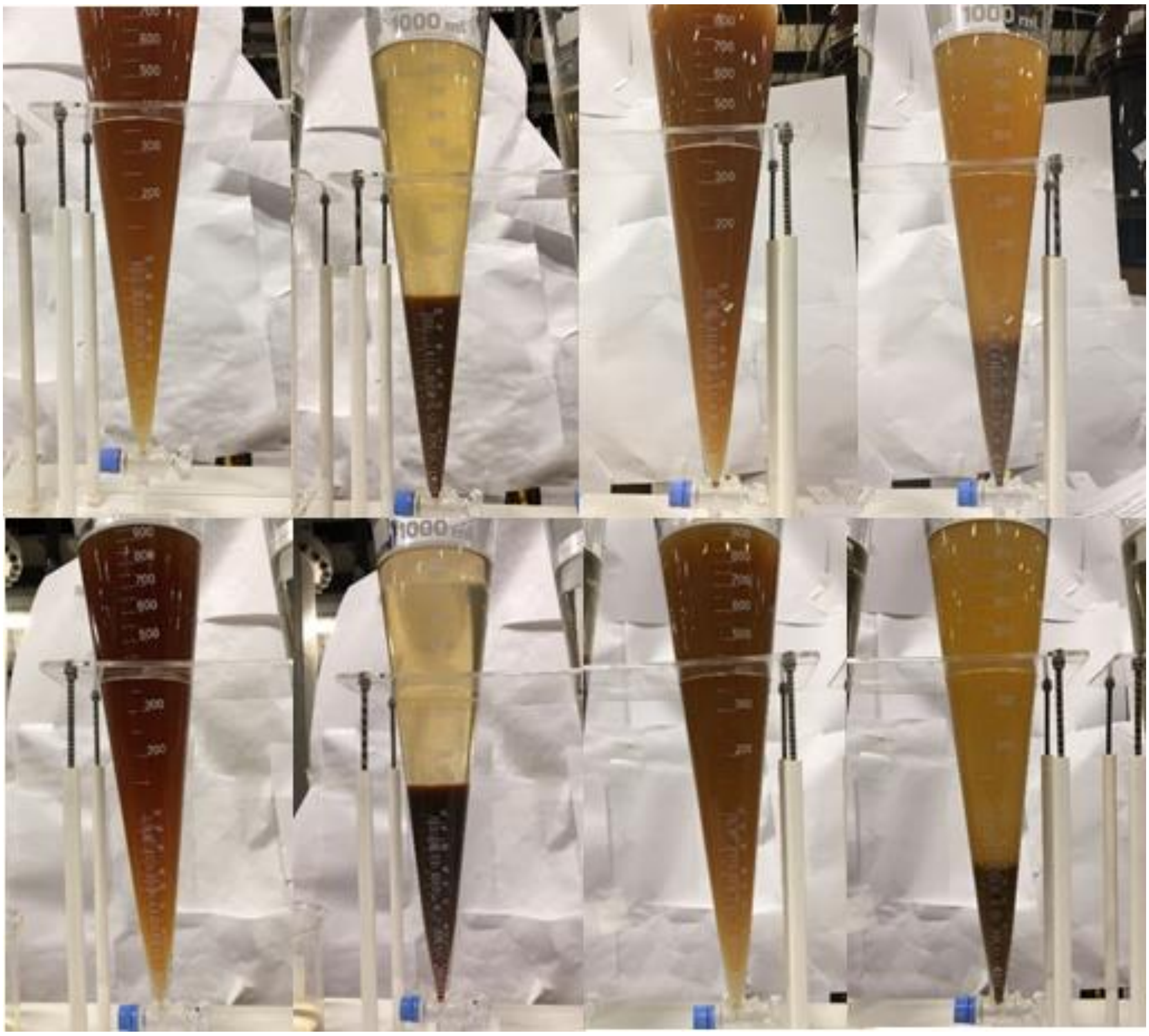
Assessment of Fe(II), Fe(III) and $NaMnO_4$ dosing for As removal <1 µg/L during aeration-filtration at WTP Prinsenbosch



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Challenge the future

Assessment of Fe(II), Fe(III) and $NaMnO_4$ dosing for As removal <1 µg/L during aeration-filtration at WTP Prinsenbosch

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Contents

Abstract

In 2013, Brabant Water (BW) adopted a new goal of <1 µg/l for As level in the drinking water, resulting in the need to enhance As removal at seven water treatment plants (WPT's), including WTP Prinsenbosch (As = 2.6 µg/l). Earlier experiences of BW at WTP Dorst had shown that dosing of $NaMnO_4$ to an aeration-filtration system efficiently reduces As concentrations. However, the so-called AOCF method had undesired operational side-effects, including decreased filter run time, breakthrough of particles and poor thickening of backwash sludge. The aim of this thesis was to investigate 3 process alternatives (respectively dosing of $NaMnO_4$, Fe(III) and Fe(II)) to enhance the As removal to < 1 µg/l at WTP Prinsenbosch, specifically including the impact on operational aspects like the filtration process and the backwash water production and sludge properties. The assessment is based on the results of (full-scale and) pilot-plant research at WTP Prinsenbosch.

It was found that Fe(III) was slightly more effective than Fe(II) and $NaMnO_4$ for the removal of As, but at doses of 1.3 mg/l $NaMnO_4$, 0.7 mg/l Fe(III) or 1.2 mg /l Fe(II) a drinking water quality of 0.7 µg As/l could be obtained with all 3 chemicals. In rapid sand filters, As(III) is oxidized biologically leading to subsequent adsorption of As(V) onto Fe(III)oxyhydroxides and Mn(IV) oxides. It was found that the adsorption capacity of the filter precipitates was relatively high, because to obtain a concentration of 0.7 µg As/l, the acceptable adsorption load was between 1.4-1.7 µg As/ mg (Fe+Mn).

Although As removal was similar for dosing either 1.3 mg/l $NaMnO_4$, 0.7 mg/l Fe(III) or 1.2 mg /l Fe(II), the impact on the filtration process and the backwash water production and sludge properties proved to be quite different. Dosing of $NaMnO_4$ and Fe(III) led to shorter filter run times, increased vulnerability to breakthrough, higher backwash water production and reduced thickening of the sludge. Contrarily, dosing of Fe(II) and the reference case (without dosing) led to longer run times, no breakthrough, lower backwash water production and superior thickening of the sludge. The differences in the impact on the filtration process and sludge properties between Fe(II) and Fe(III) and $NaMnO_4$ are most likely explained by a different density of the Fe(III)oxyhydroxides and Mn(IV) oxides formed in the filter. The different density may be related to the formation process (biotic or abiotic oxidation of Fe and Mn, homogeneous or heterogeneous precipitation of Fe(III)oxyhydroxides and Mn(IV) oxides) and the crystal structure and density (which may be influenced by E_h and pH).

The conclusion of the research for WTP Prinsenbosch is that Fe(II) is the preferred chemical in view of the superior operational aspects. It is also cheaper than $NaMnO_4$ (both chemical costs and sludge disposal costs) and easier to handle.

Preface

During my (many) years as a student, I gradually started doubting my earlier choice to drop out of the University of Utrecht. I knew that if I would have had a slightly better attitude/work ethic I would have easily passed. This doubt soon became regret and so the idea of somehow still getting my MSc-degree was born. Most of all I wanted to prove to myself that I had it in me. So when being interviewed for a job at Brabant Water, I immediately said that this was something I wanted to do. They agreed on the condition that I finished another study first. So two years later, now exactly five years ago, I started my studies at TU Delft.

I thought I knew what I was getting into and the impact it might have on my personal life, family and professional career, but I can now say that that was a mistake... I've had my share of ups and downs and even thought about quitting more than once. It might not have helped that in the last 5 years I also got married, bought a house and became a father… But now looking back I'm glad I pulled through and I'm certain that it has been worth it.

For the past five years I have been working on arsenic removal at Brabant Water, so the choice for my MSc-thesis was easy. At BW we were the first to apply $NaMnO_4$ to enhance As-removal, which meant that we were also the first to see the drawbacks of it. I feel that we have come full circle, now that BW will be the first to replace $NaMnO_4$ by $FeCl_2$ (partly as a result of my MSc-thesis).

I want to end my preface with some words of thanks. First of all to my graduation committee, Luuk Rietveld, Doris van Halem, Pieter Stuyfzand and Stephan van de Wetering. Without their guidance and support I could not have completed this project. A special thanks to Stephan, my boss, for making this all possible and being so lenient and understanding these past years.

I also want to thank Jink Gude (friend and PhD-student) for being always available as a sparring partner and helping me out where need be. Adriaan Schuijers and his team helped me to build the pilot-plant. Tim Machielse assisted me with the settling and thickening experiments. I also want to thank the whole operations department, for helping me wherever needed. Finally, I want to thank Patrick van der Wens, Martijn Groenendijk and Jasper Verberk for making my MSc-study possible and my colleagues Axel, Giel, Hans and Melanie for always being there (even though I often wasn't..).

To my parents, Atty and Hans: during the last 5 years your house was my library, cafeteria, study hall, laundry room and much more. I think it is safe to say that without both your help I would not have made it. I love you very much and want to thank you for everything you have done for me, not only during these last few years.

Last but not least I want to thank my wife Marijke. Without your love, understanding and sacrifice, I would have never been able to finish. You were always there when I needed you. Marijke also gave me the wonderful present of my daughter Zoë (2-5-2018), who lights up my day, every day, no matter what!

List of abbreviations

AOCF	Advanced Oxidation Aeration Filtration
As	Arsenic
BW	Brabant Water
DS	Dry Solids (%)
EPS	Extracellular Polymeric Substances
Fe	Iron
GFH	Granular Ferric Hydroxide
HFO	Hydrous Ferric Oxides
IOB	Iron Oxidizing Bacteria
MAC	Maximum Allowable Concentration
Mn	Manganese
mWc	meter Water column
SS	Suspended Solids (mg/l)
VEWIN	Vereniging Exploitanten Waterleidingbedrijven In Nederland
WTP	Water Treatment Plant

1. Introduction

1.1 Background

Removal of arsenic (As) from groundwater became a topic in the Netherlands in recent years as a result of the debate on the adverse impact of As on public health. This debate intensified after a paper was published in 2008 (Bakker, van Halem et al. 2008). In this paper, the health risk of As in drinking water was reviewed and an appeal was made to the Dutch water companies to reduce the maximum allowable concentration (MAC) in the drinking water from 10 µg/l (which is the legal standard set by the Dutch Drinking Water Law) to 1 µg/l. Brabant Water was among the first to respond to this appeal and initiated a policy debate on this topic in the Dutch drinking water sector (Van der Wens, Baken et al. 2016). After intensive discussions and additional research, the VEWIN Steering Group on Water Resources and Water Quality drafted a VEWIN recommendation of 1 µg/l by the end of 2015. The VEWIN Board decided to support the proposal as a precautionary measure. Meanwhile, most Dutch drinking water companies have adopted the policy to enhance the As removal in their treatment plants to the 1 µg/l level.

As naturally occurs in the groundwater in the Netherlands in concentrations of 0.01-70 µg/l (Ahmad, Kools et al. 2015). The anaerobic/anoxic groundwater, which is used as a source for drinking water production, usually contains the elements iron (Fe), manganese (Mn) and As in the reduced forms of Fe(II), Mn(II) and As(III). Conventional drinking water treatment consists of aeration and rapid sand (or dual media) filtration (de Moel, Verberk et al. 2006). Aeration increases the concentration of O_2 and the redox potential E_h, with the result that the metals may be oxidized (abiotically or biotically) to Fe(III), Mn(IV) and As(V). Fe (III) and Mn(IV) can be removed in the rapid sand filters in the form of precipitates ($Fe(OH)_3$ and MnO_2, which may be formed by different means, either homogenous in the water phase or heterogeneous on the filter grains. The As(V) may also be partially removed by adsorption to the Fe- and Mn-precipitates (Katsoyiannis and Zoubalis 2004, Katsoyiannis and Zoubalis 2004, Yang, Sun et al. 2015). In Dutch drinking water practice, As is only partially removed, resulting in concentrations that may exceed the 1 µg/l level. Depending on the raw water quality, it may thus be necessary to enhance the As removal.

In 2013, Brabant Water (BW) was the first Dutch water drinking water company to adopt the goal of <1 µg/l for the As level in the drinking water (van Dijk and van der Wens 2016). This meant that the As removal had to be enhanced at 7 water treatment plants, of which WTP Dorst had the highest level in the treated water (6 µg/l).

The AOCF method (Advanced Oxidation Coagulation Filtration) to enhance As removal is based on $NaMnO_4$ dosing before the rapid sand filters (Ahmad, Van De Wetering et al. 2014). After years of research Brabant Water successfully implemented this method at WTP Dorst (April 2016) and WTP Prinsenbosch (April 2017). However in operational practice it was found that the AOCF method has some limitations, including:

- The filter run time decreases strongly and the backwash water production increases accordingly;
- The filtration process is sensitive to the breakthrough of particles;
- The backwash sludge quickly settles, but thickens poorly in the existing tanks and ponds.

As removal can also be enhanced by dosing of Fe(III) (Katsoyiannis, Zikoudi et al. 2008). Pilot studies at WTP Prinsenbosch revealed that dosing of Fe(II) could also remove As to <1 µg/l (van Dijk 2017). However, these studies did not focus at the above mentioned potential operational limitations. Consequently, Brabant Water felt the need to compare the feasibility of the 3 chemicals for enhanced As removal: dosing of Fe(II), Fe(III) and the oxidant $NaMnO_4$. This study compares the 3 chemicals with respect to the As removal to < 1 µg/l, but also takes into account the impact on the filtration process and the backwash water production and sludge properties.

1.2 Full scale plant of WTP Prinsenbosch

WTP Prinsenbosch is a typical ground water treatment plant, consisting of aeration and rapid filtration (anthracite-sand). In figure 1.1 the treatment scheme is given.

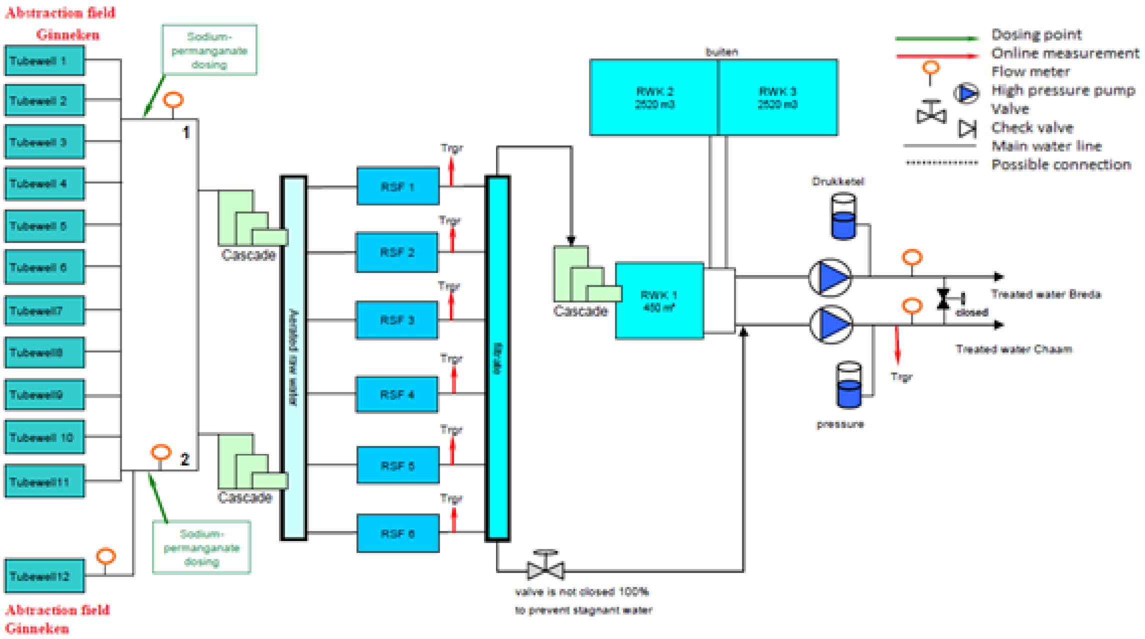

Figure 1.1: Treatment scheme of WTP Prinsenbosch

The ground water is pumped from 12 wells (of two abstraction fields) into two feed lines. Both feed lines are equipped with an $NaMnO_4$ dosing to enhance the As removal. Next, the water is aerated by means of cascades. This increases the concentration of O_2 and reduces the concentrations of CO_2 with the result that the pH increases. Next the water is passed through the rapid dual-media filters. In these filters, Fe, Mn an As are (partially) removed and NH_4^+ is converted biologically to NO_3^-. The raw water and clear water quality of the full scale plant in 2016 (before $NaMnO_4$ dosing) is given in table 1.1.

Table 1.1: Raw and treated water quality of WTP Prinsenbosch

	Raw water			**Treated water**		
	Average	Min	Max	Average	Min	Max
pH	7.5	7.5	7.6	7.7	7.7	7.8
Fe (µg/l)	1822	1450	2228	<14	<10	40
Mn (µg/l)	50.8	44.6	56.7	<10	<10	<10
As (µg/l)	4.8	3.7	6.7	2.6	2.4	2.7
NH_4^+ (mg/l)	0.6	0.6	0.7	<0.03	<0.03	<0.03
HCO_3^- (mg/l)	231	226	236	224	216	230

Other parameters in the raw water include (average concentration in mg/l): CO_2 (9.6), Cl^- (9.3), P (0.19), SO_4^{2-} (<1), Na^+ (6.1), Ca^{2+} (62), Mg^{2+} (5.1), SiO_2 (18.8).

Impact of enhanced As removal (by AOCF)

From April 2017 onwards, 1.3 mg/l $NaMnO_4$ is dosed to enhance the removal of As to <1 µg/l. The impact on the clear water quality is shown in figure 1.2. The variation in the data is mainly caused by some operational problems such as failure of dosing pumps. Initially, the dose was also somewhat adjusted and optimized. The dosing of $NaMnO_4$ has also led to a decrease in the filter run time from ±110 to ±41 hours.

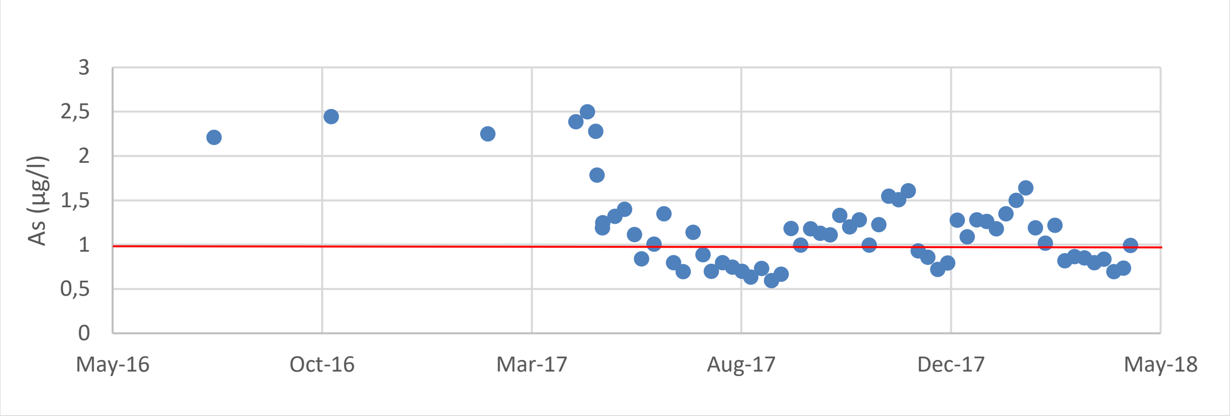

Figure 1.2: As concentration (µg/l) in drinking water before and after dosing of 1.3 mg/l NaMnO4 at WTP Prinsenbosch

Backwash water and sludge treatment

The backwash water from the filters is collected in a storage reservoir and transported to a settling basin (figure 1.3). After settling, the supernatant is discharged (over a weir) into a surface water stream. Before the implementation of AOCF, the backwash water production was 82,000 m^3/y (1.8% of the drinking water production). After implementation of AOCF, and optimization of the backwash program, the backwash water production increased to 125,000 m^3/y (2.7% of the drinking water production). The settling basin is 120 m long and 20 m wide, so the maximum surface load is 0.33 m/h (at a backwash water flow of 800 m3/h). Before AOCF, the dry solids content (DS) of the sludge in the settling basin (where it has had 20^+ years to settle and thicken) was around 15%. After AOCF, the DS-concentration decreased to 2%. It should be noted that the latter value was determined after a few months of operation only, so it may change in time. It is noted that at WTP Dorst after implementation of AOCF, the DS content of the backwash water sludge also decreased strongly (from 7% to 2%). In this case the annual exploitations costs for sludge disposal increased from 30K to 130K Euro.

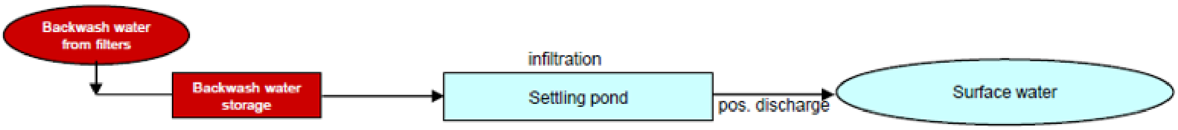

Figure 1.3: Scheme of the backwash water and sludge treatment

1.3 Fe and Mn removal during aeration-filtration

Most textbooks view flocculation-filtration as the primary removal mechanism for Fe in groundwater filtration (de Moel, Verberk et al. 2006). The Fe(II) from the groundwater is first oxidized by oxygen (introduced by the aeration step), next the Fe(III) hydrolyses and forms $Fe(OH)_3$ flocs which are removed in the sand or dual-media filters. However, Van Beek, Hiemstra et al. (2012) distinguished three processes in the oxidation and precipitation of Fe(II) into hydrous ferric oxides (HFO):

homogeneous (= flocculent) oxidation, **heterogeneous** (= adsorptive, autocatalytic or contact-) oxidation and **biological** oxidation.

Homogenous oxidation occurs in the water phase, once oxygen has been introduced by the aeration. The rate equation may be represented as:

$$-\frac{d[Fe(II)]}{dt} = k_1 * \frac{[Fe(II)] * [O_2(aq)]}{[H^+]^2} \qquad (1)$$

The value for the rate constant k_1 at 10 ° C equals $1.08*10^{-14}$ mol/l/s (Stuyfzand 2007, Van Beek, Hiemstra et al. 2012). Using this rate constant, the half-life of Fe(II) can be calculated. At a pH of 7.5 and a concentration of O_2 of 8 mg/l, the half-life becomes 4.3 minutes. From a practical point of view, this means that the oxidation of Fe (II) will not be completed in the cascade step. According to equation 1, the reaction rate will be 100 times faster if the pH is increased by 1 unit.

Heterogeneous oxidation occurs at the surface of previously precipitated Fe(III) oxyhydroxides, which act as a sorbent for Fe(II). The rate equation may be represented by:

$$-\frac{d[Fe(II)]}{dt} = k_2 * \frac{[S - OH^0] * [Fe(II)] * [O_2(aq)]}{[H^+]} \qquad (2)$$

In this relation (S-OH) represents the concentration of Fe(III)oxyhydroxides in mmol/l. The value of k_2 depends in the structure and the magnitude of the surface area of the Fe(III)oxyhydroxides. Fe(III) oxyhydroxides occur as various minerals, with different solubilities and specific surface area, as given in figure 1.4

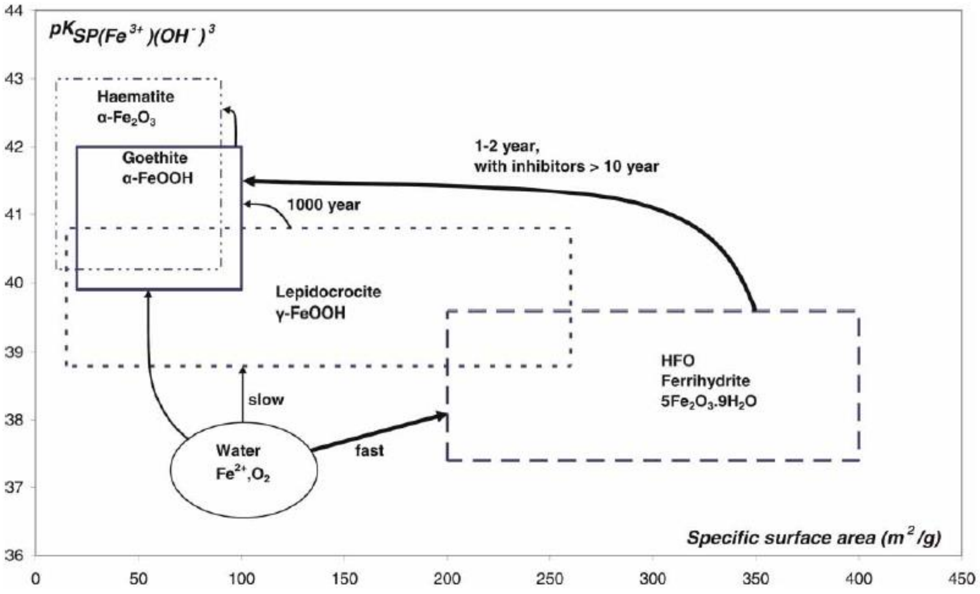

Figure 1.4: Solubility product and specific surface area of various Fe(III)oxyhydroxides (van Beek et al. 2012)

The value of k_2 for HFO equals $1.46*10^{-3}$ mol/l/s (Tamura, Kawamura et al. 1980). Using this rate constant, the half-life of Fe(II) can be calculated. For various concentrations of HFO, the half-life is represented in figure 1.5 as a function of pH and O_2 (Van Beek, Hiemstra et al. 2012). Equation 2 shows that a one-unit change in pH results in a 10-fold change in reaction rate and that the rate is inversely proportional to the concentration of O_2 and HFO.

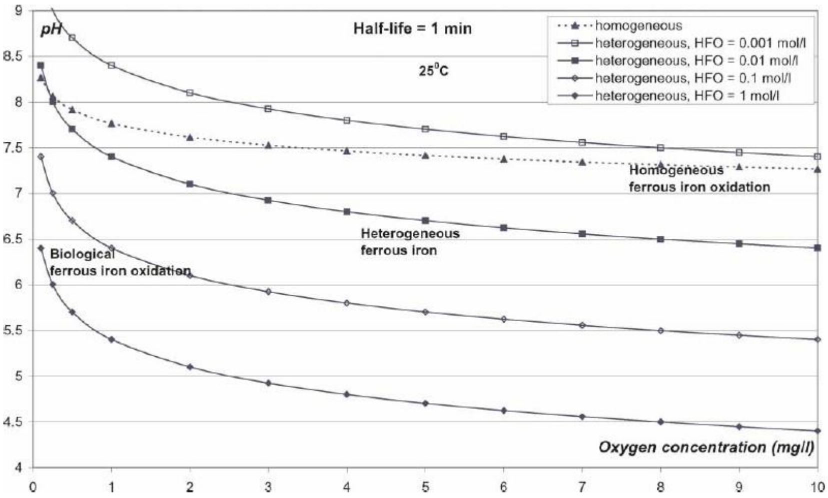

Figure 1.5: Half-life of 1 min for homogeneous and heterogeneous oxidation of Fe(II) as a function of O_2 concentration and pH at 25C^0 and various concentrations of HFO. Conditions where homogeneous, heterogeneous or biological Fe oxidation might be dominated are indicated as well (van Beek et al. 2012).

The heterogeneous oxidation was previously investigated by Sharma (2001), who named it adsorption-filtration.

Biological oxidation of Fe(II) may occur in filters by Iron Oxidizing Bacteria (IOB), such as *Gallionella ferrugina* and *Leptothrix ochracea.* As the precipitation of Fe(III) oxyhydroxides produces only little energy, IOB's need to convert large quantities of Fe(II). This is only possible at oxygen-iron (II) interfaces, characterized by low oxygen concentrations and slightly acidic to neutral conditions.

De Vet (2011) and van Beek, Dusseldorp et al. (2016) also researched biological oxidation and filtration. They stated that as soon as IOB are present, biological oxidation may substantially contribute. As the oxidation step is preceded by an adsorption step, the competition between heterogeneous and biological oxidation is not determined by the oxidation step, but by the adsorption step. Extracellular polymeric substances (EPS) excreted by all kinds of bacteria, may serve as initial adsorbent for both Fe(II) and Fe(III) hydroxides.

Impact on filtration process

van Beek, Dusseldorp et al. (2016) concluded that homogeneous (flocculent) formation of HFO is favored by high oxygen concentrations and long detention times in the supernatant and will lead to small low density flocs, shorter run times and frequent backwashing. They also concluded that heterogeneous oxidation of Fe(II) leads to growth of filter grains. They state that heterogeneous oxidation forms the major mechanism in practice (50-95%). At low oxygen concentrations, biological oxidation may also play a part (25-50%). The biological oxidation leads to firm, high density sludge and long filter run times. This confirms the earlier findings of van Dijk, van Wijk et al. (1986), who found that the density of Fe-flocs in groundwater filtration were significantly higher than those of surface water filtration (where Fe(III) is dosed, which will rapidly form large HFO flocs with a low density).

Sharma (2001) also claims that the adsorption filtration/heterogeneous filtration mechanism leads to more dense deposits which are not completely removed during backwashing. Consequently, some growth of the filter medium by coating with Fe deposits occurs which leads to a growing filter bed height.

The removal of Mn in ground water filtration differs somewhat from the removal of Fe. Homogeneous oxidation of Mn is very slow with a half-life of 3168 minutes (Katsoyiannis, Zoubalis et al. 2004). Heterogeneous oxidation and biological oxidation can both play a role in practice and have been studied by Bruins, Petrusevski et al. (2015).

1.4 As removal during aeration-filtration

The combined removal of Fe, Mn and As during aeration-filtration has been well researched. Katsoyiannis and Zoubalis (2002) found, during experiments on anaerobic groundwater treated by aeration and two-stage upflow fixed bed filters, that after a ripening period (and under the conditions of 2.7 mg/l O_2, pH=7.2 and E_h= 280-290 mV) not only Fe and Mn were removed (to below the MAC of 200 and 50 µg/l respectively), but also As was removed (to below the MAC of 10 µg/l). The following concept for the process mechanisms was derived:

- As(III) is likely to be oxidized to As(V) by indigenous bacteria as physico-chemical oxidation would require higher E_h and pH and As(III) is not likely to be removed by adsorption as it is present in the non-ionic form of arsenious acid H_3AsO_3.
- The oxidized As(V) is likely to be removed by adsorption on the Fe-oxyhydroxides and Mn-oxides as As(V) is present in the form of anions ($H_2AsO_4^-$ and $HAsO_4^{2-}$, with pK_1= 2,19 and pK_2=6,94 respectively) which are likely to be adsorbed on the positively charged Fe oxyhydroxides and Mn oxides.

Oxidation of As(III)

The abiotic oxidation of As(III) has been well researched. Clifford, Ceber et al. (1983) observed that only a few percent of As(III) was oxidized within 7 days in the presence of air. Kim and Nriagu (2000) reported a half-life of the abiotic oxidation on As(III) by dissolved air of 2.2 days. Consequently, it can be concluded that the abiotic oxidation of As(III) is slow. This was confirmed by Gude, Rietveld et al. (2016) who found that after aeration As remained largely present as As(III). After extending the residence times from 3-5 to 60 minutes, most As(III) remained mobile.

Katsoyiannis, Zoubalis et al. (2004) found that the biological oxidation had a half-life of only 3 min. The rapid oxidation was confirmed by Gude, Rietveld et al. (2016), who observed in rapid sand filters an instant acceleration of the As(III) removal. In another paper the biological filtration concept was proven (Gude, Rietveld et al. 2018). It was found that biological oxidation of As(III) developed rapidly in sand filters. The growth of biomass was confirmed with ATP-analysis and a microbial community analysis showed a high relative abundance of α- and β- Proteobacteria, the same classes where most As-oxidizing bacteria are placed.

$NaMnO_4$ can also be used for the oxidation of As(III). The stoichiometric factor of the reaction is 0.67 and the reaction is virtually complete within 1 minute (Ghurye and Clifford 2001).

Sorption of As(V)

The adsorption of As(V) on Fe(III)oxyhydroxides has been well researched. It was found that the arsenate anions can be adsorbed by the positively charged Fe-oxides (Katsoyiannis and Zoubalis 2002). The kinetics of the adsorption of As onto granular ferric hydroxide (GFH) have been investigated by Banerjee, Amy et al. (2008). They found that As(V) was faster adsorbed than As(III) and that a lower pH had a positive impact. Obviously, the As-removal will also depend on the water composition. van Halem (2011) found a detrimental effect of the presence of 0.01 mmol/l phosphate, 0.2 mmol/l silicate and 1 mmol/l nitrate on the As-removal during Subsurface Iron Removal. She also found a smaller negative impact of 1.2 mmol/l Ca.

The adsorption of As(V) on Mn oxides was also studied and found to be effective (BajPai and Chaudhuri 1999, Katsoyiannis, Zoubalis et al. 2004, Dalvi, Ajith et al. 2015, Yang, Sun et al. 2015).

The adsorption capacity on Mn oxides was even found to be as high as 13.5 µg As/mg Mn, which is similar to the adsorption capacity on Fe(III)oxyhydroxides.

In view of the crucial role of the adsorption of As(V) on the Fe(III)oxyhydroxides and Mn(IV) oxides, it could be expected that dosing of additional Fe or Mn should have a positive impact as the adsorption load (µg As/mg Fe or µg As/mg Mn) will decrease. Indeed, Pokhrel and Viraraghavan (2001) found a positive impact of increasing the Fe/As ratio.

1.5 Scope of this thesis

Objective

The objective of this research is to compare the 3 process alternatives (respectively dosing of $NaMnO_4$, Fe(III) and Fe(II)). The assessment is not limited to the As removal to <1 µg/l , but also includes the impact on operational aspects such as the filtration process and the backwash water production and sludge properties. The assessment will be based on the results of (full-scale and) pilot-plant research at WTP Prinsenbosch.
The scientific goal of this thesis is to shed more light on the understanding of the mechanisms involved in the combined removal of As, Fe and Mn in the filtration process and how this relates to the properties of the deposits/precipitates in the filter, the backwash water production and the sludge properties.

Research questions

For the comparison of the three alternatives the following questions need to be considered:

1. How much chemical dose is required for each alternative to reduce the As concentration to <1 µg/l?
2. What is the impact of the dose on the filter run time and consequently the backwash water production?
3. How sensitive is the filtration process with regard to breakthrough?
4. What is the impact on the sedimentation velocity of the backwash water?
5. What is the impact on the sludge characteristics (in particular the thickening potential)?

The results will be discussed in the framework of literature and modeling. What do we know about the mechanisms involved? When and why do they occur? Is it possible to come to a better understanding on how these mechanisms determine the removal of As and how they relate to the properties of the deposits/precipitates in the filter, the backwash water production and the sludge properties?

Approach

The assessment is based on the results of full-scale and pilot-plant research at WTP Prinsenbosch. For the pilot plant research, two aeration/filter columns were available. Throughout the project, one column served as a reference and treated groundwater without chemical dosing. The other column was used to study the impact of the three chemicals. The results of the filter columns were used to answer the above mentioned research questions 1-3. The backwash water from the pilot filters was used to answer the research questions 4-5, by performing sedimentation tests and gravity thickening in an Imhoff cone. The results of the three chemicals were finally compared to the reference column and the results of the full-scale plant (which was operated in the AOCF mode).

Hypothesis of the thesis

It is expected that all three chemicals will be able to remove As to <1 µg/l. Different results are expected regarding the operational aspects. In this respect, it is expected that Fe(II) is the best option as it leads to the formation of more dense/crystalline precipitates on the filter media, as a result of which the filter run time will be longer, filter breakthrough will not occur, less backwash water will be produced and the thickening of the backwash water sludge will be superior.

Water companies know from operational experiences that the acceptable filter load of Fe(II) (such as in groundwater filtration) is much higher than the acceptable load of Fe(III) (such as in surface water filtration) (de Moel, Verberk et al. 2006). Fe(III) forms voluminous amorphous flocs with a high water content and a low density, whereas the precipitates formed from removal of Fe(II) from groundwater are usually twice as dense (van Dijk, van Wijk et al. 1986). Consequently in the case of Fe(II) the filter run time is longer, the backwash water production is lower and the backwash water sludge thickens better. AOCF and Fe(III) both result in the formation of oxidized Fe in the supernatant water phase, that forms less dense and more hydrous flocs.

2. Materials and methods

2.1 Pilot filter setup

The pilot (figure 2.1) consists of two cascades and consequently two pilot filter columns and a dosing pump for $NaMnO_4$, Fe(II) and Fe(III) dosing. The cascade has five steps of 40 cm. The filtration columns are 0.3 m diameter and 2.5 m in height. The columns contained 1.6 m filtration media consisting of 0.8 m sand (0.4-0.8 mm) and 0.8 m anthracite (1.0-1.6 mm) (both virgin media). The overflow of the filters was connected to a reservoir (225 l) to collect the backwash water. The pilot was fed with raw water from the southern raw water pipe. After a startup period of over two months, the columns performed similar to the full scale filters. This period is described in Annex 1.

Throughout the project, one column served as a reference and treated groundwater without chemical dosing. The other column was used to study the impact of the three chemicals: $NaMnO_4$, Fe(III) and Fe(II). Each chemical was dosed for at least one month to obtain stable results (the filter run period was around 50 hours, so the filters were backwashed some 12 times during one month).

The required dose for each chemical was initially based on previous studies (van Dijk 2017). Based on the results the doses were adjusted to obtain <1 µg/l As in the filtrate. This led to doses of 1.7 mg/l Fe(II), 0.7 mg/l Fe(III) and 1.3 mg/l $NaMnO_4$. At the end of the experimental period the Fe(II) dose was lowered to 1.2 mg/l.

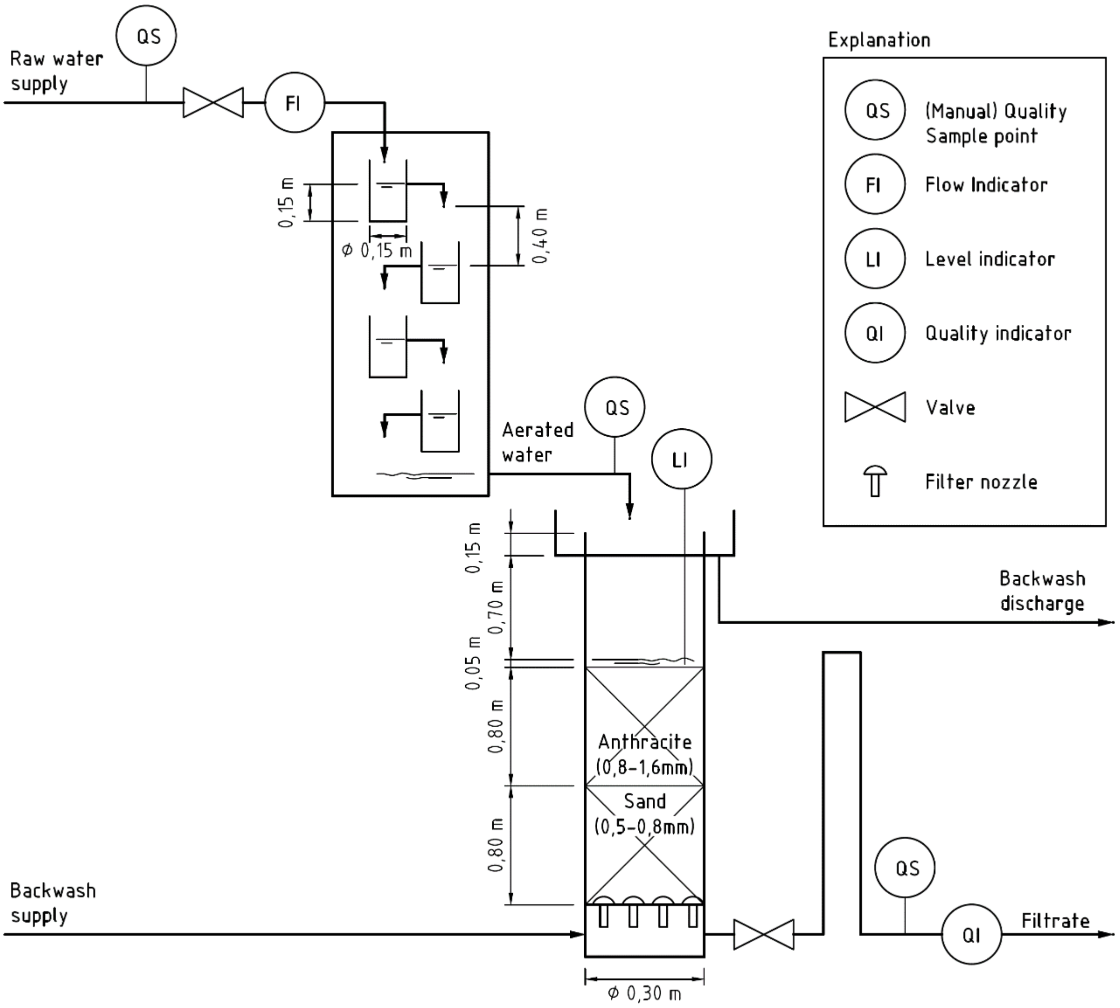

Figure 2.1: Schematic representation of pilot plant setup

The sampling points (QS) for the raw water, the aerated water, and the filtrated water are indicated in the drawing. To differentiate between dissolved and particulate matter, samples were also filtered over 0.45 µm filters.

The filters were operated at 4 m/h (283 l/h) and the clean bed supernatant level was set at approximately (Huisman 2004) 0.05 m above the filter bed, using a syphon. The filters had multiple sampling points over the height of the column as well as the filtrate. The filtered water was continuously passed through a turbidity meter (Sigrist AquaScat 2) to see if the filters were operating properly and to detect breakthrough. The filters were backwashed when they reached their run time or for practical/ planning reasons.

2.2 Filter run time

Two criteria were set to determine the filter run time, either head loss or the occurrence of breakthrough.

Head loss

Maximum head loss H was set at 0.70 mWc. In practice, the clean bed head loss H_0 of the filters at WTP Prinsenbosch is around 0.05 mWc. During the filter run the deposited particles fill the pores, so the porosity p decreases and the head loss increases. The volume of the deposits σ_v increases in proportion to the filtration rate v, the filter run time T and the influent concentration c, but is inversely proportional to the density ρ of the particles, in accordance with equation 3 (Huisman 2004):

$$\sigma_v = \frac{v * T * c}{L * \rho_s} \tag{3}$$

The foul bed head loss H increases rapidly when the volume of the deposits approaches the initial porosity p_0, in accordance with the following equation:

$$\frac{H}{H_0} = (\frac{p_0}{p_0 - \sigma_v})^2 \tag{4}$$

Equation 4 shows the large impact of the density ρs on the foul bed head loss. When the density of the particles reduces, the volume of the deposits σ_v increases and so does the foul bed head loss.

Breakthrough

Breakthrough of particles in the effluent of a filter usually occurs when the pores of the filter are substantially filled with deposits. In that case the remaining porosity becomes low and the 'real' velocity in the pores becomes high. It is noted that a lower density ρ_s increases the susceptibility to breakthrough as this increase the volume of the deposits. Breakthrough can be detected with a turbidity meter. In this study the filter run time was ended if filtrate turbidity reached 0.05 NTU.

2.3 Backwash procedure

When the filter had reached its run time the filter was backwashed. The backwash procedure was developed in the startup phase. This was done only with water (backwash with pressured air caused anthracite to flow out of the filters). Each filter was backwashed with 200 l (4.4 bed volumes), so the concentration in the backwash water could be calculated. The backwashing flow was regulated at around 20 m/h to obtain an expansion of 0.7 m (43%). At the end of the backwashing, the flow was gradually reduced to allow proper settling of the filter material.

2.4 Sedimentation velocity of the back wash water

Theoretically, the sedimentation velocity of discrete settling of the backwash sediment can be calculated with the equation of Stokes (Huisman 2004):

$$V_s = \frac{1}{18} * \frac{g}{\nu} * \frac{\rho_s - \rho_w}{\rho_w} * d^2 \tag{5}$$

Equation 5 shows the large impact of the density ρ_s and the diameter d. Through collision, particles may also increase in size during settling, thereby increasing the settling velocity. This process is known as flocculent settling. In practice flocculent settling can be recognized by the impact of the detention time and thus settling height.

The sedimentation velocity can been determined experimentally with a conventional settling test (as shown in figure 2.3).

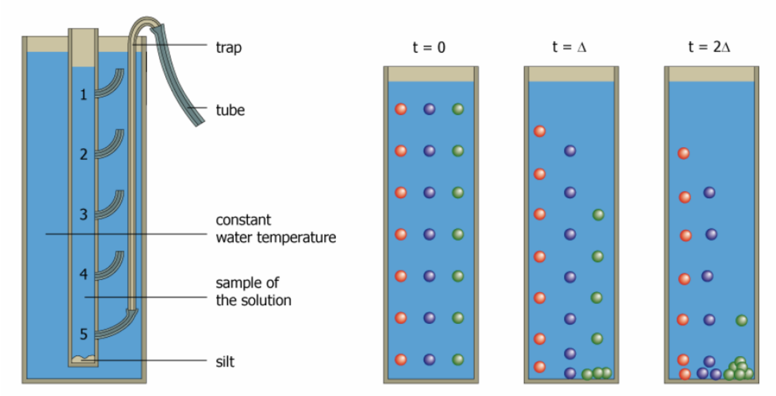

Figure 2.3: Conventional settling test (Huisman 2004)

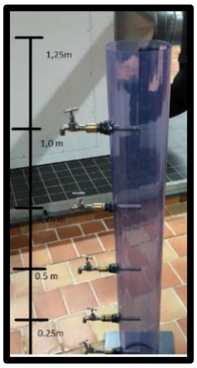

Figure 2.4: Settling test pilot

In this research a pilot column was designed, a 1.25 m long pipe with a diameter of 0.15 m and sampling points at 1, 0.75, 0.5 and 0.25 m (see figure 6.3). The pilot was filled with a homogeneous (mixed) sample of the backwash water and left to settle. The backwash sediment of the 3 alternatives and the reference has been tested in duplicate to establish the sedimentation curve of all backwash water types. Samples were taken over time after 7.5, 15, 30, 45, 60, 90, 120, 180, 240 and 300 minutes. Each test was performed at least two times after a complete filter run. The data of the sampling point at 0.5 and 0.75 m were used to calculate the distribution of the sedimentation velocities.

2.5 Thickening potential of the sludge

Theoretically, the composition of the backwash water and the sludge can be calculated with a mass balance. Neglecting the concentrations of Fe, Mn and As in the drinking water and assuming no retention on the filter media, the concentrations in the backwash water can be calculated from the concentrations in the raw water and the concentration factor (CF). The concentration factor itself is equal to the ratio of the production PROD of the filter (in m^3) and the backwash water consumption BWC (also in m^3). The production of the filter equals the filtration velocity v times the filter run time T and the surface area A:

$$c_{backwash} = c_{raw\ water} * CF \tag{6}$$

$$CF = \frac{PROD}{BWC} \tag{7}$$

$$PROD = v * T * A \tag{8}$$

The volume of the sludge V (in ml/l) can be calculated from the concentration of the backwash water (in mg/l) divided by 10 times the dry solids content of the sludge DS (in %, which equals 10 g/l):

$$V = \frac{c_{backwash}}{(\frac{DS}{10})} \tag{9}$$

Table 2.1 gives the results of an example calculation which shows the potential, theoretical impact of dosing of 2 mg/l Fe and the reference case and the dry solids content of the sludge on the sludge volume and the sludge composition. Table 2.1 illustrates that substantial differences can occur, which can be measured with an Imhoff cone of 1 liter. In the reference case, the sludge volume at a DS of 0,1% will be as high as 272 ml. At a DS of 10% the sludge volume will be only 3 ml. After dosing of 2 mg/l Fe, the sludge volume will be somewhat higher at the same DS content.

Table 2.1: Theoretical sludge volume of 1L backwash water in an Imhoff cone for the reference case and dosing of 2 mg/l Fe

	Feed	**Volume sludge at DS**		
	water	**0.10%**	**1%**	**10%**
Reference case	mg/l	ml	ml	ml
Fe	1.8	265	26	3
Mn	0.05	7	1	0
+2 mg/l Fe	mg/l	ml	ml	ml
Fe	3.8	508	51	5
Mn	0.05	7	1	0

Figure 2.4: Imhoff cone

To study the thickening potential of the sludge Imhoff© cones were used, as shown in figure 2.4. The procedure 2540F in the Standard Methods (Rice, Baird et al. 2017) was used to determine the sludge volume.
The 1 l cones were filled with 1 L of the backwash water and left to settle. After 45 minutes the cones were swirled to detach sediment from the inner side of the cone. After 1 hour, the amount of settled solids was noted down to compare the results.
The procedure was extended and the samples were left to settle over a longer period of time (up to 1 month), while the amount of settled solids was noted regularly.

2.6 Analysis

All samples were analyzed at the laboratory of Aqualab Zuid.
Determining of metals (Fe, As, Mn) was carried out by Inductive Coupled Plasma followed by Mass Spectrometry (ICP-MS). These samples were preserved in bottles which contained 250 µg/l of concentrated ultra-pure nitric acid. For filtering the samples, GE's GD/XP disposable syringe filters were used. For determining metals from the backwash water, the samples were digested in acid and microwave before ICP-MS. NH_4, NO_3 and NO_2 were determined by spectrophotometry. Aqualab Zuid is an accredited lab via NEN-EN-ISO/IEC 17025:2005.

Figure 2.5: Sampling bottles, syringe and filters.

During the experimental period samples collected from the raw water, supernatant and pilot filtrate during multiple filters runs at each setting.
The sampling program of the filters is given in table 2.2. Parameters in between brackets were not always included.

Table 2.2: Sampling program of the filters at various settings

Sampling point	Reference	Fe(II)	Fe(III)	$NaMnO_4$
Raw water	Fe, As, Mn, NH_4^+	Fe, As	Fe, As	Fe, As, Mn
Supernatant	Fe, As Filtered: Fe, As	Fe, As Filtered: Fe, As	Fe, As Filtered: Fe, As	Fe, As, Mn Filtered: Fe, As, Mn
Filtrate	Fe, As, (NH_4^+, NO_2, Mn) Filtered: Fe, As, Mn	Fe, As, (NH^{4+}, NO_2^-, Mn) Filtered: Fe, As, (Mn)	Fe, As, (NH_4^+, NO_2^-, Mn) Filtered: Fe, As, (Mn)	Fe, As, Mn,(NH_4^+, NO_2^-) Filtered: Fe, As, Mn
Frequency	2 x per filter run	2 x per filter run	2x per filter run	2x per filter run

3. Results

After startup of the pilot filters, they were operated for 3 months. During this period, the filter material ripened and the removal of all relevant components (Fe, Mn, As) improved until steady state results were obtained. In Annex 1 the results of this start-up period steady situation are presented in detail.

3.1 Water quality: impact of aeration

The mobility of Fe, Mn and As was defined as the difference between the total concentration and the concentration after filtration over 0.45 µm. Table 3.1 shows that in the reference case (without dosing) almost all of the Mn (99%) and As (92%) was mobile/dissolved, whereas a substantial part (61%) of the Fe was already present as precipitate/filterable matter. In the case of dosing of Fe(II), these percentages remained roughly the same. In the case of dosing of Fe(III), the mobility of Fe decreased considerably and the mobility of As decreased slightly. In the case of dosing of $NaMnO_4$ the mobility of all parameters decreased considerably.

Table 3.1: Total, filtered and mobile Fe, Mn and As concentrations after aeration

	Fe			**Mn**			**As**			**pH**
	Total (µg/l)	Filtered (µg/l)	**mobile %**	Total (µg/l)	Filtered (µg/l)	**mobile %**	Total (µg/l)	Filtered (µg/l)	**mobile %**	-
Reference	1622	982	**61%**	51.7	51.3	**99%**	4.6	4.2	**92%**	7.88
Fe(II) (1.2 mg/l)	2934	1680	**57%**	56.5	55.2	**98%**	4.3	3.8	**89%**	7.90
Fe(III) (0.7 mg/l)	2547	1051	**41%**	53.6	53.8	**100%**	4.8	4.4	**91%**	7.87
$NaMnO_4$ (1.3 mg/l)	1891	143	**7%**	586.8	172.9	**29%**	4.8	1.0	**20%**	7.91

It is noted that some additional change in the mobility will take place in the supernatant water due to the detention time there, which is max. 11 minutes (at the maximum supernatant water level of 0.75 m and a filtration rate of 4 m/h). However the impact of this was not measured during this study.

3.2 Water quality: impact of filtration

3.2.1 Overall comparison

The results of all filtration experiments are presented in figure 3.1. This shows that enhanced As-removal to a concentration <1 µg/l could be achieved with all 3 alternatives. It is noted that the full-scale plant (operating at a dose of 1.3 mg/l $NaMnO_4$) achieved similar results as the pilot-plant (with dosing of $NaMnO_4$). Some slight differences can be attributed to the different design and operating conditions (dosing point and mixing, variation in filtration speed and filter run time). Figure 3.2 gives a Box-Whisker plot, which shows limited variation in the results.

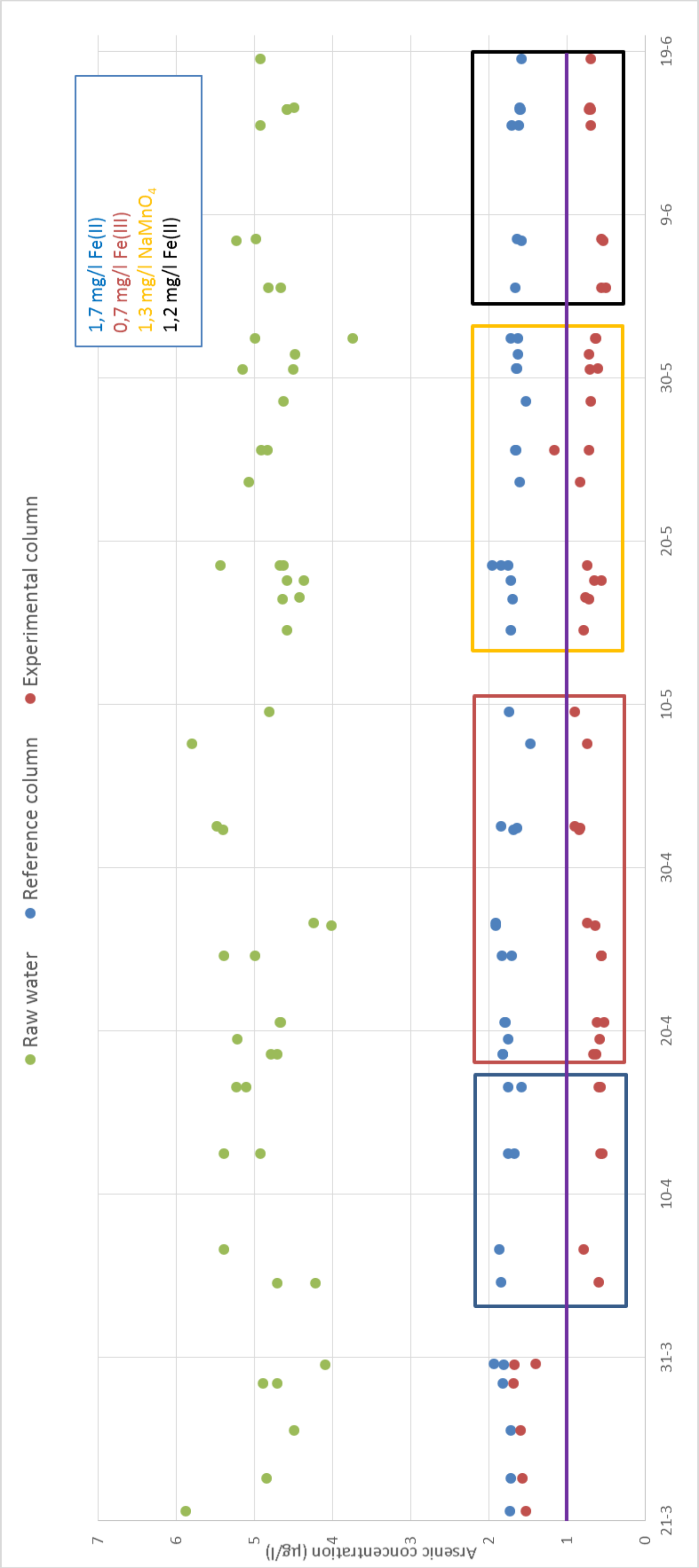

Figure 3.1: As concentrations in the filtrate of all experiments

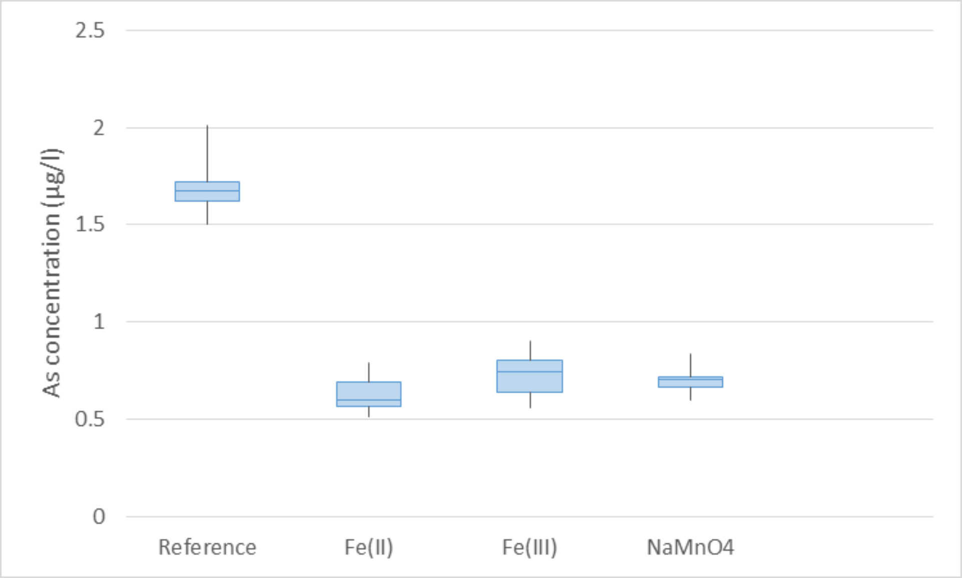

Figure 3.2: Boxplot of the filtrate As concentration of the 3 alternatives and the reference case

During the experimental period, multiple samples were analyzed for various components. Some of the most relevant results are summarized in table 3.2. It is noted that the ammonia removal that was always complete (<0.03 mg/l) during the whole experimental period.

Table 3.2: Average concentrations of various components in the filtrate

	Fe	**As**	**Mn**	**pH**
	µg/l	µg/l	µg/l	(-)
Reference	9.9	1.75	0.7	7.77
Fe(II) (1.2 mg/l)	11.7	0.63	0.5	7.72
Fe(III) (0.7 mg/l)	11.3	0.77	0.7	7.73
$NaMnO_4$ (1.3 mg/l)	5.7	0.76	1.6	7.84

The pH was slightly lower in the cases of Fe(II) and Fe(III) as compared to the reference. This can be explained by the combination of the acidic impact on the formation of $Fe(OH)_3$ (de Moel, Verberk et al. 2006) and the acidity of the $FeCl_2$ and $FeCl_3$ solutions. Contrarily the pH was slightly higher in the case of $NaMnO_4$. This can be explained by the different oxidation reaction and the pH of the dosing solution. It is noted that the same differences in pH were also found in the backwash waters from the different alternatives.

The Mn removal was similar for the alternatives of Fe(II) and Fe(III) and the reference case. However in the case of dosing $NaMnO_4$ the effluent quality of Mn was somewhat compromised. After implementation of $NaMnO_4$ in WTP Dorst and Prinsenbosch this was also found. It is noted that the feed water concentration of Mn was increased from 50 to 610 µg/l Mn by the chemical dosing, but the removal efficiency of Mn remained approximately 99%.

3.2.2 Reference column

The reference filter treated the aerated raw ground water without any chemical dosing. Throughout the research period the filter was able to remove Fe and Mn well (<10 µg/l and <1 µg/l). As expected the effluent concentration of As was above 1 µg/l, as shown in figure 3.3.

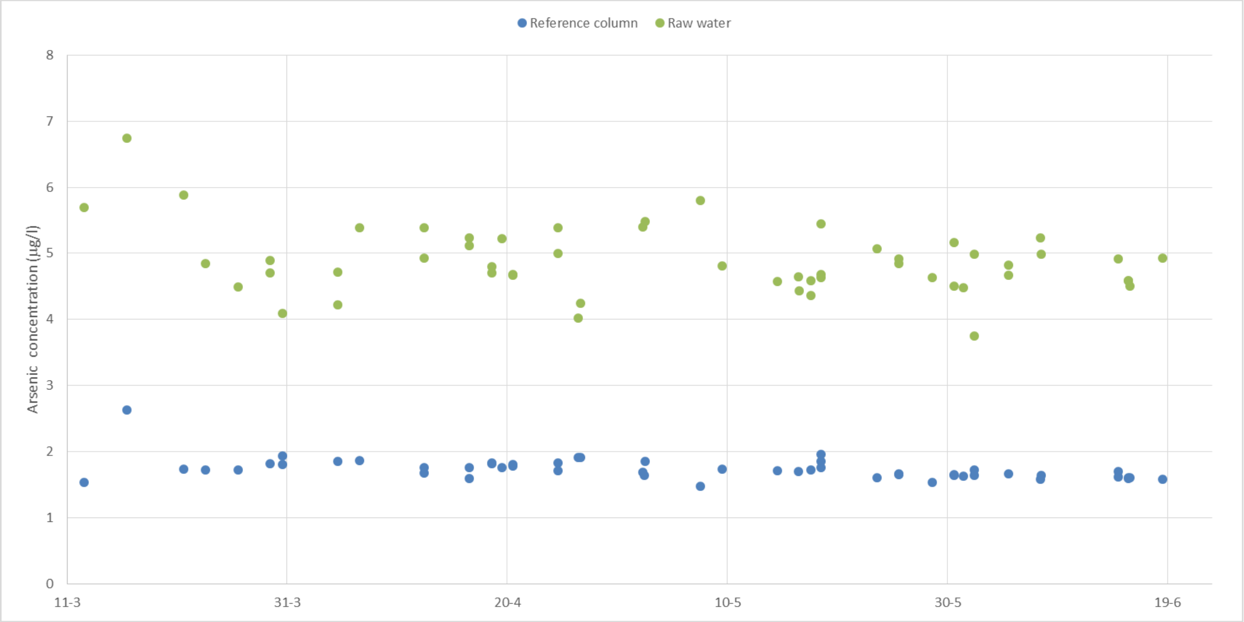

Figure 3.3: As concentrations in the raw water and the filtrate of the reference column

The removal of Fe, Mn and As during the whole experimental period is summarized in table 3.3. Throughout the period the results were stable, with limited variations and only a few outliers. As the samples were taken at different times in a filter run (begin, middle and end), it can be concluded that the water quality was stable during the filter run.

Table 3.3: Concentration of As, Fe and Mn in the filtrate of the reference column

	Total					*Filtered*				
	average	min	max	std	n	**average**	min	max	std	n
As	**1.7**	1.5	2.0	0.1	49	**1.7**	1.5	2.0	0.1	26
Fe	**9.9**	4.2	18.1	4.3	49	**8.3**	4.5	15.0	3.1	26
Mn	**0.7**	0.3	1.6	0.3	17	**0.7**	0.3	1.5	0.3	17

3.2.3 Dosing of Fe(II)

During the first experimental period 1.7 mg/l Fe(II) was dosed. This reduced the As-level to some 0.6 µg/l. During the second period, it was found that the same As removal could be achieved by dosing just 1.2 mg Fe(II)/l.

During a filter run, the results were stable as shown in table 3.4 for the dose of 1.7 mg/l and in table 3.5 for the dose of 1.2 mg/l.

Table 3.4: Concentrations of As, Fe and Mn in the filtrate during 1.7 mg/l Fe(II) dose

	Total					*Filtered*				
	average	min	max	std	n	**average**	min	max	std	n
As (µg/l)	**0.6**	0.5	0.7	0.1	10	**0.6**	0.5	0.7	0.1	8
Fe (µg/l)	**11.7**	4.9	23.5	7.2	10	**10.3**	2.3	21.2	7.1	8
Mn (µg/l)	**0.5**	0.4	0.6	0.1	4	**0.7**	0.5	0.8	0.2	4

Table 3.5: Concentrations of As, Fe and Mn in the filtrate during 1.2 mg/l Fe(II) dose

	Total					*Filtered*				
	average	min	max	std	n	**average**	min	max	std	n
As (µg/l)	**0.6**	0.5	0.8	0.1	10	**0.6**	0.6	0.6	0.0	2
Fe (µg/l)	**7.3**	4.4	16.0	3.7	10	**5.0**	3.9	6.0	1.5	2
Mn (µg/l)	**0.8**	0.5	1.0	0.2	4	**0.9**	0.9	1.0	0.1	2

3.2.4 Dosing of Fe(III)

The initial dosing of $FeCl_3$ was quite high at 2.8 mg/l Fe(III), which resulted in effluent As values of approximately 0.6 µg/l. The dosing was decreased to 1.7 mg/l and still 0.6 µg/l effluent values were obtained. The final dosing set at 0.7 mg Fe(III), which was still able to obtain As-levels of <1 µg/l (0.75-0.9 µg/l). The removal of Fe and Mn was comparable to the reference filter. The water quality results are summarized in table 3.6.

Table 3.6: Concentrations of As, Fe and Mn in the filtrate during dosing of 0.7 mg/l Fe(III)

	Total					*Filtered*				
	average	min	max	std	n	**average**	min	max	std	n
As (µg/l)	**0.8**	0.6	0.9	0.1	11	**0.8**	0.7	0.9	0.1	8
Fe(µg/l)	**7.9**	4.7	16.1	3.5	10	**7.2**	3.4	18.3	5.3	8
Mn (µg/l)	**0.7**	0.5	1.0	0.4	2	**0.9**	0.4	1.3	0.6	2

3.2.5 Dosing of $NaMnO_4$

From initial experiments, it was revealed that a dose of 1.0 mg/l $NaMnO_4$ was able to remove As to 1.3 µg/l As. The dosing was increased to 1.3 mg/l $NaMnO_4$ which was sufficient to remove As down to <1 µg/l. The removal of Fe was comparable to the reference filter, but the removal of Mn was slightly less (to 1.6 µg/l instead of 0.9 µg/l). This will probably be related to the dose of $NaMnO_4$. The water quality results are summarized in table 3.7.

Table 3.7 Concentrations of As, Fe and Mn in the filtrate during dosing of 1.3 mg/l $NaMnO_4$

	Total					*Filtered*				
	average	min	max	std	n	**average**	min	max	std	n
As (µg/l)	**0.8**	0.6	1.2	0.2	8	**0.8**	0.6	1.3	0.2	10
Fe (µg/l)	**5.7**	4.3	7.3	1.3	7	**5.0**	2.9	9.9	2.4	9
Mn (µg/l)	**1.6**	0.9	2.3	0.5	9	**1.5**	0.9	2.2	0.5	9

3.3 Filter run times

3.3.1 Overall comparison

The results of all experiments are summarized in table 3.8. In this table the results obtained during optimization of the dosing are mentioned separately. The table shows that the dosing of Fe(III) and $NaMnO_4$ lead to a considerably lower run time as compared to the dosing of Fe(II).

Table 7.8: Average filter run times and backwash criterion at different experiments

	filter run time (hours)				**Backwash criterion**
	average	min	max	n	
Reference	101.1	85.65	119.9	10	Head loss
Fe(II) 1.7 mg/l	48.6	48.0	49.3	3	Head loss
Fe(II) 1.2 mg/l	73.1	72.0	74.7	7	Head loss
Fe(III) 0.7 mg/l	49.8	48.7	50.8	5	Head loss*
Fe(III) 1.7 mg/l	28.1	27.6	28.6	2	Water quality
Fe(III) 2.8 mg/l	24.3	24.3	24.3	1	Water quality
$NaMnO_4$ 1.3 mg/l	48.8	45.0	51.5	5	Water quality

*after 56 hours breakthrough occurred (the head loss reached 0.75 m after 50 hours already)

The susceptibility to breakthrough was also greater in case of dosing of Fe(III) and $NaMnO_4$. Figure 3.7 shows turbidity peaks during backwash, but for $NaMnO_4$ turbidity also increased at the end of a filter run. The breakthrough during Fe(III) experiments only occurred at higher dosage or prolonged filter run times. This is discussed in Annex 2.

It is noted that the filter run time of the full-scale plant (operating at a dose of 1.3 mg/l $NaMnO_4$) was even slightly lower than the pilot-plant (41 hours vs 48 hours). It is believed that this difference was caused by the variation in filtration speed in the full-scale plant, which necessitated earlier backwashing to avoid breakthrough.

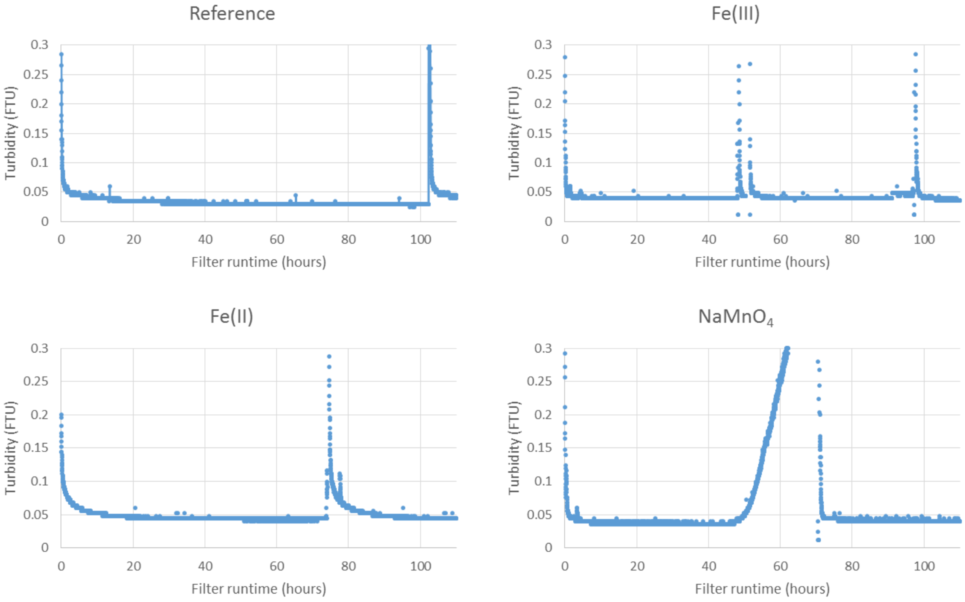

Figure 3.7: Turbidity of filtrate during filter runs at the different experiments

3.3.2 Reference column

The filter run time (determined by 0.75m foul head loss) was around 100 hours. Figure 3.8 gives an example of head loss and turbidity during a filter run.

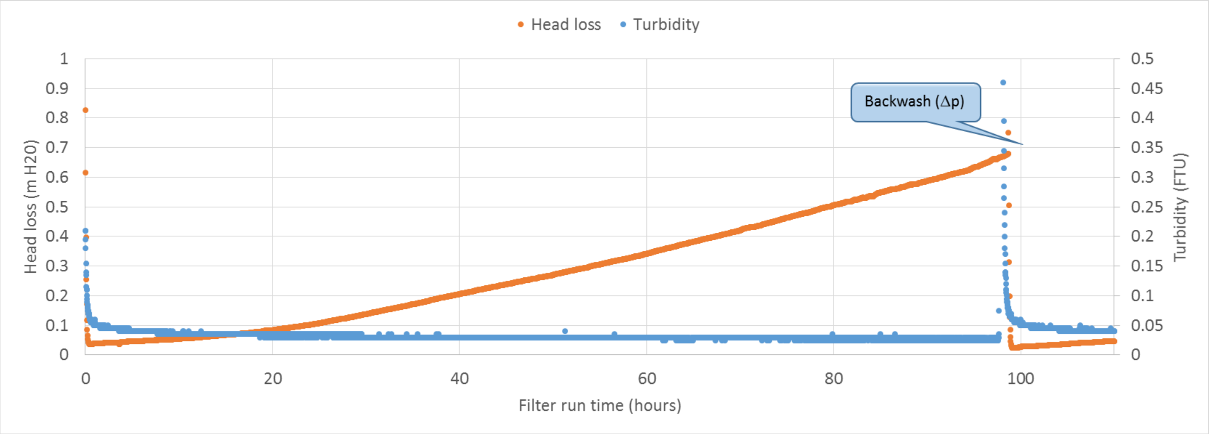

Figure 2.8: Head loss and turbidity during reference setting

Breakthrough never occurred. The turbidity peak was caused by the backwashing, during normal operation the turbidity was low and stable. This is in conformity with the constant water quality data reported earlier.

3.3.3 Dosing of Fe(II)

It was found that the filter run time was considerably lower than in the reference filter. At a dosing of 1.7 mg/l the average filter run time (based on 0.75 m foul head loss) was 49 hours. At the dosing of 1.2 mg/l the filter run time (based on 0.75 m foul head loss) was around 73 hours. An example is given in figure 3.9.

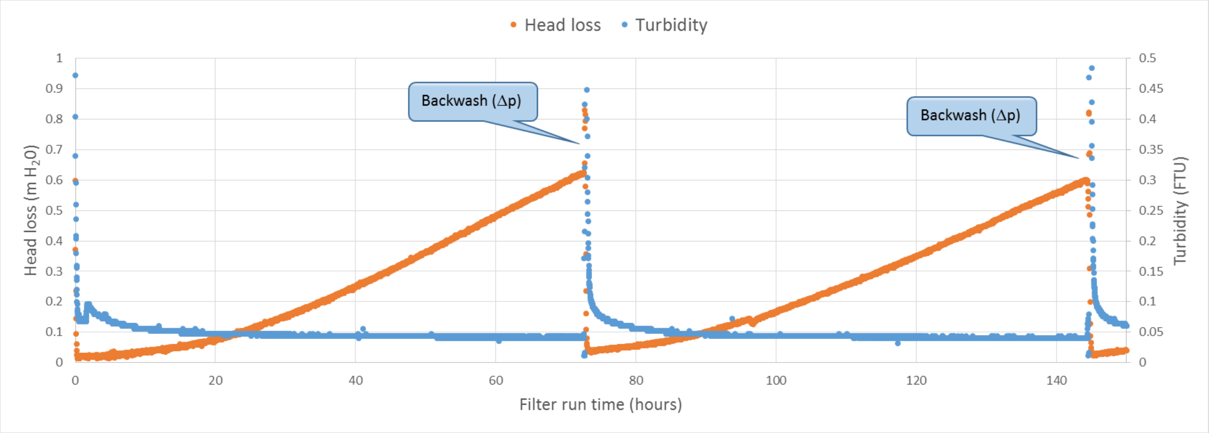

Figure 3.9: Head loss and turbidity during dosing of $FeCl_2$

3.3.4 Dosing of Fe(III)

The filter run time was reduced to an average of 50 hours. It is noted that the filter was also more susceptible to breakthrough as can be seen from figure 3.10.

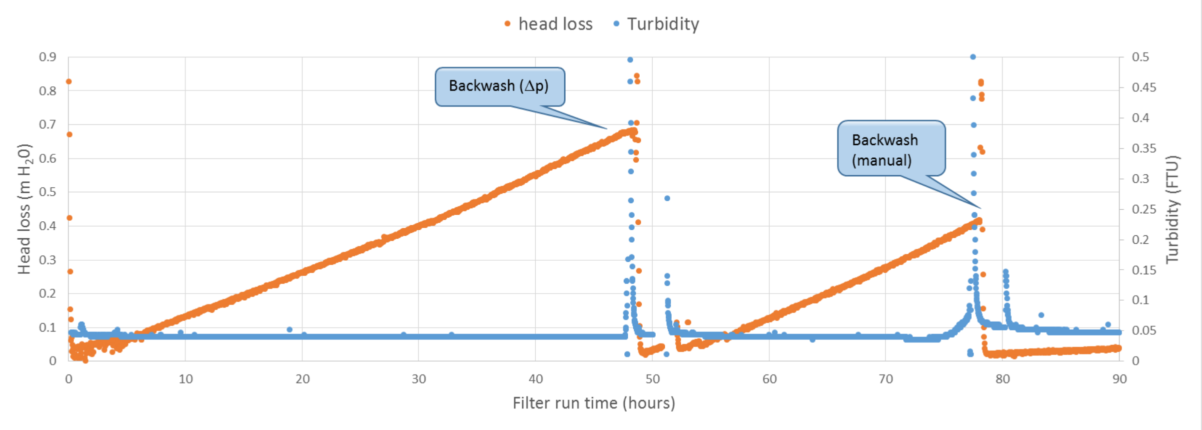

Figure 3.10: Head loss and turbidity during dosing of FeCl$_3$

3.3.5 Dosing of NaMnO$_4$

As previously observed in the full scale filters, the filter run time was much lower than in the reference case; average 49 hours. More importantly, the run time was determined by breakthrough instead of foul head loss as can be seen from figure 3.11. The figure shows that during the first run at around 46 hours the turbidity started to increase and at 49 hours (and 0.05 FTU) the filter should have been backwashed. As it was in the weekend, the filter was backwashed later. During the second run the filter was backwashed in time.

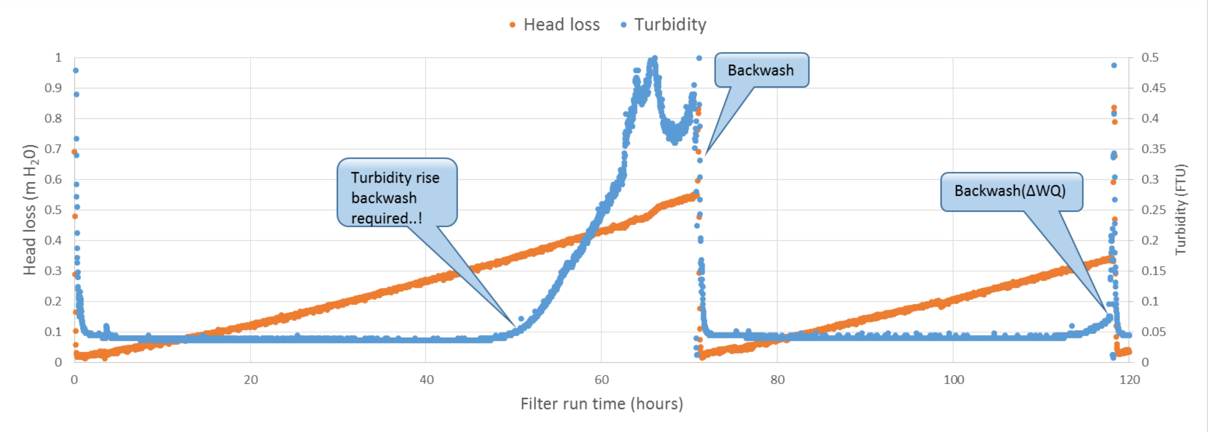

Figure 3.11: Head loss and turbidity during dosing of NaMnO$_4$

3.4 Settling velocity of the backwash water

Typical results for the cumulative frequency distribution of the four settings are presented in figure 3.12. This shows that in all cases the sediment readily settled and the dosing of Fe(III) and $NaMnO_4$ had a positive impact on the sedimentation velocity. It is noted that all experiments were duplicated and found to be reproducible. The sedimentation velocity of the backwash sediment of the full-scale plant (operating at a dose of 1.3 mg/l $NaMnO_4$) was similar to the pilot-plant as shown in annex 3.

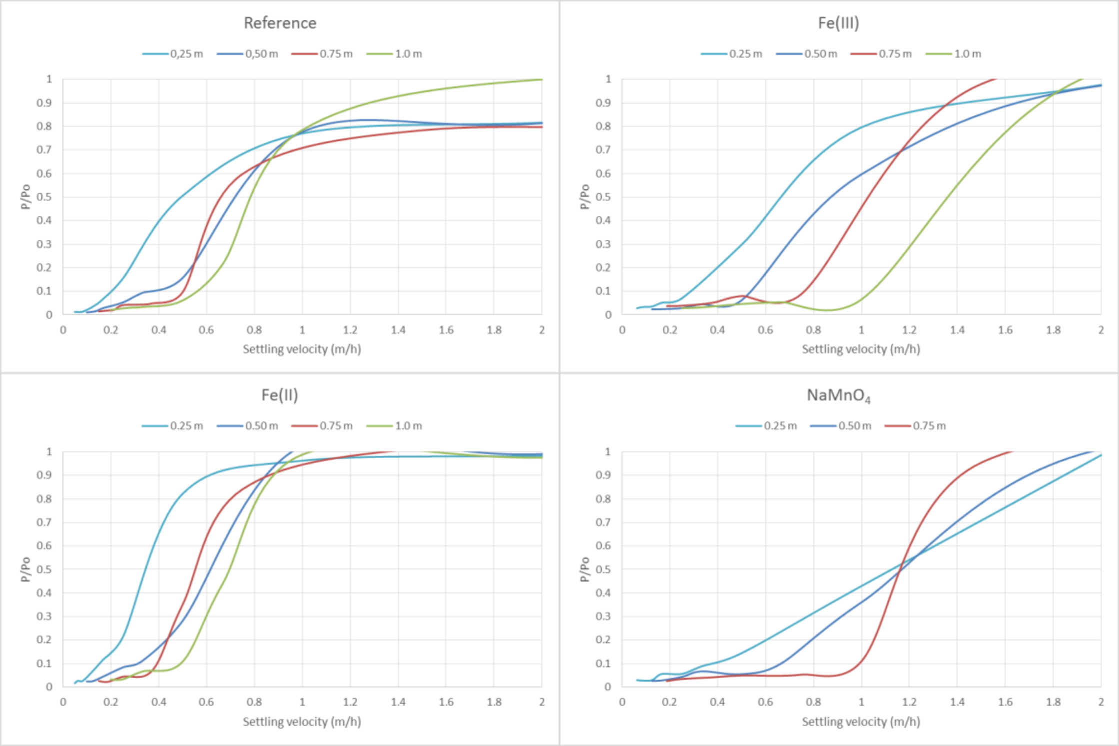

Figure 3.12: Settling velocities at different heights for the different settings

The results are summarized in table 3.9, which gives the settling velocity of the 90%-percentile (which means that 90% of the particles settled faster that the velocity indicated) at the 0.75 m sampling point as this was the most reliable sampling point. At the top of the column the impact of decreased water level (via sampling) was considerable, at the bottom of the column the impact of the settling of particles from higher sections could impact the results (as can be seen by the green line in the $NaMnO_4$ graph). The table confirms that the settling velocity was increased by the dosing of Fe(III) and $NaMnO_4$. Moreover, figure 3.12 also shows that dosing of Fe(III) and $NaMnO_4$ lead to a more flocculent settling behavior as shown by the increase in settling velocity at greater sampling depth (corresponding to higher detention time). This seems to confirm the flocculent nature of the formed hydrous ferric oxides (HFO). Contrarily, in the reference case and with dosing of Fe(II), the sedimentation curves overlapped, indicating discrete settling.

Table 3.9: Average settling velocities of the 90% percentile for the different settings at the 0.75 m sampling point

	Settling velocity	**Settling type**
ref	0.43 m/h	discrete
Fe(II)	0.36 m/h	discrete
Fe(III)	0.58 m/h	flocculant
$NaMnO_4$	0.96 m/h	flocculant

3.5 Thickening potential of the sludge

The results of the Imhoff cone for the four alternatives are given in table 3.10. This shows that the dosing of Fe(III) and $NaMnO_4$ lead to a significantly compromised thickening as compared to the reference case and the dosing of Fe(II). It is noted that all experiments were duplicated and found to be reproducible. The thickening of the backwash sludge from the full-scale plant (operating at a dose of 1.3 mg/l $NaMnO_4$) was comparable to the pilot-plant (operating at the same dose).

Table 3.10: Sludge volume in the Imhoff cone at different times for the different settings

	1 hour	End of test
	ml	ml
Reference	40	13 (576 h)
Fe(II) (1.2 mg/l)	70	20 (744 h)
Fe(III) (0.7 mg/l)	125	30 (699 h)
$NaMnO_4$ (1.3 mg/l)	165	31 (840 h)

All data of the Imhoff cone tests are given in figure 3.13. This figure also gives best fit curves that were used to extrapolate the results of the test. The sludge thickened readily. Obviously in practice the sludge detention time may be 1 year or more, so the sludge volume can be expected to decrease further.

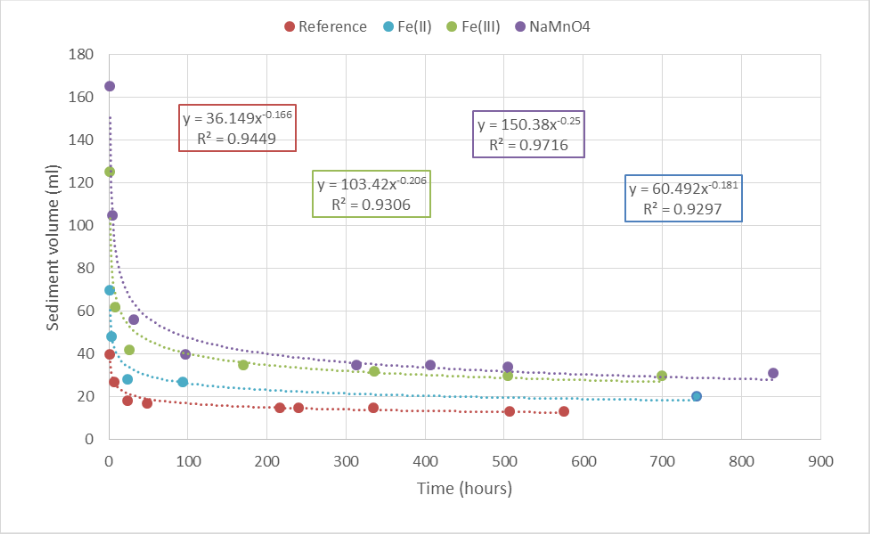

Figure 3: Measured and best-fit curves of the sludge volume for the different settings

The results of the Imhoff cone tests were also used to calculate the dry solids (DS) concentration of the sludge by using the mass balance from equations 6-9 (combined with lab analyses from the back wash water of the amount of suspended solids (SS)). The results are presented in table 3.11. It is noted that in practice the DS content will increase even further as a result of combined effect of stirring (if applied) and the weight of the sludge column compressing the sludge (in practice the sludge column will be in the order of meters instead of the few centimeters in the Imhoff cone).

Table 3.11: Suspended solids (SS) and calculated dry solids (DS) content at the end of the test of the sludge for the different alternatives

	SS	**DS**
	(mg/l)	End of test (%)
Reference	510	3.88 %
Fe(II) (1.2 mg/l)	667	3.99 %
Fe(III) (0.7 mg/l)	305	1.48 %
$NaMnO_4$ (1.3 mg/l)	312	0.95 %

4. Discussion

4.1 Water quality: impact of aeration

The results of table 3.1 show that in the reference case As remained largely (99%) mobile. This high mobility is most conveniently explained by the fact that As is not yet oxidized to As(V), in the relatively short detention time (1.3 min.) of the aeration cascades. This was shown earlier by Gude, Rietveld et al. (2016), who proved that As was not yet oxidized to As (V) by speciation analysis during similar experiments. It was also found that even during prolonged detention times (up to 1 hour) most of the As remained mobile and could not be removed by filtration over a 0.45 µm filter. Speciation analysis during earlier experiments at WTP Prinsenbosch confirmed that the mobile As was indeed As(III) (van Dijk 2017). This also confirms the findings of Katsoyiannis, Zoubalis et al. (2004), that abiotic oxidation of As is slow with a half-life of 3168 minutes. It is assumed that in the cascades the biotic oxidation can be neglected as no growth supporting contact area is available.

The results on the mobility of Fe and Mn were also similar to those of Gude, Rietveld et al. (2016), who investigated 3 treatment plants and found a mobility range of 90-99% (Mn) and 20-80% (Fe). The high mobility of Mn seems to indicate that also this compound is not (yet) oxidized in the aeration cascades. This conforms with literature that abiotic oxidation of Mn is slow (Bruins, Petrusevski et al. 2015) with a half-life of 7700 minutes (Katsoyiannis and Zoubalis 2004).

The reduced mobility of Fe indicates that a significant abiotic oxidation of this compound occurs in the aeration cascades. Using equation 1, the rate constant and the relevant data for our experiments (four cascades with 14 seconds detention time each, pH increasing from 7.6-7.9 in the 4 cascades and O_2 increasing from 3-9 mg/l in the 4 cascades), oxidation percentage of 56% of the Fe can be calculated, which is close to the 61% of table 3.1.

It is noted that the formation of particulate Fe in the cascades and supernatant water is generally not considered as favorable, as it may lead to the formation of small, low density flocs of hydrous ferric oxides (HFO), which may foul the cascades and lead to increased pressure drop in the filter (Teunissen 2007, Van Beek, Hiemstra et al. 2012). Later, van Beek, Dusseldorp et al. (2016) stated that oxidation and precipitation within the filter bed is preferred, as this leads to longer filter run times and higher density sludge. From this point of view a decreased mobility and an increased formation of precipitates in the aeration should be considered a disadvantage. Thus dosing of Fe(III) has the disadvantage of increasing the amount of HFO (which will form rapidly after dosing, as the hydrolysis reaction is fast) (Van Beek, Hiemstra et al. 2012). Dosing of $NaMnO_4$ has the same disadvantage as it will rapidly oxidize Fe(III) and thus also lead to the formation of HFO. Moreover, it has the additional disadvantage of increasing the amount of precipitates of Mn and As in the filter feed water (as shown by the reduced mobility).

4.2 Water quality: impact of filtration

The results of table 3.2 show that it was possible to enhance the As-removal to <1 µg/l for all 3 alternatives. However, different doses were required to reach this result. Considering that the adsorption of As(V) to the formed Fe(III)oxyhydroxides and Mn(IV) oxides is the bottleneck in the process, it should be interesting to calculate the adsorption load q, i.e. the amount of As removed (in µg/l) divided by the amount of Fe(III)oxyhydroxides and Mn(IV) oxides (in mg/l) formed in the filter. In the equilibrium, the adsorption load is directly related to the effluent concentration c (in mg/l) according to the well-known Freundlich isotherm (Banerjee, Amy et al. 2008):

$$q = K_f * c^{(\frac{1}{n})} \tag{10}$$

In this equation, K and 1/n are constants, indicating respectively the adsorption capacity of the sorbent and the intensity of adsorption.
Banerjee, Amy et al. (2008) performed laboratory experiments with distilled water and granular ferric hydroxide and found that at 20 °C and pH 6,5 K_f was 3.13 µg As/mg Fe and 1/n was 0.23. Obviously, the adsorption capacity of the Fe(III)oxyhydroxides and the Mn(IV) oxides need not be the same. To tackle this point, first the adsorption on the Mn(IV) oxides is neglected. The adsorption data from this study with this assumption is given in table 4.1. The adsorption load q has been expressed as Δµg As (concentration in raw water minus concentration in filtrate) per *mg of Fe* (concentration of Fe in raw water plus dosing).

Table 4.1: Adsorption data for Fe at the different settings

	c	ΔAs	Fe	q
	µg/l	µg/l	µg/l	µg As/ mg (Fe)
Reference	1.75	3.11	1825	1.70
Fe(II) (1.7 mg/l)	0.61	4.25	3526	1.21
Fe(II) (1.2 mg/l)	0.63	4.23	3026	1.40
Fe(III) (0.7 mg/l)	0.77	4.09	2526	1.62
Mn (0.6 mg/l)	0.76	4.1	1826	2.25

Table 4.1 seems to indicate that the allowable adsorption load is considerably higher in the case of dosing of $NaMnO_4$. It could be speculated that this is caused by the faster oxidation of As(III) in the supernatant, with the result that it can be faster adsorbed onto available Fe in the top of the filter bed. Without $NaMnO_4$ part of the As will be oxidized lower in the filter bed, where part of the Fe is no longer available. However, on the other hand, neglecting the adsorption on the Mn(IV) oxides seems unrealistic as several authors found that adsorption on Mn oxides is also quite efficient (BajPai and Chaudhuri 1999, Dalvi, Ajith et al. 2015, Yang, Sun et al. 2015). The adsorption capacity on Mn oxides was even found to be as high as 13.5 µg As/mg Mn, which is similar to the adsorption capacity on Fe(III)oxyhydroxides (Bissen and Frimmel 2003). Therefore, in table 4.2, the absorption load q has been expressed as Δµg As (concentration in raw water minus concentration in filtrate) per *mg of Fe+Mn* (concentration of Fe+Mn in raw water plus dosing).

Table 4.2: Adsorption data for Fe+Mn at the different settings

	c	ΔAs	Fe+Mn	q
	µg/l	µg/l	µg/l	µg As/ mg (Fe+Mn)
Reference	1.75	3.11	1876	1.71
Fe(II) (1.7 mg/l)	0.61	4.25	3576	1.19
Fe(II) (1.2 mg/l)	0.63	4.23	3076	1.38
Fe(III) (0.7 mg/l)	0.77	4.09	2576	1.59
Mn (0.6 mg/l)	0.76	4.1	2426	1.69

As can be seen from tables 4.2, the allowable adsorption load in the case of dosing of $NaMnO_4$ is much closer to the allowable adsorption load in the other cases. It could be speculated that this confirms that the adsorption on the Mn(IV) oxides is indeed relevant. On the other hand, the adsorption load is still somewhat higher which may support the relevance of the oxidation concept. In this respect it is also noted that the data are averages for the whole filter whereas in reality most of the adsorption will occur in the top layer.

The adsorption data of the experiments are also given in figure 4.1 together with the adsorption isotherm data of Banerjee, Amy et al. (2008)

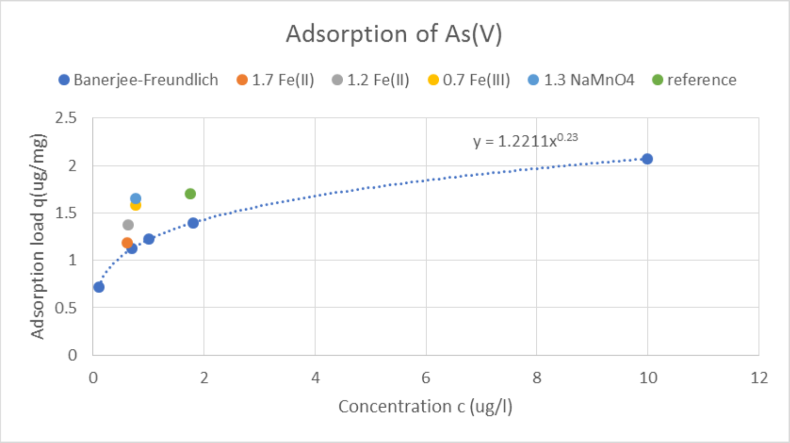

Figure 4.1: Adsorption isotherm data of Banerjee and the adsorption data (expressed as µg As/mg (Fe+Mn))

Notwithstanding the large difference between the experimental settings of Banerjee and this study, the data seem remarkably close. The somewhat higher acceptable adsorption load of our experiments may be explained by the differences in water composition and sorbent. Regarding the water composition it is noted that the pH of 7.6 in this study is considerably higher than the pH of 6.5 of Banerjee. Gude, Rietveld et al. (2017) found that As adsorption at pH 7.7 was 30% higher than As adsorption at pH 7.0. Regarding the sorbent, Gude, Rietveld et al. (2018) already suggested that different Fe-minerals (such as ferrihydrite, goethite and magnetite) could have different site-densities and sorption properties. Moreover, Sowers, Harrington et al. (2017) found that the adsorption of As(V) to environmental Fe(III) minerals was up to 3 times higher than the adsorption on synthetic ferrihydrite. They suggested that this increased adsorption was due to changes in the nature of the surface sites and/or to the incorporation of biomass and polysaccharides. Bai, Yang et al. (2016) also studied the adsorption on biogenic Fe-Mn oxides (BFMO) and concluded that it was very effective.

The data points also show a remarkable similarity in the results of the different alternatives. Similar effluent levels of 0.7 µg/l could be obtained at roughly similar adsorption loads for all three chemicals. Looking in detail, it seems that Fe(III) and $NaMnO_4$ are slightly more efficient that Fe(II), as the adsorption load is somewhat higher. In fact, $NaMnO_4$ has the highest adsorption load, so it seems to be the most efficient.
All in all, it seems that the concept of the Freundlich isotherm provides a useful and adequate understanding for the adsorption of As onto the Fe- and Mn oxides which are formed in the filter and these precipitates may even be better adsorbents than synthetic ferrihydrite.

4.3 Filter run times and breakthrough

The results of table 3.8 show that the filter run times were much shorter in the case of Fe(III) and $NaMnO_4$. This seems to indicate that the precipitates have a lower density (ρ_s) as the density of the precipitates determines the pore filling and the foul bed head loss (equation 4). This is also evident from table 4.3, which specifies the total Fe and Mn load (for reasons of simplicity expressed as kg (Fe+Mn)/m^2) for the different settings. The total acceptable filter load is much lower in the case of Fe(III) and $NaMnO_4$ as compared to the reference case and dosing of Fe(II). In the next sections some aspects relating to this phenomenon will be explored.

Table 4.3: Filter run time and filter load at different settings

	filter run time	**filter load**
	hours	kg (Fe+Mn)/m^2
Reference	101	0.73
Fe(II) (1.2 mg/l)	73	0.88
Fe(III) (0.7 mg/l)	50	0.50
NaMnO$_4$ (1.3 mg/l)	49	0.47

Impact of supernatant water level on pressure drop

During a filter run, the increasing head loss leads to an increasing supernatant water level. An increase in supernatant water level leads to an increase in detention time in the supernatant, so the oxidation of Fe(II) to Fe(III) will increase. Consequently the formation of hydrous ferric oxides (HFO) will also increase somewhat. This is expected to lead to an increased head loss (de Moel, Verberk et al. 2006, Van Beek, Hiemstra et al. 2012). According to the theory of deep bed filtration (Huisman 2004), the relationship between foul bed head loss and run time is quadratic, so the head loss should increase considerably near the end of the filter run. To investigate this phenomenon, the foul bed head loss of the different alternatives was compared and is given in figure 4.2.

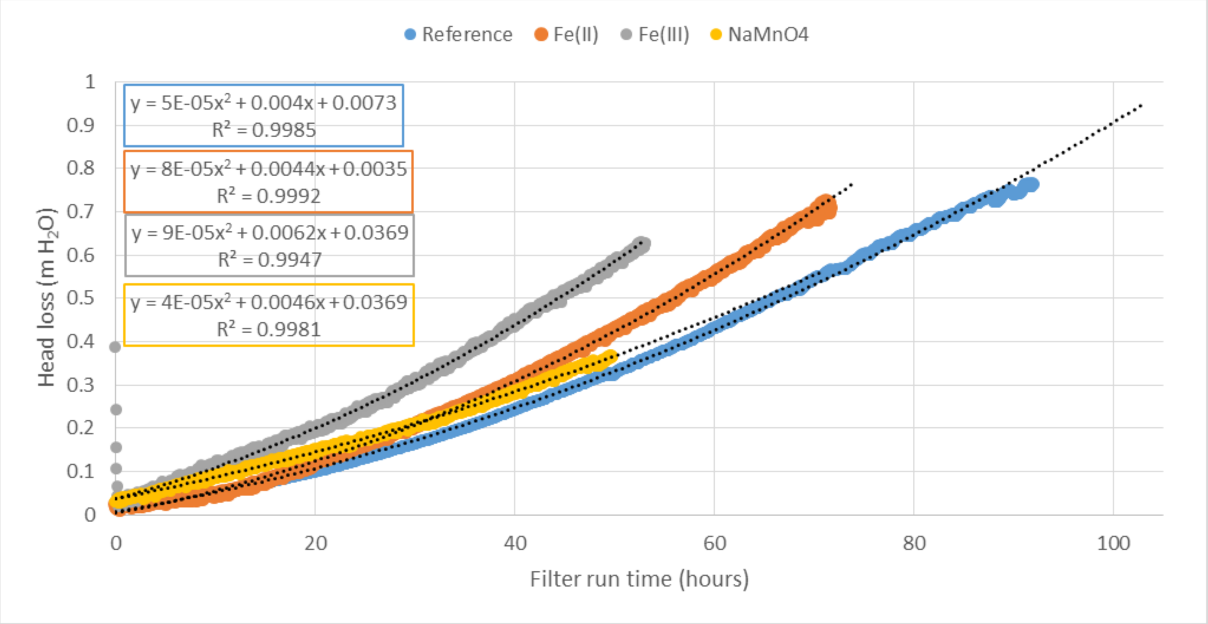

Figure 4.2: Head loss of the different settings

Figure 4.2 shows that the shape of the head loss curves does not considerably increase near the end of the filter run time. This was confirmed by measurements over the height of the filter bed, which showed that the head loss was equally distributed. Therefore the impact of an increasing supernatant water (and the related increasing HFO formation in the supernatant) on the pressure drop cannot be confirmed. Apparently, the impact of this phenomenon is relatively small as compared to the processes occurring in the filter itself.

Mass balance of the filter material

One might argue that the mass balance of the filter material might be one factor that influences the filter run time. It might be that the efficiency of the backwashing is not 100% in all cases so that some accumulation of precipitates might occur in the filter. As a matter of fact, both from practice and from literature (Teunissen 2007, Van Beek, Hiemstra et al. 2012, van Beek, Dusseldorp et al. 2016) it is well known that some accumulation of precipitates may occur, which manifests itself in the form of growth of the filter bed. To investigate this a mass balance of the filter was prepared (for Fe and Mn).

The mass balance enables a calculation of the theoretical concentration of the backwash water from the concentrations of the raw water, the dose and the clear water, assuming 100% of the precipitates are removed by the backwashing (as described in equation 6-9). This was compared to the measured concentration in the backwash water and is presented in the table 4.4.

Table 4.4: Mass balance of backwash water (% removed Fe and Mn found in backwash water samples) for different settings

	Fe(II)	**Fe(II)**	**Ref**	**Fe(III)**	**Fe(III)**	**NaMnO4**	**NaMnO4**	**NaMnO4 full scale**
Fe	80%	84%	81%	88%	99,8%	101%	90%	104%
Mn	9%	8%	7%	13%	9%	85%	95%	56%

Table 4.4 shows that for Fe nearly 100% of the deposits is removed by backwashing in the cases with Fe(III) and $NaMnO_4$. In the reference case 88-104% of the deposits is removed and with dosing of Fe(II) this percentage is also somewhat lower (80-84%), so some accumulation on the filter grains and growth of the filter bed may be expected. The latter conforms with the findings in ground water filtration practice and literature on the filtration of groundwater (Van Beek, Hiemstra et al. 2012, van Beek, Dusseldorp et al. 2016). In itself the phenomenon of accumulation of precipitates cannot explain the observed differences in filter run time as an increased accumulation (of the same precipitates) would contrarily lead to a decreased filter run time. However, the accumulation of precipitates in the case of Fe(II) does indicate that heterogeneous oxidation and/or biological filtration occurs rather than homogeneous oxidation.

Consequently, the results of the backwashing efficiency are most conveniently explained by assuming that in the cases and Fe(III) and $NaMnO_4$ (where the majority of the Fe is present in the form of Fe(III)), (more) homogeneous oxidation will take place and (more) HFO-solids will be formed. It is known that these HFO-solids can be easily removed by backwashing. In the reference case and with dosing of Fe(II), heterogeneous oxidation-filtration and/or biological oxidation filtration will be favored. In this case the precipitates are not easily removed by backwashing and may lead to growth to the filter bed material (Van Beek, Hiemstra et al. 2012, van Beek, Dusseldorp et al. 2016).

Density of the solids

The results of the filtration experiments can be used to get a first impression of the difference in the density of the formed precipitates. Using the simplified filter model (equation 2 and 3) the following floc densities can be calculated and are given in table 4.5.

Table 4.5: Calculated densities for the different settings (using the filter model)

	floc density kg/m³
Reference	3.25
Fe(II) (1.7 mg/l)	3.03
Fe(II) (1.2 mg/l)	3.87
Fe(III) (0.7 mg/l)	2.22
$NaMnO_4$ (1.3 mg/l)	2.37

These results seem to confirm that the precipitates which are formed in the reference case and in the case of dosing Fe(II) have a much higher density than those formed in the case of dosing of Fe(III) and $NaMnO_4$. This confirms the earlier findings of van Dijk, van Wijk et al. (1986), who found that the density of Fe-flocs in groundwater filtration were significantly higher than those of surface water filtration.

Crystallinity of the solids

Most of the debate in literature has been on the oxidation concept of Fe, Mn and As and the related homogeneous or heterogeneous nucleation of the Fe(III)oxyhydroxides and Mn(IV) oxides in the water and/or on the filter grains. Only limited attention has been given to the type, crystallinity and density of the precipitates itself. This is remarkable as this might have a big impact on the properties and in particular on the density and thickening potential.

Depending on the process conditions, a great many Fe oxides/hydroxides or oxide/hydroxides can be formed (Cornell and Schwertmann 2004, Schwertmann and Cornell 2004), which are summarized in table 4.6. The most reported compounds in water treatment are indicated in bold.

Structure	Name	Properties
Iron oxide/hydroxides		
α-FeOOH	**Goethite**	Thermodynamically stable , very homogeneous crystal
β-FeOOH	Akaganéite	Requires presence of Cl^- or F^-
γ-FeOOH	**Lepidocrocite**	Layered structure, forms from Fe(II) solutions, rust, slow oxidatior
δ-FeOOH	Feroxyhyte	Forms under high pressure
FeOOH	High pressure FeOOH	Forms under high pressure
$FeOOH.0.4H_2O$	**Ferrihydrite**	Poorly ordered, forms from rapidly hydrolized Fe(III) solutions
$Fe_{16}O_{16}(OH)_y(SO4)_x.nH2O$	Schwertmannite	Poorly ordered, requires presence of Cl^- and SO_4^{--}
Iron hydroxides		
$Fe(OH)_3.nH_2O$	Bernalite	
$Fe(OH)_2$	Iron(II)hydroxide	
$Fe^{III}_xFe^{II}_y(OH)_{3x+2y-z}(Cl,0.5SO_4)_z$	Green rust	
Iron oxides		
α-Fe_2O_3	Hematite	Forms at high temperatures, thermodynamically stable
FeO	Iron(II)oxide, Wüstite	
Fe_3O_4	Iron(II,III)oxide, **Magnetite**	Forms from mixed Fe(II)/Fe(III) solutions
Fe_4O_5, Fe_5O_6, Fe_5O_7,$Fe_{25}O_{32}$,$Fe_{13}O_{19}$	Various mixed oxides	

Table 4.6 : List of different Fe oxides/hydroxides structures, names and properties

In solutions containing Fe(III), the Fe hydrolyses rapidly and a red-brown polynuclear compound (HFO) is formed. What happens next is primarily determined by the supersaturation, i.e. the rate at which the hydrolyzed species are supplied (Cornell and Schwertmann 2004). This governs the oxide/hydroxide formed from the polynuclear compound and its crystallinity. The factors which determine the supersaturation and direct this process are mainly pH and the concentration of Fe(III).

In general poorly ordered (amorphous) ferrihydrite is formed at a high crystallization speed (high supersaturation), whereas a slow crystallization speed (low supersaturation) leads to the more crystalline oxides/hydroxides such as goethite (Cornell and Schwertmann 2004).

It is noted that the solubility product of goethite (pK=40-42) is much lower than that of ferrihydrite (pK= 37.7-39.5). The specific surface area of goethite (20-80 m^2/g) is also much lower than that of ferrihydrite (200-400 m^2/g). Consequently, goethite crystals are much more compact/dense than the amorphous ferrihydrite particles. Lepidocrocite is an intermediary compound in this respect.

In time, ferrihydrite and lepidocrocite may be transformed into the thermodynamically most stable goethite, but this transformation may take minutes to years depending on process conditions.

In solutions containing Fe(II), also different oxides/hydroxides may be formed, depending on the process conditions. Again goethite will be formed at low supersaturation and low oxidation speeds, whereas at higher speeds lepidocrocite and finally ferrihydrite will be favored. However, in this case also the mixed Fe(II)/Fe(III) oxide magnetite may be formed, in particular at limited oxidation speeds.

Recently, a number of papers have been published which confirm the above mentioned textbook information. Researchers from EAWAG studied the filtration of aerated Fe(II) and As(III) containing groundwater (Kaegi, Voegelin et al. 2010, Voegelin, Kaegi et al. 2010, Senn, Kaegi et al. 2015). They found that poorly crystalline ferrihydrite was formed at high supersaturation and more crystalline lepidocrocite at lower supersaturation. Van Genuchten, Pena et al. (2014) studied the precipitates formed on Fe(0) electrocoagulation electrodes in groundwater. They found primarily magnetite with minor fractions of goethite at the low supersaturation created by the electrodes (Van Genuchten, Pena et al. 2014, van Genuchten and Pena 2017). Bai, Yang et al. (2016) identified the biogenic Fe oxide formed in their experiments as lepidocrocite.

Based on the above literature, it can be hypothesized that at certain process conditions more crystalline Fe deposits (lepidocrocite, magnetite, goethite) may be formed. Furthermore, the density of a poorly crystalline deposit such as ferrihydrite may differ, depending on process conditions.

The more crystalline deposits will have a higher density and a lower water content, so this would explain the advantages of a longer filter run, better filtrate quality, shorter filter ripening time and less backwash water and sludge production. Favorable process conditions may include the Fe(II) dosing, which may promote the formation of magnetite. Dosing of Fe(II) will also lower the redox potential and thus the driving force for the formation of Fe(III)oxides/hydroxides, which may also stimulate the formation of more crystalline and dense deposits (lepidocrocite).

Obviously, this difference will have a big impact on the precipitation and filtration processes in the filter. When Fe is present in the form of Fe(III), the formation of poorly ordered, hydrous ferric oxides (HFO) such as ferrihydrite will be favored. When Fe is present in the form of Fe(II), the formation of more dense solids will be favored.

4.4 Settling velocity of backwash water

The results of the sedimentation tests show that dosing of Fe(III) and $NaMnO_4$ resulted in a higher sedimentation velocity. This was also found by Ahmad, van Dijk et al. (2017) and can be most conveniently explained by the good flocculation properties of Fe(III). According to Stokes law, the sedimentation velocity is primarily determined by the size of the solids, as this is a quadratic function. It is believed that dosing of Fe(III) and $NaMnO_4$ will lead to larger particles as a result of the superior flocculation properties of Fe(III). When Fe(III) is dosed, the formation of larger flocks with higher sedimentation velocities are promoted. Dosing of $NaMnO_4$ also stimulates the fast oxidation of Fe(II) to Fe(III) and the subsequent flocculation. In addition, MnO_2 is known to promote floc growth and improve the settling rate (Liu, Sun et al. 2011).

4.5 Thickening potential of sludge

The results of the Imhoff cone experiments can be used to get an impression of the impact of the process conditions on the thickening potential and the relation with the density. The best-fit curves of figure 3.13 have been used to extrapolate the tests to a sludge thickening time of 1 year in the table 4.7.

Table 4.7: Calculated dry solids content at two different settling times

	calculated DS content (%)	
	End of test (time varies)	After T= 1 year
Reference	3.88	6.3
Fe(II) (1.2 mg/l)	3.99	6.8
Fe(III) (0.7 mg/l)	1.48	2.7
$NaMnO_4$ (1.3 mg/l)	0.95	2.2

These data also confirm that the solids with a high density (reference and Fe(II)) have superior thickening potential properties as compared with the solids with a lower density (Fe(III) and $NaMnO_4$).

This is also known from literature as Georgaki, Dudeneu et al. (2004) found that most Fe sludges consisted of amorphous ferrihydrite, which adsorbs large quantities of water. Densification of sludge implies loss of water and/or increase in structural order. During thickening the free water is removed and with ageing a slow conversion (half-life of 3 years) of amorphous ferrihydrite to substantially crystalline goethite was also found in his research. He also found a correlation between increases in density and degree of crystallinity. Cornwell and Koppers (1990) report a large difference in compressibility and dewaterability between Fe sludge originating from surface water and ground water: the ground water sludge dewaters much easier than the surface water sludge (originating from coagulation with Fe(III)).

4.6 Overall comparison

An overall comparison of the assessment of the three alternatives is given in table 4.8. The table includes operational aspects and costs and a weighting appraisal of the different aspects determined by Brabant Water (Cardol and Vos 2018, Machielse 2018).

Table 4.8 Integral assessment of the 3 alternatives

	Fe(II)	**Fe(III)**	**$NaMnO_4$**	**Weight BW**
Filtration properties				
Chemical dosing to reach <1µg/l	0	+	0	less important
Filter runtime	+	-	-	Important
Breakthrough	+	0	-	Important
Filtrate quality	+	+	+	important
Backwash/sludge properties				
Backwash prodution	+	0	-	important
Sedimentation velocity	-	+	++	less important
Thickening potential	+	--	--	important
Operational aspects				
Safety	0	0	-	important
Handling	0	0	-	important
Reliability/uptime	0	0	--	important
Costs				
Chemical costs	++	++	0	less important
Sludge costs	++	+	0	less important

The grading of the alternatives can be clarified as follows:

- Chemical dosing Fe(III) is graded with + because less chemical is required as compared to Fe(II) and $NaMnO_4$
- Filter run time is indicated with ++ when <20% less than reference, + when 20-30% less, 0 when 30-40% less, - when 40-50% less, and -- when >50% less
- Breakthrough is indicated with + when it does not occur during run time (and prolonged runtime), 0 when it doesn't occur during run time, - when it is back wash criteria
- Filtrate quality is indicated with + when sum of changed water quality parameters is positive, 0 when it stays equal, - when it is negative
- Backwash production is indicated with ++ when <20% less than reference, + when 20-30% less, 0 when 30-40% less, - when 40-50% less, and -- when >50% less
- Sedimentation velocity is indicated with -- when >25 % less than reference, - when between 25% less and equal, 0 when 0-25% increase, + when 25-50% more, ++ when >50% more
- Thickening potential is indicated with ++ when DS content is >25% then reference, + when 25-0% better, 0 when 0-25% less, - when 25-50% less, -- when >50% less
- Safety: $NaMnO_4$ is graded with -, because of the exothermic oxidative properties of the chemical ((Cardol and Vos 2018)).
- Handling: $NaMnO_4$ is graded with -, because it has a higher hazard class (Cardol, 2018).

- Reliability/uptime: $NaMnO_4$ is indicated with - -, because of the problems experienced with storage and dosing facilities in practice. (Cardol and Vos 2018)
- Chemical costs are compared to current $NaMnO_4$ dose, and are indicated with ++ when >50K/year less, + when 50-25K/year less, 0 when 0-25k/year less, - when 0-25k/year more, -- when >25k/year more ((Machielse 2018)). This is based on wholesale prices of 3500 Euro/ton 40% NaMnO4 and 200 Euro/ton for 30% $FeCl_2$ and $FeCl_3$.
- Disposal costs are compared to current $NaMnO_4$ and are indicated with ++ when the DS content is increased by >100%, + when DS > 50%

Based on the assessment of table 8.6, Brabant Water has selected Fe(II) as the preferred chemical. Currently preparations are ongoing to the replace the $NaMnO_4$ dosing by Fe(II) at WTP Prinsenbosch. Also, plans are being made to implement Fe(II) dosing at the other 6 WTP’s involved. For some of these WTP’s (such as Dorst) which have a higher raw water arsenic concentration, additional research is foreseen to check the feasibility.

5. Conclusions and recommendations

5.1 Conclusions

Based on the presented research in this thesis the following main conclusions can be drawn:

- Pilot column experiments showed that the required doses to achieve As <1 µg/L at WTP Prinsenbosch were 0.7 mg/l for Fe(III), 1.2 mg/l for Fe(II) and 1.3 mg/l for $NaMnO_4$.
- The impact on the filtration process (filter run time, breakthrough, backwash water production) was much less/better in the case of Fe(II). The filter run times were 73h for Fe(II) as compared to approximately 50 h for both Fe(III) and $NaMnO_4$.
- The settling experiments confirmed earlier findings that settling is faster for Fe(III) and $NaMnO_4$. It also revealed that the settling velocity is adequate for WTP Prinsenbosch for all alternatives (>0,3 m/h).
- The sludge thickening experiments also showed much better results for Fe(II). The DS content was 3.9% after approximately 1 month as compared to 1.5%-1.0% for Fe(III) and $NaMnO_4$ respectively.

An explanation for the shorter run times and lower thickening potential in the case of Fe(III) and $NaMnO_4$ can be the type and crystallinity of the precipitates of Fe and Mn. The results of this study could most conveniently be explained by assuming that depending on the process conditions different precipitates with different crystallinity and/or density may be formed.

- Dosing of Fe(III) and $NaMnO_4$ leads to short filter run times and breakthrough. This indicates that the precipitates have a low density. These precipitates can be easily removed by backwashing and the backwash sludge settles fast. However, the sludge thickens poorly, which also seems to indicate a low density. All these properties can be explained by assuming that the precipitates are poorly ordered/crystalline and have a lower density, e.g. HFO/ferrihydrite.
- Dosing of Fe(II) leads to a longer run time and the absence of breakthrough. This indicates that the precipitates have a higher density. These precipitates are less easily removed by backwashing and some growth of the filter bed occurs. The backwash sludge settles slower, but thickens better. These properties point to precipitates which are more ordered/crystalline and have a higher density, e.g. lepidocrocite or magnetite.

The overall conclusion for WTP Prinsenbosch is that dosing of Fe(II) has crucial advantages over Fe(III) and $NaMnO_4$, as it can achieve similar As concentrations in the filtrate at considerable longer filter run times, with the absence of breakthrough and superior thickening potential. It is also cheaper than $NaMnO_4$ (>52.000 Euro/y for WTP Prinsenbosch) and easier to handle and operate.

It is expected that for WTP Prinsenbosch the results can be even further improved as compared to the pilot-plant results as the acceptable foul head loss in the full scale plant is higher (1.0 vs 0.75 m). This provides the option of either increasing the dose (thereby obtaining lower As-levels) or increasing the filter run time (thereby further reducing the backwash water consumption). These improvements are not possible in the cases of Fe(III) and $NaMnO_4$ as breakthrough will occur there.

5.2 Recommendations for further research

Regarding practical applications the results of this study are quite satisfactory and convincing: Fe(II) dosing is the best alternative (better than AOCF at the full scale plant) and gives adequate results in all aspects. The As removal is sufficient (<1 µg/l), the filter run time is the longest and the thickening of the backwash sediment is the best of the alternatives.

Further on-site research at WTP Prinsenbosch is recommended to address the following questions:

- What is the additional advantage of dosing $FeCl_2$ in the last cascade instead of the raw feed line (as close to supernatant as possible)?
- What is the additional advantage when allowing foul bed head loss of 1 mWc (vs 0.75 cm)
- What is the impact of changes in filtration velocity (2.5-6 m/h vs 4)?
- What is impact of a filter bed height of 1.8 m (as available at WTP Prinsenbosch) as compared to the 1.6 m (as available in the pilot plant)?

In addition future scientific research is recommended including:

- Determining the crystallinity and density of the solids in the filters (XRD, XAS) in different cases/process conditions in order to understand the impact on the filtration process. What is the impact of the type of precipitates on the adsorption of As? Is it possible to optimize the adsorption load throughout the filter bed?
- Determining the biological activity (PCR, *Gallionella*, *As oxidizers*) in the filters in order to understand the impact on the filtration process.
- What is the impact of changing process conditions on the processes in the filters? A lower oxygen concentration and a lower pH may favor crystallinity and density of Fe deposits and As removal, but may jeopardize other processes such as Mn removal.
- What is the influence of other water quality parameters such as silica and phosphate on the total performance of the filter, regarding Fe, Mn and As?

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Annex 1: Startup phase

Both pilot filters were started on January 11th at a filtration velocity of 1.5 m/h (ca. 106 l/h). From experience some 6-8 weeks for startup of rapid sand filters was expected. The startup period was not relevant for this study, so after approximately 6-7 weeks the first samples were taken to check the status of the processes. On 20-2 the filtration velocity was adjusted to 4 m/h. Table A1.1. shows that the NH_4^- conversion was almost complete at that time. This can be seen by the fact that it was almost completely removed and that there was still some NO_2^- present in the filtrate. The Mn removal was also almost complete. At the first sampling some Mn was present in the filtrate of filter 1, which was completely removed two samplings later. Filter 2 had some more Mn in the filtrate, but also showed complete removal after the 3rd sampling. As removal increased in the start-up phase, indicating that is also (partly) a biological process. This confirms the findings of earlier studies done by Gude et al (2017) and van Dijk (2018). Dosing started 31-3, when all the processes were working properly and stable.

Table A1.1: As, Fe, Mn, NH_4^- and NO_2 concentrations of the filtrate of both pilot filters during the end of the startup period

	Filter 1 (experimental)					**Filter 2 (reference)**				
	As	Fe	Mn	NH4	NO2	As	Fe	Mn	NH4	NO2
	ug/l	ug/l	ug/l	mg/l	mg/l	ug/l	ug/l	ug/l	mg/l	mg/l
20-2-2018	2.7	327	2.5	0.12	0.050	2.4	92.6	46.6	0.12	0.078
23-2-2018	4.3	248	6.6	0.19	<0.01	3.5	8.9	7.0	0.19	<0.01
8-3-2018	2.2	10.4	0.60	<0.03	<0.01	2.7	8.6	0.5	<0.03	<0.01
12-3-2018	1.5	6.2	0.53	<0.03		1.5	3.5	0.3	<0.03	
16-3-2018	1.9	14	<0.4			2.6	8.1	<0.4		
21-3-2018	1.5	19				1.7	17			
23-3-2018	1.6	8.8				1.7	6.4			
26-3-2018	1.6	19				1.7	17			

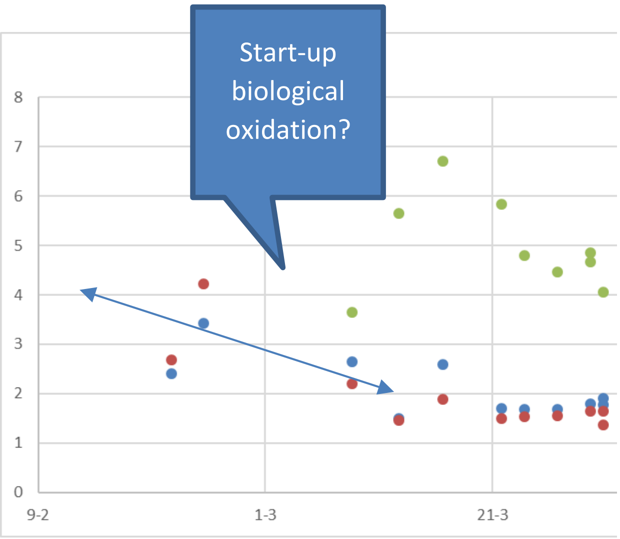

Figure A1.1: As concentration during the startup period of both filter columns

Annex 2: Breakthrough with Fe(III)

The first dose of Fe(III) was 2.8 mg/l. At this dose, the turbidity started to rise after 22 hours, and backwash was required not long after. At this time the head loss was only 0.4 m. This is shown in figure A2.1.

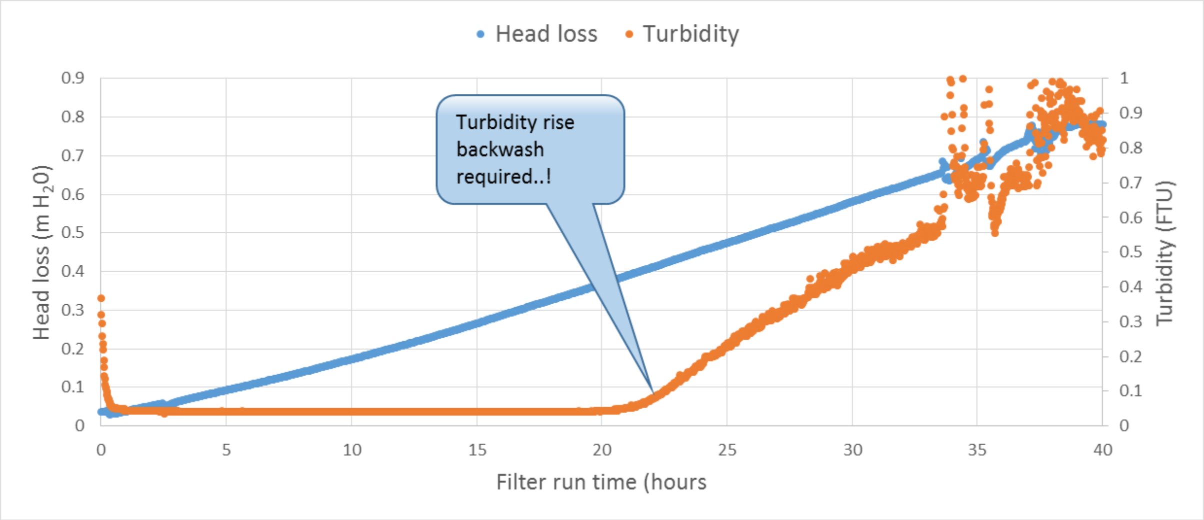

Figure A2.1: Head loss and turbidity during a filter run with dosing 2.8 mg/l Fe(III)

When dosing 1.7 mg/l, breakthrough started to occur around 24 hours, resulting in a run time of 28 hours, when the backwash criteria of 0.05 FTU was reached. Again the head loss at this time was only approximately 0.45 m. This is shown in figure A2.2.

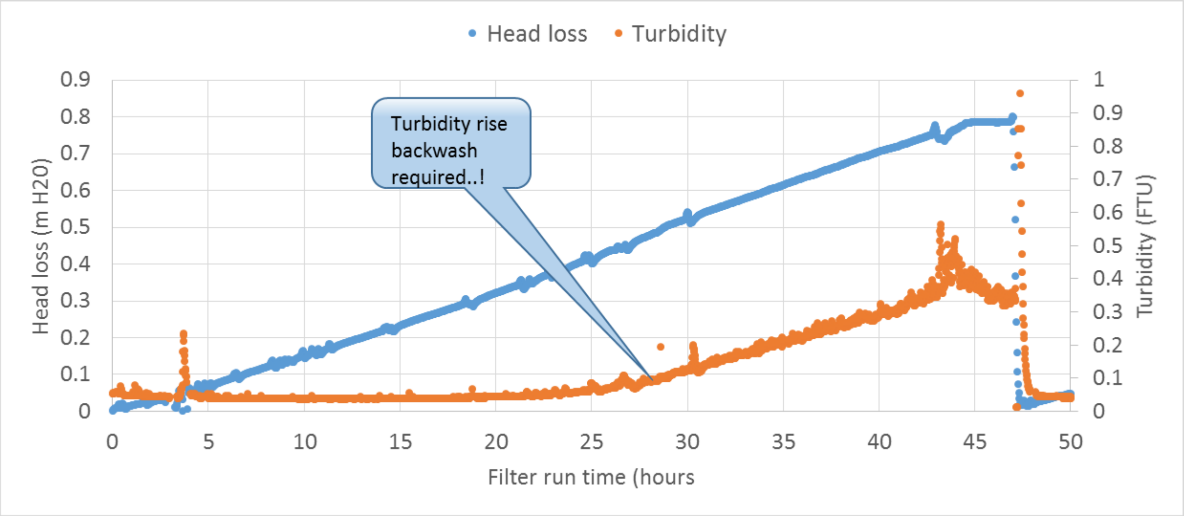

Figure A2.2: Head loss and turbidity during a filter run with dosing 1.7 mg/l Fe(III)

When dosing 0.7 mg/l Fe(III), backwashing was required after 49 hours, when head loss reached 0.7 m. When continuing the run, it was found that breakthrough started shortly thereafter, around 53 hours. This indicated that both backwash criteria were (almost) at their maximum. This is shown in figure A2.3.

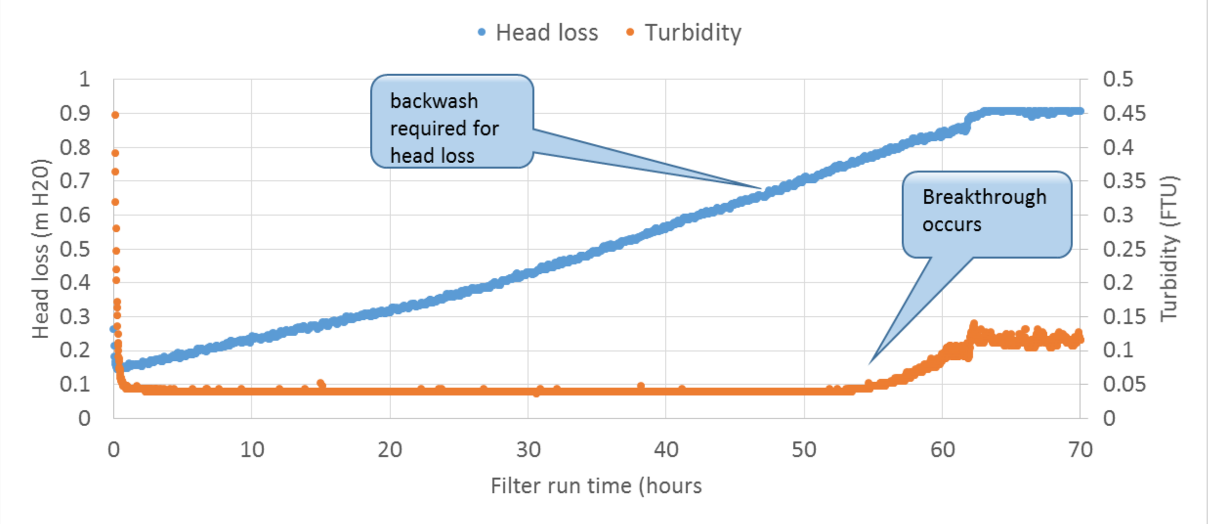

Figure A2.3: Head loss and turbidity during a filter run with dosing 0.7 mg/l Fe(III)

All graphs show that when dosing Fe(III) the process is not robust and vulnerable to breakthrough. Even with dosing 0.7 mg/l and a run time of 49 hours, breakthrough will almost occur. In practice with varying filtration velocities the process may be even more vulnerable. Therefore the filter run times need to be shortened to create margin for safety, as breakthrough is to be avoided.

Annex 3: Settling test back wash water from full scale plant

Figure A3.1 shows that the distribution of the settling velocities is similar for the full scale plant and the pilot filter (both dosing 1.3 mg/l $NaMnO_4$). In both cases the settling velocities are very high. At the sampling point at 0.25m the velocities are almost equal and at 0.5m and 0.75m they are very similar. At the 1 m sampling point the image is distorted by sludge settling from higher levels.

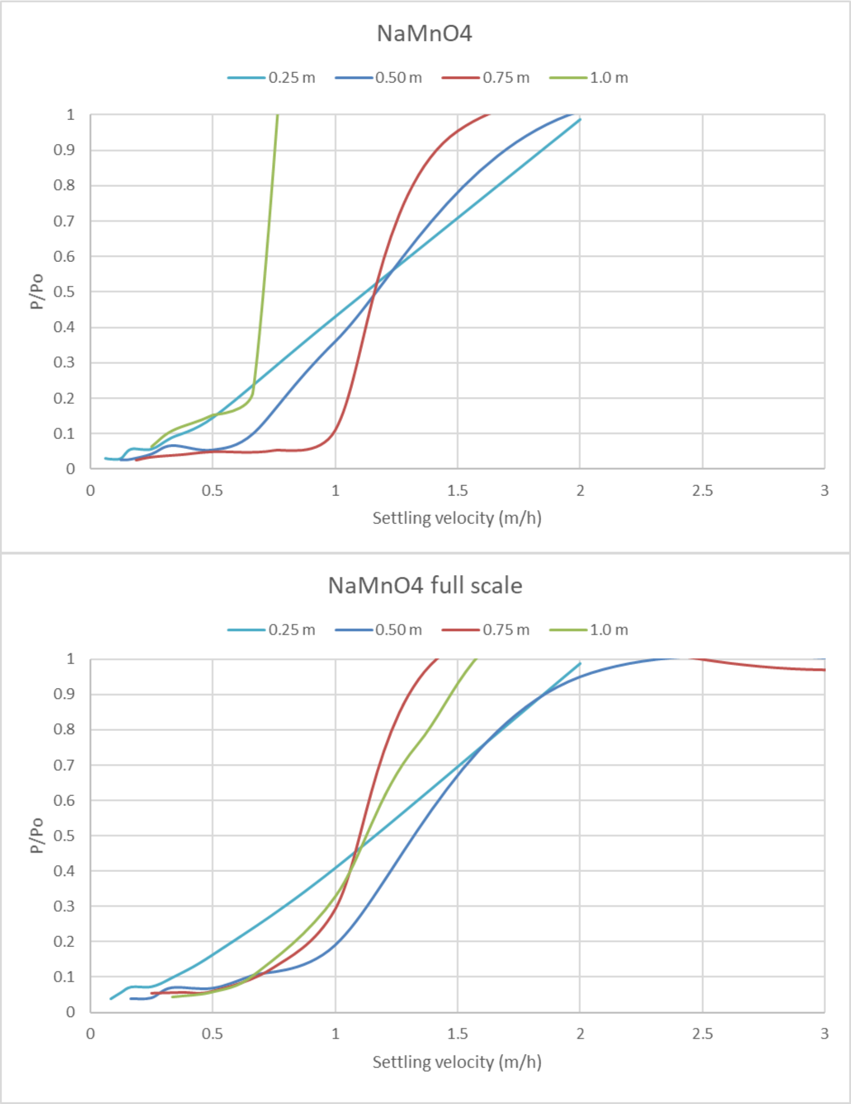

Figure A3.1: Settling velocity distribution of the backwash water of both the full scale and pilot filter when dosing 1.3 mg/l $NaMnO_4$