-1} sludge) and low phosphorus (not detectable) content. About 95% of the external sludge originates from two cheese factories which use Fe(III) as flocculent.

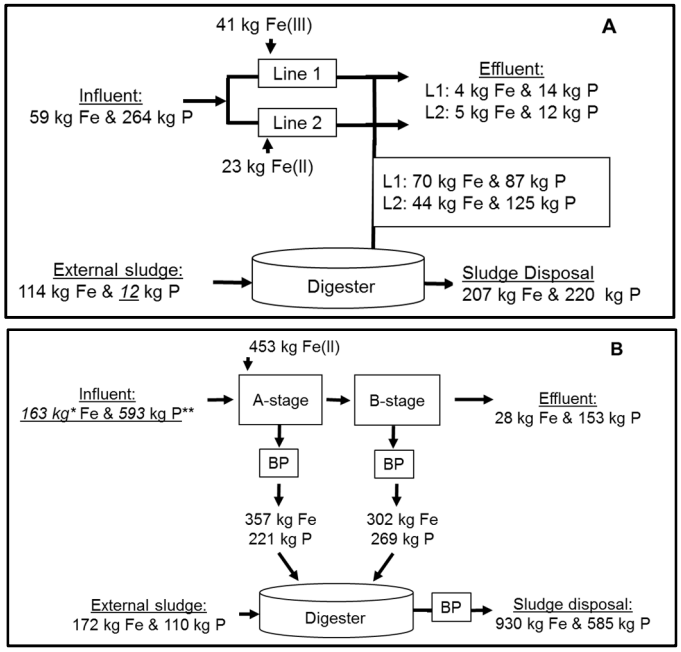


Figure 4-1: Daily mass balances for iron and phosphorus in the STPs Leeuwarden (A) and Nieuwveer (B). Underlined numbers were calculated (BP = belt press).

For Nieuwveer, the mass balance showed that, dosed iron is about three times the iron entering via the influent (Figure 4-1B). The effluent load was 15% of the influent iron and 25% of the influent phosphorus. The iron and phosphorus loads from the A and B stage to the anaerobic digestion are similar. During digestion, the molar Fe:P ratio increased, due to external sludge, from 0.76 to 0.89.

The mass balances were established by a single sampling campaign in Nieuwveer and three sampling campaigns in Leeuwarden. It was not intended to make a comprehensive mass balance which would require several samplings throughout the year. The mass balance served to identify main iron sources and sinks in the STPs. For Nieuwveer, the calculated phosphorus loads of the influent, effluent and into the digester were about 20% higher, the external sludge phosphorus input about 20% lower when compared to the average yearly phosphorus loads for 2014 which were determined from daily phosphorus measurements on pooled samples (number from yearly balance/from our balance): influent (460 vs 593 kg P d^{-1}), effluent (118 vs 153 kg P d^{-1}), external sludge (139 vs 110 kg P d^{-1}) and to the digester (411 vs 490 kg P d^{-1}). Since loads (except for

the external sludge) were consistently higher for our measurements it can be assumed that patterns of iron and phosphorus loads represent typical situations for the STP. For Leeuwarden, average yearly phosphorus loads in 2014 in the influent were also about 20% higher (318 vs 264 kg P d^{-1}) and almost the same for the effluent (28 vs 26 kg P d^{-1}). Phosphorus flows into the digester are not regularly determined in Leeuwarden.

The maximum gap for the mass balance was about 15% for iron in the STP Nieuwveer, mainly caused by an excess of iron leaving the digester. In contrast, the gap in the phosphorus mass balance was only 5%. The gap in the iron balance is most likely due to the lack of a representative external sludge sample. In Nieuwveer, external sludge is delivered in irregular intervals from various STPs applying CPR (Al/Fe dosing) and EBPR respectively. The external sludge sample in Nieuwveer was taken from a storage tank that, most likely, contained sludge also from a non-iron dosing plant. This explained why we underestimate iron input into the digester whereas the phosphorus loads can be traced back.

4.3.2 Dissolved Fe(II) & Fe(III)

Fe(II) and Fe(III) stock solutions were added (n=3) to filtrates, obtained from digested sludge and from surplus sludge of Line 1 in Leeuwarden, to test the reliability of the ferrozine method (Table 4-1). In filtrates from surplus sludge, Fe(II) was overestimated by about 7% and Fe(III) by about 4%. In filtrates from digested sludge Fe(II) was added. Here, Fe(II) was underestimated by 2% and Fe(III) overestimated by about 5%. When Fe(III) was added it was overestimated by about 1%. These results indicate that the method can reliably detect dissolved Fe(II) and Fe(III) in sewage samples.

After digestion, dissolved iron in Leeuwarden sludge was surprisingly dominated by Fe(III), 1.6 mg L^{-1} (Table 4-1). Also in digested sludge in Nieuwveer about half of the dissolved iron was detected as Fe(III), 3.0 mg L^{-1}. In general, dissolved iron in most samples was dominated by Fe(III). This Fe(III) could be free Fe(III) or Fe(III) which was complexed by organic ligands such as humic substances (Table 4-1, Buffle, 1990).

Although standard addition was successful, the results should, especially after digestion, be regarded with some caution. Fe(II)/Fe(III) were determined reliably, even in the presence of dissolved organic matter (DOM, 16–25 mg DOC L^{-1}) using the ferrozine method (Verschoor and Molot, 2013; Viollier et al., 2000). However, Viollier et al., 2000, added Fe(III) only. Verschoor and Molot, 2013 found Fe(II) and Fe(III) successfully back. Yet, when added, Fe(II) could be present as free Fe(II), whereas the Fe(II) that was already in the sample could partly also be present in complexed forms (Buffle, 1990). In surplus sludge, dissolved organic matter was on the same order of magnitude (Nieuwveer A-stage: 15 mg DOC L^{-1}, Leeuwarden Line 1: 20 mg DOC L^{-1}) compared to the successful standard additions described before. In digested sludge, DOC concentrations were much higher, in Nieuwveer, 320 mg DOC L^{-1} and in Leeuwarden, 126 mg DOC L^{-1}.

With the ferrozine assay, as we applied it, only free Fe(II) was detected (Jackson et al., 2012). When part of the Fe(II) was complexed by DOM, it was not detected in our first step, in which

Fe(II) is quantified. Subsequently, to determine Fe(III), the sample pH was lowered, a reducing agent was added and the sample incubated (12 h). Under these conditions, complexed Fe(II) is mobilized and could be incorrectly assigned to Fe(III) (Gaffney et al., 2008; Jackson et al., 2012; Rasmussen and Nielsen, 1996). That also explains why total iron levels from ICP-OES and from the ferrozine measurements matched very well. With ICP-OES free and complexed iron is detected. To measure free and total Fe(II) in the samples the method of Gaffney et al., 2008 could be established for sewage samples. Additionally, a complementary method to determine iron speciation e.g. by voltammetry would help to eliminate analytical uncertainties (Buffle, 1990). In Leeuwarden, samples from Lines 1 and 2 and from the influent were on-site filtered and directly added in ferrozine to test if free Fe(II) is present, no colour reaction was visible.

Despite all efforts, it cannot be excluded that part of the Fe(II) was oxidized during sampling or sample processing due to high sensitivity of Fe(II) to oxygen (Verschoor and Molot, 2013). Subsequently, total dissolved iron concentrations may decrease due to precipitation of ferric iron oxides. Ferrous iron can even get microbial oxidized in absence of oxygen (Nielsen and Nielsen, 1998). An opposing mechanism, that could occur after sampling and during sample transport, is the conversion of solid Fe(III) oxides to soluble Fe(II) by iron reducing bacteria (IRB). Accordingly, dissolved Fe(II) concentrations doubled within 24 h in samples from the A-stage and B-stage in Nieuwveer when they were incubated at 30 °C (data not shown).

Classifying complexed Fe(II) as Fe(III) by the ferrozine assay and oxygen contamination, could explain the presence of dissolved Fe(III) after the anaerobic digestion. From a chemical point of view all dissolved iron should be present as Fe(II). During anaerobic digestion, highly reducing conditions, including the formation of strong reducing agents like sulphide, prevail for more than three weeks. Also others found significant amounts of dissolved Fe(III) after similar periods of anaerobic incubation (Cheng et al., 2015). An increase of the oxidation-reduction potential over time could indicate that anaerobic conditions did not prevail in these experiments. In our discussion we will focus on total dissolved iron levels instead of the oxidation state of the dissolved iron.

Table 4-1: Dissolved Fe(II) and Fe(III) measurements from the STPs Leeuwarden and Nieuwveer.

	ID	Fe(II) mg L^{-1}	Fe(III) mg L^{-1}	Fe (total) mg L^{-1}
Leeuwarden	Surplus sludge Line 1, Fe(III)	0.1	0.5	0.6
	Activated sludge Line 2, Fe(II)	0.1	0.5	0.6
	Surplus sludge Line 2, Fe(II)	0.6	0.6	1.1
	Digested sludge	0.6	1.6	2.1
Nieuwveer	A-stage: after FeII dosing	0.0	0.8	0.8
	A-stage: Surplus Sludge	18.3	12.7	31.0
	B-stage: Surplus Sludge	0.0	1.9	1.9
	Digested sludge	0.1	3.0	5.9
Standard addition	Filtrate (undigested) + Fe(II): 11.8 mg L^{-1}	12.7 (±0.24)	0	12.7
	Filtrate (undigested) + Fe(III): 11.1 mg L^{-1}	0	11.6 (±0.0)	11.6
	Filtrate (digested) + Fe(II): 11.3 mg L^{-1}	11.1 (±0.08)	0.6 (±0.14)	11.7
	Filtrate (digested) + Fe(III): 10 mg L^{-1}	0	10.1 (±0.5)	10.1

4.3.3 Solids

4.3.3.1 XRD

XRD analyses revealed that vivianite and quartz were present in all samples (all XRD diffractograms and peak assignments are included in the supporting information). In the STP Leeuwarden, struvite was the dominating crystalline phosphorus phase (Table 4-2). During anaerobic digestion the relative share of struvite decreases compared to quartz and vivianite. In the STP Nieuwveer, vivianite, as the only phosphorus containing crystalline phase, was detected in all samples. In digested solids and both A-stage samples from Nieuwveer, a peak at around 29.4 °2Th with intensities between 3.9 and 8.6% could not be assigned.

Table 4-2: Results of semi quantitative XRD and VS analyses expressed as % of the total solids.

	Sampling station	Quartz (%)	Vivianite (%)	Struvite (%)	XRD amorphous (%)	VS (%)
Leeuwarden	Line 1, Fe(III): Surplus sludge	7	2	11	80	70
	Line 2, Fe(II): Activated sludge	7	3	10	79	66
	Line 2, Fe(II): Surplus sludge	6	3	7	84	68
	Digested sludge	21	6	11	63	62
Nieuwveer	A-stage: Activated Sludge	10	7	0	83	78
	A-stage: Surplus Sludge	8	6	0	86	80
	B-stage: Surplus Sludge	11	8	0	81	78
	Digested sludge	21	16	0	63	60

4.3.3.2 SEM-EDX

In both STPs, no large particles with an overlap of iron and phosphorus were found before the anaerobic digestion using SEM-EDX. Iron and phosphorus were homogenously distributed in the samples. After anaerobic digestion larger FeP particles (between 20 and 150 µm in diameter) with different crystalline morphologies were found (Figure 4-2). These particles showed Fe:P ratios between 1.1 and 1.7 when measured by EDX.

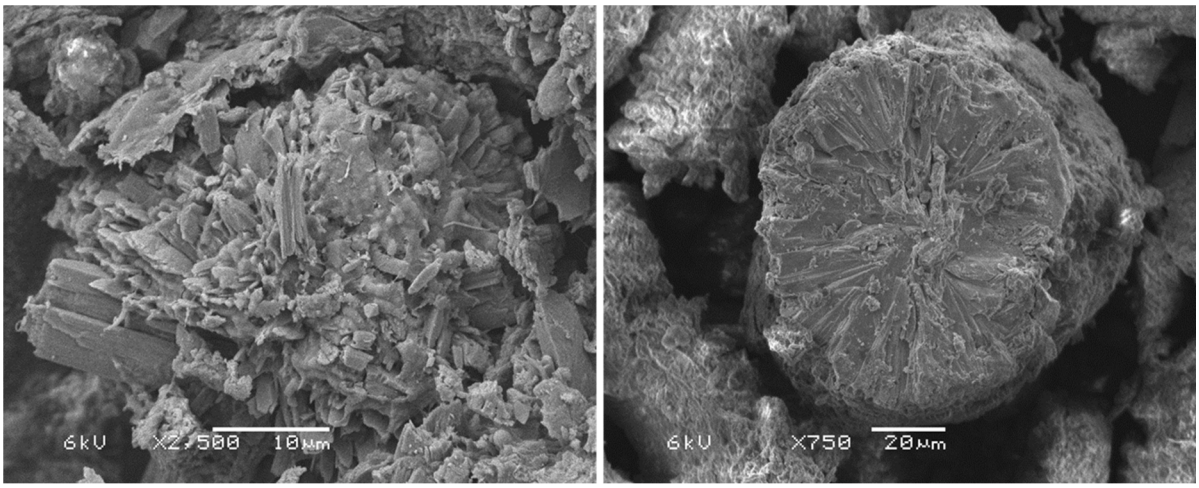


Figure 4-2: SEM images of particles in digested sludge solids sampled in Leeuwarden (left) and Nieuwveer (right). EDX showed Fe:P ratios of 1.1 (Leeuwarden) and 1.7 (Nieuwveer).

4.3.3.3 Mössbauer spectroscopy

Results of Mössbauer measurements at 4 K are summarized in Table 4-3 (all spectra and measurements at 300 K are included in the supporting information). Mössbauer spectroscopy at liquid helium temperature is more powerful as it reveals unambiguously the oxidation states and magnetic properties of the different iron structures. The samples from Leeuwarden with digested solids and the vivianite standard showed signs of oxidation (25 to 28% of vivianite was oxidized in the standard and in digested sludge respectively). Before measurements, these samples were sealed followed by storage at ambient atmosphere inside glass bottles with screw caps for about 1 month. Subsequently, other samples were stored inside the glovebox until measurement and no signs of oxidation were visible, as indicated by the absence of oxidized vivianite.

The spectra acquired with the vivianite standard (Figure 4-3) showed that about 75% of the vivianite was not affected by oxidation and allowed to obtain a spectrum with parameters that are in good agreement with the literature for the two Fe(II) sites (Gonser and Grant, 1976). The oxidized magnetically split Fe(III) species in this standard might be an intermediate valence state between Fe(III) and Fe(II) like in magnetite (Harker and Pollard, 1993). Others suggested that oxidation of vivianite results in the formation of amorphous FeP (Miot et al., 2009), Lepidocrocite (Roldan et al., 2002) or lipscombite, beraunite or rockbridgite (Leavens, 1972).

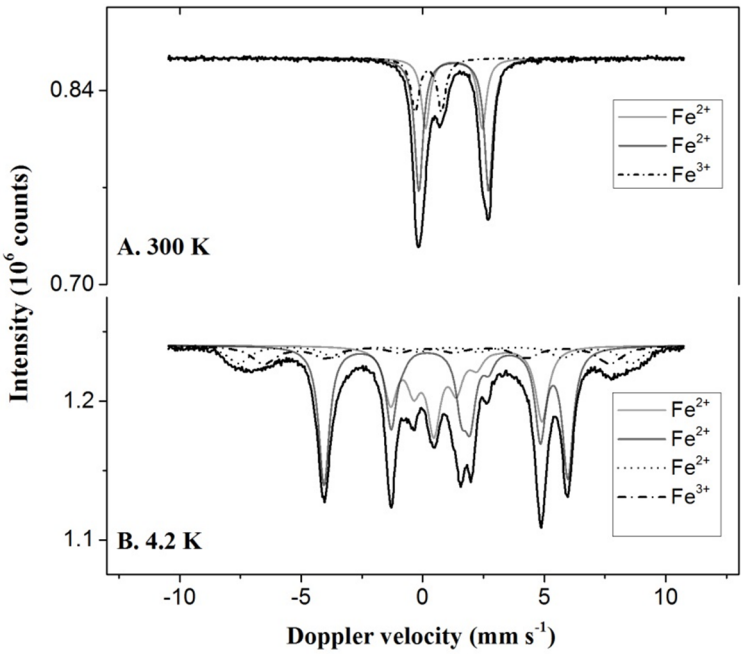


Figure 4-3: Mössbauer spectra obtained at different temperatures with the vivianite standard.

Samples taken from Line 1, Fe(III) dosing and Line 2, Fe(II) dosing in Leeuwarden were virtually the same. Between 94 and 96% of the total iron was Fe(II). Iron in vivianite represented 36 and 32% of the total iron in Lines 1 and 2 respectively. The significant (33 and 35%) paramagnetic contribution to the spectra which was not magnetically split at 4 K was assigned to Fe(II) in pyrite, FeS_2. All other iron species in these samples (summing up to about 30%) could not be decisively assigned. Mössbauer spectra of a digested sludge sample taken in Leeuwarden to which sulphide was added contained the unknown Fe(II) compound that was still paramagnetic at 4 K (data not shown as this sample was exposed to oxygen), which contributed 20-21% to the total iron pool in the samples from Lines 1 and 2. Thus, we assumed this very well defined compound (Γ = 0.4 mm s^{-1}) is a sulphur phase. However, many iron sulphide (FeS_x) and iron sulphate compounds can be excluded as they are magnetic split at 4 K or because they have different Mössbauer parameters (Mullet et al., 2002; Sklute et al., 2015; Yoshida and Langouche, 2013). The presence of FeP minerals cannot be excluded (Dyar et al., 2014), for instance, the Mössbauer parameters of anapaite, $Ca_2Fe^{2+}(PO_4)_2{\cdot}4H_2O$ are close to the values we obtained (Eeckhout et al., 1999). Overall, we cannot assign this spectra to a certain iron phase. The Fe(III) phase is an iron oxide possibly hematite, Fe_2O_3 (Murad and Cashion, 2004).

The spectra obtained for the digested sludge sample in Leeuwarden showed that vivianite was the only FeP present (73%). About 28% of iron comes from oxidized vivianite and 45% of the iron from vivianite unaffected by oxidation. The remaining 27% of Fe(II) in this sample was pyrite.

In the samples from the STP Nieuwveer, Fe(II) dominated as well. The samples contained vivianite, pyrite, an Fe(III) phase having Mössbauer parameters resembling those of hematite,

Fe_2O_3 (Murad and Cashion, 2004) and a paramagnetic (doublet) Fe(II) species that might be assigned to vivianite. The isomer shift of this Fe(II) is close to the one of vivianite, and the quadrupole splitting is also consistent with paramagnetic vivianite. Our measurements were made close to the Neel temperature (magnetic ordering temperature) of vivianite (12 K). It could be that some dispersed vivianite structures or vivianite structures with impurities are still paramagnetic at 4 K. The quantification of vivianite using XRD suggested that this unknown Fe(II) is vivianite (Table 4-4). However, this Fe(II) could also be vivianite overlapping with another phase; as well as it can be another iron compound other than vivianite. In the surplus sludge of the A-stage about 69% of the iron was present as vivianite, additional 18% as the potential vivianite phase, 9% as pyrite and 4% as Fe_2O_3. The iron in the surplus sludge sampled from the B-stage was assigned to vivianite (55%), to the potential vivianite phase (33%), pyrite (7%) and to Fe_2O_3 (5%). In digested solids, 54% of the iron could be firmly assigned to vivianite, 27% were assigned to the potential vivianite phase, the share of pyrite was (15%) and the remaining iron (4%) was assigned to Fe_2O_3. For the subsequent discussions, it was assumed that the Fe(II) species that could not clearly be assigned to vivianite with Mössbauer spectroscopy was in fact vivianite.

In all samples from Nieuwveer and in digested sludge from Leeuwarden no iron phosphate minerals besides vivianite were present. In surplus sludge from Leeuwarden the presence of other FeP phases than vivianite, cannot be excluded. Only, minor fractions of phosphorus can be adsorbed to Fe_2O_3.

Table 4-3: Results of Mössbauer measurements at 4 K. Experimental uncertainties: Isomer shift (IS): ± 0.01 mm s^{-1}; Quadrupole splitting (QS): ± 0.01 mm s^{-1}; Line width (Γ): ± 0.01 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

Sample	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
Leeuwarden Surplus Sludge Line 1: (Fe(III) dosing	0.27	0.88	-	0.84	Fe^{2+} Pyrite	33
	0.37	0.05	51.8	0.58	Fe^{3+} Fe_2O_3	6
	0.93	-	19.3	0.74	Fe^{2+}	5
	1.29	2.47	-	0.47	Fe^{2+}	20
	1.01	1.00	11.4	1.07	Fe^{2+} Vivianite I	14
	1.26	3.71	24.8	1.07	Fe^{2+} Vivianite II	22
Leeuwarden Surplus Sludge Line 2: (Fe(II) dosing)	0.29	0.84	-	0.87	Fe^{2+} Pyrite	35
	0.37	-0.20	51.4	0.58	Fe^{3+} Fe_2O_3	4
	1.07	-	24.7	0.77	Fe^{2+}	8
	1.31	2.48	-	0.46	Fe^{2+}	21
	1.01	0.61	11.4	1.07	Fe^{2+} Vivianite I	15
	1.11	3.37	26.4	1.07	Fe^{2+} Vivianite II	17
Leeuwarden digested solids	0.42	0.79	-	0.72	Fe^{2+} Pyrite	27
	0.50	-0.84	46.0	1.41	Fe^{3+} Oxidized	15
	0.71	0.81	46.3	1.41	Fe^{2+} vivianite	13
	1.20	0.50	10.0	1.18	Fe^{2+} Vivianite I	24
	1.25	2.70	26.7	1.18	Fe^{2+} Vivianite II	21
Nieuwveer Surplus sludge A-stage	0.27	1.00	-	0.92	Fe^{2+} Pyrite	9
	0.38	-0.19	51.9	0.86	Fe^{3+} Fe_2O_3	4
	1.21	2.79	-	0.79	Fe^{2+} Dispersed vivianite	18
	1.22	2.27	15.0	0.64	Fe^{2+} Vivianite I	21
	1.21	3.13	26.4	0.64	Fe^{2+} Vivianite II	48
Nieuwveer Surplus sludge B-stage	0.33	0.88	-	0.87	Fe^{2+} Pyrite	7
	0.37	-0.14	49.8	0.86	Fe^{3+} Fe_2O_3	5
	1.16	2.92	-	0.92	Fe^{2+} Dispersed vivianite	33
	1.26	2.23	14.9	0.93	Fe^{2+} Vivianite I	18
	1.18	3.32	26.2	0.93	Fe^{2+} Vivianite II	37
Nieuwveer Digested solids	0.33	0.88	-	0.87	Fe^{2+} Pyrite	15
	0.37	0.20	48.9	0.86	Fe^{3+} Fe_2O_3	4
	1.21	2.86	-	1.23	Fe^{2+} Dispersed vivianite	27
	1.16	2.21	15.0	0.77	Fe^{2+} Vivianite I	15
	1.20	3.05	26.8	0.77	Fe^{2+} Vivianite II	39
Vivianite Standard	0.35	0.45	44.2	1.24	Fe^{3+} Oxidized	13
	0.77	-0.54	50.2	1.15	Fe^{2+} vivianite	12
	1.35	2.36	14.8	0.64	Fe^{2+} Vivianite I	29
	1.36	3.14	27.4	0.53	Fe^{2+} Vivianite II	46

4.3.3.4 Extractions

Water, pyrophosphate and ammonium oxalate were used to extract Fe from digested sludge sampled in Leeuwarden and Nieuwveer (Figure 4-4). Water was the mildest extract and dissolved 0.3 and 1% of the total solid iron in Leeuwarden and Nieuwveer respectively. This was expected, considering the relatively low solubility of FeS_x and vivianite that dominated the digested sludge samples (Al-Borno and Tomson, 1994; Davison, 1991). However, in both STPs about 60% of the water extractable iron was Fe(III). During pyrophosphate extraction all dissolved iron species were quantified, summing up to between 40% (Nieuwveer) and 60% (Leeuwarden) of the iron. Considering the Mössbauer measurements, iron bound in pyrite or vivianite must be part of this fraction. Thus, the iron extracted using pyrophosphate was mainly

of non-organic origin. Pyrophosphate extracts rather iron from vivianite than from FeS_x (Carliell-Marquet et al., 2009). In Leeuwarden, the iron fraction in pyrophosphate (58±7%) is in a similar range as vivianite (57%, Mössbauer spectroscopy). However, in Nieuwveer, the pyrophosphate extracted iron (41±1%) was much less than iron bound in vivianite (81%, Mössbauer spectroscopy). Ammonium oxalate extracted from Leeuwarden digested sludge all iron (85% as Fe(II)) and around 80% of the iron in Nieuwveer digested sludge (65% as Fe(II)). Compared to the Mössbauer measurements, this indicates that the oxalate extraction and subsequent spectrophotometric determination of Fe(II)/Fe(III) overestimate the Fe(III) content by about 10 and 25%. The described uncertainties for the spectrophotometric measurements for dissolved Fe(II)/Fe(III) could also affect the results of the iron extraction.

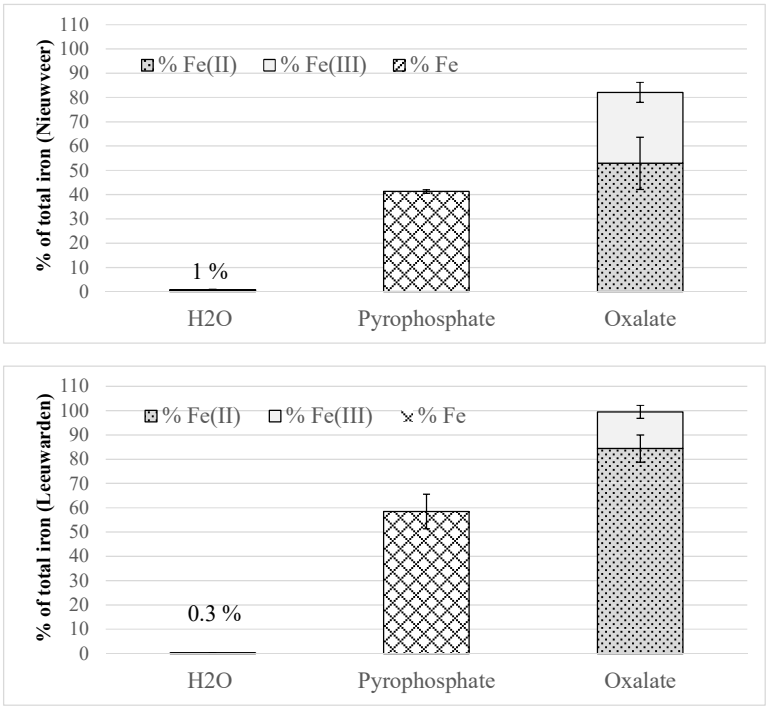


Figure 4-4: Extraction of iron from digested sludge using different extracts. The error bars indicate standard deviation (n=3).

4.3.3.5 Phosphorus bound to FeP

The maximum amount of phosphorus that could be bound to iron was estimated by using the elemental composition of the solids. Sulphide extraction was used to dissolve phosphorus bound to iron. Phosphorus bound in vivianite was determined by semi-quantitative XRD and by Mössbauer spectroscopy (Table 4-4). The results for Leeuwarden indicate that in surplus sludge between 9% (Mössbauer spectroscopy) and 13% (XRD) and after digestion between 18% (XRD) and 29% (Mössbauer spectroscopy) of the phosphorus is bound in vivianite. According to XRD, the majority of phosphorus was bound in struvite in surplus (43%) and digested sludge (35%). These values are higher than the maximum values obtained from the elemental compositions. Thus, semi quantitative XRD overestimated the struvite content in the sludge.

In the A-stage and the B-stage, estimates were in good agreement, about 50% of the phosphorus in the A-stage and about 40% of the phosphorus in the B-stage were bound in vivianite. After digestion, the estimates differ considerably between sulphide extraction (31% of phosphorus bound to iron) and Mössbauer spectroscopy and XRD (the latter two suggested 47 and 53% of the phosphorus are bound in vivianite). Additional, in Nieuwveer and Leeuwarden a maximum of 25 and 8% of the total phosphorus could be bound to Al respectively.

Table 4-4 indicates that, the elemental compositions of the samples tends to overestimate phosphorus bound to iron as it does not take into account non-iron-FeP species (e.g. iron oxides, FeS_x or organic bound iron). The same principle applies in estimating phosphorus bound to Mg in struvite or to aluminium in aluminium phosphorus compounds (AlP). XRD may underestimate phosphorus bound to iron as only the phosphorus bound to vivianite is detected. Also Mössbauer spectroscopy may underestimate phosphorus bound to iron as not all compounds were identified and as the Fe_2O_3 can bind phosphorus.

Table 4-4: Estimating phosphorus bound to FeP in different sewage (sludge) samples (n.d. = not determined).

Leeuwarden	**Average Line 1 & 2**		**Digested Sludge**	
	% of total P		% of total P	
	Vivianite/FeP	Struvite/MgP	Vivianite/FeP	Struvite/MgP
qXRD	13	43	18	35
Mössbauer	9	-	29	-
Elemental composition	26	36	36	25
Sulfide	11	-	26	-

Nieuwveer	**A-stage Surplus sludge**		**B-stage Surplus Sludge**		**Digested Sludge**	
	% of total P		% of total P		% of total P	
	Vivianite/FeP	Struvite/MgP	Vivianite/FeP	Struvite/MgP	Vivianite/FeP	Struvite/MgP
qXRD	54	0	37	0	53	0
Mössbauer	52	-	38	-	47	-
Elemental composition	55	15	43	14	59	14
Sulfide	n.d.	-	n.d.	-	31	-

4.4 Discussion

Significant iron loads entered both STPs via the influent, which could originate from the municipal sewage itself, from groundwater infiltration and from iron dosing into the sewer system (Hvitved-Jacobsen et al., 2013; van den Kerk, 2005). This often neglected, but nevertheless, large iron input could assist in phosphorus removal in STPs (Gutierrez et al., 2010). Despite of its significant contribution, the speciation of the influent iron and whether it can support CPR or not was not determined. The iron dosing in both STPs (as for most other STPs in The Netherlands) was relatively low. The molar ratios of iron dosed to phosphorus entering via the influent was in Leeuwarden 0.13 and in Nieuwveer 0.42 (Figure 4-1). External iron sources (i.e. influent and external sludge) contributed to about 80% of the total iron in the STP Leeuwarden. Here, a large input of iron via the external sludge into the digester was identified. This suggests that iron dosing can be significantly reduced, the external iron input is sufficient to prevent H_2S emissions during anaerobic digestion. In Nieuwveer, the dosed iron contributed more significantly to the total iron budget, yet still 35% of the total iron load originated from the inflowing sewage and from external sludge.

Dissolved iron was measured to identify equilibrium concentrations with iron compounds. However, it turned out that during the dynamic conditions in the treatment lines of any STP (oxidizing and reducing conditions coupled to high microbial activities) measuring of a static/equilibrium iron concentration is arbitrary. Thus, the reported dissolved iron levels should be seen as an order of magnitude for these zones. Except for the influent and effluent samples, by far most of the iron is part of the solid fraction. Accordingly, it was shown that even Fe(II), as product of IRB, can remain part of the solid phase (Rasmussen and Nielsen, 1996). The high dissolved iron concentrations in the surplus sludge of the A-stage in Nieuwveer (about 30 mg Fe L^{-1}) highlighted the possibility of a slow or insufficient Fe(II) oxidation resulting in small dispersed Fe(III) and dissolved Fe(II). Sufficient oxidation and formation of Fe(III) oxides would cause a more rapid precipitation compared to Fe(II) (Ghassemi and Recht, 1971; Oikonomidis et al., 2010). Improving the aeration of Fe(II) or dosing of Fe(III) may help to improve the limited COD removal in the A-stage of this STP (De Graaff et al., 2015).

The methodology which we employed for ammonium oxalate extraction gave only rough estimates about the Fe(II)/Fe(III) content in the sludge. The pyrophosphate extraction did not reliably extract organic iron, as explained earlier (Stucki, 2013). In this study, Mössbauer spectroscopy was the most reliable method for quantifying and identifying iron and FeP compounds. In contrast to XRD, Mössbauer spectroscopy can detect also amorphous iron and FeP phases with very small particle sizes in low abundances provided appropriate standards have been prepared. On the other hand XRD detects all crystalline phosphorus compounds, also the ones that do not contain iron. Mössbauer spectroscopy and XRD collectively showed that the solid iron compounds of surplus sludge and anaerobic digested sludge were dominated by the ferrous phosphate mineral vivianite. Ferric iron did not play a significant role in any of the solid samples. Besides vivianite, the other major iron compound was pyrite (Table 4-3).

In a membrane bioreactor with anoxic/aerobic zones, Fe(III) dominated the solid iron pool (Wu et al., 2015) also in sludge sampled from the aeration tank of an STP using Fe(II) for CPR, ammonium oxalate extraction showed that Fe(III) dominated (Rasmussen and Nielsen, 1996). However, in our samples, regardless of aerobic zone in the STPs, Fe(II) was dominant.

How is that possible? First, despite aerated areas, the sludge itself is partly non-aerated e.g. during low loading rates on weekends or in the night, in settlers and in the anoxic zones allowing the reduction of Fe(III). In flocs, oxygen free conditions can prevail throughout the treatment process due to diffusion limitation and when relatively low dissolved oxygen set-points are used. Thus, once vivianite is formed, anoxic conditions in flocs may help to channel it, without oxidation, through the aerated nitrification zone. Both, ours (SEM-EDX) and earlier research (Frossard et al., 1997; Zelibor et al., 1988) showed that vivianite is often part of an organic matrix.

High activity of IRB in STPs has been measured which could result in rapid Fe(III) reduction and thus vivianite production (Cheng et al., 2015; Rasmussen and Nielsen, 1996). Assuming the reduction rates from Rasmussen and Nielsen, 1996, it would take between 19 h and 4 days

in Leeuwarden and between 24 h and 5 days in Nieuwveer to reduce all solid iron in the surplus sludge. These figures also indicate that Fe(III) reduction after sampling could influence the oxidation state of the iron in samples. Once vivianite is formed, its chemical oxidation is relatively slow, on the time scale of weeks (Miot et al., 2009; Roldan et al., 2002). The oxidation by anaerobic nitrate-reducing iron-oxidizing bacteria was faster: it took approximately 16 days for complete oxidation (Miot et al., 2009). We could not find information on how long iron-oxidizing bacteria in the presence of oxygen would need for the oxidation of Fe(II) in vivianite.

In Nieuwveer and in Line 2 in Leeuwarden, where Fe(II) is dosed for CPR, the mechanisms of vivianite formation were not obvious. Vivianite could either directly precipitate from solution or formed as a result of Fe(III) reduction. Indirect chemical Fe(III) reduction, induced by e.g. sulphide, FeS_x or via humic substances (Biber et al., 1994; Golterman, 2001; Kappler et al., 2004) or direct Fe(III) reduction by IRB (Azam and Finneran, 2014; Cheng et al., 2015; Nielsen, 1996; Zhang, 2012) may have caused the formation of Fe(II) and subsequent precipitation of vivianite. Vivianite could also be precipitated directly from solution as a result of Fe(II) dosing, possibly combined with insufficient oxidation of Fe(II) (Ghassemi and Recht, 1971). In Line 1 in Leeuwarden where Fe(III) is dosed, also most of the solid iron was present as Fe(II), mainly as vivianite. Here, chemical or biologically Fe(III) reduction must play a role. To what extent vivianite forms already in the sewer systems cannot be determined by our measurements.

When Fe(III) is used for CPR, it was suggested that first Fe(III) oxides form which cause the phosphorus removal via co-precipitation or adsorption (Smith et al., 2008). If the Fe:P ratio of these initial ferric FeP is higher than the one of vivianite (molar Fe:P=1.5) as suggested before by Fulazzaky et al., 2014 and Luedecke et al., 1989, then Fe(III) reduction and subsequent formation of vivianite can act as a net sink for phosphorus. Hence, oxidation of Fe(II) in vivianite could result in phosphorus release due to a higher molar Fe:P ratio in the formed products (Miot et al., 2009; Roldan et al., 2002). In case of FeP with a molar Fe:P of 1 (e.g. strengite), Fe(III) reduction would cause a slight net phosphorus release. However, more significant phosphorus release could only be expected when vivianite formation would be prevented as documented in the presence of sulphide when FeS_x are formed (Roden and Edmonds, 1997). Accordingly, in our experiments, addition of sulphide to the vivianite containing sludge caused a relatively quick (4 h) and significant phosphorus release.

Vivianite is very efficient in removing phosphorus from solution due to a very low solubility ($pksp \approx 36$, Al-Borno and Tomson, 1994). Fe(II) dosing for o-P removal in oxygen free conditions resulted in vivianite formation (Ghassemi and Recht 1971). The same researchers demonstrated that, in pure water, stoichiometry of o-P removal was more efficient with Fe(II) compared to Fe(III), resulting in lower residual o-P concentrations at optimum pH, and Fe(II) showed an optimum pH for o-P removal (pH=8) closer to common sewage. On the other hand, faster kinetics of Fe(III)P formation, faster settling of the formed Fe(III)P, a broader pH range for o-P removal and better COD flocculation properties were found for Fe(III) (Ghassemi and Recht, 1971; Gregory and O'Melia, 1989). In oxygen free freshwater (O'Connell et al., 2015; Rothe et al., 2014) and even in marine sediments (Jilbert and Slomp, 2013), in anoxic soils

(Nanzyo et al., 2013; Peretyazhko and Sposito, 2005) and in septic tanks (Azam and Finneran, 2014) vivianite received attention as it plays an important role in phosphorus retention (see recent review by Rothe et al., 2016). For the formation of spherical vivianite in sediments a model has been suggested based on the presence of polymeric gel structures (Zelibor et al., 1988). At least one of the crystals we found in Nieuwveer (Figure 4-2) resembles the crystals produced by Zelibor et al., 1988, indicating that the mechanism of vivianite formation could be similar in sediments and in biological STPs.

Similar to Frossard et al., 1997, with SEM-EDX we found larger crystals (up to 150 µm in diameter) with a Fe:P ratio close to the one of vivianite in digested sludge. Such large crystals were not found before digestion. The growth of the vivianite particles during digestion may be the result of the additional SRT of several weeks under constantly anaerobic conditions. Ostwaldt ripening, particle aggregation or crystal growth at elevated temperature in the digester may have caused the growth of vivianite particles/crystals. However, vivianite showed relatively slow crystal growth rates in pure solutions with higher vivianite supersaturations than observed in our samples (Madsen and Hansen, 2014) and vivianite is not stable in the presence of sulphide (Nriagu, 1972). Moreover, various inhibitors of Ostwald ripening, like DOC, are present during the digestion process. The apparent growth of vivianite particles during the digestion process is not yet fully understood.

XRD could not detect crystalline FeS_x in any of the samples analysed. Whereas Mössbauer spectroscopy revealed that pyrite contributed significantly to the solid iron pool and even was present in the surplus sludge (9–33% of the total iron). The pyrite in these solids could originate from the sewer system or they were formed during the treatment process (Ingvorsen et al., 2003; Nielsen et al., 2005; van den Brand et al., 2015). Oxidation of FeS_x in STPs is on a time scale of hours (Gutierrez et al., 2010; Ingvorsen et al., 2003; Nielsen et al., 2005), it could occur in aerated zones of the STPs. However, if located in the core of the sludge flocs, FeS_x might, similar to vivianite, pass aerated zone without being oxidized.

Quantification of phosphorus bound in FeP was performed by various approaches (Table 4-4). Vivianite bound phosphorus contributed in Leeuwarden about 10% before digestion and around 30% after digestion to the total solid phosphorus, according to Mössbauer spectroscopy. The quantifications using XRD suggested, phosphorus in struvite contributes before digestion around 43% and after digestion about 35% of the total phosphorus. This decrease can be explained by the external input of iron in the digester. The dissolved phosphorus concentrations are usually quite high in anaerobic digesters due to organic matter degradation and, in EBPR plants, due to the release of polyphosphates from phosphate accumulating organisms. Thus, vivianite formation is not limited by the supply of phosphorus. The iron from the external sludge will partly react with phosphorus to form vivianite, iron dosing to anaerobic digesters is also a measure to prevent struvite scaling as vivianite is preferably formed (Mamais et al., 1994). Some of the added iron could react with sulphide to form FeS_x. Further phosphorus could be bound in biomass (phosphate accumulating organisms, cell material and debris) or in amorphous compounds associated with metals like aluminium, magnesium or calcium. To be

able to identify and quantify these phosphorus species would require the application of techniques like ^{31}P-NMR, sequential extraction or X-ray absorption spectroscopy (e.g. Frossard et al., 1994; Wu et al., 2015). If, however, sufficient Fe(II) is available, vivianite is expected to be the dominant inorganic solid phosphorus compound in digesters. This would make a recovery technology targeting vivianite vastly more attractive. For Nieuwveer, Mössbauer spectroscopy indicates a decrease in vivianite bound phosphorus during digestion. Here the Fe:P increases only slightly due to external sludge input. Thus, the formation of FeS_x during anaerobic digestion on expenses of vivianite causes a decrease in phosphorus bound to vivianite.

XRD might not be able to detect small particles of vivianite and amorphous FeP which Mössbauer spectroscopy does detect. We consider XRD as a semi-quantitative method. In contrast to our expectations, XRD did not underestimate the vivianite bound phosphorus and results of Mössbauer spectroscopy were very similar (Table 4-4). This apparent match supports the assumption that the Fe(II) fraction in Nieuwveer, that Mössbauer spectroscopy could not clearly assign to vivianite, is actually vivianite. However, also the XRD results in Nieuwveer bear some uncertainty due to the presence of a peak that could not be assigned. Maximum quantities of phosphorus bound in FeP, AlP and MgP were estimated using the elemental composition of the TS. It was assumed that all iron, aluminium and magnesium is bound to phosphorus and thus other fractions of these elements were neglected. However, the elemental composition was, at least for the iron, able to give good estimates on phosphorus bound to iron. Sulphide was added to sludge to extract phosphorus bound to iron (Kato et al., 2006). In Leeuwarden, the sulphide extractable phosphorus fractions in digested sludge and in surplus sludge from Line 1 matched very well with phosphorus in vivianite obtained from Mössbauer spectroscopy. In Nieuwveer, the release of phosphorus from digested sludge in response to sulphide addition was much lower (31%) compared to the phosphorus bound in vivianite (about 50%). However, also the molar Fe:P was about 20% lower in the sludge that was used for sulphide extraction. Translating the phosphorus release efficiency of sulphide to the sludge with the 20% higher Fe:P ratio, we would expect a phosphorus release of about 40%. Hence, sulphide extraction and Mössbauer spectroscopy would match better. It seems likely that the gap between sulphide extraction and the other methods is due to a difference in the sludge samples. Perhaps the released phosphorus, re-precipitated with other metals. However, from potential counter ions (magnesium, calcium and aluminium), only calcium concentrations dropped noteworthy by 2 mmol L^{-1} (net phosphorus release was 13 mmol L^{-1}). Or else vivianite particles were present in Nieuwveer in another form (see Mössbauer results) then the ones in Leeuwarden (e.g. more crystalline, enclosed by other minerals/organic) that made vivianite less reactive/unreactive to sulphide exposure. Overall, all methods gave good estimates for phosphorus bound to iron and for phosphorus bound in vivianite. The elemental composition is the easiest method but gives the less accurate result. Sulphide extractions is relatively simple, here phosphorus is released from all iron compounds without determining the type of FeP present. XRD is a popular and common method. It allows the quantification of crystalline FeP

only. In our case all iron bound phosphorus was vivianite, hence the quantification worked well. In sludge with amorphous FeP or dispersed vivianite, XRD will not be able to quantify phosphorus bound to iron. Mössbauer spectroscopy is, however, able to detect amorphous and crystalline iron compounds very accurately. In Nieuwveer, about 1/3 of the Fe(II) that was assigned to vivianite could also be another Fe(II) phase. Preparation of appropriate standards may help to identify this Fe(II) using Mössbauer spectroscopy in future. In general, Mössbauer gives very accurate qualitative/quantitative results but it should be used in combination with other complementary methods like XRD.

4.5 Conclusion

Mössbauer spectroscopy indicated that vivianite and pyrite were the dominating solid iron compounds in the surplus and anaerobically digested sludge from two STPs applying CPR and EBPR. XRD confirmed that vivianite was the major FeP in the samples. None of the sludge samples contained a significant amount of Fe(III) although besides Fe(II) also Fe(III) was dosed. Likely, this is related to fast iron reduction processes and slow vivianite oxidation rates. Studying iron chemistry, helped to identify measures on how sewage treatment can be improved. In Leeuwarden, iron dosing, to prevent sulphide emissions, can be reduced. In Nieuwveer, improving the aeration to form Fe(III) would improve COD removal in the A-stage. To assess the role of vivianite and the potential of a phosphorus recovery technology targeting on FeP, further STPs with different treatment designs (higher iron dosing and particularly higher Fe(III) dosing) should be analysed as well. If vivianite is a general iron precipitant in STPs it could offer new routes for phosphorus recovery.

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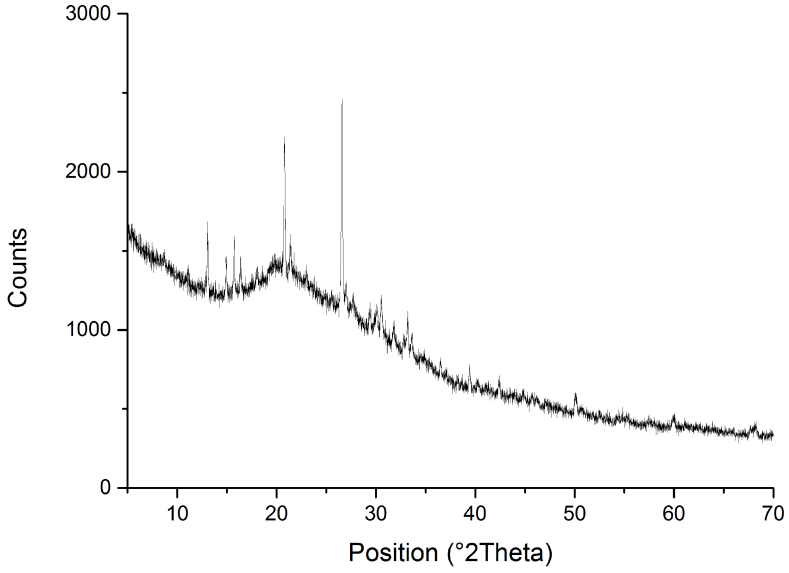
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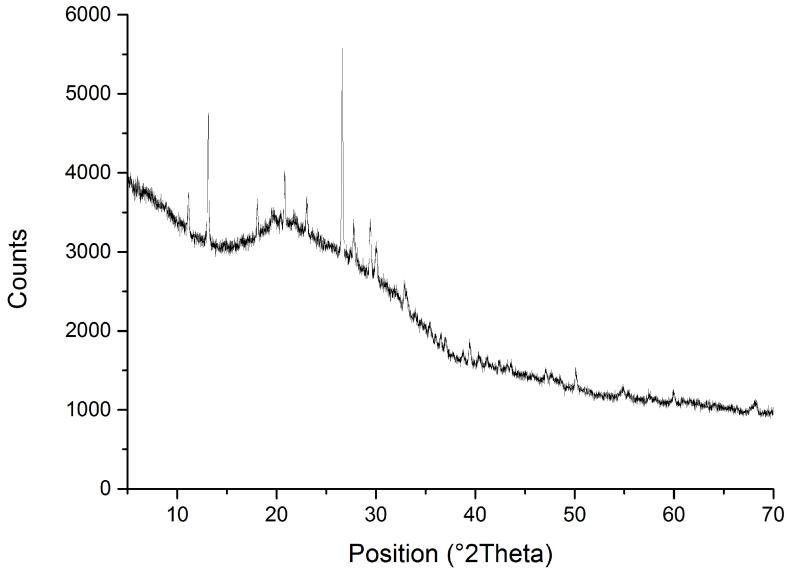
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Supplementary Information



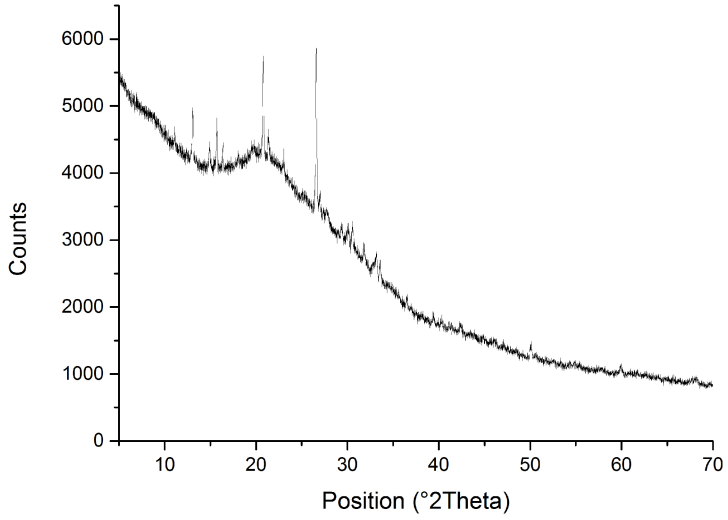
Pos. [°2Th.]	Matched by
11.090	Vivianite
13.065	Vivianite
14.913	Struvite
15.736	Struvite
16.387	Struvite
18.020	Vivianite
20.796	Quartz
21.377	Struvite
22.974	Vivianite
26.582	Quartz
27.011	Struvite
27.707	Struvite
29.441	Struvite
30.087	Struvite
30.552	Struvite
31.794	Struvite
32.802	Struvite
33.216	Struvite
33.603	Struvite
36.496	Quartz
39.422	Quartz
40.267	Quartz
42.412	Quartz
44.867	Struvite
50.004	Quartz
59.961	Quartz
68.204	Quartz

Figure S 4-1: XRD diffractogram including peak list and peak assignment for surplus sludge solids sampled in Line 1 (Fe(III) dosing) in Leeuwarden.



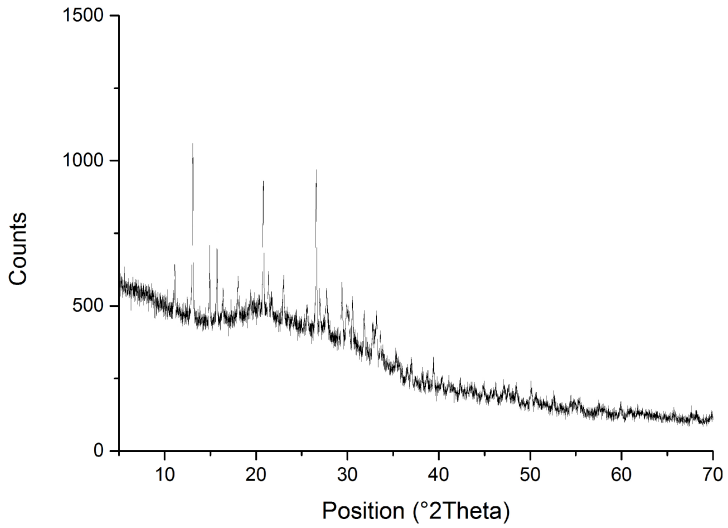
Pos. [°2Th.]	Matched by
13.062	Vivianite
14.905	Struvite
15.723	Struvite
16.380	Struvite
20.813	Quartz
21.355	Struvite
23.020	Vivianite
26.599	Quartz
26.992	Struvite
27.752	Vivianite
29.352	Struvite
30.149	Vivianite
30.560	Vivianite
31.814	Struvite
33.170	Vivianite
33.558	Struvite
35.031	Struvite
36.514	Quartz
39.424	Quartz
40.297	Quartz
42.397	Quartz
46.159	Vivianite
49.997	Quartz
57.730	Vivianite
59.915	Quartz
68.197	Quartz

Figure S 4-2: XRD diffractogram including peak list and peak assignment for activated sludge solids sampled in Line 2 (Fe(II) dosing) in Leeuwarden.



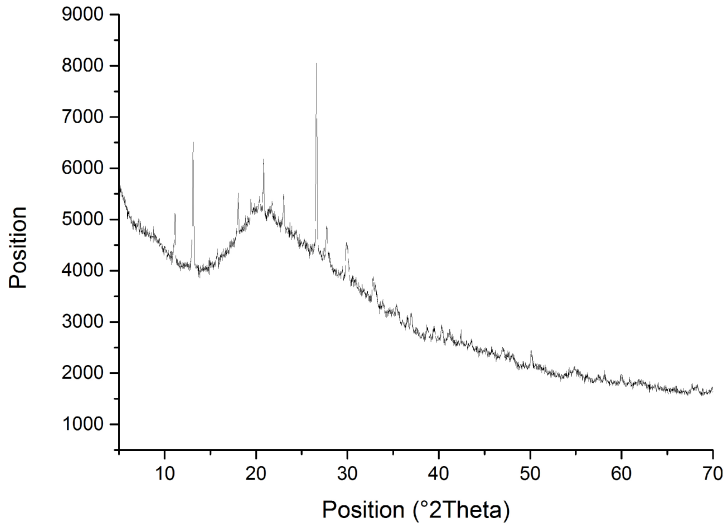
Pos. [°2Th.]	Matched by
11.104	Vivianite
13.077	Vivianite
14.922	Struvite
15.728	Struvite
16.356	Struvite
20.785	Quartz
21.376	Struvite
26.541	Vivianite
27.706	Vivianite
29.416	Struvite
30.084	Vivianite
30.531	Struvite
31.821	Struvite
33.140	Vivianite
33.597	Struvite
36.486	Vivianite
39.408	Vivianite
40.305	Vivianite
42.410	Quartz
50.090	Vivianite
59.902	Vivianite
68.220	Vivianite

Figure S 4-3: XRD diffractogram including peak list and peak assignment for surplus sludge solids sampled in Line 2 (Fe(II) dosing) in Leeuwarden.



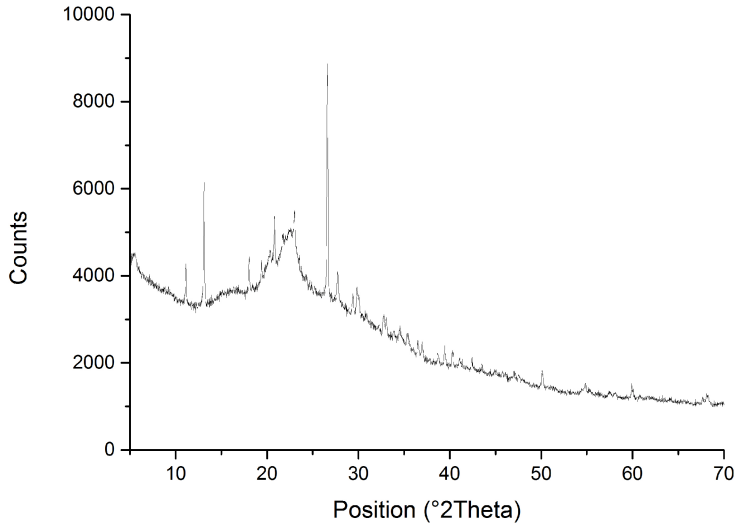
Pos. [°2Th.]	Matched by
11.104	Vivianite
13.077	Vivianite
14.922	Struvite
15.728	Struvite
16.356	Struvite
20.785	Quartz
21.376	Struvite
26.541	Vivianite
27.706	Vivianite
29.416	Struvite
30.084	Vivianite
30.531	Struvite
31.821	Struvite
33.140	Vivianite
33.597	Struvite
36.486	Vivianite
39.408	Vivianite
40.305	Vivianite
42.410	Quartz
50.090	Vivianite
59.902	Vivianite
68.220	Vivianite

Figure S 4-4: XRD diffractogram including peak list and peak assignment for digested sludge solids sampled in Leeuwarden.



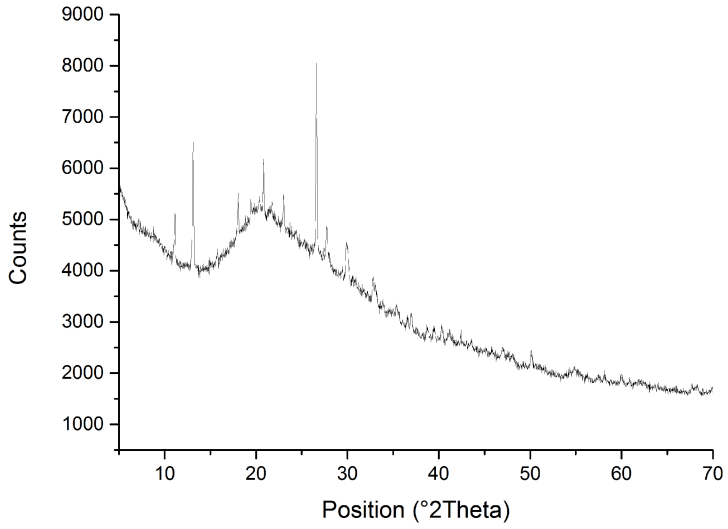
Pos. [°2Th.]	Matched by
11.117	Vivianite
13.115	Vivianite
18.026	Vivianite
20.823	Quartz
23.004	Vivianite
26.596	Quartz
27.743	Vivianite
29.397	*Unassigned*
29.948	Vivianite
32.759	Vivianite
34.615	Vivianite
35.390	Vivianite
36.517	Quartz
39.410	Quartz
40.388	Quartz
42.435	Quartz
45.862	Quartz
50.097	Quartz
54.865	Quartz

Figure S 4-5: XRD diffractogram including peak list and peak assignment for A-stage solids sampled directly after Fe(II) dosing in Nieuwveer.



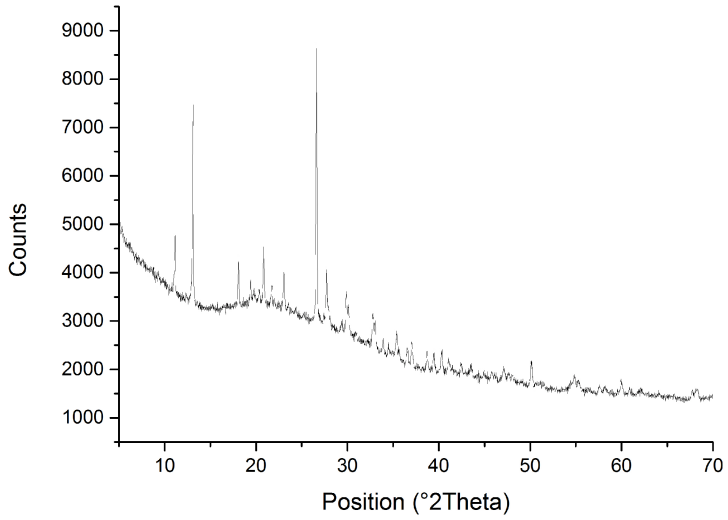
Pos. [°2Th.]	Matched by
11.119	Vivianite
13.110	Vivianite
18.042	Vivianite
19.393	Vivianite
20.302	Vivianite
20.819	Quartz
21.723	Vivianite
23.010	Vivianite
26.596	Quartz
27.725	Vivianite
29.402	*Unassigned*
29.834	Vivianite
30.073	Vivianite
32.726	Vivianite
33.030	Vivianite
34.544	Vivianite
35.359	Vivianite
36.519	Quartz
36.957	Vivianite
38.677	Vivianite
39.433	Quartz
40.258	Quartz
41.063	Vivianite
42.443	Quartz
43.506	Vivianite
47.074	Vivianite
50.096	Quartz
54.838	Quartz
59.897	Quartz
68.198	Quartz

Figure S 4-6: XRD diffractogram including peak list and peak assignment for surplus A-stage sludge solids sampled in Nieuwveer.



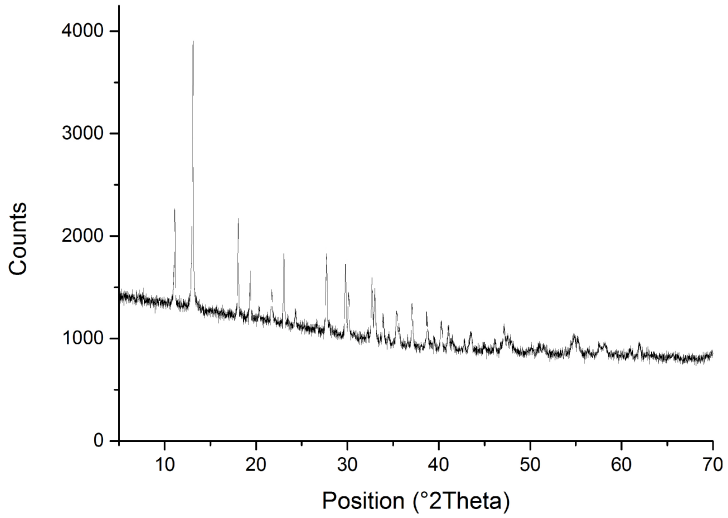
Pos. [°2Th.]	Matched by
11.133	Vivianite
13.115	Vivianite
18.068	Vivianite
19.421	Vivianite
20.829	Quartz
21.622	Vivianite
23.032	Vivianite
26.602	Quartz
27.733	Vivianite
29.865	Vivianite
32.772	Vivianite
33.922	Vivianite
35.455	Vivianite
36.986	Vivianite
38.748	Vivianite
39.478	Quartz
40.356	Quartz
41.159	Vivianite
47.015	Vivianite
50.091	Quartz
54.884	Quartz
59.970	Quartz
68.248	Quartz

Figure S 4-7: XRD diffractogram including peak list and peak assignment for surplus B-stage sludge solids sampled in Nieuwveer.



Pos. [°2Th.]	Matched by
11.135	Vivianite
13.104	Vivianite
18.090	Vivianite
19.408	Vivianite
20.341	Vivianite
20.816	Quartz
21.739	Vivianite
23.042	Vivianite
26.616	Quartz
27.725	Vivianite
29.372	*Unassigned*
29.886	Vivianite
30.125	Vivianite
32.769	Vivianite
33.032	Vivianite
33.926	Vivianite
35.382	Vivianite
36.589	Quartz
37.039	Vivianite
38.699	Vivianite
39.455	Quartz
40.302	Quartz
41.091	Vivianite
42.434	Quartz
43.624	Vivianite
45.926	Quartz
47.158	Vivianite
50.094	Quartz
54.897	Quartz
57.575	Vivianite
59.991	Quartz
62.061	Vivianite
67.717	Quartz
68.244	Quartz

Figure S 4-8: XRD diffractogram including peak list and peak assignment for digested sludge solids sampled in Nieuwveer.



Pos. [°2Th.]	Matched by
11.103	Vivianite
13.090	Vivianite
18.044	Vivianite
19.360	Vivianite
20.331	Vivianite
21.733	Vivianite
23.051	Vivianite
24.301	Vivianite
26.611	Vivianite
27.707	Vivianite
29.781	Vivianite
30.103	Vivianite
32.656	Vivianite
32.964	Vivianite
33.874	Vivianite
34.513	Vivianite
35.369	Vivianite
37.039	Vivianite
38.692	Vivianite
39.517	Vivianite
40.254	Vivianite
41.016	Vivianite
41.406	Vivianite
42.800	Vivianite
43.479	Vivianite
44.983	Vivianite
46.168	Vivianite
47.151	Vivianite
47.529	Vivianite
47.896	Vivianite
50.152	Vivianite
51.008	Vivianite
51.392	Vivianite
54.819	Vivianite
55.237	Vivianite
57.581	Vivianite
58.141	Vivianite
60.933	Vivianite
61.955	Vivianite
69.949	Vivianite

Figure S 4-9: XRD diffractogram including peak list and peak assignment for the vivianite standard.

Table S 4-1: Results of Mössbauer measurements at 300 K.

Sample	*IS* ($mm \cdot s^{-1}$)	*QS* ($mm \cdot s^{-1}$)	*Hyperfine field (T)*	*Γ* ($mm \cdot s^{-1}$)	*Phase*	*Spectral contribution (%)*
Leeuwarden	0.27	0.84	-	0.50	Fe^{3+}	57
Surplus sludge Line	1.28	2.40	-	0.36	Fe^{2+}	20
1: Fe(III) dosing	1.49	2.58	-	0.38	Fe^{2+}	17
	1.36	0.96	-	0.31	Fe^{2+}	6
Leeuwarden	0.28	0.87	-	0.49	Fe^{3+}	56
Surplus sludge	1.24	2.36	-	0.30	Fe^{2+}	19
Line 2: Fe(II) dosing	1.47	2.53	-	0.34	Fe^{2+}	18
	1.22	1.13	-	0.28	Fe^{2+}	7
Leeuwarden Digested	0.27	0.93	-	0.54	Fe^{3+}	62
solids	1.17	2.46	-	0.32	Fe^{2+}	14
	1.44	2.57	-	0.39	Fe^{2+}	24
Nieuwveer	0.20	0.89	-	0.31	Fe^{3+}	11
Surplus sludge	1.08	2.67	-	0.30	Fe^{2+}	33
A-stage	1.31	2.74	-	0.34	Fe^{2+}	56
Nieuwveer	0.31	0.85	-	0.48	Fe^{3+}	44
Surplus sludge	1.08	2.66	-	0.33	Fe^{2+}	21
B-stage	1.39	2.57	-	0.39	Fe^{2+}	35
Nieuwveer	0.30	0.91	-	0.51	Fe^{3+}	45
Digested solids	1.07	2.66	-	0.32	Fe^{2+}	19
	1.37	2.64	-	0.39	Fe^{2+}	36
Vivianite	0.23	1.09	-	0.41	Fe^{3+}	20
Standard	1.27	2.33	-	0.42	Fe^{2+}	28
	1.27	2.87	-	0.42	Fe^{2+}	52

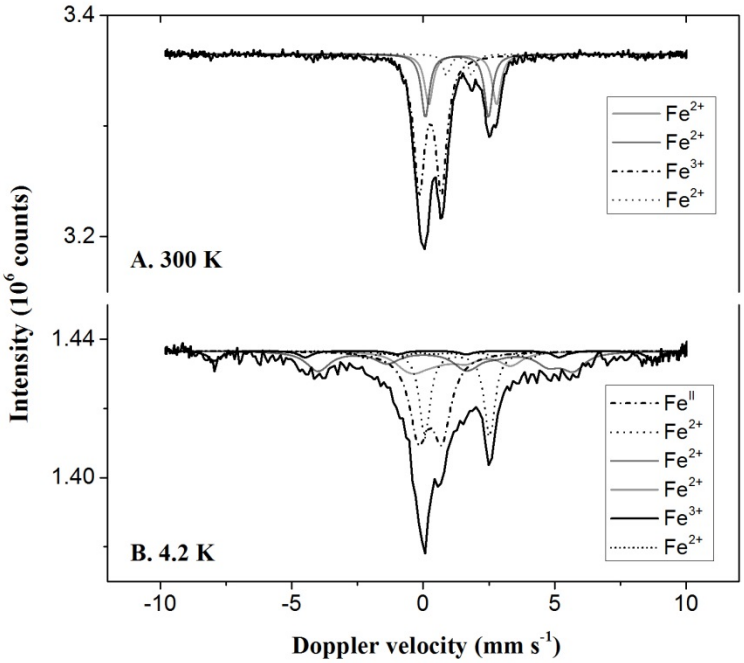


Figure S 4-10: Mössbauer spectra obtained at different temperatures with the surplus sludge solids sampled in Line 1 (Fe(III) dosing) in Leeuwarden.

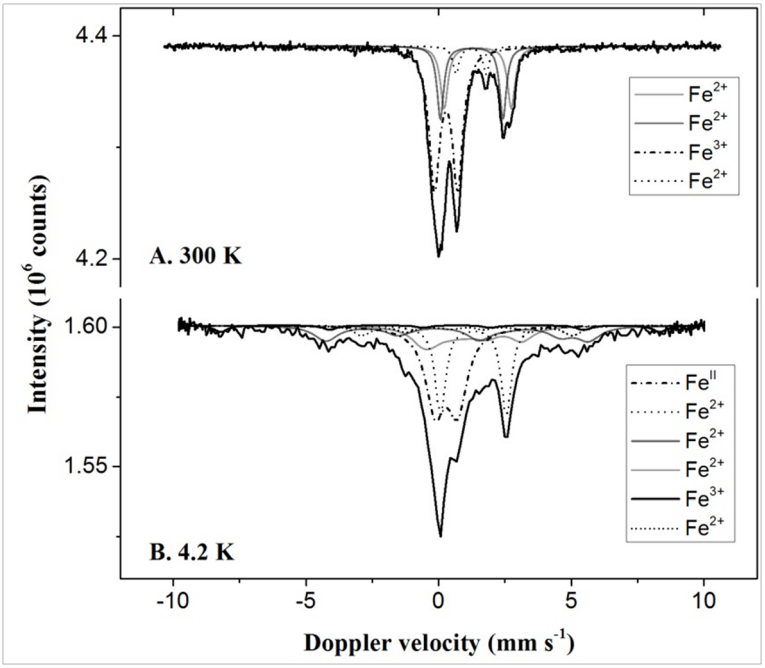


Figure S 4-11: Mössbauer spectra obtained at different temperatures with the surplus sludge solids sampled in Line 2 (Fe(II) dosing) in Leeuwarden.

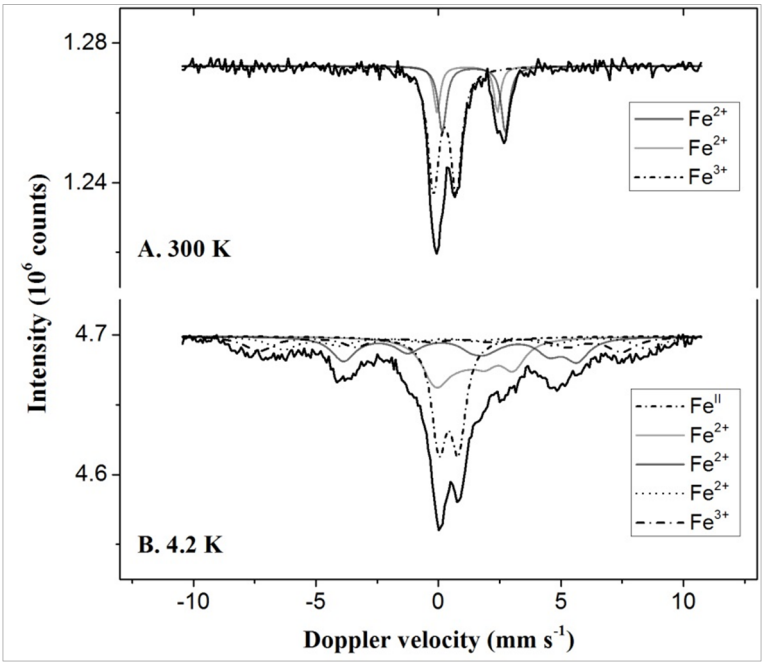


Figure S 4-12: Mössbauer spectra obtained at different temperatures with the digested sludge solids sampled in Leeuwarden.

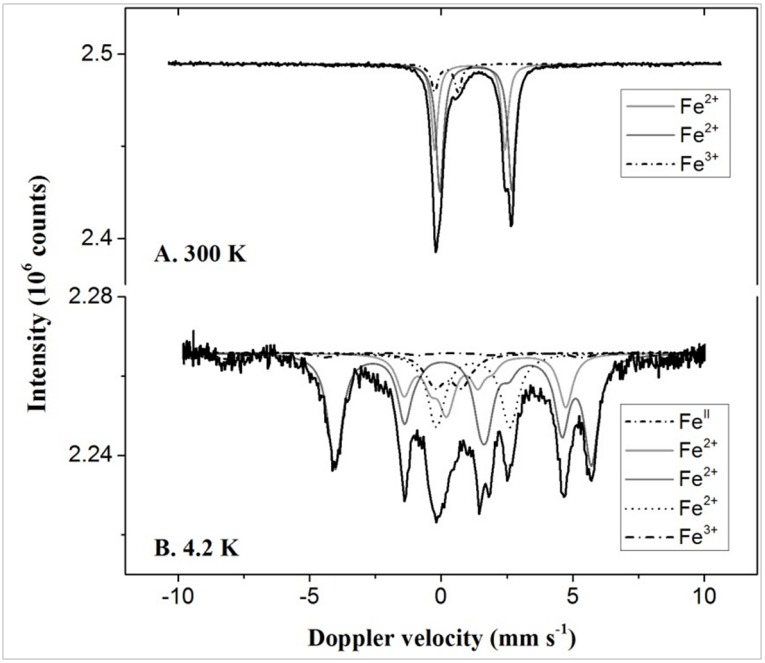


Figure S 4-13: Mössbauer spectra obtained at different temperatures with A-stage sludge solids sampled in Nieuwveer.

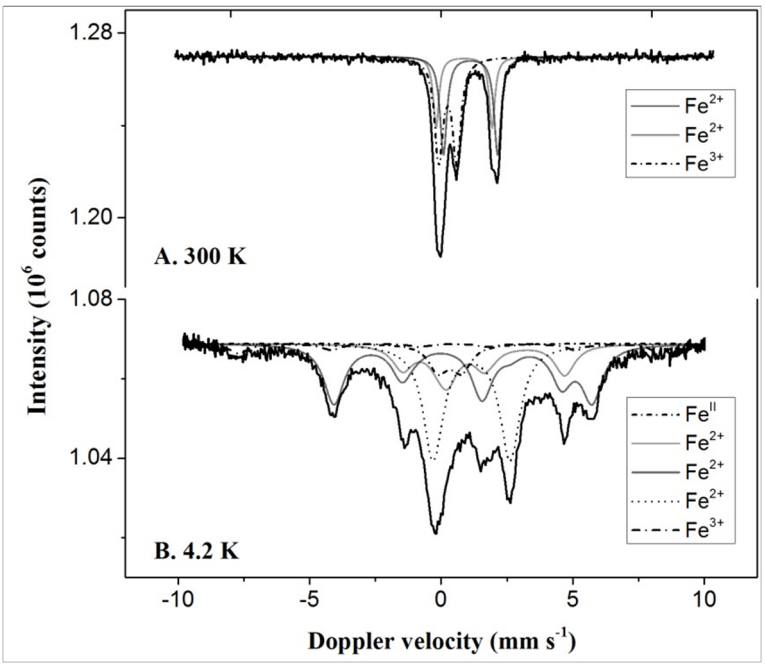


Figure S 4-14: Mössbauer spectra obtained at different temperatures with B-stage sludge solids sampled in Nieuwveer.

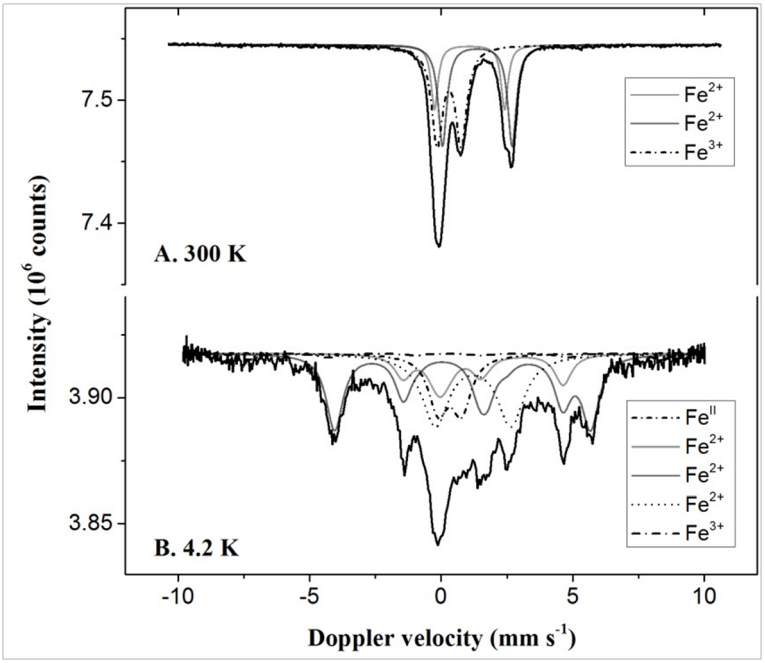


Figure S 4-15: Mössbauer spectra obtained at different temperatures with digested sludge solids sampled in Nieuwveer.

Table S 4-2: Measured parameters in the STP Leeuwarden. The reported values are the mean and the standard deviation of the three measurement campaigns between December 2013 and February 2014. In each campaign measurements were made in triplicates. The effluent from line 2 was only measured once.

LWD	T (°C)	pH	ORP (mV)	TS (g/kg)	VS (g/kg)	TA (mEq/L)	Fe(II) (mg/L)	Fe(III) (mg/L)	Total Dissolved Fe-Ferrozine (mg/L)	Total Dissolved Fe-ICP (mg/L)	Total Fe (mg/kg)	Total Solid Fe (mg/g TS)	o-P (mg P/L)	Total Dissolved P (mg/L)	Total P (mg/kg)	Total Solid P (mg/g TS)	S-SO4 (mg S/L)	Total Dissolved S (mg/L)	Total S (mg/kg)	Total Solid S (mg/g TS)
Influent	11.6 (4.6)	7.9 (0.1)	-195 (61)	1.2 (0.2)	0.4 (0.1)	10.4 (4.4)	0	0.3	0.3 (0)	0.2 (0.1)	1.7 (0.4)	1.2 (0.2)	4.5 (2.8)	5.3 (3.1)	7.5 (3.8)	2.1 (1)	9.6 (1.9)	9.4 (3.1)	18.2 (8.3)	7.5 (7.6)
Effluent line 1	11.2 (1.6)	7.6 (0.2)	62 (63)	0.7 (0.2)	0.1 (0.0)	6.9 (0.5)	0	0.1	0.1 (0.1)	0.1 (0.0)	0.3 (0.1)	0.1 (0.1)	0.4 (0.3)	0.5 (0.4)	0.9 (0.4)	0.5 (0.4)	11 (1.2)	10.5 (1.2)	15.7 (5.5)	8.4 (10.2)
Effluent line 2	12.2	7.8	45	0.9	0.1 (n.d.)	5.6 (n.d.)	0	0.1	0.1	0.1	0.5	0.4	0.2	0.3	0.4	0.2	12.4	13	13.6	0.7
Before Fe dosing line 2	11.4 (4.6)	7.4 (0.1)	-156 (35)	4.2 (0.1)	3 (0.2)	9.1 (1.5)	0.1	0.6	0.7 (0.3)	0.7 (0.3)	52.5 (9.5)	12.2 (2.0)	10.1 (9.9)	11.2 (10.4)	109.8 (16.9)	23.4 (1.4)	11 (1.8)	10.1 (2.6)	38 (1.8)	6.6 (0.6)
After Fe dozing line 2	11.7 (4.5)	7.3 (0.0)	-18 (40)	4.7 (0.4)	3.2 (0.3)	7.6 (0.9)	0.1	0.5	0.6 (0.3)	0.5 (0.3)	59.1 (16.3)	12.7 (3.7)	1.6 (0.6)	2 (0.8)	119.8 (19.9)	25.2 (2.2)	11.3 (1)	10.4 (2.5)	41.8 (10.1)	6.7 (1.8)
Surplus sludge line 1	12.3 (2.7)	7.4 (0.1)	-42 (75)	69 (0.7)	4.9 (0.7)	8.9 (0.7)	0.1	0.5	0.6 (0.1)	0.5 (0.1)	106.4 (25.2)	15.3 (2.7)	2.7 (1.2)	3.4 (1.4)	188.9 (9.1)	27.1 (2.2)	11.4 (1.2)	10.5 (2.1)	53.9 (5.1)	6.4 (0.4)
Surplus sludge line 2	12.4 (3.7)	7.3 (0.0)	-90 (8)	69 (0.3)	4.9 (0.1)	9.5 (0.7)	0.6	0.6	1.1 (0.3)	1.2 (0.4)	96.8 (37.8)	13.8 (4.9)	4.3 (0.4)	5.6 (0.0)	192 (5.7)	26.9 (0.6)	11.2 (1.6)	11 (3.5)	58.3 (8.3)	6.9 (0.4)
Digested sludge	29.3 (0.2)	7.4 (0.1)	-380 (27)	45.6 (0.7)	28.4 (0.8)	157.8*/211.7** (11.9/30.8)	0.6	1.6	2.1 (0.2)	1.7 (0.4)	1849.7 (92.3)	40.5 (1.9)	169.6 (22.4)	179.3 (33.6)	1970.6 (149.1)	39.4 (3.3)	5.1 (2.4)	7.1 (1.8)	418.5 (21.6)	9 (0.4)

*Supernatant after centrifugation

** Raw sludge

LWD	Total Dissolved Al (mg/L)	Total Al (mg/kg)	Total Solid Al (mg/g TS)	Total Dissolved Mg (mg/L)	Total Mg (mg/kg)	Total Solid Mg (mg/g TS)	Total Dissolved Ca (mg/L)	Total Ca (mg/kg)	Total Solid Ca (mg/g TS)	Total Dissolved K (mg/L)	Total K (mg/kg)	Total Solid K (mg/g TS)	Total Dissolved Na (mg/L)	Total Na (mg/kg)	Total Solid Na (mg/g TS)
Influent	<0.1	<1.25	-	12.3 (0.7)	13.9 (2.4)	1.7 (2.4)	64.1 (12.3)	75 (9.7)	10.6 (9.3)	20.6 (9.8)	25.8 (14.6)	4.5 (4.1)	178.6 (43.8)	213.6 (14.6)	34.1 (29.9)
Effluent line 1	<0.05	<1.25	-	10.3 (1.6)	11 (1.6)	1.1 (0.6)	58.4 (11.2)	64 (9)	8.8 (4.9)	13.5 (2)	15.4 (2.8)	2.2 (2.9)	164.3 (48.2)	173.5 (45.7)	14 (7.3)
Effluent line 2	<0.05	<1.25	-	12.9	13.2	0.3	72.4	75.2	3.3	13.2	17.4	4.8	194.5	201	7.7
Before Fe dosing line 2	<0.2	21.2 (1.2)	5 (0.4)	13.6 (1.5)	34.4 (1.8)	4.9 (0.1)	59.8 (15.9)	151.3 (17.6)	21.7 (7.4)	21.1 (7.4)	54.1 (2.1)	7 (1.2)	168.1 (61.7)	181.8 (61.9)	3.4 (1.1)
After Fe dozing line 2	<0.1	23 (1.5)	5 (0.6)	11.7 (1.6)	36.9 (3.7)	5.4 (0.6)	61 (12.2)	158.2 (22.2)	20.7 (3.9)	16.2 (1.9)	57.64 (2.7)	36.8 (49.1)	154.3 (43.6)	168.2 (46.6)	3.1 (0.8)
Surplus sludge line 1	<0.2	34.3 (7.9)	5 (0.7)	11.8 (1.5)	50.5 (2)	5.7 (0.7)	58.8 (10.8)	207.8 (11.3)	22 (3.8)	18.1 (0.3)	78.7 (5.4)	25 (27.2)	168.2 (50.4)	191.5 (43.4)	3.6 (1.3)
Surplus sludge line 2	< 0.2	34.7 (7.6)	5 (0.9)	13 (2.9)	51 (3)	5.5 (0.2)	59.8 (15.6)	205.8 (0.4)	21.3 (3.1)	19.8 (1)	76.7 (10.0)	8.3 (1.0)	163.7 (47.1)	171.8 (45.0)	1.3 (0.3)
Digested sludge	<0.5	239.8 (17.4)	5.3 (0.4)	5.4 (4.5)	370.8 (37.5)	8 (0.8)	49.9 (5.2)	1901 (183.7)	40.6 (3.5)	500.4 (29.2)	551.4 (29.0)	1.6 (0.6)	263.2 (12.2)	289.8 (49.5)	0.8 (0.8)

Table S 4-3: Measured parameters in the STP Nieuwveer. Nieuwveer was sampled once in March 2014. The reported values are the mean and standard deviation of triplicate measurements.

Nieuwveer	T (°C)	pH	ORP (mV)	TS (g/kg)	VS (g/kg)	TA (mEq/L)	Fe(II) (mg/L)	Fe(III) (mg/L)	Total Dissolved Fe-Ferrozine (mg/L)	Total Dissolved Fe-ICP (mg/L)	Total Fe (mg/kg)	Total Solid Fe (mg/g TS)	o-P (mg P/L)	Total Dissolved P (mg/L)	Total P (mg/kg)	Total Solid P (mg/g TS)	S-SO4 (mg S/L)	Total Dissolved S (mg/L)	Total S (mg/kg)	Total Solid S (mg/g TS)
Influent	9.8	7.3	10	0.4 (0.01)	0.1 (0.01)	4.6	0	0.3 (0.0)	0.3 (0.0)	0.2	0.86 (0.0)	1.4	1.6	2.0	2.9 (0.0)	2.3	10.8	10.8	11.3 (0.2)	1.4
Effluent	9.7	7	117	0.3 (0.02)	0.08 (0.0)	2.1	0.0	0.1 (0.0)	0.09 (0.0)	0.1	0.23 (0.0)	0.5	0.8	1.1	1.3 (0.0)	0.7	10.8	9.9	10.4 (0.1)	1.6
A-stage	9.4	7.1	-90	3.6 (0.1)	2.8 (0.1)	11.8	0.0	0.8 (0.1)	0.8 (0.1)	0.8	82.5 (2.1)	22.4	1.0	1.5	57.7 (0.5)	15.4	12.0	11.2	20.9 (2.1)	2.7
A-stage: Surplus sludge	10	6.8	-264	18.6 (0.1)	14.8 (0.1)	13.2	18.3 (1.1)	12.7 (0.1)	31 (1.2)	32.4	436.7 (23.6)	21.8	18.9	31.2	290.2 (15.3)	13.9	10.0	16.8	89.5 (2.6)	3.9
B-stage: Surplus sludge	9.4	7	-109	14.9 (0.3)	11.6 (0.2)	9.1	0.0	1.9 (0.0)	1.9 (0.03)	1.4	426.7 (9.4)	28.6	5.5	7.2	375 (7.1)	24.8	10.9	11.4	107.8 (3.5)	6.5
External sludge before digestion	17	6	-294	75.9 (8.1)	58.3 (5.9)	30.2	70.7 (1.2)	26.8 (26.9)	97.6 (7.8)	90.0	1747 (139)	21.8	12.9	54.8	1121.8 (82.9)	14.1	18.6	15.3	347 (21.6)	4.4
Digested sludge	27	7.7	-322	41.6 (0.1)	24.8 (0.7)	140.7	0.1 (0.0)	3.0 (0.1)	3.1 (0.1)	3.0	2389 (78.7)	57.4	70.2	73.8	1558.2 (29.2)	35.8	7.1	14.5	442.2 (8.4)	10.3

Nieuwveer	Total Dissolved Al (mg/L)	Total Al (mg/kg)	Total Solid Al (mg/g TS)	Total Dissolved Mg (mg/L)	Total Mg (mg/kg)	Total Solid Mg (mg/g TS)	Total Dissolved Ca (mg/L)	Total Ca (mg/kg)	Total Solid Ca (mg/g TS)	Total Dissolved K (mg/L)	Total K (mg/kg)	Total Solid K (mg/g TS)	Total Dissolved Na (mg/L)	Total Na (mg/kg)	Total Solid Na (mg/g TS)
Influent	<0.1	0.3 (0.0)	0.9	5.2	5.6 (0.0)	1.2	44.0	45.7 (0.1)	4.7	14.0	14.6 (0.2)	1.5	48.8	47.1 (0.2)	-
Effluent	<0.05	<0.2	-	4.5	4.7 (0.1)	0.7	37.3	37.9 (0.5)	2.2	11.2	12.9 (0.2)	5.5	43.6	42.7 (0.7)	-
A-stage	<0.5	19.4 (1.6)	5.3	4.7	<17	-	40.3	143.3 (5.2)	28.3	13.1	34.8 (0.7)	6	45.4	<83	-
A-stage: Surplus sludge	<0.2	82.2 (7.3)	4.4	10.7	39.7 (2.8)	1.6	88.5	373.3 (23.6)	15.4	34.7	69.7 (4.7)	1.9	56.7	<83	-
B-stage: Surplus sludge	<0.2	77.5 (1.2)	5.2	5.6	46 (0.9)	2.7	39.8	309.5 (10.1)	18.2	20.5	100.5 (4.9)	5.4	44.4	<83	-
External sludge before digestion	<0.5	451.5 (50.4)	5.9	34.2	137.2 (4.6)	1.4	215.5	1226.4 (40.5)	13.5	107.5	252.3 (12.4)	2	62.5	<170	-
Digested sludge	<0.5	479.9 (5.2)	11.5	12.5	170.9 (4.2)	3.8	41.8	1251.2 (13.9)	29.1	196.0	267.3 (2.5)	1.9	81.1	<160	-

Chapter 5: Vivianite as a key mineral in sewage treatment plants and its potential role for phosphate recovery



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5.1 Introduction

Phosphate has to be used more sustainably in future, including its recycling from secondary resources (Carpenter and Bennett, 2011; Childers et al., 2011). Sewage sludge is such a phosphate rich secondary source (van Dijk et al., 2016). However, current phosphate recovery technologies have limitations in recovery efficiencies and applicability. Agricultural use of sewage sludge is a simple way to reuse the nutrients in the sludge, but this route has logistic constraints (Macdonald et al., 2011) and pollutants in the sludge are a concern (Clarke and Smith, 2011). Recovery of phosphate from sewage sludge ashes has the potential for high recovery efficiencies, but requires the realization of dedicated sewage sludge incinerators that are expensive to build. Phosphate recovery via struvite is frequently suggested as a promising route but the recovery efficiency is relatively low, only between 10–50 % of all influent phosphate can be recovered (Egle et al., 2015; Ewert et al., 2014). Additionally, struvite recovery is only possible in sewage treatment plants (STPs) with enhanced biological P removal (EBPR) (Wilfert et al., 2015a). More often just iron salts are used for chemical phosphate removal (CPR), or EBPR supported by CPR is used for phosphate removal to meet stringent effluent phosphate regulations (Wilfert et al., 2015a). Iron and aluminium are present in sewage sludge due to CPR but also because of other reasons such as iron rich groundwater infiltration into the sewer system, iron dosing to mitigate sulphide emissions, because iron naturally occurs in human excreta and because both elements are used as coagulants. These metals can lower the recovery efficiency for struvite further (Korving et al., 2017). Thus, there is still a need for economic phosphate recovery technologies from sewage sludge without sludge incineration and for sludge from CPR plants that dose iron.

The ferrous iron phosphate mineral vivianite ($Fe(II)_3(PO_4)_2x8H_2O$) is forming in anaerobic systems with relatively low sulphide concentrations when iron and phosphate are present (Rothe et al., 2016). Such conditions occur in STPs, especially during anaerobic sludge digestion. Accordingly, several authors found indications for vivianite in STPs (Frossard et al., 1997; Roussel and Carliell-Marquet, 2016; Singer, 1972; Wilfert et al., 2016) or in systems were wastewater was kept under anaerobic conditions (Azam and Finneran, 2014; Cheng et al., 2015; Zhang, 2012) or in experiments where ferrous iron, Fe(II) was added to oxygen free wastewater (Ghassemi and Recht, 1971). However, only in two of these studies the vivianite was quantified (Frossard et al., 1997; Wilfert et al., 2016).

In a recent publication (Wilfert et al., 2016) we hypothesised that the amount of phosphate that is bound in vivianite is positively correlated with the molar Fe:P ratio in digested sludge. Because under conditions that occur in anaerobic digesters, vivianite is likely thermodynamically the most stable phosphate phase in the sludge (Nriagu and Dell, 1974). Furthermore, the formation of vivianite can be quick as substantial amounts of it were formed, due to iron reduction, in experiments with septic wastewater within 48 h (Azam and Finneran, 2014). Vivianite can also directly precipitate from solution at circumneutral pH (Ghassemi and Recht, 1971; Roldan et al., 2002). If these assumptions are correct, then this would imply that under reducing conditions most phosphate is bound in one relatively homogenous mineral

phase, i.e. vivianite. Its formation would mainly be limited by the phosphate that is bound in organic structures and by the presence of sulphide, that has a higher binding strength to ferrous iron than phosphate (Nriagu, 1972). If one were be able to separate the vivianite from the sewage sludge it should be possible to achieve higher phosphate recovery efficiencies compared to struvite. Struvite based recovery technologies show a relative low recovery efficiency because part of the phosphate is bound to other, less soluble phases than struvite, such as iron or aluminium phosphates (Baker et al., 2006; Doyle and Parsons, 2002; Mamais et al., 1994; Neethling and Benisch, 2004). There are reports that significant quantities of vivianite can already be formed before the anaerobic digestion in surplus sludge (Frossard et al., 1997; Wang et al., 2017; Wilfert et al., 2016). Also there are regular reports of vivianite precipitation in pipe lines at sewage treatment sites (Marx et al., 2001). Nevertheless, research reports on vivianite in sewage sludge do not report size, purity, composition and % of phosphate that is bound in vivianite before and after digestion nor the mechanism of vivianite formation. Often samples are prepared in such a way that vivianite gets oxidized. The best practice is to dry the samples at anaerobic conditions to prevent oxidation processes that can modify the mineral composition of the sample (Kraal et al., 2009). It is possible to find vivianite when samples are dried at room temperature, even in the presence of oxygen. Above 70 °C, in the presence of oxygen, vivianite is transformed within hours into amorphous iron phosphate compounds (Čermáková et al., 2015; Poffet, 2007).

In this study we sampled and analysed sludge from several full scale STPs in Europe with different molar Fe:P ratios to be able to reject or accept the hypotheses that (I) the extent of phosphate that is bound in vivianite is a function of a molar Fe:P ratio in digested sludge and that (II) significant amounts of vivianite are already formed in the surplus sludge prior to the anaerobic digestion process.

We chose a combination of Mössbauer spectroscopy, XRD and SEM-EDX/eSEM-EDX for analysing sludge before and after the anaerobic digestion process to determine the vivianite content and to characterize the vivianite in the samples.

5.2 Material and Methods

Sampling, sample handling and sample analyses (Mössbauer spectroscopy, XRD, TS/VS, dissolved elemental composition and dissolved Fe(II)/Fe(III)) was done as previously described (Wilfert et al., 2016). In short, all samples were taken after a period of 48 h without precipitation. Surplus sludge samples were taken from settled sludge before dewatering and before it was pumped into the anaerobic digester. Digested samples were sampled directly after the digestion process before sludge dewatering. The samples were stored in glass bottles and transported in cooling boxes on ice to minimize microbial activity until analyses started in the laboratory, about 3 – 6 hours after sampling. Sample drying started at most 8 h after sampling and was completed within 24 h. Sampling and sample processing were done under anaerobic conditions. Total elemental compositions of the samples were determined after a microwave assisted acid digestion (HNO_3=69%, 15 min, 180 °C) followed by ICP-OES. Additionally, the elemental composition of the sludge solids was determined using XRF. For XRF analyses the

samples were pressed into powder tablets, using an organic binder. The measurements were performed with a Panalytical Axios Max WD-XRF spectrometer and data evaluation was done with SuperQ5.0i/Omnian software. Total solids (TS) and volatile solids (VS) were measured according to standard methods (APHA, AWWA, WEF, 1998). Inside an anaerobic glovebox (95% N_2 and 5% H_2, O_2<20 ppm) the sludge samples were transferred into plastic centrifuge tubes and centrifuged outside the glovebox (15 min, 3200 G). Dissolved elemental compositions (ICP-OES), dissolved anions (IC) and dissolved Fe(II)/Fe(III) (Viollier et al., 2000) were determined after filtration of the supernatant (0.45 µm) inside the glovebox. Solid material was derived from centrifuge pellets of the samples. Inside the glovebox, pellets were finely spread on glass plates, dried (25 °C, 24 h, in the dark) and afterwards grinded. Samples for XRD analyses were filled in glass capillaries and sealed first with modelling clay and then superglue. Right before analyses, glass capillaries were sealed using a burner. The measurements were done on a PANalytical X´Pert PRO diffractometer with Cu-Ka radiation (5-80 º2θ, step size 0.008º). The results from XRD analyses were made semi-quantitative by determining the amorphous and crystalline area of the spectra (Origin Pro 9). This allows the determination of the degree of crystallinity and thus of the total mineral share of the sample. Spectra for digested sludge samples using XRD were further fitted by Rietveld refinement using the software GSAS (Larson and Dreele, 1994; Toby, 2001). The samples before the anaerobic digestion showed a large amorphous fraction and Rietveld refinement did not give reliable results. These results were still made semi-quantitative by using the output of the program package HighScore (version 4.6.1, 2017) to compare these measurements with the results obtained from Mössbauer spectroscopy. Vivianite was prepared (Roldan et al., 2002) and added to digested sewage sludge in Dokhaven in different quantities to test the reliability of the method. Vivianite could be tracked back with an error of 7% (Table S 5-1 and Table S 5-2, all spectra and peak assignments are included in the supplementary information).

For Mössbauer analyses, samples were filled in plastic rings, sealed with Kapton tape and super glue and then wrapped in parafilm. Transmission ^{57}Fe Mössbauer spectra were collected at 4 and 300 K and for some samples at 100 K with conventional constant-acceleration and sinusoidal velocity spectrometers using a ^{57}Co(Rh) source. Velocity calibration was carried out using an α-Fe foil. The Mössbauer spectra were fitted using Mosswinn 4.0 (Klencsár, 1997). All Mössbauer spectra and related hyperfine parameters are in the supplementary information (Figure S 5-1 to Figure S 5-5 and Table S 5-6).

Morphology and elemental compositions of sludge particles in the grinded solids were also analysed by eSEM-EDX and SEM-EDX. Samples for eSEM-EDX and SEM-EDX were exposed to air during measurements. Samples for eSEM-EDX were vacuum dried on the sample holder inside the instrument vacuum chamber. For SEM-EDX dried and grinded sample was used. For these analyses first an EDX scan with low magnification was performed to identify particles with high Fe:P molar ratio. Some of these particles were randomly chosen to determine their elemental composition.

All sampled STPs also had an anaerobic digestion stage. The plants were mainly chosen according to the molar Fe:P in the digested sludge. Relevant plant parameters and treatment designs are summarized in Table 5-1. Table S 5-3 and Figure S 5-4 show the composition of the sludge samples. Note, that sometimes the iron content (and thus the molar Fe:P ratio in the solids, Table 5-1) in the digested sludge samples was significantly different to the samples before the anaerobic digestion. This may be due to external sludge input in the digester (e.g. Leeuwarden, Wilfert et al., 2016) because of additional iron dosing before the digester (Dokhaven), because of fact that iron rich secondary sludge was sampled and that this sludge was combined with primary settled sludge in the digester (Cologne, Berlin and Finland) or because of a combination of these factors (Dokhaven).

*Table 5-1: Details about the STPs that were sampled during this study (*indicates SRT in AB plants, A-stage/B-stage; ** the load is given in 150 g COD/day as yearly average; ^indicates Primary Sludge / Thickened Sludge; n.d. = not determined).*

			SRT (days)		Loads (kmol/d)					Molar Fe:P measured	
STP	P Removal	Load** (p.e. / day)	Before digestion	During digestion	S^{2-} influent	Fe Influent	Fe Dosing	P Influent	P Effluent	Before digestion	After digestion
Asten (NL)	EBPR	76,000	15	49	n.d.	n.d.	0.0	3	0.4	0.14	0.17
Leeuwarden (NL)	EBPR + Fe(II)/Fe(III)	226,000	15	42	1.18	1.1	1.1	8.5	0.8	0.25	0.55
Nieuwveer, Breda (NL)	Fe(II)	440,000	0.6 / 15*	25	n.d.	2.9	8.1	19.1	3.5	0.86	0.85
Dokhaven, Rotterdam (NL)	Fe(III)	564,000	0.3 / 5.5*	35	3.17	15.6	5.6	25.7	2.4	0.85	1.07
Rodenkirchen, Cologne (Ger)	Fe(III)	70,000	12	21	0.17	0.5	4.8	3.3	0.1	1.38	1.55
Münchehofe, Berlin (Ger)	Fe(II)	320,600	0.7	30	14.86	1.8	21.7	16.2	0.7	1.87	1.57
Espoo (Fin)	Fe(II)	321,045	6-10	13-14	n.d.	5.6	44.4	21.2	0.7	2.19	2.4

5.3 Results

5.3.1 XRD and Mössbauer

5.3.1.1 Fe(II) content of the samples

Mössbauer spectra obtained at 4 K for several sludge samples showed ferrous iron as the dominant form of iron (>90%) in digested sewage sludge (Table 5-2). This was expected since during anaerobic digestion strongly reducing methanogenic conditions prevail. Here, chemical and / or biological iron reduction will turn Fe(III) into Fe(II). The sample from Leeuwarden showed some signs of oxidation because the sample was not protected well enough against oxidation as explained earlier (Wilfert et al., 2016). Surprisingly, before digestion, in the surplus sludge samples, Fe(II) was also the dominant iron phase. In sludges with lower iron content (Fe:P<1.0), Fe(II) made up 94-96% of all iron, even when Fe(III) was used for phosphate elimination. In plants with higher iron dosing (Berlin and Cologne) 50 - 60% of all iron was present in its reduced form. The Fe(III) in these samples is present as iron oxides.

Table 5-2 Fe(II)/Fe(III) content in surplus and digested sewage sludge (from Mössbauer measurements at 4 K). Iron and phosphorus concentrations were determined using XRF.

		Surplus Sludge		Digested Sludge	
	Dosing	Molar Fe:P	Fe(II) (%)	Molar Fe:P	Fe(II) (%)
Leeuwarden (Line 1)	Fe(II)/Fe(III)	0.4	94	0.5	85*
Nieuwveer A-Stage	Fe(II)	0.9	96	0.8	96
Nieuwveer B-Stage	Fe(II)	0.6	95		
Dokhaven A-Stage	Fe(III)	0.8	91	1.1	n.d.
Berlin	Fe(II)	1.7	63	1.6	n.d.
Cologne	Fe(III)	2.1	50	1.6	91
Espoo	Fe(II)	2.5	n.d.	2.4	100

*Exposed to air

5.3.1.2 Quantification of vivianite in the samples

The vivianite content in the samples in surplus and digested sludge was determined by using Mössbauer spectroscopy at different temperatures and by semi-quantitative XRD. This data was plotted against the molar Fe:P ratio as obtained from XRF (Figure 5-1 and Figure 5-2). Additionally, data from an earlier study (Frossard et al., 1997) was included.

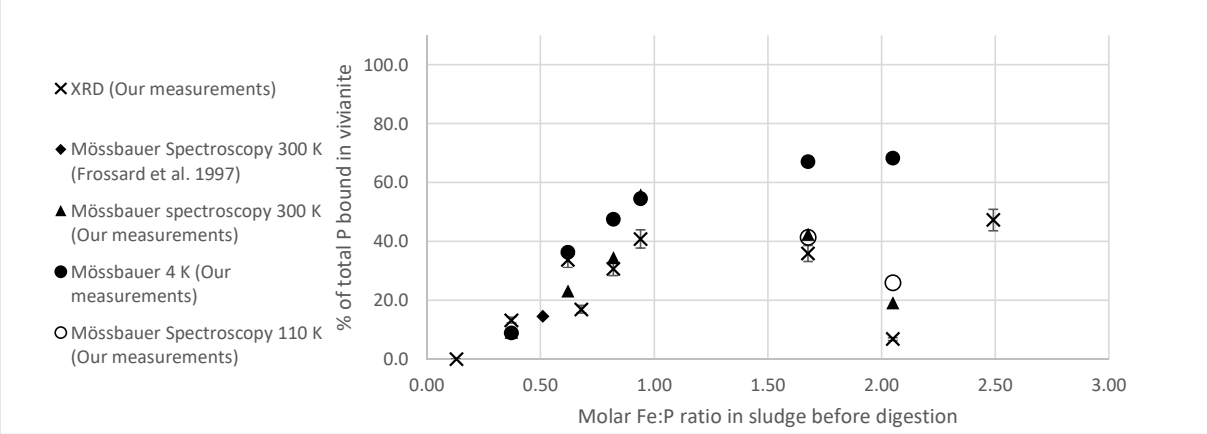


Figure 5-1: Molar Fe:P and % of total phosphorus bound in vivianite in surplus sludge (error bars for semi quantitative XRD indicate error as determined by standard addition for digested sludge sampled from Dokhaven). Mössbauer spectra obtained at 300 K (room temperature, RT).

The Mössbauer measurements obtained at 300 K clearly showed that vivianite is present with parameters that are in agreement with earlier measurements on vivianite standards (Gonser and Grant, 1976; Wilfert et al., 2016). However, at 4 K the spectra become less clear and very complex, still vivianite was detected in these measurements. Thus, because interpretation and fitting of 4 K data was difficult it was decided to re-measure some samples at 100 K to be able to quantify vivianite more easily, as the Mössbauer f-factors of the different species present are assumed to be similar at this temperature. The latter measurements again indicate that vivianite is present in the samples. Due to difficulties in the spectra fitting and interpretation, measurements at 4 K are used for discussions related to the oxidation state of iron in the samples

mainly. For sake of completeness, the quantification of vivianite in the sewage sludge using the data obtained at 4 K was plotted as well in Figure 5-1 and Figure 5-2.

In most samples measured at 4 K a paramagnetic (doublet) Fe(II) species that might be assigned to vivianite were found in significant amounts as described before (Wilfert et al., 2016). This phase is listed as "vivianite impure" in Table S 5-6. The isomer shift of this Fe(II) and the quadrupole splitting are close to the one of vivianite. It could be that some dispersed vivianite structures or vivianite structures with impurities are still paramagnetic at 4 K which is close to the magnetic ordering temperature of vivianite (12 K). For further discussions, it was assumed that the Fe(II) species that could not clearly be assigned to vivianite with Mössbauer spectroscopy at 4 K was in fact vivianite with impurities as discussed earlier (Wilfert et al., 2016).

We prepared standards with different degrees of impurities of magnesium and calcium. The presence of vivianite was confirmed with XRD. Unfortunately, the samples partly oxidized before Mössbauer spectra were obtained. Thus, a clear pattern of impurities vs. site ratios was not visible because of the two antagonistic effects on the site ratio, i.e. oxidation vs. impurities. What we could see, however, was that the impurities affected the oxidation of vivianite. Vivianite with impurities was almost completely oxidized within 48 hours (about 89% of all Fe(II) got oxidized) as indicated by Mössbauer spectroscopy (data not shown). This was much quicker and to a much larger extent compared to pure vivianite in earlier studies, where oxidation took several weeks and only part of the vivianite got oxidized and turned into Fe(III) oxides (Miot et al., 2009; Roldan et al., 2002). It was observed that at room temperature after about an year the Fe(III) concentration in synthetic vivianite stabilized at 50% in vivianite when just chemical oxidation takes place (Rouzies and Millet, 1993).

Before the anaerobic digestion, sludges with a molar Fe:P ratios below 1 show a clear increase of phosphate bound in vivianite with an increase of iron content in the sludge (Figure 5-1). From these sludges, the highest Fe:P ratio of about 0.95 was found in the A-stage of Nieuwveer. Here, between 41 and 56% of all phosphate was bound in vivianite according to XRD and Mössbauer spectra. All results for these low iron sludges are in relative good agreement, also the ones determined by Frossard et al. are in line with our measurements.

At higher molar Fe:P ratios, however, the vivianite quantification differed more clearly between the methods and a relation between the Fe:P molar ratio and the vivianite content in the sludge was not obvious. In surplus sludge from Berlin, with a molar Fe:P ratio of about 1.7. Mössbauer measurements made at 300 and 100 K and the quantification using XRD agree well. Between 36 and 43% of all phosphate is bound in vivianite. However, the measurements at 4 K indicate that much more, about 67%, of all phosphate is bound in vivianite. In the sludge from Cologne, only Mössbauer quantifications from the measurements at 100 and 300 K match well, giving vivianite contents between 19 and 26%. The data at 4 K again suggests a much higher vivianite content of 68%. In contrast, quantification using XRD gives a much lower share of phosphate bound in vivianite (7%). The spectra obtained at 4 K were difficult to interpret as discussed

below (section 5.4.3). In Cologne and Berlin, before the anaerobic digestion, for the Fe(II) spectra obtained at 4 K, it was assumed that the phase which could not be clearly assigned to vivianite is indeed vivianite. This assumption obviously leads to a higher vivianite content in the samples as determined at 4 K compared to the other measurements. Assuming that the impure vivianite is in fact not vivianite would mean that in Cologne about 27% and in Berlin about 37% of all phosphate would be bound in vivianite. In the surplus sludge from Finland (molar Fe:P = 2.5) only XRD measurements were made, according to these measurements about 50% of all phosphate was bound in vivianite.

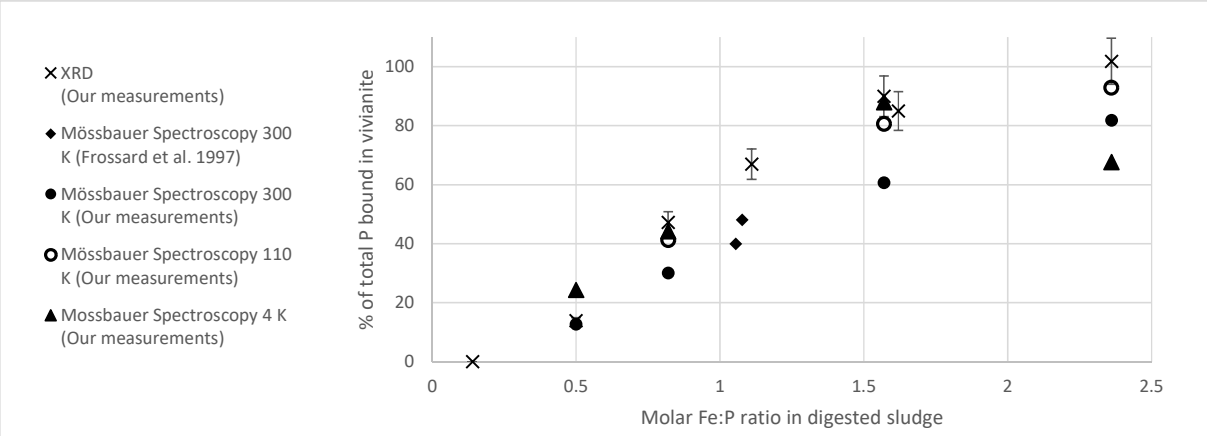


Figure 5-2: Molar Fe:P and % of total phosphorus bound in vivianite digested sludge (error bars for semi quantitative XRD indicate error as determined by standard addition for digested sludge sampled from Dokhaven). Mössbauer spectra obtained at 300 K (room temperature, RT).

After the anaerobic digestion, all measurements show an increase of the vivianite content in the sludge with a simultaneous increase of the iron content (Figure 5-2). The measurements from Frossard and co-workers (Frossard et al., 1997) are again in line with our data. All methods showed that phosphate bound in vivianite started to level off in the sludge with the highest iron content that was sampled in Finland (molar Fe:P =2.5). The absolute values of the vivianite in the Finnish sludge differed but both Mössbauer measurements at 100 K and XRD suggest that almost all phosphate can be bound in vivianite. Between 67% (4K), 82% (300 K), 93% (100 K) and 101% (±7.8; XRD) of all phosphate is contained in vivianite according to these measurements. The data obtained at 4 K suggests a lower vivianite content compared to the measurements at 300 and 100 K which is in contrast to the measurements before the digestion. The data obtained with Mössbauer spectroscopy at 300 K gives, except for the sample in Finland, the lowest vivianite content in the digested sludge samples. Whereas XRD data tends to give higher vivianite amounts than the data from Mössbauer spectroscopy.

5.3.2 SEM-EDX and eSEM-EDX

Particles with a size distribution between 20 – 100 µm and elemental composition close to the one of vivianite were found by analysing the digested sludge samples using SEM-EDX. The composition of some particles with crystalline appearance and high iron and phosphate content is summarized in Table 5-3. All particles consisted mainly of iron and phosphate but also always

some impurities were present. The iron and phosphate content of the particles increases with the iron content of the sewage sludge. Except of Finland samples, all samples showed molar Fe:P ratios below the one of vivianite (1.5). In the Finnish STP large quantities of iron are added to remove phosphate. Besides iron and phosphate also calcium, magnesium and some aluminium were present in all particles.

Table 5-3: Elemental composition of crystalline particles in the dried digested sewage sludge sample. The particles were analysed using SEM-EDX.

	Fe:P	Ca:P	Mg:P	Al:P
Leeuwarden (n=3)	1.1 (0.06)	0.1 (0.00)	0.2 (0.00)	0.0 (0.00)
Nieuwveer (n=4)	1.4 (0.30)	0.3 (0.29)	0.1 (n=1)	0.1 (0.15)
Dokhaven (n=7)	1.4 (0.52)	0.3 (0.32)	0.1 (0.03)	0.1 (0.04)
Cologne (n=4)	1.5 (0.17)	0.1 (0.03)	0.1 (0.03)	0.0 (0.04)
Espoo (n=4)	2.0 (0.30)	0.2 (0.13)	0.1 (0.20)	0.1 (0.12)

Subsequently, digested sewage sludge samples from Berlin and Dokhaven were also analysed using environmental (e)SEM-EDX. For this purpose the samples were rapidly vacuum dried inside the instrument. A higher abundance of particles with high iron and phosphate content and with diameters similar to the ones detected by SEM-EDX were found in these samples (Figure 5-3, Table S 5-5). The particles were free, i.e. not covered by organic coating. These particles were better visible and more abundant in samples that were analysed using SEM-EDX. Probably, the slow drying of the samples for SEM-EDX at room temperature can result in organic coating of the vivianite compared to the quick vacuum drying were the sample morphology is more fibrous. We concluded that the vivianite particles are present as free particles in the sludge as opposed to earlier observations (Frossard et al., 1997).

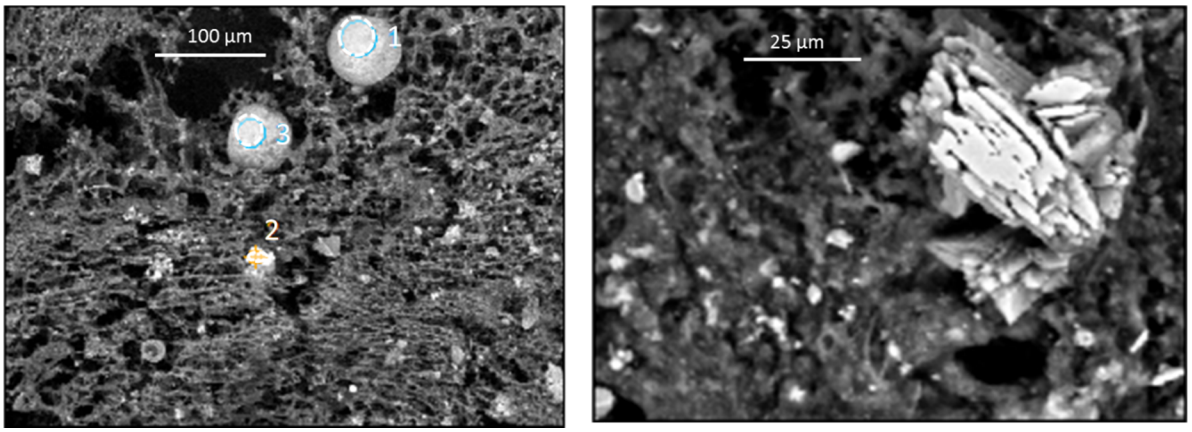


Figure 5-3: Images obtained with eSEM using sludge sampled in Dokhaven (composition of the spots 1,2 and 3 from the left image and the composition of the particle on the right are listed in the appendix, Table S 5-5).

5.4 Discussion

5.4.1 Vivianite quantification before the anaerobic digestion

Mössbauer spectra obtained at liquid helium temperature revealed that Fe(II) dominates the iron pool in surplus (≥50%) and digested sewage sludge (>90%) although in the plants Fe(III) was dosed and despite the fact that the sludge solids passed also aerated sections in the STPs. In all STPs where Fe(III) was dosed, vivianite was present as indicated by XRD and Mössbauer spectroscopy. At molar Fe:P ratios below 1 in the surplus sludge, always more than 90% of all iron was present as Fe(II). Because Fe(III) was dosed, the dominance of Fe(II) in the surplus sludge before anaerobic digestion indicates that chemical or biological Fe(III) reduction must occur in the STPs. Iron could be reduced by reduced sulphide compounds (Biber et al., 1994; Nielsen et al., 2005), organics (Cornell et al., 1989) indirectly via fermenting bacteria (Kappler et al., 2004) or directly via iron reducing bacteria (Nielsen, 1996). Another important source for iron in the sludge is the incoming raw sewage (Table 5-1). Probably, this iron pool was in our STPs dominated by Fe(II), because sulphidic conditions prevailed in most influents (Table 5-1). From all surplus sludges the highest Fe(III) content was found in Cologne. Here about 50% of all iron was present as Fe(III) in iron oxides, probably a mixture of ferrihydrite and goethite as indicated by Mössbauer spectroscopy. The presence of ferrihydrite would be surprising because it transforms quickly into lepidocrocite and/or goethite in the presence of Fe(II). Here relatively large amounts of Fe(III) are added to remove phosphate. Obviously, iron reduction is not quick enough to turnover all of this Fe(III). In Cologne also the lowest sulphide influent load was measured, whether this has an effect on the iron speciation cannot be concluded from the present data.

In Dokhaven STP quick Fe(III) reduction took place. Here Fe(III) is dosed in the aerated A-stage, where the SRT is only 8 hours. This short retention time does not give much time for microbial Fe(III) reduction (Nielsen et al., 1997). The influent sulphide load would be enough to reduce all dosed Fe(III) and could explain the dominance of Fe(II) in the aerated A-stage. Additionally, the large contribution of influent iron (3 times the dosed iron), probably as Fe(II), to the total iron pool is a reason for the dominance of Fe(II) in this sludge. In Dokhaven the ORP of the incoming raw sewage was -290 mV.

Also in Berlin the influent sulphide load was relatively high, which is related to high sulphate levels in the drinking water of Berlin and long wastewater retention times in the sewer systems (Heinzmann, B., pers. Communication). About 60% of all iron was ferrous iron in Berlin before the digestion and about 37% of the iron in the surplus sludge was present as iron oxide, most likely as goethite (Mössbauer quadrupole splitting of goethite was 0.25 mm/s) which can efficiently bind phosphate by adsorption and is probably relative insensitive to chemical and biological reduction on a time scale of STPs (Canfield, 1989; Lovley, 2013). Earlier studies on activated sludge in Münchehofe STP showed, that most phosphate was extracted in the reductive soluble phosphate pool and only 10% of the phosphate was in the NaOH fraction where vivianite would be expected (Röske and Schönborn, 1994; Uhlmann et al., 1990). This difference could be explained by the fact that in the earlier study activated sludge from the

aeration tank was sampled. In our study surplus sludge was analysed. Surplus sludge (and thus settled sludge) is exposed to oxygen free conditions during settling (retention time in sludge blanket is several hours) which could allow Fe(III) reduction. After sampling, our samples were kept on ice. Yet, we cannot exclude that Fe(III) reduction in the samples was ongoing until sample drying started (for Berlin about 6 hours after sampling) (Nielsen, 1996; Rasmussen and Nielsen, 1996). This could result in changes of the iron pool. In addition, the presence of Fe(II) can induce recrystallization of ferric iron oxides (especially for less stable forms such as ferrihydrite) even in non-biological systems (Latta et al., 2012). On the other hand, vivianite extraction characteristics are not fully understood as it occurs in different forms (particle sizes, impurities) and crystallinity and thus most extraction procedures can only give rough estimates for the vivianite content in samples (Rothe 2016).

A large difference between the vivianite content as determined by using XRD and by Mössbauer spectroscopy was measured in Cologne and Berlin for the surplus sludge. This is probably because only Mössbauer spectroscopy is able to detect not very well defined (freshly formed?) vivianite in these two samples and because the unknown Fe(II) species was assigned to impure vivianite. We can however, not definitely conclude that this impure vivianite is really vivianite.

Results from measurements in Leeuwarden and Nieuwveer were adopted from an earlier study and were discussed in detail before (Wilfert et al., 2016). Overall, no clear pattern of Fe:P vs phosphate bound in vivianite before digestion was visible. This is likely related to the large variation in conditions in individual activated sludge processes (e.g. dissolved oxygen set-points, Fe(II)/Fe(III) dosing, different redox zones and retention times in settler sludge blanket etc.) and varying significance of iron and sulphide loads from the inflowing sewage.

5.4.2 Vivianite quantification after the digestion

After the anaerobic digestion vivianite was the dominating iron phase. As thermodynamics predict always some iron bound in FeS_x was present (Nriagu, 1972). Figure 5-2 shows that the vivianite content in the digested sludge increases with the iron content in the samples. In the pure EBPR plant Asten (with a low molar Fe:P of 0.14) XRD could not detect any vivianite. This suggests that at low iron levels vivianite is present in low quantities or not present at all because of a shortage of iron. The iron that is present in this sludge is partly not available for vivianite formation as it reacts with sulphide to form FeS_x. At intermediate iron content in the sludge (Fe:P > 0.5 – 1.1) again part of the iron is bound in FeS_x. The residual iron is available for vivianite formation to bind some but not all of the phosphate that would theoretically be available for vivianite formation. In sludge with even higher iron content and molar Fe:P ratios of around 1.5 (Cologne and Berlin) it seems that vivianite formation is already starting to level off due to limited phosphate availability. In Cologne, Mössbauer indicates that between 61 and 88% and semi quantitative XRD shows that 90% of all phosphate is bound in vivianite. In Espoo, Finland it seems that almost all phosphate is bound in vivianite. XRD measurements agree with the 100 K Mössbauer measurements which indicate that between 93% and 100% (±8) of all phosphate is bound in vivianite. It is unlikely that all phosphate is bound in vivianite

as organic bound phosphate is present which should only be recoverable if all organics are broken down e.g. during incineration or at alkaline pH. The stronger binding of iron with sulphide suggests that excess iron is required for complete vivianite formation with the available phosphate. Molar iron to phosphate ratios slightly lower or equal to the stoichiometry of vivianite are sufficient to complete vivianite formation in the digested sewage sludge. The amount of iron that gets bound to sulphides seems to more or less correspond with the amount of phosphate that is not available for vivianite formation in waste sludge digestion.

Assuming only organic bound phosphate is limiting vivianite formation, how much phosphate could then be bound in organics and thus limit the formation of vivianite? It was suggested that activated sludge from Berlin Münchehofe contained 25% of all phosphate in the form of organics (Uhlmann et al., 1990). In another study, between 7 and 16% of all phosphate was assigned to organic phosphates before anaerobic digestion in STPs using iron or aluminium respectively for phosphate removal (Alvarenga et al., 2017). In digested sludge with a molar Fe:P of about 1.2, Carliell-Marquet et al., 2009 reported that only about 12% of all phosphate was present as organic phosphate. Similarly, other results show that up to 86% of all phosphate in digested sludge was inorganic phosphate (Frossard et al., 1994). Thus, based on these reports of organic phosphates in digested sludge it is feasible that roughly 90% of all phosphate could be available for vivianite formation.

5.4.3 Vivianite characterization method

Some controversial observations were made during the quantification of vivianite bound phosphate in the sludge. As discussed above, after the anaerobic digestion, XRD suggests that all phosphate is bound in vivianite, 101% (±8%). This seems unlikely because we expect that part of the phosphate is also bound in organic matter or in other inorganic phases. Additionally, deviations in the vivianite content of the sludges as determined by using Mössbauer spectroscopy and XRD were observed and the Mössbauer measurements at different temperatures also gave different vivianite contents for some sludges (Figure 5-1 & Figure 5-2).

Why is the quantification of vivianite so difficult? Our EDX analyses (Table 5-3) and earlier analyses (Roussel and Carliell-Marquet, 2016) indicate that the vivianite particles in the sludge contain impurities. In general, vivianite is known to contain impurities (Rothe et al., 2016) and also earlier Mössbauer and XRD studies, using mineral vivianite specimens also always contained a certain degree of impurities and/or the vivianite was partly oxidized during handling of the samples (Gonser and Grant, 1976; Rodgers and Henderson, 1986). Pure vivianite will hardly be encountered in environmental or engineered systems like STPs. The degree and type of impurities (e.g. magnesium, manganese, copper, arsenic) probably varies from one place to the other as the impurities partly mirror the composition of the host solution were it was formed (Rothe et al., 2016). We should refer to vivianite like structures rather than to vivianite when talking about the compounds that we found in the sewage sludge. It seems logical that impurities affect the thermodynamic properties, stability and solubility in chemical extraction schemes of the vivianite. Furthermore, the impurities can hinder the identification and quantification of vivianite in samples. A standard addition of synthetic (pure) vivianite to digested sewage sludge

from Dokhaven showed that our method, to semi quantitatively determine vivianite in the sludge using XRD, is relative reliable (±7%, Table S 5-1). This further suggests that XRD is not able to distinguish between vivianite with and without impurities. Likely, part of the iron in the sludge vivianite was replaced by other cations (such as copper or magnesium) which could explain why the vivianite content in digested sludge, as quantified by XRD, is often higher than the numbers from the more specific Mössbauer spectroscopy. Also phosphate in the vivianite structure can be replaced by other elements such as arsenic (Muehe et al., 2016). For XRD the quantification of vivianite is further hindered by the presence of unassigned peaks in some samples and by the fact that quartz and vivianite had some overlapping peaks in our measurements (see peak assignments in the supplementary information). Also the Rietveld refinement and the determination of the amorphous share of the samples introduce some uncertainty.

Although, the hyperfine parameters obtained by Mössbauer spectroscopy clearly show that vivianite is present in the samples, some observations remain unclear. Iron in vivianite is present in two distinct octahedral sites. The ratio for these sites is usually 2 (Site B : Site A = 2, Mori and Ito, 1950). However, in our case the ratio was often lower than 2 (ranging from 1.2 – 2). Frossard et al., 1997 used Mössbauer spectroscopy at 300 K only to determine the vivianite in one activated sludge and two digested sewage sludge samples. Only one of the three samples (surprisingly the activated sludge sample which is more subjected to oxygen exposure) had a site ratio close to 2 (1.9). In the other two samples much higher ratios of 4 and 6 were found. The authors concluded that this deviation is caused by oxidation although the high ratio is far higher than expected for oxidized vivianite. In our case oxidation is probably not the reason for the lower site ratio because literature shows that the oxidation takes (at least initially) preferably place at site A which would rather increase the site ratios (Rouzies and Millet, 1993). Also most of our samples showed no signs of oxidation, e.g. no presence of oxidized vivianite as determined by Mössbauer spectroscopy (i.e. only limited quantities of ferric iron were present and they were not identified as oxidized vivianite). Literature indicates that elemental substitutions of iron can affect Mössbauer spectra (Amthauer and Rossman, 1984; Dyar et al., 2014). In baricite (the magnesium analogue of vivianite) substitution takes preferably place at site B which indeed cause a decrease in the iron site ratios (Yakubovich et al., 2001). Similarly, Manning et al., 1991 further hypothesized that substitutions at site B by manganese or Fe(III) could change the site ratios. Additionally, they claimed that part of the iron at the A site could actually not be part of the vivianite but part of clay minerals. Some iron containing chlorite and clay minerals have similar hyperfine parameters as vivianite. Manning suggested to recalculate the real vivianite content by assuming FeA:FeB = 2 and then derive the phosphate content from it. This would mean that we would currently over quantify vivianite bound phosphate in our samples by using Mössbauer spectroscopy. On the other hand, if impurities are present and we assume that substitution takes mainly place on site B then an adaption of the site ratio to 2 would be necessary to take the iron (from site B) into account that was replaced by cations such as calcium or magnesium. This would mean that we are underestimating the phosphate bound

in vivianite by our Mössbauer measurements. The latter case is rather unlikely as in the digested sludge sample from Finland more than 100% of all phosphate is bound in vivianite. Also both phenomena could occur in our samples. Overall, despite uncertainties, Mössbauer Spectroscopy and XRD show a clear increase of the vivianite content in the samples with an increase of the molar Fe:P in the digested sewage sludge. Additionally, our data clearly show that anaerobic digesters are places of very significant vivianite formation.

Another option for quantifying vivianite in the sludge is modelling, which is a strong tool for estimating which phosphate compounds could possibly form in STPs. However, modelling has also drawbacks in complex systems like STPs for determining the vivianite content of the sludge due to: (I) molar Fe:S ratios of iron sulphides, that will probably form prior to vivianite, range from one (mackinawite) to two (pyrite, Peiffer et al., 2015); (II) kinetics of mineral formation are difficult to model, certainly in presence of organic complexes; (III) for some minerals, possibly more stable than vivianite (e.g. anapeit, Nriagu and Dell, 1974) and for amorphous compounds thermodynamic data is missing and therefore such compounds are not included in the corresponding databases (V) metals in sludge can be complexed by dissolved organic compounds which are ubiquitous in wastewaters, this makes modelling more difficult and (VI) sometimes the modelling input is biased and minerals, such as vivianite, have even been neglected in studies (Flores-Alsina et al., 2016). Besides modelling, chemical extractions have been used for vivianite determination, however, results were also inconsistent for environmental samples (Rothe et al., 2016). It seems that all approaches, including our combination of spectroscopic methods have problems to determine the vivianite content in the samples.

5.4.4 From vivianite quantification to phosphate recovery

Analogously to struvite, it has been reported that vivianite can cause problems in STPs especially during thermophilic digestion (Marx et al., 2001; Reusser, 2009). Obviously, when iron is used for phosphate removal the biogeochemical conditions in STPs that are required for successful sewage treatment drive vivianite formation without additional measures. Vivianite solubility will depend on the activity of the iron, it is likely that vivianite is the phosphate compound with the lowest solubility in digested sewage sludge (Nriagu and Dell, 1974). Our data suggests that it is time to make use of the formation of vivianite in STPs and develop strategies to recover phosphate in form of vivianite from sewage sludge.

The characteristics of vivianite observed in STP sludges in this study indicates limitations related to the recovery of the mineral. Separation via magnetism or density separation may provide ways to recover vivianite. Our measurements on vivianite in sludges, backed by solubility products for minerals, suggest that much higher phosphate recovery efficiencies can be achieved compared to struvite recovery routes. The potential of struvite recovery is limited because part of the phosphate is bound to compounds with lower solubility than struvite solubility, such as aluminium or iron phosphates (Baker et al., 2006; Doyle and Parsons, 2002; Mamais et al., 1994). This would not be the case for vivianite as it has a very low solubility, probably also compared to amorphous aluminium phosphates. Solubility is, in our opinion, a

reason why phosphate bound vivianite could not efficiently be recovered via dissolution of ferric or ferrous phosphate in the sludge. Phosphate from vivianite could e.g. be released via microbial Fe(III) oxidation (Miot et al., 2009) or by making use of sulphide (Kato et al., 2006; Suschka et al., 2001). But the released phosphate will form precipitates with other elements in the sludge liquor or bind to other inorganic phases in the sludge solids. Similar observations were made for sediment systems (Boström and Pettersson, 1982; Richardson, 1985; Roden and Edmonds, 1997). Thus, a separation technology for vivianite, instead of other recovery routes, seems most logical. The current form of vivianite detected is, however, present in very small particles. For efficient recovery, methods to form larger vivianite particles need to be developed.

5.5 Conclusion

This study shows that vivianite is the most important iron and phosphate phase in digested sewage sludge with high iron content. Between 70 to 90% of all phosphate in sewage sludge can be bound in vivianite. This vivianite will contain impurities and it is therefore better to call it vivianite like structures. The eSEM-EDX analyses indicate that the vivianite is present as free particles, which would theoretically allow their separation from the sludge. Thereby higher recovery efficiency compared to struvite recovery routes can be achieved. Hereto more knowledge on vivianite formation in sewage sludge is necessary (density, impurities, size distribution, % of free vivianite particles) in order to induce growth of larger crystals in the sludge which will be easier to separate. Dosing iron for phosphate and COD removal is in line with energy producing STPs of the future (Wilfert et al., 2015a). Recovery of vivianite can amend these treatment facilities with an effective phosphate recovery technology.

5.6 References

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Supplementary Information

Table S 5-1: Results of vivianite standard addition and quantification of vivianite in the sludge using XRD on digested sewage sludge sampled in the STP Dokhaven.

	Vivianite added (g)	Vivianite according to qXRD (g)	Recalculate initial vivianite content (g)	Average
Raw Sludge	0	194		175
Sludge +10% vivianite	20	214	160	StDev
Sludge +50% vivianite	121	315	186	13
Sludge +100% vivianite	235	429	179	(7%)

Table S 5-2: Vivianite and quartz content in digested sludge samples taken at the STP Dokhaven.

	Vivianite	Quartz
Sludge Raw	52	48
Sludge Raw + 10 % Vivianite	58	42
Sludge Raw + 25 % Vivianite	69	31
Sludge Raw + 50 % Vivianite	81	19

Table S 5-3: Characteristics of the sludges that were analysed in this study.

	pH	TS (g/kg)	VS (g/kg)	Ferrozine Fe(II) (mg/L)	Ferrozine Fe(III) (mg/L)	Total Dissolved Fe-ICP (mg/L)	o-P (mg P/L)	Total Dissolved P (mg/L)	Total Dissolved S (mg/L)	Total Dissolved Al (mg/L)	Total Dissolved Mg (mg/L)	Total Dissolved Ca (mg/L)	Total Dissolved K (mg/L)	Total Dissolved Na (mg/L)
Berlin Surplus Sludge	7.1	9.13	5.44	7.3	2.8	9.6	3.8	8.3	63.0	<0.5	19.3	109.0	52.8	132.0
Berlin Digested Sludge	7.2	21.96	12.10	13.2	2.5	14.6	20.7	13.6	5.6	<0.5	24.0	199.5	64.7	128.0
Finland Surplus Sludge	7.7	12.48	9.70	22.8	2.6	24.3	<0.5	1.2	27.4	<0.5	6.7	29.1	30.5	44.5
Finland Digested Sludge	7.2	23.72	14.40	38.0	5.8	40.6	<0.5	0.3	7.5	<0.5	26.3	41.5	93.3	60.4
Asten Surplus Sludge	n.d.	9.56	7.15	0.1	0.3	0.3	8.5	8.3	19.4	<0.5	13.7	63.3	45.4	88.1
Asten Digested Sludge	n.d.	44.27	30.17	1.8	0.0	1.8	573.3	528.0	14.9	<0.5	5.4	23.6	603.0	87.5
Cologne Surplus Sludge	7.2	6.52	3.57	1.2	10.3	2.8	0.0	0.4	33.4	<0.5	11.1	72.0	16.7	101.2
Cologne Digested Sludge	7.5	25.93	13.38	5.5	16.8	8.5	0.3	0.8	10.5	<0.5	42.7	140.3	142.7	138.3
Dokhaven A-stage Surplus Sludge	7.0	12.60	9.96	4.6	3.0	7.8	0.4	3.8	23.0	<0.5	12.3	96.0	28.0	93.2
Dokhaven Digested Sludge	6.9	31.90	18.77	3.0	0.0	5.9	41.2	44.5	6.9	<0.5	17.9	97.7	153.0	87.4

Table S 5-4: Elemental composition of sludge solids determined by using XRF.

g/kg TS

	Leeuwarden Surplus Sludge	Leeuwarden Digested Sludge	Berlin Surplus Sludge	Berlin Digested Sludge	Finland Surplus Sludge	Finland Digested Sludge	Asten Surplus Sludge	Asten Digested Sludge	Cologne Surplus Sludge	Cologne Digested Sludge	Dokhaven A-stage Surplus Sludge	Dokhaven Digested Sludge	Nieuwveer A-stage Surplus Sludge	Breda Digested Sludge
Fe	24.4	43.4	118.7	103.5	84.4	134.7	8.1	11.0	124.1	100.6	39.3	73.9	29.5	61.6
P	36.3	47.8	39.3	35.4	18.8	31.7	34.8	43.3	33.5	35.5	26.7	36.8	17.4	41.8
Si	28.2	30.5	9.2	18.3	7.0	15.7	17.4	22.9	29.1	46.6	12.6	32.7	22.4	36.1
Ca	23.5	41.5	27.6	38.3	14.9	21.1	16.5	25.2	18.8	35.3	25.7	35.0	18.5	32.4
Al	9.5	9.7	4.7	9.8	3.2	7.7	11.6	21.4	12.2	15.8	4.5	12.1	8.1	17.9
S	4.9	6.2	6.4	26.4	4.3	8.3	6.0	8.7	4.1	8.1	7.0	11.4	3.8	8.4
Mg	9.0	10.8	3.8	3.0	2.1	2.6	9.4	5.2	4.5	4.7	3.1	5.1	2.6	5.6
K	9.6	7.9	3.5	0.7	1.8	1.1	8.8	13.4	4.7	1.8	3.2	2.5	2.7	4.9

Table S 5-5: Elemental compositions of particles in the sludge obtained from eSEM-EDX analyses.

% atomic

	Carbon	***Nitrogen***	***Oxygen***	***Sodium***	***Magnesium***	***Aluminum***	***Silicon***	***Phosphorus***	***Sulfur***
Fig. 2a, Spot 1	28.1	17.4	47.9	0.3	0.2	0.2	0.5	1.7	0.4
Fig. 2a, Spot 2	52.2	-	19.1	0.3	0.1	0.2	0.7	0.6	12.3
Fig. 2a, Spot 3	40.4	-	50.5	0.5	0.2	0.3	0.6	2.4	0.4
Fig. 2b	22.2	-	65.6	-	22.2	0.1	0.3	4.4	-

	Chloride	***Potassium***	***Calcium***	***Iron***	***Copper***	***Manganese***	***Molar Fe:P***	***Molar Fe:S***
Fig. 2a, Spot 1	0.3	0.2	1.5	1.4	-	-	0.8	3.9
Fig. 2a, Spot 2		0.1	0.5	13.9	-	-	23.5	1.1
Fig. 2a, Spot 3	0.3	0.2	1.6	2.6	0.07	-	1.1	5.9
Fig. 2b	0.1	0.1	0.4	5.4	0.04	0.11	1.2	

Table S 5-6: Results of Mössbauer measurements at different temperatures.. Experimental uncertainties: Isomer shift (IS): ± 0.01 mm s^{-1}; Quadrupole splitting (QS): ± 0.01 mm s^{-1}; Line width (Γ): ± 0.01 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

Sample	*IS ($mm·s^{-1}$)*	*QS ($mm·s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm·s^{-1}$)*	*Phase*	*Spectral contribution (%)*
Dokhaven	0.21	0.51	51.3	0.85	Fe^{3+}	4
A – stage	0.47	0.61	39.8	0.85	Fe^{3+}	5
4K	0.32	0.58	-	0.74	Fe^{II} (Pyrite)	8
	1.18	3.03	-	1.03	Fe^{2+} (Viv. Imp.)	34
	1.12	2.62	14.9	0.70	Fe^{2+} (Viv. I)	16
	1.18	2.85	27.3	0.70	Fe^{2+} (Viv. II)	33
Dokhaven	0.24	0.92	-	0.42	Fe^{3+}	35
A – stage	1.25	2.29	-	0.35	Fe^{2+} (Viv. I)	28
300 K	1.27	2.78	-	0.35	Fe^{2+} (Viv. II)	37

Sample	*IS ($mm·s^{-1}$)*	*QS ($mm·s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm·s^{-1}$)*	*Phase*	*Spectral contribution (%)*
Berlin Before	0.46	-0.18	46.3	0.85	Fe^{3+}	19
4 K	0.54	-0.26	41.5	0.85	Fe^{3+}	18
	0.32	0.58	-	0.74	Fe^{II} (Pyrite)	3
	1.07	3.29	-	1.70	Fe^{2+} (Viv. Imp.)	27
	1.17	1.80	12.3	0.70	Fe^{2+} (Viv. I)	12
	1.12	3.60	25.3	0.70	Fe^{2+} (Viv. II)	21
Berlin Before	0.32	0.85	-	0.49	Fe^{3+}/Fe^{II}	63
100 K	1.29	2.37	-	0.34	Fe^{2+} (Viv. I)	18
	1.21	3.10	-	0.34	Fe^{2+} (Viv. II)	19
Berlin Before	0.37	0.78		0.46	Fe^{3+}	62
300 K	1.23	2.20		0.34	Fe^{2+} (Viv. I)	18
	1.21	2.85		0.34	Fe^{2+} (Viv. II)	20

Sample	*IS ($mm·s^{-1}$)*	*QS ($mm·s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm·s^{-1}$)*	*Phase*	*Spectral contribution (%)*
Cologne Before	0.31	0.07	46.8	1.10	Fe^{3+}	22
4 K	0.44	-0.19	41.8	1.10	Fe^{3+}	28
	1.13	3.05	-	1.59	Fe^{2+} (Viv. Imp.)	30
	1.13	2.67	12.7	0.70	Fe^{2+} (Viv. I)	7
	1.10	3.02	25.0	0.70	Fe^{2+} (Viv. II)	13
Cologne Before	0.38	0.78		0.5	Fe^{3+}/Fe^{II}	81
100 K	1.14	2.68		0.3	Fe^{2+} (Viv. I)	10
	1.19	3.08		0.3	Fe^{2+} (Viv. II)	9
Cologne	0.37	0.79	-	0.55	Fe^{3+}	86
Before	1.19	2.14	-	0.32	Fe^{2+} (Viv. II)	5
300 K	1.13	2.75	-	0.32	Fe^{2+} (Viv. I)	9

Sample	*IS* *(mm·s^{-1})*	*QS* *(mm·s^{-1})*	*Hyperfine field (T)*	*Γ* *(mm·s^{-1})*	*Phase*	*Spectral contribution (%)*
Cologne Digested	0.43	-0.34	50.0	0.85	Fe^{3+}	6
4 K	0.44	-0.43	41.6	0.85	Fe^{3+}	3
	0.32	0.58	-	0.74	Fe^{II} (Pyrite)	7
	1.12	3.21	-	2.16	Fe^{2+} (Viv. Imp.)	41
	1.20	2.69	14.3	0.70	Fe^{2+} (Viv. I)	14
	1.21	3.30	26.4	0.70	Fe^{2+} (Viv. II)	29
Cologne Digested	0.39	0.51		0.56	Fe^{3+}/Fe^{II}	23
100 K	1.18	2.58		0.34	Fe^{2+} (Viv. I)	35
	1.21	3.16		0.34	Fe^{2+} (Viv. II)	42
Cologne Digested	0.37	0.37	-	0.56	Fe^{3+}	43
300 K	1.22	2.14	-	0.44	Fe^{2+} (Viv. II)	38
	1.27	2.90	-	0.44	Fe^{2+} (Viv. I)	20

Sample	*IS* *(mm·s^{-1})*	*QS* *(mm·s^{-1})*	*Hyperfine field (T)*	*Γ* *(mm·s^{-1})*	*Phase*	*Spectral contribution (%)*
Finland Digested	0.32	0.58	-	0.74	Fe^{II} (Pyrite)	12
4 K	1.18	3.23	-	3.14	Fe^{2+} (unknown)	45
	1.12	2.16	14.6	0.70	Fe^{2+} (Viv. I)	15
	1.17	3.02	26.8	0.70	Fe^{2+} (Viv. II)	28
Finland Digested	1.21	3.15		0.31	Fe^{2+} (Viv. II)	34
110 K	1.21	2.62		0.31	Fe^{2+} (Viv. I)	25
	1.24	2.13		0.36	Fe^{2+} (unknown)	31
	0.16	0.75		0.46	Fe^{II} (Pyrite)	10
Finland Digested	1.22	3.15		0.30	Fe^{2+} (Viv. II)	30
300 K	1.21	2.62		0.30	Fe^{2+} (Viv. I)	22
	1.24	2.13		0.37	Fe^{2+} (unknown)	41
	0.20	0.75		0.40	Fe^{II} (Pyrite)	7

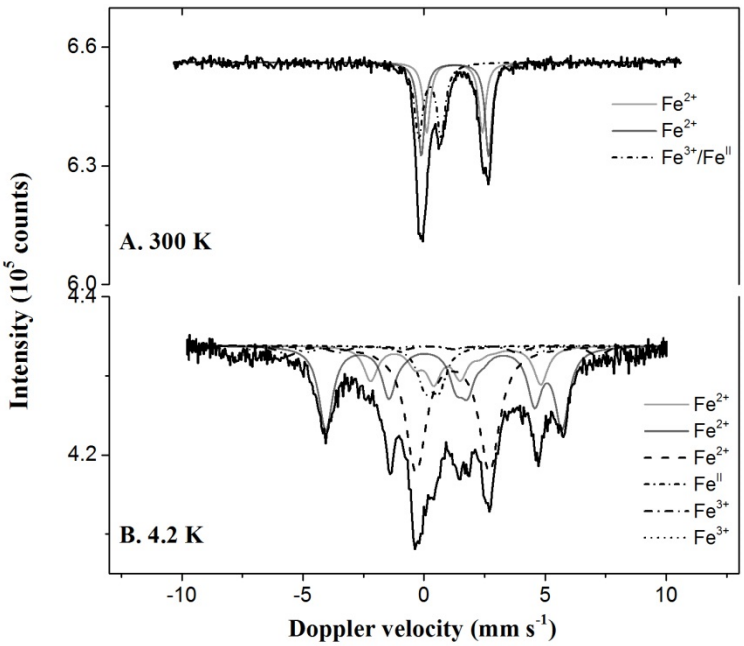


Figure S 5-1: Mössbauer spectra obtained at different temperatures with A-stage sludge solids from Dokhaven.

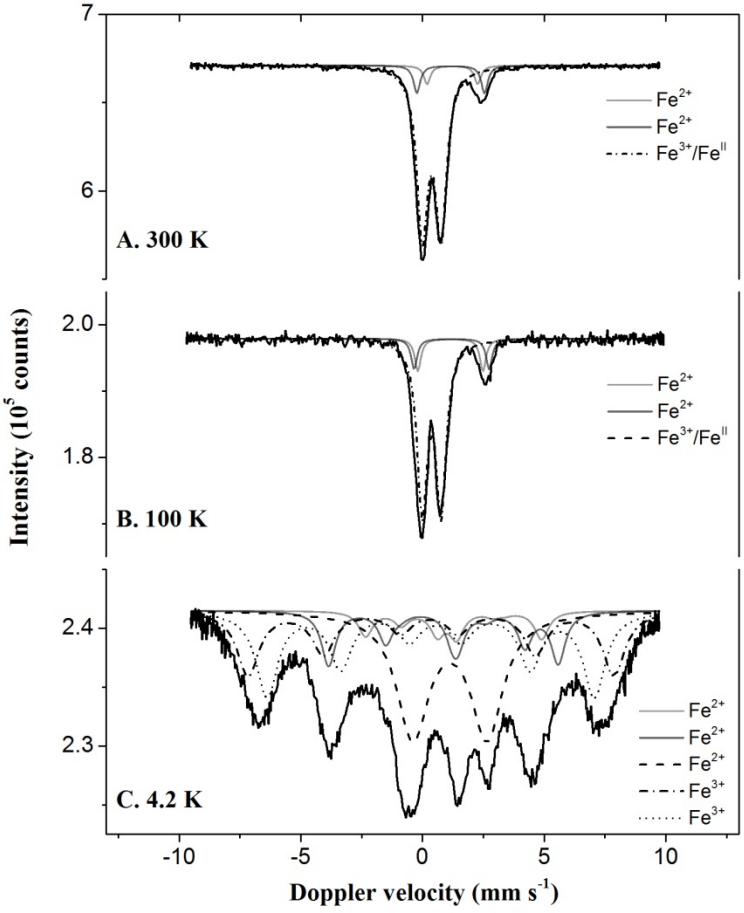


Figure S 5-2: Mössbauer spectra obtained at different temperatures with surplus sludge solids from Cologne.

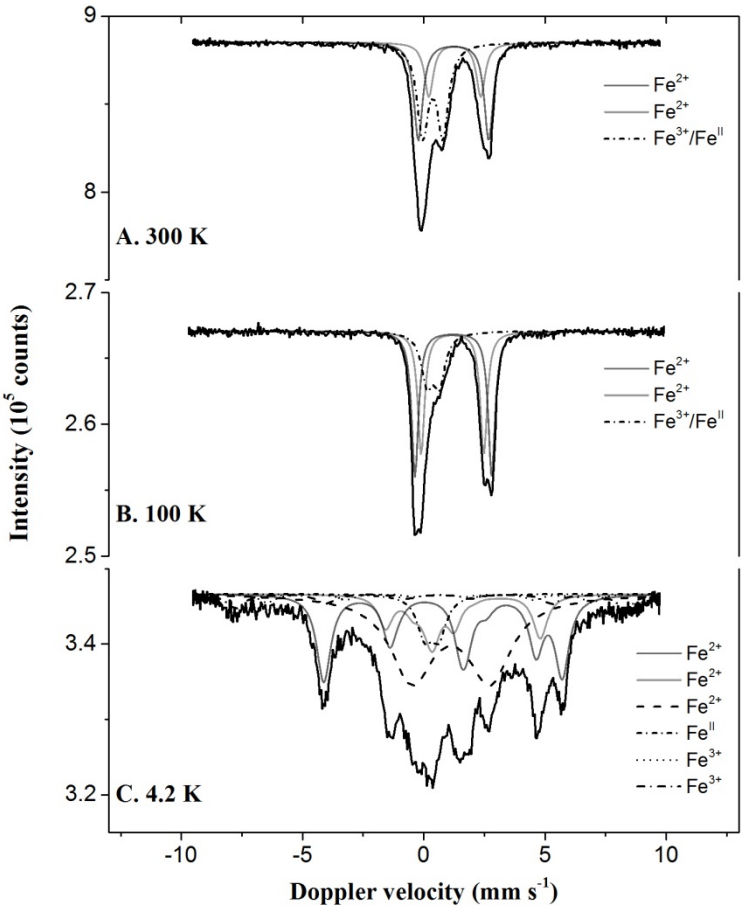


Figure S 5-3: Mössbauer spectra obtained at different temperatures with digested sludge solids from Cologne.

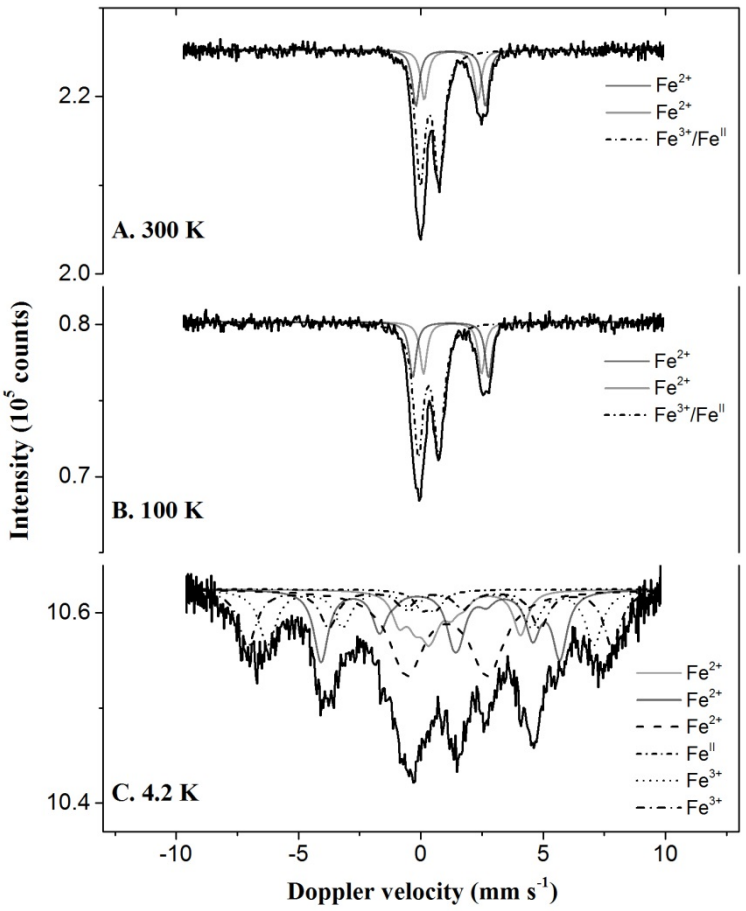


Figure S 5-4: Mössbauer spectra obtained at different temperatures with surplus sludge solids from Berlin.

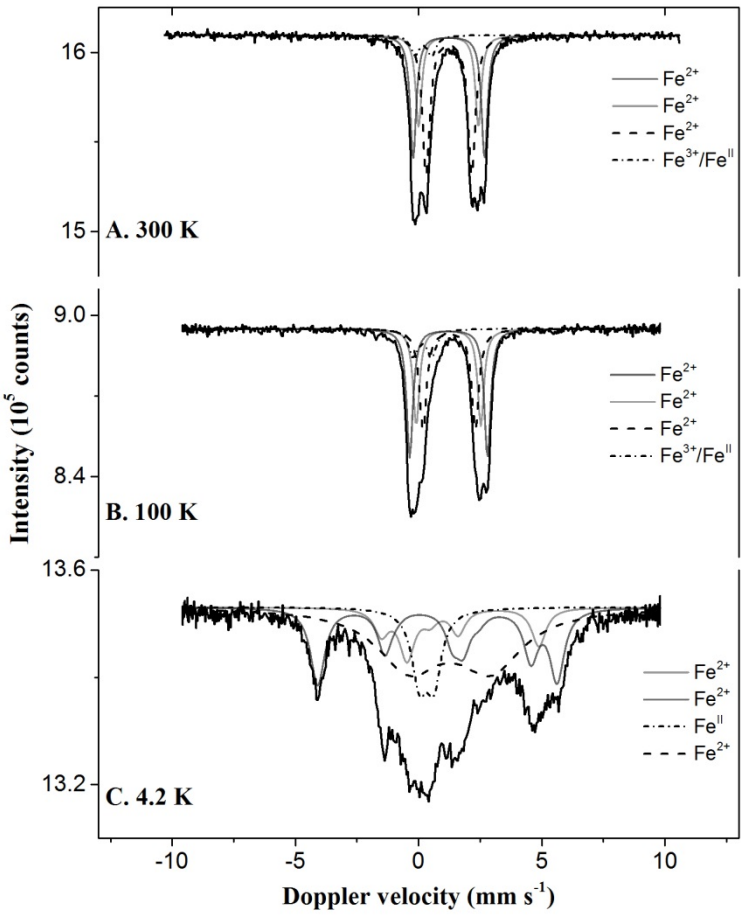
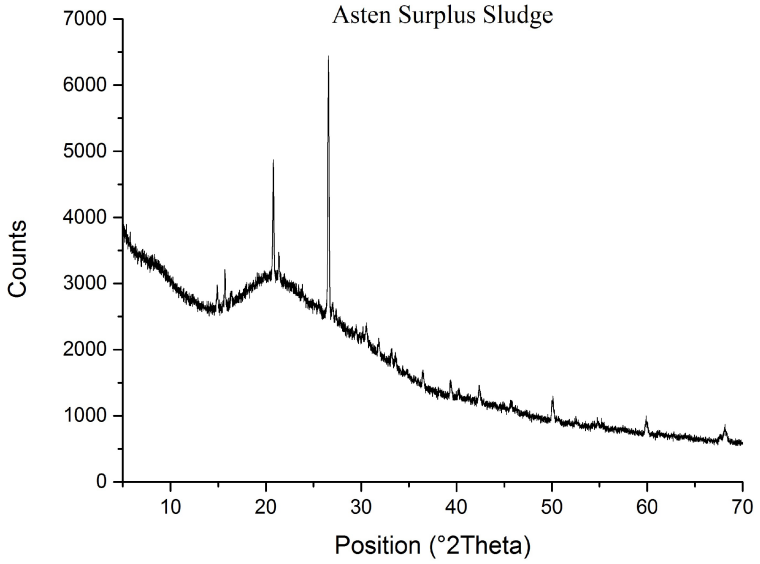
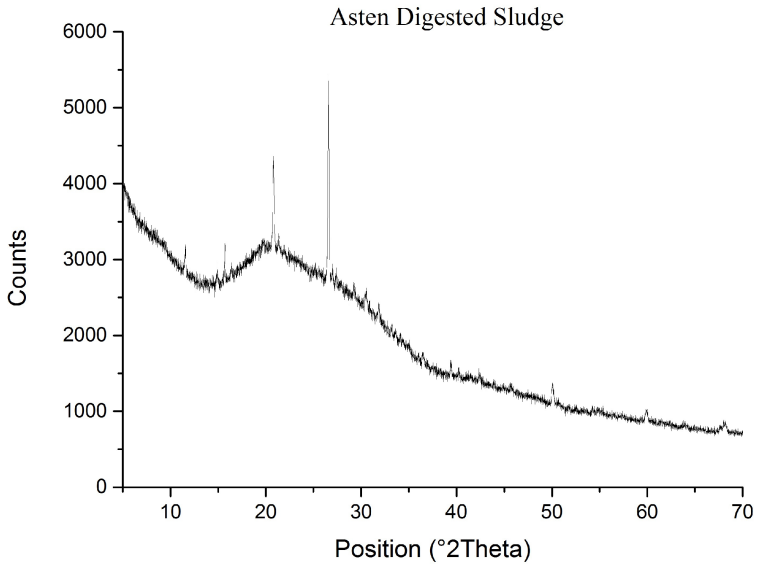


Figure S 5-5: Mössbauer spectra obtained at different temperatures with digested sludge solids from Finland.

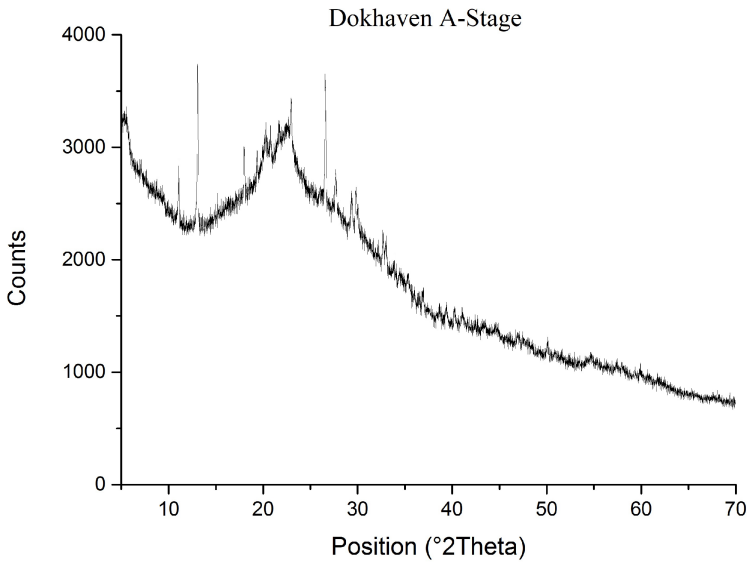
XRD diffractograms for all samples including peak list and peak assignment.



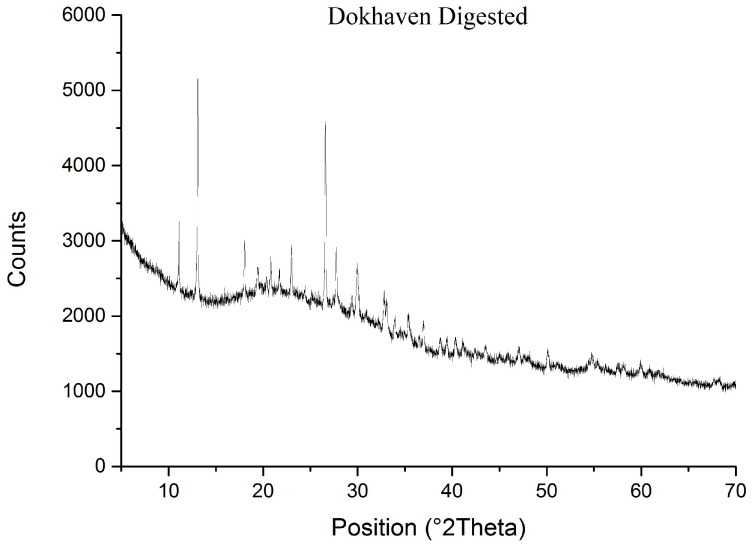
Pos. [°2Th.]	Matched by
14.922	Struvite
15.733	Struvite
16.385	Struvite
20.776	Quartz; Struvite
21.359	Struvite
26.526	Quartz
26.579	Quartz
27.006	Struvite
29.491	Struvite
30.543	Struvite
31.83	Struvite
33.193	Struvite
36.443	Quartz
39.379	Quartz
40.241	Quartz
42.379	Quartz; Struvite
45.717	Quartz; Struvite
50.107	Quartz; Struvite
52.585	Struvite
54.818	Quartz; Struvite
59.876	Quartz; Struvite
68.132	Quartz
73.461	Quartz; Struvite
75.646	Quartz; Struvite



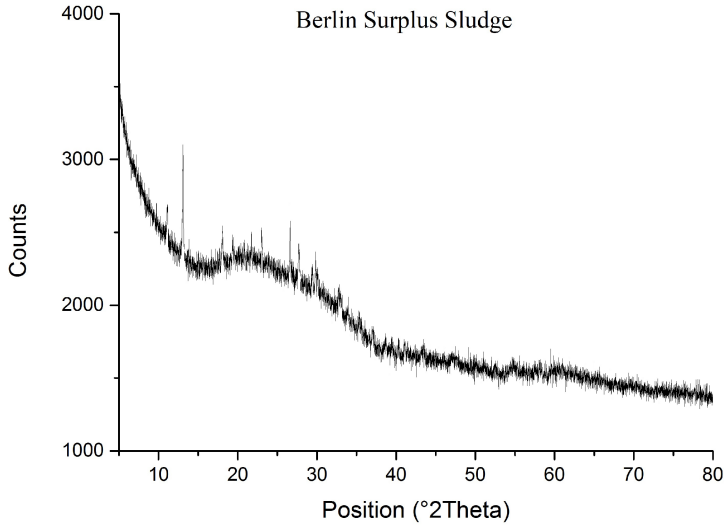
Pos. [°2Th.]	Matched by
11.570	Calcium Hydrogen Phosphate
14.902	Struvite
15.733	Struvite
16.392	Struvite
20.787	Quartz; Struvite; Calcium Hydrogen Phosphate
21.366	Struvite
26.551	Quartz
27.368	not assigned
29.253	Calcium Hydrogen Phosphate
30.531	Struvite; Calcium Hydrogen Phosphate
31.842	Struvite; Calcium Hydrogen Phosphate
33.200	Struvite
36.471	Quartz; Calcium Hydrogen Phosphate
39.382	Quartz
42.393	Quartz; Struvite
45.721	Quartz; Struvite; Calcium Hydrogen Phosphate
50.052	Quartz; Calcium Hydrogen Phosphate
59.910	Quartz; Struvite
68.208	Quartz



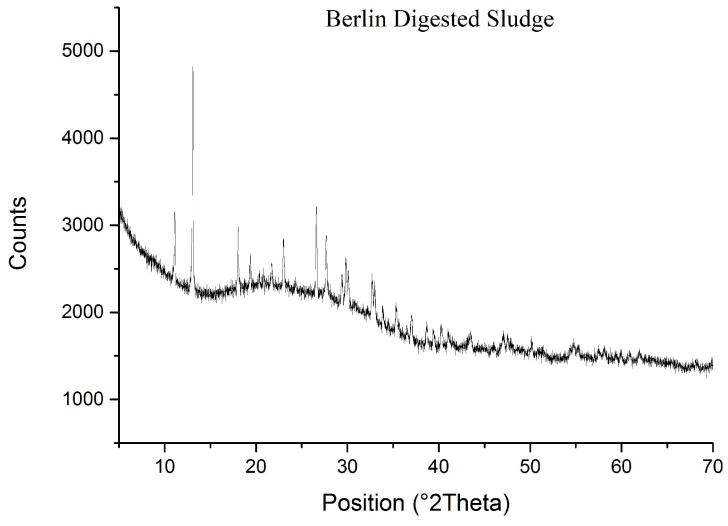
Pos. [°2Th.]	Matched by
11.088	Vivianite
13.068	Vivianite
17.990	Vivianite
19.358	Vivianite
20.277	Vivianite
20.790	Quartz
21.676	Vivianite
22.967	Vivianite
26.555	Vivianite
27.677	Vivianite
29.329	not assigned
29.802	Vivianite
32.685	Vivianite
32.971	Vivianite
33.833	Vivianite
35.304	Vivianite
36.850	Vivianite
38.693	Vivianite
39.390	Vivianite
40.258	Vivianite
41.059	Vivianite
44.672	not assigned
47.219	Vivianite
50.096	Vivianite
57.762	Vivianite
59.763	Vivianite



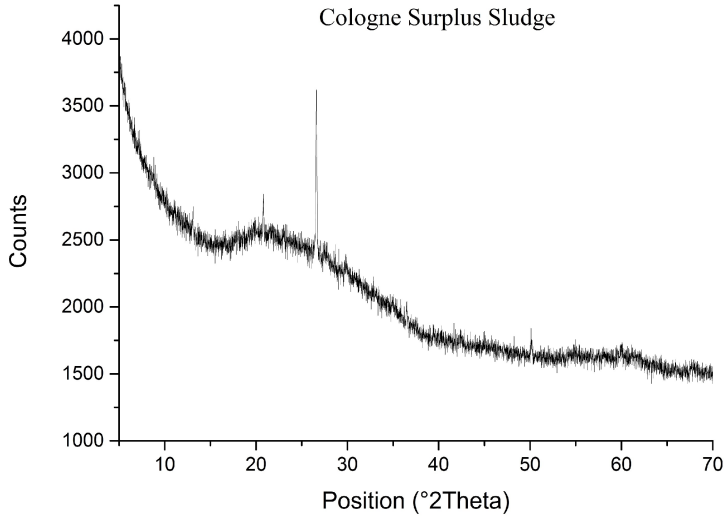
Pos. [°2Th.]	Matched by
11.104	Vivianite
13.089	Vivianite
18.032	Vivianite
19.433	Vivianite
20.364	Vivianite
20.829	Quartz
21.718	Vivianite
22.990	Vivianite
24.414	Vivianite
26.577	Vivianite; Quartz
27.712	Vivianite
29.392	
30.016	Vivianite
32.789	Vivianite
33.071	Vivianite
33.914	Vivianite
35.328	Vivianite
36.492	Vivianite; Quartz
36.975	Vivianite
38.772	Vivianite
39.448	Vivianite; Quartz
40.334	Vivianite; Quartz
41.134	Vivianite
42.431	Quartz
43.544	Vivianite
45.909	Vivianite; Quartz
47.083	Vivianite
50.105	Vivianite; Quartz
54.827	Vivianite; Quartz
55.377	Vivianite; Quartz
57.505	Vivianite
58.137	Vivianite
59.958	Vivianite; Quartz
60.826	Vivianite
67.998	Vivianite; Quartz
69.933	Vivianite



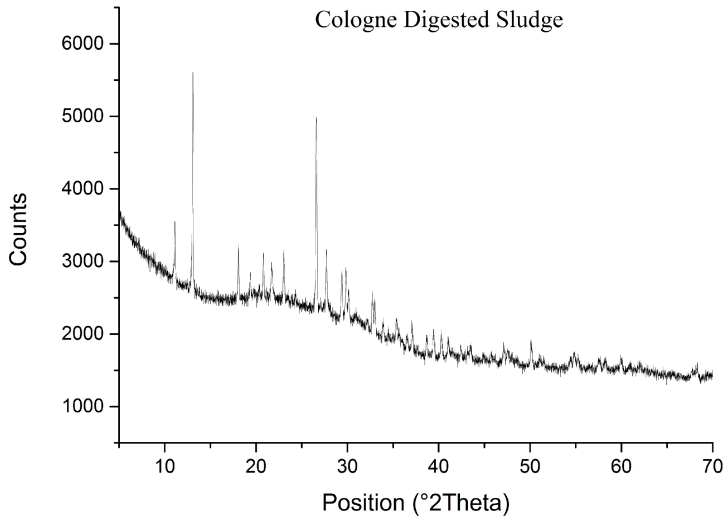
Pos. [°2Th.]	Matched by
11.104	Vivianite
13.104	Vivianite
18.071	Vivianite
19.365	Vivianite
20.865	Quartz
21.717	Vivianite
22.989	Vivianite
26.621	Vivianite; Quartz
27.709	Vivianite
29.431	not assigned
29.831	Vivianite
30.152	Vivianite
32.85	Vivianite
33.917	Vivianite
35.385	Vivianite
36.935	Vivianite
39.488	Vivianite; Quartz
40.304	Vivianite; Quartz
41.184	Vivianite
43.38	Vivianite
47.354	Vivianite
50.108	Vivianite; Quartz
54.64	Vivianite; Quartz
57.954	Vivianite



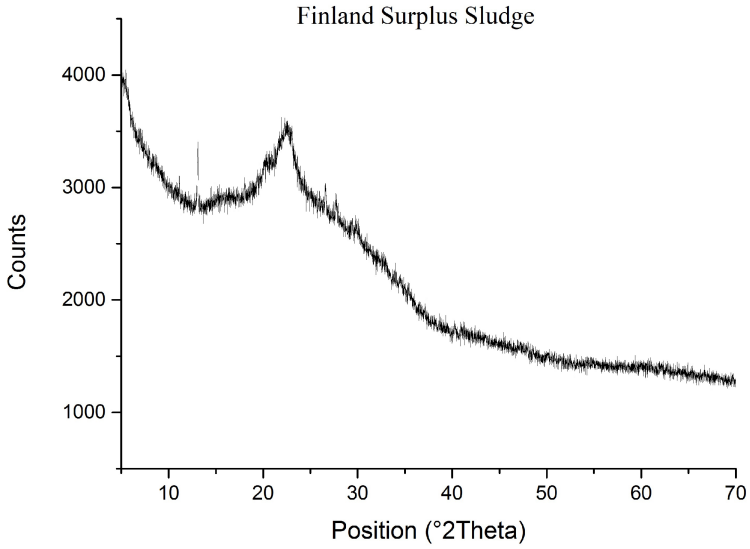
Pos. [°2Th.]	Matched by
11.109	Vivianite
13.077	Vivianite
18.053	Vivianite
19.377	Vivianite
20.337	Vivianite
20.815	Quartz
21.697	Vivianite
22.990	Vivianite
24.277	Vivianite
26.593	Vivianite; Quartz
27.658	Vivianite
29.386	not assigned
29.788	Vivianite
30.077	Vivianite
32.684	Vivianite
32.979	Vivianite
33.862	Vivianite
35.336	Vivianite
36.519	Vivianite; Quartz
37.015	Vivianite
38.638	Vivianite
39.410	Vivianite; Quartz
40.200	Vivianite; Quartz
40.990	Vivianite
43.468	Vivianite
47.038	Vivianite
47.570	Vivianite
50.158	Vivianite; Quartz
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55.237	Vivianite; Quartz
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58.107	Vivianite
59.389	Vivianite
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61.976	Vivianite
68.174	Vivianite; Quartz
69.924	Vivianite



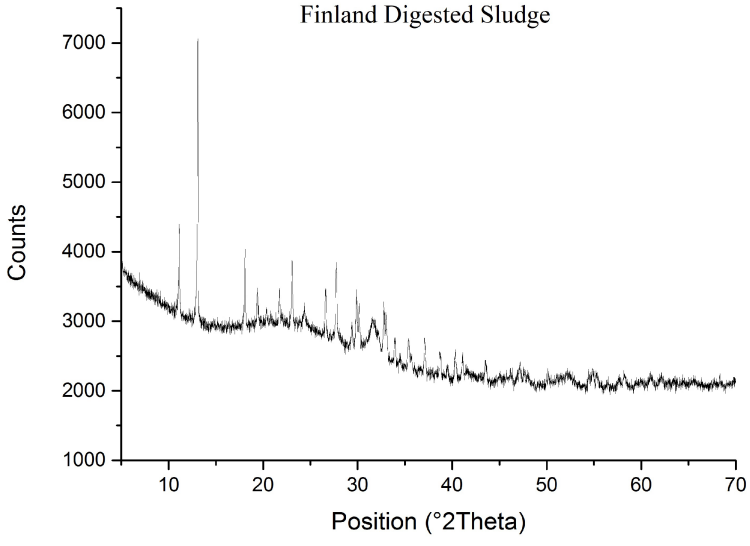
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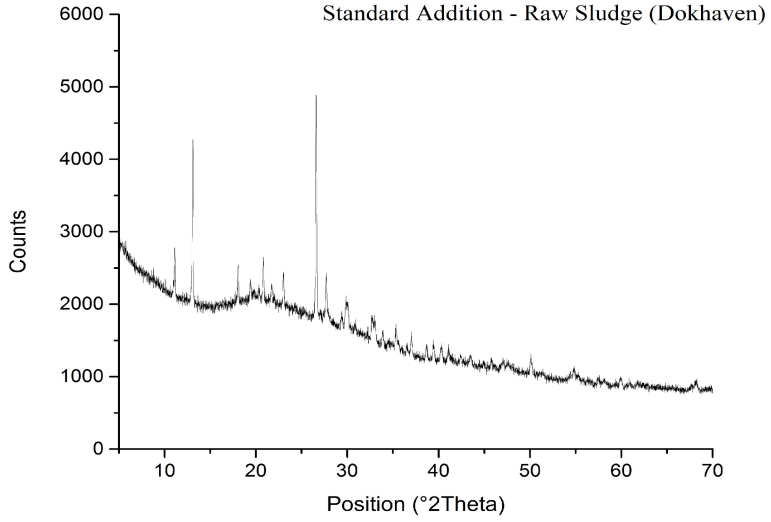
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33.908	Vivianite
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37.051	Vivianite
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40.297	Vivianite; Quartz
41.030	Vivianite
42.407	Quartz
43.451	Vivianite
45.943	Vivianite
47.120	Vivianite
47.537	Vivianite
50.098	Vivianite; Quartz
51.188	Vivianite
54.434	Vivianite
54.797	Vivianite; Quartz
55.247	Vivianite; Quartz
57.591	Vivianite
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60.883	Vivianite
62.048	Vivianite
68.259	Vivianite; Quartz



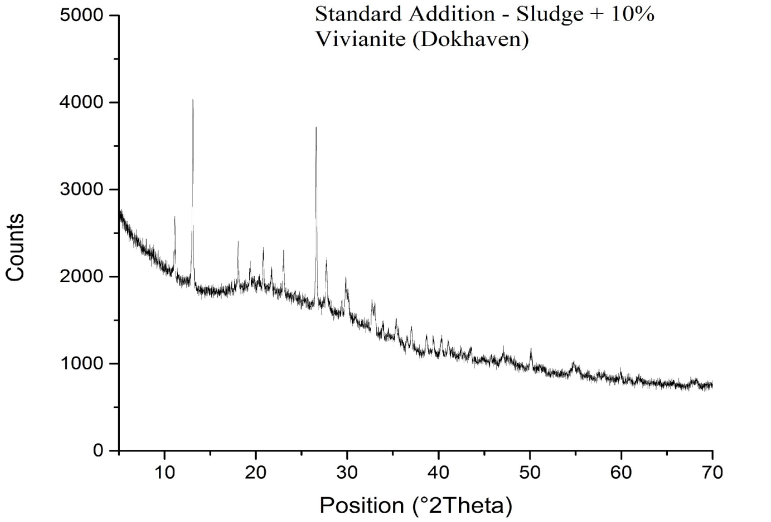
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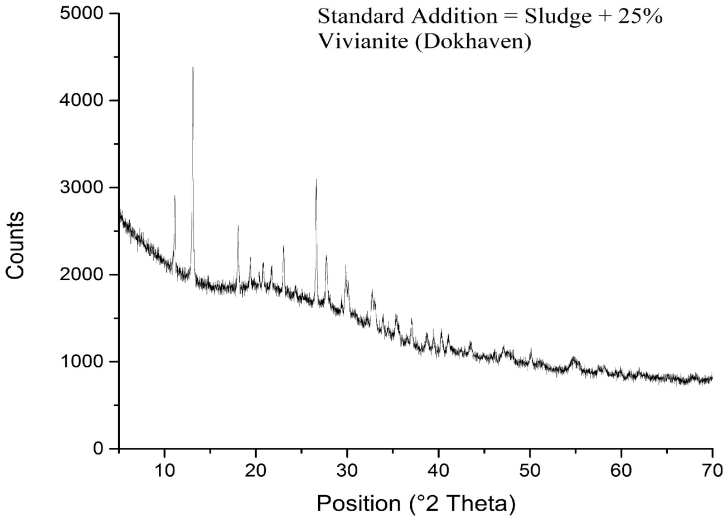
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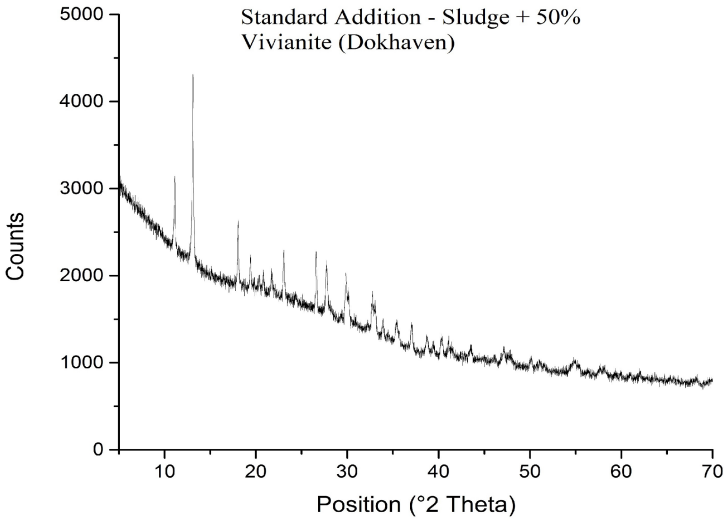
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43.521	Vivianite
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50.069	Quartz; Vivianite
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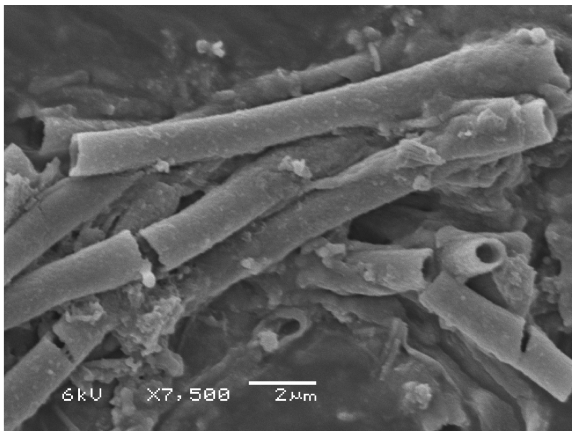


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33.908	Vivianite
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37.079	Vivianite
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40.304	Quartz; Vivianite
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51.366	Vivianite
54.757	Quartz; Vivianite
57.404	Quartz; Vivianite
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61.965	Vivianite



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27.723	Vivianite
29.841	Vivianite
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32.731	Vivianite
33.074	Vivianite
33.919	Vivianite
34.428	Vivianite
35.444	Vivianite
37.031	Vivianite
38.737	Vivianite
39.443	Quartz, Vivianite
40.269	Quartz, Vivianite
41.066	Vivianite
43.544	Vivianite
46.085	Vivianite
47.157	Vivianite
47.868	Vivianite
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57.943	Vivianite
59.948	Quartz, Vivianite
62.045	Vivianite
68.243	Quartz, Vivianite

Chapter 6: Fe(III) reduction and vivianite formation in activated sludge



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Wang, R., Wilfert, P., Dugulan, I., Goubitz, K., Korving, L., Witkamp, G.J., van Loosdrecht, M.C.M., 2018. Fe(III) reduction and vivianite formation in activated sludge.

6.1 Introduction

Dosing iron salts is a convenient, effective and popular method to eliminate phosphate from sewage (WEF, 2011). Usually, for iron based chemical phosphate removal (CPR) ferrous iron (Fe(II)) or ferric iron (Fe(III)) is used. Fe(II) is often dosed in aerated tanks of the sewage treatment plant (STP) to allow its oxidation to Fe(III), which is often considered to result in better phosphate removal capacity. Literature shows that mechanisms for phosphate removal by dosing Fe(II) or Fe(III) are mainly via adsorption to Fe(III) oxides which are rapidly formed when Fe(III) comes in contact with water (Lu et al., 2016; Mao et al., 2016; Wendt von, 1973). Several factors like aging / recrystallization of the precipitates, bacterial activity and pH variations can result in the transformation of these initial precipitates, which can also affect their phosphate retention capacity (Senn et al., 2017; Smith et al., 2008; Szabo et al., 2008). Fe(III) reduction occurs in STPs and this reduction can be chemically, direct biologically or indirect biologically induced (Kappler et al., 2004; Nielsen, 1996; Nielsen et al., 2005; Pyzik and Sommer, 1981; van den Brand et al., 2015). Fe(III) reduction is often considered to cause net mobilization of phosphate, however, in environmental systems some doubts have been risen about this hypotheses (Gächter and Müller, 2003; Golterman, 1995, 2001; Roden and Edmonds, 1997). Also some studies / observations on wastewater systems indicate that the mobilization of phosphate via Fe(III) reduction is not necessarily true. During anaerobic digestion, when strong reducing conditions prevail for a long period, all Fe(III) is likely reduced to Fe(II) (Ivanov et al., 2003). However, still the phosphate is largely retained in the solid fraction of the sludge at molar Fe:P ratios of around 2 (Stabinov et al., 2005; Thomas, 1965). Furthermore, several studies show that Fe(II) is very efficient in removing phosphate, in some respective even more efficient than Fe(III) (Ghassemi and Recht, 1971). Azam and Finneran, 2014 studied phosphate removal in septic tanks. Within 30 h, phosphate was removed in solutions containing complexed Fe(III), phosphate and Fe(III) reducing bacteria. In the same study, during experiments with real septic water, the bulk phosphate was removed within 2 days via Fe(III) reduction. In both experiments complexed Fe(III) was used, which should not result in significant phosphate removal and therefore it was clear that Fe(III) reduction was the main reason for phosphate removal. The ferrous iron phosphate mineral vivianite, ($Fe(II)_3[PO_4]_2 \cdot 8H_2O$) was identified in these experiments using XRD. Similarly, in longer running experiments, Zhang, 2012 found that Fe(III) reduction caused phosphate removal in septic tanks and also here vivianite was formed. For sewage, some information on phosphate removal in response to Fe(III) reduction exist. Stabinov et al., 2005 report that Fe(III) reduction resulted in effective removal of phosphate during anaerobic digestion of sewage. Ivanov et al., 2003 showed that Fe(III) reducers can be used to eliminate phosphate and xenobiotics from sludge liquor. Cheng et al., 2015 stored activated sludge under anaerobic conditions. They claim that Fe(III) reduction and the decrease in dissolved phosphate resulted from the formation of vivianite without giving experimental evidence. In a later study with a similar experimental set-up (although with a significant drop in pH) Fe(III) reduction did obviously not result in substantial phosphate removal. In purely chemical experiments, it was shown that within 1-5 hours efficient phosphate removal can be achieved in secondary effluents when Fe(II) is dosed

in the absence of oxygen and XRD indicated that vivianite was formed. Note, that here the residual phosphate levels were lower as compared to experiments when Fe(III) was used for phosphate removal at the optimum pH = 8 (Ghassemi and Recht, 1971).

With this knowledge it is not surprising that vivianite was found in digested sludge (Frossard et al., 1997; Singer, 1972; Wilfert et al., 2016). However, vivianite was also found in sludge before the anaerobic digestion. Here the sludge passes, besides anoxic and sometimes anaerobic zones, also aerated tanks. In an earlier publication (Wilfert et al., 2016) it was hypothesized that the presence of vivianite in surplus sludge before the anaerobic digestion can be explained by fast Fe(III) reduction rates (Nielsen, 1996), subsequent fast vivianite formation (Azam and Finneran, 2014) and slow oxidation of the formed vivianite (Miot et al., 2009; Roldan et al., 2002). Fe(III) reduction has been detected in STPs (Nielsen, 1996) however it was not studied what the products of the Fe(III) reduction are and if notorious Fe(III) reducing bacteria are present. Identifying Fe(III) reducing bacteria is important because Fe(III) reduction can also be induced by other bacteria via indirect mechanisms e.g. electron shuttling (Kappler et al., 2004) or sulphide (Pyzik and Sommer, 1981) or via other non-enzymatic pathways (Lovley et al., 1991a).

In this study we determined Fe(III) reduction rates using HCl extraction of the produced iron phases, studied the iron reducing community using deep sequencing (NGS) and analysed products of Fe(III) reduction in activated sludge systems using XRD and Mössbauer spectroscopy of a STP using Fe(III) for CPR and a STP where enhanced biological phosphate removal (EBPR) is applied. We hypothesized that (1) Fe(III) reduction rates are higher in the CPR plant, (2) Fe(III) reducing bacteria show a higher relative abundances in the CPR plant and that (3) vivianite is formed in both treatment plants as Fe(III) reduction commences.

6.2 Material and Methods

6.2.1 Sample origin

Activated sludge samples were obtained from aerated tanks of the STP Cologne-Rodenkirchen (Capacity: 70,000 p.e.; in 150 g TOC/d) where Fe(III) is dosed for CPR and from the STP Leeuwarden (226,000 p.e.; in 150 TOC/d) where EBPR is applied which is supported by CPR using Fe(III) salts. The SRTs in the activated sludge systems are 15 days in Leeuwarden and 12 days in Cologne. The elemental composition of the initial sludge (Table S 6-1) was determined using a microwave assisted acid digestion (MD, 9.0 mL of 70% HNO_3 on 1 g sample and heating for 20 minutes at 200 °C in closed Teflon vessels) followed by ICP-OES. Total and volatile solids (TS and VS respectively) were determined according to standard methods (APHA, AWWA, WEF, 1998). After sampling the sludge was settled for about 3-4 hours to increase the TS content by a factor 7 for Leeuwarden and 5 for Cologne (Table 6-1 and Table S 6-1). The supernatant was discarded and further experiments were performed with the settled sludge (Table 6-1). Due to the settling time we assume that anaerobic conditions occurred in the sludge.

Table 6-1: Characteristics of the settled sludge that was used in the batch experiments.

Parameter	Leeuwarden	Cologne
Temperature (°C)	19.6	18.0
pH	7.31	7.16
ORP (mV)	-34	-120
TS (g/kg sludge)	8.8	13.5
VS (g/kg sludge)	6.4	8.7
Molar Fe : P ratio	0.22	1.24
Total iron concentration (mg Fe/ kg sludge)	100	1190
Dissolved iron (mg Fe/ kg sludge)	0.1	0.1
Dissolved sulphate (mg SO_4^{2-}/ kg sludge)	33.6	132.5

6.2.2 Experimental design

To determine the total Fe(III) reduction rates in the activated sludge, $Fe(III)Cl_3 \cdot 7H_2O$ (1.0 g / kg settled sludge) was added inside an anaerobic glovebox (95% N_2 and 5% H_2) to the settled sludge. In the following total iron/all iron refers to the initially present iron (Leeuwarden: 100 & Cologne: 1190 mg Fe/kg settled sludge respectively) plus the Fe(III) that was added to the sludge (200 mg Fe / kg settled sludge). 100 mL of this mixture was filled in butyl rubber stoppered serum bottles (n=3 per time interval) and equipped with magnetic stirring bars. Samples were then incubated at 25 °C, for up to 24 h while stirring (400 rpm) and sampled at different time intervals. This was the experimental group aiming to obtain the total Fe(III) reduction rates. To determine chemical Fe(III) reduction rates in the sludge, a control group was treated analogue to the samples in the experimental group, however, this gravity settled sludge was autoclaved (30 min, 121 °C) before the experiments. Fe(III) reduction rates were calculated using the slope of the linear fitting of decreasing Fe(III) concentrations over time. The biological Fe(III) reduction rates reported are the difference between total and chemical Fe(III) reduction rates. Specific Fe(III) reduction rates were expressed per kg VS.

6.2.3 Sampling and sample preparation

At each time interval, prior to (destructive) sampling, temperature, pH and ORP of the samples were determined potentiometric (Figure S 6-1). The Fe(III) reduction rates were determined using 0.5 M HCl (Nielsen et al., 2005; Rasmussen and Nielsen, 1996). In short, 4 mL of sludge was filled in plastic centrifuge tubes containing 16 mL oxygen free 0.5 M HCl and glass beads. The samples were immediately flushed with N_2 to remove gaseous H_2S. The extraction was continued for one hour while shaking the samples at 1200 rpm. After extraction the samples were centrifuged (10 minutes, 3500 G) and Fe(II)/Fe(III) was measured using the ferrozine method (Viollier et al., 2000).

At the beginning and at the end (24 h) of the experiment about 2 mL sample were taken for DNA analyses. These samples were centrifuged (2 minutes, 8000 G), the pellet was collected and stored at -20ºC for one day until DNA was extracted using the Mo-Bio PowerSoil kit. The extracted DNA was stored at -20ºC until sequencing. Sequencing and basic data analysis were delegated to GATC. Amplification and high-throughput sequencing bacterial 16S rRNA was used for studying the phylogeny and taxonomy of the sludges. In case of paired end sequencing where amplicons are sequenced in both the directions, the resulting read pairs were merged based on overlapping bases using FLASh with maximum mismatch density of 0.25 (Magoč und Salzberg 2011). The sequence data was compressed by performing sequence clustering based on 99% similarity accounting for PCR and sequencing errors (<1%) using cd-hit (Li und Godzik 2006). Chimera check was performed with UCHIME (Edgar et al. 2011). Data that were not qualified as reliable was discarded. All qualified sequences where submitted to the NCBI database for a BLAST search (E-value cutoff 1e-06). All hits were utilized and the similarity was set above 97%.

The remaining sample was filled in plastic centrifuge tubes, the lids were sealed with parafilm and samples were centrifuged (10 min, 3500 G). Back in the glovebox the supernatant was filtered (0.45 µm) to determine the dissolved Fe(II)/Fe(III) concentration using the ferrozine method (Viollier et al., 2000) and the dissolved elemental and ionic composition using ICP-OES and IC respectively. Iron concentrations measured by the ferrozine method after HCl extraction are indicated as $Fe(II)_{Fer}$, $Fe(III)_{Fer}$ and $Fe(tot)_{Fer}$. Elemental concentrations measured by ICP-OES in the supernatant and in the total sludge are recorded as $X(aq)_{ICP}$ and $X(tot)_{ICP}$. Ionic composition in supernatant, was determined by using IC, these values are labelled as $X(aq)_{IC}$.

For XRD and Mössbauer analyses, the centrifuge pellet from the sample centrifugation was two times washed with oxygen free acetone and centrifuged (10 min, 3500 G) and then spread on glass plates inside the glovebox. The samples were apparently dry within 30 – 60 minutes but drying was continued in the dark, overnight inside the glovebox. For XRD analyses, the dried and grinded sample from one of the triplicates was filled in 0.7 mm glass capillaries and sealed first with modelling clay and then superglue. Just before the measurements started, glass capillaries were burnt off to be able to mount them in the sample holder. The measurements were done on a PANalytical X´Pert PRO diffractometer with Cu-Ka radiation (5-80 º2θ, step size 0.008º). For Mössbauer analyses, dried and grinded samples were filled in plastic rings, sealed with Kapton tape and super glue and then wrapped in parafilm. Transmission ^{57}Fe Mössbauer spectra were collected at 100 K with conventional constant-acceleration and sinusoidal velocity spectrometers using a $^{57}Co(Rh)$ source. Velocity calibration was carried out using an α-Fe foil. The Mössbauer spectra were fitted using Mosswinn 4.0 (Klencsár, 1997).

6.3 Results

6.3.1 Fe(III) Reduction

Figure 6-1 shows the average Fe(II), Fe(III) and total iron concentrations over the time period of the batch test experiments. All iron concentrations in this graph were measured using the ferrozine method after a 0.5 M HCl extraction. On average 82% of all iron was released from Leeuwarden activated sludge, while 86% could be extracted from the Cologne activated sludge compared to the total iron content as determined by using the microwave assisted acid digestion followed by ICP-OES. In both sludges, Fe(III) dominated at the start of the experiment. Initially, 93% of $Fe(tot)_{Fer}$ in Leeuwarden and 92% of $Fe(tot)_{Fer}$ in Cologne was $Fe(III)_{Fer}$. In Leeuwarden about 75% of $Fe(tot)_{Fer}$ and in Cologne 58% of $Fe(tot)_{Fer}$ was reduced within 24 h and 24.5 h respectively. The chemical $Fe(III)_{Fer}$ reduction rates, determined in experiments with autoclaved sludge, was only about 5% of the $Fe(tot)_{Fer}$ reduction rate in both sludges. The specific $Fe(III)_{Fer}$ reduction rates in Cologne sludge (2.99 mg-Fe g VS^{-1} h^{-1}) was almost 3 times higher than the one in Leeuwarden sludge (1.02 mg-Fe g VS^{-1} h^{-1}).

Fe(III) bio-reduction with Fe(III) oxyhydroxides follows first order kinetics (Bonneville et al., 2009; Hacherl et al., 2003; Liu et al., 2002). Hence, the first order rate constant (k) was determined by linear fitting of ln(Fe(III)) versus time. The k value (95% CI) for Leeuwarden was 0.06 ± 0.001 h^{-1}, while for Cologne it was 0.05 ± 0.007 h^{-1}. An t-test showed that there is a statistical difference between the constants ($p<0.05$, $t=0.03$). However, the k value of the EBPR sludge from Leeuwarden was only 1.14 times higher than the one obtained from measurements on Cologne sludge. In practice, one can consider the potential iron reduction rate in Leeuwarden as being equal to the one of Cologne. Thus, the biological induced Fe(III) reduction rates in Cologne and Leeuwarden should be equal when both sludges contain the same quantities of iron.

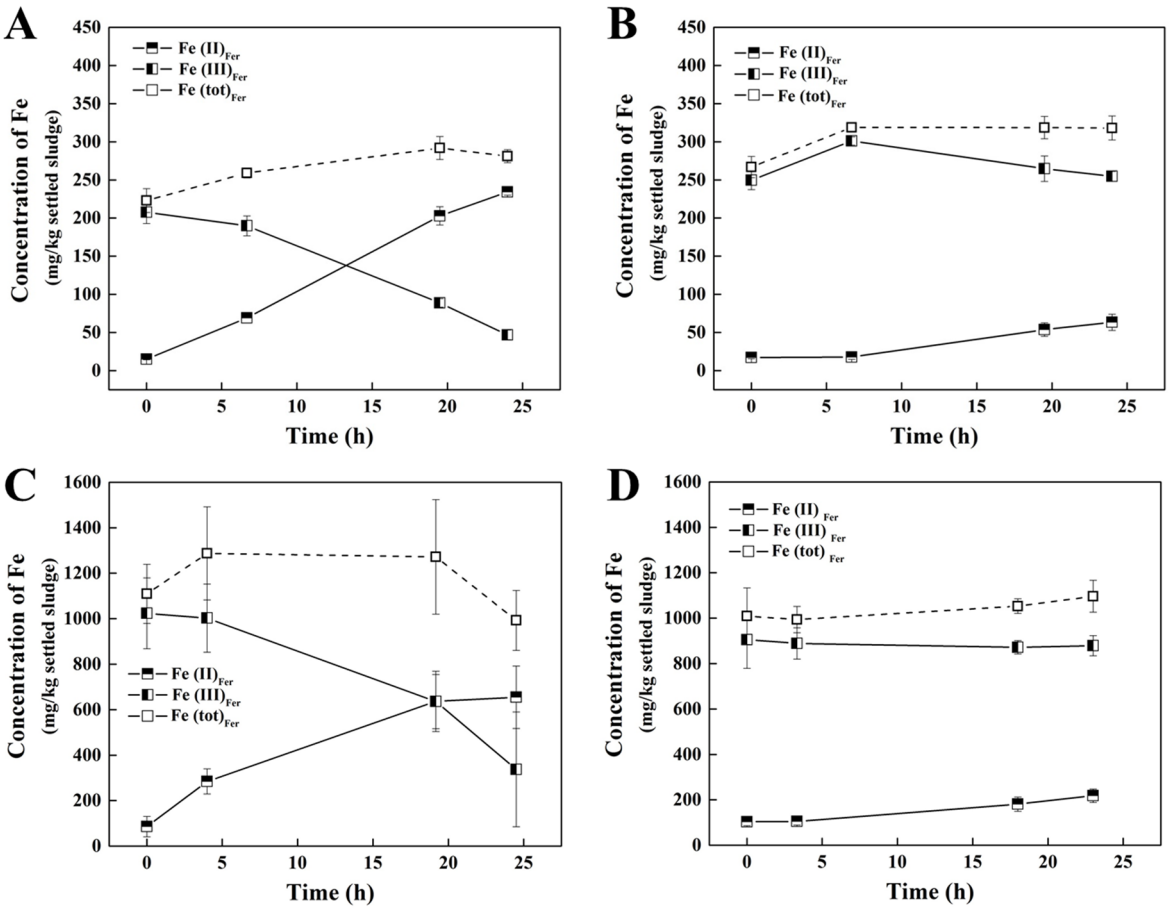


Figure 6-1: Iron concentrations in activated sludge during batch test experiments determined by the ferrozine method. A & C refer to sludge from Leeuwarden STP and Cologne STP respectively, while B & D refer to autoclaved sludge.

6.3.2 Dissolved elemental composition

The behaviour of dissolved compounds in the sludge suspension during the iron reduction experiments (Figure 6-2, Figure S 6-2 & Figure S 6-3) shows that in the EBPR sludge from Leeuwarden significant amounts of phosphate are released within the first few hours of the experiment. This is accompanied by a release of potassium and magnesium. Phosphate accumulating organisms (PAOs) are probably responsible for this phenomenon (Jardin and Pöpel, 1994; Wentzel et al., 1992). Initially, dissolved calcium concentrations drop which could indicate calcium phosphate precipitation. However, during the course of the experiment calcium concentrations rise again. Despite apparent Fe(III) reduction, dissolved iron levels remain relatively low at 0.16±0.06 mmol Fe/kg sludge. In the control group from Leeuwarden iron and potassium remained relatively constant over time, whereas phosphate, calcium and magnesium increased within 24 h of anaerobic storage. This increase could be due to cell lyses in response to the autoclaving.

In contrast to the EBPR sludge from Leeuwarden, phosphate levels did not increase in CPR sludge from STP Cologne, the dissolved phosphate levels remained constantly low at 0.07±0.02 mmol P/kg sludge throughout the experiment. The dissolved iron concentration clearly

increased from 0.3 mmol Fe/kg sludge at the beginning of the experiments to about 1.24 mmol Fe/kg sludge after 24 h of anaerobic incubation. As the pH in the batch test was kept above 6.0, the dissolved iron is supposedly rather present as Fe(II) rather than Fe(III) (Tilley, 2005). In the control group from Cologne, no large changes of dissolved elemental concentrations were observed. Dissolved iron and phosphate remained on a relatively low level.

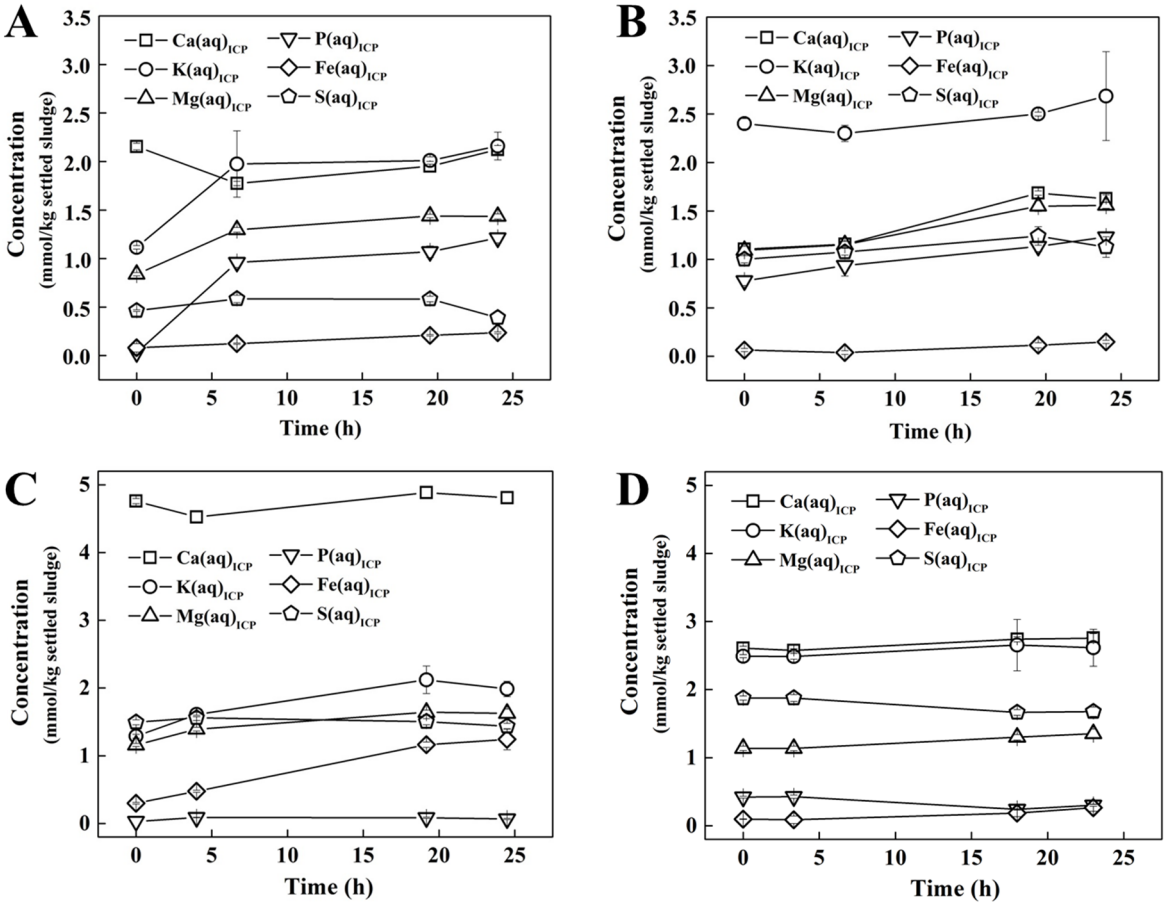


Figure 6-2: Elemental concentrations in activated sludge during batch test experiments determined by ICP. A & C refer to sludge from Leeuwarden STP and Cologne STP respectively, while B & D refer to autoclaved sludge.

6.3.3 Microbial communities in the activated sludges

Samples of the sludges used in the study were sent for metagenome sequencing. The dominant phylum in both sludges was proteobacteria (Figure S 6-4) comprising between 68 and 89% of all OTUs. Betaproteobacteria formed the dominant class of OTUs observed (Figure S 6-5). The predominant microbial genera in the sludges are shown in Figure 6-3 and in Table S 6-2. As expected for activated sludge communities (Zhang et al. 2012) the diversity of the system was high with many different OTUs, each comprising only a small fraction of the total community.

The genus diversity in the two sludges were high with 103 OTUs in the STP Cologne and 107 OTUs in the STP Leeuwarden. Both sludges showed a similar Simpson index (between 0.95 and 0.96) and Shannon index (between 3.62 and 3.74) indicating a comparable richness and evenness on the genus level. The top 3 genera in the EBPR sludge from the STP Leeuwarden

were *Flavobacterium* (11.7%), *Novosphingobium* (9.4%) and *Rhodoferax (*8.9%). While in the CPR sludge from STP Cologne, the observed top 3 bacterial genera were *Novosphingobium* (10.8%), *Dechloromonas* (9.3%) and *Rhodoferax* (8.9%).
The CPR sludge from the STP Cologne showed a higher abundance of the genera *Rubrivivax* (3.4% compared to 0.6% in Leeuwarden) and *Leptothrix* (3.2% in STP Cologne vs 0.6% in the STP Leeuwarden), but lower abundance in the genera *Flavobacterium* (4.6% vs 11.7%), *Trichococcus* (0.6% vs 6.8%) and *Janibacter* (0.2% vs 3.1%).
After anaerobic incubation for 24 h, the abundance of several genera changed. In EBPR sludge, the abundance of *Novosphingobium* increased from 9.4% to 12.0%. In CPR sludge the abundance of *Dechloromonas* decreased from 9.3% to 3.6%.

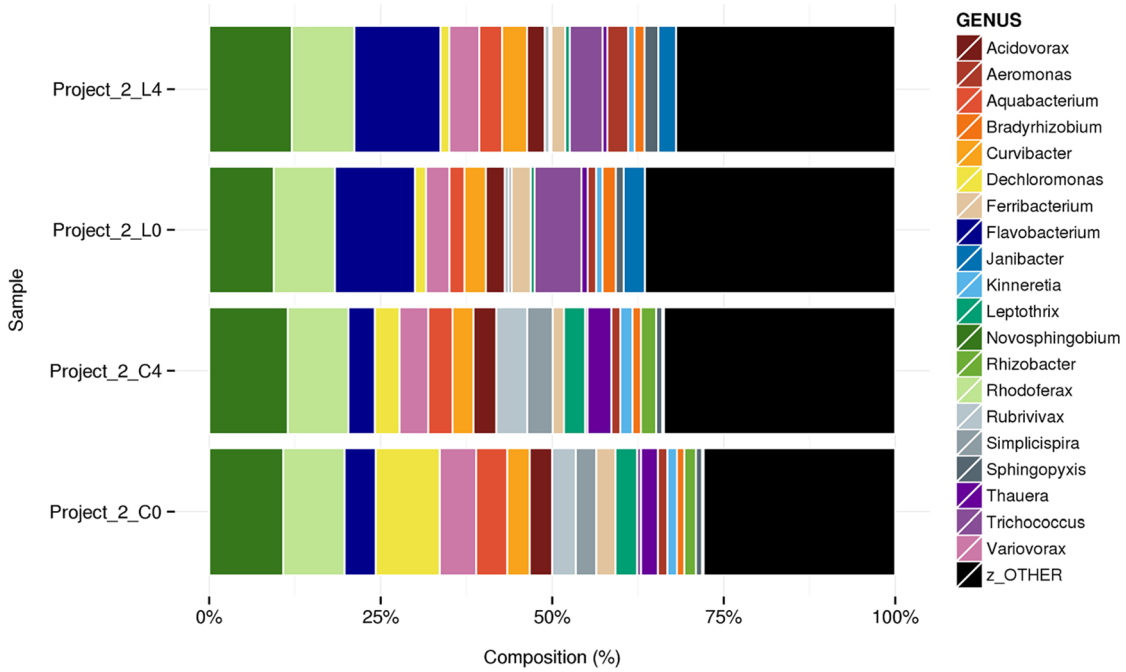


Figure 6-3: Genus wise OTU distribution in the activated sludge samples (Top 20 OTUs contain 68% of total OTU assigned reads).

6.3.4 Vivianite formation

6.3.4.1 XRD

The degree of crystallinity was relatively low in all samples, probably due to their large organic content and due to the presence of amorphous inorganic phases (all spectra including peak assignments are included as supporting information, Figures S6-6 to S6-9). Despite the low crystallinity several crystalline phases could be identified in the samples. Samples taken from the activated sludge tanks in Leeuwarden contained only quartz as crystalline material at the beginning and after 24 h of anaerobic incubation (Table 6-2). The samples from Cologne also contained quartz at the beginning and end of the experiment but the dominant crystal was calcium carbonate. After 24 h of anaerobic incubation the typical peaks of vivianite appeared

in the sample. Vivianite contributed 29% to the total crystalline material in the Cologne activated sludge after 24 h of incubation (Table 6-2).

Table 6-2: Results of XRD measurements on dried activated sewage sludge solids from STP Leeuwarden and STP Cologne.

ID	Compound	Share (% of crystalline material)	
		t = 0 h	t = 24 h
Cologne	Quarz (SiO_2)	19	15
	Vivianite ($Fe^{II}_2PO_4^{3-}x8H_2O$)	-	29
	Calcium Carbonate ($CaCO_3$)	81	57
Leeuwarden	Quarz (SiO_2)	100	100

6.3.4.2 Mössbauer spectroscopy

Vivianite was identified and quantified in all samples by Mössbauer spectroscopy. The spectra were obtained at 100 K. Note that the results from Mössbauer spectroscopy refer to total iron in the samples. The total iron content in both samples differed considerably (Table 6-1).

The spectra obtained from the samples showed Mössbauer parameters for vivianite in agreement with the vivianite data that was obtained by Gonser and Grant, 1976. However, the ratio of the two iron sites in vivianite should be 2 (Rouzies and Millet, 1993, Mori and Ito, 1950) but deviated from 2 in our measurements (for Leeuwarden: 1.4 for Cologne: 1.1, Table 6-3).We believe that impurities in the vivianite are the reason for deviation of the site ratio compared to the standard measurements. Substitution of iron by other cations in iron phases can affect Mössbauer measurements (Gil et al., 1992), also the site ratios in iron phases (Amthauer and Rossman, 1984). For baricite (the analogue of vivianite with some magnesium as iron substitute) iron substitution takes preferably place at site 2 (Yakubovich et al., 2001). If iron substitution in vivianite also takes dominantly place at site 2 then an iron site ratio <2 can be expected. Indeed, vivianite is notoriously known to contain impurities (Rothe et al., 2016; Taylor et al., 2008). In sewage sludge dissolved metals, such as calcium or magnesium, occur that could be incorporated in the vivianite structure. With this line of reasoning we hypothesize that the vivianite in our samples is rather a vivianite like structure, i.e. that some of the iron was replaced (data indicate that the replacement takes preferably place at site 2) by other metals such as magnesium or calcium. When we refer to vivianite in the following we actually refer to the vivianite like structures with unknown degrees of impurity. Oxidation of vivianite can also change the site ratios but it was observed that initial oxidation rather increases than decreases the site ratio i.e. that it leads rather to a Fe site ratio>2 (Rouzies and Millet, 1993).

Mössbauer spectroscopy showed (Table 6-3) that vivianite was initially present only in small fractions in the sludge from Leeuwarden (5% of all iron was bound in vivianite) and Cologne (8% of all iron bound in vivianite) respectively. After about 24 h of anaerobic incubation the vivianite content in both samples increased substantially. At the end of the experiments

vivianite was the dominating iron phase in the samples from Leeuwarden, here the Fe(II) in vivianite summed up to 53% of all iron. In Cologne about 34% of all iron was in vivianite after 24 h of incubation. The vivianite structures in the Leeuwarden sample (after 24 h) have Mössbauer parameters that are closer to those of standard vivianite (compared to the Cologne sample at 24 h). Also the site ratio is higher – it seems the Leeuwarden vivianite is better defined compared to the vivianite in Cologne.

The Fe(II) content in the two activated sludge samples, as determined by HCl extraction combined with photometric determination of Fe(II)/Fe(III), was different than the Fe(II) content determined by Mössbauer spectroscopy. After 24 h Mössbauer spectroscopy suggested that in Leeuwarden 53% and in Cologne 34% of all iron is Fe(II). In contrast, HCl extraction showed that in the same samples 83% (Leeuwarden) and 66% for (Cologne) of all iron is Fe(II). For Leeuwarden, the extraction efficiency was with about 92% relatively high. In Cologne only 71% of all iron was extracted after 24 h by using HCl and hence a comparison between HCl extraction and Mössbauer spectroscopy is difficult in this case. Using Mössbauer spectroscopy for obtaining the oxidation state of the iron is not straight forward when samples are not measured at 4 K. In Table 6-3, Fe^{3+} refers to high-spin Fe(III) (that could e.g. be an iron oxide); Fe^{2+} to high-spin Fe(II) (vivianite or disordered/impure vivianite) and Fe(II) to low-spin Fe(II) (probably pyrite). For spectra obtained at 100 K, the Fe^{3+} (iron oxide) can overlap with Fe(II) (pyrite) – it can be any of the two alone or a mixture, but not an intermediate species. Thus, by assuming HCl extraction as accurate in accounting for all Fe(II) in Leeuwarden sludge, then the difference between Mössbauer and HCl extraction should be the iron that is bound in pyrite (about 30%). The elemental composition of the sludge solids, indeed suggests that up to 50% of all iron could be bound in pyrite in Leeuwarden (Table S 6-1). Thus, we can assume 30% of all iron in Leeuwarden is bound in pyrite, 53% in vivianite and the remaining 17% in another, unknown iron phase which is probably a ferric compound. Differences between HCl extractions and Mössbauer could be related to differences in sample handling (wet vs dried sample) or the presence of other low spin Fe(II) species with Mössbauer parameters close to the one of pyrite (but different stoichiometry / elemental composition).

Table 6-3: Mössbauer results obtained with the samples from the STPs Leeuwarden and Cologne at the beginning of the experiments and after 24 h of anaerobic incubation.

Sample	Temperature (K)	IS ($mm \cdot s^{-1}$)	QS ($mm \cdot s^{-1}$)	Γ ($mm \cdot s^{-1}$)	Phase	Spectral contribution (%)
Leeuwarden t=0	100	0.37	0.68	0.49	Fe^{3+}/Fe^{II}	95
		1.25	2.36	0.30	Fe^{2+} (Vivianite I)	2
		1.25	2.97	0.30	Fe^{2+} (Vivianite II)	3
Leeuwarden t=24 h	100	0.39	0.70	0.54	Fe^{3+}/Fe^{II}	47
		1.16	2.64	0.39	Fe^{2+} (Vivianite I)	22
		1.22	3.17	0.39	Fe^{2+}(Vivianite II)	31
Cologne t=0	100	0.36	0.74	0.48	Fe^{3+}/Fe^{II}	91
		1.19	2.45	0.32	Fe^{2+} (Vivianite I)	3
		1.19	2.98	0.32	Fe^{2+}(Vivianite II)	5
Cologne t=24 h	100	0.38	0.72	0.46	Fe^{3+}/Fe^{II}	66
		1.14	2.59	0.34	Fe^{2+} (Vivianite I)	16
		1.19	3.03	0.34	Fe^{2+}(Vivianite II)	18

Note: Experimental uncertainties: Isomer shift: I.S. ± 0.01 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.01 mm s^{-1}; Line width: Γ ± 0.01 mm s^{-1}; Spectral contribution: ± 3%.

6.4 Discussion

6.4.1 Fe(III) reduction in activated sludge

The iron reduction rates measured in the activated sludge after storing it under oxygen free conditions for 24 h are in the range of earlier measurements (Nielsen, 1996; Nielsen et al., 1997; Rasmussen et al., 1994). By compiling all these data, the trend for increasing iron reduction rates in sludge with higher iron content is obvious (Figure 6-4), which is consistent with the view that iron reduction exhibits first order kinetics. However, also some data show Fe(III) reduction rates that significantly deviate from the general trend (Figure 6-4). These differences can be caused by 1) differences in the type of oxidized iron phases that are present; 2) presence of different types of iron reducing bacteria; 3) different mechanisms of microbial Fe(III) reduction; 4) different reaction conditions and 5) presence and availability of organics as electron donors. In our study, Mössbauer spectroscopy and XRD indicate that poorly crystalline Fe(III) phases were formed/present in the sludge (the line width of the Mössbauer signal is considerably higher compared to very crystalline structures with values of about 0.25 mm/s). Such iron phases usually have a high surface area and the iron in these compounds is readily available to Fe(III) reducers compared to more crystalline ferric iron forms (Lovley, 2013). The apparent increase of iron reduction rates with the higher iron content in the sludge, presumably under similar experimental conditions, follows first order kinetic. This suggests that the iron reduction rate is rather physical than biological driven. In this context, it could be a limitation

of mass transport that is usually a function of the surface area of the iron phases in the sludge. In other words, by assuming that the type of iron compounds in the sludges are the same, then a higher iron content will result in higher availability of iron because of reduced transport limitations. Experimentally, this hypothesis can be tested by adding different quantities of iron to sludge under the same experimental conditions until the reduction rate is plateauing. Hence, the scattering of data points in Figure 6-4 could partly be explained by the presence of iron phases with different mineralogy and thus with a different availability of the iron to the bacteria and/or a different surface area. In the other studies no additional iron was added and the iron that was initially present in the sludge was not characterized. We can therefore not conclude that the type of iron in the sludges could explain some of the observed deviations. Furthermore, the type of organic substrates that are present in the sludges can explain deviations. Yet, Nielsen et al., 1997 claim that the rates after adding lactate were only about 20-30% higher than the ones in samples without additional substrate addition.

In the present study, although the Fe(III) reduction rates in Cologne sludge was 3 times higher compared to Leeuwarden sludge, the potential of Fe(III) reduction rate for these two sludges was similar assuming first order kinetics. This would imply that the reduction rates for both sludges at similar iron concentrations would be more or less similar.

Besides direct microbial Fe(III) reduction also indirect microbial induced chemical reduction via sulphide production or via organic electron shuttles could be responsible for the turnover of iron in the samples. Out of 1 mol of sulphate 1 mol of sulphide can be formed that subsequently reduce 2 mol of Fe(III) to Fe(II). In Cologne dissolved sulphate levels dropped from 132 to 117 mg SO_4^{2-}/kg sludge indicating that at most 0.31 mmol Fe(III)/kg sludge can be reduced. In Leeuwarden sulphate dropped from 33.5 to 14.3 mg SO_4^{2-}/kg sludge indicating that a maximum of 0.4 mmol Fe(III)/kg sludge could be reduced. The indirect Fe(III) reduction by sulphide could therefore at maximum explain 7% and 1% of the observed iron reduction in Leeuwarden and Cologne respectively. The exact magnitude of Fe(III) reduction rate by sulphide is unknown but during the whole experiments neither a sulphide smell nor black colouration of the samples was observed. To what degree other mechanisms contributed to the reduction of Fe(III) in our samples is unknown.

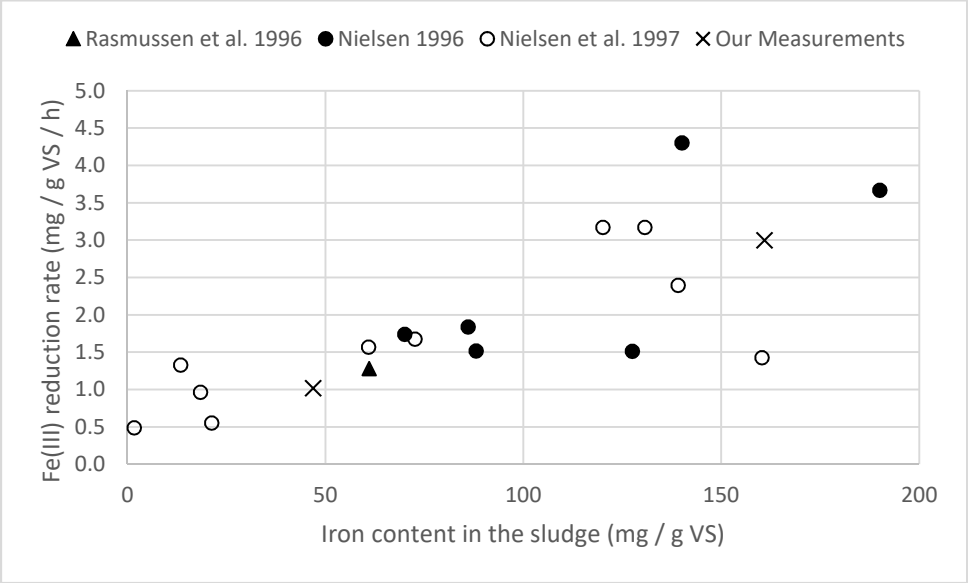


Figure 6-4: Iron reduction rates in activated sludge samples. Rates marked with dots and circles refer to rates that were determined after adding lactate to the sludge. The other rates (triangles and crosses) were determined without organics addition. The rates are plotted versus the iron content of activated sludge. Rates determined by Nielsen, 1996 are average values.

Control incubations with autoclaved sludge were performed to identify the chemical / non-biological Fe(III) reduction in the sludge. In both control incubations, a slight but steady increase of Fe(II) over time was measured but the computed Fe(III) reduction rates are only about 5% of the total rates. This is in accordance to earlier studies, where sterilized sediments showed only little Fe(III) reduction capacity in contrast to non-sterilized sediment (Lovley et al., 1991b). The chemical reduction in our study could be due to the presence of reduced compounds in the sludge, such as reduced sulphur species (Pyzik and Sommer, 1981), that can be produced in-situ or originate from the incoming raw sewage (Hvitved-Jacobsen et al., 2013; van den Brand et al., 2015). Additionally, organic compounds are able to transfer electrons to Fe(III). Organic molecules are e.g. used as electron shuttles by microorganisms (Kappler et al., 2004; Lovley et al., 1996), are probably released as external electron donors to access insoluble Fe(III) phases (Richter et al., 2012) and additionally some organic ligands, like cysteine, are capable of reducing Fe(III) (Cornell et al., 1989). Since the interaction between Fe(III) and dissolved sulphide are usually relatively quick (Poulton et al., 2004) we suggest that mainly organic compounds or other reduced compounds such as FeS_x are responsible for the Fe(III) reduction in the control incubations. The autoclaving could further increase the abiotic Fe(III) reduction potential due to cell lyses and thus an additional release of organics with reducing properties into the solution. We suggest to consider further non-destructive control incubations in future, such as cooling of the samples to reduce the activity of microorganism, to be able to distinguish between chemical and biological Fe(III) reduction better.

For calculating the time it takes to turnover all Fe(III) to Fe(II) in the sludge, the Fe(III) reduction rates (2.99 and 1.02 mg-Fe g^{-1} VS h^{-1} respectively) at the total iron content of the experiments were used and assumed to be constant over time. According to these calculations

it would take 15 h in Leeuwarden and 44 h in Cologne to reduce the naturally present iron (i.e. the iron from the influent and the iron that is dosed for CPR) in the sludge from Fe(III) to Fe(II). Note that significant amounts of Fe(III) would still be present after this time when the iron turnover is calculated by using the first order rate constants, in Cologne 10% and in Leeuwarden 40% of all iron would not be reduced after 15 and 44 h respectively. Yet, it was decided not to use the rate constants because the reaction can change order when it progresses and then another step could become rate limiting.

The SRT in the plants are about 14 days and half of this time in oxygen free tanks. In Leeuwarden besides anoxic also anaerobic tanks exist for EBPR. Earlier Mössbauer measurements on surplus sludge (i.e. sludge after settling but before dewatering that is brought into the digester/recirculated in the sludge line) from Leeuwarden show that indeed all iron in this sludge was Fe(II) (Wilfert et al., 2016). The findings from Leeuwarden match with the first part of our hypothesis (Wilfert et al., 2016): Fe(III) reduction and subsequent formation of vivianite is quick and once vivianite is formed its re-oxidation is slow. In Cologne, however, earlier Mössbauer data obtained at 4 K, indicates that not all but only about 57% of all iron in the surplus sludge was Fe(II), this sludge was taken right before it was pumped into the anaerobic digester (Wilfert et al., 2017a). The activated sludge that we used in our experiments was taken from the aerated tank of the activated sludge process, here Fe(III) was dominant (90%). Note, that about 15% of all iron was added as Fe(III) at t=0 and that the extraction efficiency was about 90% at t=0. Still, there is obviously a difference in the iron chemistry between surplus and activated sludge. Sludge and thus the containing iron can encounter oxygen free conditions for some time in STPs, e.g. in settlers, inside flocs with limited oxygen diffusion or in anaerobic/anoxic tanks that are required for successful nutrient elimination. Apparently, in Cologne the reduction is not quick enough to turn over all Fe(III), perhaps due to the presence of aerated tanks or because the conditions in our batch experiments are different to the ones encountered in the treatment lines. Else, Fe(III) reduction would theoretically be quick enough to reduce all Fe(III) and re-oxidation of Fe(II) to Fe(III) would be slow assuming the presence of pure vivianite (Roldan et al., 2002). Nielsen, 1996 and Nielsen et al., 2005 showed that most, but not all Fe(II) could be re-oxidized after intense aeration for several days of sludge that was stored under anaerobic conditions before. Since vivianite oxidation is supposedly a slow process (Miot et al., 2009; Roldan et al., 2002). It could be that this phenomenon can be explained by the presence of vivianite in these experiments. On the one hand, the activated sludge in Cologne, contained little vivianite and little Fe(II), showing that our hypothesis is not entirely true. On the other hand, surplus sludge sampled in Cologne contained about 60% of all iron as Fe(II) (Wilfert et al., 2017a) showing that our hypothesis proves to be partly true.

6.4.2 Microbial analysis in activated sludge

The metagenome analysis was performed for both sludges before and after anaerobic incubation for 24 h under endogenic conditions. Since marginal growth and decay will occur the communities would be expected to be highly similar or identical. For Leeuwarden this is more or less the case, but for the Cologne samples there seem to be differences. This might be related

to the change in iron valency. DNA extraction methods are sensitive to many factors and the presence of different forms of metals might influence the DNA extraction (Matheson et al. 2009). Since the transformation of Fe(III) to Fe(II) in the sludge sampled in STP Cologne was quicker it seems logically that the detrimental effects on the genetic analyses was larger for the Cologne samples. The discussion section will therefore focus on the microbial community in both of the sludges at the start of the anaerobic incubation (t=0 h).
Similar to earlier studies proteobacteria were the dominant phylum in the activated sludges (Ferrera und Sánchez 2016). Table S 6-2 shows the top 20 genera in EBPR and CPR sludge with their abundances. Half of the top 20 genera in both sludges are common genera that are encountered in STPs. Some of their common traits are given in Table S 6-3. *Rhodoferax, Dechloromonas, Acidovorax* and *Bradyrhizobium* are common denitrifiers while *Trichococcus* and *Bradyrhizobium* are organic degrading organisms. *Dechloromonas, Rubrivivax, Simplicispira, Janibacter* and *Sphingopyxis* are known PAOs but it has not been proven yet that these organisms carry this metabolism also out in activated sludge systems (Terashima et al. 2016; Thomsen et al. 2007; Godoy et al. 2003; Tsai et al. 2005; Abma et al. 2007; Tsai et al. 2005; Lu et al. 2007). Saunders et al. (2016) analysed the microbial communities in 13 Danish STPs and found the predominant genera in these plants were *Trichococcus, Flavobacterium* and *Comamonadaceae*. Zhang et al. (2012) investigated the bacterial communities of activated sludge from 14 STPs, *Zoogloea, Trichococcus* and *Dechloromonas* were the core genera in each sample. This suggests that the microbial composition in STPs is relatively similar.

The top genera in the EBPR sludge and in the CPR sludge were similar, however they occurred with different abundances (Table S2). Higher abundances (at least 2 times higher) of *Dechloromonas, Aquabacterium, Rubrivivax, Thauera, Leptothrix* and *Simplicispira* were observed in the CPR sludge compared to the EBPR sludge. Some species in these genera, e.g. *Dechloromonas*, *Aquabacterium*, *Leptothrix* and *Simplicispira* are related to Fe(II) oxidation / Fe(III) reduction (Wang et al. 2015; Corstjens et al. 1992; Chang et al. 2015). In EBPR sludge, higher abundance of *Flavobacterium*, *Trichococcus* and *Janibacter* were observed. *Flavobacterium* and *Trichococcus* are commonly known in STPs for their roles in nitrogen removal and organics degradation respectively (Zhang et al. 2012; Saunders et al. 2016). As for *Janibacter*, no reports about its role in STPs are available.

Iron reducing bacteria (IRB) can directly reduce Fe(III) to Fe(II). However, most of the IRB are able to carry out various other metabolic conversions, besides iron reduction (Lovley 2013). Furthermore, next to direct iron reduction also indirect chemical or biological iron reduction can take place which is induced by various groups of microorganisms (Lovley 2013; Kappler et al. 2004; Pyzik and Sommer 1981). Among the genera found in the activated sludge samples, direct iron reduction has been related to members of the genera *Rhodoferax*, *Dechloromonas*, *Ferribacterium* and *Aeromonas*. *Rhodoferax ferrireducens* was reported as a facultatively anaerobic bacterium that oxidize acetate with the reduction of Fe(III) (Finneran et al. 2003). However, the other *Rhodoferax* species, e.g. *Rhodoferax antarcticus*, *Rhodoferax fermentans* and *Rhodoferax saidenbachensis* have not been reported to have ability of Fe(III) reduction,

some species in this genus are phototrophs. *Dechloromonas hortensis* was found to have the ability of reducing ferric oxides and oxidizing Fe(II) (Wang et al. 2015). Other *Dechloromonas* species, e.g. *Dechloromonas agitata* and *Dechloromonas aromatica* were reported to be Fe(II) oxidizers (Shi et al. 2012; Ilbert und Bonnefoy 2013). *Ferribacterium limneticuma*, as the only species in the genus *Ferribacterium* reduces Fe(III) with acetate as electron donor (Cummings et al. 1999). Bacteria of the genus *Aeromonas* are often human pathogens (Banerjee et al. 2017), from 14 species in this genus *Aeromonas hydrophila* was reported to be a Fe(III) reducer (Liu et al. 2014; Ventura et al. 2015). The higher iron content in sewage sludge from the STP in Cologne could explain the higher abundance of genera that comprise some iron oxidizing bacteria (IOBs) such as *Aquabacterium*, *Dechloromonas*, *Acidovorax*, *Leptothrix* and *Curvibacter* (Chang 2015; Wang et al. 2015; Corstjens et al. 1992) in CPR sludge compared to the EBPR sludge sampled in the STP Leeuwarden.

6.4.3 Vivianite is formed in both treatment plants as Fe(III) reduction commences

The phosphate removal is efficient in Cologne with effluent levels of 0.33 mg P/L (average in June 2017) although significant amounts of iron are present as Fe(II) in the surplus sludge (Wilfert et al., 2017a). In our experiments no substantial amounts of phosphate were released despite more than 50% of the Fe(III) was reduced during the experiment. This phosphate could be retained by excess Fe(III) that was present but at least a significant part of the phosphate was also retained as vivianite. Both XRD and Mössbauer spectroscopy confirmed the presence of vivianite after 24 h of anaerobic incubation in the activated sludge in Cologne. Taking the molar Fe:P ratio of the Cologne sludge (1.24, Table 6-1), the molar P:Fe ratio of vivianite (0.66) and the % of iron bound as vivianite (34%, Table 6-3) into account then about 30% of all phosphate should be bound in vivianite (compared to 7% at the start of the experiment) in Cologne. In Leeuwarden, about 8% of all phosphate is bound in vivianite at the end of the experiment. Thus, both, Mössbauer spectroscopy and XRD measurements show that substantial amounts of vivianite can form within 24 h and thus within time scales of STPs. Our data shows that vivianite can form as a response to Fe(III) reduction and that this Fe(III) reduction does not necessarily result in net phosphate release (Ivanov et al., 2003; Stabinov et al., 2005). Vivianite has been identified in wastewater treatment systems with oxygen free stages as an important phosphate phase (Azam and Finneran, 2014; Frossard et al., 1997; Nriagu, 1972; Singer, 1972; Wilfert et al., 2016; Zhang, 2012). Our data shows that its formation can take already place before the anaerobic digestion process in short time frames when the oxygen free conditions occur in the treatment lines within the activated sludge process. This explains why considerable amounts of vivianite have been found in surplus sludge before digestion (Frossard et al., 1997; Wilfert et al., 2016). Also our Mössbauer measurements indicate that the sludge that was sampled in aerated tanks of the STPs contained before the start of the experiment small amounts of vivianite, and that the oxidation of vivianite is a relatively slow process. Indicating that its formation already takes place in the activated sludge of the STPs. This vivianite fraction was not detectable by XRD, either because it is highly dispersed vivianite with small particle size

or because its amount was below detection limit. How fast the oxidation of the vivianite like structures in the sludge is has yet to be determined.

Our experiments furthermore show what will happen when sewage sludge is brought to an anaerobic digester. During anaerobic digestion the sludge is usually retained for about 2-4 weeks under methanogenic conditions. During this time all Fe(III) should be transformed to Fe(II), since dissolved phosphate is present vivianite can form. Thermodynamic calculations indicate that, under the conditions that occur in digesters, vivianite is more stable than most other phosphate minerals (Nriagu and Dell, 1974). If enough iron is present in the sludge, as in the case of Cologne, then the formation of vivianite during anaerobic digestion is also not hampered by the formation of insoluble iron sulphide compounds FeS_x, (Chen et al., 2008; van den Brand et al., 2015). This line of reasoning underlines the important role vivianite plays for STPs using iron for CPR. When vivianite forms, then the expected net phosphate release is very little during the anaerobic digestion (Nriagu, 1972). Accordingly, in Cologne the phosphate concentration in the liquor of the digested sludge was only 0.8 mg P/L at a pH of 7.5.

In both sludges Mössbauer spectroscopy showed that vivianite formed although different treatment designs are applied. In STP Leeuwarden EBPR with little Fe(III) dosing is applied and the STP Cologne relies solely on CPR using Fe(III). We suggest that the mechanisms of vivianite formation in the two STPs were different (Figure 6-5). In Cologne, most iron bound phosphate is initially adsorbed to amorphous ferric iron oxides (Lu et al., 2016; Mao et al., 2016). During the reduction of ferric iron (phosphate) phases some phosphate is released and re-precipitates with the dissolved Fe(II) as vivianite. Additionally, adsorbed phosphate will precipitate in response to iron reduction as vivianite due to the very low solubility of vivianite. The kinetics and importance of these two processes have to be established. In Leeuwarden, initially most phosphate is bound inside the PAOs with only little amounts of phosphate adsorbed to ferric iron oxides. While storing the samples under oxygen free conditions, PAOs release polyphosphates which are hydrolyzed and at the same time Fe(II) is brought in solution via iron reduction. Besides phosphate the PAOs also release potassium and magnesium. Ammonium levels are increasing in solution from 0.65 to 3.69 mmol/L in the first 20 h and then sharp decreasing to 0.16 mmol/L at 24 h, theoretically struvite could form in the samples, but XRD could not detect it. Perhaps it was below detection limit of XRD or present with small particle size. Mössbauer spectroscopy indicated that vivianite formed in the sludge in Leeuwarden, perhaps this vivianite formation was on expenses of struvite due to a lower solubility of vivianite compared to struvite (Mamais et al., 1994; Nriagu and Dell, 1974).

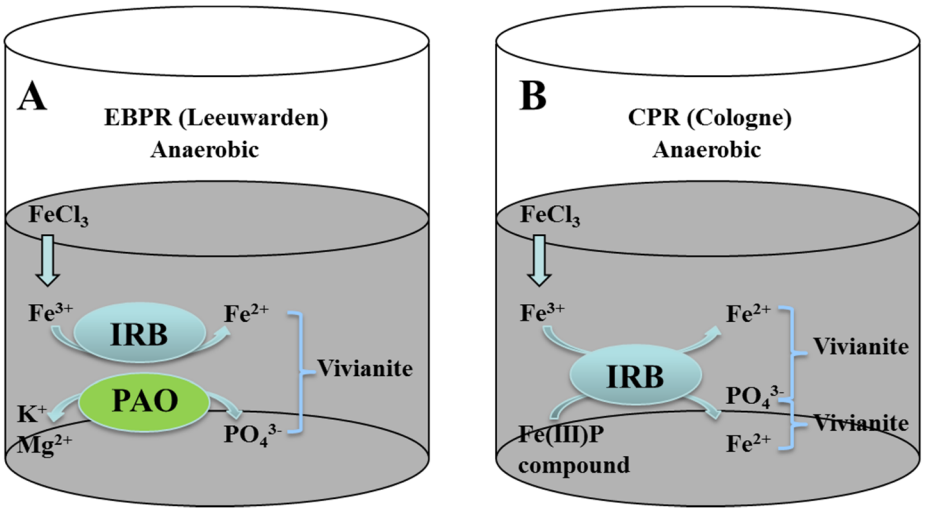


Figure 6-5: Conceptual model of vivianite formation in response to Fe(III) addition and subsequent Fe(III) reduction in sludge from a EBPR plant (with low initial Fe(III) content) and in a CPR plant where Fe(III) is already present.

6.5 Conclusion

Our results on activated sludge sampled in two full scale STPs indicate that all Fe(III) that is present in the sludge can be reduced within few days provided oxygen free conditions occur. Under the measurement conditions the Fe(III) reduction rate in Cologne sludge was 3 times higher than that in Leeuwarden sludge. Since Fe(III) reduction is thought to follow first order reaction kinetics, the difference in rates can be explained by differences in the iron concentration and the potential Fe(III) reduction rate (i.e. the first order reaction constant) for both sludges is therefore comparable. In both plants, Mössbauer spectroscopy showed that initially little vivianite was present in the sludge and the iron pool was dominated by Fe(III). With ongoing Fe(III) reduction also formation of vivianite proceeded without significant release of phosphate from the sludge. At the end of the experiment in the treatment plant with high iron dosing (Cologne) 34% of all iron was bound in vivianite compared to 53% in the plant that relied mainly on enhanced biological phosphate removal (Leeuwarden).This equals 30% and 7% of all phosphate in Cologne and Leeuwarden respectively. Our short term (24 h) batch tests were similar to conditions that occur during anaerobic digestion. Indicating that vivianite is the dominating iron and phosphate phase in digested sludge where vivianite formation can proceed for 20 – 30 days. Furthermore, our measurements show that vivianite formation can start already under oxygen free conditions in the treatment line before the anaerobic digestion. To predict the role of vivianite in STPs the re-oxidation kinetics of vivianite in sludge need still to be investigated. Metagenomics show the presence of genera with species that are involved in iron oxidation and iron reduction. These analyses further indicate that such genera are more abundant in CPR sludge with high iron content compared to EBPR sludge sampled in the STP Leeuwarden with a lower iron content. We suggest that mechanisms of vivianite formation in plants with chemical phosphate removal using Fe(III) (Cologne) and in plants that make use of EBPR (Leeuwarden) are different. In the STP Cologne, ferric (phosphate) compounds are reduced by bacteria to release Fe(II) and phosphate. The released Fe(II) reacts with phosphate

to form vivianite. While in the STP Leeuwarden PAOs release phosphate under anaerobic conditions. Fe(III) present in the sludge is reduced by bacteria to Fe(II), this Fe(II) reacts with phosphate to form vivianite. Due to the lower solubility of vivianite, its preferential formation over struvite or other phosphate phases is proposed.

6.6 References

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Supplementary Information

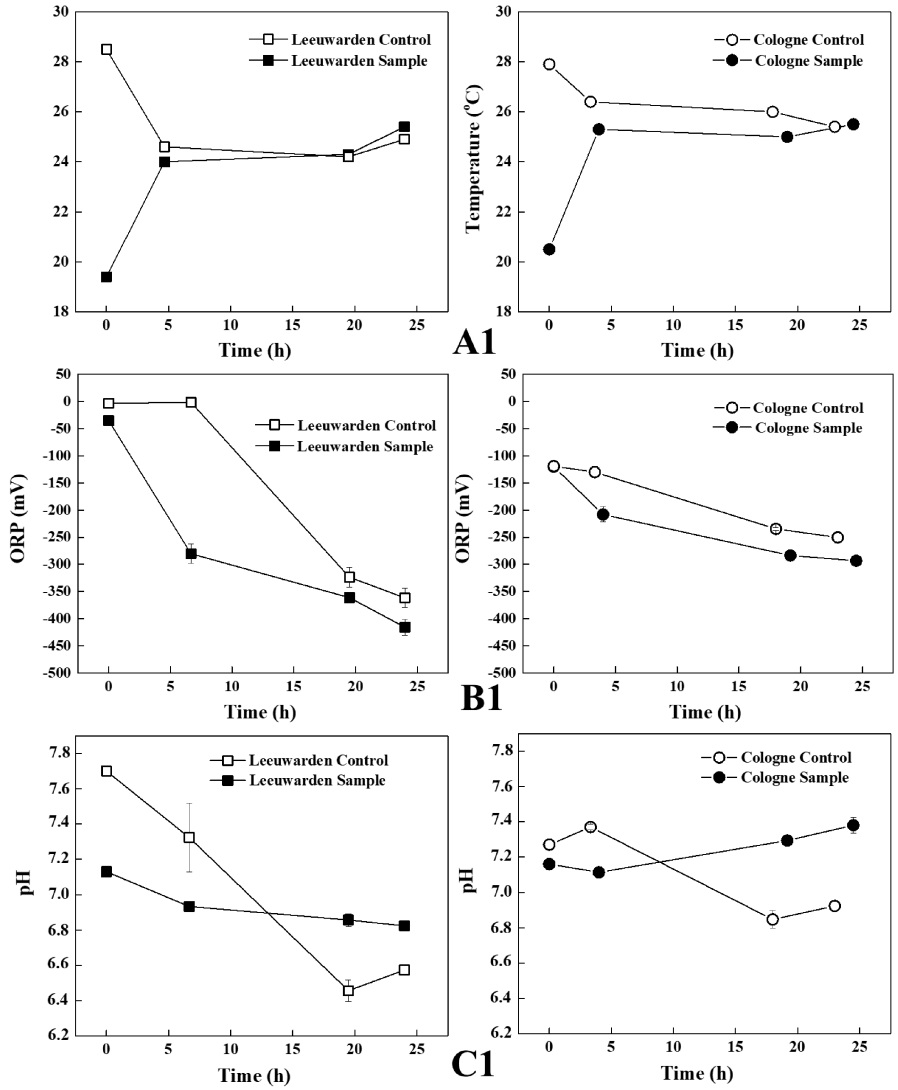


Figure S 6-1: Temperature (A), ORP (B) and pH (C) vs time in batch test experiments.

Table S 6-1: Elemental compositions of the activated sludges from Cologne and Leeuwarden determined by microwave assisted acid digestion using concentrated nitric acid.

Elemental composition in activated sludge from STP in Leeuwarden (g/kg TS)								
Items	Calcium	Iron	Magnesium	Aluminium	Potassium	Phosphorus	Sulphur	Silicon
Sample 1	25	11	7	<28	11	27	8	8
Sample 2	24	10	7	31	14	26	7	8
Sample 3	26	11	7	31	14	28	7	9
Average	25	11	7	31	13	27	7	8
Sdev	1.14	0.66	0.00	0.00	1.31	1.14	0.66	0.66
Elemental composition in activated sludge from STP in Cologne (g/kg TS)								
Items	Calcium	Iron	Magnesium	Aluminium	Potassium	Phosphorus	Sulphur	Silicon
Sample 1	51	90	5	6	9	40	11	8
Sample 2	50	86	5	5	9	39	11	8
Sample 3	51	88	5	6	8	39	11	8
Average	51	88	5	6	9	39	11	8
Sdev	0.86	1.86	0.00	0.43	0.43	0.74	0.00	0.00

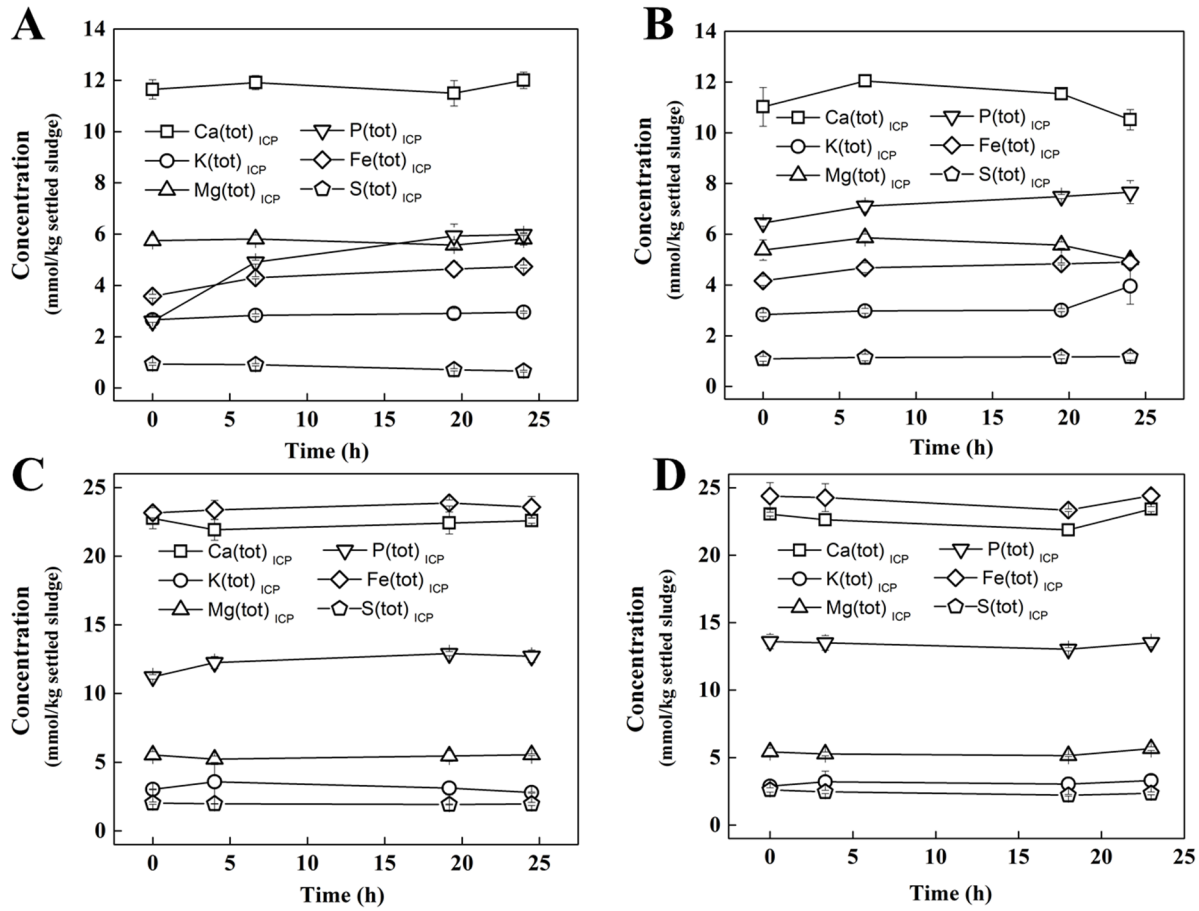


Figure S 6-2: Dissolved elemental concentrations determined by ICP in batch test systems. A: With activated sludge from STP Leeuwarden; B: With autoclaved activated sludge from STP Leeuwarden; C: With activated sludge from STP Cologne; D: With autoclaved activated sludge from STP Cologne.

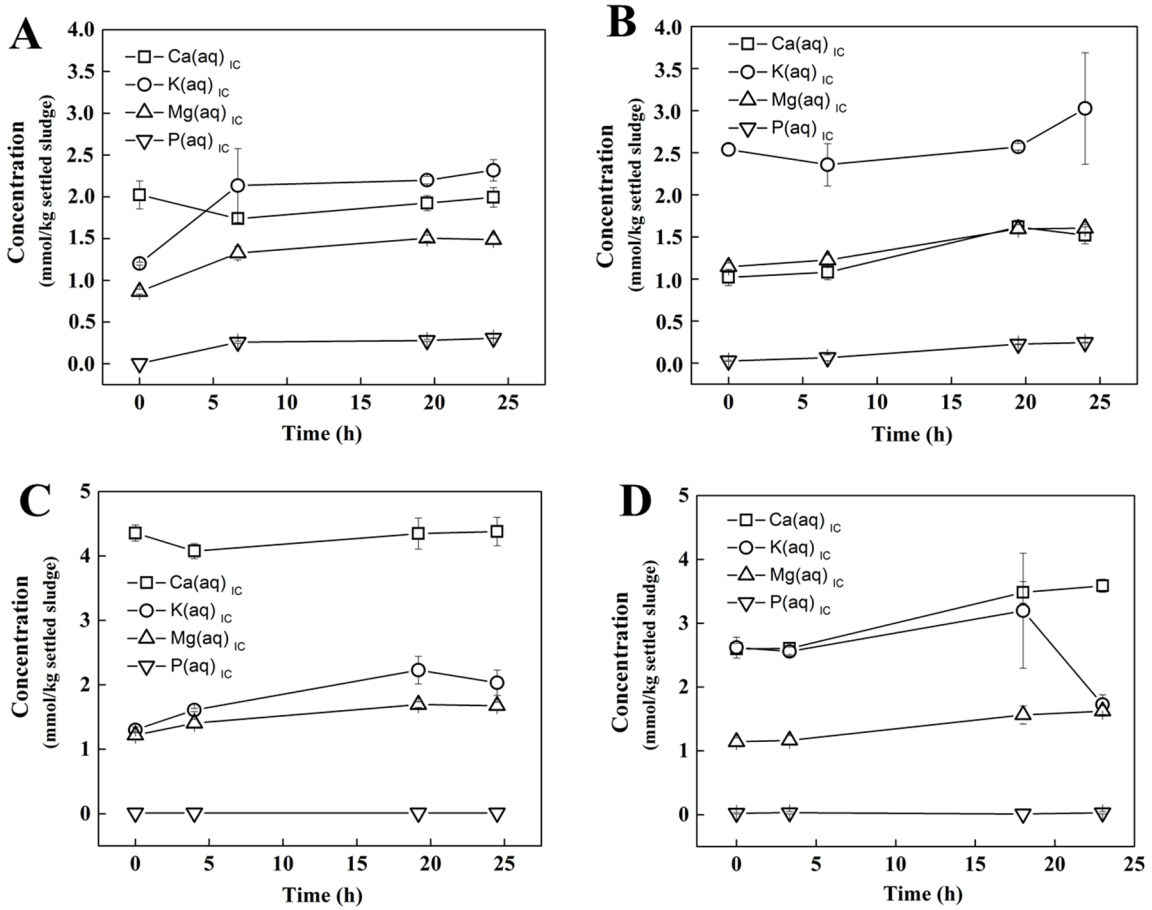


Figure S 6-3: Dissolved elemental concentrations determined by IC in batch test systems. A: With activated sludge from STP Leeuwarden; B: With autoclaved activated sludge from STP Leeuwarden; C: With activated sludge from STP Cologne; D: With autoclaved activated sludge from STP Cologne.

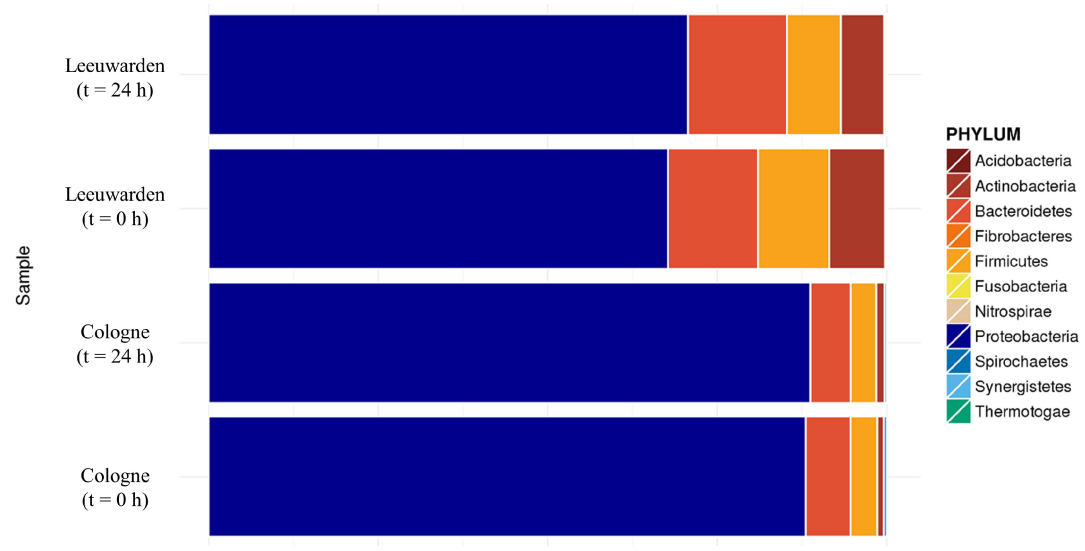


Figure S 6-4: Phylum wise OTU distribution in the samples (Top 11 OTUs contain 100% of total OTU reads).

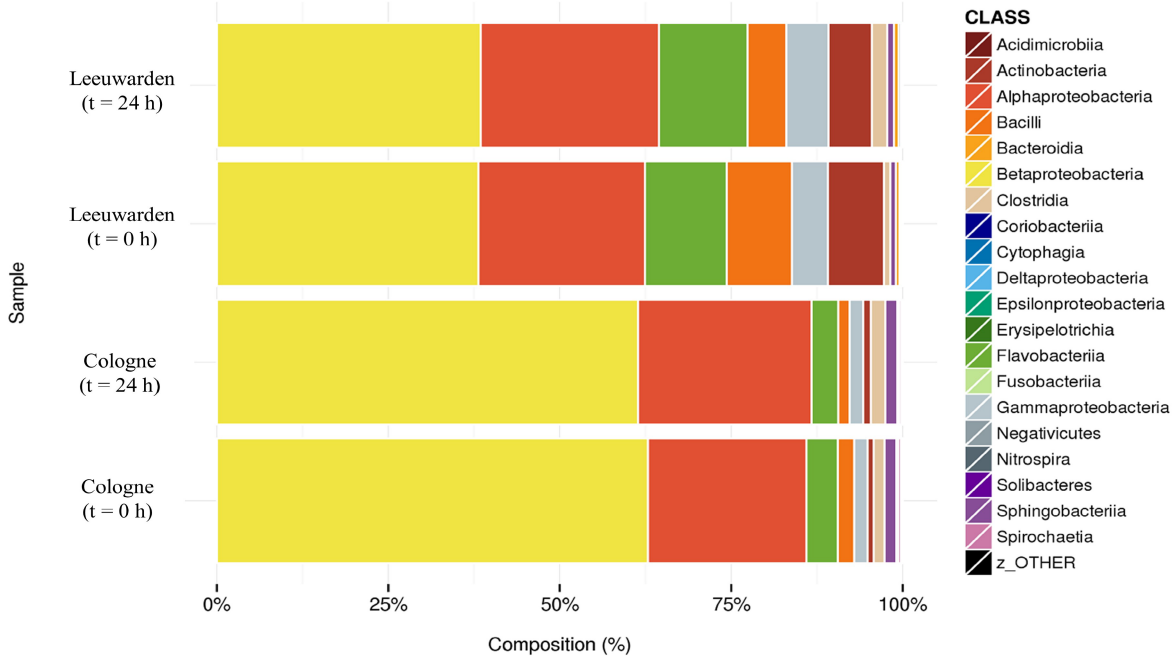


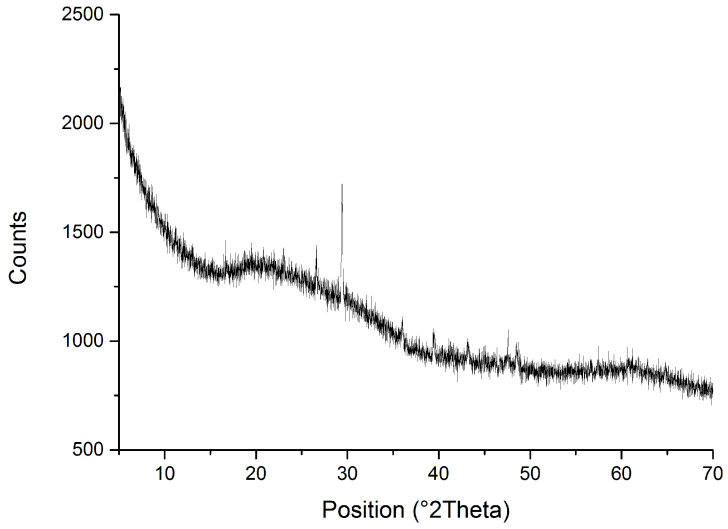
Figure S 6-5: Class wise OTU distribution in the samples (Top 20 OTUs contain 100% of total OTU reads).

Table S 6-2: Genus distribution table for the sludge samples.

GENUS	Cologne (t = 0 h)	Cologne (t = 24 h)	Leeuwarden (t = 0 h)	Leeuwarden (t = 24 h)
Novosphingobium	10.79	11.46	9.42	12.04
Rhodoferax	8.94	8.84	8.91	9.13
Flavobacterium	4.55	3.86	11.68	12.56
Variovorax	5.3	4.19	3.42	4.36
Dechloromonas	9.33	3.59	1.6	1.29
Aquabacterium	4.53	3.54	2.19	3.33
Curvibacter	3.27	3.05	3.12	3.62
Trichococcus	0.56	0.34	6.83	4.79
Acidovorax	3.28	3.34	2.76	2.59
Ferribacterium	2.8	1.63	2.78	2.02
Rubrivivax	3.44	4.51	0.57	0.68
Thauera	2.47	3.48	0.91	0.68
Leptothrix	3.16	3.09	0.56	0.66
Simplicispira	2.98	3.71	0.44	0.29
Aeromonas	1.38	1.3	1.23	3.05
Janibacter	0.24	0.23	3.08	2.59
Bradyrhizobium	1.08	1.22	1.94	1.44
Kinneretia	1.39	1.78	0.93	0.93
Sphingopyxis	0.88	0.9	1.16	2.01
Sulfuritalea	1.07	0.89	1.64	0.9

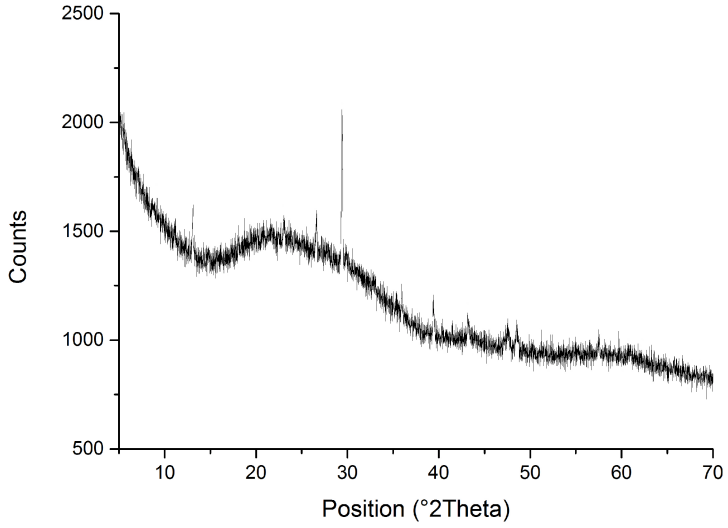
Table S 6-3: Characteristics of the dominant genera that were detected in the activated sewage sludge samples in the STPs Leeuwarden and Cologne. Data obtained from MiDAS (http://www.midasfieldguide.org/).

Canonical Name	**Phylum**	**Predominant in**	**Filamentous**	**PAO**	**Nitrite reduction**	**Fermentation**
Novosphingobium	Proteobacteria	Activated sludge	NEG		NEG	NEG
Rhodoferax	Proteobacteria	Activated sludge	NEG	NEG	POS	V
Flavobacterium	Bacteroidetes	Influent	V			V
Dechloromonas	Proteobacteria	Activated sludge	NEG	V	POS	NEG
Trichococcus	Firmicutes	Influent	V		NEG	POS
Acidovorax	Proteobacteria	Influent	NEG		POS	NEG
Ferribacterium	Proteobacteria	Activated sludge	NEG		NEG	NEG
Thauera	Proteobacteria	Influent	NEG	NEG	V	NEG
Leptothrix	Proteobacteria	Activated sludge	V			
Simplicispira	Proteobacteria	Influent	NEG			
Bradyrhizobium	Proteobacteria		NEG		POS	POS
Sphingopyxis	*Proteobacteria*	Activated sludge	NEG		NEG	NEG



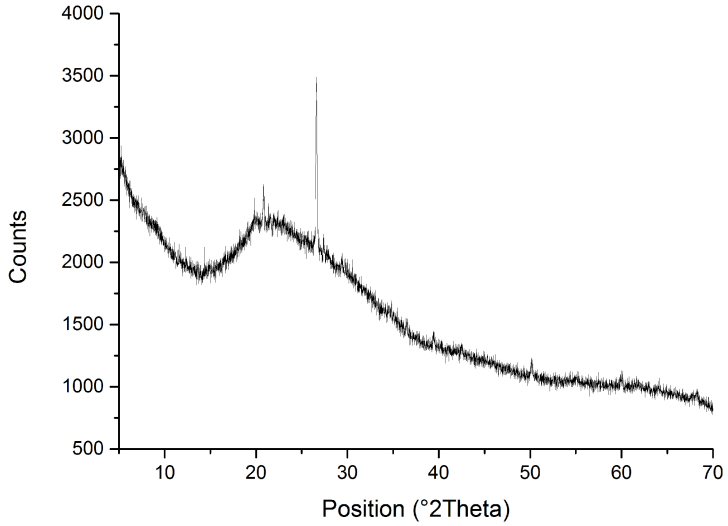
Pos. [°2Th.]	Matched by
23.057	Calcium carbonate
26.602	Quartz
29.397	Calcium carbonate
35.995	Calcium carbonate
39.373	Calcium carbonate
43.209	Calcium carbonate
47.575	Calcium carbonate
48.523	Calcium carbonate
50.136	Quartz
57.409	Calcium carbonate

Figure S 6-6: XRD diffractogram including peak list and peak assignment for Cologne at t=0.



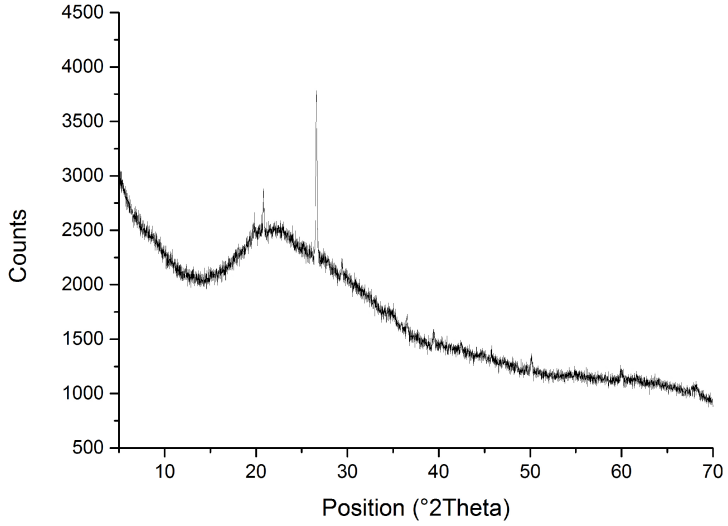
Pos. [°2Th.]	Matched by
11.119	Vivianite
13.096	Vivianite
20.824	Quartz
23.060	Calcium carbonate; Vivianite
26.624	Quartz; Vivianite
29.372	Calcium carbonate
33.041	Vivianite
35.965	Calcium carbonate; Vivianite
39.397	Calcium carbonate; Quartz
43.179	Calcium carbonate; Vivianite
47.553	Calcium carbonate; Vivianite
48.507	Calcium carbonate
57.501	Calcium carbonate; Vivianite
60.968	Calcium carbonate; Vivianite

Figure S 6-7: XRD diffractogram including peak list and peak assignment for Cologne after 24 h of incubation (t=24 h).



Pos. [°2Th.]	Matched by
19.848	not assigned
20.833	Quartz
26.617	Quartz
29.345	not assigned
36.519	Quartz
39.445	Quartz
42.436	Quartz
50.147	Quartz
60.006	Quartz
68.089	Quartz

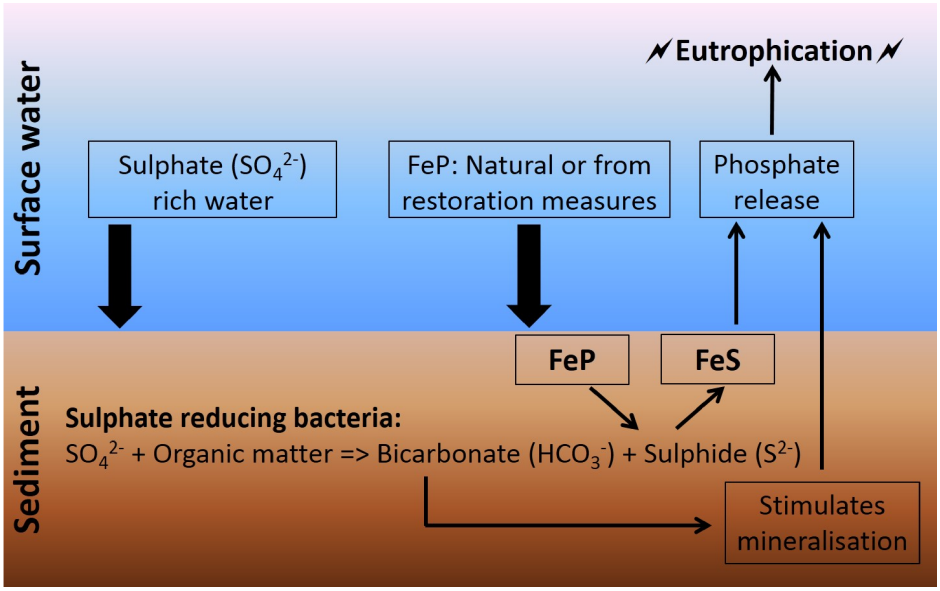
Figure S 6-8: XRD diffractogram including peak list and peak assignment for Leeuwarden at t=0.



Pos. [°2Th.]	Matched by
19.805	not assigned
20.821	Quartz
26.588	Quartz
29.394	not assigned
35.066	not assigned
36.531	Quartz
39.430	Quartz
42.494	Quartz
45.734	Quartz
50.190	Quartz
59.934	Quartz
68.242	Quartz

Figure S 6-9: XRD diffractogram including peak list and peak assignment for Leeuwarden after 24 h of incubation (t=24 h).

Chapter 7: Sulphide induced phosphate release from iron phosphate



7.1 Introduction

Achieving a circular economy requires a more sustainable use of phosphate and thus its recovery from secondary resources such as sewage sludge (Childers et al., 2011). In many industrial countries with high life stock density excess phosphate is already present in the 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. This means phosphate recovery from sewage sludge should yield a pure product that can be used for the production of phosphate fertilizer which can easily be exported to countries with phosphate deficient soils.

Iron salts are often used to eliminate phosphate from sewage (WEF, 2011). The iron bound phosphate ends up in the sewage sludge. Only if this sludge is anyway burnt in relative expensive mono-incinerators phosphate recovery can be efficient and economic. Phosphate recovery alone will not be enough to make these incinerators economic (Egle et al., 2014, 2015). The recovery of phosphate from digested sludge liquor in the form of struvite in sewage treatment plants that make use of biological phosphate removal has a low recovery efficiency, when expressed in percent of the incoming phosphate, and is only of interest if no iron or aluminium salts are used for phosphate removal (Cornel and Schaum, 2009; Korving et al., 2017). Economic phosphate recovery from iron phosphate rich sewage sludge without sludge incineration is still not economically feasible although iron based phosphate recovery routes would have benefits such as a high recovery efficiency (Korving et al., 2017) and iron has many properties that are beneficial for modern sewage treatment as it can be used as a coagulant, to prevent sulphide emissions and to efficiently remove phosphate (Wilfert et al., 2015a).

Sulphide and iron can react in various ways with each other. In the presence of ferric iron (Fe(III)), sulphide acts as a reducing agent that produces dissolved ferrous iron (Fe(II)) and elemental sulphur (Poulton et al., 2004). Together with ferrous iron, sulphide can form various iron sulphide 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 sulphide 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 sulphide ratio in the system (Peiffer et al., 2015) or the pH (Rickard, 2006).

It was shown that sulphide can effectively mobilize iron bound phosphate from sediment systems (Caraco et al., 1989; Roden and Edmonds, 1997; Smolders et al., 2006; Zantout et al., 2011). It has also been observed that iron reduction alone, be it chemically or biologically induced, can mobilize phosphate from iron phosphates (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). The re-precipitation of phosphate with iron is not possible when iron reacts with sulphide

to form FeS_x and consequently a more significant phosphate release can be expected (Hupfer and Lewandowski, 2008; Roden and Edmonds, 1997).

In the framework of sewage treatment, sulphide 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 sulphide production is probably limited by the supply of sulphate in the sludge. If substantial amounts of sulphide were formed during the anaerobic digestion, iron bound phosphate would dissolve and remain in solution as sulphide 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 sewage treatment plants requires that most phosphate remains in the sludge solids. High phosphate levels in the filtrate would prevent efficient phosphate removal. The limited amount of sulphide formed during digestion is explaining why iron addition can be used for efficient phosphate removal even in plants with anaerobic digesters (Thomas, 1965).

Sulphide is readily available and cheap since it is produced in installations for biogas cleaning and sulphur is a waste product of the oil industry (Graaff et al., 2012; STOWA, 2011). On the other hand, sulphide is very toxic to higher organisms.

Sulphide has been used in earlier studies for releasing phosphate to study the phosphate recovery from waste streams (Kato et al., 2006; Likosova et al., 2013; Suschka et al., 2001). Likosova et al., 2013 efficiently released phosphate from synthetic ferric phosphate and from sludge that originated from a drinking water treatment plant. They suggest that a low pH should be used for the sulphide 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) sulphate salt to eliminate phosphate from sewage and incubated the formed sludge containing ferric phosphate under oxygen free conditions. Subsequently, they observed microbial sulphide 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 sulphide induced phosphate release. They found out that sulphide can be used as a selective extractant to release iron bound phosphate, because phosphate was only released from sludge in case significant amounts of iron were present. These studies suggest that sulphide is indeed an interesting option to release phosphate from iron phosphate rich sewage sludge where most of the phosphate is bound to iron.

For a phosphate recovery process ideally digested sewage sludge (which is already concentrated in phosphate due to organic matter degradation) could be brought to a separate tank where phosphate is released. Then the sludge is dewatered to obtain a phosphate rich solution. The phosphate in this solution can be precipitated as struvite or calcium phosphate. Unfortunately, the phosphate release from digested sewage sludge using sulphide has not been studied yet.

Many different iron compounds exist and the phosphate can be bound in various ways to these iron phases (Wilfert et al., 2015a). It could be that the type of iron phosphate can also affect sulphide induced phosphate release, i.e. the total phosphate release or how much phosphate can

be released per mol sulphide. In sewage treatment plants ferrous and ferric iron phosphates can occur or a combination of both (Frossard et al., 1997; Thistleton et al., 2001; Wilfert et al., 2016; Wilfert et al., 2017a).

In a set of experiments the phosphate release from synthetic ferrous and ferric phosphate precipitates triggered by sulphide was studied to evaluate whether there is a difference between these compounds in phosphate release patterns/efficiency or not. Furthermore, it was tested if the reduction of ferric iron by sulphide could result in more efficient phosphate release compared to experiments where FeS_x are formed (higher phosphate release per mol sulphide added). Finally, sulphide was added to several digested sludge samples from full scale sewage treatment plants to have a comparison with the results obtained from the experiments with the synthetic precipitates.

7.2 Material and Methods

7.2.1 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 - 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 minutes, 3600 G) and the supernatant was filtered with nitrogen flushed syringes through nitrogen washed 0.45 µm filters. During the experiments a sulphide solution was dropwise added through a septum on top of the reactor with a syringe (or a pump in the slow addition experiments). The concentrations of the sulphide solutions varied from experiment to experiment (described in further detail below). All dissolved sulphide concentrations were determined using the methylene blue method after fixation of the samples in 0.5 M ZnAc. Dissolved inorganic phosphate was measured using the molybdenum blue method and ion chromatography. The elemental composition of the samples was determined using ICP-OES. 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.

7.2.2 Experiments with synthetic iron phosphates

7.2.2.1 Pulse addition

In one set of experiments, sulphide was continuously added dropwise to different iron phosphate precipitates until the desired Fe:S ratio of 1 was reached (Table 7-1 & Table 7-2) to determine the kinetics of phosphate release, the total phosphate release and to study the

efficiency of phosphate release, i.e. how many moles of phosphate can be released per mol of sulphide. The molar ratio of 1 was chosen as it was expected that amorphous FeS_x 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 7-1 & Figure S 7-1). Vivianite and ferric phosphates were chosen for the experiments as both play probably a significant role during sewage treatment (Wilfert et al., 2017a). One of the ferric phosphates was iron(III) phosphate dihydrate purchased from Sigma Aldrich, labelled as Sigma Fe(III)P in the following. The ferric and ferrous phosphate precipitates were prepared in nitrogen bubbled oxygen free Milli-Q water while 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 hour. For the ferric phosphate, potassium phosphate was precipitated using ferric chloride, this precipitate is referred to as Fe(III)P in the following. Vivianite was produced by precipitating phosphate with ferrous sulphate. For more details about the precipitates refer to Table 7-1. For all experiments a 0.8 M sulphide solution was prepared using Na_2S flocks and oxygen free Milli-Q water. The efficiency of phosphate release, i.e. how many moles of phosphate were released per mole of sulphide 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 sulphide to it. The input for Minteq was equal to the experimental conditions. 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 sulphides more crystalline than mackinawite (such as pyrite).

7.2.2.2 Slow addition

In this experiments it was tested if the reduction of ferric iron by sulphide 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. Precipitates were separated by centrifuging and discarding of the supernatant. Phosphorus and iron levels were measured in the solid and liquid phase. The obtained precipitates with a molar Fe:P ratio of 1.07 were dried at 30 °C. For these experiments the sulphide was added in two different ways to evaluate how different experimental conditions affect phosphate release from the precipitates. In experiment I, a 0.5 molar sulphide solution was added with a dosing rate of 0.03 mL/min to a suspension containing 1.6 mmol/L of the iron phosphate precipitates until a molar ratio S:Fe of 0.2 was reached. In experiment II, a 8 molar sulphide solution was added with a dosing rate of 1 mL/min to a suspension containing 30 mmol/L iron phosphate precipitates until a molar ratio S:Fe of 0.12 was reached.

7.2.3 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 that rely on chemical phosphate removal using ferrous (Nieuwveer) and ferric iron (Dokhaven). Sulphide 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 sulphide 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 supplementary information (Table S 7-4).

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

Equation 7.1:

$$Filterability = \frac{\Phi\,(\mu \,.\, c)}{CST}\left[\frac{g^2}{s^2 m^4}\right]$$

Φ = 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)

7.3 Results and Discussion

7.3.1 Synthetic FeP

7.3.1.1 Pulse addition

In a series of batch experiments, synthetic iron phosphates and sulphide were mixed to evaluate the total phosphate release and the kinetics of phosphate dissolution. The maximum phosphate release from the synthetic iron phosphate precipitates was reached within one hour (Figure 7-1, respective Fe:S ratios are listed in Table 7-1). From vivianite about 92% of the phosphate was released after the sulphide was added (Table 7-1). In this experiment enough sulphide was added to bind all iron (assuming the formation of 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 theoretically 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 76% (Table 7-1). However, during experiments with Fe(III)P the 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 was almost identical.

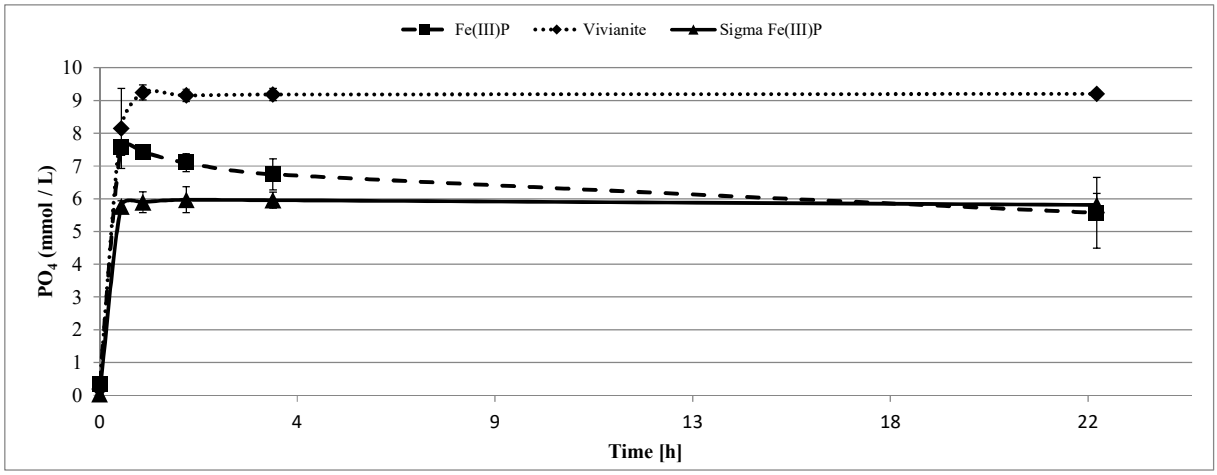


Figure 7-1: Patterns of phosphate release over time after adding sulphide to different iron phosphate phases. Sulphide in all experiments was added to a final Fe:S ratio of 1. The Fe:P ratios of the initial precipitates ranged between 1 (Sigma Fe(III)P), 1.53 (Vivianite) and 1.55 (Fe(III)P.

For the preparation of the vivianite and 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 ferric iron. The product of phosphate removal using Fe(II) was vivianite and for Fe(III) amorphous ferric phosphate. Probably, with the Fe(III) addition to the phosphate solution, iron oxides or hydroxides, that can bind the phosphate via adsorption, were formed (Smith et al., 2008). The sulphide induced phosphate release was higher for vivianite than for Fe(III)P despite an identical sulphide input. This is because sulphide reacts directly with vivianite to form FeS_x and releases phosphate (equation 7.3), thus there is no additional investment of sulphide required for reducing Fe(III) to Fe(II). At the same time Fe(II) (in vivianite) is more efficient in phosphate binding compared to many ferric iron oxides. In vivianite 1.5 mol of iron are required to bind 1 mol of phosphate. 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, 2010b; Luedecke et al., 1989; Schulz and Zabel, 2006). However, at low Fe:P ratios also iron phosphates with an initial Fe:P ratio close to one can form (see section 7.2.2). During aging and at higher iron dosing the molar Fe:P of the precipitates will probably increase. We did not determine the Fe:P ratio of the iron phosphate precipitates in this experiment.

For ferric phosphates the reaction with sulphide is more complicated. It is likely that sulphide first reduces Fe(III) to Fe(II), while sulphide is oxidized to elemental sulphur (equation 7.2, Poulton et al., 2004). Formation of elemental sulphur 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 sulphide to form FeS_x (equation 7.3). The formation of FeS_x prevents precipitation of Fe(II)P, as Fe(II) is no longer available for precipitating phosphate. Thus, to form out of one mol ferric iron 1 mole of FeS 1.5 mol sulphide would be required. Note that the sulphide input can be higher in case FeS_x with a different stoichiometry, such as pyrite, are formed. In experiments with ferric phosphate the sulphide dose (Fe(III):S = 1) is, according to

these assumptions, enough to release 66% of all phosphate from the iron. However, the net phosphate release through the addition of sulphide 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). Sulphide should theoretically react preferably 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 sulphide and iron oxides (Biber et al., 1994). For our experiments that would mean that sulphide can be used up without any release of phosphate to the solution.

Equation 7.2: $3Fe(III)P + 1.5\ S^{2-} <=> (Fe(II))_3(P)_2 + 1.5\ S^0 + PO_4$

Equation 7.3: $(Fe(II))_3(P)_2 + 3\ S^{2-} <=> 3\ FeS + 2\ PO_4$

Phosphate release from Fe(III)P was, at its maximum, higher as stoichiometry would suggest. About 0.80 instead of 0.66 mol P released per mol sulphide 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 (Figure 7-1). 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 0.45 µm filtration step at the end of the experiment as reported earlier (Likosova et al., 2013). High quantities of iron and sulphide were measured in solution in this experiment. Our measurements methods are not able to distinguish between iron and sulphide that is free and iron and sulphide that is bound in dissolved (complexed / colloidal) FeS_x. But it can be assumed that this black coloration was due to the presence of colloidal FeS_x because the molar Fe:S ratio in solution was approximately 1 (Table S 7-1). To calculate the efficiency of phosphate release in this experiment it was assumed that iron and sulphide occur in a molar ratio of 1 in solution. This means that all added sulphide was used up during this experiment and that no free (dissolved) sulphide was present. Only, in the experiment with vivianite significant amounts of sulphide remained in solution after 22 h (0.34 mmol S^{2-}/L; Table S 7-1). Dissolved and precipitated FeS_x can still react with Fe(III) as they can, according to thermodynamics, reduce ferric iron phases. To evaluate whether sulphide can be used as reducing agent to release phosphate more efficiently from ferric phosphate a slower dosing rate was tested in subsequent experiments.

Table 7-1: Characteristics of the iron phosphate precipitates and phosphate release during the sulphide addition experiments (Figure 7-1). Initial o-P indicates the phosphate levels at the start of the experiment before adding sulphide. 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	$Fe(III)PO_4^{2-}x2H_2O$ XRD: Amorphous n=3	10	10	0.04	1.00	1.00	60 (4.1)	0.60 (0.040)
Vivianite	o-P precipitated using $Fe(II)SO_4x7H_2O$ 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 $Fe(III)CL_3x6H_2O$ XRD: Amorphous n=3	10	15	0.34	1.55	1.00	75 (2.6)	0.80 (0.053)

7.3.1.2 Slow addition

During the first 1.5 hours of experiment I, no black colouration (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 / mol sulphide invested, 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 7.3). Thus, it can be assumed that chemical iron reduction by sulphide is responsible for initially observed phosphate release. After 1.5 h, coinciding with the colour change, the extraction efficiency decreased to about 0.7 mol phosphate / mol sulphide (between 2 - 24 h). Theoretically, 1 mol of sulphide 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 2, where a higher concentrated sulphide solution (8 mol /L) was added to 30 mmol//L iron phosphate, no colour change in the reactor was visible in the first hour. 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 sulphide 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 sulphur) was not observed.

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, the 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). Obviously, after some time sulphide was accumulating in the reactor and FeS_x was supersaturated which resulted in its precipitation.

7.3.2 Digested sewage sludge and incineration ash

7.3.2.1 Our observations

After sulphide addition to the incineration ash only about 1.5% (=0.42 mmol/L) of all phosphate was released after about 1 h of reaction time (Table 7-2). Subsequently, the phosphate in solution decreased continuously to levels below the initial ones at the start of the experiment (24 h, Table S 7-3). In a control experiment, without sulphide addition, phosphate levels also decreased slightly from 0.15 at the beginning of the experiment to 0.10 mmol/L after 24 hours (data not shown). Apparently the dissolved phosphate rebinds over time to other compounds in the ash. The phosphate phases in the sewage sludge ash are obviously relatively inert towards sulphide resulting in only little phosphate release. Accordingly, one would not expect a phosphate release from most of the minerals which were found in sewage sludge ash because these phosphate minerals do not contain iron (Adam et al., 2009). It is, however, possible that higher quantities of phosphate were initially released before the first sample was taken after one hour.

In the digested sludges an higher iron content resulted in a higher sulphide induced phosphate release (Table 7-2). 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. Sulphide was added in excess in Amersfoort (S:Fe =2) and in equimolar ratios in Leeuwarden (S:Fe =1). In the experiments with Leeuwarden sludge no residual sulphide was detected in contrast to the experiments with the Amersfoort sludge where about 5 mmol S^{2-}/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 sulphide was added in molar Fe:S ratio of 1. About 1.3 times more phosphate (29% of all phosphate) was released from another digested sludge sample from the same treatment plant at a higher molar S:Fe ratio of 1.5. Accordingly, in an earlier study 1.2 times more phosphate was released (26% of all phosphate) from Leeuwarden digested sludge compared to our experiment. Although the sludges had identical Fe:P molar ratio (0.55). In the earlier study sulphide was added until a molar S:Fe ratio of 1.5 was reached, in the current experiment sulphide was added to a molar Fe:S ratio of 1 (Wilfert et al., 2016). This again indicates that a higher sulphide input results in more phosphate release.

It was assumed that adding sulphide in a molar ratio of 1 is enough to release all phosphate from iron phosphate in the sludge because: 1. iron was present in its reduced form in the digested sludge (Wilfert et al., 2017a), 2. part of the iron was anyway present as iron sulphide (Wilfert et al., 2017a) and 3. that the freshly formed amorphous iron sulphide compounds have a molar Fe:S ratio equal or slightly above 1 (Rickard, 2006).

In earlier studies at pH=4 an increase in the sulphide 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). However, Kato et al., 2006 reported that phosphate release levelled already off at S:Fe ratios between 1-2 in surplus sewage sludge. It is possible that different FeS_x with different molar Fe:S ratios form and that thus varying sulphide input is required to release the phosphate.

From Dokhaven sludge about 30% of all phosphate could be 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. It was expected that most of the phosphate in this sludge is bound to iron. Earlier studies indicate that iron bound phosphate (as vivianite) accounts in Leeuwarden for around 20 – 30%, in Nieuwveer for around 40% and in Dokhaven for about 65% of all phosphate (Wilfert et al., 2016; Wilfert et al., 2017a). Only in Leeuwarden the sulphide induced phosphate release (18%) comes close to the one determined by Mössbauer spectroscopy and XRD. In the other sludges the phosphate release is only about the half of the expected release. Why is the phosphate release lower than expected? The earlier measurements showed some inconsistencies which are discussed in these studies (Wilfert et al., 2016; Wilfert et al., 2017a). So it could be that iron bound phosphate was overestimated. For this, and all other sludges, it is, however, also possible that part of the released phosphate precipitates with other substances that are in solution 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 sulphide 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 sulphide were still present at the end of the experiment (Table S 7-2 and Table S 7-3).

The efficiency of phosphate release was expressed as the sulphide 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 sulphide 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 sulphide concentrations is not free of doubts since free sulphide 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 release 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 sulphide that was removed from solution was actually not used up during the reaction with iron. This could happen when e.g. H_2S gasses out of solution or if sulphide precipitates in other forms, e.g. as polysulphides (Wan et al., 2014). Care was taken to fix sulphide with ZnAc and additionally outgassing of sulphide at circumneutral pH should not be very significant. However, it cannot be excluded that some of

the sulphide emitted as H_2S from solution. Polysulphides were not quantified during the experiments.

During the experiment with sludge a strong decrease in the viscosity was observed. To evaluate if sulphide could also influence the dewaterability of the sludge CST measurements were carried out. The filterability in digested sludge (0.13 ±0.015 $g^2(s^2\ m^4)^{-1}$) was clearly higher compared to the same sludge after sulphide addition (0.06 ±0.004 $g^2(s^2\ m^4)^{-1}$). This strongly suggests that sulphide 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 wastewater treatment plants (Mikkelsen, 2002). Similar to our findings, earlier research showed that the addition of sulphide 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).

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 should 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 sulphide it can modify these structures which would then result in the deterioration of the sludge dewaterability (Liu and Fang, 2003). The mechanism of the decrease in viscosity and filterability remains unclear.

Table 7-2: Experimental results of sulphide addition to various sewage sludges and sewage sludge ash.

	Iron content (mmol/kg sample)	Phosphorus content (mmol/kg sample)	Initial P Dissolved (mmol / kg sample)	Molar Fe:P	Molar Fe:S	P Release (% of total solid)	Mol P release vs Mol S^{2-} consumed
Digested sludge Amersfoort	18	39	3.4	0.49	0.5	14	0.12
Leeuwarden Control	34	67	4.8	0.55	-	-1	-
Leeuwarden #1	31	63	4.1	0.53	2.2	11	0.42
Leeuwarden #2	34	67	4.9	0.55	1.0	18	0.36
Digested sludge Nieuwveer	34	50	3.5	0.74	1.0	22	0.28
Digested sludge Nieuwveer	40	50	2.7	0.73	0.7	29	0.12
Digested sludge 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.

7.3.2.2 Comparison to other studies

It is possible to release significant amounts of phosphate from activated sludge and digested sewage sludge through the addition of sulphide. 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., 2017a). In digested sludge most iron is present as Fe(II) (Frossard et al., 1997; Wilfert et al., 2017a). From both, ferrous and ferric iron bound phosphate the phosphate can be released by adding sulphide. Our 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. The sulphide induced phosphate release is thus more efficient from Fe(II) in case FeS_x are formed because additional sulphide / electron investment for Fe(III) reduction is not necessary. In case sulphide 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 could result in a lower net phosphate release.

Table 7-3: Results of sulphide addition to synthetic iron phosphates and sludges.

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	Maija 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)	Maija Likosova et al. 2013
Sigma Fe(III)P	4	1	0.40	90 (±6)	Maija Likosova et al. 2013
Synthetic Fe(III)P	5.3-7.0	1	0.50	93	Kato et al. 2006

It seems concerns (Likosova et al., 2013) about the formation of colloidal FeS_x are no issue for the 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 sulphides were present in the supernatant (visible by a slightly black colour 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 sulphide overdose, were very similar despite differences in pH during the experiments (Table 7-3).

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 suggests that more phosphate could be released from iron using sulphide (Wilfert et al., 2017a). Also a much higher release of phosphate from drinking water sludge was measured by Likosova et al., 2013 (Table 7-3). 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 compounds in this 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 sulphide input

(relative to the iron in the sludge). Thus, it cannot be excluded that higher sulphide/iron dosing would indeed have resulted in higher phosphate mobilization from the sludges. In their activated sludge, probably more phosphate is bound in organic matter, compared to digested sludge, which is not solubilized by sulphide, which would thus negatively affect their release efficiency. The sulphide investment is also dependent on the presence of iron phases that are not iron phosphates such as ferric iron oxides. Probably, the sulphide 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 sulphide addition can be expected which would result in high costs for sludge disposal (Nielsen and Keiding, 1998).

Sulphide 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, sulphide 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 sulphide addition from 3.4 to 7.4 mmol/L. During struvite recovery only dissolved phosphate in the digested sludge can be recovered. Thus, sulphide could increase the recovery potential by a factor of two in this plant. However, the sludge we tested was sampled before thermal hydrolysis (resulting in an extra organic phosphate release) and a stripping process to enhance bio-P release were implemented in this plant. Still, we expect a significant phosphate release for the thermally hydrolyzed sludge after sulphide addition.

7.4 Conclusion

Overall, sulphide addition could be a useful tool for phosphate recovery, e.g. to increase phosphate release in plants where struvite recovery is limited by the phosphate that is bound to iron. Of course, it can also be used 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 sewage sludge are constraints. Understanding the mechanisms for both of these phenomena might help to use sulphide in a more effective way for recovering phosphate from iron phosphate containing sludge. 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 sulphide addition. Furthermore, for struvite precipitation magnesium has to be added to the sewage sludge which could counteract and perhaps even neutralize the deterring effect of sulphide on the filterability. The limitation in phosphate release in response of sulphide addition (be it sulphide acts 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.

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Supplementary Information

Table S 7-1: Results of the experiments with synthetic iron phosphate precipitates.

Sigma Fe(III)-P (n=3)	ID	time (h)	PO_4 (mmol/L)	StDev	S^{2-} (mmol/L)	StDev	Fe (mmol/L)	StDev
	T0	0	0.04	0.009	10.00	0	0.00	0.002
	T1	0.5	5.77	0.170	2.66	0.756	3.44	0.474
	T2	1	5.90	0.318	3.06	0.755	3.65	0.638
	T3	2	5.97	0.395	3.24	0.955	3.58	0.552
	T4	4	5.96	0.242	3.23	0.810	3.57	0.497
	T5	23	5.81	0.350	1.93	0.276	2.08	0.840

Vivianite (n=3)	ID	time (h)	PO_4 (mmol/L)	StDev	S^{2-} (mmol/L)	StDev	Fe (mmol/L)	StDev
	T0	0	0.20	0.052	15.00	0	0.40	0.398
	T1	0.5	8.15	1.222	2.94	0.911	0.01	0.007
	T2	1	9.25	0.230	1.78	0.076	0.02	0.019
	T3	2	9.16	0.189	1.43	0.120	0.01	0.010
	T4	4	9.19	0.189	0.85	0.100	0.02	0.016
	T5	23	9.21	0.109	0.34	0.318	0.00	0.002

Fe(III)-P (n=3)	ID	time (h)	PO_4 (mmol/L)	StDev	S^{2-} (mmol/L)	StDev	Fe (mmol/L)	StDev
	T0	0	0.34	0.005	15.00		0.00	-
	T1	0.5	7.57	0.239	5.43	0.603	2.92	-
	T2	1	7.43	0.206	0.69	0.237	4.97	-
	T3	2	7.10	0.271	0.28	0.092	3.22	-
	T4	4	6.75	0.473	0.17	0.075	2.57	-
	T5	23	5.57	1.077	0.05	0.022	1.38	-

Table S 7-2: Sulphide addition experiments using sludge from Leeuwarden.

Leeuwarden Fe:S=2.2	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)	Fe (mmol/L)
	T0	0	3.77	14.21	0.04
	T1	0.5	6.97	1.75	0.01
	T2	1	7.48	0.99	0.00
	T3	1.5	8.06	0.62	0.00
	T4	2	8.95	0.44	0.01
	T5	3	9.52	0.61	0.01
	T6	6	9.44	0.12	0.02
	T7	23	9.76	0.00	0.01

Leeuwarden Fe:S=1	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)	Fe (mmol/L)
	T0	0	4.87	32.36	0.03
	T1	0.7	7.90	4.97	0.00
	T2	1.3	10.42	4.26	0.00
	T3	1.6	11.81	2.51	0.00
	T4	2	11.77	3.71	0.00
	T5	2.5	12.87	2.63	0.00
	T6	3	12.35	2.36	0.00
	T7	3.5	12.77	3.02	0.00
	T8	23	16.06	1.17	0.00

Leeuwarden Control (no S^{2-})	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)	Fe (mmol/L)
	T0	0	4.66	0.00	0.02
	T1	0.5	4.28	0.00	0.02
	T2	1	4.16	0.00	0.05
	T3	1.5	4.19	0.00	0.03
	T4	2.5	4.53	0.00	0.03
	T5	3.5	4.53	0.00	0.02
	T6	21	3.81	0.00	0.01

Table S 7-3: Sulphide addition experiments using sludge and ash.

Amersfoort sludge (n=1)	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)
	T0	0:00:00	3.42	36.43
	T1	0:35:00	4.29	6.15
	T2	1:05:00	4.58	8.65
	T3	1:38:00	4.71	7.29
	T4	21:05:00	7.29	5.46
	T5	24:35:00	7.39	4.34
	T6	42:15:00	7.32	5.14

Nieuwveer (n=1)	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)
	T0	0	3.52	34.00
	T1	24	9.74	14.00
	T2	36	10.60	11.69
	T3	48	11.37	6.03
	T4	72	11.26	6.77

Dokhaven (n=1)	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)
	T0	0	1.65	42.00
	T1	0.5	n.d.	31.90
	T2	0.75	1.66	30.55
	T3	2	5.52	21.06
	T4	7	6.97	21.13
	T5	23.5	8.94	11.21
	T6	46.5	9.39	15.10

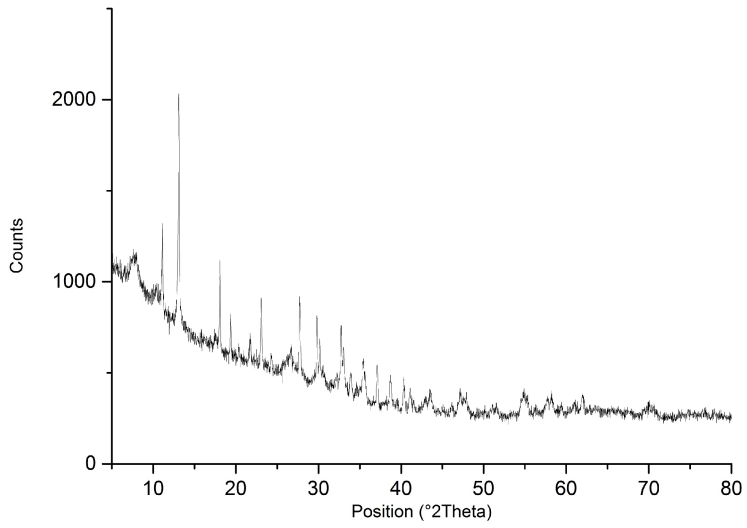
Dokhaven (n=1)	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)
	T0	0	2.83	58.50
	T1	24	10.74	27.13
	T2	48	14.26	13.98
	T3	72	12.45	15.53
	T4	144	12.00	10.29
	T5	168	11.84	n.d.

Ash	ID	time (h)	PO_4 (mmol/L)	S^{2-} (mmol/L)
	T0	0	0.09	n.d.
	T1	1	0.42	n.d.
	T2	2	0.04	n.d.
	T3	3	0.04	n.d.
	T4	4	0.04	n.d.
	T5	5	0.06	n.d.

Table S 7-4: Characteristics of the digested sewage sludge and the sewage sludge ash that was used in the sulphide addition experiments.

	pH	TS (g/kg)	Total Dissolved Fe (mg/L)	Total Fe (g/kg)	Total Dissolved P (mg/L)	Total P (g/kg)	Total Dissolved S (mg/L)	Total S (g/kg)
Leeuwarden	7.4	39	3.0	1.87	128	2.02	9.0	0.49
Amersfoort	7.1	28	3.2	1.00	118.0	1.21	11.0	0.32
Nieuwveer	7.7	42.5	1.1	1.91	109.0	1.54	6.6	0.49
Dokhaven	7.1	28.3	1.0	2.20	87.9	1.26	7.4	0.55
Ash	-	-	-	76.54	-	83.20	-	21.27

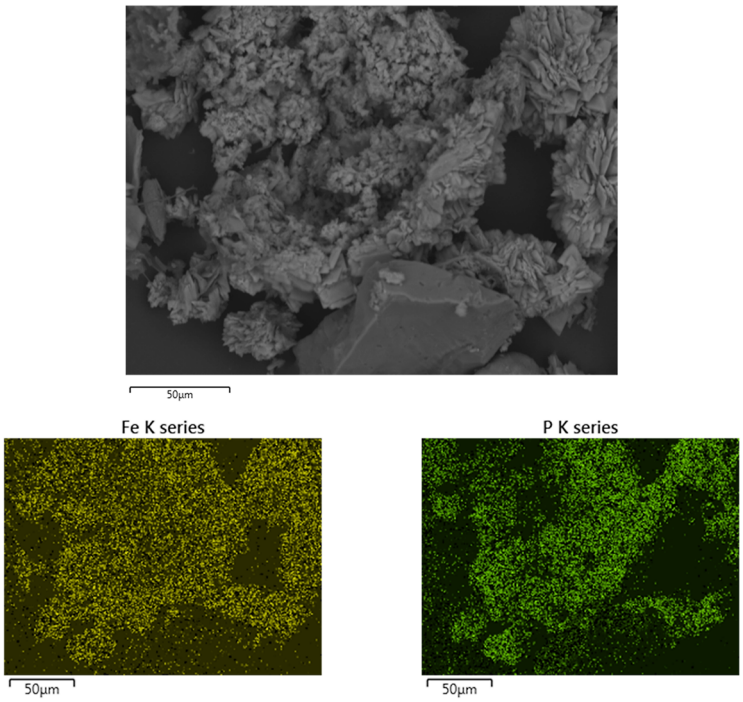
	Total Dissolved Al (mg/L)	Total Al (g/kg)	Total Dissolved Mg (mg/L)	Total Mg (g/kg)	Total Dissolved Ca (mg/L)	Total Ca (g/kg)	Total Dissolved K (mg/L)	Total K (g/kg)
Leeuwarden	3	0.15	14.0	0.35	60.0	2.01	429	0.54
Amersfoort	0.3	0.54	16.0	0.16	51.0	0.76	359	0.20
Nieuwveer	<0.5	0.52	5.1	0.19	45.6	1.24	212	0.30
Dokhaven	<0.5	0.21	20.1	0.14	58.1	1.05	140	0.27
Ash	-	48.11	-	16.70	-	140.16	-	n.d.



Pos. [°2Th.]	Matched by
7.758	not assigned
11.133	Vivianite
13.108	Vivianite
18.074	Vivianite
19.377	Vivianite
20.360	Vivianite
21.726	Vivianite
23.073	Vivianite
24.314	Vivianite
26.660	Vivianite
27.735	Vivianite
29.829	Vivianite
30.139	Vivianite
32.266	Vivianite
32.751	Vivianite
33.050	Vivianite
33.880	Vivianite
35.411	Vivianite
37.095	Vivianite
38.693	Vivianite
40.305	Vivianite
41.085	Vivianite
43.556	Vivianite
46.156	Vivianite
47.182	Vivianite
47.869	Vivianite
51.305	Vivianite
54.717	Vivianite
58.191	Vivianite
62.000	Vivianite

Figure S 7-1: XRD spectra and peak list of vivianite that was formed when phosphate was precipitated with Fe(II) during experiments with synthetic iron phosphates.

Chapter 8: Phosphate recovery via magnetic separation of vivianite from digested sewage sludge



This chapter was patented as:
Wilfert, P., Korving, L., Rem, P., Witkamp, G.J., van Loosdrecht, M.C.M., Dugulan, I., Goubitz, K., 2017. Method and system for phosphate recovery from a stream.

8.1 Introduction

Phosphate has to be removed from sewage to prevent eutrophication of effluent receiving surface waters. For this reason, iron salts (e.g. iron chloride or iron sulphate) are often dosed in sewage treatments plants to form iron phosphate precipitates (WEF, 2011). These precipitates end up in the sewage sludge which is usually brought to an anaerobic digester for biogas production. Several studies prove that the iron phosphate mineral vivianite, ($Fe(II)_3[PO_4]_2x8H_2O$) forms during the anaerobic digestion process and during anaerobic storage of wastewater (Azam and Finneran, 2014; Cheng et al., 2015; Frossard et al., 1997; Marx et al., 2001; Seitz et al., 1973; Singer, 1972; Wilfert et al., 2016). Thermodynamic data accordingly suggests that, in the presence of iron, vivianite preferably forms over most other inorganic phosphate phases (Nriagu and Dell, 1974). And indeed our research showed that vivianite will be the dominant inorganic phosphate phase in digested sludge provided enough iron (molar ratio Fe:P >1.5) is present (Wilfert et al., 2017a). We hypothesized that the amount of phosphate that is bound in vivianite is limited only by the organic phosphate fraction if enough iron is present. Organic phosphate makes up between 10-15% of all phosphate in digested sewage sludge where iron / aluminium were dosed for chemical phosphate removal (Carliell-Marquet et al., 2009; Frossard et al., 1994). Accordingly, our measurements showed for the first time that 80-90% of the total phosphate in sewage sludge could be bound in vivianite (Wilfert et al., 2017a). Thus, a recovery route via vivianite has the potential to yield much higher phosphate recovery efficiencies compared to traditional struvite technologies. In struvite only 10–50 % of the total phosphate from the influent can be recovered also because other, more insoluble inorganic phosphate compounds are present (Cornel and Schaum, 2009). This is illustrated by the fact that iron dosing can be applied to prevent struvite scaling in pipe lines after anaerobic digestion of sewage sludge (Mamais et al., 1994).

The vivianite is present as small particles in the sludge (crystals and/or aggregates, size 10-150 µm, Frossard et al., 1997; Wilfert et al., 2017a). These particles consist mainly of iron and phosphate but also of impurities like magnesium or calcium. Due to the impurities it would be more appropriate to refer to vivianite like structures. It is well known that natural vivianite contains impurities (Rothe et al., 2016; Taylor et al., 2008) and thus we refer simply to vivianite in the following. These impurities make the quantification of vivianite difficult. Additionally, they will also change the properties of the vivianite such as the magnetic susceptibility or other physical parameter such as the density or the colour. Vivianite is paramagnetic and simple magnetic systems have been used to concentrate vivianite in sewage sludge to be able to identify it more easily using XRD (Seitz et al., 1973). With this knowledge we evaluated whether magnetic separation of vivianite using Jones separators from sewage sludge is feasible or not. In the following we will discuss the results of these experiments and suggest, based on these results, how a phosphate recovery route via vivianite could look like.

8.2 Material and Methods

The vivianite occurs in the wet sewage sludge as free particles (Wilfert et al., 2017a). Drying could lead to vivianite particles that are covered in an organic matrix (Frossard et al., 1997;

Wilfert et al., 2017a). Accordingly, magnetic separation of vivianite from dried sewage sludge using a Frantz separator was not possible in our trial runs. Although, Seitz et al., 1973 were able to concentrate vivianite magnetically in dried, digested sewage sludge.

Subsequently, we developed a wet magnetic separation set-up tailor made for vivianite based on a magnetic Jones separator (Wills and Finch, 2015). The technical drawings of the set-up and of the Jones plates made are shown in Figure 8-1 and Figure 8-2. Digested sludge from Dokhaven and Espoo (Wilfert et al., 2017a) was used for the experiments. The molar iron to phosphate ratios in the sludges were 1.1 and 2.36 and the volatile solids made up 58.9 and 58.7% of all solid material in Dokhaven and Espoo sludges respectively.

The Jones separator was submerged in a tank filled with water. The water surface was just below the openings of the Jones plates. Then sludge was dropwise added via a pipe between the Jones plates with flow rates between 4 – 20 mL/min for 30 seconds. Afterwards MilliQ was pumped with the same hydrodynamic regime through the plates for 1 min to remove non-magnetic material that got stuck between the magnets. Afterwards, a strong flow of MilliQ was used to wash the vivianite of the plates into an aluminium drawer. The material was dried in a vacuum oven at 30 °C. The dried solids were analysed using XRD, SEM-EDX and the elemental compositions was determined using concentrated nitric acid and a microwave assisted acid digestion (20 min at 200 °C) followed by ICP-OES.

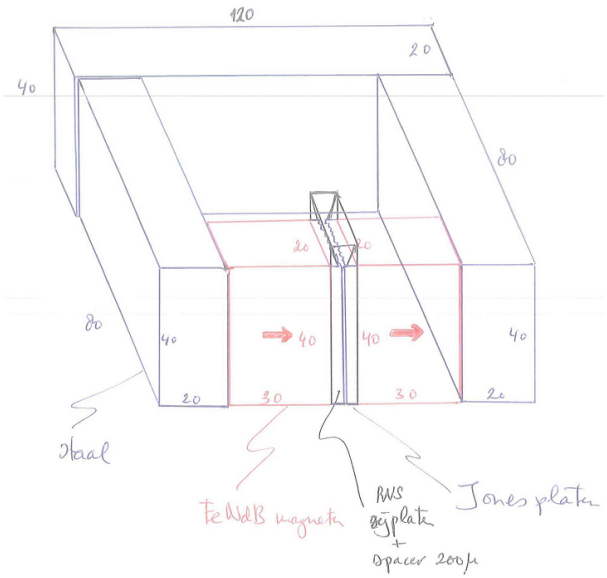


Figure 8-1: Set-up for magnetic separation of vivianite from sewage sludge using Jones plates (all linear dimensions in mm). Drawings by Prof. Dr. Peter Rem and Peter Berkhout.

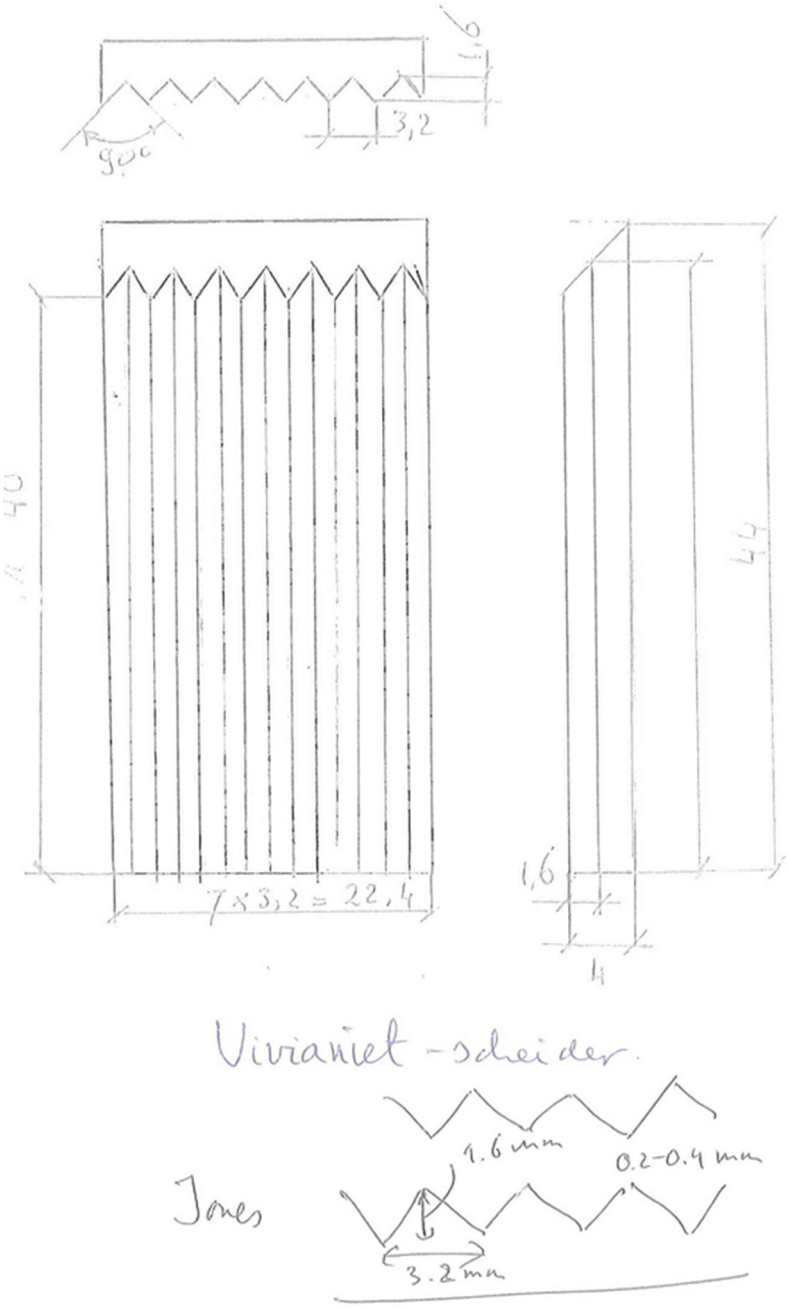


Figure 8-2: Dimensions of the Jones plates used for the magnetic separation of vivianite from sewage sludge (all linear dimensions in mm). Drawings by Prof. Dr. Peter Rem and Peter Berkhout.

8.3 Results

8.3.1 Elemental composition of separated material

The material that was separated by using the magnetic separator was analysed and compared with the initial sludge composition. All results from flowrates which caused a reduction of the volatile solids in the separated material by less than 10% were not included in Table 8-1. We considered such separations as not efficient enough. As expected, low feeding rates produced a

low purity material with volatile solid contents similar to the ones of the initial sludge. For low feeding rates the corresponding efficiencies of phosphate recovery were high, sometimes 100% but the material that we separated resembled the initial sludge solids. Hence, these results were not considered as a successful separation.

Table 8-1 shows that up to 60% of all phosphate could be separated from sludge sampled in Espoo using higher flowrates with a simultaneous decrease in the volatile solid content of the separated material (between 80-90% of all phosphate is bound in vivianite according to earlier measurements Wilfert et al., 2017a). In Dokhaven, where earlier measurements showed that about 65% of all phosphate is bound in vivianite (Wilfert et al., 2017a), up to 40% of all phosphate could be recovered. In our trials the phosphate content in the separated material could easily be doubled compared to the initial sludge solids. In material separated from Dokhaven sludge and for the lower flowrates even a 3 times higher phosphate content in the separated material was observed.

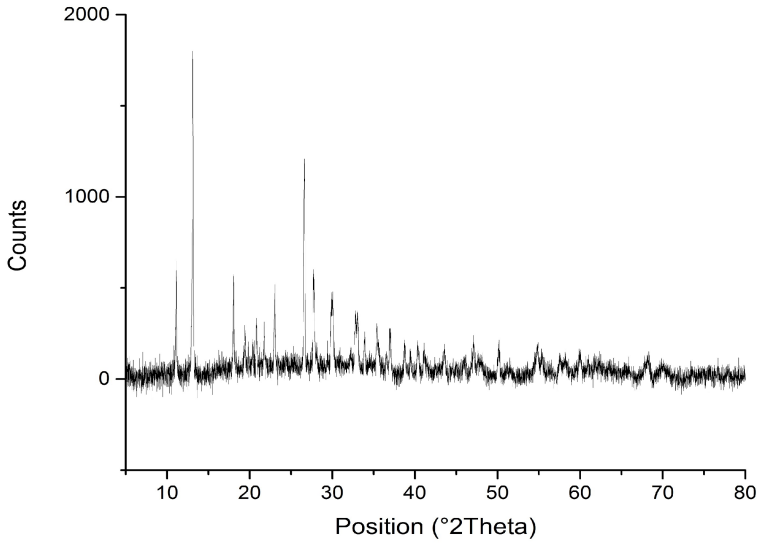
These results show that magnetic separation of vivianite from sewage sludge using conventional mining equipment is feasible. Yet, the efficiency of separation is smaller than earlier quantifications of vivianite in these sludge would suggest (Wilfert et al., 2017a). Additionally, the volatile solid fractions in the separated material are still relatively high. Both sludge solids had initially a volatile solid content of about 59%, which was reduced to values between 31 and 41% in Dokhaven and values between 42 and 45% in Espoo in the separated material. This relatively high volatile solid content could be explained by the presence of organic compounds or other compounds that lose weight during the heating (such as carbonates or minerals that lose crystal water at temperature below 550 °C, Weliky et al., 1983). Note, that vivianite itself loses about 25% of its weight around 100 °C due to the loss of crystal water (Čermáková et al., 2015).

Table 8-1: Results of magnetic separation at different flow rates using sludges from Espoo and Dokhaven respectively. The efficiency column indicates how much (%) of all the phosphorus / iron that was fed into the separator could be retrieved in the magnetic separation step. The enrichment column indicates how much (more) iron / phosphorus were present in the solid fraction of the magnetically separated material compared to the initial sludge solids, i.e. a value of 2 indicates that the magnetic separated solids contained x2 more phosphorus per mass solid material compared to the solids in the sludge that was fed into the separator.

		Efficiency (% of total)		**Enrichment**		
Origin	**Flowrate (mL/min)**	**Fe**	**P**	**Fe**	**P**	**VS (%)**
Dokhaven	8	49	40	3.4	2.8	31.1
Dokhaven	16	34	28	3.3	2.7	36.0
Dokhaven	20	17	13	2.5	2.0	42.3
Espoo	16	54	62	1.9	2.1	44.3
Espoo	20	48	52	1.6	1.7	45.3

8.3.2 XRD analysis of separated material from Dokhaven

XRD showed that quartz and vivianite were in the magnetically separated material from Dokhaven (Figure 8-3). Semi quantitative results from the XRD software PANalytical HighScore showed that the crystalline material consisted mainly of vivianite (68%). Surprisingly the residual fraction was non-magnetic quartz (32%). The XRD spectra shows that the amorphous fraction in the separated material was relatively low compared to earlier XRD analyses on digested sewage sludges (Figure 8-3 & Figure S 8-1).



Pos. [°2Th.]	Matched by
11.145	Vivianite
13.116	Vivianite
18.069	Vivianite
19.446	Vivianite
20.827	Quartz
21.752	Vivianite
23.047	Vivianite
26.604	Quartz
27.718	Vivianite
29.896	Vivianite
30.087	Vivianite
32.806	Vivianite
33.097	Vivianite
33.911	Vivianite
35.395	Vivianite
36.982	Vivianite
38.746	Vivianite
39.480	Quartz
40.304	Quartz
41.123	Vivianite
43.575	Vivianite
46.010	Vivianite
47.125	Vivianite
47.918	Vivianite
50.206	Quartz
54.872	Quartz
55.381	Quartz
57.553	Vivianite
59.959	Quartz
68.302	Quartz

Figure 8-3: Results of XRD analyses obtained from material that was magnetically separated from digested sewage sludge sampled in Dokhaven.

8.3.3 SEM-EDX analyses of separated material

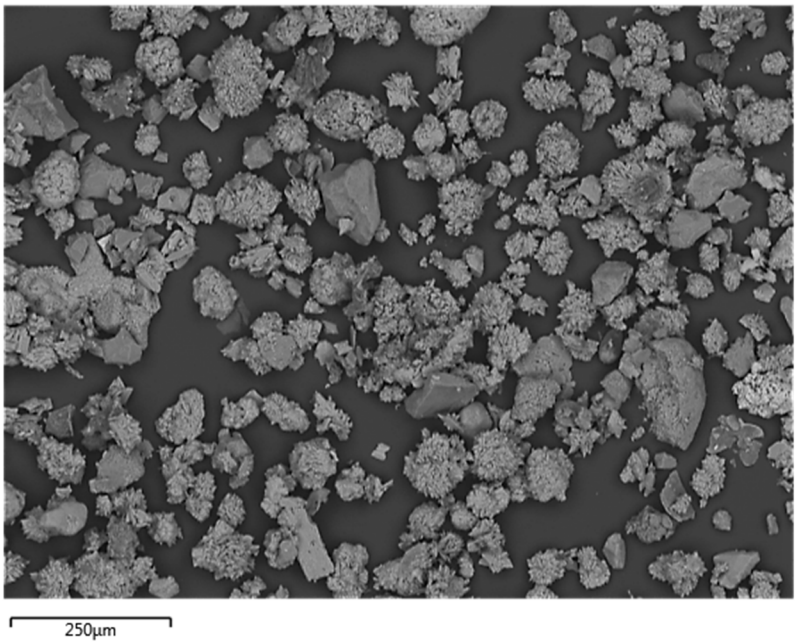


Figure 8-4: The SEM image shows material that was separated using the magnetic separator. 10 mL digested sludge from Dokhaven was pumped within one minute through the magnets. Particles with a cauliflower appearance were crystalline particles with a high iron and phosphate content.

SEM analyses showed that the separated particles had size ranges between 20-100 µm (Figure 8-4). The molar Fe:P ratio of the section in Figure 8-4 was 1.8. Significant amounts of silicon and calcium were present (Table 8-2, Figure S 8-2). No apparent overlap of iron and silicon was visible that would explain the presence of silicon in the magnetically separated fraction (Figure S 8-2). Images, similar to the one in Figure 8-4 with comparable elemental compositions were obtained from both sludge samples using flow rates above ≥ 8 mL/min.

Table 8-2: Elemental composition of the section shown in Figure 8-4.

Element	Wt %	Wt% Sigma	Atomic %
Mg	0.32	0.02	0.19
Al	0.32	0.02	0.17
Si	1.02	0.03	0.53
P	1.85	0.05	0.87
S	0.28	0.03	0.13
K	0.08	0.02	0.03
Ca	0.80	0.03	0.29
Mn	0.14	0.03	0.04
Fe	6.06	0.11	1.58
Cu	0.38	0.06	0.09
Zn	0.39	0.06	0.09

8.4 Discussion

The set-up we designed using magnetic Jones plates is able to separate vivianite from digested sewage sludge with efficiencies between 40 – 60%. The iron and phosphate content in the separated material can easily be doubled or even be tripled by means of the magnets compared to the initial sludge solids. Most likely higher separation efficiency can be achieved. The separation process could be further optimized to achieve higher separation efficiencies by e.g. more homogeneous feeding or an improved rinsing procedure or by obtaining more detailed information related to the magnetic susceptibility of the vivianite particles in the sludge. Further characterisation of the separated material is thus necessary. Separating and analysing the vivianite structures in the sludge is also required to be able to evaluate for which applications they could be used. If indeed organic matter is part of the separated material an additional step could be introduced to liberate vivianite particles from the organic matter (e.g. by using a hydrocyclone). Another option would be to increase the size of the vivianite particles which would then allow a more efficient separation.

The separated vivianite may find use as such in certain industries. Vivianite has been used as a colour pigment (Čermáková et al., 2015), it plays a role during production of lithium ion batteries (Recham et al., 2009) and it has been applied as fertilizer occasionally (Roldan et al., 2002). After optimization of the magnetic separation, larger quantities of vivianite should be separated and analysed for the elemental composition including trace elements such as arsenic or cadmium. Then it can be evaluated whether the impurities hinder this direct application or could even proliferate it.

For a later recovery process in sewage treatment plant we envisage a process (Figure 8-6) where iron is overdosed. This would result not only in low effluent phosphate concentrations but, additionally, vivianite formation is not limited by iron during the anaerobic digestion and this would probably result in the transformation of all available phosphate to vivianite. Then the vivianite can be separated using a magnetic separator (as it is applied in the mining industry, Žežulka et al., 2004; Figure 8-5). This separation could be combined with a liberation or pre-separation step by using e.g. a hydrocyclone.



Figure 8-5: SLon® vertically pulsating high-gradient magnetic separator from Outotec.

The vivianite could directly be used (see examples above). It could also be used as seeding material, similar to what has been done for calcium phosphate (Kempter et al., 2014), for growing larger particles that are easier to separate from the sludge. If a direct application of vivianite is not possible it could also be further processed by means of an alkaline treatment using potassium hydroxide to produce a concentrated potassium phosphate solution and an iron oxide precipitate. Potassium phosphate solutions can be directly used for fertilizer production. The iron oxide precipitate could be transformed into iron chloride using hydrochloric acid. It can then be reused for sewage treatment.

For operators of wastewater treatment plants, the recovery of vivianite also presents an opportunity to reduce their sludge volume. The vivianite content in sewage sludge can be up to 20% of the dry matter (dm). Recovery of the vivianite from this stream will therefore significantly reduce the amount of sewage sludge that needs to be disposed. The removal of the vivianite will also increase the heating value of (dried) sewage sludge and in this way make the sludge more useful as an energy source. Furthermore, the remaining sludge is more valuable for agricultural use in regions with a phosphate surplus as it contains valuable organic matter but is depleted in phosphate.

Current disposal costs for sewage sludge in The Netherlands and in Germany are roughly 200-300 €/ton dm (personal communication L. Korving; Wiechmann et al., 2013). Recovery of vivianite would present a resource value of circa 40 €/ton dm, assuming prices for iron ore (75 €/ton, worldbank.org, 2017) and phosphate rock (100 €/ton, indexmundi.com, 2017). The comparison of our recovery product with phosphate rock and iron ore can give a rough estimate only because the products that are produced during vivianite recovery are of equal quality as iron ore / phosphate rock. The real market value of the retrieved vivianite has to be established first to make more precise calculations. A 20% volume reduction suggests a benefit of 40-60 €/ton dm. The total benefit of vivianite recovery could therefore be ca. 80-100 €/ton solids

assuming a recovery efficiency of 80%. Initial estimates show that the retrieval costs may vary between 15-20 €/ton solids (Table S 8-1), which is several factors lower than the sum of the product value and sludge disposal savings, however pilot projects need to show that a net benefit is also obtained when considering all costs during on-site large-scale implementation.

In theory, this process could be used for similar waste streams where ferrous iron and phosphate are present and thus where the formation of vivianite can take place. Such conditions could for instance be met in case biogas production from manure would take place in the presence of sufficient quantities of iron. We could not, however, find any reports on the occurrence of vivianite in manure. It could be that its formation is limited by the supply of iron in this matrix.

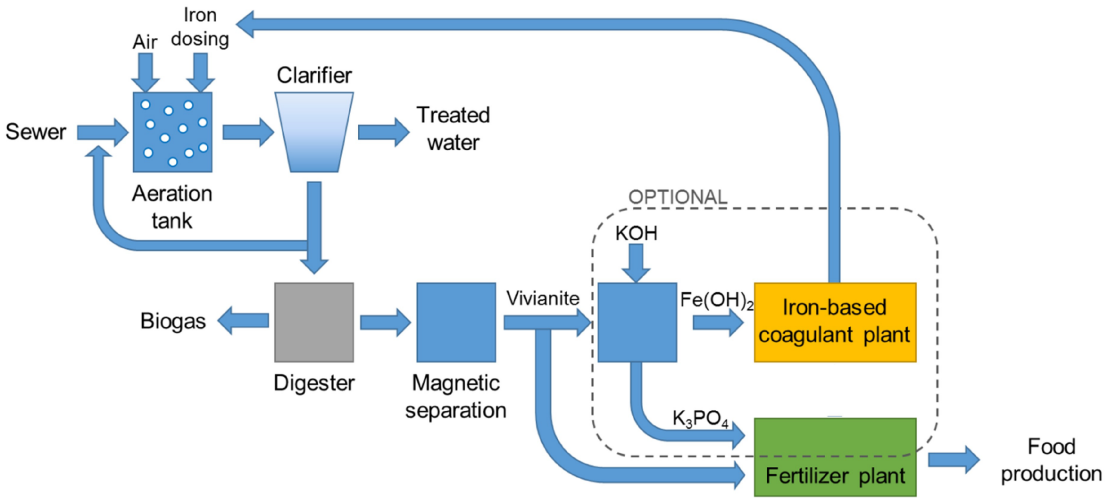


Figure 8-6: A vision of a phosphate recovery process in sewage treatment plants based on magnetic separation of vivianite from digested sewage sludge (Wilfert et al., 2017b).

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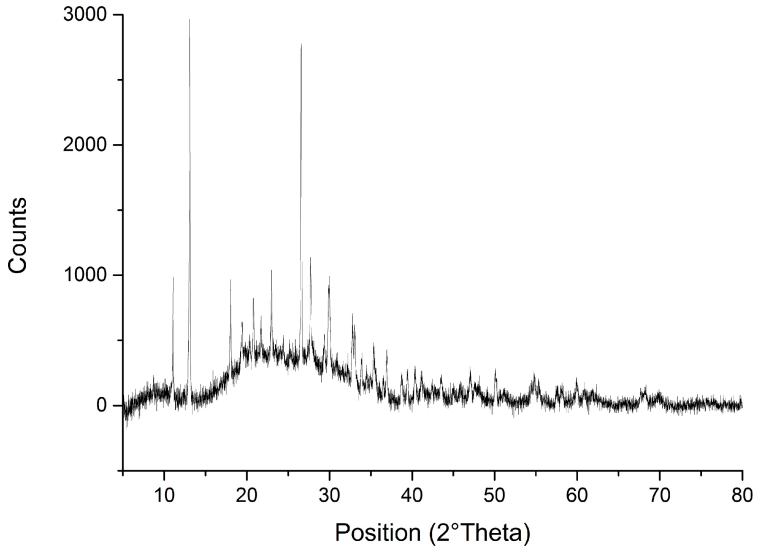
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Supplementary Information



Pos. [°2Th.]	Matched by
11.118	Vivianite
13.309	Vivianite
18.052	Vivianite
19.380	Vivianite
20.351	Vivianite
20.809	Quartz
21.723	Vivianite
23.005	Vivianite
26.587	Quartz; Vivianite
27.691	Vivianite
29.393	not assigned
29.838	Vivianite
30.087	Vivianite
30.897	Vivianite
32.691	Vivianite
33.018	Vivianite
33.876	Vivianite
35.350	Vivianite
36.529	Quartz; Vivianite
37.015	Vivianite
38.730	Vivianite
39.411	Quartz; Vivianite
40.272	Quartz; Vivianite
41.094	Vivianite
42.392	Quartz
43.554	Vivianite
45.771	Quartz; Vivianite
47.081	Vivianite
50.085	Quartz; Vivianite
54.822	Quartz; Vivianite
57.499	Vivianite
59.953	Quartz; Vivianite
60.866	Vivianite
68.187	Quartz; Vivianite

Figure S 8-1: Results of XRD analyses obtained from digested sewage sludge solids sampled in Dokhaven.

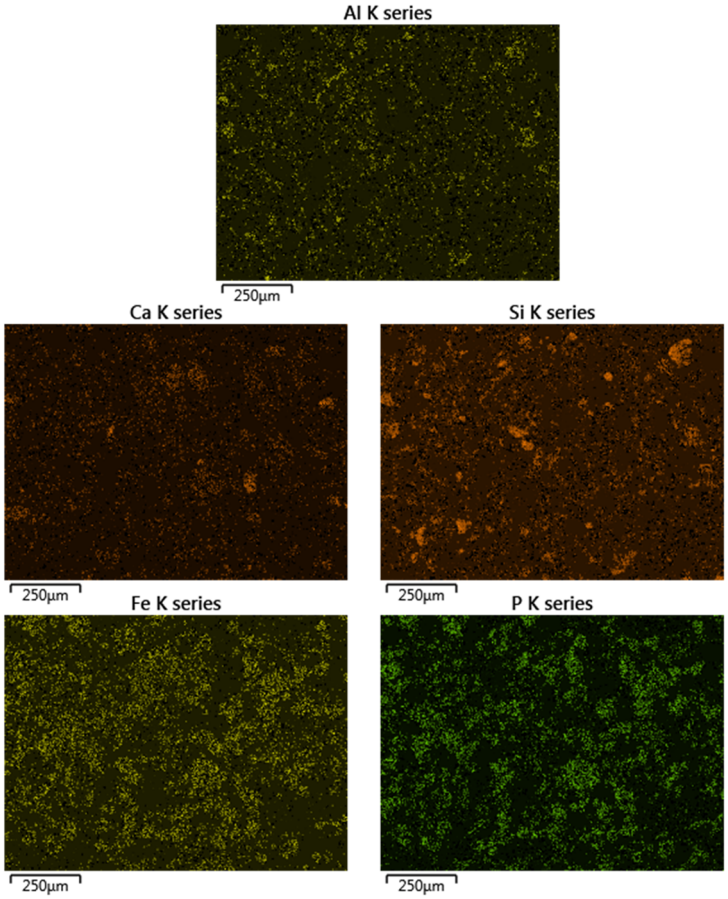


Figure S 8-2: Elemental imaging using EDX on the SEM section that is visualized in Figure 8-4.

Table S 8-1: Economics of high-intensity magnetic separation by means of a Jones separator.

Basic numbers for a Jones separator (Wills and Barley, 1986)

Nominal capacity for minerals: 30 tons of solids/h

Investment: € 173,000

Power consumption: 90 kW

Yearly cost of maintenance: € 8,000/y

It is assumed that these units require no operator, but this may be different for non-traditional applications. Assuming 0.2 additional operator * 5 shifts = € 45,000/y

Sludge application

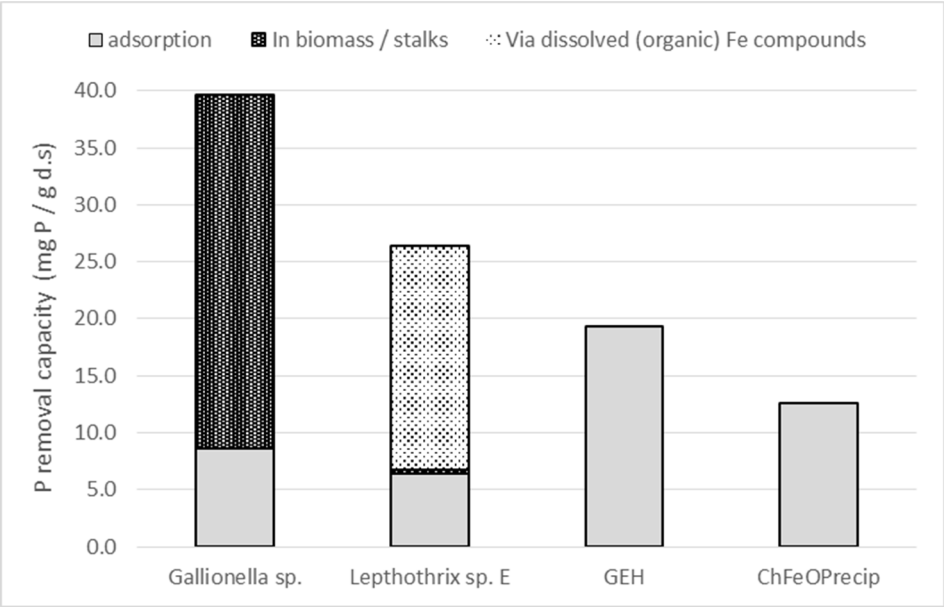
Minerals application assumes minerals of 5000 kg/m^3 in density. The average density of solids in sewer sludge is approx. 4 times lighter due to the high organics content. Since the capacity of the Jones is related to the volume of solids, this would imply a reduction of the capacity to 7.5 tons of solids/h. Since part of the solids in sludge is fibrous, a less efficient particle shape, a further reduction of capacity by a factor of 2 is expected resulting in a capacity of 3.75 tons of solids/h.

Estimation of cost per ton of dry solids for sludge:

Yearly capacity: 24 h/day X 300 d/year X 3.75 tons/h	27,000 tons/y
Investment costs (five years, interest rate 3%):	€ 37,000/year
Electricity costs (€0.1/kWh):	€ 66,000/year
Maintenance costs:	€ 8,000/year
Operator:	€ 45,000/year
Total:	€ 156,000/year
	€ 6/ton dry solids

It is quite common that a circuit of 3 Jones separators is used to get an optimal grade and recovery of the magnetic product. So total costs are expected to be approx. Euro 18/ton of dry solids.

Chapter 9: Biogenic iron oxides for phosphate removal



This chapter was submitted to Environmental Technology as:
Buliauskaitė, R., Wilfert, P., Kumar, P.S., De Vet, W.W.J.M., Witkamp, G.J., Korving, L., van Loosdrecht, M.C.M., 2018. Biogenic Iron Oxides for Phosphate Removal.

9.1 Introduction

Adsorption has the potential to reduce phosphate levels in wastewaters to as low as 20 µg P/L, (Zelmanov and Semiat, 2011) which could help to prevent eutrophication, and even to substitute iron salts dosing for phosphate removal during sewage treatment (Wilfert et al., 2015). Achieving very low phosphate concentrations (0.3 µg P/L) may restrict biofouling in drinking water production and distribution systems (Vrouwenvelder et al., 2010). An ideal adsorbent has good adsorption capacity, high affinity and selectivity towards phosphate and can be produced at relatively low cost. Adsorption is also a reversible process which allows for the adsorbent reuse via regeneration and thereby allowing phosphate recovery (Loganathan et al., 2014).

Biogenic iron oxides (BioFeO) are complex aggregates of organic material, bacterial cells and iron (oxyhydr)oxides, which contain impurities, such as sorbed or structural phosphate, silicon, SO_4, manganese, aluminium, etc. Extracellular BioFeO can be formed by iron oxidizing bacteria (FeOB) such as *Gallionella* sp. or *Leptothrix* sp. (Fortin and Langley, 2005). BioFeO are widespread in the environment, have large surface areas and reactive surface properties, which would have a positive effect on phosphate adsorption (Fortin and Langley, 2005; Suzuki et al., 2012). Accordingly, *Leptothrix* sp. deposits showed relatively high adsorption capacities between 10.8 to 39.9 mg P/g d.s., dried solids (Rentz et al., 2009) comparing to the values of ChFeO (Wilfert et al., 2015). The adsorption capacities of *Leptothrix* sp. deposits were high when expressed in terms of iron, with adsorption capacities between 46.9 to 165.0 mg P/g iron (Rentz et al., 2009) which corresponds with a molar phosphate/iron ratio of up to 0.3. This implies that the iron in the BioFeO is efficiently used to bind phosphate. Additionally, De Vet et al., 2012 showed that in the presence of *Gallionella* sp., phosphate levels were reduced to such an extent that growth of autotrophic bacteria was minimized. In contrast, in the presence of ChFeO these bacteria could grow. This observation indicates that BioFeO can be applied to reduce dissolved phosphate to levels where even biofouling is diminished (De Vet et al., 2012; Emerson and De Vet, 2015). BioFeO have also been used for arsenic remediation (Ahoranta et al., 2016; Bai et al., 2016; Katsoyiannis and Zouboulis, 2006; Pokhrel and Viraraghavan, 2009). The aim of this study was to investigate if and why BioFeO have superior phosphate adsorption characteristics compared to ChFeO. We studied the differences in phosphate binding capacity, the morphology and chemical composition between BioFeO and ChFeO, which included a commercial iron based adsorbent (GEH®) with large surface area and high phosphate adsorption capacity (Genz et al., 2004) and chemical precipitates from groundwater.

9.2 Material and Methods

9.2.1 Biogenic iron oxides of *Leptothrix* sp. and *Gallionella* sp.

Leptothrix sp. deposits were collected between December 2015 and February 2016 from ditches with groundwater seeps in Earnewâld (53.145270, 5.954955), Beetsterzwaag (53.053125, 6.118824) and Lettelbert (53.192624, 6.425097). The water overlaying the deposits had a neutral pH, temperatures between 4-8 °C and dissolved oxygen concentrations between 4-6 mg/L. The loosely accumulated deposits were collected using sterile 100 ml plastic syringes and stored at 4 °C (Earnewâld's sample was kept for 27 days and *Leptothrix* sp. from

Beetsterzwaag and *Lettelbert* were kept for 3 days*)* until the experiments started. *Gallionella* sp. stalks originated from a set-up designed for biological iron oxidation (De Vet et al., 2011).

Light microscopy and scanning electron microscopy (SEM) were used to identify *Leptothrix* sp. and *Gallionella* sp. and to check if the characteristic shape of the BioFeO was intact (Figure S 9-1). Samples for SEM analyses were rinsed with PBS before dehydration in an ethanol series (Heim et al., 2015). Samples for XRD analyses were air-dried.

Total solids (d.s.) and volatile solids (VS) were determined according to the standard methods (Clesceri et al., 1999). The elemental composition of the samples was determined using ICP-OES after a microwave assisted acid digestion (15 minutes at 180°C) using concentrated HNO_3.

9.2.2 Chemically formed iron oxides

Granulated ferric hydroxide (GEH®) is a commercially available adsorbent, which consists of akaganeite (Genz et al., 2004). For experiments, grinded GEH® was used (≤ 100 µm) to allow a fair comparison with the BioFeO which were in powdered form. Additionally, chemical iron oxide precipitates (ChFeOPrecip) were used, which were formed by bubbling oxygen trough raw groundwater.

9.2.3 Phosphate adsorption experiments

Leptothrix sp. and *Gallionella* sp. deposits were washed with MilliQ (MQ) until total iron in the supernatant (0.45 µm polycarbonate filtered) was <0.2 mg Fe/L (Hach Lange disc kit and ICP-OES).

Preliminary experiments showed no significant difference between dry and wet samples. For all experiments MQ washed and vacuum dried (25 °C) precipitates of *Gallionella* sp. were used. To prevent structural changes in iron oxides, the drying temperature was kept below 40 °C (Schwertmann and Cornell, 2000). However, for the experiments with *Leptothrix* sp. wet samples were used to allow a better comparison with Rentz et al., 2009.

The adsorption experiments were carried out in batch mode (initial conditions: 5-6 mg P/L, pH 6.5 ± 0.2, 25 °C, stirred manually once per day) in duplicates. For determining phosphate adsorption kinetics, an adsorbent concentration of 0.5 g/L was used and the solutions were sampled after 1, 2, 3, 4 and 7 (or 8) days. The data was fitted with the non-linear form of a pseudo-second order kinetic model. This model is based on the assumption of chemisorption (Ho and McKay, 1999) as is the case with phosphate adsorption onto iron oxides (Cornell and Schwertmann, 2003). For isotherm experiments, the adsorbent concentrations used were 2, 1, 0.5, 0.25, 0.125, 0.062 or 0.031 g/L. Phosphate adsorption studies with ChFeO showed that the time taken to reach adsorption equilibrium can vary between 1 to 28 days (Borggaard et al., 2005; Chitrakar et al., 2006; Genz et al., 2004; Yoon et al., 2014). From an application point of view, it is not practical to run adsorption on a very long time scale and hence it was decided that 4 days were enough to perform all isotherm experiments (Table S 9-3). Samples were filtered (0.45 µm polycarbonate membrane filter), phosphate concentrations were determined by IC and total phosphorus using ICP-OES (Table S 9-2).

9.3 Results and Discussion

9.3.1 Washing of BioFeO and ChFeO prior to phosphate adsorption experiments

During experiments with non-washed deposits of *Leptothrix* sp. dissolved iron was detected, therefore, it was decided to wash the deposits. Also Rentz et al., 2009 washed *Leptothrix* sp. deposits once with a saline solution (100 mM NaCl) prior to adsorption experiments to remove background phosphate. We have not performed experiments with deposits of *Leptothrix* sp., which have been washed just once, because significant amounts of soluble iron was still in the supernatant after a single washing step. This indicates that the sample preparation in this previous study was not optimal. Iron release for *Leptothrix* sp. deposits washed with saline solution was greater compared to MQ washed samples. Perhaps due to a higher solubility of Na-organic linkages, which can cause an increase in organically complexed metals in solution (Nelson and Oades, 1998). Thus, it was decided to wash BioFeO and ChFeO with MQ before the adsorption experiments.

Our study showed that *Leptothrix* sp. required more intensive washing to remove soluble iron then *Gallionella* sp. deposits, ChFeOPrecip and GEH®. *Leptothrix* sp. normally occurs in waters rich in organic matter (Harder, 1919). It is well known that dissolved organics have the ability to retain iron (as ferrous and ferric iron) in solution/suspension (Lobartini et al., 1998). Thus, organically complexed iron could be the reason for the high concentration of iron in solution (up to 19.4 mg Fe/L when deposits were washed with saline solution) measured during washing of *Leptothrix* sp. and explains why intensive washing was necessary.

9.3.2 Phosphate adsorption kinetics of BioFeO and ChFeO

Adsorption capacities of MQ washed *Leptothrix* sp. from Beetsterzwaag and Lettelbert were similar to adsorption capacity of MQ washed *Leptothrix* sp. from Earnewâld, therefore, only kinetics with non-washed vs MQ washed for *Leptothrix* sp. from Earnewâld were performed. Figure 9-1 shows the adsorption kinetics for phosphate on ChFeO and *Leptothrix* sp E. According to the pseudo-second order kinetic model, more than 95% of the adsorption equilibrium was reached within 4 days for the non-washed BioFeO of *Leptothrix* sp. E and grinded GEH® (Table S 9-3). For ChFeOPrecip and *MQ* washed BioFeO of *Leptothrix* sp. E 90% and 76% of the adsorption equilibrium was reached respectively. In the adsorption experiments by Rentz et al., 2009 the equilibrium was reached within 1 day using deposits of *Leptothrix* sp. This might be due to the less intense washing and the use of saline solution for washing which causes more intensive iron release which precipitates with the phosphate thereby accelerating the phosphate removal. The slow kinetics in experiments with washed BioFeO of *Leptothrix* sp. E could be related to the complex nature of BioFeO (Fortin and Langley, 2005). The organics in the BioFeO structure could slow down the phosphate diffusion and adsorption to the adsorption sites.

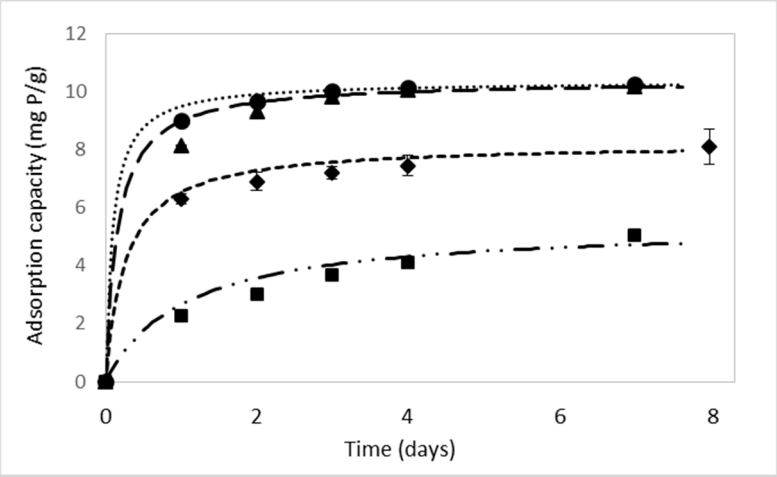


Figure 9-1: Phosphate adsorption kinetics for different adsorbents. Markers represent the actual adsorption capacities (n = 2) and dashed lines represent the corresponding fitting using the pseudo-second order kinetic model

• Leptothrix sp E: non-washed; ▲ GEH; ♦ ChFeOPrecip; ■ Leptothrix sp E: MQ washed.

9.3.3 Phosphate adsorption isotherms of BioFeO and ChFeO

Figure 9-2 shows the adsorption isotherms of BioFeO and ChFeO. The Langmuir adsorption model was only fitted for GEH® and non-washed BioFeO of *Leptothrix* sp. E since adsorption to these two samples reached most close to equilibrium (Table S 9-3). Maximum phosphate adsorption of non-washed *Leptothrix* sp. E obtained with Langmuir model was 24.7 ± 0.2 mg P/g d.s. and it is in the 10.8-39.9 mg P/g d.s. range reported by Rentz et al., 2009 (q_e is in the range of 12-19 mg P/L, Table S 9-4). The maximum experimentally observed adsorption capacities for all the adsorbents are listed in Table S 9-5 in mg P/g d.s. and mg P/g Fe.

Adsorption capacity of MQ washed *Leptothrix* sp. E was 6.4 mg P/g d.s., which is about 4 times lower compared to non-washed *Leptothrix* sp. E. Isotherms of MQ washed BioFeO of *Leptothrix* sp. from all three origins showed the same pattern with adsorption capacities between 6.4-8.4 mg P/g d.s. Also, dissolved iron (up to 2.2 mg Fe/L) was measured for the MQ washed *Leptothrix* sp. samples in the supernatant of the adsorption experiments. This indicates continuous release of dissolved iron from *Leptothrix* sp. deposits, which implies that even in washed samples, the phosphate removal could be a combination of adsorption and precipitation. Dissolved iron concentrations in the supernatant correlated well (R^2=0.95-0.99) with DOC (Figure S 9-2). Organic matter is a potent complexing agent for iron (Lobartini et al., 1998). Rentz et al., 2009 showed that *Leptothrix* sp. deposits have very high phosphate adsorption capacity. However, the results they report are most likely a combination of adsorption and precipitation of phosphate by organic-iron complexes (Gerke, 2010a; Weir and Soper, 1963). It is important to distinguish between these two mechanisms. Adsorption enables phosphate release and recovery as well as reusability of the adsorbent. When the phosphate precipitates, it can only be partly released and recovered. Furthermore, precipitation is not as selective as adsorption (Li and Stanforth, 2000b; Loganathan et al., 2014). Therefore, biogenic iron oxides

produced by *Leptothrix* sp. are not a suitable material for phosphate removal with subsequent recovery.

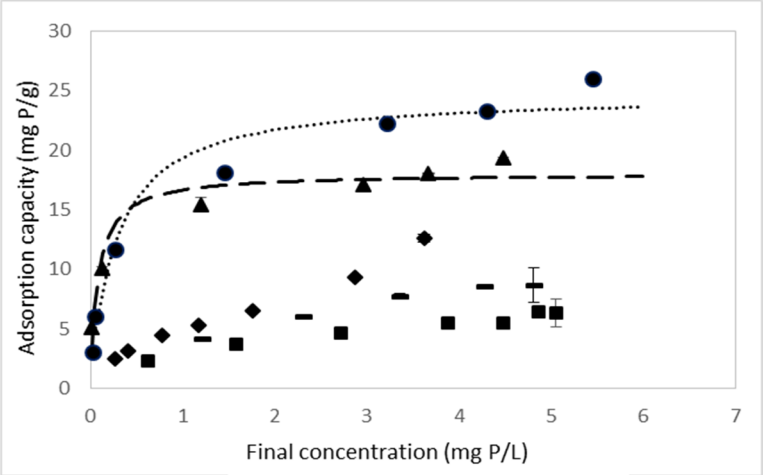


Figure 9-2: Isotherms fitted according to Langmuir adsorption model for phosphate adsorption to 5 different iron based adsorbents after 4 days, mg P/g d.s (n = 2)

• Leptothrix sp. E: non-washed; ▲ GEH; ♦ ChFeOPrecip; ▬ Gallionella sp: MQ washed; ■ Leptothrix sp. E: MQ washed.

Phosphate was apparently immobilized by sorption and/or co-precipitation during the growth of *Gallionella* sp. stalks. The phosphate in the stalks before the adsorption experiments amounted to 31.0 mg P/g d.s., which gives Fe:P molar ratio of 7 (Table S 9-1). A similar Fe:P molar ratio of 10 was reported in literature for *Gallionella* sp. sampled from drinking water systems with low phosphate concentrations (Ridgway et al., 1981). Our *Leptothrix* sp. samples had a Fe:P molar ratio of 40. Studies on *Leptothrix* sp. samples from a freshwater purification system showed a Fe:P molar ratio of 80.(Hashimoto et al., 2007) This high phosphate content of the *Gallionella* sp. precipitates could not only explain the strongly reduced phosphate levels in the residual water (De Vet et al., 2012) but also the retardation of the heterogenic (autocatalytic) chemical iron oxidation (van der Grift et al., 2016) observed by De Vet and co-workers in 2012.

During isotherm experiments the pH of the solution containing *Gallionella* sp. increased up to 7.5, whereas the pH for *Leptothrix* sp. and GEH® remained stable (6.5±0.3). Additional experiments showed that even when the pH was kept constant for all adsorbents at 7.5, the adsorption capacity for the biogenic adsorbents were lower than GEH® (Figure S 9-3). XRD measurements showed that no crystalline material was present in the samples and thus that the iron structures of *Gallionella* sp. and *Leptothrix* sp. were amorphous. The difference in adsorption capacity (mg P/g d.s.) between MQ washed *Gallionella* sp. stalks and *Leptothrix* sp. sheets is not high (Figure S 9-3). Therefore, it is also concluded that the structure of BioFeO tested does not have an influence on phosphate adsorption capacity.

Based on our measurements we hypothesize that both *Gallionella* sp. and *Leptothrix* sp. remove phosphate via multiple mechanisms. Their overall phosphate removal capacity is high, with *Gallionella* sp. and *Leptothrix* sp. *E* removing 39.6 and 26.3 mg P/g d.s., respectively. The

phosphate removal attributed to adsorption is significantly lower, with 8.6 and less than 6.4 mg P/g d.s, for *Gallionella* sp. and *Leptothrix* sp. *E*, respectively. Figure 9-2 shows that the adsorption capacity of the biogenic adsorbents were much lower than the chemical adsorbent GEH®. These values are in general lower than the adsorption capacities of ChFeO (Wilfert et al., 2015). However, the overall ability to immobilize large quantities of phosphate from solutions indicate that BioFeO could play an important role in environmental and engineered systems, which focus on removal rather than recovery. Next to efficient removal of phosphate to prevent bacterial growth and fouling, these BioFeO are also good candidates for removing arsenate, which has similar structure and reactivity to phosphate (Antelo et al., 2005; Violante and Pigna, 2002) and preventing its leakage from sediments of marine and freshwater ecosystems (Bai et al., 2016), groundwater (Katsoyiannis and Zouboulis, 2006; Pokhrel and Viraraghavan, 2009) and mine drainage systems (Ahoranta et al., 2016).

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Supplementary Information

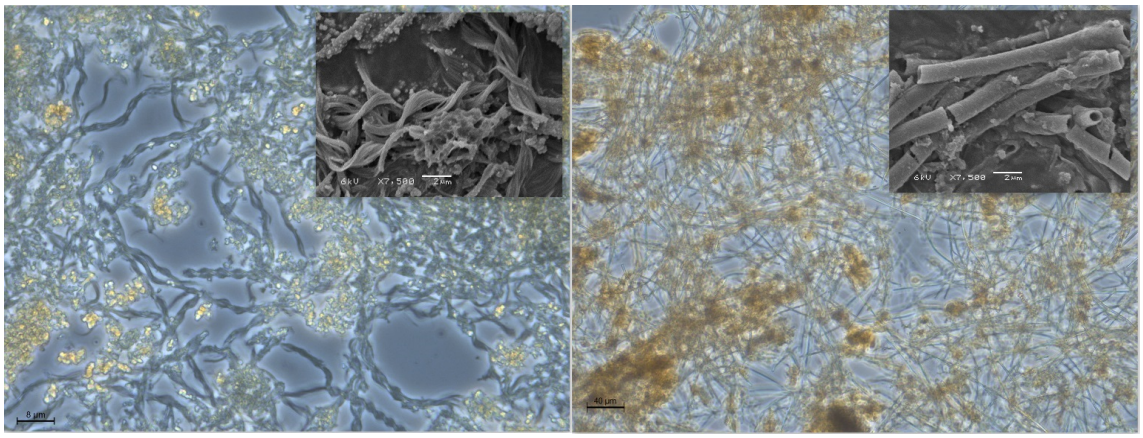


Figure S 9-1: Light microscopy and SEM images of Gallionella sp. stalks (left) and Leptothrix sp. sheats (right). Leptothrix sp. is a sheathed filamentous bacterium and produces oxyhydroxides in the form of hollow microtubes. Gallionella sp. produces iron oxides, which have the shape of twisted stalks.

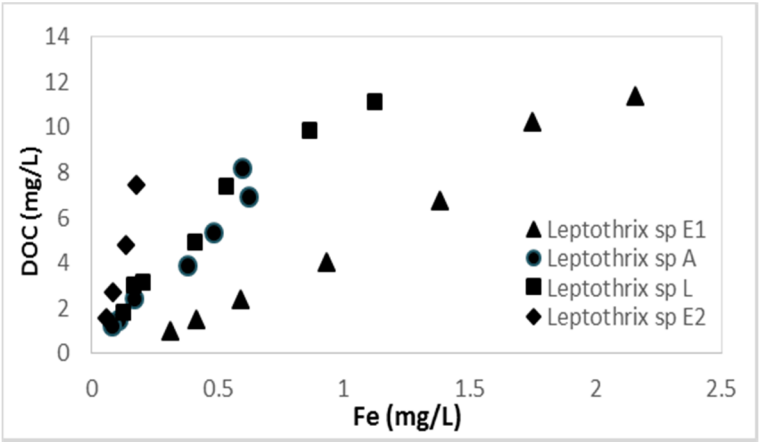


Figure S 9-2: Correlation of DOC and iron concentrations in the supernatant after isotherm experiments using MQ-washed BioFeO of Leptothrix sp.. E, A and L refer to the sampling locations (see text).

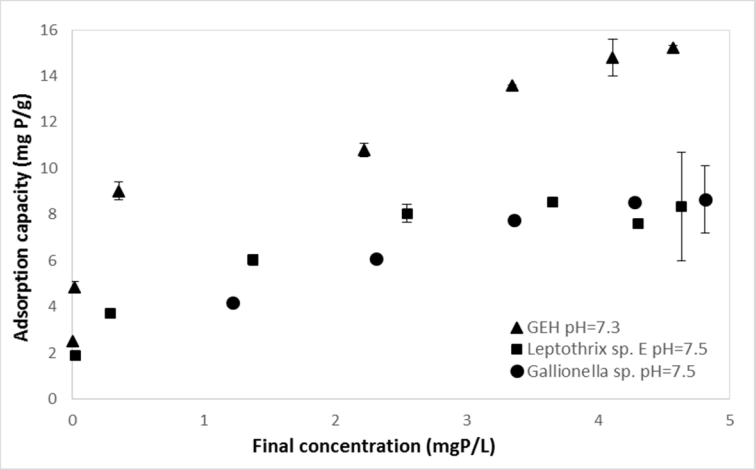


Figure S 9-3: Isotherms for GEH and Leptothrix and Gallionella at around pH = 7.5.

Table S 9-1: Characteristics of BioFeO, ChFeOPrecip and GEH.

	***Leptothrix* sp. E non-washed**	***Leptothrix* sp. E saline-washed**	***Leptothrix* sp. E, A, L MQ washed**	***Gallionella* sp. MQ washed**	**ChFeO Precip MQ-washed**	**GEH MQ-washed**
Fe mg Fe/g	237.4 ± 4.0 (n=2)	204.7 ± 0.4 (n=2)	235.7 ± 13.0 (n=6)	390.8 ± 10.3 (n=2)	339.2 ± 4.3 (n=2)	566.1 ± 4.9 (n=2)
P mg P/g	<0.3 ± 0.1 (n=2)	<0.4 ± 0.0 (n=2)	3.3 ± 2.6 (n=6)	31.0 ± 0.3 (n=2)	10.4 ± 0.4 (n=2)	<0.4 ± 0.0 (n=2)
Ca mg Ca/g	25.0 ± 0.2 (n=2)	3.3 ± 0.1 (n=2)	10.3 ± 3.4 (n=6)	31.7 ± 0.4 (n=2)	35.6 ± 0.2 (n=2)	<0.4 ± 0.0 (n=2)
VS g/kg d.s.	365.8 ± 34.6 (n=9)	476.3 ± 8.2 (n=4)	447.1 ± 69.6 (n=12)	–	–	–
Fe/P molar ratio	>337.6	>291.1	39.6	7.0	18.1	>805.1
XRD	–	–	amorphous	amorphous	–	–

Table S 9-2: P_{total} and o-P concentrations in the supernatant after adsorption experiments with BioFeO, $P_{initial}$ = 5-6 mg P/L (Leptothrix sp. from Earnewâld after 7 days, Leptothrix sp from Alddjp and Lettelbert after 4 days).

d.s. g/L	***Leptothrix* sp. E non-washed**		***Leptothrix* sp. E MQ washed**		***Leptothrix* sp. E saline washed**		***Leptothrix* sp. A MQ washed**		***Leptothrix* sp. L MQ washed**		***Gallionella sp.* MQ washed**	
	o-P mg/L	**$P_{total,}$** mg/L	**o-P** mg/L	**P_{total}** mg/L	**o-P** mg/L	**P_{total}** mg/L	**o-P** mg/L	**P_{total}** mg/L	**o-P** mg/L	**P_{total}** mg/L	**o-P** mg/L	**P_{total}** mg/L
0.2	-	-	0.3 ± 0.0	0.4 ± 0.0	0.1 ± 0.0	-	0.1 ± 0.0	0.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	-	-
0.1	0.0 ± 0.0	-	1.0 ± 0.0	1.2 ± 0.0	0.5 ± 0.0	-	0.6 ± 0.1	0.7 ± 0.1	0.7 ± 0.3	0.8 ± 0.4	-	-
0.05	0.1 ± 0.0	0.2 ± 0.0	2.2 ± 0.2	2.2 ± 0.2	1.4 ± 0.0	1.8 ± 0.0	1.8 ± 0.1	1.9 ± 0.1	1.5 ± 0.0	1.7 ± 0.0	1.2 ± 0.0	1.2 ± 0.0
0.025	1.1 ± 0.1	-	3.5 ± 0.1	3.4 ± 0.1	2.4 ± 0.1	3.0 ± 0.1	3.1 ± 0.0	3.2 ± 0.0	2.9 ± 0.0	3.0 ± 0.0	2.3 ± 0.0	2.2 ± 0.0
0.0125	2.6 ± 0.1	2.8 ± 0.0	4.2 ± 0.1	4.0 ± 0.1	3.3 ± 0.0	4.0 ± 0.0	4.0 ± 0.0	4.0 ± 0.1	3.8 ± 0.0	3.9 ± 0.0	3.4 ± 0.0	3.1 ± 0.0
0.00625	3.6 ± 0.2	-	4.7 ± 0.0	4.4 ± 0.0	3.7 ± 0.0	4.5 ± 0.1	4.4 ± 0.0	4.4 ± 0.0	4.2 ± 0.2	4.3 ± 0.2	4.3 ± 0.0	4.0 ± 0.2
0.00313	4.8 ± 0.1	-	4.9 ± 0.0	4.6 ± 0.0	4.0 ± 0.0	5.0 ± 0.0	4.6 ± 0.0	4.5 ± 0.0	4.6 ± 0.0	4.6 ± 0.0	4.8 ± 0.1	4.5 ± 0.2

Table S 9-3: Kinetic parameters for the adsorption of phosphate by BioFeO, ChFeOPrecip and GEH.

Sample	q_e, mg P/g (fitted)	q_e, mg P/g (experimental, after 4 days)	k, µg P/g min	q_e reached experimentally in comparison to q_e estimated with model (%)
***Leptothrix* sp. E non-washed**	10.3 ±0.0	10.1 ±0.0	$7.5 \times 10^{-1} \pm 1.1 \times 10^{-1}$	98.0
***Leptothrix* sp. E MQ washed**	5.4 ± 0.1	4.1 ±0.0	$1.3 \times 10^{-1} \pm 1.7 \times 10^{-3}$	75.9
ChFeOPrecip MQ washed	8.2 ± 0.6	7.4 ±0.4	$3.3 \times 10^{-1} \pm 1.1 \times 10^{-1}$	90.2
GEH grinded, ≤100 µm	10.4 ± 0.0	10.0 ±0.05	$4.3 \times 10^{-1} \pm 2.1 \times 10^{-2}$	96.1

The pseudo second order kinetic model is described by the following equation:

$$q_t = \frac{(kq_e{}^2 t)}{(1 + (kq_e t))}$$

where,

q_t is the adsorption capacity at time t,

k is the rate constant of adsorption (g/mg min),

q_e is the adsorption capacity at equilibrium.

The difference between q_e determined by fitting with model and q_e reached experimentally is a measure of how close the samples were to adsorption equilibrium.

Table S 9-4: Langmuir isotherms constants for the adsorption of phosphate by Leptothrix sp and GEH. (1RMSE - Root-mean-square error for the fit of experimental data to the isotherms model using non-linear regression).

Sample	q_m, mg P/g dried solids	q_m, mg P/g Fe	K_l, L/mg P	RMSE[1]
***Leptothrix* sp., Rentz et al., 2009 saline washed (once), non-dried**	10.8-39.9	46.9-165.0	-	-
***Leptothrix* sp. E non-washed, non-dried**	24.7 ± 0.2	109.6 ± 1.0	3.6 ± 0.1	1.7 ± 0.0
GEH grinded, ≤100 µm	18.0 ± 0.3	31.8 ± 0.5	12.1 ± 0.8	1.3 ± 0.2

The Langmuir adsorption model is expressed as follows:

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)}$$

where,

q_m = Maximum adsorption capacity (mg P/g),

q_e = Adsorption capacity at equilibrium (mg P/g),

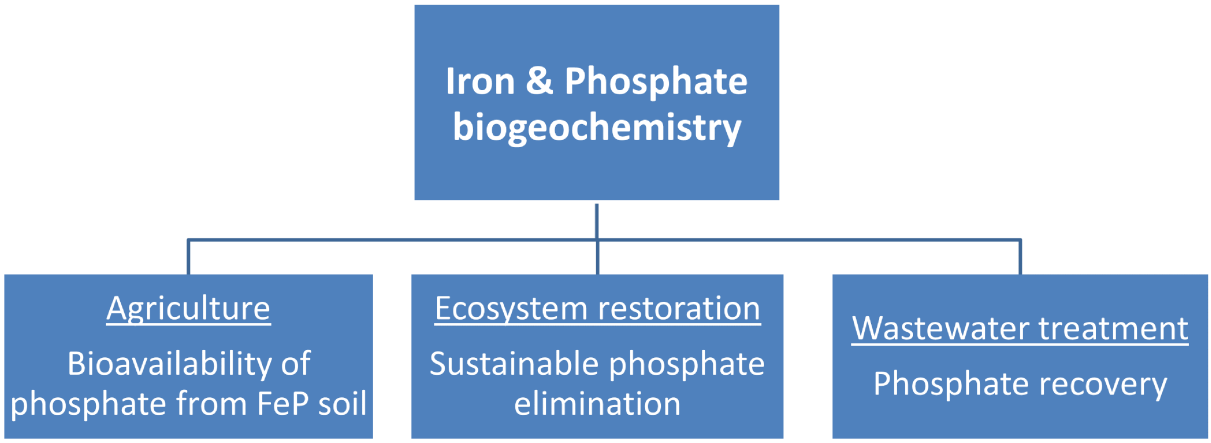
C_e = Concentration at equilibrium (mg P/L),

K_L = Equilibrium constant for the Langmuir adsorption (L/mg P).

Table S 9-5: Actual maximum phosphate adsorption capacities observed after 4 days adsorption by BioFeO and GEH.

Sample	Actual adsorption capacities, mg P/g dried solids	Actual adsorption capacities, mg P/g Fe	Final P concentration in the solution, mg P_{ortho}/L
***Leptothrix* sp. E non-washed non-dried**	26.0 ± 0.3	115.3 ± 1.4	5.4 ± 0.0
***Leptothrix* sp. E MQ washed non-dried**	6.4 ± 1.2	27.5 ± 5.2	5.1 ± 0.0
***Leptothrix* sp. E, A, L MQ washed non-dried**	7.3 ± 0.7	31.0 ± 3.1	4.8 ± 0.3
***Gallionella* sp. MQ washed dried**	8.7 ± 1.5	22.1 ± 3.8	4.8 ± 0.1
GEH grinded (≤100 µm) dried	19.3 ± 0.1	34.1 ± 0.2	4.5 ± 0.0
ChFeOPrecip MQ washed dried	12.6 ± 0.3	37.2 ± 0.9	3.6 ± 0.1

Chapter 10: Thesis Conclusion & Outlook



10.1 Conclusion

Major targets and major outcomes of this thesis

The scope of this thesis was to investigate interactions between iron and phosphate in the context of sewage treatment plants (STPs) and specifically digested sewage sludge. This research should clarify whether or not it is possible to develop technologies to recover phosphate from sludge that originates from municipal wastewater treatment plants that rely on iron based precipitation of phosphates. An additional premise was that such a technology can be integrated in current, hence conventional, sewage treatment plants without changing the treatment process significantly.

As a major outcome of this research, the iron phosphate mineral vivianite ($Fe(II)_3[PO_4]_2 \cdot 8H_2O$) was identified as the main phosphate compound in iron rich digested sewage sludge. Based on this finding a new route for phosphate recovery was patented and will be tested on a pilot scale from 2018 onwards (ViviMag project). Additionally, other spin-off ideas on vivianite related research were identified (e.g. stimulating crystal growth to facilitate vivianite separation or inducing vivianite formation in manure; see outlook for more details).

Lack of knowledge related to iron and phosphate biogeochemistry

Scientific literature on natural systems such as soils or sediments, showed that the interactions between iron and phosphate are important and manifold (Chapter 2). The presence and type of iron affects the availability and mobility of phosphate. Depending on the system considered, it is sometimes anticipated that phosphate remains locked and immobilized in the solid fraction, i.e. that it is tightly bound to iron (e.g. during lake restoration, in natural aquatic sediment systems or in chemical phosphate removal during sewage treatment). However, in other systems it might be anticipated that the phosphate is released (e.g. in iron rich agricultural soils, during phosphate recovery from sewage sludge or when iron based phosphate adsorbents are regenerated). Due to the central role iron plays for phosphate mobility and availability, much information regarding interactions between these elements was created and documented by researchers from various research disciplines.

For sewage systems, the information found was limited. Mechanisms, that appear relatively simple at a first glance, like iron based chemical phosphate removal and the fate of the formed iron phosphate precipitates, remained (and still remain) largely unknown due to controversial findings in this field of research. In contrast to phosphate, iron receives little attention in sewage treatment plants. It is surprising that only limited information / knowledge is available since iron plays an important role during sewage treatment. The controversial or non-existing information related to iron in STPs can probably be related to its very complicated biogeochemistry and the difficulties in measuring iron speciation in general. Measuring for e.g. the speciation of dissolved iron (not only in STPs) is a very difficult task. This information is extremely important but not available for sewage treatment systems. The iron speciation is required for reliable thermodynamic modelling of mineral formation in sludges.

Studying iron and phosphate compounds

For a few parameters, however, some relatively simple to use and readily available tools exist which allow to obtain more information related to the fate of iron during sewage treatment. This knowledge would allow a more effective use of iron. In two treatment plants, where we studied the fate of iron in more detail, we helped to improve the treatment process and could reduce the costs for iron dosing. In the STP Leeuwarden, a relatively simple mass balance for iron was made and will help to reduce the operation costs related to iron dosing significantly. In the STP Nieuwveer, high dissolved iron concentrations related to an insufficient oxidation of Fe(II) to Fe(III) in the A-stage of this plant explained why the COD removal was limited. Improving the aeration in the A-stage or dosing Fe(III) will probably enhance the COD removal.

XRD is a very common method and can help to identify vivianite in sewage sludges, provided the sample preparation is appropriate (i.e. the sample is dried at room temperature – ideally in the absence of oxygen). Obviously, sample preparation in many studies was not properly done or vivianite could not be quantified as its significance was not noticed before. XRD is able to give orders of magnitudes on the vivianite content in the sludge. A bit more advanced than XRD but not as available as XRD is Mössbauer spectroscopy. Mössbauer spectroscopy is a very sophisticated and useful tool to study iron. Mössbauer analyses enabled us to show that most iron in surplus sewage sludge is Fe(II). This would suggest that dosing of more expensive Fe(III) salts is not required for phosphate removal if it is anyway reduced to Fe(II) during the treatment process. On the other hand, HCl extractions and earlier studies showed Fe(III) as the dominant iron phase in activated sludge (Chapter 2, 4 and 5). This means that either discrepancies between the measurements methods exist or that iron phases between surplus (i.e. settled activated sludge) and activated sludge (sampled in the treatment line of the plant) differ. Using rather Fe(II) than Fe(III) for phosphate removal in treatment plants is a pre-mature conclusion. Fe(II) can very efficiently remove phosphate. Yet, possible effects of Fe(II) on COD removal (see STP Nieuwveer), floc formation or kinetics of iron phosphate precipitation (i.e. its removal from solution) are not fully resolved.

HCl extractions together with XRD and Mössbauer spectroscopy showed relatively high iron reduction rates in activated sludge and vivianite formation within 24 h in this sludge when it was incubated under anaerobic conditions. Furthermore, we showed that iron reduction rates were a function of the iron content in the sludges. It remained unknown to what degree the formed vivianite can be re-oxidized during sewage treatment and what kind of mechanism (chemical or direct / indirect biological iron reduction) is responsible for the iron reduction.

Similarly to the interactions between iron and phosphate during phosphate removal in activated sludge tanks, the fate of iron and phosphate during the anaerobic digestion process received only limited attention as well. This is surprising because iron based chemical phosphate removal is a relatively old and well established method. Furthermore, the forms of phosphate in the sludge will affect further use of sludge such as its application on agricultural land and of phosphate recovery technologies that target on iron rich digested sewage sludge.

Vivianite as a key mineral in sewage treatment plants

Our Mössbauer and XRD measurements suggested that vivianite is the most important phosphate phase in sewage sludge. Between 70-90% of all phosphate in digested sludge and between 40–70% of all phosphate in surplus sludge was bound in vivianite. Although these two methods agree more or less well, some uncertainties remained about the absolute vivianite content in the sludge. In some sludges we analysed, about 1/3 of the Fe(II) could not be assigned clearly to vivianite by Mössbauer spectroscopy. This suggests that we overestimate the iron (and phosphate) bound in vivianite in the sludge. This uncertainty is probably related to the substitution of iron in the vivianite structures by other metallic cations or by the fact that mixed mineral phases occur.

Also after adding sulphide to the sewage sludge, which specifically extracts iron bound phosphate, less phosphate was released as expected / indicated by the Mössbauer spectroscopy and XRD measurements. This finding would again suggest that we overestimate vivianite bound phosphate in the sludge. However, it is very well possible that, similar to observations made for sediments systems, phosphate sorption or precipitation of phosphate decreases the net phosphate release from sludge. On the other hand, extraction of vivianite from sewage sludge using magnets that were specifically designed for vivianite showed that up to 60% of all phosphate could be separated from sewage sludge. Meaning that our results from Mössbauer and XRD measurements are in the right range albeit potentially overestimating the amount of vivianite.

New opportunities for phosphate recovery routes

These observations cleared the way for a new phosphate recovery route via vivianite using well established and affordable magnetic equipment from the mining industry. Thermodynamics and our spectroscopic measurements suggest that this route is promising. Vivianite is anyway formed in sewage treatments plants with iron dosing. Hence, no additional measures are necessary to induce vivianite formation. In addition, vivianite is less soluble than struvite and most other phosphate minerals in the sludge. Thus, a higher phosphate recovery efficiency is possible compared to struvite recovery from rejection water from sewage sludge dewatering or directly from sewage sludge (e.g. by the airprex system). Moreover, struvite recovery is only feasible in plants with enhanced biological phosphate removal. Vivianite recovery routes could be an alternative to technologies that rely on sludge incineration (and the related expensive mono-incinerators) or that produce struvite from sludge liquor. The research in this study could be the nucleus for new phosphate recovery routes via vivianite. Such technologies can help to use phosphate (and iron) more circular. The theoretical framework is set, now the ViviMag pilot has to show if this route is feasible.

Using sulphide to recover phosphate from iron phosphate rich sludge

The possibility to recover phosphate via sulphide addition to digested sewage sludge was evaluated. Sulphide is a specific extractant for iron bound phosphate. Phosphate release from

the sludge was lower than expected because Mössbauer spectroscopy and XRD suggested that more phosphate is bound to iron, i.e. is bound in vivianite. We hypothesize that this could be related to re-binding of released phosphate by other dissolved elements or by its adsorption to the sludge solids which thereby reduces the net phosphate release in solution. Capturing phosphate by a resin (with a high affinity for phosphate) or complexing the iron to prevent re-precipitation could solve this issue. Another weak point in this route is the negative effect of sulphide on the dewaterability of the sludge. Sulphide amended sludge showed a significant deterioration in its dewaterability. The reason for this drop cannot be explained and should be studied in further detail by evaluating e.g. effects of sulphide on the floc structure in the sludge. Phosphate can be released from the sludge using sulphide but the disposal costs would rise due to a decrease in the sludge dewaterability.

Overall, it seems that separating or concentrating phosphate phases such as vivianite from or in the sludge, analogue to struvite recovery, is more efficient compared to technologies that dissolve phosphate from sludge. Sorption and precipitation of released phosphate and the dissolution of unwanted compounds has to be prevented if phosphate is brought into solution. When a concentrated phosphate stream is produced (consisting of vivianite or struvite) then it can be treated much more efficient and re-precipitation of the phosphate would probably not be so significant.

Biogenic iron oxides

Equipped with methods and knowledge related to iron and phosphate interactions the fascinating case of biogenic iron oxides was studied in a side project. It was reported that these microbial produced iron oxides bind phosphate in very effective ways by adsorption. We could find indications that several mechanisms, next to adsorption, are involved in phosphate removal by these iron rich structures (and that adsorption plays only a minor role). This means that phosphate, and other contaminants such as arsenic, can effectively be locked away by biogenic structures but that the recovery of phosphate would probably be difficult. The suggested mechanisms are hypothesized but have to be experimentally confirmed. These biogenic iron oxides are an interesting research topic, they show how complex the interactions between iron and phosphate are.

10.2 Outlook

Vivianite like structures

This thesis opened up the way to a field which deserves more research. For instance, our characterisation of the vivianite like structures in the sludge was incomplete. There is good evidence that vivianite occurs with impurities in the sludge but we could only hypothesis that these impurities make its characterisation and quantification such difficult. It is not known whether these vivianite like structures vary from STPs in one region to STPs in other regions and how these impurities could influence the separation and further application of vivianite. Impurities influence chemical and physical parameters of vivianite. More experiments with vivianite that contains different extents/types of impurities should be performed. In this way some of the controversial observations related to the extractability or oxidation behaviour of vivianite could possibly be explained. Characterization of larger quantities of separated material from different plants would help to increase the knowledge related to impurities and how they affect its separation from sewage. Such a characterisation will be part of the ViviMag pilot stage for magnetic separation of vivianite from sewage sludge. For this technology an overdosing of iron for phosphate removal is recommended. This ensures that vivianite formation is not limited by the availability of iron and it helps to reach low phosphate levels in the effluent of the STP. Dosing iron for phosphate and COD removal is also in line with energy producing STPs of the future.

Unravelling: How much phosphate is bound in vivianite (like structures)?

At the end of the day a separation method, such as the one that will be used in the pilot stage, has to prove if the hypothesized high recovery efficiency of phosphate by retrieving vivianite likes structures from sludge is possible as our measurements suggest. Thus, this pilot stage or other separation methods and technologies (based e.g. on seeding or density separation) will finally show if we bet on the right horse.

Despite the uncertainties in Mössbauer spectroscopy and XRD, thermodynamics back up our hypothesis as modelling suggests that significant amounts of phosphate are bound in vivianite. Thus, it seems likely that vivianite is a promising route for phosphate recovery. The suggested recovery method, based on magnetic separation of vivianite from sewage sludge, is relatively cheap and comprises well-established methods. Furthermore, vivianite formation is taking place anyway when sewage sludge is anaerobically digested and provided sufficient iron is present, no additional measures are required for its formation. There are indications that vivianite formation could even be more significant if thermophilic digestion is applied because vivianite scaling was particularly observed in such plants. This phenomenon deserves more attention in research. It has to be shown whether or not higher temperatures indeed favour the formation/growth of vivianite in these systems. Additionally, the role of aluminium on the extent of vivianite formation has not been solved yet. Thermodynamic modelling suggests that some aluminium phosphate minerals could be more stable than vivianite under the conditions that are encountered during sewage treatment. Sometimes aluminium is used for phosphate

removal and significant amounts of aluminium can occur in sewage sludge. Although, no crystalline aluminium phosphates were found using XRD, it can still be that amorphous aluminium phases bind part of the phosphate (which would not be available for vivianite formation).

Vivianite in environmental and engineered systems

Understanding the presence of vivianite in sludge may also be interesting for the application of sewage sludge on agricultural land. Vivianite could determine the availability of phosphate for plants. Here impurities may also play a role as they could affect the oxidation kinetics of vivianite (i.e. its breakdown) and the vivianite solubility. Simple XRD studies on vivianite containing sludge could for e.g. be used to show how fast this mineral decomposes after it has been brought to the fields.

The impurities could be contaminants such as arsenic but also beneficial micronutrients such as zinc. At the same time the impurities make vivianite quantification probably difficult. Economic calculations following the pilot stage, will also be influenced by the type and degree of impurities, and thus impurities will also influence the decision if vivianite recovery technologies are feasible.

Several publications show the importance of vivianite in limnic and even marine sediments. This indicates that vivianite is not only for engineered but also for environmental systems an interesting mineral to study. The open questions related to vivianite affect researchers in both disciplines. Multidisciplinary collaboration would certainly help to answer questions related to vivianite like (1) its crystal growth mechanisms, crystal growth kinetics and nucleation in a complex matrix (such as sludge / sediment / soil) (2) its actual quantitative role in environmental / engineered systems (3) the role of microorganism in vivianite formation and dissolution.

The future of phosphate recovery

In case the pilot stage gives positive results, a full scale installation can be envisaged in near future. However, also other directions related to phosphate recovery by using vivianite are possible if the magnetic separation approach in the ViviMag project fails. Vivianite separation would probably be facilitated if larger vivianite crystals could be produced in the sludge. This could be achieved by seeding or by increasing the solid retention time of vivianite during the digestion process. Also vivianite growth on specific surfaces could be proliferated. These surfaces can be separated from sewage sludge more easily.

Finally, if vivianite recovery technologies proof to be successful, then these could also be used to recycle phosphate from other phosphate rich waste streams such as manure. In the presence of iron, vivianite should be the most stable compounds in these systems as well – provided an oxygen free stage exists (e.g. during biogas production). Experiments in which waste streams are spiked with iron and subsequent vivianite formation is measured could be a first step.

Probably, sewage treatment will evolve to other designs than the ones we see today. In future sewage treatment plants will supply the society with nutrients and other useful compounds such

as chemical elements or energy or bioplastics. They will be urban mines. Most likely new treatment designs such as granular aerobic sludge processes (e.g. the NEREDA process), A-stage plants combined with cold anammox and / or source separated technologies will replace current classical activated sludge systems. However, phosphate recovery will be necessary in all these systems. It cannot be predicted how phosphate recovery will be achieved in future, but it seems likely that iron remains a reliable partner for phosphate because iron is often present in the sewage and because it has a high affinity for phosphate. Thus, iron has to be taken into account to achieve successful phosphate recovery with a high efficiency from such waste streams.

Phosphate recovery is necessary because of an imbalance of phosphate in the world regions. It seems unlikely that phosphate occurrences can be balanced because of 21st century phenomena such as urbanization. Phosphate rich sewage sludge is produced in highly populated areas and requires application on the agricultural soils that might be far away from the places where the phosphate rich waste occurs. Even if these logistic issues could be solved, vivianite separation from sewage sludge could be interesting. Because the separation of vivianite from sewage sludge could not only allow the production of low value phosphate fertilizers but also allow the production of higher value products. Such products could be colour pigments, lithium iron phosphate batteries but also the interesting photo-electrochemistry of vivianite could have potential applications in future. Thus, STPs have the potential to provide us with products that are more valuable than just nutrients. Studying vivianite in sewage treatment plants and vivianite as a mineral itself in more detail will show if it can indeed be used for developing higher value sewage derived products.

Even if agricultural soils would not contain excess nutrients, due to excess manure or fertilizer input, as currently observed in many industrial countries, good reasons argue against a direct application of sewage sludge in agriculture (although it has been done in the past and although it is still practiced in many regions). The nutrient composition of sludge does often not match with the nutrient demand of crop. Contaminants, which are contained in sludge, could be spread on fields. Whether or not a recovery route via vivianite would be better, in terms of soil contamination, is unknown. Thus, it has to be studied which contaminants end up in the fertilizer that will be produced from vivianite. To be able to compare contamination in fertilizer produced from phosphate rock and from vivianite, mass balances for the usual suspects (such cadmium, arsenic and micropollutants) have to be made.

We need a new perspective on sewage

A collaboration with artists in the USA working on vivianite (www.nativepaintrevealed.com and www.copperwomanstudio.com) will hopefully help to present sewage to the public in a more proper light. The artists were able to produce colour pigments out of vivianite scaling that was retrieved from the STP Venlo. Colour pigments based on vivianite have already been used in ancient paintings by Dutch masters such as Johannes Vermeer van Delft and by Native Americans. The cover of this thesis shows a picture that was painted with vivianite scaling by

Heidi Gustafson and Melonie Ancheta. This illustrates that prestigious resources can be available from sewage. Sewage and also our other waste products should be seen as sources for valuable goods in our society rather than a disposable material.

Chapter 11: Kids' summaries of thesis chapters



11.1 Introduction

Often attributed to Albert Einstein are these words of wisdom “If you can't explain it to a six year old, you don't understand it yourself.” It is indeed useful when researchers are able to communicate their work in simple words to public audience. In the following chapter the main outcomes of this thesis were explained to young people of different ages. The research was then summarized by these youngsters. This chapter provides readers with simple summaries of the research content of this thesis.

11.2 Material and Methods

Test persons, their birth date and the chapter(s) that were explained to them are listed in Table 11-1.

Table 11-1: Overview of individuals and the research that was explained to them.

Chapter(s)	**Name**	**Date of Birth**
Chapters 2 & 3: Relevance of iron and phosphate interactions during sewage treatment	Marwin Wilfert	30.11.2007
Chapters 4, 5 and 6: Relevance of vivianite during sewage treatment	Maya Stegmüller	12.10.2002
Chapter 7: Using sulphide for phosphate recovery	Lotta Wilfert	20.05.2010
Chapter 8: Magnetic separation of vivianite from sewage sludge	Jonas Stegmüller	14.03.2001
Chapter 9: Biogenic iron oxides for phosphate removal and recovery	Hannes Stegmüller	12.10.2002

The author of this thesis had five minutes time to give an overall introduction about phosphorus and phosphorus recovery using a power point presentation. This step was meant to convey the following key messages related to phosphorus recovery:

- Phosphorus is a chemical element that all living organisms require. It is important for life and thus phosphorus is a major ingredient of fertilizers. Without phosphorus, there is no food for you.
- Humans, for instance, have phosphorus in bones as calcium phosphorus. A similar material, calcium phosphorus rock, is our main source for phosphorus today.
- This phosphorus rock is mined from finite phosphorus rock reservoirs. The environment is damaged during the mining. We use the phosphorus that we consume one single time and then throw it away. Is that not stupid? I think we should recycle or reuse it, just as we do it with glass bottles or like the old toys you inherited from your siblings, friends or from other family members.
- How could we reuse phosphorus? Most of the phosphorus we eat is excreted via our pee and poo and thus it ends up in sewage treatment plants. This phosphorus mainly

ends up in sewage sludge which is the end product of sewage treatment. Phosphorus is now a waste product because it comes along with some other stuff that we do not like to reuse or like to have on our agricultural fields.

- Why is the phosphorus ending up in the sewage sludge? Because phosphorus is removed in sewage treatment plants from water.
- Phosphorus can swim in water, it is dissolved. People in the treatment plant make it solid, it cannot swim and everything that cannot swim ends up in sewage sludge.
- If phosphorus is not removed from wastewater it ends up in rivers or lakes where it also acts as a fertilizer. On land phosphorus is used to grow useful crop. However, in waters often algae grow that are toxic when phosphorus is present, the produced toxins can even kill fish.
- Phosphorus should not stay in the water that comes from sewage treatment plants effluent and that flows in lakes or rivers. What do people do in the treatment plant? They throw iron or rust into the wastewater. Phosphorus and iron like each other a lot. So they start holding hands. Can iron swim? No! Iron is so heavy and hugs the phosphorus, so both of them sink, as a couple, to the bottom of the tanks. They form sewage sludge which is not part of the water anymore. So the water contains no swimming phosphorus anymore and can be released to lakes and rivers.
- What is happening to the phosphorus containing sludge? It is often discarded or burnt and then discarded. Thus, phosphorus is not re-used and that means new phosphorus has to be mined and again the environment is damaged.
- My topic was to break the relation between the couple iron and phosphorus to release phosphorus in a separate tank and to produce a fertilizer out of it. Instead of throwing phosphorus away after using it one time.

After the general introduction, the research content of one or more chapters was explained to the individuals within 5-10 minutes (by using a pencil and a piece of paper only). The main explanation points are given in the result section before the summary of the individuals. The individuals were allowed to make notes. Afterwards the individuals had as much time as they wanted (usually between 5-10 minutes) to digest the research pitch. In a subsequent step questions were allowed to be asked to clarify unclear points. There was time to summarize the main points by writing short texts or by drawing sketches. This text was later on translated from German to English without any further modifications and included in this chapter.

11.3 Results

11.3.1 Chapters 2 & 3: Relevance of iron and phosphate interaction during sewage treatment

11.3.1.1 Bullet points from the tutor for explaining the research content to the test person

- Believe it or not nobody knows how to make fertilizer out of iron phosphorus containing sewage sludge in an affordable way.
- And even worse many people work on stuff which does not make so much sense to me. They recover a phosphorus mineral called struvite from sewage.
- This is only possible when instead of iron, bacteria fall in love with phosphorus. These bacteria can take up a lot of phosphorus. For producing fertilizer the bacteria should release the phosphorus again later on. That works a bit. Part of the phosphorus is still sticking to other elements in the sludge or is part of the bacteria. So they do not like to give it away.
- This means in this process only a small fraction of the phosphorus (maximum 50%) can be released to produce fertilizer.
- If iron is present, phosphorus sticks to iron (and to other elements or bacteria) because these two like each other most. So if you target on iron and phosphorus much more phosphorus can be captured to produce fertilizer.
- We think you should use iron for phosphorus removal rather than bacteria. Because if you find a way to unlock phosphorus from iron. You get much more phosphorus out of the sludge.
- How to do that?
- Many people see that iron is good in binding phosphorus but they say that when phosphorus is bound to iron it cannot be released to produce fertilizer.
- Many plants and bacteria have developed strategies to dissolve phosphorus from iron. Why should we not use these strategies to develop a technology to release phosphorus from sewage and to produce a fertilizer from it?

11.3.1.2 Summary of the research by the test person

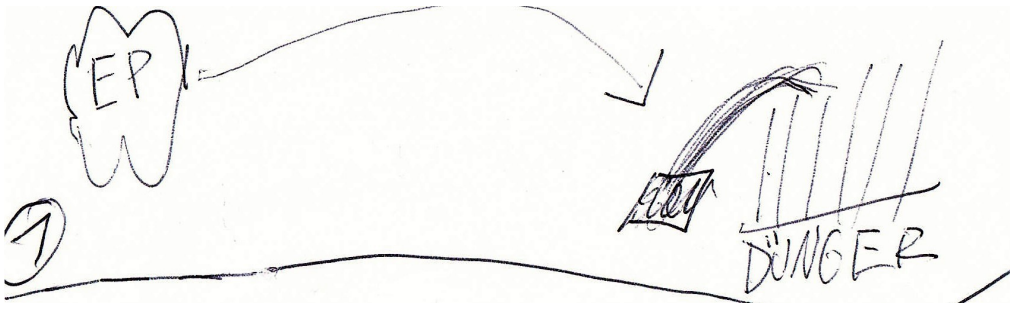


Figure 11-1: We like to make fertilizer out of iron phosphorus. EP stands for iron phosphorus and Dünger means fertilizer in German.

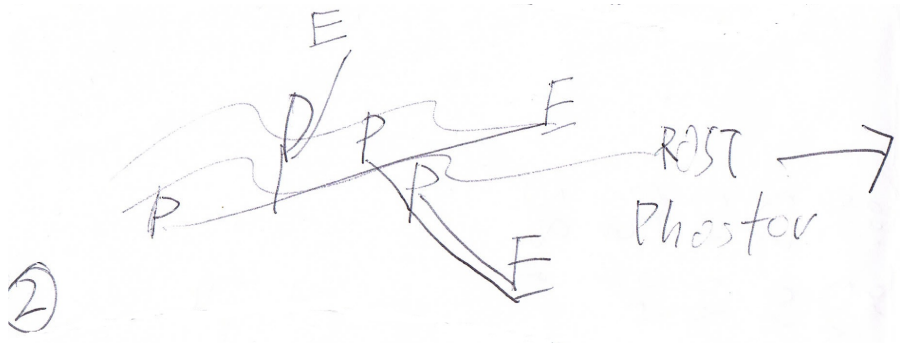


Figure 11-2: When one adds rust in water almost all phosphorus sticks to it. Rost means rust in German, E stands for iron (Eisen in German) and P for phosphorus.

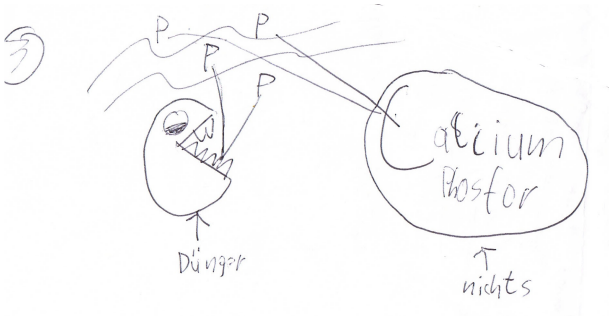


Figure 11-3: When bacteria are put into the water then only a part of the phosphorus stays with the bacteria; the other part sticks to something else. The problem is: that fertilizer can only be produced from phosphorus that is in the bacteria. Dünger means fertilizer in German and nichts means nothing.



Figure 11-4: Other people say that phosphorus cannot be dissolved from iron. However, some plants (Pflanzen) and bacteria can do that. EP stands for iron phosphorus (Eisen Phosphor in German).

11.3.2 Chapters 4, 5 and 6: Relevance of vivianite during sewage treatment

11.3.2.1 Bullet points from the tutor for explaining the research content to the test person

- From the introduction we learned that phosphorus in sewage sludge is bound to iron. We like to release this phosphorus from iron to produce fertilizer.
- We read science books and found that bacteria, fungi and plants can release phosphorus from iron. That is what we want. So we checked if nature has already invented tricks for us that we can use to release phosphorus from iron.
- We continued reading and actually found that there are many different types of iron phosphorus. The way how plants, fungi and bacteria release phosphorus from iron depends on the type of iron phosphorus. Just as every lock has a unique key – for different iron phosphorus compounds different ways of releasing phosphorus from it exist.
- That means before we continue our work on how to release phosphorus from iron phosphorus in sewage sludge we need to do what? Right, try to find out which type of iron phosphorus is in sewage sludge (Comment by tutor: Correctly answered by test person). However, this was not known.
- We used different methods to find out which iron phosphorus compound is in sewage sludge and took samples from various sewage treatment plants.
- We always found one and the same mineral. Do you know the name of one mineral / what a mineral is? (Answer test person: quartz). We found a mineral called vivianite which contains iron and phosphorus. Always the same, no matter where we went (Finland, Germany or Netherlands). Provided enough iron is present in the sludge it was always there. And most phosphorus is bound in this mineral.
- That means we now could start to find ways on how we can recover the phosphorus from the vivianite containing sludge.
- And even more we could start thinking if this mineral is not more valuable than the phosphorus which is contained in it. For instance, vivianite is used as a colour pigment.

11.3.2.2 Summary of the research by the test person

- Phosphorus is a main component of fertilizer. No fertilizer no food.
- Sewage contains phosphorus.
- Phosphorus is removed from the sewage using iron.
- Iron and phosphorus need to be separated.
- In nature plants and substances exist that are able to do so.
- But there are many different iron phosphorus compounds. For every compound substances are required that can split the bond between iron and phosphorus.
- It was one of the targets to find the appropriate substance for splitting the iron and phosphorus that is in the sludge.
- The iron phosphorus compound vivianite was found in the sludge
- Once separated from iron, phosphorus that is contained in the sludge can be used to produce fertilizer or paint.

11.3.3 Chapter 7: Using sulphide for phosphorus recovery

11.3.3.1 Bullet points from the tutor for explaining the research content to the test person

- Key role here plays sulphur gas. This is this rotten smelling gas that you sometimes smell maybe you noticed it at shores of lakes or rivers. When you fart you can also sometimes smell it because bacteria produce it in your intestines where no air is present.
- This sulphur gas is very toxic but not when it is bound to iron. And it loves iron. And iron loves sulphur. Iron loves the sulphur gas so much that it rather holds hands with sulphur gas than with phosphorus.
- So first iron and phosphorus hold hands in the sewage sludge, they like each other a lot. But then a better friend of iron (namely sulphur) comes along, iron leaves phosphorus alone and goes in a relation with sulphur.
- So we want to release phosphorus from iron phosphorus in sewage sludge, why not using sulphur gas. Because once phosphate is free we can produce a fertilizer from it.
- We tried this: We added sulphur gas to iron phosphate rich sewage sludge. You know what happened? It worked!
- But only a bit.
- Only some phosphorus was released. Do you know why? What are you doing if a friend does not want to hang around with you anymore? Right, you try to find another friend that you can hang around with. I think when the iron and sulphur became friends the phosphorus found other friends e.g. calcium. Because also calcium and phosphorus are good friends (if iron is not around). That means no phosphorus is released. Only a limited fertilizer production is possible.
- And another problem: When you get rid of sewage sludge you dump it somewhere. But it contains a lot of water. The more water, the more space it occupies and the more it costs to dispose and transport (just as the costs you have at home for garbage).
- Therefore people usually dewater sludge by squeezing it. Just as wine was produced. Then they have to pay less for getting rid of it.
- And when the sulphur gas made friends with the iron in the sludge, somehow it was not possible to dewater the sludge so nicely any more. And we have no idea why.
- Because we got only a bit phosphorus out of sludge and because disposal costs of the sludge rise after adding sulphur, we summarized, it is currently not useful to go in this direction.

11.3.3.2 Summary of the research by the test person

- One could squeeze the sewage sludge at the same time when the sulphur gas is added.

11.3.4 Chapter 8: Magnetic separation of vivianite from sewage sludge

11.3.4.1 Bullet points from the tutor for explaining the research content to the test person

- From the introduction we learnt that phosphorus in sludge is bound to iron.
- We found out, almost all phosphorus is bound to the iron in a mineral called vivianite. Do you know what a mineral is, do you know an example of a mineral (Answer test person: quartz).
- Vivianite occurs in very small particles in the sludge. Imagine the thickness of a 1 Eurocent coin. The vivianite particles are about 1/10 of this thickness.
- We would like to get this vivianite out of the sludge. Because we could use it to produce fertilizer, but people use it e.g. as a paint, also. So we could get money for the vivianite provided we get it out of this sewage sludge.
- Any idea how to get something with iron out of a complex matrix like sewage sludge?
- Bingo, magnetism (Comment tutor: correctly answered by test person). The vivianite is paramagnetic, that means it gets indeed attracted by magnets. People in the mining industry already have invented sophisticated magnetic separators cheap to operate. But nobody has tested them on sewage sludge before.
- We did some tests and indeed we could get up to 60% of all phosphorus out of the sludge.
- That was nice. So we filed a patent on this process.
- What would you do next? Answer test person: Test the invention in a real sewage treatment plant.
- But we still have some open questions:
  - Why do we not get more phosphorus out of sludge (only 60%)?
  - What can we do with the vivianite?
- Therefore, we will check in subsequent steps:
  - Can we, before magnetic separation, make a pre-separation? We will try to separate the stuff in the sewage sludge by density. Just as people do it when they search for gold. And perhaps then the magnetic separation works better.
  - What can we do with vivianite? Could we produce colour pigments or use it as a fertilizer?

11.3.4.2 Summary of the research by the test person

- Rust added to sewage sludge binds phosphorus to form vivianite particles.
- These particles can be separated from sewage sludge using magnets.
- 60% of all phosphorus can be separated from the sludge in this way.
- Several passes through the magnetic separator do not make this process more efficient.
- The biggest economic value of vivianite is probably the production of colour pigments.

11.3.5 Chapter 9: Biogenic iron oxides for phosphate removal and recovery

11.3.5.1 Bullet points from the tutor for explaining the research content to the test person

- You know what rust is, right? Where do you see it usually? Answer test person: On bike chain or my parents' car.
- Rust forms on iron and thus part of it is iron.
- This rust can bind phosphorus very well. Just as we saw in the introduction it can be sometimes nice to bind phosphorus. Can you remember why? Answer test person: Because it can remove phosphorus to prevent fertilization of lakes and rivers and thus prevent that algae grow that can release toxins.
- This rust, like the rust from your bike, is good in removing phosphorus and often used for phosphorus removal. That means a tiny bit of rust can be used to remove a lot of phosphorus from water.
- Rust can be formed without any living organisms involved (just as if forms on your bike chain). But some bacteria produce rust, just as you poo poo they poo rust.
- Mark, my professor, and one of his students found out that this rusty poo from one bacteria species is actually even better in removing phosphorus than the rust on your bike chain that is formed without any living organisms involved. Better means it can reduce phosphorus to very low concentrations. So that no organism can grow at all in this water (remember all organisms require phosphorus to survive). Rust produced without bacteria was not able to do so.
- Sometimes it can be useful when other organisms are not able to grow. For instance, in some companies they filter water to clean it. They have the problem that a lot of bacteria grow on the filter. What happens then? Right, the bacteria clog the filter and no water can pass any more. Imagine you could prevent bacterial growth by removing phosphorus using rusty poo.
- The rusty poo from bacteria is even more interesting. Someone in the USA found out that phosphorus can be very efficiently removed from water by rusty poo from another type (species) of bacteria. Efficient means, you need only a tiny bit of rusty poo to remove a lot of phosphorus.
- We wanted to know how this is possible. Because you would expect rust is rust, no? So we did some experiments. We analysed how much phosphorus normal rust and how much rusty poo can take up. And we analysed the composition of the rusty poo.
- We think we could find answers to these two questions:
  - What did Mark and his student see? Well, what we think is that while the bacteria are pooing rust, some phosphorus was already so excited to see the iron that it hugged the iron (before the pooing was done).The phosphorus got incorporated into the poo. It is really locked away and difficult to reach for other organisms.
  - The researchers from the USA made probably a mistake. Because we could not see that rusty bacteria poo is better in removing phosphorus than the normal rust (in terms of the amount of rust you need). We

think this was because the rusty poo had some loose iron on the surface of the poo. So one iron after the other went away from the poo structure to find and hug a phosphorus which then became solid. We think this is because we found some iron swimming in our water (where it should actually be in the poo). Whereas, when the poo is intact only the surface of the rusty poo can bind phosphorus. We have two different mechanisms here. When we washed away the loose iron on the surface of the rusty poo, we saw phosphorus removal was not better than for normal rust. We think that the researchers in the USA simply did not wash away all loose iron.

11.3.5.2 Summary of the research by the test person

- Rust pooing bacteria exist.
- The rusty poo from bacteria can take up more phosphorus compared to usual rust.
- The rusty poo retains the phosphorus in such a way that it cannot be accessed any more.

11.4 Discussion

All test persons showed a great interest in the research that was explained to them. Some of the summaries were short but still showed that the main items were understood. For instance in the sulphur gas case, the summary comprised of only one sentence. This sentence was a good suggestion on how to improve the explained process.

It was very challenging to summarize the thesis research without falling back into the technical language. Different ages of the test persons were an additional challenge.

While explaining the research in simple language it became clear that some topics were explained in too complicated ways or described too detailed, e.g. the description of the mechanisms why biogenic iron oxides are special. Most of these poor explanations were reflected in the summary and in the faces of the test persons.

Based on the observation made in this chapter it is strongly suggested, that researchers communicate their scientific work to their families, friends or public audience. Ideally, the audience comprises kids. Kids think very logical and do not dare to ask simple questions (which are often the hardest ones). The communication can be done in various ways such as cartoons, books, presentations or articles in newspapers. This approach assures that the research was really understood well by the researcher and it raises awareness for science.

Summary

The scope of this thesis was to lay the basis for a phosphate recovery technology that can be applied on sewage sludge containing iron phosphate. Such a technology should come with minimal changes to the existing sludge treatment configuration while keeping the use of chemicals or energy as small as possible. The research focused on understanding the exact mechanism for phosphate release from iron in sewage sludge in order to find a method to release phosphate in an elegant way. Phosphate is an essential nutrient for plant growth, but at the same time the resources of phosphate are limited and concentrated in a few countries outside Europe. Recovery of phosphate can secure the access to phosphate for food production and is therefore an important topic.

Iron based phosphate removal is still used by a majority of sewage treatment plants (STPs) but no viable technology is available to recover phosphate from sludge without sludge incineration. The addition of iron is a convenient way for removing phosphate from wastewater, but this is often considered to limit phosphate recovery. Struvite precipitation is currently used to recover phosphate, and this approach has attracted much interest. However, it requires the use of enhanced biological phosphate removal (EBPR). Phosphate removal relying solely on EBPR is not yet widely applied and the recovery potential is low (<50%). Other phosphate recovery methods, including sludge application to agricultural land or recovering phosphate from sludge ash, also have limitations. Energy-producing STPs increasingly rely on phosphate removal using iron, but the problem (as in current processes) is the subsequent recovery of phosphate from the iron. In contrast, phosphate is efficiently mobilized from iron by natural processes in sediments and soils. Iron–phosphate chemistry is diverse, and many parameters influence the binding and release of phosphate, including redox conditions, pH, presence of organic substances, and particle morphology. The current poor understanding of iron and phosphate chemistry in sewage systems is preventing processes being developed to recover phosphate from iron–phosphate rich wastes like municipal wastewater sludge. In the first chapter parameters that affect phosphate recovery were reviewed, and methods are suggested for manipulating iron–phosphate chemistry in wastewater treatment processes to allow phosphate to be recovered.

Iron is omnipresent in STPs. It can be present unintentionally, for e.g. due to groundwater seepage into sewers, or it is intentionally added for odour and corrosion control, phosphate removal or prevention of hydrogen sulphide emissions into the biogas. The strong affinity of iron to phosphate has advantages for efficient removal of phosphate from sewage but it may also reduce recovery efficiencies in struvite precipitation technologies or for some phosphate recovery methods from ash. On the other hand iron may also have positive effects on phosphate recovery. Acid consumption was reported to be lower when leaching phosphate from sewage sludge ash with higher iron content. Also, phosphate recovery efficiencies may be higher if an iron phosphate compound, like vivianite, $Fe(II)_3(PO_4)_2x8H_2O$, could be harvested from sewage

sludge. Developers of phosphate recovery technologies should be aware of the potential and obstacles the iron and phosphate chemistry bears.

The mineral vivianite, is already present in digested sewage sludge and can be an alternative phosphate recovery option to current technologies. To evaluate this, surplus and digested sewage sludge was sampled from full-scale STPs and analysed using XRD, (e)SEM-EDX and Mössbauer spectroscopy. Vivianite was observed in all plants where iron was used for phosphate removal. In surplus sludge before the anaerobic digestion ferrous iron dominated the iron pool (≥50%). XRD and Mössbauer spectroscopy showed no clear correlation between vivianite bound phosphate versus the iron content in surplus sludge. In digested sludge, ferrous iron was the dominant iron form (>85%). Phosphate bound in vivianite increased with the iron content of the digested sludge but levelled off at high iron levels. 70-90% of all phosphate was bound in vivianite in the sludge with the highest iron content (molar Fe:P = 2.5). The quantification of vivianite was difficult and bears some uncertainty probably because of the presence of impure vivianite as indicated by SEM-EDX. eSEM-EDX indicates that the vivianite occurs as relatively small (20 -100 μm) but free particles that could potentially be separated from the sludge. We hypothesize that chemical/microbial Fe(III) reduction is relatively quick and triggers vivianite formation in the treatment lines. Once formed, vivianite may endure oxygenated treatment zones due to slow oxidation kinetics and due to oxygen diffusion limitations into sludge flocs.

It was shown that vivianite can indeed form relatively quickly in activated sludge systems. Kinetics of iron reduction, the microbial community and the mechanism of vivianite formation in activated sludge from two STPs were studied; one STP with a low iron dosing (STP Leeuwarden, EBPR) and the other STP with a high iron dosing (STP Cologne, applying chemical phosphorous removal, CPR) were studied. The sludges were incubated under anaerobic conditions in batch experiments. The iron reduction rate in the CPR sludge (2.99 mg-Fe g VS^{-1} h^{-1}) was 3 times higher than the rate observed in the EBPR sludge (1.02 mg-Fe g VS^{-1} h^{-1}). The higher iron reduction rate in the CPR sludge is probably caused by its 3 times higher iron content. The rate constants (k) in both sludges are comparable (0.06 h^{-1} in EBPR sludge vs 0.05 h^{-1} in CPR sludge), thus the potential rates in both sludges are similar. For calculating the time it takes to turn over all Fe(III) to Fe(II) in the sludge, the Fe(III) reduction rates at the total ferric iron content of the experiments were used and assumed to be constant over time. Calculations then suggest that all iron in STP Leeuwarden and STP Cologne can be turned over within 15 h and 44 h respectively. Sequencing showed that both of the sludges were dominated by proteobacteria (65 – 89% of all operational taxonomic units, OTUs) and that the dominant class of bacteria were β-proteobacteria (38-63% of all OTUs). The microbial communities in both sludges contained genera that comprise iron oxidizing and iron reducing bacteria. These genera were more abundant in the CPR sludge with a higher iron content. XRD and Mössbauer spectroscopy showed that significant quantities of vivianite were formed in the sludges within 24 h. Our study suggests that iron metabolizing bacteria are more abundant in sludge which is

rich in iron and that significant vivianite formation can already take place before the anaerobic digestion process.

Based on the findings, vivianite is the most important phosphate phase provided enough iron is present, vivianite separation from sewage sludge was studied using a tailor made magnetic separator. Vivianite particles are paramagnetic and present as free particles. Magnetism is an elegant technology as it exclusively separates the liberated and paramagnetic vivianite (and perhaps some pyrite or iron carbonates that are present in the sludge). For this purpose a magnetic separator with Jones magnetic plates was designed and tested on two digested sewage sludges with different iron content. Varying feeding rates were used for the separation. A higher phosphate separation efficiency was achieved with sludge that contained more iron (up to 60% of all input phosphate was recovered) compared to the sludge with lower iron contents (up to 40% of all phosphate could be recovered). The iron and phosphate content was double sometimes even three times higher in the separated (magnetic) fraction when compared to the initial sludge solids. The crystalline fraction of the separated material consisted mainly of vivianite (68%) but also quartz was found (32%) as shown by XRD. The separated material had still a relatively high volatile solid content ranging between 30 – 40% of the dry matter. This fraction is related to organic compounds and other compounds that lose weight during heating (such as carbonates or vivianite). Based on these observations a new phosphate recovery technology for vivianite containing sludge was proposed that makes use of relatively cheap magnetic separation equipment from the mining industry. In this process iron is dosed in high quantities during the treatment process. This would result not only in low effluent phosphate concentrations but, additionally, vivianite formation is not limited by iron during the anaerobic digestion and this would probably result in the transformation of all available phosphate to vivianite. Then vivianite can be separated using a magnetic separator. This separation could be combined with a liberation or pre-separation step by using e.g. a hydrocyclone. Once vivianite is separated from sludge it could be directly used, preferably to produce high valuable products, or it could be dissolved to produce fertilizer. Pure vivianite can easily be dissolved at alkaline pH of about 12. At this pH, phosphate goes in solution and iron and most other metals remain in the precipitate. The phosphate solution obtained from the separated vivianite can directly be used for fertilizer production. Iron could be re-used for phosphate elimination in the STP.

In another study it was tested whether sulphide can help to release and recover phosphate from sewage sludge. A series of batch experiments were conducted on different synthetic iron phosphates: Fe(III)P purchased from Sigma, Fe(III)P synthesized in the lab and vivianite. Sulphide was added to these different iron phosphates in a molar Fe:S ratio of 1 to evaluate the total phosphate release and the kinetics of phosphate release into solution. Phosphate release was usually completed within 1 hour. The maximum phosphate release was 92%, 60% and 76% from vivianite, Sigma Fe(III)P and Fe(III)P synthesized in the lab, respectively. However, rebinding of the released phosphate by Fe(II), only in the experiment with Fe(III)P that was synthesized in the lab, reduced the net phosphate release to about 56%. Sulphide induced phosphate release from vivianite is more efficient because sulphide reacts directly with Fe(II)

to form FeS_x and releases phosphate. No additional sulphide is needed for reducing Fe(III) to Fe(II). At the same time Fe(II) in vivianite is probably more efficient, or as efficient, as Fe(III) in retaining phosphate. Phosphate release from Fe(III)P was, at its maximum (before re-sorption/re-precipitation of the phosphate to other compounds in the sludge) higher than stoichiometry would suggest. Probably because sulphide was acting as a reducing agent, without significant formation of FeS_x. FeS_x formation requires a larger sulphide input. The high efficiency (moles P released / moles S input) of sulphide acting as a reducing agent to release phosphate was confirmed in additional experiments where sulphide was slowly added to Fe(III)P. Moreover, sulphide addition experiments showed that up to 30% of all phosphate could be released from digested sewage sludge. The highest phosphate release was achieved in experiments with the highest iron content. The total phosphate release from digested sludge was not as high as expected, earlier measurements using XRD and Mössbauer spectroscopy, that were used to quantify iron bound phosphate in the digested sludges, suggested that more phosphate should be iron bound and hence sulphide extractable. The dewaterability (determined using capillary suction test) in digested sludge (0.13 ± 0.015 $g^2(s^2\ m^4)^{-1}$) dropped significantly after sulphide was added (0.06 ± 0.004 $g^2(s^2\ m^4)^{-1}$). This strongly suggests that sulphide addition to sewage sludge will result in higher sludge disposal costs. Only insignificant phosphate release (1.5%) was observed from sewage sludge ash in response to sulphide addition. Overall, sulphide showed to be a useful tool to release phosphate bound to iron from sewage sludge for its subsequent recovery. Drawbacks are the deterioration of the sludge dewaterability and a net phosphate release that is lower than expected.

In a side project of this thesis biogenic iron oxides (BioFeO) formed by *Leptothrix* sp. and *Gallionella* sp. were compared with chemically formed iron oxides (ChFeO) for their suitability to remove and recover phosphate from solutions. The ChFeO used for comparison included a commercial iron based adsorbent (GEH®) and chemical precipitates. Despite contrary observations in earlier studies, our batch experiments showed that BioFeO do not have superior phosphate adsorption capacities compared to ChFeO. However, it seems multiple mechanisms are involved in phosphate removal by BioFeO which make their overall phosphate removal capacity higher than that of ChFeO. The overall phosphate removal capacity of *Leptothrix* sp. was 26.3 mg P/g dry matter (d.m.), of which less than 6.4 mg P/g d.m. was attributed to adsorption. The main removal is likely due to formation of organic iron phosphate complexes (19.6 mg P/g d.m.). *Gallionella* sp. had an overall phosphate removal capacity of 39.6 mg P/g d.m. Significant amounts of phosphate were apparently incorporated into the *Gallionella* sp. stalks during their growth (31.0 mg P/g d.m.) and only one fourth of the total phosphate removal can be related to adsorption (8.6 mg P/g d.m.). Their overall ability to immobilize large quantities of phosphate from solutions indicates that BioFeO could play an important role in environmental and engineered systems for removal of contaminants such as phosphate or arsenic.

This thesis showed that the iron phosphate chemistry in STPs has been neglected in the past and that more research is necessary to understand the complex interactions between iron and

phosphate. This knowledge would help to improve the use of iron in STPs for phosphate removal further and pave the way for new phosphate recovery technologies from iron rich sewage sludge. Within the framework of this research the mineral vivianite was identified as a main iron phosphate phase in sewage sludge. Phosphate recovery technologies via vivianite might lead to a significantly higher recovery efficiency compared to routes relying on struvite. Magnetic separation of vivianite from sewage sludge was achieved using equipment from the mining industry. This process will be tested on pilot scale next. Future research related to vivianite based phosphate recovery has to focus on (I) understanding the formation of vivianite in STPs, (II) improving the separation efficiency of vivianite from sewage sludge using equipment that is tailor made for the type of vivianite which is contained in the sludge (density, magnetic susceptibility etc.) or by manipulating the formation of vivianite (by e.g. increasing its particle size) and (III) evaluating the purity of vivianite in sewage sludge to determine its economic value.

Samenvatting

Dit onderzoek beoogde het fundament te leggen voor een techniek voor de terugwinning van fosfaat uit ijzerfosfaat houdend zuiveringsslib. Deze techniek zou zo weinig mogelijk aanpassingen moeten vergen van de huidige configuratie van een rioolwaterzuivering en slibbehandeling en zo weinig mogelijk chemicaliën en energie moeten gebruiken. Het onderzoek richtte zich daarom op het begrijpen van de mechanismen die kunnen leiden tot het vrijmaken van fosfaat van het ijzer in zuiveringsslib. Fosfaat is een essentieel nutriënt voor de groei van planten, maar tegelijkertijd zijn de voorraden van fosfaaterts beperkt en bevinden zij zich buiten Europa. Terugwinning kan toegang tot fosfaat voor de voedselproductie zeker stellen en is daarom een belangrijk thema.

Verwijdering van fosfaat met ijzerzouten is nog steeds een techniek die gebruikt wordt door een grote meerderheid van rioolwaterzuiveringen, maar tot op heden is er geen techniek die het fosfaat direct kan terugwinnen uit ijzerhoudend slib. Dosering van ijzerzouten wordt veelal gezien als een eenvoudige manier voor fosfaatverwijdering, maar wordt daarentegen vaak gezien als een belemmering voor fosfaatterugwinning. Precipitatie en daaropvolgende winning van struviet wordt nu al toegepast voor het terugwinnen van fosfaat en krijgt veel aandacht. Deze techniek vergt echter biologische fosfaatverwijdering (Bio-P). Bio-P wordt weliswaar steeds meer toegepast, maar wereldwijd overheerst chemische fosfaatverwijdering, soms ook als aanvulling op Bio-P. Bovendien zijn de terugwinrendementen voor struvietwinning relatief laag. Andere methoden voor fosfaathergebruik, zoals toepassing van slib in de landbouw en terugwinning uit de as na verbranding, hebben ook beperkingen. Er is een trend dat rioolwaterzuiveringen toegaan naar een concept waarbij zij netto energie produceren en in de meest vergaande varianten zullen veelal ijzerzouten gebruikt worden voor fosfaatverwijdering. Fosfaatwinning is dan nu niet mogelijk. Daarentegen wordt fosfaat in natuurlijke processen in waterbodems en grond zeer efficiënt gemobiliseerd. De ijzer-fosfaat chemie is divers en er zijn veel parameters die de binding en het vrijmaken van fosfaat beïnvloeden, zoals redox condities, zuurgraad, aanwezigheid van organische verbindingen en de morfologie van de deeltjes. Het geringe begrip van deze ijzer-fosfaat chemie in afvalwatersystemen verhindert de ontwikkeling van processen om fosfaat terug te winnen uit ijzerfosfaat rijke stromen zoals communaal zuiveringsslib. Het eerste hoofdstuk inventariseert de parameters die van invloed zijn op het terugwinnen van fosfaat en stelt methoden voor om door manipulatie van de ijzer fosfaat chemie het fosfaat in afvalwatersystemen terug te winnen.

IJzer is alom aanwezig in rioolwaterzuiveringen. Het kan onopzettelijk aanwezig zijn door bijvoorbeeld intrusie van ijzerrijk grondwater of kan opzettelijk toegevoegd zijn vanwege bestrijding van geur, beheersing van corrosie, verwijdering van fosfaat of tegengaan van zwavelwaterstof emissies. De sterke affiniteit van ijzer voor fosfaat heeft voordelen voor een efficiënte verwijdering van fosfaat uit rioolwater. Tegelijk beperkt het de mogelijkheden om fosfaat terug te winnen via struviet precipitatie of bij sommige technieken voor de winning van

fosfaat uit as van zuiveringsslib. Anderzijds kan ijzer ook positieve effecten hebben voor fosfaat terugwinning. Zo rapporteerden onderzoekers dat minder zuur nodig was voor het uitlogen van fosfaat uit de as van zuiveringsslib. De terugwin efficiëntie kan ook groter zijn als een ijzerfosfaatverbinding als vivianiet, $Fe(II)_3(PO_4)_2x8H_2O$ gewonnen zou kunnen worden uit zuiveringsslib. Ontwikkelaars van fosfaat terugwintechnieken zouden daarom op de hoogte moeten zijn van de potentie en beperkingen die de ijzer-fosfaat chemie met zich mee brengt.

Het mineraal vivianiet is al aanwezig in vergist zuiveringsslib en kan een alternatieve manier zijn voor het terugwinnen van fosfaat ten opzichte van de nu beschikbare technieken. Om dit te onderzoeken is surplus slib en vergist slib bemonsterd in rioolwaterzuiveringen en geanalyseerd met XRD, (e)SEM-EDX en Mössbauer spectroscopie. Vivianiet werd gevonden in alle zuiveringen die ijzer gebruiken voor de verwijdering van fosfaat. In het surplus slib voor de vergisting domineerde tweewaardig ijzer (>50% van alle ijzer). XRD en Mössbauer spectroscopie lieten in dit slib geen duidelijke correlatie zien tussen in vivianiet gebonden fosfaat en het ijzergehalte van het slib. In vergist slib overheerste tweewaardig ijzer (>85% van alle ijzer). Het gehalte in vivianiet gebonden fosfaat nam toe met het ijzer gehalte in het vergiste slib, maar bereikte een plafond bij hogere ijzer gehaltes. Bij de hoogste ijzergehaltes (molaire verhouding Fe:P=2,5) was 70-90% van alle fosfaat gebonden als vivianiet in het zuiveringsslib. De kwantificering van vivianiet is moeilijk en brengt enige onzekerheid met zich mee, waarschijnlijk vanwege de aanwezigheid van onzuiverheden in het vivianiet zoals ook SEM-EDX liet zien. eSEM-EDX liet zien dat het vivianiet aanwezig is als relatief kleine (20-100 µm), maar vrije deeltjes in het slib, die in potentie kunnen worden afgescheiden. We veronderstellen dat chemische of microbiële reductie van driewaardig ijzer in het actief slib relatief snel is en leidt tot de vorming van vivianiet. Eenmaal gevormd, overleeft het vivianiet de beluchte delen van een zuivering vanwege de langzame oxidatie kinetiek en beperkingen in de diffusie van zuurstof naar de slibvlokken.

Het onderzoek toonde aan dat vivianiet inderdaad snel gevormd kan worden in actief slib systemen. De kinetiek van de reductie van ijzer, de microbiële gemeenschap en de mechanismen voor de vorming van vivianiet werden onderzocht in twee rioolwaterzuiveringen met respectievelijk lage (Leeuwarden, voornamelijk fosfaatverwijdering via bio-P) en hoge (Keulen, chemische fosfaatverwijdering, Chem-P) doseringen van ijzer. De slibben werden onder anaerobe condities getest in batch experimenten. De ijzerreductiesnelheid in het slib uit Keulen (2,99 mg-Fe g VS^{-1} h^{-1}) was drie keer hoger dan de reductiesnelheid in het bio-P slib uit Leeuwarden (1,02 mg-Fe g VS^{-1} h^{-1}). De hogere reductiesnelheid in het slib uit Keulen wordt waarschijnlijk veroorzaakt door de drie keer zo hoge ijzer concentratie. De reactiesnelheidsconstanten (k) waren voor beide slibben vergelijkbaar (0,06 ± 0,001 h^{-1} voor het slib uit Leeuwarden vs 0,05 ± 0,007 h^{-1} in het slib uit Keulen) hetgeen laat zien dat de ijzerreductie in beide slibben vergelijkbaar is qua snelheid. Om de tijd te berekenen waarbij alle Fe(III) in het slib is omgezet naar Fe(II), zijn de Fe(III) reductiesnelheden bij de Fe(III) gehaltes van de experimenten genomen en is aangenomen dat deze constant zijn in de tijd. In dat geval kan alle ijzer in het slib van Leeuwarden en Keulen in respectievelijk 15 en 44 uur kan worden

omgezet in tweewaardig ijzer. NGS liet zien dat beide slibben voornamelijk proteobacteriën bevatten (65-89% van alle OTEs) en dat de dominante klasse betaproteobacteriën was (38-63% van alle OTEs). De microbiële gemeenschappen in beide slibben bevatten genera die ijzer oxiderende en ijzer reducerende bacteriën bevatten. Deze genera waren overvloediger aanwezig in het chem-P slib uit Keulen met een hoger ijzergehalte. XRD en Mössbauer spectroscopie lieten zien dat significante hoeveelheden vivianiet werden gevormd in de slibben binnen een periode van 24 uur. Onze studie suggereert dat ijzer omzettende bacterien overvloediger aanwezig zijn in ijzerrijke slibben en dat significante vorming van vivianiet al kan plaats vinden voor de anaerobe vergisting van het slib.

Omdat dit onderzoek aantoonde dat vivianiet de belangrijkste fosfaat verbinding is in zuiveringsslib (mits er voldoende ijzer aanwezig is), is magnetische scheiding van vivianiet uit slib onderzocht. De vivianiet deeltjes zijn immers paramagnetisch en aanwezig als vrije deeltjes. Magnetisme is een elegante techniek omdat het alleen het vrije en paramagnetische vivianiet afscheidt (en wellicht wat pyriet of ijzercarbonaat aanwezig in het slib). Voor dit doel is een magnetische scheider met Jones-type magnetische platen ontworpen en getest op twee vergiste zuiveringsslibben met verschillende ijzergehalten. Bij de scheiding werden verschillende voedingsdebieten getest. Een hogere scheidingsefficiency werd bereikt voor het slib met een hoog ijzergehalte (tot 60% teruggewonnen van alle fosfaat in het slib) in vergelijking met slib met een lager ijzergehalte (tot 40% teruggewonnen van alle fosfaat in het slib). Het ijzer en fosfaat gehalte in de magnetische fractie verdubbelde en in sommige gevallen verdrievoudigde in vergelijking met de concentraties in het oorspronkelijke slib. Met XRD werd vastgesteld dat het kristallijne deel in de afgescheiden fractie voornamelijk bestond uit vivianiet (68%) en wat kwarts (32%). De afgescheiden factie had nog wel een relatief groot (30-40%) aandeel aan vluchtige organische verbindingen. Deze fractie zal bestaan uit organische verbindingen, kristalwater uit het vivianiet en carbonaten. Op basis van deze bevindingen kan een nieuwe techniek voor fosfaatwinning voorgesteld worden die gebruik maakt van relatief goedkope en al beschikbare, magnetische scheidingstechnologie uit de mijnbouwindustrie. In deze aanpak wordt ijzer in voldoende grote hoeveelheden gedoseerd in de rioolwaterzuivering. Hiermee worden lage effluent waarden voor fosfaat bereikt, maar wordt ook bereikt dat de vorming van vivianiet niet beperkt wordt door de beschikbaarheid van ijzer tijdens de anaerobe vergisting, waardoor alle beschikbare ijzerfosfaat omgezet kan worden in vivianiet. Het vivianiet kan dan afgescheiden worden met een magnetische scheider. Deze scheiding kan eventueel worden voorafgegaan door een stap waarbij het vivianiet wordt vrijgemaakt van de slibvlokken en/of wordt voorgeconcentreerd, bijvoorbeeld in een hydrocycloon. Als het vivianiet eenmaal is afgescheiden kan het direct worden gebruikt, bij voorkeur in hoogwaardige producten, of het kan worden opgelost voor de productie van kunstmest. Zuiver vivianiet kan eenvoudig opgelost worden door alkalische behandeling bij een pH van ongeveer 12. Bij deze pH gaat alle fosfaat in oplossing en het ijzer en de meeste andere (zware) metalen blijven achter als een neerslag. De verkregen fosfaatoplossing kan

direct gebruikt worden in de productie van kunstmest. Het ijzer zou, na behandeling, hergebruikt kunnen worden voor fosfaatverwijdering in de rioolwaterzuivering.

In een andere studie is onderzocht of sulfide gebruikt kan worden om fosfaat vrij te maken en terug te winnen uit zuiveringsslib. In een serie van batch experimenten zijn verschillende synthetische ijzerfosfaten (één soort ijzer(III)fosfaat aangekocht van Sigma, één soort ijzer(III)fosfaat gesynthetiseerd in het lab en vivianiet) gemengd met sulfide in een molaire verhouding van Fe:S van 1. Het doel was het rendement en de kinetiek voor het vrijmaken van het fosfaat te onderzoeken. Meestal was na 1 uur alle fosfaat vrijgemaakt. Uit vivianiet kon 92% van alle fosfaat worden vrijgemaakt, van het ijzer(III)fosfaat van Sigma werd 60% vrijgemaakt en van het zelf gesynthetiseerde ijzer(III)fosfaat maximaal 76%. Doordat een deel van het vrijgemaakte fosfaat weer neersloeg was het netto rendement voor het vrijmaken van het fosfaat uiteindelijk slechts 56%. Het vrijmaken van fosfaat met sulfide is efficiënter omdat het tweewaardige ijzer in het vivianiet direct reageert met het sulfide tot ijzersulfide waardoor het fosfaat wordt vrijgemaakt. Er is geen extra sulfide nodig om het ijzer eerst te reduceren van driewaardig naar tweewaardig ijzer. Aan de andere kant is het tweewaardige ijzer in vivianiet efficiënter of net zo efficient als driewaardig ijzer om fosfaat vast te leggen. Uit ijzer(III)fosfaat werd op het maximale punt (dus voordat het weer opnieuw adsorbeerde of precipiteerde) meer fosfaat vrijgemaakt dan de stoichiometrie van de reactie suggereert. Dit komt doordat de reductie van het driewaardige ijzer door het sulfide eerst zorgt dat een groot deel van het fosfaat vrijgemaakt wordt. Daarna slaat een deel van het fosfaat weer neer met het gevormde tweewaardige ijzer. Dit effect werd ook bevestigd in aanvullende experimenten waarbij het sulfide langzaam werd toegevoegd aan het ijzer(III)fosfaat. Additie van sulfide aan vergist slib liet zien dat tot 30% van het fosfaat kon worden vrijgemaakt en het hoogste rendement werd behaald bij de hoogste ijzer concentraties. Tegelijkertijd nam echter de ontwaterbaarheid van het slib (bepaald met de capillary suction test) sterk af door de additie het sulfide (van 0,13 $\pm$0,015 $g^2(s^2\ m^4)^{-1}$naar 0,06 $\pm$0,004 $g^2(s^2\ m^4)^{-1}$). Dit suggereert dat sulfide additie het moeilijker zal maken om het slib op praktijkschaal te ontwateren waardoor de slibverwerkingskosten zullen toenemen. De behandeling van slibverbrandingsas met sulfide leidde nauwelijks tot het vrijmaken van fosfaat uit de as (1,5%). Sulfide kan kortom een nuttige manier zijn om fosfaat vrij te maken uit ijzergebonden fosfaat in zuiveringslib zodat het fosfaat kan worden teruggewonnen, bijvoorbeeld door precipitatie als struviet zoals nu ook al gebeurd. De afname van de ontwaterbaarheid van het slib en de lager dan verwachte vrijmaak efficiency beperken de toepasbaarheid van deze methode.

In een zijproject werd de potentie voor fosfaatverwijdering en terugwinning vergeleken van biogene (BioFeO) en chemisch gevormde (ChFeO) ijzeroxides. De biogene ijzeroxides waren gevormd door *Leptothrix* sp. en *Gallionella* sp. De chemische ijzeroxides omvatten een commercieel op ijzeroxide gebaseerd adsorbent en chemisch gevormde neerslagen. Ondanks dat andere studies andere observaties rapporteerden, kon in deze studie in batch experimenten niet aangetoond worden dat BioFeO hogere adsorptie capaciteiten heeft in vergelijking met ChFeO. Desondanks lijken er verschillende mechanismen tegelijkertijd een rol te spelen bij de

verwijdering van fosfaat door BioFeO waardoor de overall verwijdering van fosfaat door BioFeO toch groter is dan bij ChFeO. De totale capaciteit voor fosfaatverwijdering door *Leptothrix sp* was 26,3 mg P/g d.s. waarvan minder dan 6,4 mg P/g d.s. toegeschreven kon worden aan adsorptie. Het grootste deel van de fosfaatverwijdering wordt waarschijnlijk bereikt door de vorming van organische ijzercomplexen (19,6 mg P/g d.s.). *Gallionella* sp. gaf een totale capaciteit voor fosfaatverwijdering zien van 39,6 mg P/g d.s.. Significante hoeveelheden fosfaat werden kennelijk ingebouwd in de *Gallionella* sp. stengels tijdens de groei van deze bacteriën (31 mg P/g d.s.) en slechts een kwart van de totale fosfaatverwijdering kan toegeschreven worden aan adsorptie (8,6 mg P/g d.s.). Deze grote totale capaciteit voor het vastleggen van opgelost fosfaat, geeft aan dat BioFeO een belangrijke rol kan spelen in ecologische en ontworpen systemen voor de verwijdering van fosfaat.

Dit proefschrift laat zien dat de chemie van ijzer en fosfaat in rioolwaterzuiveringen in het verleden onderbelicht is geweest en dat meer onderzoek nodig is om de complexe interacties tussen ijzer en fosfaat te begrijpen. Deze kennis kan helpen om de dosering van ijzer voor fosfaatverwijdering in rioolwaterzuiveringen te verbeteren. Tegelijk kan deze kennis helpen om het pad te plaveien voor nieuwe technieken voor het terugwinnen van fosfaat uit ijzerhoudend zuiveringsslib. Dit onderzoek identificeerde het mineraal vivianiet als de belangrijkste ijzerfosfaat verbinding in zuiveringsslib. Terugwintechnieken op basis van vivianiet hebben waarschijnlijk een significant hogere terugwin potentie dan technieken die zich baseren op de vorming van struviet. Magnetische scheiding van vivianiet uit zuiveringsslib was mogelijk met behulp van apparatuur die algemeen gebruikt wordt in de mijnbouw industrie en deze techniek wordt binnenkort op pilot schaal getest. Verder onderzoek naar op vivianiet gebaseerde terugwintechnieken voor fosfaat moeten zich richten op (I) het begrijpen van de vorming van vivianiet in rioolwaterzuivering, (II) het verbeteren van het scheidingsrendement van vivianiet uit slib met behulp van apparatuur die specifiek ontworpen is voor het vivianiet zoals het aanwezig is in slib (bv. dichtheid, magnetische gevoeligheid, etc.) of door de vorming van vivianiet te beïnvloeden (bijvoorbeeld door de deeltjesgrootte te vergroten) en (III) het onderzoeken van de zuiverheid van het vivianiet om zo de economische waarde te bepalen.

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Curriculum vitae



Philipp Wilfert (*24.09.1982 in Stuttgart, Germany) obtained his university entrance diploma from the Mildred-Scheel-Schule, Böblingen in 2005. After completing the civilian service at a German environmental NGO (BUND) he started studying Biology at the University of Applied Sciences in Bremen. He made his bachelor thesis related to the chemical composition of sediment pore waters and its effect on an aquatic macrophyte under the supervision of Prof. Dr. Dietmar Zacharias in close collaboration with researchers from the University of Nijmegen. During the bachelors' studies Philipp spent one year in Namibia for internships at marine research institutes and he studied one semester marine biology at the National University of Ireland in Galway. From 2010 until 2012 he studied biological oceanography at the GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel in Kiel. The final master thesis, supervised by Prof. Dr. Tina Treude, was about a methane blowout in the North Sea and its effects on the microbial methane degrading community in the sediment. From 2013 on Philipp started the PhD project "phosphate release from sewage sludge containing iron phosphate" which was initiated by the TU Delft and Wetsus, European centre of excellence for sustainable water technology in Leeuwarden. The results produced within the project period are documented in this work.

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- *Farm* –unkown photographer on https://static.pexels.com

Chapter 4:

- *Sampling from dawn till dusk in the sewage treatment plant Leeuwarden* – A. Mandalidis, December 2014.

Chapter 5:

- Vivianite scaling from the sewage treatment plant Venlo - own image

Chapter 6

- SEM image of *Lepthothrix* sp. in an environmental sample from Earnewâld – Prashanth Kumar Suresh & Raimonda Buliauskaitė

Chapter 7:

- Sulfide induced phosphate release from sediments - Modified from Smolders A.J.P., Lamers L.P.M., Lucassen E.C.H.E.T., Van der Velde G. & Roelofs J.G.M. (2006) Chem Ecol 22, pp.: 93–111.

Chapter 8:

- SEM image of vivianite in sewage sludge including an EDX scan from the same particles - own image

Chapter 11:

- Vivianite from Anloua, N´gouandere in Cameroon (Museum für Naturkunde Berlin) – own image.