

FROM WASTE TO VALUE

Vivianite Precipitation:
*a novel concept to remove
iron from groundwater*

by Roos Goedhart



Vivianite Precipitation: a Novel Concept to Remove Iron from Groundwater

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Cover image: *50 Shades of Vivianite*

Visualising my thesis in a painting made with, needless to say, aquarelle paint.



Abstract

The removal of iron from groundwater is essential to avoid aesthetic issues of the produced drinking water and to reduce maintenance cost of the system. The most applied iron removal method of oxidation and filtration produces large volumes of aqueous iron sludge of little value and the method is more likely to fail at high iron concentrations. This research investigates the novel concept of removing iron(II) anaerobically from groundwater by precipitation as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) by dosing phosphate to the water.

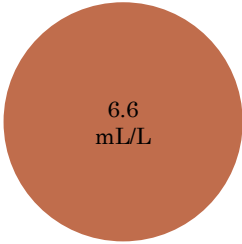
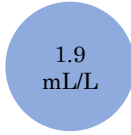
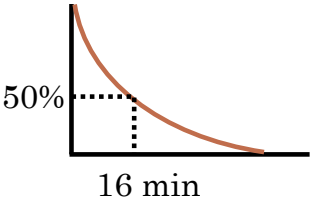
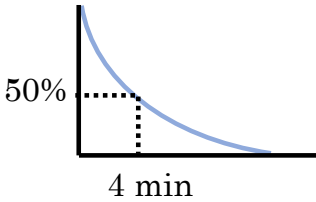

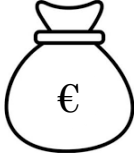
Natural groundwater was used to investigate the proposed method. A better understanding of the iron-phosphate chemistry was obtained in experiments with a synthetic iron solution. To find a possible alternative to the limited resource phosphate, the possibility of removing iron by forming a compact mineral was also tested by dosing sulphate and carbonate. The chemical equilibriums and carried out experiments were evaluated by a geochemical model and the reaction products were analysed by X-ray diffraction.

Up to 93% of iron removal by vivianite precipitation was obtained by dosing phosphate to anaerobic groundwater spiked with 100 mg Fe/L. An additional aeration step increased the efficiency to 99.9%, a higher total removal efficiency compared to the conventional aeration-filtration technique. The geochemical model showed that the anaerobic removal stopped when the saturation index (SI) of vivianite drops below 4, which explains why the last 7% were not removed anaerobically. Increasing the pH increases the SI of vivianite and can enhance further removal. Theoretically iron can be removed by vivianite precipitation starting from a concentration of 1 mg/L at a pH of 8.5. A second order kinetics was found for the removal of iron by vivianite precipitation at pH 7 with a rate constant of 2.27 M/s. The corresponding half life of iron is 4 minutes, while the half life of iron oxidation is 16 minutes at the same pH. Vivianite was the only crystalline end product detected and this decreased the sludge volume by a third compared to the sludge currently produced with oxidation and filtration.

The total iron removal by sulphate addition only reached 73%, probably caused by the formation of iron(III)-sulphate complexes, and is therefore not a proper alternative to phosphate. The addition of carbonate reached an anaerobic removal of 59% and was increased to 99.9% by aeration. The formed sludge contained of a mixture of several oxidised compounds and the volume was almost 6 times higher compared to the currently produced aqueous iron sludge, which is why carbonate is not considered as an interesting alternative.

The possibility of removing iron(II) anaerobically from groundwater by forming a compact mineral is successfully demonstrated. This method can increase the efficiency of drinking water production: higher throughput rates can be reached and a valuable end product with interesting reuse opportunities is created, provided that the phosphate can effectively be recovered from the water. It can decrease the operational costs of groundwater production substantially. The proposed novel method is a promising alternative to the conventional treatment method of oxidation and filtration, especially at plants where large iron sludge volumes are currently produced caused by elevated iron concentrations.

Graphical Abstract

	Conventional method Oxidation and filtration	Novel method Anaerobic vivianite precipitation
End product	Iron hydroxides $Fe(OH)_3$	Vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$
Sludge volume	 6.6 mL/L	 1.9 mL/L
Kinetics iron removal pH 7	 50% 16 min	 50% 4 min
Market value sludge	 €50/ton	 €10.000/ton

Acknowledgement

You are currently reading the result of 9 months of hard work with which I finish my master, thank you for your interest. I enjoyed diving into this new concept to remove iron from groundwater by vivianite precipitation and it felt really good to work in a lab again. The topic was a perfect blend of my obtained knowledge during my BSc Molecular Life Sciences (WUR) and my MSc Environmental Engineering (TU Delft). Finishing my thesis is not only the end of my master, it feels like the end of an era. And that is why I took the freedom to write an extensive acknowledgement.

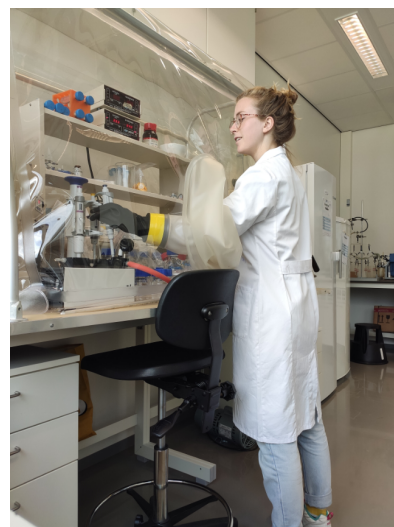
Although writing a MSc thesis is known to be challenging, I must say that I look back at it with grateful feelings. I owe this feeling to many people and I would like to start by thanking my supervisors. Simon Müller, you are an exemplary daily supervisor. Always there for me when I needed you, but never asking too much. Doris van Halem, thank you for your endless motivation and your believe in me. I am looking forward to being mentored by you for many more years, a real honour. Mark van Loosdrecht, you helped me finding answers when I was lost. Thank you for you guidance. All three of you have always given me very valuable and especially positive feedback, which I have found to be quite rare in academic environments. It highly encouraged me.

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It might be unusual, but in my believe very important: I would also like to thank myself. Although my favourite 'uitlaatkleppen' were all shut down and despite the many hours behind my desk in my sleepingroom, I stayed very enthusiastic and motivated and I can't wait to continue my career as a researcher. I could maintain this positive attitude because I feel empowered by the beautiful people around me.

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1 Introduction

The volume of water available below our feet is tremendous, it is estimated that 30.1% of freshwater present on earth is stored below the ground [2]. This voluminous water body is already used for at least 5000 years as the most used source of drinking water and serves approximately half the world population [3]. For the Netherlands, around 60% of the drinking water is produced out of groundwater [4].

Being stored deep in the ground, the resource is barely susceptible to pollution [5], which makes it particularly interesting as a source for drinking water. Anthropogenic activities, such as the increase in agriculture and industry, are however becoming a treat for the quality. Besides anthropogenic effects, the chemical quality of the water is mainly depending on hydro-geological conditions. The most common issue regarding water quality are elevated concentrations of iron and manganese present [4]. Natural variations in ammonium are also common. Other quality problems can be caused by the hardness or salinity of the water and in specific regions in the world, problems with arsenic, nitrate, hydrogen sulphide and methane can occur [6]. Proper treatment is therefore essential to ensure public health and safety when used as source for drinking water.

This research focuses on the removal of iron (Fe) from groundwater. Remaining iron present in drinking water can increase the turbidity of the water, causing aesthetic issues such as an unpleasant taste and colour and should therefore be removed. Maintenance costs and growth of bacteria on deposition in the pipelines are other reasons why removal of iron is essential [7]. The common treatment method to remove iron is oxidation followed by filtration, resulting in aqueous iron sludge as a waste product [4].

In this thesis a new approach is explored for the removal of iron from groundwater. Instead of converting the iron from the reduced iron(II) state to the oxidised iron(III) state as is commonly done, the environment is kept anaerobic to maintain the ferrous iron(II) state. It is explored if iron can precipitate with an anion, ideally forming a valuable and compact iron mineral as end product.

The research presented in this proposal is part of the overall RedOx filter project, in which a new approach is investigated aiming at making the treatment of groundwater more controlled, while also achieving higher throughput rates. It focuses on the biological and chemical redox reactions of the main groundwater constituents such as iron. By controlling the oxidation-reduction potential certain processes can be favoured, leading to more understanding of the reactions happening and the products formed. This research is a collaboration between Vitens, Dunea, NWO domain AES and TU Delft. Researching the anaerobic iron removal fits within this project, since it can contribute to understanding the interactions occurring in the systems and it might result in faster removal rates.

To introduce the topic of iron removal from groundwater, first an overview is given of common groundwater properties. Afterwards, a scheme of a common groundwater treatment chain is provided and the mechanisms of iron removal are discussed, including the characteristics of the iron sludge formed. An outlook of iron treatment in the future is given and subsequently the possibility of anaerobic removal is more extensively discussed. The chapter ends with the research questions defined for this thesis.

1.1 Groundwater Properties

The composition and quality of groundwater can vary per area, influenced by both anthropogenic and natural causes such as different soil types. Knowing the common constituents of groundwater is essential for understanding the processes occurring and therefore typical groundwater properties are assessed in this section. Each component is shortly discussed and, if applicable, the possible influence and interactions with iron are emphasized. This section will help to estimate which possible minerals might form with iron(II) or which constituents might hinder the formation of certain iron(II) minerals.

Since the quality can vary a lot per groundwater well, an overview is given in Table 1.1 of the average values derived from 21 different groundwater wells at different areas in the Netherlands from drinking company Vitens between 2018 and 2020 [8]. To give an idea about the range in which the concentrations can fluctuate, also the minimal and maximal values are given.

Table 1.1: The average, lowest and highest values of the main groundwater constituents in 21 wells from Vitens.

Compound	Average	Lowest	Highest	Unit
H ⁺	7.4	6.6	7.9	pH
Fe ²⁺	4.15	0.3	13.5	mg/L
Mg ²⁺	6.99	2.19	29.5	mg/L
Ca ²⁺	65.97	33.58	126	mg/L
NH ₄ ⁺	0.86	0.11	4.34	mg/L
HCO ₃ ⁻	221.77	81.3	466.9	mg/L
SO ₄ ²⁻	22.4	<2.0	60.8	mg/L
Cl ⁻	35.9	8.0	151.6	mg/L
NO ₃ ⁻	8.92	<1.0	15.3	mg/L
SiO ₄ ⁴⁻	28.45	17.4	52.3	mg/L
CH ₄	5.14	<0.005	42.8	mg/L
Mn ²⁺	0.35	0.082	1.1	mg/L
HPO ₄ ²⁻	0.50	<0.057	1.1	mg/L

pH: The values for pH in the wells measured from Vitens are fluctuating around a neutral pH. Minor changes can already have a large influence on chemical reactions. The effect of pH on the appearance of iron is visible in the pourbaix diagram of iron (Figure 1.1). The pH will not only affect the appearance of iron, but the appearance of every specie present and therefore influence the possible interactions with iron. Also the oxidation rate of iron is strongly depending on pH, a 100 times increase is expected for each unit pH increase. A low pH means a slow oxidation [4].

Iron: The occurrence of iron in water is natural, since it is one of the most abundant metals of the Earth's crust. In anaerobic conditions and with the presence of reducing agents such as organic matter (OM), iron can be released from iron containing rocks [4]. An anthropogenic origin of iron in groundwater resulting from mining [9] or by leaching from a landfill [10] is also possible. The variation in iron concentration (0.3 - 13.5 mg/L) is quite large, which is important to keep in mind since iron is the target component in this research. The concentrations reported in Table 1.1 are not very high, but concentrations up to 50 mg Fe/L are common globally [9]. Also in the Netherlands, there are areas where such high iron concentrations are present [11]. The iron is mainly present as the divalent ion Fe(II) in groundwater, oxidation of iron results in ferric hydroxides, which can cause blockage in the network [12].

Magnesium and calcium: The concentration of magnesium and calcium ions determine the hardness of the water. In general the water of Vitens is semi-hard. Varieties are caused by differences in the amount of lime present in the soil [12]. Both magnesium and calcium are also divalent cations, competition during precipitation with an anion can be expected. This might decrease the removal efficiency of iron and this

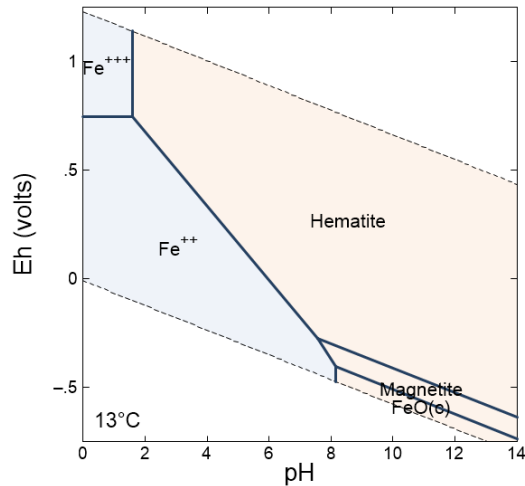


Figure 1.1: Pourbaix diagram of the iron species under different conditions, created with GWB® Act2. Concentration iron 4.15 mg/L (as in Table 1.1).

influence is important to consider when exploring the possibilities of anaerobic iron(II) removal.

Ammonium: High ammonium concentration are often reported in the Netherlands, mainly due to high organic matter (OM) content [13]. It is not expected that this constituent has much influence on the anaerobic removal of iron(II).

Carbonate: When infiltration of rain- or irrigation-water occurs, certain rocks (e.g. limestone and dolomite) can release carbonate. This can increase the concentration in groundwater [14]. It can alter the pH and carbonate can precipitate with iron(II) to form siderite (FeCO_3) [15]. Concentrations of carbonate are therefore important in this research.

Sulphate: Sulphate in groundwater is very mobile and can be reduced and eventually precipitate to iron(II) sulfide (FeS) or pyrite (FeS_2). When traces of iron(III) are present, the formation of green rust ($[\text{Fe}_4^{2+}\text{Fe}_2^{3+}(\text{OH})_{12}]^{2+} \cdot [\text{SO}_4^{2-} \cdot 2\text{H}_2\text{O}]^{2-}$) is also possible [16]. In general the concentration of sulphate is decreasing with time in the Netherlands, but the concentrations as in Table 1.1 are relatively high and the possible effect of sulphate should be kept in mind.

Chloride: The concentration of chloride varies due to intrusion of salt water. Concentration differences in the Netherlands are common. Water is called brackish when it has a concentration of more than 150 mg Cl- per litre [12]. The highest value is just above this value, but in general it can be concluded that Vitens has mainly fresh water in the researched wells. Salt formation out of iron(II) and chloride is not expected.

Nitrate: Fertilisers can increase the concentration of nitrate in the groundwater, which is a serious threat when ending in drinking water [12]. Since it is a very mobile compound, the concentrations can vary quite a lot since it is easily flushed to ground- and surface-water. Under anaerobic conditions, denitrification (if OM is present) takes place which removes the nitrogen from the groundwater. The target value determined by RIVM is 25 mg/L [12]. The values obtained by Vitens are well below this value, probably due to nitrification.

Silicate: As many constituents, also silicate ends up in groundwater by water-rock interactions. The variation in concentration is mainly depending on the contact time with the rocks and therefore depends on the residence time [17]. It can form several minerals with iron, such as minnesotaite, olivine and fayalite. The formation rate of silica rich minerals is however often low [18], but the possible formation might influence the iron removal. Silica is known to interfere with the iron removal process, it can react with the iron hydroxides affecting crystallinity and eventually the floc formation [4].

Methane: The variation in concentration of methane is large. Methane can either have a microbiological origin or the gas can migrate into the aquifers from reservoirs or leaking infrastructure. The presence of methane itself in the groundwater is not a direct threat to human health, but it does contribute to higher anthropogenic emissions of greenhouse gasses [19]. It can also change the redox conditions in the water, which can influence the state of iron (Figure 1.1) and the possible formation of minerals with iron. The variation in methane concentration in Table 1.1 is very large, so it is expected that the effect will vary largely per location.

Manganese: Manganese is an important constituent that should be removed before the water is distributed as drinking water. It is also a divalent cation and it can compete [20] or co-exist [21, 22] with iron in certain minerals which might hinder the removal efficiency of iron. The average concentration is lower than iron, but also fluctuating per well. The influence on iron removal probably depends on the available concentration of both iron and manganese and is important to consider.

Phosphorus and phosphate: Phosphorus and phosphate are again products of the break down of OM. Since it is one of the main components of fertilisers, increased levels are detected in shallow and semi-shallow groundwater [13]. Also sewage discharges is a cause of elevated levels in the environment. It is not a dangerous compound for humans, but can cause eutrophication in the environment. The mineral vivianite can form with iron(II) and phosphate, often detected in wastewater treatment plants [23, 24] and anaerobic natural environments [21, 25]. This makes it an interesting compound for the possible removal of iron(II) from groundwater.

Oxygen: Two other important properties of groundwater not noted in Table 1.1 are the oxygen concentration and the temperature. The oxygen concentration is very important to consider for the removal of iron(II), since it influences the state of the iron ions. When iron(II) is oxidised to iron(III), it is not soluble anymore and the ions will directly react to form different kind of compounds, mainly hydroxides [26]. In general, the groundwater is in anoxic conditions and it is expected to find very low values of dissolved oxygen (DO).

Temperature: The temperature of groundwater at 125 meters depth is generally around 13 °C [27]. The temperature is often very stable and possible fluctuations will have a limited affect on the state of iron and the possible minerals that can form [15, 28, 29]

1.2 Iron Removal in Groundwater Treatment

Several methods exist to effectively remove iron from groundwater and the best strategy often depend on the quality of the raw water. The methods can be divided in 4 different types of strategies; several conventional strategies exist, biological strategy, membrane technology-based strategy and nanotechnology based strategy [30]. The most commonly applied method around the globe is the conventional strategy of oxidation and filtration [4], of which a possible treatment chain is depicted in Figure 1.2. During oxidation the common groundwater constituents iron, manganese and ammonium are converted to the oxidised form. Soluble, ferrous iron is hereby converted to its ferric form which is insoluble. Advantages of this relatively easy treatment chain is the simple operation and oxidation also strips several gasses such as CO₂, H₂S and CH₄. An oxidising agent is sometimes dosed to enhance oxidation [30], but in many cases no chemicals are required [4]. The produced water is either ready for distribution, or an extra treatment step is necessary such as ion exchange or membrane filtration [31] to obtain the recommended iron concentrations in the product water.

The World Health Organization (WHO) recommends to have a maximum iron concentration of 0.3 mg/L in the production water. The European Union sets a higher standard of 0.2 mg/L and the guideline in the Netherlands is a concentration below 0.05 mg/L. The Dutch drinking water companies even aim at a max of 0.03 mg/L, to reduce the maintenance cost to the system [4].

1.2.1 Method of Oxidation and Filtration

Although the method of oxidation and filtration is commonly applied, not all interactions are fully understood yet. Three processes are known to play a major role in the removal of iron; homogeneous, heterogeneous

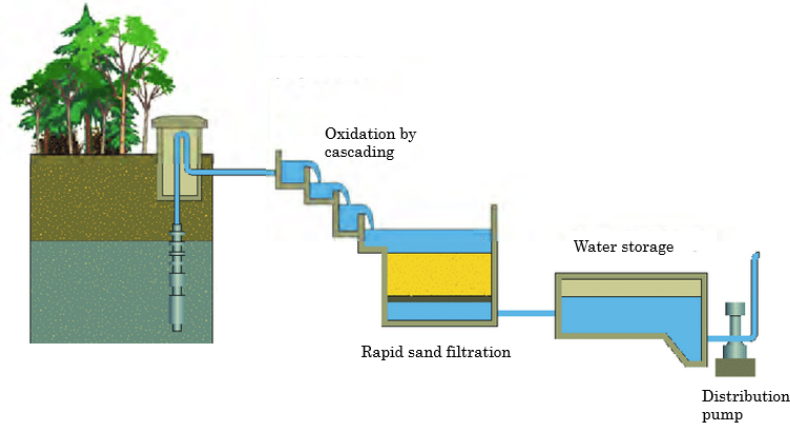


Figure 1.2: A common treatment chain applied in groundwater treatment including oxidation and filtration. Modified figure from De Vet [1].

and biological oxidation [32]. In the first process, soluble iron(II) is oxidised to iron(III) and subsequently precipitates [32]:



In heterogeneous oxidation iron(II), binds to the filtermedia after which oxidation to iron(III) occurs [32]. This layer stimulates the adsorption of other iron(II) molecules, which are subsequently oxidised. The latter mechanism occurs mainly when oxygen concentrations are lower and the pre-oxidation time limited, but often both processes are observed during treatment [33].

The mechanism of biological removal is less known, but increasingly reported [34]. The efficiency and lower costs makes it an interesting mechanism [34]. It is expected that the bacteria need large amounts of iron to grow [35].

1.2.2 Kinetics Iron Oxidation

In this research, the goal is to remove the iron by forming a compact mineral with iron(II). To evaluate the outcomes a comparison will be made with the oxidation and filtration method. The anaerobic iron removal will be compared to the conventional homogeneous removal efficiency, since vivianite formation is also a homogeneous and abiotic reaction. The kinetics of homogeneous oxidation follows first-order removal with respect to iron(II) at constant pH and is frequently reported; different values for the rate constant of k are published, depending on different parameters of the system. In this study the rate constant determined by Schenk and Weber Jr [36] at 25 °C is used: $k = 2.1 \cdot 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$. The rate law of iron removal by oxidation becomes [37]:

$$\frac{d}{dt}[Fe(II)] = k[OH^-]^2 P_{O_2} [Fe(II)] \quad (1.2)$$

The rate of removal is strongly depending on pH. To visualise this, Figure 1.3 shows the iron removal over time at pH 7 and P_{O_2} of 0.21 atm and the range of this removal between pH 6.5 (slower removal) and 7.5 (faster removal). This is a visualisation of the integrated rate law, which is:

$$[Fe(II)] = [Fe(II)]_0 e^{k_1 t} \quad (1.3)$$

in which

$$k_1 = k \cdot [OH^-]^2 \cdot P_{O_2} \quad (1.4)$$

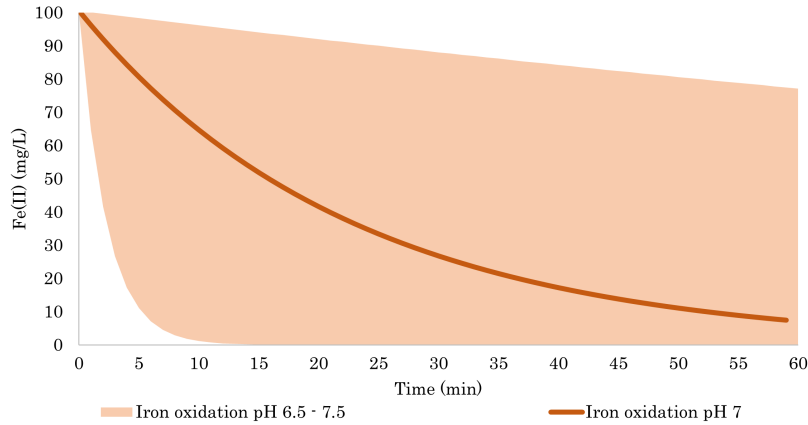


Figure 1.3: The kinetics of iron removal in natural groundwater for iron oxidation between a pH of 6.5 (upper limit, slower removal) and 7.5 (lower limit, faster removal) at a P_{O_2} of 0.21 atm.

1.2.3 Iron Sludge

Precipitated iron in the filter is removed from the filterbed by backwashing and separated from the stream by settling [38]. The formed iron sludge is produced in large quantities around the world. Treating 5000 ton of groundwater with an iron concentration of 7 mg/L results in approximately 1 ton of sludge [39]. It is estimated that 10,000 ton of sludge is produced per day globally [40] and that this production will double over the coming decade [41].

The marketvalue of the sludge depends on the end-use. In certain countries, the sludge is treated as waste and ends up in an incinerator or in landfill [38, 42]. In the Netherlands, the company Aquaminerals handles the produced sludge from treatment plants all over the country. Their currently published value of iron sludge is approximately €50/ton and mainly used as a sulphur neutraliser in biogas plants [43].

1.2.4 Iron Removal in the Future

Oxidation and filtration is already used for centuries and will probably remain a common method for the removal of iron from groundwater. At higher iron concentrations or when iron has formed complexes with organic matter (OM) the method is however limited [4]. At high OM, the iron(III) is known to reduce back to iron(II). Different strategies exist to solve these problems, such as the more recently developed membrane and nanotechnology-based solutions [30]. Membrane based technologies are however known to be relatively expensive and a disadvantage of nanotechnologies are the possible need of costly and toxic chemicals [30].

Reusing the iron sludge is considered as the most important step in increasing the sustainability of the industry [42]. Aquaminerals is reporting an increase in earnings for iron sludge [43], but the expected increase in sludge production should be acknowledged. For Vitens, the costs of sludge discharge are often still higher than the earnings [44] which, together with a need to increase the sustainability, are important reasons for the need of an efficient alternative.

1.3 Anaerobic Iron Removal

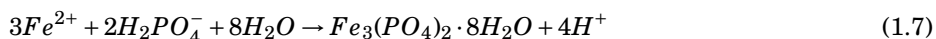
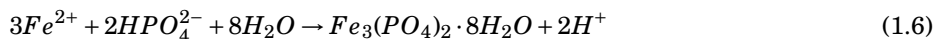
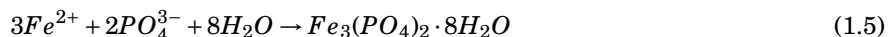
To full fill this need, a new approach of removing iron from groundwater is investigated in this research. Up to now, the iron removal processes are mainly based on oxidation to the insoluble iron(III). In this research, a novel concept of removing iron(II) anaerobically from groundwater by precipitation to a mineral is investigated.

This concept is coming from the field of wastewater treatment, reactions with iron(II) are here used to recover phosphate from the water as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) [23, 29, 45, 46, 47, 48]. Iron(II) and phosphate often occur naturally in wastewater and iron can also be dosed to improve the settleability of sludge [49] and for odour control [50]. Several studies have revealed that vivianite is actually the major iron-phosphate compound found in wastewater sludge [24, 48, 51] and that iron(III) is barely present [52].

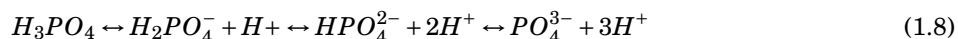
The hypothesis of this research is based on this concept: iron(II) can be removed from groundwater by anaerobically dosing phosphate to form the mineral vivianite. Forming a compact mineral might decrease the volume and increase the value of the sludge produced, contributing to a more sustainable treatment chain. Dosing phosphate, a limited resource on earth, to recover the abundant element iron is however counter intuitive. Therefore, this research will also look into alternatives to phosphate; other anions that can precipitate anaerobically with iron(II) are also considered. Since vivianite recovery is already studied a lot in wastewater treatment systems, a review on the thermodynamics and general process conditions under which this can form is given in the next section, to assess the possibility of formation in groundwater environments.

1.3.1 Vivianite

Vivianite can form with iron(II) and phosphate with either free [46] or protonated phosphate [29]:



The speciation of phosphate is depending on pH and shown in Figure 1.4. The corresponding reaction equation is described as follows:



At pH levels commonly present in groundwater (pH 5-8), phosphate is mostly protonated. The formation of vivianite will release protons, thereby causing a drop in pH. The speciation of phosphate influences the saturation index (SI) of vivianite, which is an indicator if the mineral can precipitate in a certain environment. The expression of the SI is [23]:

$$SI = \log \frac{IAP}{K_{sp}} \quad (1.9)$$

Different solubility constants are reported for vivianite [29], but the one mostly reported is determined by Al-Borno and Tomson [28]; $K_{sp} = 10^{-36}$. With the formula of vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ the ion activity product (IAP) follows:

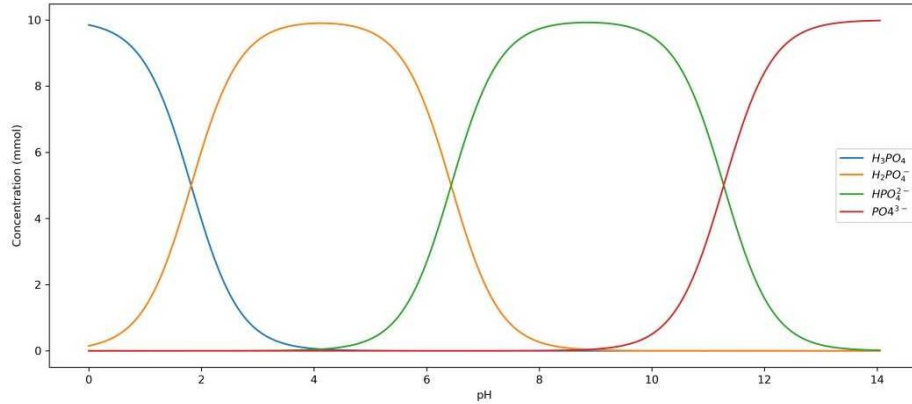


Figure 1.4: Phosphate speciation of 10 mM H₃PO₄ solution at 20 °C between pH 1 and 14 modelled with PHREEQC Version 3 by Simon Müller.

$$IAP = (\gamma_{Fe^{2+}} \cdot C_{Fe^{2+}})^3 (\gamma_{PO_4^{3-}} \cdot C_{PO_4^{3-}})^2 \quad (1.10)$$

in which the activity coefficient is determined with the Guntelberg approximation of the Debye-Hückle limiting law [29]:

$$\log \gamma_i = -Az_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (1.11)$$

and

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (1.12)$$

with

- SI: saturation index
- IAP: ion activity product
- K_{sp} : solubility product of vivianite, value for 25 °C: $K_{sp} = 10^{-36}$ [28]
- γ : activity coefficient of the denoted ion in the solution (mol/L)
- A: temperature dependent parameter, value for water, 25 °C: 0.51 (-)
- z_i : charge of ion i
- I = ionic strength
- c = concentration (mol/L)

Theoretically formation of vivianite can occur when its SI is positive, the higher the value the more likely the formation. This parameter is however limited, factors like kinetics and activation energy also play a role in the

formation but are not included in this definition [23]. Liu et al. [29] found that the formation of vivianite was greatly enhanced at a SI between 4 and 11. Below 4, the formation is very slow and above 11 the metastable limit is reached. At a pH below 6, the SI is insufficient for vivianite to precipitate [29]. There are 3 factors influencing the SI value of vivianite formation caused by pH differences; 1) the speciation of both iron and phosphate depend on the pH (Figure 1.1 and Figure 1.4), 2) a shift in pH changes the concentrations of OH^- and H^+ ions, effecting the ionic strength (Equation 1.11), and 3) at a higher pH more OH^- is available to trap the free iron(II) ions making them unavailable for vivianite precipitation [46].

Besides the possibility of vivianite formation, indicated by the SI, the rate of vivianite formation is also of importance when applied in a drinking water system. Liu et al. [29] assumed a zero order kinetics and determined a nucleation rate constant for vivianite formation of $5 \cdot 10^{-06}$ M/s. This is the only reported study to the kinetics of vivianite formation so far and therefore the kinetics will also be calculated for the experiments done in this research and compared to the published value and to the kinetics of iron removal by oxidation.

1.4 Research Questions

The novel concept of removing iron(II) from groundwater is investigated in this study. The main research question defined is:

How can iron(II) be removed from groundwater anaerobically by forming a compact mineral and what is the efficiency compared to the conventional method of oxidation and filtration?

The question consist out of two parts, of which the first one will be determined by a chemical laboratory study. The results will give an outlook for the second part of the question; if this can make drinking water more efficient than the conventional method. The main question is broad, to find the answer to this question the research is divided in several parts for which sub questions are defined. In the first part, the focus is on obtaining a proper understanding of the iron-phosphate chemistry to find out if vivianite can form under groundwater conditions:

- What is the removal efficiency of iron by vivianite precipitation and how does this depend on kinetics, initial iron concentration and the ratio of dosed phosphate to iron?

In the second part, finding an alternative to phosphate is the main goal:

- Which anions can precipitate with iron(II) under groundwater conditions and what is the efficiency compared to dosing phosphate?

To compare the concept of anaerobic iron removal to the currently applied technique of oxidation and filtration, the following sub questions are defined:

- What is the removal efficiency of iron by anaerobic removal compared to the conventional method of oxidation and filtration?
- What is the difference in sludge volume formed during anaerobic iron(II) removal compared to the currently produced iron sludge?
- What is the value of the sludge formed during anaerobic iron(II) removal compared to the currently produced iron sludge?
- What is the difference in operational costs of anaerobic iron(II) removal compared to the conventional method of oxidation and filtration?

Eventually, an outlook will be given of the possibilities of applying anaerobic iron(II) removal in practice:

- How can anaerobic iron(II) removal be applied in a current existing groundwater treatment plant?

2 Methodology

2.1 Outline Experiments

The experiments done to investigate the possibility of anaerobic iron removal from groundwater, can be divided in 3 parts. An overview of the experiments is given in Figure 2.1. Several experiments were also simulated with the geochemical model Geochemist's Workbench[®] (GWB) (Student Edition) as indicated in the figure. In the first two parts a synthetic iron solution was used, experiments with natural groundwater were done in the third part.

The main goal of the first set of experiments was to understand the interaction between phosphate and iron and finding out if iron can indeed be removed by forming a mineral. The kinetics, ratio of dosed phosphate and the initial iron concentration were varied in these experiments. Eventually, the formed product is analysed.

In the second part, the experiments focused on finding an alternative to phosphate. Which anions can function as an alternative was first determined by making pourbaix diagrams with GWB[®]. With the possible alternatives, the anaerobic and aerobic removal efficiencies and the sludge properties were determined.

In the third part the composition of the natural groundwater was analysed and two sets of experiments were done; one using the natural iron concentration of the water and one with an overdose of iron. The kinetics, total removal and the sludge properties were again determined. The experiments simulated with the geochemical model were compared to the laboratory outcomes. More details of this model are given in the next section.

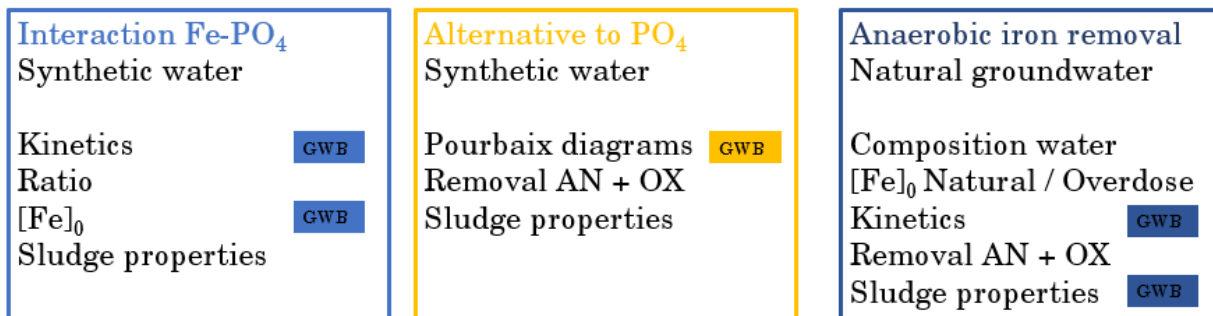


Figure 2.1: An overview of the experiments done and labelled with GWBB[®] (Geochemist Workbench) if the experiments were modelled.

2.2 Geochemical Model

To evaluate the experiments carried out in this research and to get an insight in the chemical equilibrium and the possibility of forming a mineral, simulations were done by *GWB*[®]. The model was used for 3 purposes: 1) to determine the saturation index for vivianite formation for a better understanding of the iron phosphate interaction, 2) to find which anions can form a mineral with iron(II) and thereby serve as an alternative to phosphate and 3) to simulate the experiments with natural groundwater.

For the first purpose, the program *Spec8* was used which can calculate speciation in solution and gives the saturation of possible minerals in the system. The input was the measured iron and phosphate concentrations, pH and temperature. An overview of the inserted data is given in Appendix B.

To find an alternative for phosphate, *pourbaix* diagrams were generated with the program *Act2*. This shows the stability of minerals under certain pH and Eh conditions. The average iron concentration of 4.15 mg/L as presented in Table 1.1 was inserted and the main anions present in groundwater with the concentrations as presented in the same table were added to the model individually, to observe the possible minerals that can form with iron(II) with each anion. *Act2* requires an activity as input, for which the activity coefficient must be determined as explained in subsection 1.3.1. This was again done with *Spec8*. All the species together in solution, as presented in Table 1.1, were inserted after which the model determined the activity coefficients.

The experiments in which natural groundwater was used were simulated by *Spec8*. This time not only iron and phosphate were inserted, but also the other compounds present in groundwater. A detailed overview of the input is given in Appendix F. As an outcome, the SI of different minerals that are thermodynamically favoured to form are expected and this is compared to the sludge formed in the laboratory experiments.

2.3 Setup

To illustrate the general setup used in the experiments, a schematic overview is given in Figure 2.2. A 500 mL reactor containing either an oxygen-free synthetic iron solution or natural groundwater was placed on a magnetic stirrer inside an anaerobic chamber. While mixing continuously, a solution containing an anion was added after which the solutions could react anaerobically for an hour. Samples taken during or after the reaction were filtered through a 0.45 μm non-sterile PDVF syringe filter, acidified with oxygen-free HCl to bring the pH below 4 and stored inside the anaerobic chamber. To prepare the samples for XRD analysis, the suspension was vacuum filtered with a 0.45 μm PALL 'supor membrane'. More details on the development of this method can be found in Appendix A. If an oxidation step was added after the anaerobic reaction, the reactor was removed from the anaerobic chamber and oxidised by flushing with compressed air. To determine the sludge volume, the suspension was transferred to a plastic Imhoff cone of 1L. The volume of the liquid and sludge was measured after a day of settling. Room temperature was used during all experiments, which was approximately 21 °C. More details on the anaerobic chamber, the chemicals, the analysis done and the probes used is presented in the coming paragraphs. Parameters that varied between the different experiments, such as initial iron concentration or the anion that was added, will be presented per experiment in section 2.4.

2.3.1 Anaerobic Environment

All anaerobic experiments were conducted in an anaerobic chamber. A vinyl (PVC) anaerobic chamber (Coy's Lab) filled with a gas mix of 5% hydrogen and 95% argon gas (impurity < 200 vpm) was used. An airlock made transfer possible, while minimizing changes in the anaerobic atmosphere. Three palladium catalysts inside kept the oxygen level at approximately 0-5 ppm. The catalysts were regenerated every week. Water vapor was entrapped by silica beads. A hygrometer tracked the water level in the anaerobic chamber and when exceeding 70% at 21°C the silica beads were refreshed.

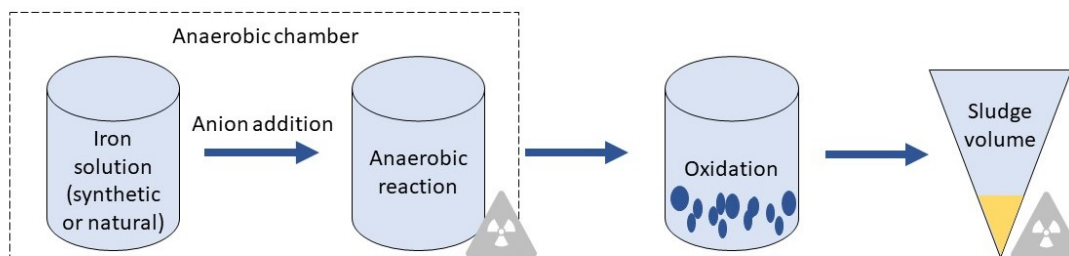


Figure 2.2: The general setup of the experiments carried out in this thesis.

2.3.2 Chemicals

All solutions prepared inside the anaerobic chamber were made with deoxygenated, demineralised water, by flushing the water with N_2 gas (impurity < 200 vpm) for at least 45 minutes before bringing the water inside the anaerobic chamber. The oxygen concentration of the solutions was always below 0.05 mg/L. The required chemical for a solution was weighted outside the anaerobic chamber and once brought inside the chamber, dissolved in the oxygen-free demineralised water and stored anaerobically. All chemicals used met or exceeded the ACS reagent grade and were used without further purification.

2.3.3 Analysis

Iron concentrations were determined with the standard method of the LCK320 kits (HACH) for iron(II)/(III). Phosphate concentrations were determined with the standard method of the LCK 348 kits (HACH). A HACH DR3900 VIS spectrophotometer was used to measure the concentrations.

In the experiments in which groundwater was used, the samples were both analysed with the HACH kits as with inductively coupled plasma mass spectrometry (ICP-MS). For the ICP-MS, total Fe and P were measured and also Na, Mg, Si, S, Ca, Mn, Zn and As. The samples for ICP-MS were acidified by adding 65% ultrapure HNO_3 to 1 volume percentage.

Analyses of the sludge formed during the reactions were done by X-ray Diffraction (XRD). The best method for the handling of these samples was determined and explained in Appendix A. After vacuum filtering a solution, the filter was sealed with aluminium foil and dried for a day. Afterwards, the filter was covered with a layer of glycerol to minimise oxidation during XRD analysis. The method with glycerol is used for handling green rust samples [53], but has not yet been tested for vivianite. It increases the ease of sample handling tremendously compared to methods reported in literature [23, 45].

A Bruker D8 Advance diffractometer with Cu-K α radiation was used for the XRD analysis. The measurements were done with coupled $\theta - 2\theta$ scan $10^\circ - 120^\circ$, step size $0.030^\circ 2\theta$, counting time per step 2 s. Bruker software DiffracSuite.Eva vs 5.2 was used for the data evaluation. The measurements and data evaluations were done by Ruud Hendriks, at the materials science and engineering department at TU Delft.

Statistical analysis were done at results where the experiments were done in duplo. To compare the results among each other an analysis of variance (ANOVA) test was done. If the change was less than 5% that the results were different by accident, corresponding with a probability value (p-value) of 0.05, the difference was considered significant.

2.3.4 Probes

The pH, ORP, EC and temperature were measured during the experiments with the SensION+ MM150 from HACH with the multisensor 5048. The dissolved oxygen concentration was measured with an optical dissolved oxygen sensor (WTW, FDO® 925). An overview of the accuracy of the probes:

pH	0.02 pH
ORP	1 mV
EC	0.5%
T	0.2 °C
DO	1.5 %

2.4 Experiments

As presented in Figure 2.1, three types of experiments were done with the previous explained setup. An overview of the parameters per experiment is given in Table 2.1. In experiments done to study the interaction between iron and phosphate and to find an alternative to phosphate, synthetic water was used. In the last part of the experiments, natural groundwater was used. The varied parameters per experiment is presented in italics. More details on each set of experiments are presented in this section.

Table 2.1: The parameters of the different experiments carried out in this thesis. The varied variable per experiment presented in italics.

Parameter	Unit	Synthetic water						Natural groundwater		
		Interaction Fe·PO ₄				Alternative to PO ₄		Anaerobic iron removal		
		Ref	Kinetics	Ratio	[Fe] ₀	CO ₃	SO ₄	Ref	PO ₄	CO ₃
Added anion		-	PO ₄	PO ₄	PO ₄	CO ₃	SO ₄	-	PO ₄	CO ₃
Initial Fe conc	mg/L	100	100	100	<i>Varies</i>	100	100	<i>3/100</i>	<i>3/100</i>	<i>3/100</i>
Reaction time AN	min	-	<i>Varies</i>	60	60	60	60	-	60	60
Aeration time	min	60	-	-	-	10	10	10	10	10
Oxidation time	min	60	-	-	-	60	60	60	60	60
Ratio anion:Fe	molar	-	1:1	<i>Varies</i>	1:1	1:1	1:1	-	1:1	1:1
Analysis		HACH	HACH	HACH	HACH	HACH	HACH	HACH/ICP-MS	HACH/ICP-MS	HACH/ICP-MS
Sludge volume		✓				✓	✓	✓	✓ (overdose)	✓ (overdose)
XRD		✓		✓		✓	✓	✓	✓	✓
Temp	°C	21	21	21	21	21	21	21	21	21

2.4.1 Interaction Iron-Phosphate

To increase the understanding of the interaction between iron and phosphate, four experiments were conducted with a synthetic iron solution. This iron solution was made from dissolving FeCl₂, for reasons discussed in Appendix A. A reference experiment with 100 mg Fe/L was done to simulate the conventional treatment of oxidation and filtration, to eventually compare the final removal efficiencies. No anion was added and no anaerobic reaction took place. The standard parameters during the anaerobic experiments were a reaction time of 60 minutes, an initial iron concentration of 100 mg/L and a 1:1 ratio of phosphate to iron added. Each of these parameters was however varied in an experiment, as marked in Table 2.1. The pH was measured at the start of each experiment and when a sample was taken during an experiment. The pH was also necessary as an input for the program SpecE8 of GWBB®, in which the explained experiments were simulated to calculate the SI of vivianite at the different process conditions.

In the experiment in which the reaction time was varied, samples were taken at minute 1, 5, 10, 15, 20, 30, 40, 50 and 60 to measure the iron concentration and determine the removal. A final sample was taken

the next day, to ensure the reaction had stopped after 60 minutes. From these results, the kinetics of iron removal by vivianite precipitation will be determined. In another experiment, the initial iron concentration was varied between 1, 5, 10, 25, 50 and 100 mg/L. To test the influence of the amount of phosphate added, the ratio phosphate:iron is varied from 0.5, 0.67 (theoretical ratio of vivianite) 1, 2 and 9. The corresponding concentrations of phosphate to these ratios are 85, 114, 170, 340 and 1530 mg PO₄/L.

2.4.2 Alternatives to Phosphate

In Figure 2.1 the experiments done in the second part are depicted in light blue. Carbonate and sulphate are tested as alternative to phosphate, based on the outcome of the GWB[®] model (subsection 3.2.1. An oxidation step was added after the anaerobic reaction step, in which compressed air was flushed through the solution for 10 minutes. Afterwards, the reactor was let exposed to air for another 50 minutes to have a total oxidation time of an hour. The compounds used as phosphate, sulphate and carbonate source were Na₂HPO₄, Na₂SO₄ and Na₂CO₃ dissolved in oxygen-free water.

2.4.3 Anaerobic Iron Removal in Natural Groundwater

In the final part of the experiments, natural groundwater was used instead of a synthetic iron solution as depicted in yellow in Figure 2.1. The groundwater was collected at well 20 at the groundwater treatment plant from Vitens in Loosdrecht. At the well, 15 mL samples were taken and acidified directly with 0.1 mL 60% HNO₃. These were analysed by ICP-MS to determine the composition of the groundwater.

The water used for the experiments with groundwater, was collected in 1L Schott bottles and transferred to the anaerobic chamber in the laboratory in Delft. To avoid oxidation to iron(III), it was made sure that no air bubbles were present in the bottles. The sampling method to achieve this, was to place the inflow water tube at the bottom of the bottle while sampling and the bottle was overflowed approximately ten times and filled completely. The bottle was closed with a rubber stop and a GL45 cap. High vacuum grease (dow corning) was used to insert the rubber stops. It was made sure that the bottles contained no air bubbles. Before the start of the experiments, the composition of the water was analysed by ICP-MS both before and after vacuum filtration and compared to the samples taken and acidified directly at the well, to check if the transport caused any conversions of groundwater constituents.

In Table 2.1 the process conditions of the experiments with groundwater are shown. Four different experiments were done, varying in the initial iron concentration (natural or overdose), and varying in the anion added (phosphate or carbonate). The groundwater was spiked with a FeCl₂ solution to increase the iron concentration to 100 mg/L in the experiments with an overdose. The total reaction time was one hour, but to determine the kinetics samples were taken during the reaction with phosphate at minute 1, 5, 15 and 60 both during the anaerobic step as during the oxidation step. For carbonate, samples were taken at minute 1 and 60 anaerobically and aerobically the same time steps were used as with phosphate. The pH was measured continuously throughout the experiments, which was also necessary to simulate the experiments with the program SpecE8 of GWB[®].

A reference experiment was carried out with groundwater, to which no anion was added and no anaerobic reaction took place. The solution was only aerated and filtered before the final iron concentration was measured. Also the two different initial concentrations were used here. For the reference experiment with natural initial iron concentration, samples were taken during oxidation at minute 1, 5, 15 and 60. For the reference experiment with an overdose of iron, samples were taken during oxidation at minute 1 and 60. The kinetics of iron removal by vivianite precipitation were calculated from the results obtained in this research and compared to the kinetics of iron removal by oxidation. The kinetics of iron removal by oxidation is widely reported and therefore the values published by [37] were used to calculate the reaction rate of iron removal in a pH range of 6.3 to 8.

3 Results

3.1 Interaction Iron-Phosphate

Iron removal by precipitation with phosphate to form vivianite was observed under most process conditions applied in the first set of experiments to study the interaction between iron and phosphate. The conditions are presented in this section: the results of the iron removal efficiency over time, the corresponding ratio of removed phosphate to iron, the removal efficiency at different dosed phosphate to iron ratios and the removal efficiency at different initial iron concentrations are presented in Figure 3.1.

A maximum iron removal of approximately 73% was observed after 10 minutes (Figure 3.1a), the kinetics are further explained in subsection 3.1.2. An additional measurement the next day, not shown in the graph, did not show any further removal. The ratio of removed phosphate to iron was always very close to the theoretical value of vivianite, which is 0.67 (Figure 3.1b). This graph also shows that the method used caused very little oxidation of iron(II) to iron(III), less than 3% was oxidised during the experiments conducted in the anaerobic chamber. An increase in removal efficiency was obtained when more phosphate was dosed; a ratio phosphate to iron of 2 caused a removal of iron of almost 98% (Figure 3.1c). When the theoretical ratio (0.67) of phosphate to iron needed to form vivianite was dosed to the iron solution, the removed ratio was also 0.67. The XRD results presented in the next section will confirm which products were formed. At iron concentrations below 25 mg/L the removal efficiency obtained in the experiments was less and little vivianite precipitation was observed (Figure 3.1d).

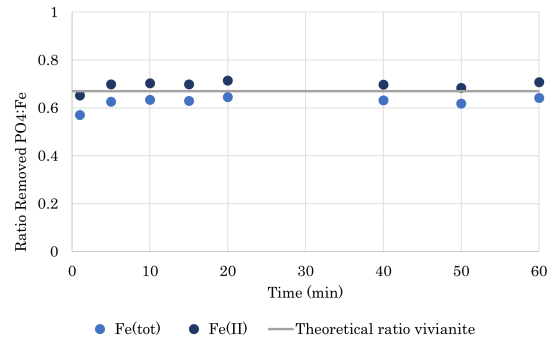
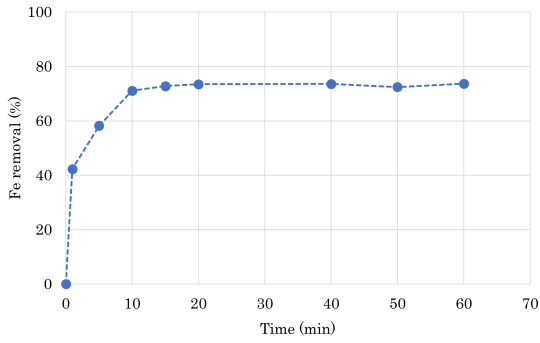
Adding an oxidation step after the anaerobic precipitation of iron with phosphate increased the removal efficiency to 99.2% as visualised in Figure 3.2. This value is very close to the 99.5% removal obtained with the reference experiment in which only iron was oxidised.

3.1.1 Saturation Index

The saturation index of each measurement point as depicted in Figure 3.1a and Figure 3.1d was determined with GWB® SpecE8. The input and detailed results are presented in Appendix B. A summary of the most important results are presented in this section. The SI is depending on pH (Equation 1.9). No pH measurements were done during the experiment in which different phosphate dosages are added, so this experiment could not be simulated.

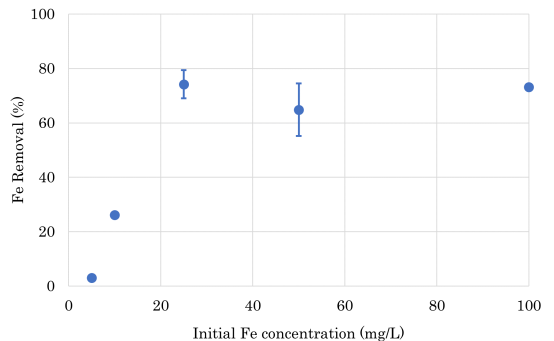
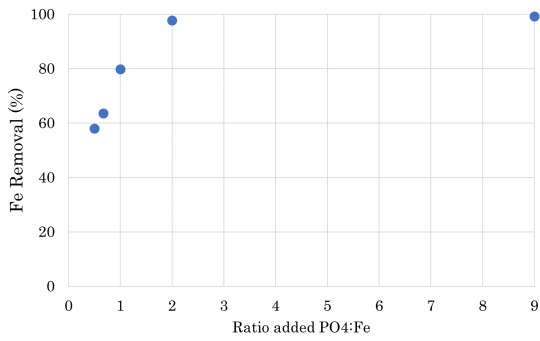
In the experiment determining the kinetics of vivianite precipitation, the pH dropped from 6.9 to 5.8 in approximately 20 minutes (Figure C.1). This pH drop together with the decrease in iron and phosphate concentration caused the SI to decrease as well, presented in Figure 3.3. After 10 minutes, no removal was observed anymore at which the SI was around 3.

In the experiments with different initial iron concentrations, the maximal iron removal was obtained at initial iron concentrations above 25 mg/L (Figure 3.1d). Below this concentration, the SI of vivianite formation was negative while the SI from 25 mg Fe/L and higher was above 5. This is presented in Figure B.1 in Appendix B, in which more details are given about the SI calculations and results.



(a) Kinetics

(b) Ratio of removed PO₄:Fe over time.



(c) Added PO₄:Fe Ratio

(d) Initial Fe concentration

Figure 3.1: Fe removal by vivianite precipitation in synthetic water, varied in (a) reaction time and (b) the corresponding removed ratio PO₄:Fe (c) added PO₄:Fe ratio and (d) initial Fe concentration added. Standard conditions (unless varied): Reaction time 60 min, initial Fe concentration 100 mg/L, ratio PO₄:Fe added 1:1.

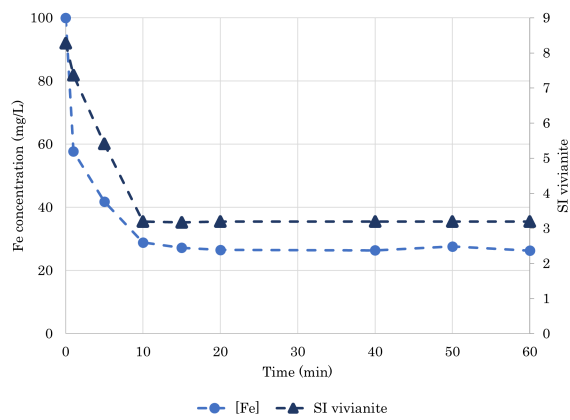
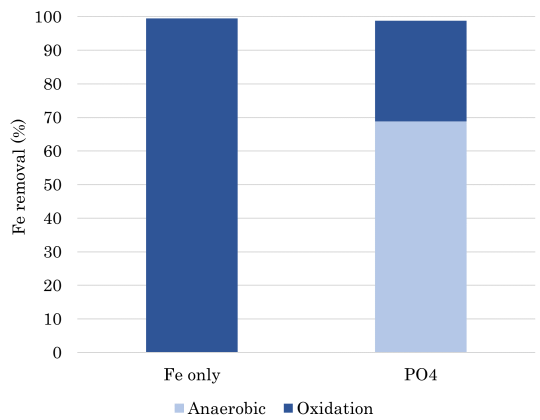


Figure 3.2: Fe removal anaerobically and aerobically in the reference experiment (Fe only) and by PO₄ addition. AN and OX reaction time 60 min, initial iron concentration 100 mg/L, ratio PO₄:Fe added 1:1 - synthetic water.

Figure 3.3: Fe removal over time and the corresponding saturation index (SI) of vivianite formation modelled with GWB® SpecE8. Initial Fe concentration 100 mg/L, ratio PO₄:Fe added 1:1 - synthetic water.

To understand why less removal was obtained below iron concentrations of 25 mg/L, the relation between the initial iron concentration and SI is modelled for several pH's between 6 and 9, visualised in Figure 3.4. The input for the model is presented in Table D.2 in Appendix D. At higher initial iron concentration and pH, the SI increases. By raising the pH, the SI can also increase at the same initial iron concentration suggesting that a better iron removal at low concentrations can be obtained by increasing the pH.

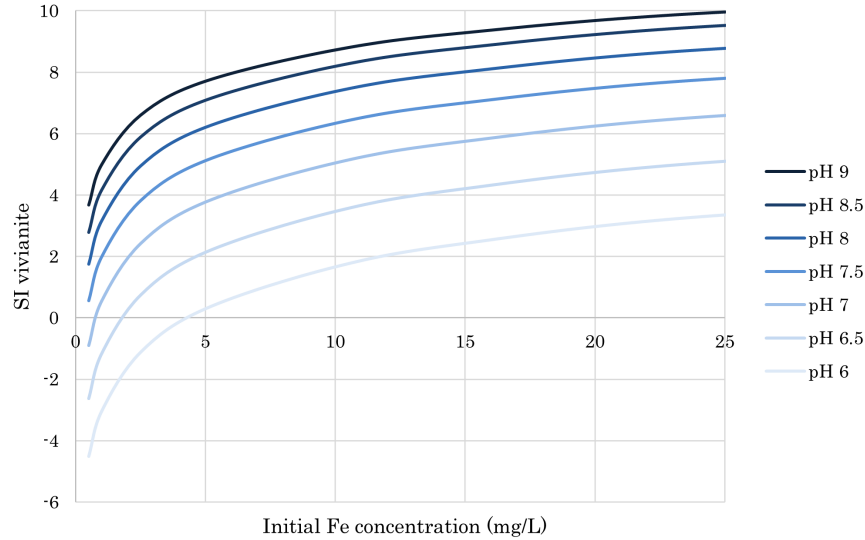


Figure 3.4: The saturation index for vivianite formation at different initial Fe concentrations and for different pH's modelled by GWB® SpecE8. Ratio $\text{PO}_4\text{:Fe}$ added 1:1 - synthetic water.

3.1.2 Kinetics Vivianite Precipitation in Synthetic Water

The removal of iron over time by vivianite precipitation in a synthetic iron solution (Figure 3.3) followed second order kinetics with a rate constant k of 2.65 M/s . Only the first ten minutes were taken into account for the calculation, since no extra removal was obtained afterwards. The derivation of the order and rate constant are given in Appendix E. The rate law becomes:

$$\frac{d[\text{Fe}]}{dt} = 2.65[\text{Fe}]^2 \quad (3.1)$$

The integrated rate law is plotted in Figure 3.5, visualising the iron removal over time. In this graph, the experimental data points are also given. A division is made between the points at which the SI was greater than 4 and removal of iron still took place and the points at which no removal was observed anymore with a SI of lower than 4. After 60 minutes, the concentration of iron decreases from 100 mg/L to 6.4 mg/L. The corresponding half life of iron when removed by vivianite precipitation is approximately 3:30 minutes.

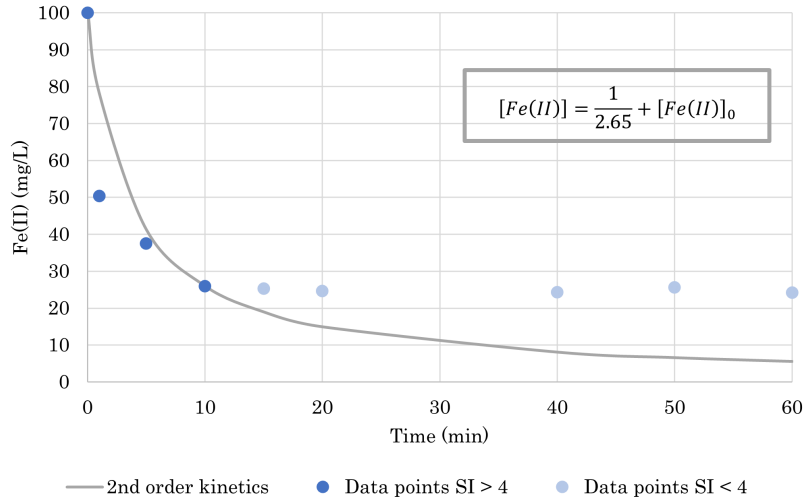


Figure 3.5: The iron removal over time in synthetic water following the integrated Equation 3.1 and the data points obtained experimentally with a SI greater than 4 depicted in light blue and with a SI lower than 4 in darkblue (SI determined by GWB® SpecE8).

3.1.3 Sludge Properties

The volume of the sludge formed by anaerobic precipitation with phosphate was significantly less compared to the reference experiment, while similar iron removal efficiencies were reached. The volume of the sludge formed was 1.9 mL per litre of treated water, a decrease of 3.3 times compared to oxidation and filtration as visible in Figure 3.6. The solution turned white blueish during anaerobic precipitation and the colour during oxidation did not change much, while the reference experiment showed the typical brown colour of iron oxides (Figure 3.7).

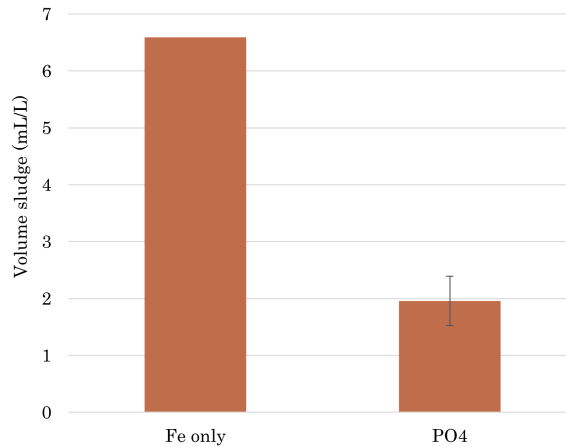


Figure 3.6: Sludge volume formed per litre of treated water for the reference experiment (Fe only) and by the anaerobic precipitation with PO₄. AN and OX reaction time 60 min, initial iron concentration 100 mg/L, ratio PO₄:Fe added 1:1 - synthetic water.

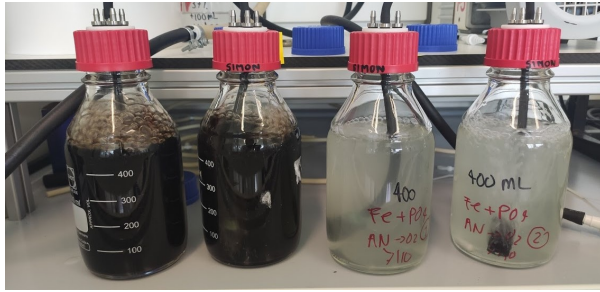


Figure 3.7: The reactors during oxidation of the reference experiment (2 reactors left) and the iron solution to which PO_4 was added (2 reactors right).

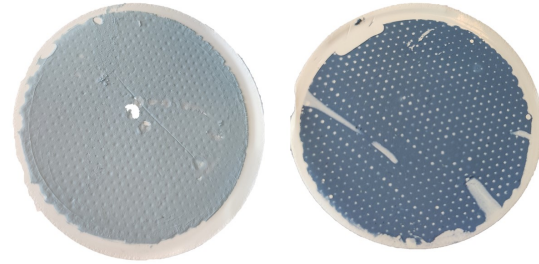


Figure 3.8: The precipitate formed after filtering the iron solution to which PO_4 was dosed stored anaerobically (left, lightblue) and when exposed to oxygen (right, darkblue).

After anaerobic iron precipitation with phosphate, the solution was filtered inside the anaerobic chamber and a light blue colour arised, typical for vivianite. When this precipitate was brought in contact with air, the colour changed into a deep blue colour. The difference is visible in Figure 3.8. The blue colour and the ratio of removed phosphate to iron are two good indicators for the formation of vivianite. The XRD analysis proved that vivianite indeed formed. The detected compounds are presented in Table 3.1 and the corresponding patterns given in Figure G.2 in Appendix G.

Sample	Compound
Fe only	Feroxyhyte FeOOH
PO_4	Vivianite $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$

Table 3.1: XRD results of the iron sludge formed in the reference experiment and by anaerobic addition of PO_4 . Initial Fe concentration 100 mg/L, reaction time 60 min - synthetic water.

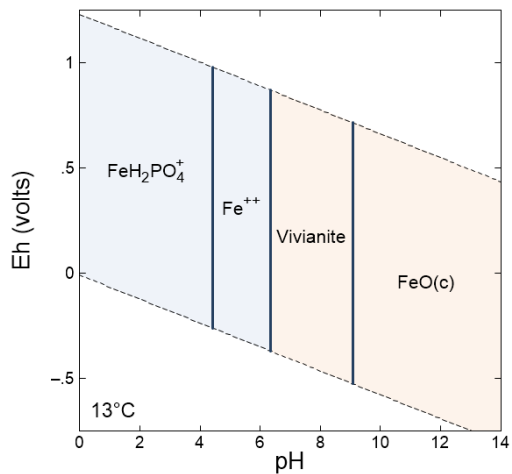
3.2 Alternatives to Phosphate

3.2.1 Pourbaix Diagrams

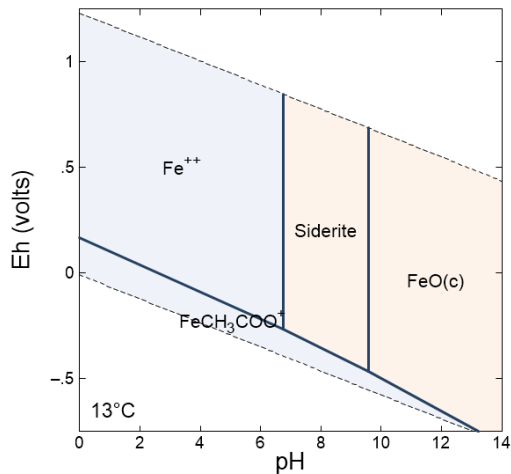
For each anion naturally present in groundwater, a pourbaix diagram with iron was made showing which minerals can form under certain pH and redox conditions. The activity coefficients needed to obtain these pourbaix diagrams are presented in Table 3.2. The final pourbaix diagrams are given in Figure 3.9.

Table 3.2: Activity coefficients of the anions present in groundwater, calculated with GWB® SpecE8. Concentrations used as presented in Table 1.1.

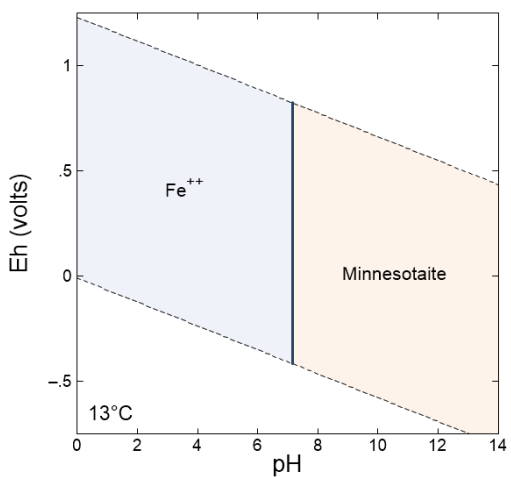
Compound	Activity Coefficient
Fe^{2+}	0.723
H_2O	1.000
HCO_3^-	0.920
SO_4^{2-}	0.712
Cl^-	0.917
NO_3^-	0.917
SiO_4^{4-}	1.000
HPO_4^{2-}	0.712



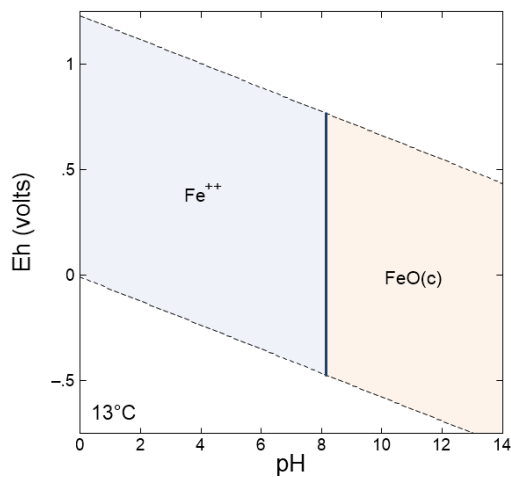
(a) Phosphate



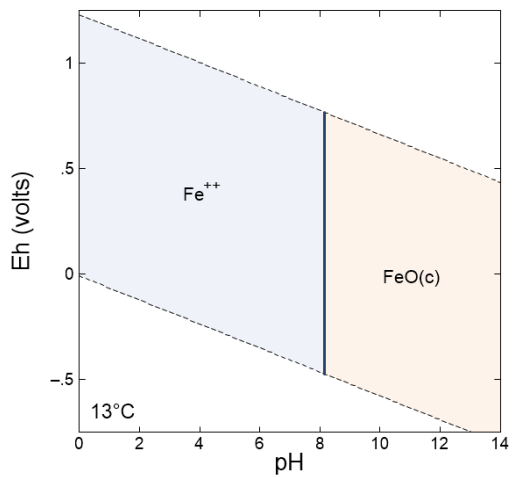
(b) Carbonate



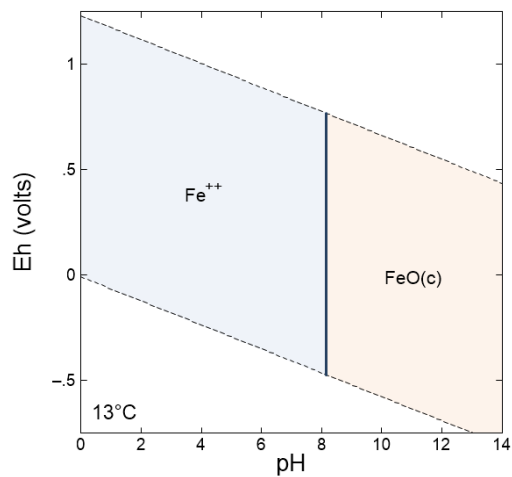
(c) Silicate



(d) Sulphate



(e) Chloride



(f) Nitrate

Figure 3.9: Pourbaix diagrams of different anions in groundwater with Fe(II). Temperature 13°, activity coefficients as in Table 3.2 and concentrations as in Table 1.1.

First the pourbaix diagram with phosphate is presented (Figure 3.9a), in which indeed the formation of vivianite is suggested at pH 6-9 as proven in the previously presented results. In the pourbaix diagram with carbonate (Figure 3.9b), it is suggested that siderite (FeCO_3) can form in the range of the common pH of groundwater. Therefore, carbonate will be tested as an alternative for phosphate to remove iron(II) anaerobically from groundwater. When silicate is added, minnesotaite ($\text{Fe}_3^{2+}\text{Si}_4\text{O}_{10}(\text{OH})_2$) can form when a pH higher than approximately 7 is present (Figure 3.9c). Since no published literature can be found about this mineral occurring in natural aqueous environments, this option is not taken into account in this research. With the other anions chloride, sulphate and nitrate, no crystal seems to form around neutral pH (Figure 3.9). For these three options, the pourbaix diagram suggest the formation of FeO above a pH of 8. To test if this indeed forms, sulphate is also tested as an alternative for phosphate for which necessary pH adjustments will be done to obtain a pH above 8. Another reason why sulphate is considered as an interesting alternative, is the possible formation of sulphate green rust ($[\text{Fe}_4^{2+}\text{Fe}_3^{3+}(\text{OH})_{12}]^{2+} \cdot [\text{SO}_4^{2-} \cdot 2\text{H}_2\text{O}]^{2-}$) at low traces of Fe(III) as introduced in section 1.1. Fe(III) was not inserted in the model and therefore green rust does not show up in the pourbaix diagram, but might form in reality.

3.2.2 Iron Removal by Carbonate and Sulphate in Synthetic Water

As expected from the pourbaix diagrams, precipitate became visible at neutral pH when carbonate was added to the anaerobic iron solution, while the iron remained in solution when sulphate was added. By increasing the pH above 8, the suspension with sulphate also became cloudy. In Figure 3.10 the anaerobic removal efficiencies are shown in light blue. The suspensions were oxidised afterwards and the increase in removal is visible in dark blue.

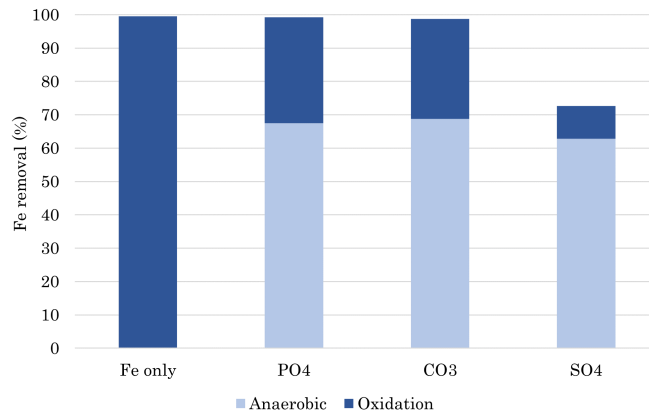


Figure 3.10: Fe removal anaerobically and aerobically with the reference experiment (Fe only) and with the addition of PO_4 , CO_3 or SO_4 . AN and OX reaction time 60 min, initial iron concentration 100 mg/L, ratio anion:Fe added 1:1 - synthetic water.

The iron removal by adding carbonate or sulphate were compared to the reference experiment in which iron was only only oxidised iron and to the addition of phosphate. The anaerobic removal was around 65% for all three anions. For carbonate and phosphate the total removal increased up to 99% after oxidation. A smaller increase in removal by oxidation was observed for the reactor with sulphate, only 73% of iron removal was reached.

3.2.3 Sludge Properties

The addition of carbonate to the anaerobic iron solution resulted in 5.9 times more sludge compared to the reference experiment with iron only and 19.5 times more compared to the addition of phosphate. The addition of sulphate caused a sludge volume increase of 2.3 times compared to the reference experiment and a 7.6 times

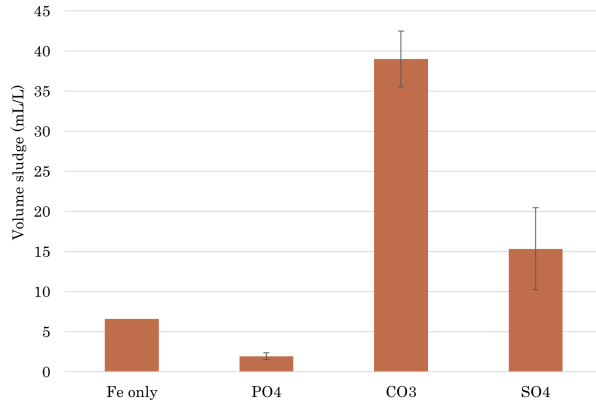


Figure 3.11: Sludge volume per litre of treated water formed by anaerobic precipitation with no addition (Fe only), the addition of PO_4 , CO_3 or SO_4 . AN and OX reaction time 60 min, initial iron concentration 100 mg/L, ratio anion:Fe added 1:1 - synthetic water.

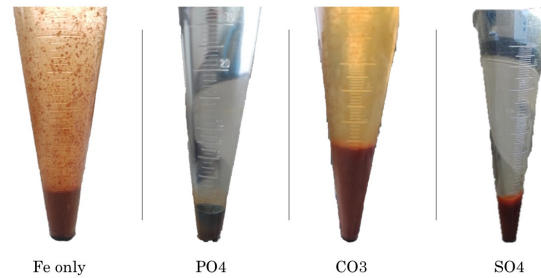


Figure 3.12: The sludge formed by anaerobic precipitation and oxidation of the reference experiment (Fe only), PO_4 addition, CO_3 addition and SO_4 addition to synthetic water.

increase compared to the addition of phosphate. These volumes are significantly different (p-value: 0.0037), an overview of the results is presented in Figure 3.11.

The appearance of the sludge is visible in Figure 3.12. The sludge formed by addition of carbonate looked similar to the reference experiment, the flocs were however more voluminous and slightly lighter in colour. Not all flocs settled that well and the water remained turbid. The sludge formed by the addition of sulphate has a slightly brighter red colour, but looks fairly similar. The settling capacity however was better, which was also the case for the sludge formed by phosphate addition. This sludge had a bright blue colour and was less fluffy compared to the other products.

The XRD analysis revealed which crystalline compounds were formed during the anaerobic reactions, presented in Table 3.3. The corresponding patterns are given in Figure G.3 in Appendix G. Several different compounds formed in the experiments with carbonate and sulphate. In the case of carbonate, no siderite was detected although this was expected from the pourbaix diagram. Magnetite, goethite and calcium iron oxide did form. For sulphate, magnetite and iron-hydroxides were formed. In the case of carbonate, no calcium was added to the reactor while a calcium containing compound was detected by XRD. The results when phosphate was added are more uniform, only the crystal vivianite was detected as expected.

Table 3.3: XRD results of the sludge formed by anaerobic Fe removal with CO_3 , SO_4 or PO_4 . Ratio anion:Fe added 1:1, initial iron concentration 100 mg/L, AN + OX reaction time 60 min - synthetic water.

Sample	Compound	Chemical Formula
CO_3	Magnetite	$\text{Fe}_{2.93}\text{O}_4$
	Goethite	$\text{FeO}(\text{OH})$
	Calcium Iron Oxide	$\text{Ca}_3\text{Fe}_{15}\text{O}_{25}$
SO_4	Green Rust	$\text{Fe}_6(\text{OH})_{12}(\text{CO}_3)$
	Magnetite	$\text{Fe}_{2.93}\text{O}_4$
	Amakinite	$\text{Fe}(\text{OH})_2$
	Feroxyhyte	FeOOH
PO_4	Vivianite	$\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$

3.3 Anaerobic Iron Removal in Natural Groundwater

3.3.1 Groundwater Composition

The average composition of the natural groundwater used is presented in Table 3.4. The 'raw at well' sample is the raw groundwater sample directly taken and acidified at the well. The 'raw in lab' sample is an average of the water that was transported from Loosdrecht to Delft in closed bottles and the 'filtered in lab' is the same water, but now filtered through a 0.45 μm filter. Iron was still present at around 3 mg/L and although minor changes did occur, the composition did not change much by transporting the samples.

Table 3.4: Concentrations of elements in the groundwater analysed by ICP-MS. Results for samples taken directly at the well and from the water transported to the lab both unfiltered and filtered. All values are in mg/L.

Element (mg/L)	Na	Mg	Si	P	S	Ca	Mn	Fe	Zn	As
Raw at well	8.68	2.25	8.54	0.15	1.37	37.03	0.11	3.45	0.058	0.0018
Raw in lab	9.07	2.23	8.54	0.09	2.01	37.03	0.11	2.88	0.057	0.0017
Filtered in lab	7.78	2.16	8.26	0.18	3.39	36.18	0.12	3.81	0.006	0.0020

3.3.2 Iron Removal by Phosphate and Carbonate

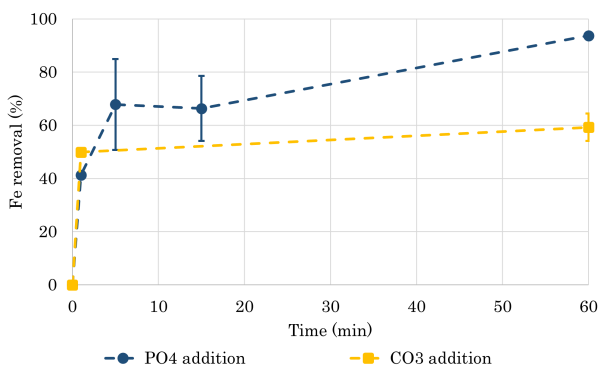
The removal efficiencies of iron from natural groundwater by the anaerobic addition of phosphate and carbonate over time are presented in Figure 3.13, for both the experiments done with natural iron concentration and with the overdose of iron.

For phosphate, an anaerobic removal of 93.7% was reached in natural groundwater with 100 mg/L of iron. This is around 20% more than obtained in the experiments with a synthetic iron solution of 100 mg/L. The maximum removal of 73% obtained with synthetic water after 15 minutes was already reached after 5 minutes when natural groundwater was used. For carbonate an anaerobic removal of 59.3% was reached in natural groundwater with 100 mg/L of iron. Most iron precipitated already after 1 minute. The iron removal with phosphate is significantly higher than the removal with carbonate (p-value $8.06 \cdot 10^{-6}$).

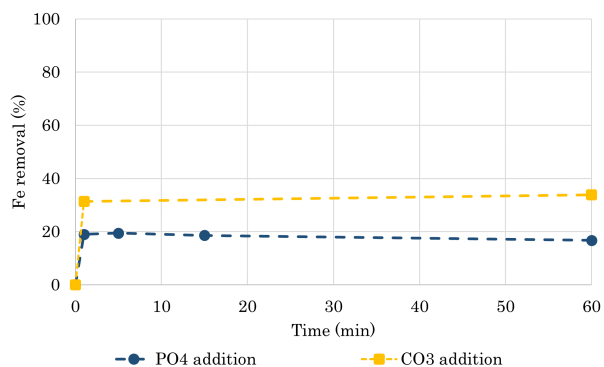
With the natural iron concentration less anaerobic iron removal was observed for both phosphate and carbonate, 19% and 34% respectively. Due to the poor removal and the low iron concentrations, very little sludge formed and therefore the sludge volume and properties discussed in the next section are only about the experiments with an overdose of iron.

With the addition of an oxidation step, the total iron removal increased for both phosphate and carbonate to 99.9% (Figure 3.14) in the experiments with an overdose of iron. This removal is more than the average removal obtained with the reference experiment with only iron, which was 85.1%. For the natural iron concentration, the oxidation step increased the removal up to 98.2% for phosphate and 87.9% for carbonate. The reference experiment with only iron showed a removal of 92.4%, which means a higher removal was obtained in the reactor with phosphate.

Not only the final concentration of iron is important, but also the residual phosphate concentration is eventually important for the production of drinking water. The initial iron concentration in the experiments with natural iron varied slightly and the removal efficiency in percentage does not reveal how much iron was left in the produced water. An overview of the start and end concentrations of iron and phosphorus for each experiment is presented in Table 3.5. The lowest iron concentration in the experiments with both natural and 100 mg/L of initial iron was reached when phosphate was added anaerobically. The final iron concentrations obtained here were even lower than obtained with the conventional treatment of oxidation and filtration. The final concentration of phosphorus are however elevated in these experiments, since a slight overdose of

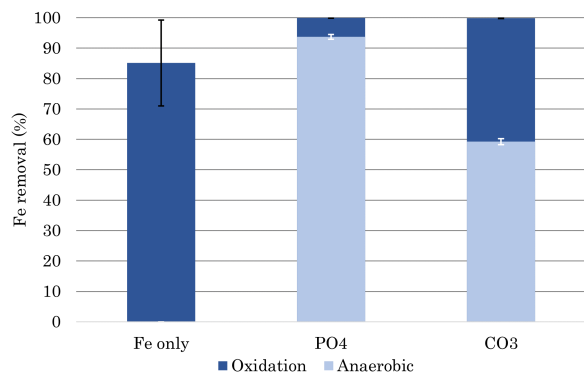


(a) Initial Fe concentration 100 mg/L (overdose).

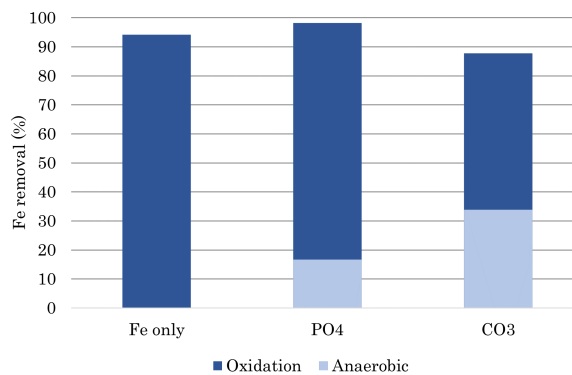


(b) Initial Fe concentration 3 mg/L (natural).

Figure 3.13: Fe removal anaerobically over time with the addition of PO_4 or CO_3 . Ratio anion:Fe added 1:1 - groundwater.



(a) Initial Fe concentration 100 mg/L (overdose).



(b) Initial Fe concentration 3 mg/L (natural).

Figure 3.14: Fe removal anaerobically and aerobically with no addition (Fe only) and with the addition of PO_4 or CO_3 . AN and OX reaction time 60 min, ratio anion:Fe added 1:1 - groundwater.

phosphorus was added to remove the iron. The concentration of phosphorus also decreased in the reference experiment and when carbonate was added anaerobically instead of phosphate, which can indicate that vivianite also formed in these experiments. This was confirmed by the XRD results discussed in subsection 3.3.5.

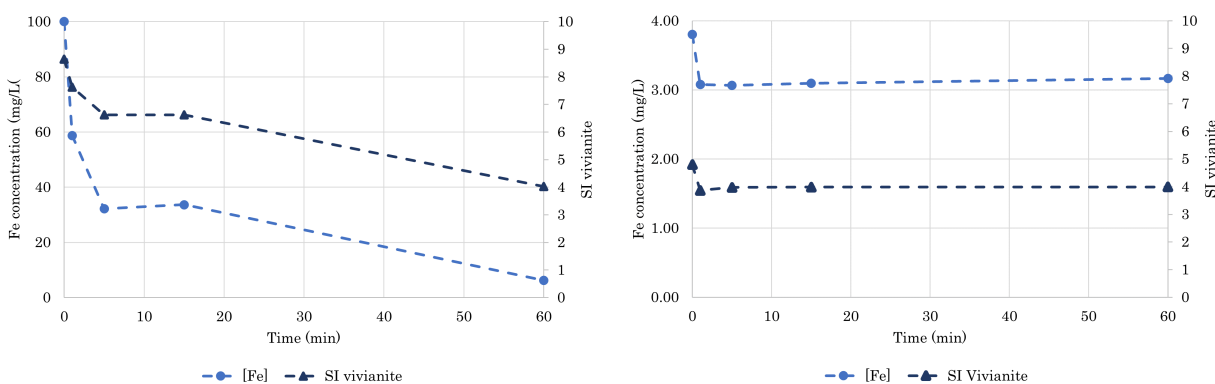
Table 3.5: The start and end concentration of Fe and P in the experiments with groundwater. The bold numbers indicate that the compound was dosed and is an elevated value compared to the natural concentration.

Experiment		start/end concentration	ICP-MS Fe (mg/L)	ICP-MS P (mg/L)
Fe only	3 mg/L	start	3.26	0.12
		end	0.21	0.04
PO4 dosed	3 mg/L	start	3.13	5.2
		end	0.07	0.97
PO4 dosed	100 mg/L	start	100	170
		end	0.08	22.44
CO3 dosed	3 mg/L	start	2.9	0.08
		end	0.52	0.04
CO3 dosed	100 mg/L	start	100	0.07
		end	0.14	0.02

3.3.3 Saturation Index

For each measurement point as depicted in Figure 3.13a and Figure 3.13b, the SI of vivianite was determined with GWB® SpecE8. The input and detailed results are presented in Appendix B. The pH decrease in the experiment with natural groundwater with 100 mg Fe/L was less compared to synthetic groundwater as can be seen in Figure C.1 in Appendix C. The pH decreased from 7.0 to 6.8 in 20 minutes. At the natural iron concentration, the pH stayed stable during the experiment as visible in Figure C.2.

The results of the iron concentration and the corresponding SI's are visualised in Figure 3.15. For the spiked groundwater with an overdose of iron, the iron removal stopped when 95% was removed. The SI was decreased to 4 at that moment. For the experiment with natural iron concentration, only some removal was observed at the first minute, in which the SI was 5. The SI dropped below 4 for the remaining time.



(a) Initial Fe concentration 100 mg/L (overdose).

(b) Initial Fe concentration 3 mg/L (natural).

Figure 3.15: Fe removal over time and the corresponding saturation index (SI) of vivianite formation modelled with GWB® SpecE8. Ratio PO₄:Fe added 1:1 - groundwater

3.3.4 Comparison Kinetics Vivianite Precipitation and Iron Oxidation

The removal of iron over time by vivianite precipitation in natural groundwater spiked with 100 mg Fe/L followed a similar trend compared to the removal in synthetic water. Second order kinetics with a rate constant k of 2.27 M/s was found. This time, also the iron concentration at minute 60 is taken into account, since removal was still observed in the last time step. For the derivation of the rate order and constant see Appendix E. The rate law becomes:

$$\frac{d[Fe]}{dt} = 2.27[Fe]^2 \quad (3.2)$$

The iron removal over time is represented by the integrated rate law given in Figure 3.16, in which the experimental data points are also shown. After 60 minutes, the concentration of iron decreased from 100 mg/L to 6.4 mg/L. The corresponding half life of iron when removed by vivianite precipitation is approximately 4 minutes.

The removal of iron by vivianite precipitation at pH 7 and for iron oxidation for a pH between 6.5 and 7.5 is given in Figure 3.17. The removal method of iron oxidation follows first order kinetics, as explained in subsection 1.2.2. The removal is pH dependent, a lower pH decreases the oxidation rate. At a neutral and common pH of 7, the half life of iron is 16 minutes when removed by oxidation. After 60 minutes, a similar final removal is obtained for both iron oxidation as vivianite precipitation.

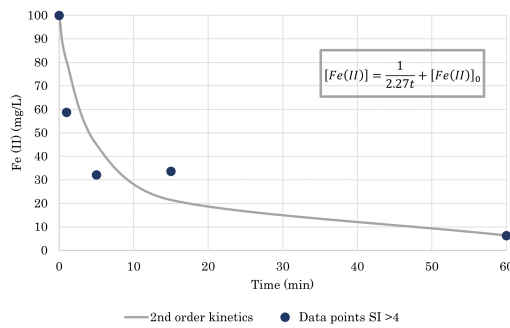


Figure 3.16: The iron removal over time in natural groundwater following the integrated Equation 3.2 and the data points obtained experimentally.

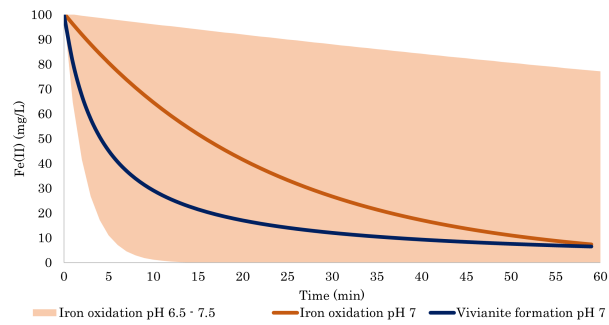


Figure 3.17: The kinetics of iron removal in natural groundwater for vivianite precipitation at pH 7 and for iron oxidation between a pH of 6.5 (upper limit) and 7.5 (lower limit).

3.3.5 Sludge Properties

In Figure 3.18 the amount of sludge produced in the experiments with an iron concentration of 100 mg/L in natural groundwater are shown. Significantly less sludge was formed when phosphate was added anaerobically compared to the reference experiment with iron only: 1.6 mL of sludge per litre of treated water was formed, which is less than a third of the 4.9 mL of sludge produced with the reference experiment. Significantly more sludge is produced with the addition of carbonate (p-value: $3.09 \cdot 10^{-5}$), 28.9 mL of sludge was produced per litre of water which is 5.9 times as much as with only iron. A picture of the appearance of the sludge, is shown in Figure 3.19.

The formed compounds during the experiments were analysed by XRD and the results are shown in Table 3.6. The corresponding patterns are given in Figure G.4 and Figure G.5 in Appendix G. As expected, vivianite and only vivianite was formed when iron and phosphate reacted anaerobically. Also after oxidation no other crystalline compound was detected by XRD.

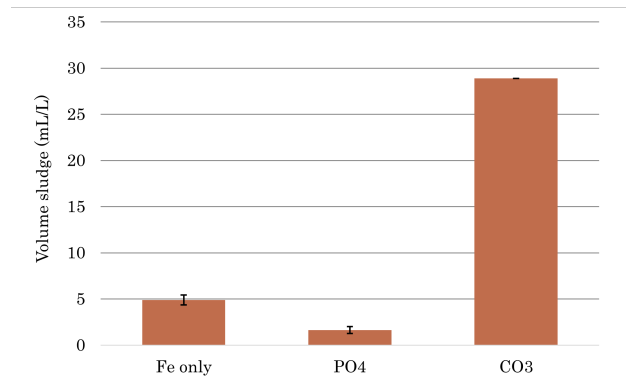


Figure 3.18: Sludge volume per litre of treated water formed by anaerobic precipitation followed by oxidation with no addition (Fe only) and with the addition of PO₄ or CO₄. Ratio anion:Fe added 1:1, initial iron concentration 100 mg/L, AN + OX reaction time 60 min - groundwater.

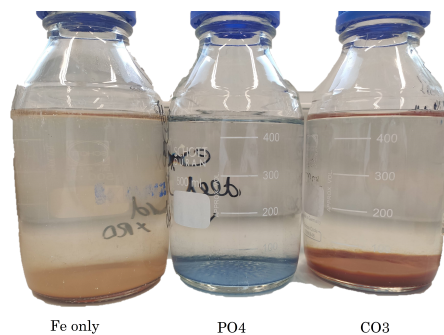


Figure 3.19: The sludge formed by anaerobic precipitation and oxidation of the reference experiment (Fe only), PO₄ addition and CO₃ addition to natural groundwater.

For carbonate, different solids were formed. During the anaerobic reaction with the natural iron concentration, vivianite was also formed as expected from the final phosphorus concentrations as shown in Table 3.5. The natural phosphate present in groundwater must have reacted with the iron. During oxidation, also feroxyhyte and zinc oxide were formed. For the higher iron concentration of 100 mg/L, green rust, lepidocrocite and calcium iron oxide were formed. The last one was also found in the experiments with synthetic water, but the other two compounds not. Magnetite and goethite formed during the experiments with synthetic water, but were not detected in the samples taken from the experiments with groundwater. Vivianite was indeed also formed when the conventional treatment method of only oxidation was applied with a concentration of 100 mg/L iron, just as feroxyhyte and zinc oxide. Other possible formed amorphous structures can not be detected by XRD.

Table 3.6: XRD results of the formed sludge by anaerobic Fe(II) removal followed by oxidation with no addition (Fe only) and with PO₄ and CO₃ addition. Ratio anion:Fe added 1:1, reaction time 60 min - groundwater.

Sample	Conc	AN/OX	Compound
Fe Only	100 mg/L	OX	Vivianite
			Feroxyhyte
			Zinc Oxide
PO ₄	3 mg/L	AN	Vivianite
PO ₄	3 mg/L	OX	Vivianite
PO ₄	100 mg/L	AN	Vivianite
PO ₄	100 mg/L	OX	Vivianite
CO ₃	3 mg/L	AN	Vivianite
		OX	Vivianite
CO ₃	100 mg/L	AN	Green Rust
			Lepidocrocite
			Calcium Iron Oxide
CO ₃	100 mg/L	OX	Vivianite
			Feroxyhyte
			Zinc Oxide

4 Discussion

4.1 Vivianite Formation

A poor understanding of the iron-phosphate chemistry is the main cause of a slow development of phosphate recovery via vivianite precipitation in the field of wastewater treatment [54]. Increasing this understanding and investigating if this method is also applicable for groundwater treatment was the main goal of the first part of this research.

Vivianite did indeed form when phosphate was added to both a synthetic iron solution and to natural groundwater in an anaerobic environment at neutral pH. This was expected from the pourbaix diagram (Figure 3.9a) and from other studies in which it is reported that vivianite is poorly soluble in water ($K_{sp} = 10^{-36}$ [28]) and stable in anaerobic conditions under pH 6-9 [54]. The first part of the main research question is hereby answered; the compact mineral vivianite can form to remove iron(II) from groundwater. Answering the second part of the research question; if this is also more efficient than the conventional treatment method of oxidation and filtration, requires a more extensive discussion provided in section 4.3. First, the results of understanding the interaction between iron and phosphate to form vivianite and finding an alternative to phosphate are discussed.

4.1.1 Kinetics

Iron removal by anaerobic vivianite precipitation was found to follow second order kinetics in groundwater with an initial iron concentration of 100 mg/L. At a pH of 7 the half life was approximately 4 minutes, which is 4 times faster compared to the oxidation of iron at pH 7. This means higher throughput rates can be achieved, which is very interesting for drinking water systems.

Only one study was done before to the kinetics of vivianite formation by Liu et al. [29], who reported a zero order dependency with a rate constant for nucleation of 0.053 M/S. A second order dependency is found in this study and contradicts the results of Liu et al. [29]. To verify this finding, a linear plot was made for the zero-, first- and second-order kinetics presented in Appendix E. The determination coefficient for zero-order was 0.69 and 0.95 for second-order, strongly suggesting second order kinetics. Creating a better understanding of the influences of e.g. pH and other process conditions might explain the different results obtained and further research is necessary. What is found in both studies though is that the vivianite precipitation only follows the determined kinetics when the saturation index of vivianite is higher than 4. Below this value, the reaction becomes very slow or completely stops.

The kinetics of vivianite formation was only determined for one set of process conditions; at room temperature, an initial iron concentration of 100 mg/L, the dosed ratio phosphate to iron was one and no pH corrections or variations were applied. The dependency of the rate constant on these factors is not yet determined. The small difference in rate constant found for vivianite formation in synthetic or natural water can be caused by the difference in pH between the two experiments; natural groundwater has a larger buffer capacity causing the pH to remain relatively stable compared to the experiments with synthetic water in which a stronger pH drop

was measured (pH graphs given in Appendix C). Another factor affecting the calculation is the sampling time. For the synthetic iron solution, only the first ten minutes were taken into account and for natural groundwater, the time gap between the sample taken at minute 15 and minute 60 causes uncertainties. It might be that the maximum removal efficiency was already reached sooner. The two rate constants obtained are however from the same order of magnitude and it is likely that the kinetics are less depending on pH variations compared to the oxidation of iron. The rate law of iron oxidation (Equation 1.2) is also depending on the pH, while the rate law of vivianite (Equation 3.2) was found to be only dependent on the rate constant and iron concentration.

4.1.2 Saturation Index and Influence of pH

In both the experiments with synthetic and natural groundwater, vivianite formation stopped under certain conditions which limited the removal of iron. The simulated experiments in GWB[®] together with the experimental results suggest that below a SI of approximately 4 no vivianite precipitates anymore. This corresponds with the findings by Liu et al. [29] in their thermodynamic study to vivianite formation and it explains many of the obtained results. The iron removal in synthetic water stagnated at 73%, the decrease in concentrations and release of H⁺ ions when vivianite is formed (shown in Equation 1.6 and Equation 1.7) caused the SI to drop below 4 at that moment. For initial iron concentrations below 25 mg/L, poor removal was observed at which the SI of vivianite formation was negative. For the experiments with groundwater, the spiked groundwater showed removal up to 96% which was substantially higher than obtained in the experiments with synthetic water. Here again, the SI dropped below 4 at the moment vivianite precipitation stopped. For the natural iron concentration only some removal was observed in the first minute, when the SI was still slightly higher than 4. After the first minute, the lower concentrations caused the SI to drop below 4 and no extra removal was observed.

It also explains the increase in removal efficiencies at higher dosed phosphate concentrations. No pH measurements of these experiments were available, but the increase in phosphate concentrations will positively effect the SI in two ways: more phosphate is available to react and the pH increases by the dosage of phosphate. However, phosphate dosage should be minimised and high concentration can be avoided by increasing the pH. At a phosphate to iron ratio of 1, the minimum iron concentration at which the SI of vivianite is above 4 is 1 mg/L at a pH of 8.5. This suggests that even at these low initial iron and dosed phosphate concentrations, iron can successfully be removed anaerobically by increasing the pH of the system.

At iron concentrations below 1 mg/L, the pH should be increased above 9 to get a SI higher than 4. However, above a pH of 9 it is expected that no vivianite precipitates anymore. From the pourbaix diagram of vivianite formation (Figure 3.9) and as reported by Wilfert et al. [54], vivianite can only form between a pH of 6-9. A pH of 9 or higher was not obtained during the experiments carried out in this thesis, but Liu et al. [29] found that the metastable zone of vivianite formation was between a SI of 4 and 11. In Figure D.1 in Appendix D the relation between pH and SI is visualised for an iron concentration of 100 mg/L, which exactly corresponds with the findings in literature; at a pH higher than 9, the SI becomes higher than 11 and at a pH of 6, the SI becomes lower than 4. The increase in OH⁻ ions at higher pH will stimulate Fe(OH)₂ formation [46], making the iron(II) unavailable for vivianite precipitation.

Vivianite formation is found to be very dependent on the saturation index. This conclusion contributes to a better understanding of the interaction between iron and phosphate, as is reported to be limited [54]. It might explain some of the contradictory results published in literature about phosphate recovery via vivianite precipitation in wastewater. Wang et al. [47] found an optimal ratio of 1 in a bioinduced vivianite recovery system, which is a small overdose of phosphate which will increase the SI by increasing the pH. Wu et al. [46] on the other hand reported that the iron concentration should be in slight excess to avoid the formation of Fe(OH)₂. Wu et al. [46] reviewed the removal efficiencies of phosphorus in WWTPs by vivianite precipitation in several studies and reported P recovery as vivianite with values varying between 23% and 95%. Calculating the SI of the difference systems might explain why such varieties in results are obtained. Adjusting the SI of the systems by e.g. increasing or decreasing the pH might lead to better phosphate recovery in wastewater treatment systems.

4.2 Alternatives to Phosphate

Carbonate and sulphate were tested as alternatives to the limited resource phosphate. The pourbaix diagrams as presented in Figure 3.9 suggest the formation of siderite (FeCO_3) when carbonate is dosed at neutral pH and FeO when sulphate is dosed and the pH is raised above 8.

For sulphate, a white precipitate formed when the pH was increased. The XRD result in Table 3.3 showed the formation of iron hydroxides (amakinite and feroxyhyte), magnetite and green rust. FeO was not detected. The possible formation of green rust with sulphate and iron is also reported in literature [16, 55]. It is however unlikely that large amounts of green rust has formed, since this mineral also consist of iron(III) molecules and in each experiment only less than 5% of iron(II) was oxidised to iron(III). Quantification of the formed minerals was not done, so no data is available on the actual amounts formed.

A remarkable result with the addition of sulphate, was the inhibition of iron removal by oxidation. A plausible explanation is the formation of iron(III)-sulphate complexes [56]. This makes the iron(III) unavailable for flocculation or adsorption on reactive surfaces. Complexes are not removed by filtration and the iron will be detected during analysis. This phenomena is important to consider in environments with a high sulphate concentration, it might reduce the efficiency of the iron removal during the oxidation step. This is however not observed during the experiments with groundwater, in which concentrations around 2 mg S/L were present. The variety of formed products, the increased amount of sludge compared to the conventional method and most importantly the poor total iron removal when sulphate was added, result in the conclusion that it does not function as a proper alternative to phosphate.

With carbonate, the total removal after an anaerobic and oxidation step resulted in similar efficiencies compared to phosphate. There are nonetheless some disadvantages with the use of carbonate. First of all, the anaerobic iron removal was almost 34% less with carbonate than with phosphate in groundwater with an iron concentration of 100 mg/L. The aerobic iron removal however, reached a similar efficiency of more than 99%. At natural iron concentrations, less total removal was observed with carbonate than with phosphate (88% and 98% respectively), but the anaerobic removal was higher this time with carbonate (34% compared to 17% with phosphate). Another major difference was the volume of sludge formed, 18 times more sludge was produced with carbonate than with phosphate. When phosphate was added, only vivianite was detected as the end product. In the case of carbonate, a mixture of all kind of different substances were formed including feroxyhyte, green rust and also vivianite. No siderite was detected by the XRD analysis, although this was the hypothesis based on the pourbaix diagram. Based on the colour and structure of the sludge (Figure 3.12 and Figure 3.19), it is likely that also amorphous structures were present, undetectable by XRD analysis.

If siderite did not form at all can not be stated for sure. It can also be that it did form, but that it was not detected by XRD. Although XRD is known to be able to detect siderite [20, 57], it might be that other compounds present dominated the XRD pattern. Another plausible reason is that the formed siderite was oxidised. Kim et al. [58] reported the formation of goethite when siderite is exposed to oxygen and the formation of magnetite by auto-oxidation (oxidation by exposure to light). These two minerals were indeed detected in the experiments with carbonate in synthetic water. The samples were covered with aluminium foil and stored in the anaerobic chamber, but during filtering and/or transport some exposure to light and oxygen probably occurred. It might also be that the protection of the glycerol layer did not work well enough to avoid some oxidation, although it worked good enough for vivianite.

In the experiments with groundwater however, no siderite, goethite or magnetite was detected. To understand why such a variety of products was formed by the addition of carbonate, the experiment was simulated with GWB® SpecE8. The input and the obtained minerals with a positive SI are given in Appendix F. The model gives a low SI of 0.2248 for siderite, which suggest that the presence of the other compounds in the water might hinder the formation of siderite. Minerals with a high SI are mainly silica containing minerals such as minnesotaite and greenalite, which were not found in the lab experiments. These two minerals also have a high positive value in the simulation of the experiments with phosphate in groundwater (Appendix F). A probable explanation why these minerals were not found is the slower kinetics of the formation of minerals

containing iron and silica [18] or the low alkalinity of the water [59]. The possible impact of silicate concentration on the removal efficiency of iron should be considered if this method is applied in practice and should be further investigated.

Since no compact and uniform mineral was formed by the addition of carbonate, it is not considered as a suitable alternative for phosphate. The removal of iron was reasonable and this should be taken into account when phosphate is dosed to form vivianite in environments with high carbonate concentrations. It might hinder the formation of vivianite, however both Liu et al. [29] and Wu et al. [46] report that precipitation with phosphate is favoured over carbonate for alkalinity up to 1000 mg/L.

4.3 Anaerobic Iron Removal in Natural Groundwater

The process of aeration followed by rapid sand filtration is the most applied method for iron removal from groundwater [4], but is less effective for elevated iron concentrations which occur more frequently due to pollution [30]. Khatri et al. [30] reviewed the currently applied strategies for iron removal from water with a special focus on elevated iron concentrations. Regarding the iron removal efficiency, the conventional strategies are known to be relatively effective and remove iron above 90%. More recent strategies such as ion exchange and supercritical fluid extraction are less effective and Khatri et al. [30] suggest that improving newer technologies such as nanotechnology are needed to manage the elevating iron concentrations in the future. Anaerobic iron removal by vivianite precipitation is, of course, not taken into account in this review but perfectly fits the prospects of the authors. It can reach similar removal efficiencies as the conventional systems, especially at the higher iron concentrations in which some conventional systems fail. For oxidation and rapid sand filtration, the main disadvantage of high iron concentration is the frequent backwashing required. The sludge volume is a third with anaerobic iron removal compared to the conventional method, which will partly erase this problem. An advantage compared to e.g. some nanotechnologies, is that no toxic chemicals have to be dosed.

No comparison in iron removal efficiencies from groundwater by vivianite precipitation can be made with other studies, since this is a new concept. However, this technique is increasingly used to recover phosphorus from wastewater treatment plant and a comparison in removal is made. Wu et al. [46] reviewed the removal efficiencies of phosphorus in WWTPs by vivianite precipitation in several studies and reported P recovery as vivianite with values varying between 23% and 95%. The high removal of 95% was obtained in a fluidized-bed crystallisation reactor in which silica was used as a seeding material and a slight excess of iron was present compared to phosphate [60]. Wilfert et al. [52] reported a total phosphorus removal of approximately 40-50% in an adsorption/bio-oxidation treatment plant in which the ratio available phosphate:iron was 1.3 during treatment and decreased to 1.1 in the digester. The final phosphorus removal efficiencies in groundwater obtained in this experiment were 81.3% for the natural iron concentrations and 86.9% when an overdose of iron was added, both at phosphate:iron ratios of 1. This is higher than the removal obtained by Wilfert et al. [24]. Besides the different environments, this will probably also be caused by the overdose of phosphate present compared to iron in their experiments. The 95% phosphorus removal reached by Priambodo et al. [60], is likely to be caused by relatively higher iron concentration present. Another major difference in their experiments was the addition of silica as a seeding material, which is known to enhance the vivianite precipitation process [29]. The possibility of applying a seeding material during groundwater treatment is further discussed in chapter 5.

Anaerobic iron removal by vivianite precipitation seems to be a good solution for upcoming challenges in water treatment. A product with a good marketvalue is created; vivianite is worth €10.000/ton [46]. An important factor towards a sustainable treatment chain is the reuse of resources [38]. Vivianite can be used for the production of Li-ion batteries [60], as an efficient slow release fertiliser or as a pigment [46]. The iron sludge produced in the oxidation and filtration still ends up in landfill in certain countries [38, 42], but is increasingly reused for e.g. sorption processes [38, 61]. The currently reported value of iron sludge by aquaminerals is approximately €50/ton of produced iron sludge [43], which suggest that the formation of vivianite instead of

iron sludge might increase the profit of iron recovery with more than 60 times.

This research insinuates that anaerobic iron removal indeed improves the efficiency of iron removal, which answers the second part of the main research question. Experimentally this is proven for high iron concentrations above 25 mg Fe/L, but the GWBB[®] model shows that it is also likely to work at low iron concentrations starting at 1 mg Fe/L by increasing the pH of the system. The iron removal process is found to be more efficient compared to the conventional method, but if it will also increase the efficiency of the complete drinking water treatment system will depend on several additional factors not taken into account in this research, such as the recovery efficiency of the dosed phosphate. Further research is needed and recommendations are listed in chapter 7.

5 Application

5.1 Implementing Anaerobic Iron Removal

Anaerobic iron removal can have some great advantages compared to the conventional treatment of oxidation and filtration. Although the study done in this thesis was mainly fundamental and additional research is needed before solid conclusions can be made about the applicability, the outcome does suggest that it can lead to a more economical favourable process. Higher production rates might be achieved since less backwashing is required, less backwash water needs to be treated and also the transport costs of the sludge will decrease.

How to implement the method of anaerobic iron removal into practice is discussed in this chapter. Two possible designs are presented first and if these designs are realistic depends, among other things, on the recovery of phosphate discussed in the second section. Adding a seeding material might be interesting for engineering application and this concept is introduced afterwards. A rough estimation is given on the costs of treating iron-rich water and the possible savings when done anaerobic instead of fully aerobic is presented in the next section. This chapters ends with an overview of locations where it might be interesting to apply anaerobic iron removal.

5.2 Design Treatment Plant

Two designs are proposed, in which a conventional existing treatment plant (as depicted in Figure 1.2) is used as the base. Constructing a completely new treatment plants is less realistic than renovating a consisting one, since treatment plants are often used for many years.

In the first design option (Figure 5.1a), phosphate is added to the anaerobic stream before the oxidation step. An optimal flow should be found in which the iron and phosphate have enough time to react, which will vary per individual plant. Reaction times might be accelerated by an increase in SI due to e.g. increasing the pH or by adding a seeding material. Vivianite will be transported in the stream during the cascading in which other constituents in the groundwater such as manganese and ammonium are oxidised. Eventually, the vivianite will be separated from the stream in the sand filter. Considering the end use of vivianite, the purity is important. The oxidation step might also oxidise the vivianite and the reactivity and stability of vivianite depends on the purity, further discussed in section 5.3. Another important parameter discussed in that section, is how the vivianite can eventually be separated from the filter bed. This first design option requires the least investment, but is less likely to produce a pure vivianite crystal.

In the second option, the aim is to remove iron from the stream before oxidation starts (Figure 5.1b). The phosphate is added to the anaerobic water stream and can react with the iron in the anaerobic reactor. In the anaerobic filter, only vivianite will be removed. If this filter can be made of simple quartz grains is not yet investigated, this will depend on the density and buoyancy of the vivianite crystals compared to the filter material. This design option will probably result in a more pure end product compared to the first design option, but also requires more renovation and construction cost.

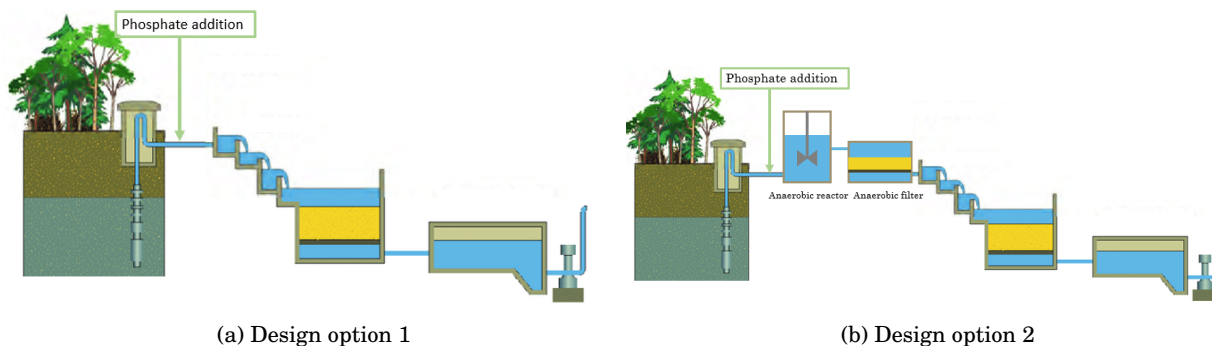


Figure 5.1: Two possible design options for the implementation of anaerobic iron removal in an existing groundwater treatment plant. Modified figures from De Vet [1].

5.3 Phosphate Recovery

Vivianite has a economical value in chemical and agricultural industries. The end use will strongly depend on the purity of the vivianite obtained and the sensitivity of vivianite to oxidation depends on the purity as well. Inserting an anaerobic reactor and filter before oxidation to harvest vivianite is expected to produce a purer end product, but further research is necessary to identify the purity of the obtained material. Currently a knowledge gap in literature exist on the purity and structure of obtained vivianite in different (waste)water systems [46]. The crystalline structure can turn into an amorphous one by replacement of iron by e.g. magnesium or calcium [23].

Before vivianite can be harvested, the product should be removed from the water stream. This can be done in a conventional way by filtering the stream and back washing the filter bed periodically. After back washing, the vivianite can be separated from the water by e.g. settling. Another separation possibility is magnetic separation [51]. Vivianite has paramagnetic properties, but during the experiments these properties were not perceived. This will strongly depend on the structure of the crystals and for vivianite it is known that the magnetism is often very weak. This method requires very high energy costs to separate the mineral based on this property [62]. However, if a more structured crystal could be obtained, the magnetic properties might strengthen. More research is needed to find out if this is possible and if magnetic separation is an option in drinking water systems.

5.4 Seeding Material

Adding a seeding material to the reactor might improve the removal efficiencies even at lower concentrations, since it can accelerate the crystallisation reactions by lowering the super saturation index needed to start the reaction [29]. Instead of homogeneous nucleation, which occurs spontaneously, heterogeneous nucleation is promoted. This can help to not only further remove iron, but can also help to improve the removal efficiencies when less phosphate is added. Instead of adding a small overdose, adding the theoretical value might be enough such that very little to no phosphate ends up in the product water. This will also save in the costs for the dosage of chemicals, which is an important factor for application. Heterogeneous crystallisation might lead to a more organised crystal structure, which can improve the paramagnetic properties of vivianite. If larger crystals and/or pellets of vivianite can form with a well organised structure, magnetic separation will become more realistic.

A possible seeding material can be quartz. Liu et al. [29] found a decrease in final phosphate concentration

when quartz was added from 10 mg/L to 6.7 mg/L and the nucleation and crystal growth started 10 minutes earlier by the addition of quartz. This increase in removal rate is interesting for the application in drinking water, especially within the RedOx filter project in which they aim at designing filters with a faster throughput rate. The hydraulic retention time can decrease and smaller reactors will become necessary.

5.5 Costs Iron Removal

If anaerobic iron removal contributes to a more efficient drinking water treatment system, depends on the costs of the removal. To get an insight in the cost difference between aerobic and anaerobic iron removal, a calculation is done with a fictitious plant representing an average plant of Vitens. In this plant, the process steps as presented in Figure 1.2 are used. An additional step is the treatment of the filter backwash water. Following the trend of water reuse, which is important to satisfy the increase in global water demand, it is assumed that the backwash water is cleaned to drinking water standards by flocculation, filtration and UV disinfection. An overview of all steps are given in Table 5.1.

Table 5.1: The process steps used in the cost calculation for the main groundwater treatment chain and for the treatment chain of the backwash water.

Process steps Treatment groundwater	Process steps Treatment backwash water
Water well	Wastewater buffer
Aeration (cascading)	Flocculation
Rapid sand filtration (open system)	Rapid sand filtration
Reuse backwash water	UV Disinfection
Water storage	
Distribution pump	

To calculate the costs of this treatment chain, the 'Kostencalculator drinkwater' developed by Royal Haskoning DHV is used (www.kostenstandaard.nl). It is assumed that the fictitious plant has a production capacity of 1000 m³ per hour and a distribution capacity of 1500 m³ per hour. Four different scenarios are compared; a conventional plant with an inlet of 3 mg Fe/L (aerobic average) and one with an inlet of 25 mg Fe/L (aerobic high) both producing only iron-hydroxides as sludge and an anaerobic plant with an inlet of 3 mg Fe/L (anaerobic average) and one with 25 mg Fe/L (anaerobic high) producing vivianite. The only variation between the scenarios is the amount of non-chemical sludge discharge, all other parameters influencing the calculations are set on standard and can be found in Appendix H.

To calculate the amount of sludge produced in the conventional treatment plant, it is assumed that all the iron is converted to iron hydroxides according to Equation 1.1. An inlet concentration of 1 mg Fe/L with a production of 1000 m³ per hour results in approximately 1.9 kg of sludge per hour, meaning that more than 16 ton of sludge is produced annually at 1 mg Fe/L. As observed in the experiments, 3 times less sludge is produced when vivianite is formed instead of iron hydroxides. This result is used for the calculations, an overview of the 4 different scenarios is presented in Table 5.2.

Table 5.2: The inlet Fe concentration and sludge discharge per scenario used in the kostencalculator.

Scenarios	Inlet Fe(II) (mg/L)	Sludge production (ton DS /year)
Aerobic average	3	49.8
Aerobic high	25	415
Anaerobic average	3	16.6
Anaerobic high	25	138

The investment (CAPEX) and operational (OPEX) costs of each step is presented in Table 5.3. From this table, it becomes clear that treating the backwash water is the most costly process step in the system and is highly depending on the concentration of iron in the inlet, since more sludge is produced at higher iron concentrations. The operational costs for an average aerobic treatment plant, considering a inlet iron concentration of 3 mg/L, is almost €11.5 million. With the assumed production rate of 1000 m³ per hour this means a cost of approximately 1.2 €/m³, which is higher than the average costs of 1 m³ of drinking water in the Netherlands which is around €0.70 [63]. In the calculations it is assumed that all backwash water is treated to drinking water standards, which is not always done in practice and probably causes the extra costs.

The costs of treating the backwash water is the main contributor to the final operational costs. This means that a 3 times sludge decrease also results in a costs decrease of approximately 3 times, which means anaerobic iron removal can drastically decrease the operational costs of drinking water treatment. The 1.2 €/m³ reduces to approximately 0.5 €/m³ when the water is treated anaerobically.

These are very rough calculations to give a first insight in the possible profit of removing iron anaerobically instead of aerobic. These results should be interpreted with care and some important considerations should be kept in mind:

- The possible profit of selling the iron sludge or vivianite is not taken into account. This might make the recovery of iron via vivianite even more interesting, since the marketvalue of vivianite is approximately 60 times higher than of iron sludge.
- Instead of treating the backwash water to drinking water, it can also be disposed on e.g. a nearby natural water body. This will reduce the costs of treating the backwash water tremendously, but a similar trend will be visible for the different scenarios. Also a 3 times reduction in costs will be observed, it will only decrease the total costs.
- Not taken into account in these calculations are the investment costs for an additional treatment step when anaerobic iron removal is considered. This is not included, since a final design is not yet determined and because the operation costs are significantly higher than the investment costs. This suggest that the possible investment costs will be earned back in a very short time. If an anaerobic filter is installed before oxidation to remove the iron and if it is assumed that the costs of such a filter is similar to a RSF, the earnback time will be approximately 1 month at the anaerobic scenario with 25 mg Fe/L, if assumed that the backwash water is treated to drinking water quality.
- The needed dosing of phosphate is not taken into account in Table 5.3. The costs of sodium phosphate will depend on the supplier and on the demanded volume. The average price for chemicals used in the Kostencalculator is 0.879 €/kg. For the anaerobic high iron concentration of 25 mg/L, this would mean an annual costs of €243,719 which is negligible compared to the savings of 46 million when iron is removed anaerobically at this concentration.
- However, also the environmental costs of phosphate should be considered, and the recover possibilities of phosphate are of importance to decide if this method is applicable, as discussed in the previous section.

Table 5.3: The CAPEX and OPEX obtained by the kostencalculator of each process step in the 4 different scenarios.

Scenario	Aerobic average		Aerobic high		Anaerobic average		Anaerobic high	
	CAPEX (€)	OPEX (€/y)	CAPEX (€)	OPEX (€/y)	CAPEX (€)	OPEX (€/y)	CAPEX (€)	OPEX (€/y)
Water well	1.927.013	306.39	1.927.013	306.39	1.927.013	306.39	1.927.013	306.39
Aeration (cascading)	496.248	52.570	496.248	52.570	496.248	52.570	496.248	52.570
RSF (open system)	3.846.595	302.413	3.846.595	302.413	3.846.595	302.413	3.846.595	302.413
Reuse backwash water	1.164.601	10.297.825	1.164.601	83.451.767	1.164.601	3.647.466	1.164.601	28.025.437
Water storage	2.592.013	140.017	2.592.013	140.017	2.592.013	140.017	2.592.013	140.017
Distribution pump	3.778.615	351.856	3.778.615	351.856	3.778.615	351.856	3.778.615	351.856
Total	13.805.085	11.451.071	13.805.085	84.605.013	13.805.085	4.800.712	13.805.085	29.178.683

5.6 Suitable Plants

Removing iron anaerobically is done successfully in this research. To implement this technique in practice, there are some considerations which are discussed in this section. The most profit can be obtained at plants with a high iron concentration in the raw water, switching towards anaerobic iron removal will substantially decrease the sludge production. An additional reason is that conventional systems are more likely to fail at high iron concentrations. Identifying which plant might benefit from anaerobic iron removal compared to aerobic iron removal should be investigated per plant individually. To give an idea of the areas where this might be beneficial, an overview is given of locations where iron concentrations are high.

In the Netherlands the iron groundwater quality is mapped by the geological survey of the Netherlands. In Figure 5.2 the results of this survey is visualised. The map is dominated by green dots, indicating an iron concentration below 5 mg/L. Although the benefits might be less, iron can be removed in these plants anaerobically by increasing the pH. In the regions in which Vitens is operating, most areas have a concentration below 5 mg/L, which is in line with the concentrations presented in Table 1.1.

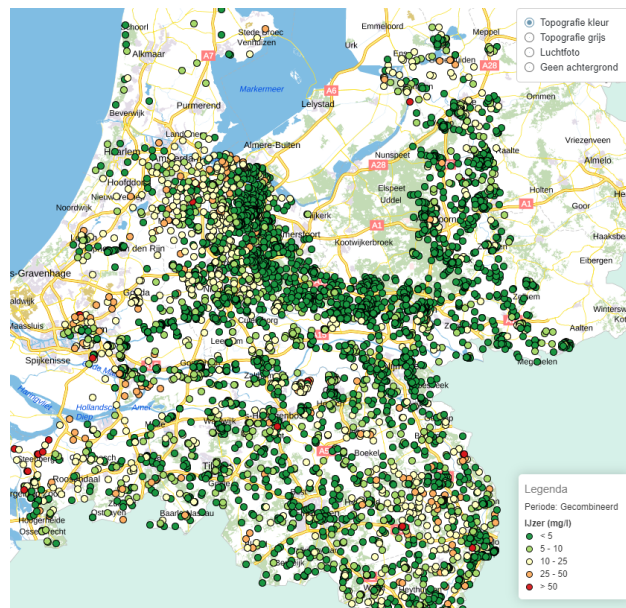


Figure 5.2: Fe concentrations in groundwater in the Netherlands.(www.grondwatertools.nl)

The method might especially be of interests in areas where elevated levels of iron in groundwater occur frequently, which are less found in the Netherlands (Figure 5.2). Higher iron concentrations can come from natural causes or an increase can be observed by pollution of e.g. a nearby landfill [10], which can cause increases of iron concentration up to 142 mg/L at landfill borders [64]. Merrill et al. [65] found an average concentration of 16.3 mg Fe/L in a rural area in northwestern Bangladesh [65]. Also in Belgium there are areas with high iron levels: in the first 100 m of the Neogene aquifer, iron concentrations up to approximately 65 mg/L are measured [66]. Also some areas in India are known for their high iron concentrations [67].

If it is worth investing in anaerobic iron(II) removal for Vitens where low iron concentrations occur, should be further investigated and will depend on e.g. the costs of dosing chemical to increase the pH. This is not taken into account in this research. It is however likely that anaerobic iron removal is an interesting option for several areas in the Netherlands and in other places around the globe where elevated iron concentration occur, leading to a more profitable and efficient groundwater treatment plant while achieving a good or even better iron removal compared to the conventional systems.

6 Conclusion

This research successfully demonstrated the novel concept of anaerobic iron(II) removal from groundwater by precipitation of vivianite. Up to 93% removal was achieved experimentally by dosing phosphate to iron(II) spiked groundwater. Increasing the pH of the system is expected to enhance the removal. An additional aeration step increased the removal up to 99.9%, which was higher than the 85.1% removal obtained with the conventional aeration-filtration technique. The anaerobic removal followed second order kinetics at a pH of 7 and the half life of iron was 4 minutes, which is 4 times faster than obtained by oxidation of iron at the same pH. Vivianite was the only crystalline product detected after anaerobic precipitation and aeration, indicating that it remains stable under oxic conditions. The volume of the vivianite sludge was a third compared to the aqueous iron sludge produced in the conventional oxidation method, which can decrease the operational costs of groundwater treatment substantially. The market value of vivianite is 60 times higher than the currently produced sludge.

Vivianite can only form when its saturation index is between 4 and 11. Increasing the pH elevates the SI and it is expected that the lowest initial iron concentration at which iron can be removed by anaerobic vivianite precipitation, is 1 mg Fe/L at a pH of 8.5. This makes the technique suitable for many locations worldwide. The largest profit compared to the conventional method can be gained for groundwater with a high iron concentration, since conventional systems are less effective in treating elevated iron concentrations while large sludge volumes are produced.

Given that phosphate is a limited resource, dosing sulphate and carbonate were investigated as alternatives to phosphate. By dosing sulphate, the iron removal by oxidation was hampered and only 73% of iron was removed in total. The anaerobic iron removal with carbonate was 59% and increased up to 88% by oxidation. No compact mineral was formed, the sludge consisted of a mixture of different crystalline and amorphous structures with a volume 18 times higher compared to the removal with phosphate.

The good removal efficiency, the fast rate and the possible economical savings make anaerobic iron(II) removal by forming vivianite a promising alternative to the conventional treatment method of oxidation and filtration. Further laboratory experiments are required to fully understand the effect of pH on this process. Another essential process not yet investigated is how vivianite can be removed from the stream in a groundwater treatment system and how phosphate can eventually be recovered for reuse.

7 Recommendations

The possibility of removing and recovering iron(II) by precipitation with phosphate to form vivianite seems promising. More research is however needed before this method can be applied in practice. Some additional knowledge is required about the fundamental processes, as well as more knowledge about the feasibility of important application features such as the recovery of phosphate. In this chapter, a list of these recommendations is given based on the findings in this study.

- Finding the optimal phosphate dosage and pH: increasing the pH increases the SI which can lead to a better iron removal. Less dosage of phosphate might be necessary while still achieving a good removal efficiency, which will also decrease the phosphate concentration in the produced water. The optimum should be found in future experiments.
- The kinetics of vivianite formation has only been determined for one certain set of process conditions; the influence of pH and other parameters such as alkalinity should be investigated.
- The structure of the formed vivianite crystals is not researched in this study. Understanding the crystallisation of vivianite better and the difference in obtained purity by using different precipitation methods will help to develop more knowledge on the possibility of recovering the vivianite by e.g. using the paramagnetic properties.
- A best method should be found for the recovery of the vivianite from the water stream. When filtration is used, the buoyancy of vivianite should be studied and compared to the filter bed material.
- A market research should be done to investigate the interest in vivianite, which purities are needed and how the market value is compared to the currently produced iron sludge. It should also include the costs of dosing phosphate to the chain and include how much phosphate can be recovered and what the (economical) costs are if not all the phosphate can be recovered.
- The possibility of adding a seeding material is an interesting next research step. This might increase the iron removal while decreasing the needed phosphate. It might decrease the reaction time and separating the crystals can get easier compared to homogeneous crystallisation. Which material is the most suitable should be investigated.
- In this study, only the possibility of removing iron(II) with anions naturally present in groundwater are studied. Exploring the method with other anions might be interesting as well. An example is sulfide; pyrite is the most commonly occurring metal in many sediments [68].
- In groundwater with elevated sulphate and silicate concentrations, the possible decrease in iron removal efficiency by forming complexes with iron(II/III) should be taken into account.
- In this research the focus was on capturing the iron while it was not yet oxidised. Another possibility to use the method of vivianite precipitation, is to reduce the iron present in the currently produced sludge back to iron(II) and let it react with phosphate subsequently.

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A Development Methodology

A.1 Methodology

A.1.1 Iron Solution

In studies to vivianite both iron chloride (FeCl_2) [29] and iron sulphate (FeSO_4) [69, 70] are used to prepare the iron solution. To determine the most suitable solution for the experiments in this research, a 100 mg/L iron solution in a reactor of 100 mL of both compounds was made to which phosphate (HNa_2PO_4) at a molar ratio of 1 is added. The efficiency of iron and phosphate removal was determined and the most suitable iron source is based on these results.

A.1.2 Sample Handling

To find out what the best method is to take samples during the experiments, several methods were tested. To a 100 mL reactor containing an iron solution of 100 mg/L, phosphate was added with a 1:1 molar ratio. 4 samples of 5 mL were taken directly after mixing 1 minute and handled in different ways. An overview of the different handling methods is given in Table A.1. The 5 mL 'raw' sample was left untouched. To the acidified sample, 0.2 mL of 0.1M HCl was added directly after sampling. Bringing the pH below 6 is expected to stop the reaction (Figure 3.9a). The 'filtered' sample was directly filtered through a $0.45\ \mu\text{m}$ non-sterile PDVF syringe filter before storage and the 'filtered and acidified' sample was first filtered and subsequently acidified in the same way. The pH values of the 4 samples were measured at minute 1 and after 2 hours. Also after 2 hours, the remaining solution in the reactors was vacuum filtered with 2 different membrane to see the influence of the pore size. Sartorius 'PESU membranes' are used for the vacuum filtration with $0.1\ \mu\text{m}$ filters and PALL 'supor membranes' for the filtration with $0.45\ \mu\text{m}$ filters. From these 6 samples, the removal efficiency of iron was determined and the ratio of removed phosphate:iron by also measuring the final phosphate concentration. To be able to measure the removal efficiency of the raw sample, it was filtered through a $0.45\ \mu\text{m}$ filter just before measuring the iron concentration.

Table A.1: The 6 different samples taken and their corresponding handling method

Sample	Method	Time (min)	Acidified	Filtered
1	Raw	t=1	x	$0.45\ \mu\text{m}$ at t=120
2	Acidified	t=1	0.2 mL 0.1M HCl	x
3	Filtered	t=1	x	$0.45\ \mu\text{m}$
4	Filtered and acidified	t=1	0.2 mL 0.1M HCl	$0.45\ \mu\text{m}$
5	Reactor filtered $0.45\ \mu\text{m}$	t=120	x	$0.45\ \mu\text{m}$
6	Reactor filtered $0.1\ \mu\text{m}$	t=120	x	$0.1\ \mu\text{m}$

A.1.3 XRD Analyses

XRD analyses were done to analyse which compounds were formed during the anaerobic and aerobic (if applicable) reactions. The standard method mentioned in literature [23, 45] with glass capillaries is not very user friendly and therefore some other methods were tested and compared.

In the experiments explained in the previous subsection about sample handling (subsection A.1.2), the reactors were vacuum filtered after 2 hours. On the filters, the solids formed during anaerobic precipitations were remained. The filters were left in the anaerobic chamber for one day to evaporate the remaining water. It was saved in a closed petridish covered with aluminium foil to prevent auto-oxidation. Afterwards, 4 samples were prepared for XRD analysis handled in different ways: in a capillary, on a Si510 zero-background-wafer and 2 were left on the 0.1 μm PESU filter of which one was covered with glycerol and the other not.

All samples were prepared inside the anaerobic chamber. For the capillary, the solids formed during anaerobic precipitation were scraped off the filter with a spatula, powdered and carefully transferred to a 0.7 mm glass capillary. To prevent oxidation, the capillary was closed with super glue. For the wafer, the solids were also scraped from the filter and powdered and transferred onto the wafer. To prevent oxidation, oxygen-free glycerol was added onto the solids which is known to inhibit oxidation of green rust (GR) [53]. This method has not been tested yet for vivianite. For the third method, the solids were left onto the filter used for vacuum filtration. The filter was cut in half. One half was covered with a layer of oxygen-free glycerol and to the other half nothing was done. An overview of the samples is given in Table A.2.

Table A.2: The four different sample preparation methods that are tested for practicality.

Sample preparation	Glycerol layer	Literature
Capillary	No	[23, 45]
Wafer	Yes	Only for GR [53]
Filter	Yes	Only for GR [53]
Filter	No	-

A.2 Results

A.2.1 Iron Solution

With the iron chloride solution, 71.4% iron was removed by the anaerobic reaction with phosphate. The ratio of removed phosphate:iron was 0.67, which suggests that vivianite did form confirmed by XRD (subsection A.2.3). With the iron sulphate solution, 67.8 % iron was removed with a ratio of 0.83. Since the removal was less and the ratio suggested that not only vivianite did form, it was chosen to continue the further experiments with iron chloride. In all further experiments in which iron is added, an iron chloride solution is used. In these solutions, approximately 2% of the iron was present in the oxidised iron(III) form, while the remaining iron was present as iron(II). The anaerobic environment together with the pH below 5 of the iron solutions kept most of the iron in the reduced state.

A.2.2 Sample Handling

The results of the 6 different methods of sampling are presented in Table A.3. Acidifying the samples brought the pH below the vivianite pH boundary of pH 6. The raw sample taken at $t=1$ that was left untouched had eventually a comparable removal efficiency as the sample taken from the reactor after 2 hours, as expected. The acidified sample showed a very low removal of iron, which is probably because the formed precipitate is dissolved again at this pH. Also the ratio suggests that no vivianite is formed. From the comparison of the sample which was only filtered and filtered and acidified, it can be concluded that acidification is essential to stop the reaction. It suggests that after filtering, the precipitation reaction continued with the remaining iron

and phosphate. The 2 samples from the reactor taken after 2 hours only differ in filter pore size, in which a 1.9% higher removal efficiency is observed for the samples filtered through a 0.1 μ m filter.

From this experiment it is decided that samples are always filtered through a 0.45 μ m filter and acidified with 0.2 mL HCl afterwards, since this is more practical than a 0.1 μ m filter and the difference is only small. The ratio of removed phosphate:iron of 0.67 suggest that vivianite is indeed formed and removed by filtering, while no extra is formed after acidification. What is important to keep in mind is that the ferrozine method used to measure the iron(II/III) concentrations only functions properly when the pH is above 3. Since the samples are often strongly diluted before measuring, this is not considered as a problem. If a sample is not diluted before measuring the iron concentration, 0.1 mL HCl instead of 0.2 mL is added and the pH is checked before measuring. The 'acidified and filtered' sample from Table A.3 had a pH above 3 after diluting.

Table A.3: The pH, removal of Fe and the removed PO₄:Fe ratio of the 6 samples with different handling methods.

Sample	Method	pH	Removal Iron (%)	Ratio Fe:PO ₄
1	Raw	6.51	72.4	0.63
2	Acidified	2.63	5.4	0.48
3	Filtered	6.75	64.4	0.63
4	Acidified and Filtered	2.45	45.8	0.67
5	Reactor filtered 0.45 μ m	5.74	73.0	0.63
6	Reactor filtered 0.1 μ m	5.74	74.4	0.63

A.2.3 XRD Analyses

Table A.4: XRD result of the samples prepared for XRD analysis in 4 different ways.

Sample preparation	Glycerol layer	Compound
Capillary	No	No result
Wafer	Yes	Vivianite Fe ₃ (PO ₄) ₂ (H ₂ O) ₈
Filter	Yes	Vivianite Fe ₃ (PO ₄) ₂ (H ₂ O) ₈
Filter	No	Vivianite Fe ₃ (PO ₄) ₂ (H ₂ O) ₈

The result of the XRD analysis is presented in Table A.4 and the patterns are given in Figure G.1 in subsection A.2.3. Since the measurement done with the capillary gave no result and because the preparation of the samples is much easier by leaving them on the filters, it is decided that in coming experiments all XRD measurements will be done on the solids that are dried and kept on the filter with which it is vacuum filtered. Glycerol is always applied, to minimise oxidation. The oxidation did not seem to have an effect on the results of this experiment, but when less mass or several compounds are formed in one solution it might be necessary.

B SI Interaction Fe-PO₄

B.1 Methodology

The saturation index of vivianite was determined theoretically for the systems at each measurement point obtained experimentally. For the experiments with synthetic water, the iron removal over time and the iron removal at different initial iron concentrations were simulated. For the experiments with groundwater, the removal over time at the two different initial concentrations were simulated. The input for the model was the iron and phosphate concentration of each measurement point and the corresponding pH. For each simulation, the Fe⁺⁺/Fe⁺⁺⁺ redox couple was set to decoupled in the model.

For the removal over time in synthetic water, the inserted concentrations were as depicted in Figure 3.1a and presented in Table B.1. For the different initial iron concentrations, the inserted concentrations were as described in subsection 2.4.1 and depicted in Figure 3.1d, the input is presented in Table B.2.

Table B.1: Data input for GWB® SpecE8 to calculate the SI of vivianite formation at the measurements points of the kinetics experiment - synthetic water

Compound	Value										Unit
Time	0	1	5	10	15	20	40	50	60		min
H2O	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	Free kg
Fe ⁺⁺	1.79E-03	1.03E-03	7.48E-04	5.17E-04	4.87E-04	4.74E-04	4.73E-04	4.94E-04	4.71E-04	4.71E-04	mol/L
Cl-	3.58E-03	2.07E-03	1.50E-03	1.03E-03	9.74E-04	9.49E-04	9.45E-04	9.88E-04	9.42E-04	9.42E-04	mol/L
HPO ₄ ⁻	0.001771	0.001344	0.001125	0.000973	0.000958	0.000931	0.000947	0.000978	0.000933	0.000933	mol/L
Na+	3.54E-03	2.69E-03	2.25E-03	1.95E-03	1.92E-03	1.86E-03	1.89E-03	1.96E-03	1.87E-03	1.87E-03	mol/L
H+	6.86	6.78	6.28	5.94	5.81	5.83	5.83	5.83	5.83	5.83	pH
Temp	21	21	21	21	21	21	21	21	21	21	C

Table B.2: Data input for GWB® SpecE8 to calculate the SI of vivianite formation at different initial iron concentrations - synthetic water

Compound	Value					Unit
Conc initial Fe	0	10	25	50	100	mg/L
H2O	0.5	0.5	0.5	0.5	0.5	Free kg
Fe ⁺⁺	1.79E-05	0.000179	0.000448	0.000895	0.001791	mol/L
Cl-	3.58E-05	3.58E-04	8.95E-04	1.79E-03	3.58E-03	mol/L
HPO ₄ ⁻	1.79E-05	0.000179	0.000448	0.000895	0.001791	mol/L
Na+	3.58E-05	3.58E-04	8.95E-04	1.79E-03	3.58E-03	mol/L
H+	7.73	6.5	6.59	6.25	6.9	pH
Temp	21	21	21	21	21	C

In the experiments in which natural groundwater was used, the iron removal over time of both the experiments with a natural initial iron concentration and with the increased iron concentration of 100 mg/L were simulated. The input is presented in Table B.4 and Table B.5 respectively. These simulations represents the experiments as depicted in Figure 3.13.

Table B.3: Data input for GWB® SpecE8 to calculate the SI of vivianite formation at the measurements points of the kinetics experiment with groundwater

Table B.4: Natural iron concentration

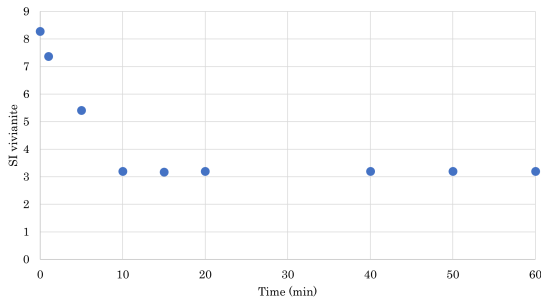
Compound	Value					Unit
	0	1	5	15	60	
Time						min
H2O	0.5	0.5	0.5	0.5	0.5	Free kg
Fe++	6.81E-05	5.52E-05	5.49E-05	5.54E-05	5.67E-05	mol/L
Cl-	1.36E-04	1.10E-04	1.10E-04	1.11E-04	1.13E-04	mol/L
HPO4-	5.47E-05	2.22E-05	2.21E-05	2.23E-05	2.14E-05	mol/L
Na+	1.09E-04	4.45E-05	4.41E-05	4.45E-05	4.27E-05	mol/L
H+	7.64	7.64	7.69	7.72	7.84	pH
Temp	21	21	21	21	21	C

Table B.5: Spiked groundwater, 100 mg Fe/L

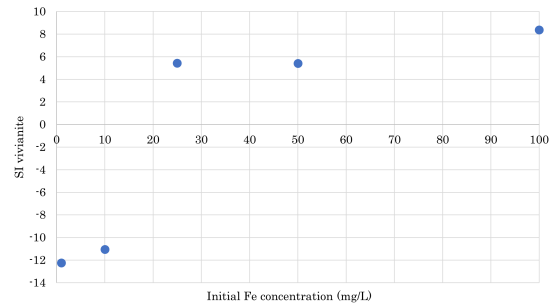
Compound	Value					Unit
	0	1	5	15	60	
Time						min
H2O	0.5	0.5	0.5	0.5	0.5	Free kg
Fe++	0.001791	0.001051	0.000576	0.000603	0.000112	mol/L
Cl-	3.58E-03	2.10E-03	1.15E-03	1.21E-03	2.24E-04	mol/L
HPO4-	0.001789	0.000454	0.000369	0.000366	0.000273	mol/L
Na+	3.58E-03	9.08E-04	7.37E-04	7.33E-04	5.46E-04	mol/L
H+	7	7.03	6.92	6.74	6.77	pH
Temp	21	21	21	21	21	C

B.2 Results

In the kinetics experiment with synthetic water, the simulated SI of vivianite formation dropped when the concentration of iron and phosphate and the pH dropped as well (Figure B.1a). No extra iron removal was observed after 10 minutes (visible in Figure 3.1a), at which the SI value was 3. For the different initial iron concentrations, the SI was negative for concentrations under 10 mg/L (Figure B.1b). From 25 mg/L the SI increased above 5, which is the minimal concentration at which removal was obtained during the experiments (visible in Figure 3.1d).



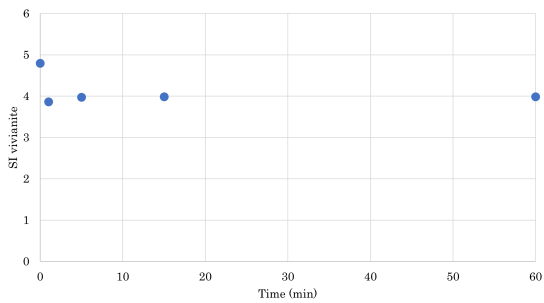
(a) Kinetics



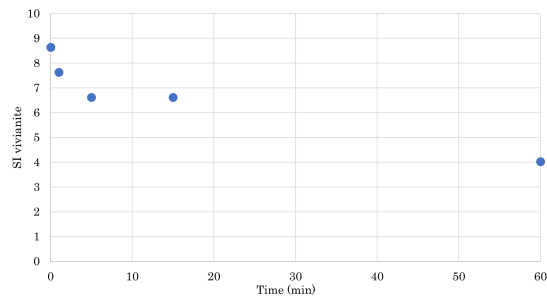
(b) Initial Iron Concentration

Figure B.1: The modelled saturation index of the removal of iron over time experiment (Figure 3.1a and at different initial iron concentrations Figure 3.1d)

In the kinetics experiment with natural iron concentrations, only some removal was observed at minute 1 (visible in Figure 3.13b). The SI value was 5 at the start of the experiment and dropped to 4 after 1 minute (Figure B.2a). No extra removal was observed afterwards and the SI of vivianite stayed stable for the remaining time. With spiked groundwater of 100 mg Fe/L, the SI decreased over time (Figure B.2b) caused by a decrease in iron and phosphate concentration (visible in Figure 3.13a) and pH. No extra removal was observed at minute 60, when the SI was approximately 4.



(a) Natural iron concentration



(b) Spiked groundwater, 100 mg Fe/L

Figure B.2: The modelled saturation index of the removal of iron over time in groundwater with a natural initial iron concentration and an initial iron concentration of 100 mg Fe/L experiments

C pH Interaction Fe-PO₄

C.1 Comparison pH Experiments Synthetic and Groundwater

The pH of the iron removal by adding phosphate is shown in Figure C.1 for the experiments with synthetic water and groundwater. In both experiments, a 100 mg/L initial iron concentration was used. After approximately 20 minutes, the pH stabilised.

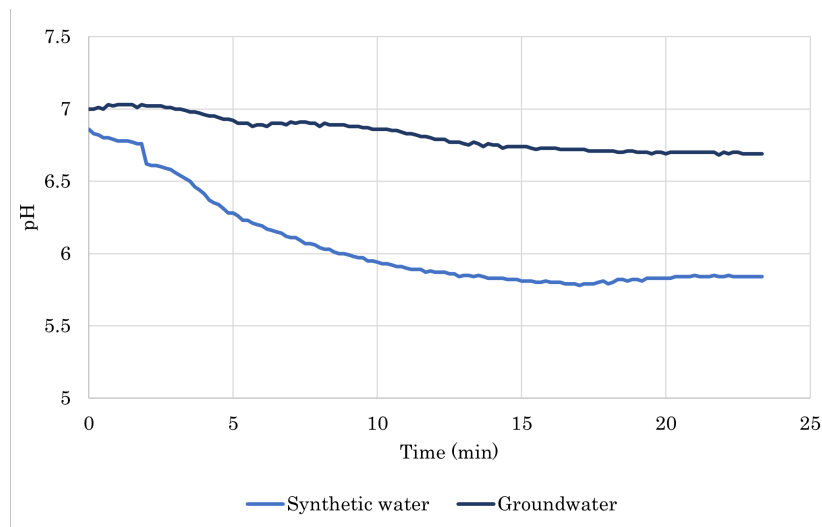


Figure C.1: The pH over time for the Fe removal experiments in which PO₄ is dosed in either synthetic or groundwater. Ratio PO₄:Fe added 1:1, initial Fe concentration 100 mg/L.

C.2 pH Initial Iron Concentrations Experiments Groundwater

In the experiments in which raw groundwater is used, two different initial iron concentrations were used; the natural concentration present of approximately 3 mg/L and an overdose of 100 mg/L. The pH gradient of these two experiments are depicted in Figure C.2 and Figure C.3 respectively.

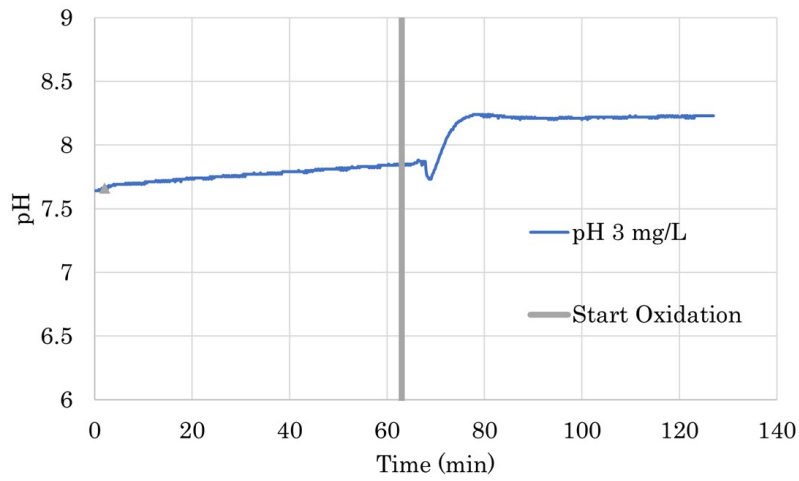


Figure C.2: The pH over time for the Fe removal experiments in which PO_4 is dosed in groundwater. Ratio $\text{PO}_4:\text{Fe}$ added 1:1, initial Fe concentration 3 mg/L.

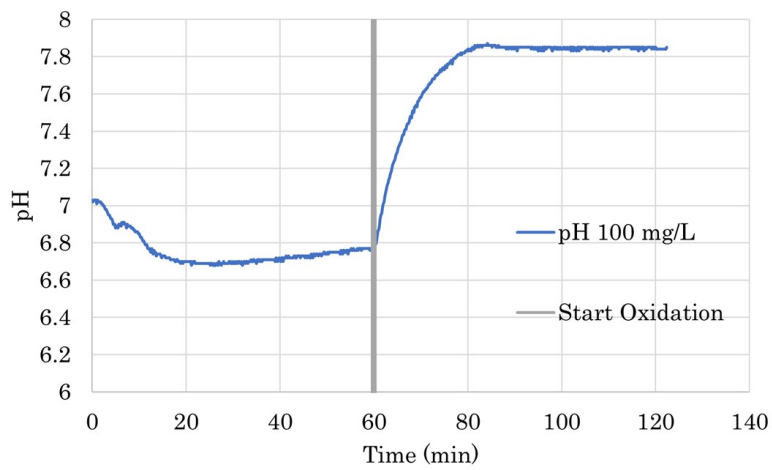


Figure C.3: The pH over time for the Fe removal experiments in which PO_4 is dosed in groundwater. Ratio $\text{PO}_4:\text{Fe}$ added 1:1, initial Fe concentration 100 mg/L.

D pH Dependency SI Vivianite

The input in GWB® SpecE8 to obtain the relation between SI and pH is given in Table D.1 and the results presented in Figure D.1.

Table D.1: Data input for GWB® SpecE8 to calculate the SI of vivianite formation at different pH's with a initial iron concentration of 100 mg/L and a dosed phosphate ratio of 1.

Compound	Value					Unit
pH	5	6	7	8	9	
H2O	0.5	0.5	0.5	0.5	0.5	Free kg
Fe ⁺⁺	1.79E-03	1.79E-03	1.79E-03	1.79E-03	1.79E-03	mol/L
Cl ⁻	3.58E-03	3.58E-03	3.58E-03	3.58E-03	3.58E-03	mol/L
HPO4 ⁻	1.79E-03	1.79E-03	1.79E-03	1.79E-03	1.79E-03	mol/L
Na ⁺	3.58E-03	3.58E-03	3.58E-03	3.58E-03	3.58E-03	mol/L
H ⁺	5	6	7	8	9	pH
Temp	21	21	21	21	21	C

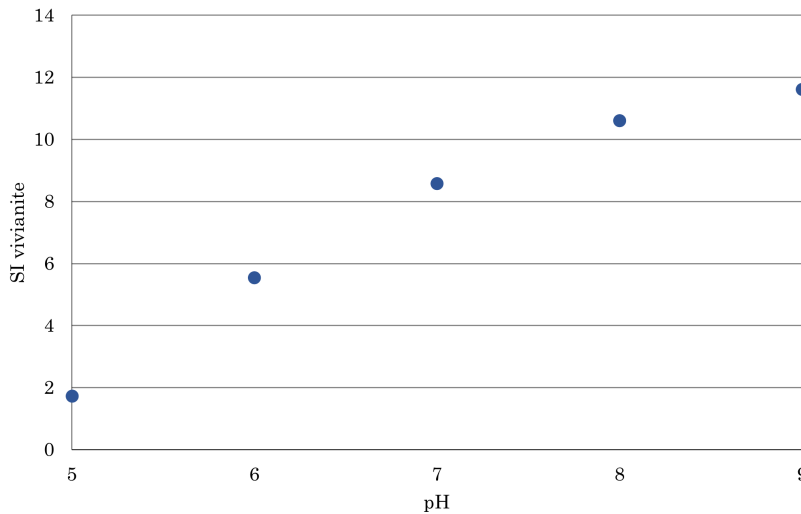


Figure D.1: The saturation index for vivianite at different pH's. Initial iron concentration 100 mg/L, Ratio PO₄:Fe added 1:1 - synthetic water.

A similar simulation is done, but now for different initial iron concentration. The SI is calculated for different pH steps between 6 and 9. The result is given in Figure 3.4. The input for the GWB® SpecE8 used to calculate the relation between SI and initial iron concentration at pH 6 to 9 is given in Table D.2.

Table D.2: Data input for GWB® SpecE8 to calculate the SI of vivianite formation at different initial iron concentration and at different pH's. Ratio phosphate to iron is 1.

Compound	Value								Unit
Conc initial Fe	1	2.5	5	10	15	25	50	100	
H2O	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	Free kg
Fe++	1.8E-05	4.48E-05	8.95E-05	0.00018	2.69E-04	4.48E-04	8.95E-04	1.79E-03	mol/L
Cl-	3.58E-05	8.95E-05	1.79E-04	3.58E-04	5.37E-04	8.95E-04	1.79E-03	3.58E-03	mol/L
HPO4-	1.8E-05	4.48E-05	8.95E-05	0.00018	2.69E-04	4.48E-04	8.95E-04	1.79E-03	mol/L
Na+	3.58E-05	8.95E-05	1.79E-04	3.58E-04	5.37E-04	8.95E-04	1.79E-03	3.58E-03	mol/L
H+	6 to 9	6 to 9	6 to 9	6 to 9	6 to 9	6 to 9	6 to 9	6 to 9	pH
Temp	21	21	21	21	21	21	21	21	C

E Order Kinetics Vivianite Formation

E.1 Synthetic Water

To determine the reaction order of the kinetics of iron removal by vivianite precipitation, 3 scenarios are simulated; the removal following zero, first or second order kinetics. In the calculations only the first 10 minutes of the iron removal (Figure 3.1a) are taken into account since the removal stops after 10 minutes and no additional vivianite is formed.

It is assumed that the iron removal is not depending on the phosphate concentration. The initial concentration of iron and phosphate is the same and the ratio of removed iron and phosphate stays equal during the entire experiment, as can be seen in Figure E.1. Since the reaction order is the sum of the individual order per compound, it will also not effect the final outcome.

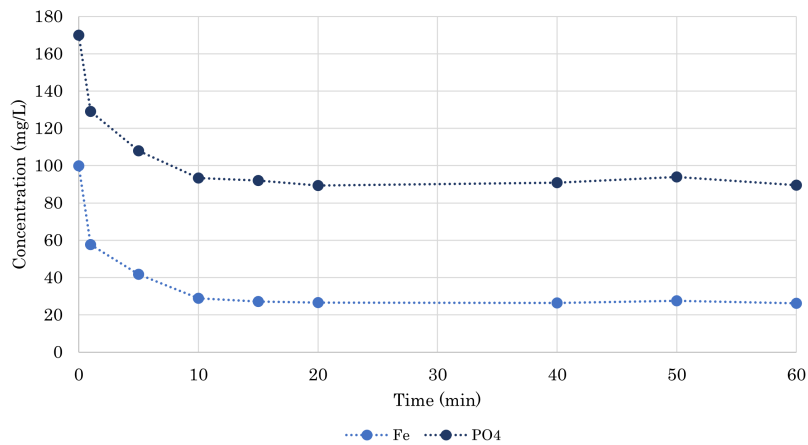


Figure E.1: The concentration iron and phosphate over time by the formation of vivianite (same data as in Figure 3.1a). Initial Fe concentration 100 mg/L, molar ratio $\text{PO}_4:\text{Fe}$ added 1:1 - synthetic water.

With this assumption, the rate law and their corresponding integration per order is given in Figure E.2. Since the order of the iron removal is determined, $[A]$ is $[\text{Fe}]$ in this research.

The linear plots to determine k for the three scenarios are depicted in Figure E.3. The determination constant R^2 is the highest for the second order plot and therefore it is concluded that iron removal by anaerobic vivianite precipitation follows a second order rate.

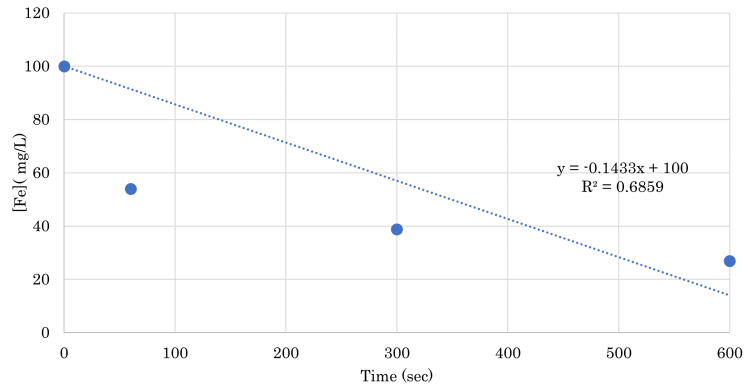
The rate constant is 2.65 M/s. The equation for the removal of iron therefore follows:

	Zero-Order	First-Order	Second-Order	n th -Order
Rate Law	$-\frac{d[A]}{dt} = k$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$ ^[8]	$-\frac{d[A]}{dt} = k[A]^n$
Integrated Rate Law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ ^[8]	$\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)kt$ [Except first order]
Units of Rate Constant (k)	$\frac{M}{s}$	$\frac{1}{s}$	$\frac{1}{M \cdot s}$	$\frac{1}{M^{n-1} \cdot s}$
Linear Plot to determine k	$[A]$ vs. t	$\ln([A])$ vs. t	$\frac{1}{[A]}$ vs. t	$\frac{1}{[A]^{n-1}}$ vs. t [Except first order]
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$ ^[8]	$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$ [Except first order]

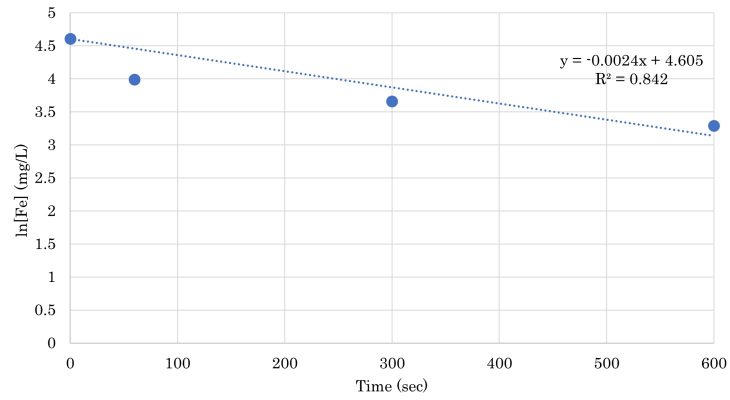
Figure E.2: Summary of equations for (integrated) rate laws for zero-, first-, second- and nth-order reactions. From: <https://courses.lumenlearning.com/boundless-chemistry/chapter/the-rate-law-concentration-and-time/>

$$\frac{d[Fe]}{dt} = 2.65[Fe]^2 \quad (E.1)$$

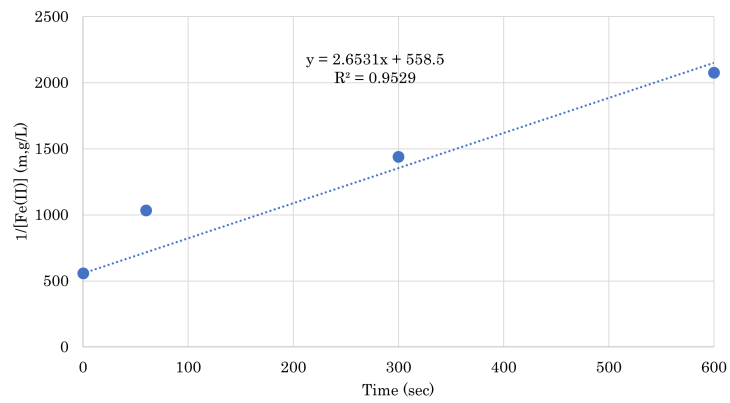
This equation only applies to a system in which the saturation index for vivianite formation is higher than 4. Below this number, no vivianite is formed. In the experiments determining the kinetics of the interaction between iron and phosphate, only in the first ten minutes removal was observed, since the SI dropped below 4 after ten minutes.



(a) Zero-order



(b) First-order



(c) Second-order

Figure E.3: Linear plots to determine k of the zero-order, first-order and second-order kinetics removal of iron by vivianite precipitation.

E.2 Groundwater

To check if the vivianite formation when natural groundwater was used also follows second order kinetics, the rate constant is again determined with a linear plot assuming a second order reaction (Figure E.4). In this case, also the measurement at $t=60$ is taken into account, since the SI did not drop below 4.

The rate constant is almost similar to the rate constant obtained with synthetic water; 2.27 M/s. The equation for the removal of iron therefore follows:

$$\frac{d[Fe]}{dt} = 2.27[Fe]^2 \quad (E.2)$$

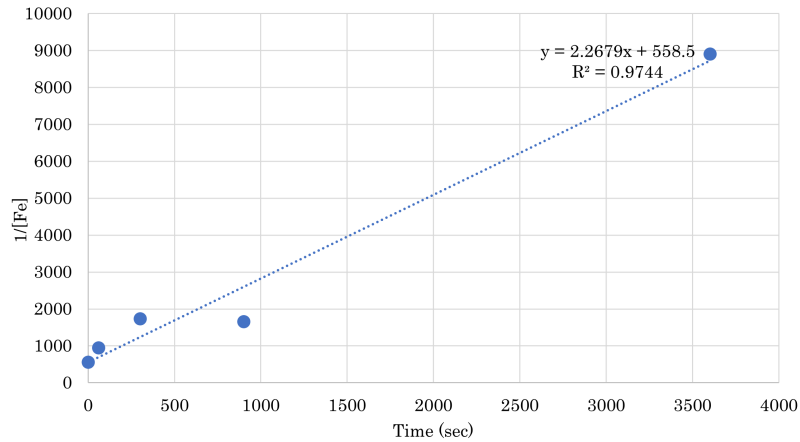


Figure E.4: Linear plot to determine k of the second order kinetics removal of iron by vivianite precipitation.

F Sludge Properties Fe removal by PO_4 and CO_3

In the experiments done in the lab with raw groundwater, carbonate and phosphate solutions were added to the groundwater to observe the effect on the iron concentration. In the experiments with phosphate, vivianite arised proven by the ratio of removed phosphate and iron and detected by XRD. Siderite was expected based on the pourbaix diagram of carbonate, but is not detected by XRD. The experiments were simulated by $\text{GWB}^{\text{®}}$ SpecE8 and the data input and results are presented in this chapter. This gives insight in the possible interactions with iron, carbonate and/or phosphate with the other compounds present in the groundwater.

F.1 Data Input

The input for the model used to simulate the reactions is the average data from the drinking water treatment plant of Vitens in Loosdrecht collected over two years from March 2018 until March 2020. Since this is an average value over a longer timespan, the input is not exactly the same as given in Table 3.4 or as the data given in Table 1.1, since the data is now coming from only 1 plant. It is chosen to use another input, since the analysis of data of the raw water used in the experiments is not complete, crucial parameters such as ammonium or methane can not be measured by ICP-MS. Another option would be to use the average data of all vitens plants as given in Table 1.1, but since Loosdrecht is a location experiencing some issues regarding iron removal and to make a more realistic comparison with the lab experiments, only the data of this plant was considered. The average data of these 2 years which were inserted in the model, are presented in Table F.1.

F.2 Results

The minerals that appeared in the model with a positive SI value are depicted in Table F.2 for phosphate and in Table F.3 for carbonate.

Table F.1: Data input for GWB® SpecE8 to simulate the reactions occurring when CO₄ or PO₄ is added to the groundwater with an overdose concentration of 100 mg Fe/L and concentrations as in Table 3.4. * Temperature as used during the experiment, not as measured by Vitens. ** Measured with ICP-MS, no Data from Vitens available.

Compound	Data Loosdrecht	CO ₃ addition	PO ₄ addition	Unit	Note
pH	7.34			-	
Temp	21.00			°C	*
Fe ⁺⁺	4.50	100	100	mg/L	
Na ⁺	8.68	49.86	49.86	mg/L	**
Ca ⁺⁺	38.49			mg/L	
Mn ⁺⁺	0.18			mg/L	
Mg ⁺⁺	2.19			mg/L	
NH ₄ ⁻	0.32			mg/L	
CH ₄	135.00			µg/L	
Cl ⁻	14.67			mg/L	
HCO ₃ ⁻	122.78	232.04		mg/L	
HPO ₄ ⁻	0.46		172.35	mg/L	
SiO ₄	23.18			mg/L	
SO ₄ ⁻	8.89			mg/L	

Table F.2: The obtained SI values from the model by the addition of PO₄ to the groundwater solution with 100 mg Fe/L.

Mineral saturation states	SI	Formula
Hydroapatite	6.9899	Ca ₁₀ (PO ₄) ₆ (OH) ₂
Minnesotaite	5.8979	(Fe ₂₊ ,Mg) ₃ Si ₃ O ₁₀ (OH) ₂
Vivianite	5.5089	Fe ₃ (PO ₄) ₂ * 8 H ₂ O
Greenalite	4.3594	(Fe ₂₊ ,Fe ₃₊) ₂ -3Si ₂ O ₅ OH ₄
Whitlockite	3.1476	Ca ₉ (MgFe)(PO ₄) ₄ PO ₃ OH
MnHPO ₄	1.5567	MnHPO ₄
Quartz	0.4308	SiO ₂
Ferrosilite	0.3398	(Mg,Fe)SiO ₃
Tridymite	0.2613	SiO ₂
Chalcedony	0.1557	SiO ₂
Fayalite	0.0217	Fe ₂ SiO ₄

Table F.3: The modelled SI values from the addition of CO₃ to the groundwater solution with 100 mg Fe/L.

Mineral saturation states	SI	Formula
Minnesotaite	5.9012	(Fe ₂₊ ,Mg) ₃ Si ₃ O ₁₀ (OH) ₂
Greenalite	4.3627	(Fe ₂₊ ,Fe ₃₊) ₂ -3Si ₂ O ₅ OH ₄
Quartz	0.4307	Fe ₃ (PO ₄) ₂ * 8 H ₂ O
Vivianite	0.3649	SiO ₂
Ferrosilite	0.3409	(Mg,Fe)SiO ₃
Tridymite	0.2613	SiO ₂
Siderite	0.2248	FeCO ₃
Chalcedony	0.1557	SiO ₂
Fayalite	0.0238	Fe ₂ SiO ₄

G XRD patterns

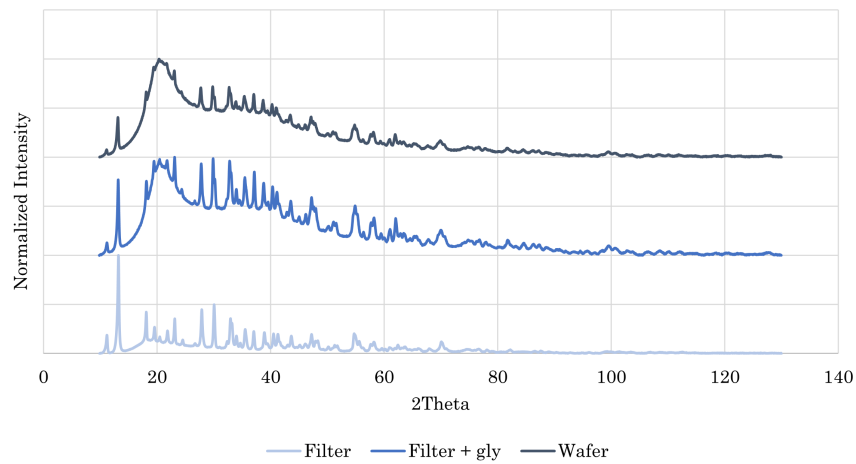


Figure G.1: XRD patterns of results presented in Table A.4

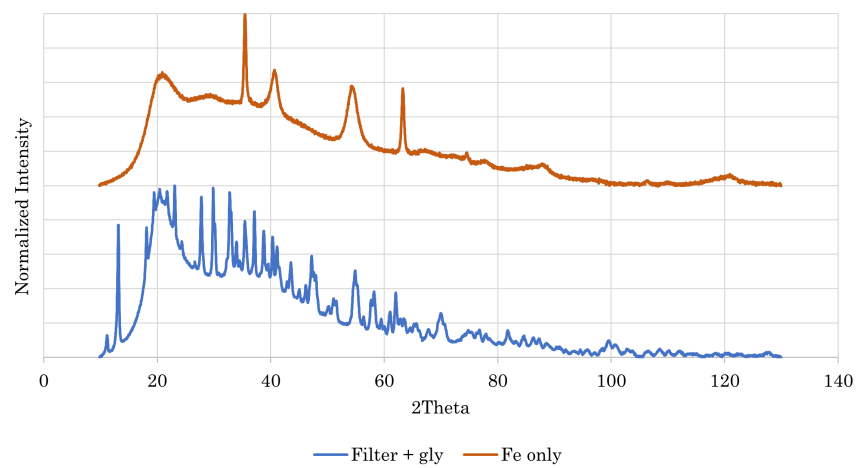


Figure G.2: XRD patterns of results presented in Table 3.1

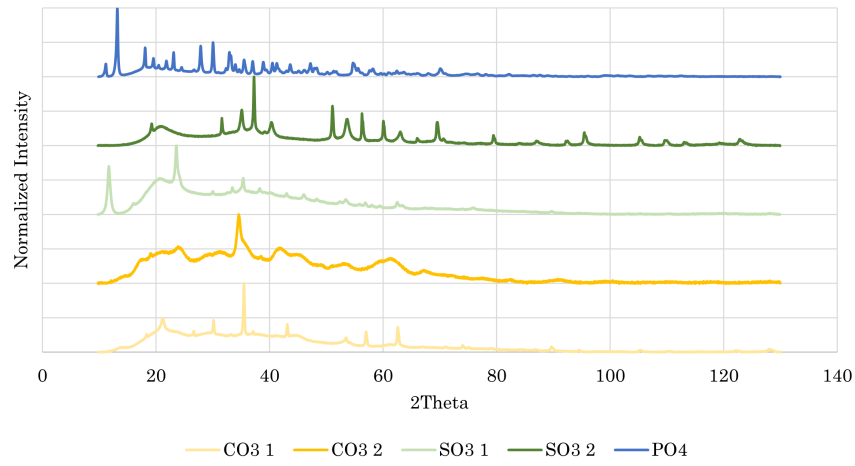


Figure G.3: XRD patterns of results presented in Table 3.3

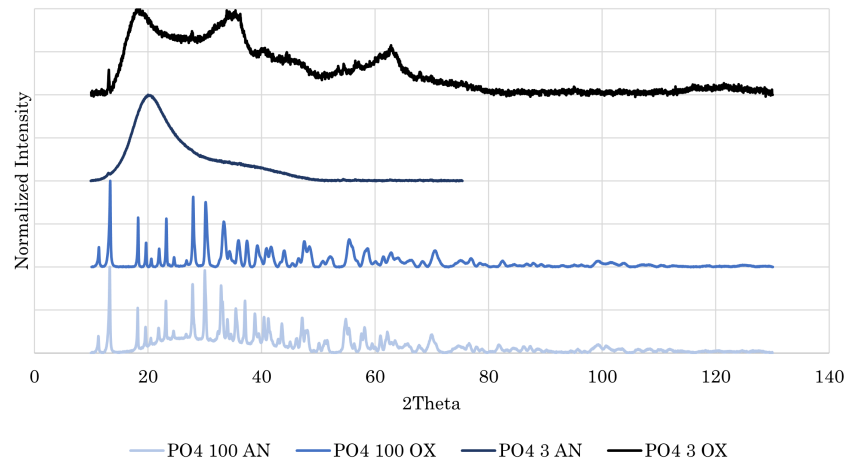


Figure G.4: XRD patterns of phosphate results presented in Table 3.6

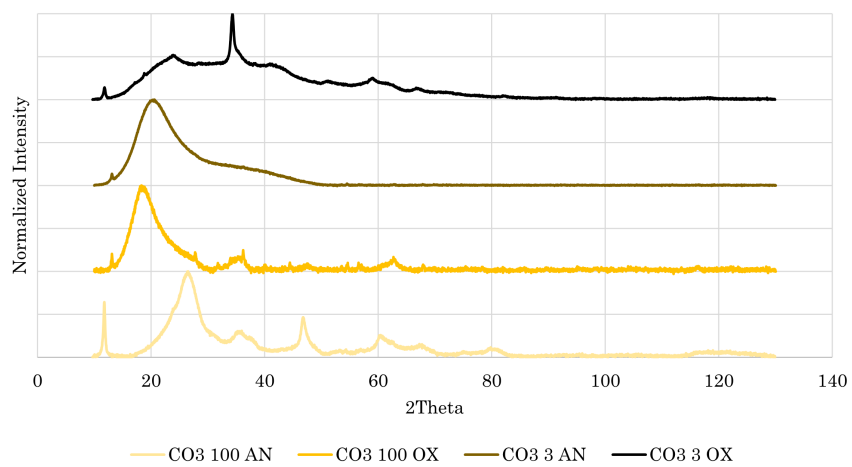


Figure G.5: XRD patterns of carbonate results presented in Table 3.6

H Kostencalculator

Table H.1: The investment parameters and the operational parameters of the different treatment steps used in the kostencalculator (table in Dutch).

1) Win- of infiltratieputten					
Parameters investeringen	waarde	unit	Parameters exploitatie	waarde	unit
Ontwerp cap. per put	75	m ³ /h	Energieverbruik	90	Wh/m ³
Reservestelling	0	I/O	Kiwapunten	0	punten /jaar
Proces Automatisering	0	%	Grondwater belas. ontrr.	0	€ / m ³ onttrekking
Bestaande capaciteit	0	%	Provinciale heffing	0,0200	€ / m ³ onttrekking
Aandeel CTB in kosten	58	%	Belas. teruggave infiltr.	0	€ / m ³ infiltr.
Aandeel WTB in kosten	14	%			
Aandeel E&I in kosten	28	%			
Verlies	0	%			
2) Cascadebeluchting					
Parameters investeringen	waarde	unit	Parameters exploitatie	waarde	unit
Ontwerp mesbelasting	150	m ³ /m/h	Energieverbruik	52	Wh/m ³
Reservestelling	0	%	Kiwapunten	0	punten /jaar
Proces Automatisering	0	I/O	Methaan (CH ₄)	1	mg/l
Bestaande capaciteit	0	%	Kooldioxide (CO ₂)	10	mg/l
Aandeel CTB in kosten	60	%			
Aandeel WTB in kosten	36	%			
Aandeel E&I in kosten	4	%			

Table H.2: Table H.1 continued.

3) Snelfiltratie (open systeem) Parameters investeringen Ontwerpsnelheid filtratie Reservestelling Proces Automatisering Hoogte zandbed Hoogte antracietbed Spoelwaterverlies Hoogte marmarbed Hoogte actief kool Bestaande capaciteit Aandeel CTB in kosten Aandeel WTB in kosten Aandeel E&I in kosten	waarde unit 7 m/h 33 % 0 I/O 1 m 1 m 2 % 0 m 0 m 0 % 52 % 33 % 15 %	Parameters exploitatie Energieverbruik Kiwapunten Uitspoeling antraciet Uitspoeling zand Verbruik marmar Uitspoeling actief kool waarde unit 12 Wh/m ³ 0 punten /jaar 2 volume % / jaar 2 volume % / jaar 0 mg/ ltr 0 volume % / jaar
4) Spoelwaterhergebruik (conventioneel) Parameters investeringen Spoelwater hergebruik Reservestelling Proces Automatisering Bestaande capaciteit Aandeel CTB in kosten Aandeel WTB in kosten Aandeel E&I in kosten	waarde unit 4 % 0 % 0 I/O 0 % 40 % 45 % 15 %	Parameters exploitatie Energieverbruik Kiwapunten slibafvoer niet chemisch Slibafvoer chemisch FeCl ₃ (100%) FeSO ₄ · 7H ₂ O (100%) PAC (Sachtoclar) (100%) AL ₂ (SO ₄) ₃ · 14H ₂ O (100%) PE (100%) waarde unit 40 Wh/m ³ 0 punten /jaar Varies ton ds / jaar 0 ton ds / jaar 150 gr /m ³ 0 gr /m ³ 0 gr /m ³ 0 gr /m ³ 0 gr /m ³
5) Reinwater berging Parameters investeringen % van maxdag IJzeren voorraad Proces Automatisering Onttrekkingen Bestaande capaciteit Aandeel CTB in kosten Aandeel WTB in kosten Aandeel E&I in kosten Paalfundering Uitvoering	waarde unit 25 % 10 % 0 I/O 0 m ³ /dag 0 % 88 % 10 % 2 % 1 - 1	Parameters exploitatie Energieverbruik Kiwapunten waarde unit 8 Wh/m ³ 0 punten /jaar
6) Reinwater pompstation Parameters investeringen Reservestelling Proces Automatisering Bestaande capaciteit Aandeel CTB in kosten Aandeel WTB in kosten Aandeel E&I in kosten	waarde unit 60 % 0 I/O 0 % 42 % 36 % 22 %	Parameters exploitatie Pompdruk Kiwapunten waarde unit 300 kPa 0 punten /jaar

