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ARSENIC REMOVAL USING MANGANESE OXIDE FOR ARSENIC OXIDATION PROCESS
Case study – Skovby waterworks, Denmark

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Abstract

Arsenic contamination has been a pressing concern in water supplies for a long time, exerting detrimental and severe impacts on human health due to its high toxicity. According to Danish drinking water criteria, the limit for arsenic is set to 5 µg/l. Skovby waterworks, a local water supply company in Denmark, is planning to increase water production by abstracting raw water from a new intake well which contains 18 µg/l of arsenic.

The study aimed to find the most practical and appropriate treatment techniques to deal with high level of arsenic in the new boring raw water at Skovby waterworks. Investigating on the oxidizing potential of solid media was also one of the objectives of this study, providing knowledge about the roles of manganese oxides coated sand in arsenic oxidation process. A review of literature on existing arsenic removal methods as well as manganese oxides 's ability to convert As(III) to As(V) were carried out. Several calculations were made to identify possible water treatment operations and systems that could manage raw water containing arsenic from new well while satisfying with safety limit.

Manganese oxides has shown good capability of oxidizing As(III) to As(V) following first-order kinetic with a half-life time of 3-6 minutes, in which manganese oxides could either be a catalyst for reaction between arsenic and dissolved oxygen or a main oxidant in direct reaction with arsenic through surface mechanism. The role was defined by the levels of interfering substances in raw water, such as sulfide, iron or natural organic matter.

High efficiency of arsenic removal could be achieved by oxidation/filtration method (also known as iron and manganese removal), in which arsenic is co-removed with natural iron content in water. Three water treatment designs and processes were studied, of which co-treatment of raw water sources and two-step arsenic treatment indicated good results while individual treatment of raw water from new well was possible if iron chemical was added.

Later experiments and bench-scale studies are suggested to better accurate the efficiency of arsenic oxidation process and arsenic removal treatment.

Keywords

Arsenic, manganese oxides, catalyst, oxidant, iron, oxidation/filtration

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1   INTRODUCTION

1.1   Current knowledge and problem formulation

Arsenic has posed a serious threat to drinking water resources around the world; thus, wide range of technologies have been studied and investigated to address this issue. Nowadays, there are various arsenic removal techniques available in the market, for example oxidation and filtration, coagulation/flocculation, lime softening, adsorption, ion exchange or membrane technology. Arsenic is most likely prevalent in the reduced form As(III) under groundwater reducing environment, which is difficult to remove due to its neutral charge. Pre-oxidation process is required to oxidize arsenite As(III) to more reactive arsenate As(V) in order to enhance arsenic removal efficiency. (Hoffman et al. 2006, 2-3; Nicomel et al. 2016, 3.) Typically, several chemical oxidants, such as chlorine, ozone, permanganate, are employed to convert arsenic to its highest oxidation state because of powerful oxidizing ability. In addition, manganese oxides have also been considered as an effective agent with regards to arsenic oxidation in natural environment, which is currently implemented in arsenic-contaminated water treatment (Oscarson et al. 1981, 50; Driehaus et al. 1995, 297-305; Ghurye & Clifford 2004, 84-96; Ramsay 2007; Zhang et al. 2011, 655-660)

Skovby is a small town located in Central Jutland, North-Eastern part of Skanderborg municipality with population of 2500. Residents in Skovby are provided water by Skovby waterworks, a private cooperative water company established in 1934. In response to town development and growth in population, Skovby waterworks has an intention of abstracting groundwater from a new borehole to complement the raw water sources extracted from three active intake wells at present. However, the concentration of arsenic is relatively high (18 µg/l), which is more than three times above Danish drinking water criteria (Maribo & Vestergaard 2016). It is essential for Skovby waterworks to take some arsenic treatment measures before drawing raw water from this new borehole.

1.2 Objectives of the study

The project study aims to provide two objectives as follows:

- To determine the most practical arsenic remediation strategies to manage high level of this contaminant in the planned raw water boring. A number of design and operation modifications will be evaluated by assessing advantages and disadvantages, providing Skovby waterworks some potential solutions to reduce the concentration of arsenic in raw water.

- To define the role of manganese oxides in arsenic oxidation process, which could be either as a catalyst or a primary oxidant. The conversion process of As(III) to As(V) will be investigated with regards to the effectiveness as well as the interference of other substances and factors.

2 SKOVBY WATERWORKS

Skovby waterworks lies in the heart of Skovby town, supplying water to 1300 consumers with approximately 150,000 m^3 annually. The main consumers include households, small industries, farms and a school (Maribo & Vestergaard 2016). Figure 1 shows the town of Skovby and Skovby waterworks location.

Figure 1. Map of Skovby and Skovby waterworks (Google maps 2017)

2.1 Raw water sources

The three active intake wells are located in the proximity of Skovby center. Two of them (Boring 1 and 2) are directly located at the site of waterworks while the other (Boring 4) is about 150 m away, all within the urban area as displayed in Figure 2. A new well (Boring 5), aiming to provide additional capacity to waterworks, is established 1200 m away to the East-South of the waterworks in the rural area. Boring 1 and 2 have been put into operation since 1970's. While Boring 4 and 5 are newer, being built in 1990 and 2002 respectively (Geologic survey of Denmark and Greenland 2017).

Figure 2. Location of intake wells in the context of Skovby waterworks (Geologic survey of Denmark and Greenland 2017)

Figure 3 demonstrates that Boring 1, 2 and 4 abstract groundwater from the same confined glacial melt water sand aquifer protected by a layer of moraine clay above. While three filters inside Boring 5 were installed in much deeper aquifers constituted mostly of gravel and covered majorly by meltwater clay. These aquifers are saturated since the groundwater table lies above the upper boundary of sand and gravel aquifers (Geologic survey of Denmark and Greenland 2017). Detailed data about four intake wells is presented in Table 1.
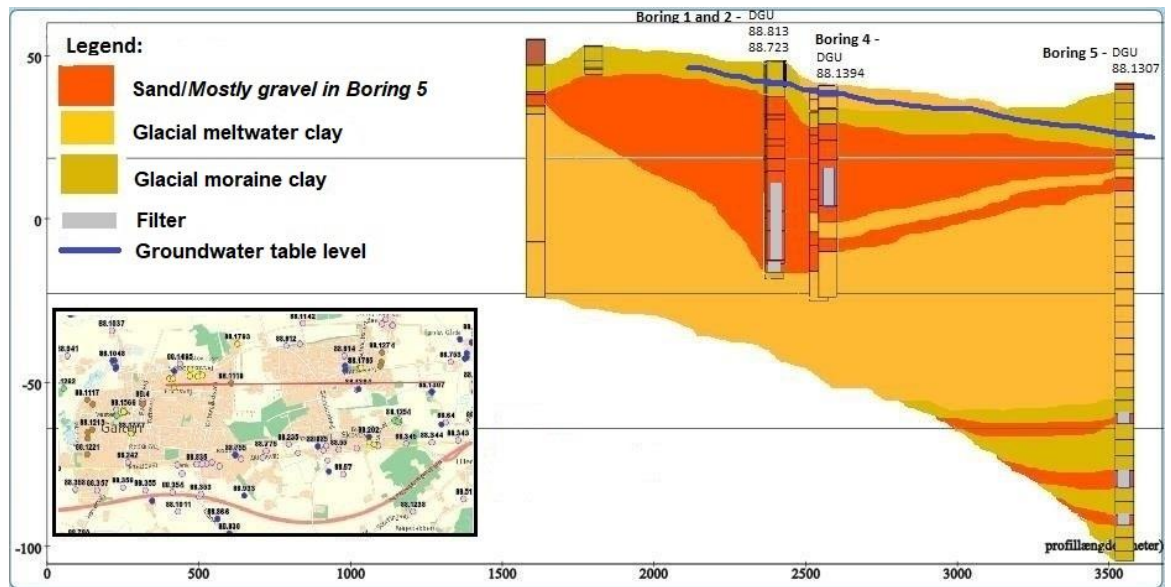
Figure 3. Geological profile of intake wells – West-East Direction Cut, 4km long with radius of 500m (Geologic survey of Denmark and Greenland 2017)

Table 1. Technical data about intake wells in Skovby waterworks (Geologic survey of Denmark and Greenland 2017)

	Boring			
	1	2	4	5
DGU number	88.813	88.723	88.1394	88.1307
Drilling year	1977	1973	1990	2002
Aquifer material	Sand	Sand	Sand	Sand/Gravel
Screened interval (m.u.t)	29-63	37-61	25-37	101-135
Thickness of protective layer (m)	13.2	11	11.7	100
Potentiometric surface (m.u.t)	8.62	7.78	1.88	19.4

In addition to the physical and geological description, chemical analysis is carried out to examine the water quality of raw water taken from four boreholes. Different water parameters are compared against Danish criteria for drinking water in order to identify exceeding water properties and further suggest solutions to remove undesirable substances before supplying clean water to customers. The most important parameters and those elements in exceedance of the water requirement are presented in Table 2. A full list of parameters in groundwater analysis can be found in Appendix 1.

Table 2. Important parameters from groundwater analysis of intake borings in Skovby waterworks, those substances exceeding limit values are marked bold in the table (Geologic survey of Denmark and Greenland 2017; Ramsay)

Parameters	Danish water criteria	Boring			
		1	2	4	5
Iron (mg/l)	0.1	**0.297**	**0.54**	**0.417**	**0.84**
Manganese (mg/l)	0.02	**0.582**	**0.446**	**0.413**	-
Ammonium (mg/l)	0.05	**0.07**	**0.06**	0.02	**0.645**
Agress.CO_2 (mg/l)	2	**<5**	<2	**<5**	-
Hydrogen sulphide (mg/l)	0.05	<0.01	<0.01	<0.01	<0.05
Methane (mg/l)	0.01	<0.01	<0.01	<0.01	<0.01
Nitrite (mg/l)	0.01	0.003	0.007	0.005	**0.012**
Arsenic (µg/l)	5	3.4	3.22	2	**18**

The levels of iron, manganese and ammonium are above Danish potable water requirement in all four wells. However, these substances can be removed in subjection to Standard Treatment System. During aeration process, aggressive CO_2 in Boring 1 and 4 is possibly reduced in concentration to safety level. There are also two substances in the Boring 5 surpassing water criteria, especially the content of arsenic is nearly four times higher than admissible level. This problem requires Skovby waterworks to implement further advanced treatment than the existing practices if raw water from Boring 5 is abstracted for water supply (Jensen 2012a, 63-67).

2.2 Water treatment system

Skovby waterworks consists of two separate treatment plants located centrally in the town of Skovby. Standard Treatment System is implemented in both treatment plants to produce clean water for residents in the region. The complex of Skovby waterworks is depicted in Figure 4 for general overview.
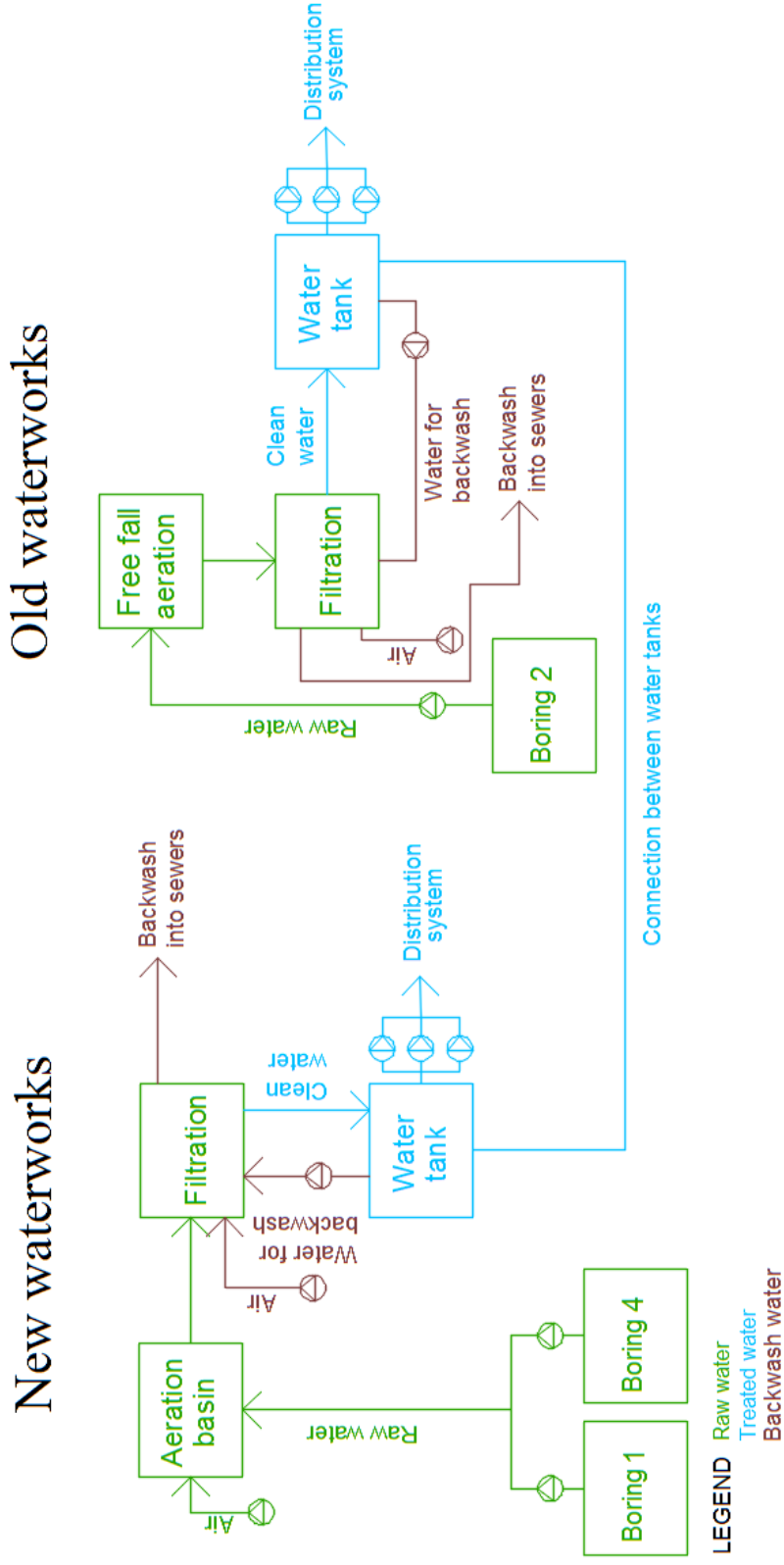
Figure 4. Scheme of Skovby waterworks, both the old and new waterworks

The old waterworks was built and began operating in 1960's with a free-fall aerator and two filters. Meanwhile, the new waterworks was constructed in 1977, equipped with an aeration basin and three filters for water treatment; yet, two out of three filters have been used in the treatment process at the moment. The treated water is then kept in two storage tanks connected to each other by a pipe with diameter of 300 mm. The total capacity of two storage tanks is 750 m^3 (Maribo & Vestergaard 2016).

Skovby waterworks performs automatically, in which raw water pumps are triggered when the level of clean water in storage tank is lowered due to consumer consumption. Raw water pumped from Boring 1 and 4 supplies to the new waterworks while old waterworks takes water pumped from Boring 2; these pumps are started alternatively (Maribo 2016). Some relevant values indicating the performance of the Skovby waterworks taken from Yearly Report 2015 are shown in Table 3.

Table 3. General information about Skovby waterworks performance (Skovby waterworks 2016)

	Old waterworks	**New waterworks**	
Boring	2	1	4
Operation time (h)	2393.2	2029.5	660.7
Raw water volume (m^3)	61087	84638	
Backwash frequency	Once/week	Every 1000 m^3	
Total amount of clean water produced in year 2015 is 144056 m^3			

In the old waterworks, raw water from Boring 2 flows down the free-fall aerator under gravity, in which aeration/stripping is achieved by water-in-air method. A cross-current flow between water and air allows exchange of gases along the thin film; oxygen can be added to water from the atmosphere; whereas methane, hydrogen sulphide and aggressive CO_2 can be stripped out during aeration process (Jensen 2012b, 73-76) The level of dissolved oxygen after water aerated is 8.6 mg/l, correspondingly 78% saturation. (Maribo 2017.) Under the free-fall aerator, there are two open gravity single-media filters filled with quartz sand coated by manganese oxides with the aim of removing critical substances like

iron, manganese and ammonium from raw water abstracted from Boring 2 (Søgaard & Madsen 2013, 233-235). Figure 5 shows aeration and filtration stages in the old waterworks.

Figure 5. Free-fall aerator and sand filters in old waterworks (Skovby waterworks 2016)

In the new waterworks, raw water is extracted from Boring 1 and 4. Boring 5 is planned to provide groundwater but it has not been put into operation yet. In the aeration step, raw water is introduced at one end of the bubble basin and flowed into filters at the other end, while air bubbles containing oxygen rises from the bottom of the basin produced by an air compressor. Cross-current flow between air and water is created by this setting, providing efficiency for aeration/stripping process. The aerated water contains 10.2 mg/l of dissolved oxygen before entering the filters, equivalent to 91% saturation. (Maribo 2017.) Two open gravity sand filters situated next to the basin receive aerated water for removal of substances above the limit from Boring 1 and 4. The filters are single-media filled with manganese oxides coated quartz sand (Søgaard & Madsen 2013, 233-235). Aeration and filtration stage in new waterworks are illustrated in Figure 6.

Figure 6. Aeration basin and sand filters in new waterwoks (Skovby waterworks 2016)

Dimension of the sand filters in the old waterworks were measured from the field inspection in 2016 due to lack of technical drawing. While Krüger A/S 's drawing (1977) provides information about the width, length and height of the filters in the new waterworks, detailed measurements can be found in Appendix 2. Different values in size of two filters in both old and new waterworks are presented in Table 4. The following table also indicates other hydraulic properties of filters, taking maximum water flow into consideration so as to represent extreme occasions when waterworks must treat the biggest amount of water while still complying with drinking water requirements.

Table 4. Dimensioning of filters in and relevant hydraulic properties in old and new waterworks (Krüger A/S 1977, Maribo 2016, Skovby waterworks 2016)

	Old waterworks	New waterworks
Width per filter (m)	1.5	2.03
Length per filter (m)	3	4
Effective height (m)	1.5	1.3
Area (m^2)	4.5	8.12
Filtration flow (m^3/h)	26.8	49
Filtration flow/filter (m^3/h)	13.4	24.5 for Boring 1
		19.5 for Boring 4
Filtration rate (m/h)	2.98	3.02 & 2.4
Empty bed contact time (h)	0.5	0.43 & 0.54

The concentrations of some substances that exceed Danish drinking water criteria (Table 1) gathered from an analysis of treated water quality are illustrated in Table 5:

Table 5. The quality of treated water in 18 May,2016 (Geologic survey of Denmark and Greenland 2017; Ramsay)

Parameter	Concentration in treated water	Danish drinking water criteria
Iron (mg/l)	0.004	0.1
Manganese (mg/l)	<0.001	0.02
Ammonium (mg/l)	<0.02	0.05
Agress.CO_2 (mg/l)	2.5	2

Overall, the two waterworks in Skovby operate well as the levels of critical substances like iron, manganese and ammonium are reduced considerably to meet the potable water requirements. However, there is only one problem with aggressive CO_2 since its content is 0.5 mg/l higher than acceptable level, indicating that better aeration would be needed to remove aggressive CO_2 to avoid any corrosion impacts on pipeline and other metallic materials in water supply system.

3 BACKGROUND

3.1 Arsenic and its characteristics

Arsenic is renowned for both positive and negative effects for a long time. The broad applicability of arsenic can be seen in many areas, including electronics, agriculture, pharmaceuticals, metallurgy or timber conservation (Nicomel et al. 2016, 1). Especially, ulcers, tuberculosis, and other illness has been cured with application of arsenic (Choong et al. 2007, 140). On the other hand, exposure to high dose of arsenic are extremely detrimental to human health. In fact, arsenic-contaminated water has caused significant number of mortality around the world; tens of thousands of peoples in Bangladesh and India exposed to high level of arsenic in drinking water. The World Health Organization named arsenic problem as "the worst mass poisoning in history". (Ramsay 2005, 10)
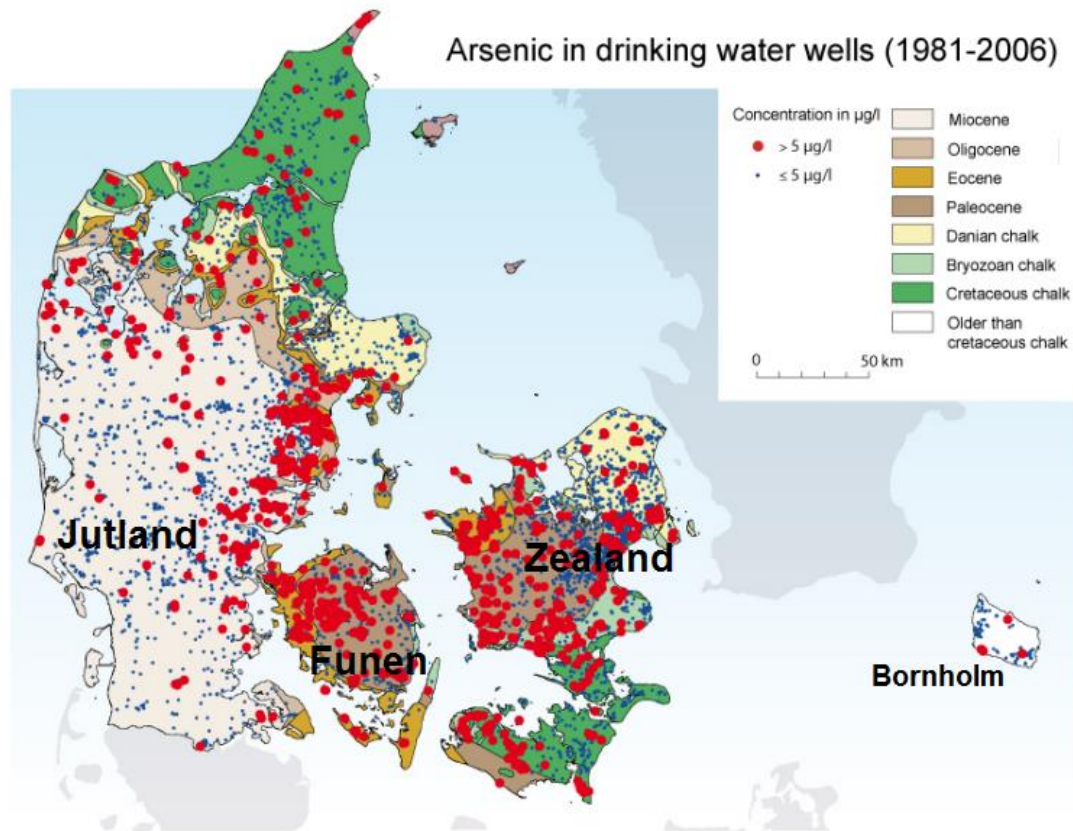
Figure 7. Arsenic concentration in borings throughout Denmark from 1981 to 2006 (Søgaard & Madsen 2013, 239)

In Danish context (Figure 7), one can notice that borings with high level of arsenic are mostly found in eastern Jutland, Funen island and around Zealand area (Ramsay 2005; Søgaard & Madsen 2013, 239). Skovby area is highly vulnerable to arsenic contamination (refer to Figure 1 for location). Of 4833 water samples taken for measuring water quality, a vast majority of samples had less than 5 µg/l of arsenic (83%), the figure for the samples whose arsenic content between 5 and 10 µg/l was 10%. Only 7% of the samples contained arsenic more than 10 µg/l (Danish Ministry of the Environment 2014, 9). It seems that groundwater from Boring 5 is one of minority of raw water sources that has high level of arsenic.

3.1.1 Arsenic sources and speciation

Arsenic is relatively abundant in the environment, staying 20th position in the list of the most prevalent chemical element in the Earth's crust (Kartinen et al. 1995,

79; Singh et al. 2015, 248; Nicomel et al. 2016, 1). Arsenic is introduced into water environment both by natural process and human activities.

The major natural sources of arsenic are dissolution and leaching of minerals containing arsenic into groundwater aquifers. In nature, arsenic is primarily present in ore minerals, created deeply underground in high temperature and regularly found in mineralized areas. Among those, arsenopyrite FeAsS accounts for major proportion of arsenic-enriched ores, following by realgar AsS or orpiment As_2S_3. Rock-forming minerals are also supposedly sources of arsenic, of which pyrite minerals have greatest amount of arsenic. Additionally, weathering of rocks or sediments results in release of arsenic although average concentration of arsenic found in wide ranges of rocks and sediments are low. Arsenic also exists in the atmosphere with insignificant amount, remained in aqueous environment by wet and dry deposition. (Smedley & Kinniburgh 2001.)

On the other hand, Thirunavukkarasu (2003) has claimed that anthropogenic activities are the main culprit of arsenic occurrence, since twice amount of arsenic released into the environment is caused by human. A number of typical human practices elevating arsenic level could be listed: mining (smelting ore and water percolation), agriculture (use of herbicides, insecticides and fertilizers) and some industrial activities (wood conservation, metallurgy or pigment and dye) (Halem et al. 2009, 30; Jiang et al. 2012, 18; Singh et al. 2015; 248)

In the periodic table, arsenic appears in period 4 and group VA, leaving five free electrons in the outer cell. Thus, this atom formation allows arsenic to be present in different compounds with various oxidation numbers. According to Jiang et al. (2013), Nicomel et al. (2016) and other researchers, existence of arsenic correspond to four oxidation states of this element, namely arsenate As^{+5}, arsenite As^{+3}, arsenic As^0 and arsine As^{-3}. In aqueous environments, arsenic can be detected in both organic and inorganic forms, though the concentration of the former is negligible and its effect are less harmful than the latter's and not a problem in drinking water treatment (Jain & Ali 2000, 4305). The level of pH and

oxidation/reduction potential are two main factors governing the existence of inorganic arsenic in solution.
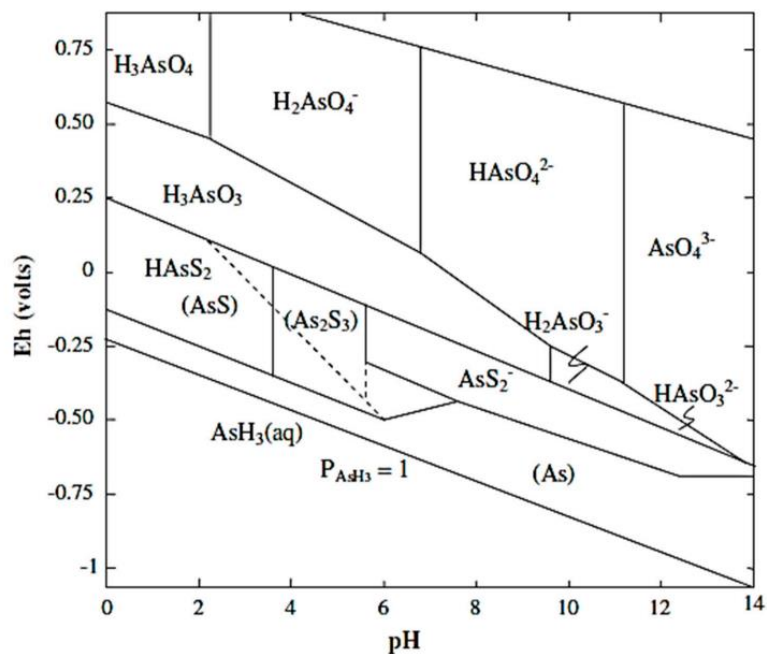

Figure 8. Arsenic element in various compounds, found in water. pH is acid/base potential. Eh is oxidation/reduction potential (Nicomel et al. 2016, 2)

Various forms of inorganic arsenic in water rely on a function of pH and redox potential (Figure 8). It is likely that inorganic arsenite and arsenate are more prominent than other forms of arsenic in water. (Jiang et al. 2013, 10.) The prevalence of arsenite As^{+3} species (H_3AsO_3, $H_2AsO_3^-$, and $HAsO_3^{2-}$) are recorded in anoxic reducing conditions like groundwater aquifer; the majority of these species exist in an uncharged form H_3AsO_3 at pH<9.2. Whereas arsenate As^{+5} species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) are stable in aerobic oxidizing environment in which the potential of oxidation is higher than that of arsenite species. Extremely acidic and alkaline environment shows prominence of H_3AsO_4 and AsO_4^{3-} respectively; while $H_2AsO_4^-$ is dominant at low to middle pH range (2 to 6.9) and $HAsO_4^{2-}$ at middle to high pH range (6.9-11.8). (Choong et al. 2007, 140; Jiang et al. 2013, 21; Nicomel et al. 2016, 1.) Reduced sulphur appearing in water with substantially high level could result in formation of dissolved arsenic-sulphide compounds. For instance, orpiment (As_2S_3), realgar (AsS) and other arsenic-sulphide species are found in reducing environments with low pH. (Smedley & Kinniburgh 2001.)

According to groundwater analysis of Boring 5 (Appendix 1), water is abstracted from strongly reduced environment with pH equal to 7.84. In addition, the level of reduced sulphur is remarkably low with less than 0.05 mg/l of hydrogen sulphide. Therefore, from Figure 9 and 10 as well as favoring conditions of arsenic state mentioned above, it can be speculated that arsenite is dominant in Boring 5 groundwater in the form of uncharged H_3AsO_3, while the percentages of AsO_3^- and arsenate species are markedly minor.
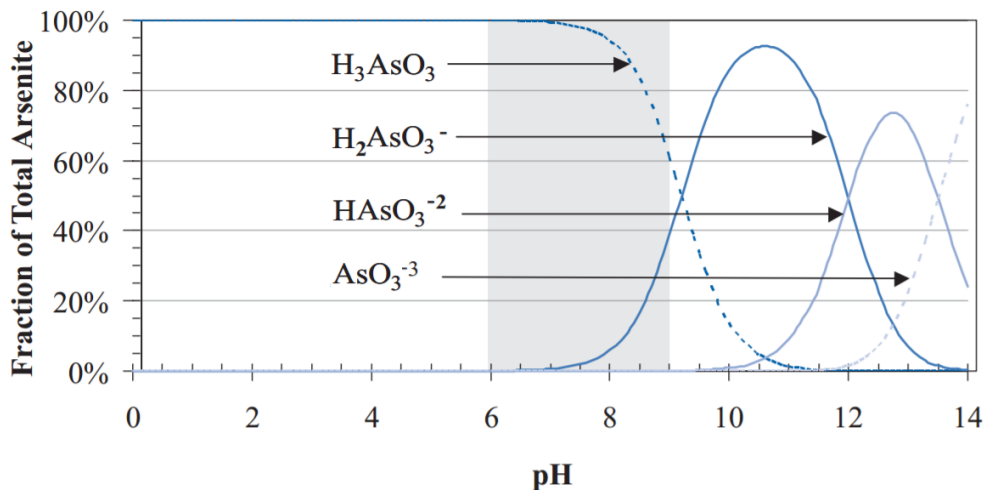

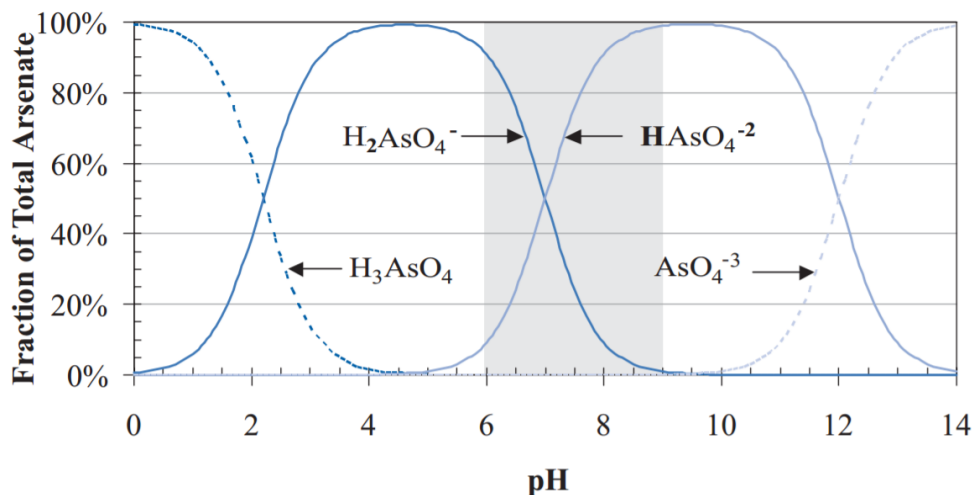Figure 9. Speciation of arsenite As^{+3} (United States Environmental Protection Agency 2003, 9)

Figure 10. Speciation of arsenite As^{+5} (United States Environmental Protection Agency 2003, 9)

3.1.2 Health impacts of arsenic and drinking water limit

The intake of arsenic in drinking water exerts negative influences on human health, corresponding to periods of exposure: acute and chronic. After a short

period of time drinking arsenic-polluted water, one is likely to suffer vomiting, stomachache and diarrhea. In some incidents, numbness, muscle cramping or even death have been documented if being poisoned to high level of arsenic.

Chronic health effects of arsenic are diverse. Apparent problems caused by long-term exposure to arsenic are related to skin, including skin lesions, hyper-pigmentation, hyperkeratosis. Moreover, arsenic is categorized as human carcinogen (group 1) where many chronic arsenic poisoning victims are diagnosed with cancers of liver, kidney, prostate and lung. Cardiovascular diseases, high blood pressure, bone marrow depression or diabetes are also supposed as one of consequences of arsenic poisoning. Birth defects, respiratory infections or retarded developments are found in utero exposure to arsenic or conceiving women who consume water polluted with arsenic (Halem et al. 2009, 30; WHO 2010; Abdul et al. 2015, 828-834).

Due to harmful health risks and a number of accidents in relation to consumption of arsenic-contaminated water, permissible level of arsenic that had been set at 50 µg/l was decreased down to 10 µg/l in 1993 by World Health Organization (Choong et al. 2007, 141). European Union restrained arsenic content to the same value five years later (1998). In 2001, Danish government implemented EU Drinking Water Directive in their legislation (Danish Ministry of the Environment 2014, 33) and not until 2003, new Danish requirement for potable water took effect, in which arsenic in drinking water was limited to 5 µg/l at waterworks and 10 µg/l at consumer taps. The difference in these arsenic levels could be attributed to the leakage of arsenic into clean water along pipeline systems (Ramsay 2005, 10)

3.2   Arsenic treatment theory

It is extremely vital for waterworks to treat arsenic containing water, minimizing any human health risks arisen from exposure to this contaminant. Several existing technologies have shown high effectiveness of arsenic treatment. Coagulation and flocculation are one of the most widely used treatment method, in which coagulants with positive charge or anionic flocculants are added into raw

water. As a result, larger particles containing arsenic is formed, precipitated and filtered out during the treatment. Arsenic is also effectively removed by attachment to solid sorbents, such as activated carbon, activated alumina or iron-based medium, through adsorption method. Another reliable treatment technique is ion exchange, in which arsenic ions are substituted by chloride or hydroxide ions due to strong exchange affinity when water passes through columns filled with exchange resin. In addition, various types of membrane (micro-filtration, ultra-filtration, nano-filtration or reverse osmosis) in operation with high pressure of water flow also provides high arsenic removal efficiency thanks to selective barrier of billions of membrane pores. In some other treatment methods, the removal of arsenic could be carried out by co-precipitation with settable particles, for example calcium carbonate in enhanced lime softening method or iron hydroxides in oxidation/filtration method (United States Environmental Protection Agency 2003; 23-36; Choong et al. 2007, 142-156; Singh et al. 2015, 252-263; Nicomel et al. 2016, 3-13)

Selecting the most appropriate arsenic removal technique with high applicability to the Skovby waterworks requires intensive considerations with regards to cost, efficiency, construction, operation and maintenance. However, the compatibility with existing waterworks settings might be utmost pivotal. A simple guideline on arsenic treatment technology is recommended, taking advantage of adsorption ability of iron to bind arsenic during water treatment. The ratio of arsenic and iron concentrations in water content would specify a proper and reasonable treatment technique within waterworks background, in which Fe:As ratio of 20:1 is considered as determinant number (Sorg 2002).
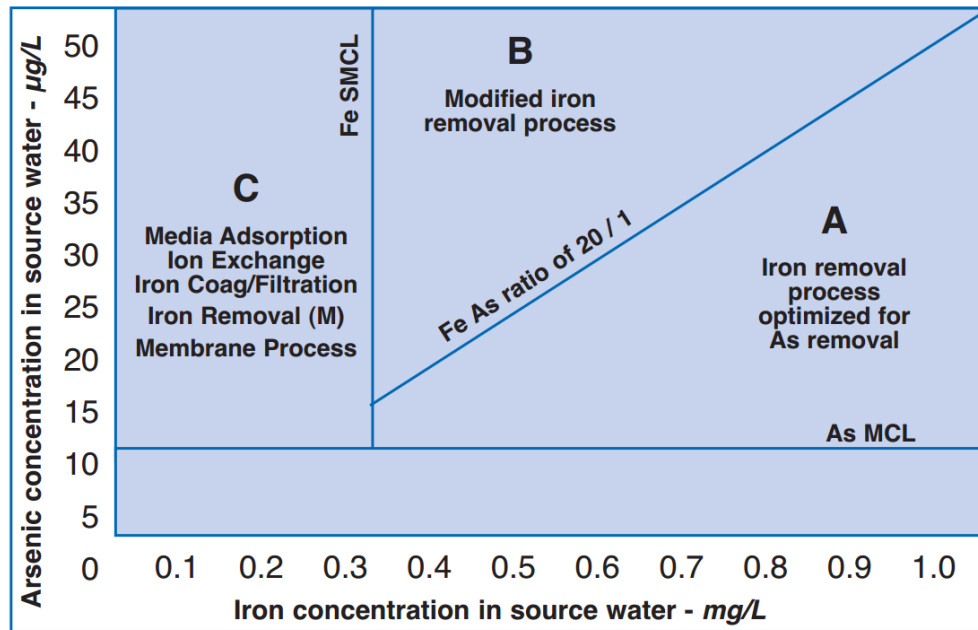
Figure 11. Arsenic treatment selection guideline based on initial levels of arsenic and iron in water. MCL: maximum contaminant level. SMCL: secondary maximum contaminant level (Sorg 2002)

Groundwater analysis of Boring 5 provides the concentrations of arsenic and iron in raw water, 18 µg/l and 0.84 mg/l (840 µg/l) respectively. One can guess the concentration ratio between iron and arsenic is greater than 20, suggesting that iron removal process would be possible for Skovby waterworks to treat arsenic-contaminated raw water abstracted from new boring.

Iron removal process is also known as oxidation/filtration method, in which iron as well as manganese are removed via two stages to avoid aesthetic problems (taste, odor and color) in clean water consumption. Reduced forms of iron and manganese with high solubility are firstly oxidized to their insoluble forms of $Fe(OH)_3$ and MnO_2, which will be eliminated by filtration in the subsequent step. If there is a presence of arsenic in raw water, it could be removed during the oxidation/filtration treatment process thanks to high binding capability of arsenic to iron (United States Environmental Protection Agency 2003, 35; Ohio Environmental Protection Agency 2010, 15).

3.2.1 Oxidation of As(III) to As(V)

The extent of adsorption of As(III) and As(V) on iron particulates are varied owing to electrical charge of arsenic speciation. Due to neutral charge, arsenite is less likely to bind to other positively charged surface of particles during treatment, hindering the efficiency of arsenic removal process. By contrast, negatively charged arsenate is more preferable because of its tendency to be attracted by positive particles; thus, removing arsenic in raw water becomes easier if the bulk of arsenic in water is arsenate (Halem et al. 2009, 32; Nicomel et al. 2016, 3). In addition, As(III) are considered more noxious than As(V) (Kim & Nriagu 2000, 72). Therefore, oxidation of arsenite to arsenate by using catalyst or oxidizing agents plays an important role in eliminating this contaminant effectively and minimizing the toxicity of arsenic in water. And this is the case of raw water from Boring 5 when neutral arsenite H_3AsO_3 is substantially prevalent than any other forms of arsenic.

Oxygen is capable of oxidizing iron and manganese in treatment process, but shows poor conversion of arsenic to its highest oxidation state. In the experiment carried out by Kim & Nriagu (2000), oxidation of arsenite by injection of pure oxygen and atmospheric air into reaction chamber was so slow that more than half of As(III) was converted into As(V) after 5 days (57% and 54% respectively). Ramsay (2007) has found that "no measurable conversion" of As(III) in aerated water is recorded in the test after 2 weeks. Despite the inconsistence in conversion rate of arsenic, oxygen is not a powerful oxidant that could facilitate the arsenic oxidation.

Besides, chemically oxidation of arsenite to arsenate is also a common technique to enhance removal efficiency of arsenic. Chlorine, ozone and potassium permanganate are among strong chemical oxidants that are able to convert arsenite to arsenate with high oxidation rate under short amount of time (Clifford and Ghurye 2001; United States Environmental Protection Agency 2005). These powerful oxidizing agents take only less than one minute to convert arsenic to its oxidation state V with efficiency of above 95%. This conversion process is almost

not influenced by pH of water and other interfering substances (United States Environmental Protection Agency 2003, 18-22)

3.2.2 Coprecipitation of As(V) with iron

To maximize the treatment capacity of arsenic-contaminated water, arsenic oxidation should be followed by adsorption/coprecipitation with iron particles as a second process (Driehaus et al. 1995, 305). After oxidation stage, arsenic, mainly As(V) and some remaining As(III), attaches to iron hydroxide solids during filtration process. Iron particles then settle down along with arsenic sorbed on surfaces when the water is filtrated through filters. Filter medium captures suspended precipitate products containing iron and arsenic, which is later removed during backwash stage.

Although manganese hydroxides are able to remove arsenic utilizing the same mechanisms as iron counterparts, amount of arsenic removed with manganese is trivial with poor efficiency. The adsorptive capacity for arsenic of iron hydroxides $Fe(OH)_3$ is immense (Pierce & Moore 1982, 1252); therefore, iron has strong affinity for arsenic, accumulating on its surface (Hoffman et al. 2006, 3). The interpretation for this strong connection could be the difference in electrical charge between iron hydroxides and arsenic, in which iron particles are positively charged while oxidized arsenic products are opposite in charge.

In simple (standard) water treatment, iron present in water has the most important and crucial role to play in arsenic removal (Ramsay 2005,11). The initial level of iron in water content is strongly associated with arsenic removal efficiency (Fields et al. 2000, 4). Higher concentration of iron will likely result in better removal of arsenic from water. The percentage of arsenic removed in relation with iron content is estimated from formula below:

$$Arsenic\ removal = \frac{K * [Fe]}{1 + K * [Fe]} * 100\% \qquad (1)$$

where   K   constant

                                     [Fe]   concentration of iron   [mg/l)]

The value of K is set to 1.45 in America (McNeil & Edwards 1997), while the figure for K in Denmark is 1.1. The reason for the difference in K value is that arsenic is present dominantly in As(III) form in Danish groundwater while most of arsenic in the United States in groundwater sources are As(V). Since As(III) is harder to remove that As(V), lower K is applied in Danish groundwater treatment context (Ramsay 2007). The relationship between the amount of iron in raw water and arsenic removal is described in the following graph (Figure 12):
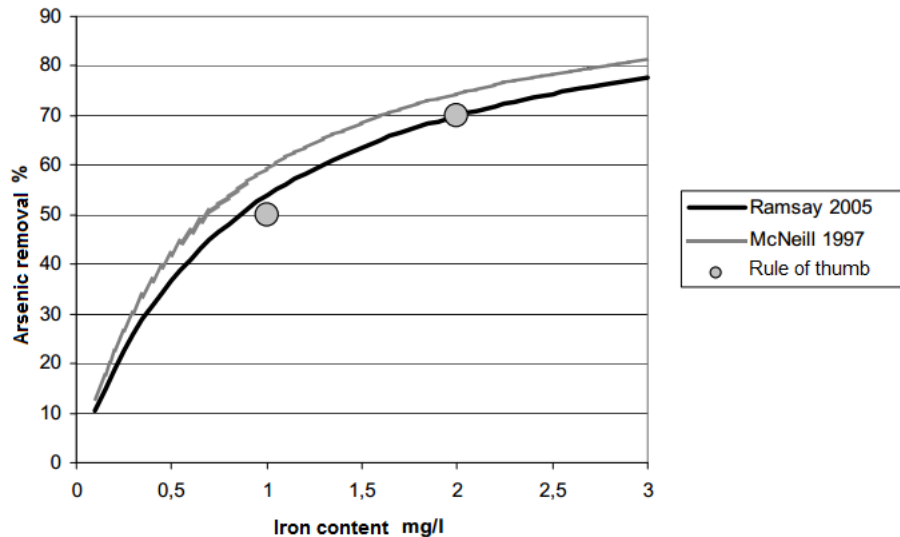

Figure 12. Arsenic removal indicated by level of iron in raw water (Ramsay 2007)

Figure 12 suggests the proportion of arsenic removed by adsorption/ coprecipitation with iron present in raw water though traditional filter. Two rule of thumb values are marked in the graph at two iron levels, 1 mg/l and 2mg/l, at which 50% and 70% of arsenic is removed respectively (Ramsay 2007).

Since co-removal of arsenic with iron involves adsorption in the process, it is necessary to study other competing substances in water that battle with arsenate

on binding sties on iron particles as well as optimal environment for arsenic adsorption and coprecipitation. Iron hydroxides usually adsorb arsenate at pH below zero-point charge pH_{ZPC} which is 7.9-8.4 (Kim & Nriagu 2000, 75); while, the maximum arsenite and arsenate adsorbed on iron particles is found under neutral/alkaline and acidic environment respectively (Pierce & Moore 1982, 1253). Other competing anions, like phosphate, silicate, natural organic matter pose unfavorable effects on arsenic removal because of their affinities to iron hydroxides (Fields et al. 2000, 4; Meng et al. 2000, 1255; Ramsay 2005;13).

3.3   Roles of manganese oxide in arsenic removal

When encountering a water boring that contains high level of arsenic, either finding a new well or integrating certain techniques in treatment process to reduce arsenic concentration could be an option (Ramsay 2005; 10). Nevertheless, arsenic-contaminated wells are scattered widely in a broad geographical area of Denmark (Figure 7.), it seems unrealistic for water companies to search for new abstraction areas, restraining them to seek treatment initiatives to deal with arsenic content in water. Yet, any attempts to remove critical substances, including arsenic, using different treatment methods other than aeration and filtration requires permission from Danish authorities. Even though the rule was loosened and lenient in 2007, permitting Danish waterworks to implement advanced methods in water treatment process, simple treatment practice without chemical addition is still favored and encouraged (Søgaard & Madsen 2013, 236-237).
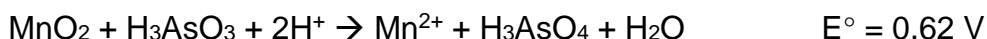
Regarding oxidation/filtration method for arsenic removal as discussed earlier, treating arsenic containing water without any usage of chemicals could be a breakthrough if successfully implemented. Since iron hydroxides formed by iron content in water adsorb arsenic on surfaces during filtration step, oxidation of arsenic might be possibly achieved by taking advantage of manganese oxides-coated sand available in the filters, which have long been researched for its capability of transforming As(III) to As(V).

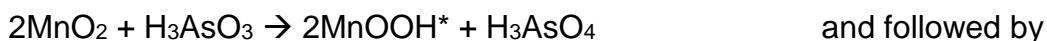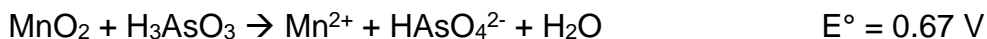### 3.3.1 Manganese oxides as an oxidant in arsenic oxidation

Oxidation of arsenite to arsenate by manganese oxides occurring in a time scale of minutes with high removal rate, have been confirmed many times by several researchers via different experiments both in laboratory and waterworks (Scott & Morgan 1995, 1898; Bajpai & Chaudhuri 1999, 782; Zhang et al. 2011, 656).

It is demonstrated that diffusion and adsorption/desorption are primary processes involved in oxidation of As(III) to As(V) (Driehaus et al. 1995, 301). These phenomena are experienced during three stages in reaction between manganese oxides and arsenic: movement of reductant to oxide surfaces, redox reaction on oxide surfaces and release of reaction products from oxide surfaces (Scott & Morgan 1995, 1899). In case of arsenic, arsenite is transported to manganese oxide surfaces in early stage. After that, arsenate is produced by oxidation of arsenite while MnO_2 is reduced to MnOOH* accumulated on oxide surfaces or further to Mn^{+2} during redox reaction. Lastly, these reaction products, As(V) and Mn^{+2}, are likely released into solution after reaction. The reactions between manganese oxides and arsenic illustrating how As(III) is oxidized to As(V) are described below, taking into account pH level of water. (Driehaus et al. 1995, 298; Kim & Nriagu 2000, 77-78; Manning et al. 2002, 976.)

- At low pH level:

$$MnO_2 + H_3AsO_3 + 2H^+ \rightarrow Mn^{2+} + H_3AsO_4 + H_2O \qquad E° = 0.62 \text{ V}$$

$$MnO_2 + H_3AsO_3 + H^+ \rightarrow Mn^{2+} + H_2AsO_4^- + H_2O \qquad E° = 0.56 \text{ V}$$

- At neutral pH level:

$$MnO_2 + H_3AsO_3 \rightarrow Mn^{2+} + HAsO_4^{2-} + H_2O \qquad E° = 0.67 \text{ V}$$

$$2MnO_2 + H_3AsO_3 \rightarrow 2MnOOH^* + H_3AsO_4 \qquad \text{and followed by}$$

$$H_3AsO_3 + 2MnOOH^* + 2H^+ \rightarrow HAsO_4^{2-} + 2Mn^{2+} + 3H2O \quad E° = 0.95 \text{ V}$$

* where MnOOH is an intermediate product having oxidation state of 3

It should be noted that these reactions are based on thermodynamic favorability, in which high redox potential E° indicates high likelihood of chemical reaction. Iron(III) hydroxides also shows potential to oxidize arsenic with slightly lower redox potentials E° in these redox reactions (0.28-0.4 V), but the oxidation reaction rate was very sluggish (Kim & Nriagu 2000, 77-78). In addition, Oscarson et al. (1981) drew a similar conclusion that Mn(IV) oxide was more effective oxidizing agent than Fe(III) oxide and conversion of As(III) to As(V) by the latter agent did not take place after 3 days due to slow kinetics of the redox reactions.

As one of reaction products resulted from chemical oxidation of As(III), Mn^{+2} is released into water. This will increase the concentration of manganese ions in raw water. Nevertheless, the rate of Mn^{+2} created as reaction product is not in accordance with stoichiometric ratio. The Mn^{+2} is released slower than As(V), which is in the form of $HAsO_4^{2-}$ in this reaction; and the amount of ion Mn^{+2} release is smaller than that of As(V). The low level of this substance could be explained by high adsorption capacity of manganese oxides, which attach released manganese ions. (Scott & Morgan 1995, 1900-1904.) Another possibility could be a formation of an arsenate-manganese ion complex $Mn_3(AsO_4)_2$ during the reaction. Because of low solubility of this complex in comparison with ion products (Mn^{+2} and AsO_4^{2-}), a decrease in amount of Mn^{+2} ion was recorded in the test (Oscarson et al. 1981, 50; Driehaus et al. 1995, 303). Or Mn(III) intermediate is a mainly reduction product of manganese oxides, blocking reactive sites on oxide surfaces for As(III) oxidation, limiting the release of Mn^{+2}. (Wu et al. 2015; 322.)

Another finding in addition to oxidation of arsenic by manganese oxides is adsorption of arsenic on oxide surfaces (Han et al. 2011, 370). It has been discovered that As(V) is adsorbed with an increasing amount by manganese oxide surfaces, forming an adsorption complex $(MnO)_2AsOOH$ between reactive hydroxyl group Mn-OH on MnO_2 surface and produced As(V), according to Manning et al. (2002). However, this adsorption occurrence was only reported by

a number of researchers while the others experienced manganese oxide adhered only small amount of As(V) during the reaction. (Driehaus et al. 1995, 298.) The conflict between experiment results could be attributed to the surface charge characteristics of arsenate and manganese oxides, which largely relies on pH level. Figure 13 presents the pH dependence of some critical substances appearing in arsenic treatment process, regarding their electrical surface charges.
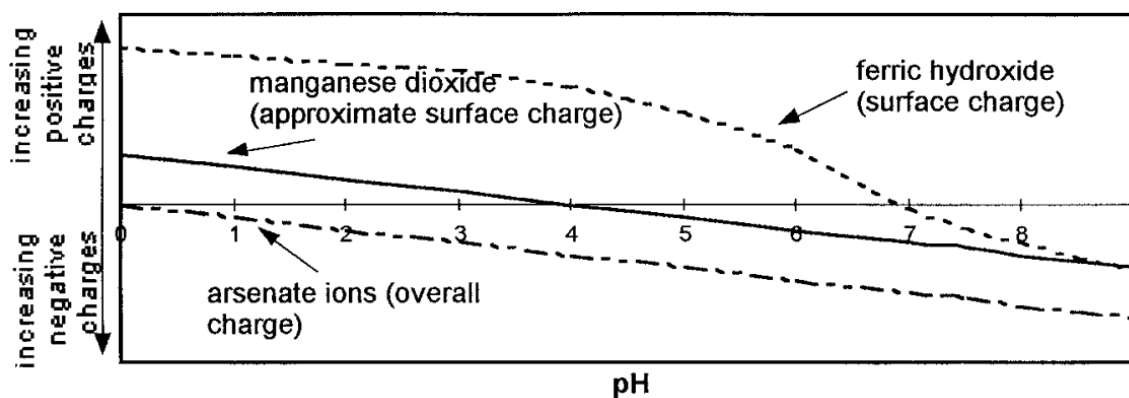

Figure 13. Electrical charges of As(V), MnO2 and Fe(OH)3 against pH (Hanson et al. 2000, 1160)

One can see that the surface charges of arsenate and manganese oxides fall as the level of pH increases, however, point of zero discharge (PZC) varies among these substances. It is expected that manganese oxides attach As(V) to surfaces when pH level of solution is below the pH_{PZC}; in contrast pH level higher than the pH_{PZC} deters manganese oxides from adsorbing As(V). (Scott & Morgan 1995, 1900.) Thus, binding force between manganese oxides and As(V) is necessarily stronger than repulsion force generated by level of pH above pH_{PZC}. Moreover, arsenate in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$ prevail in the solution as chemical products as well as in the neutral pH environment. These arsenate species are also negatively charged, unlikely being adsorbed by manganese oxide (Oscarson et al. 1981, 50; Zhang et al. 2011, 657.). It seems that those researchers who found adsorption of As(V) on manganese oxide surfaces carried out experiments under acidic conditions while low attraction of manganese oxide to As(V) is expected in tests with neutral or alkaline pH environment.

During arsenic oxidation stage, it is analyzed that there are no significant effects on reaction rate regarding level of pH. The greatest rate is measured under condition of acidity (pH 4 as in experiments), but differences in the rate are not appreciable when rising pH level. The increasing arsenic oxidation rate is apparently proportional to rising level of temperature. Ions like calcium Ca^{2+}, manganese Mn^{+2}, might slightly diminish the oxidation rate; whereas phosphate PO_4^{3-}, which shares acid-base properties and affinity characteristic in common with arsenate As(V), has no effects on oxidation rate. Especially, iron Fe^{2+} exhibits a great negative influence on As(III) oxidation, for instance, competitive oxidation and formation of iron particles around manganese oxide surfaces. (Han et al. 2011, 369-372; Wu et al. 2015, 327.) The effect of dissolved oxygen in water is of minimal significance on rate of reaction. The initial concentrations of As(III) and manganese oxides (or initial molar ratio) should also be borne in mind since the rate is dependent on the content of manganese oxide and As(III) (Driehaus et al. 1995, 300-303; Scott & Morgan 1995, 1901-1903; Zhang et al. 2011, 657).

3.3.2 Manganese oxides as a catalyst in arsenic oxidation

Investigations on the oxidation of As(III) to As(V) by manganese oxides through surface mechanism mentioned above is challenged by another research that points out the lacking discussion of existence of interfering substances in raw water during arsenic oxidation process in the studies, such as manganese, iron, hydrogen sulfide or Total Organic Carbon. In the presence of these elements, it is found that dissolved oxygen is primarily an oxidizing agent that reacts with As(III). This discover, in fact, contradicts with the argument stated by Scott & Morgan (1995), in which the oxidation rate is not influenced by dissolved oxygen in water. If, however, there is an abundance of dissolved oxygen and presence of interfering substances in water, solid-oxidizing media, which is manganese oxides in this case, will catalyze arsenic oxidation process and achieve complete oxidation after few minutes. Otherwise, there is a strong probability that arsenic is oxidized by direct reaction with manganese oxides in the absence of interfering reductants (Ghurye & Clifford 2001, 1-2; Ghurye & Clifford 2004, 84).

In addition to the oxidation of arsenite to arsenate that requires available dissolved oxygen in water, a number of chemicals also compete with arsenic to take up oxidizing matter during oxidation process with manganese oxides as catalyst. Ferrous iron and manganese ions react with dissolved oxygen to reach their highest oxidation states, from II to III and from II to IV respectively; while oxygen converts hydrogen sulfide gas to insoluble sulfur. Those products expectedly precipitate in filter media and being removed during backwash. Reactions involved in this process are given below along with oxygen demand for oxidation calculated based on stoichiometric ratio (United States Environmental Protection Agency 2003, 23):

$$2H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4- + 2H^+ \qquad\qquad 0.21 \text{ mg } O_2/\text{mg As(III)}$$

$$4Fe^{2+} + 3O_2 + 6H_2O + 2e^- \rightarrow 4Fe(OH)_3 \qquad\qquad 0.43 \text{ mg } O_2/\text{mg Fe}^{2+}$$

$$Mn^{2+} + O_2 + 2e^- \rightarrow MnO_2 \qquad\qquad 0.58 \text{ mg } O_2/\text{mg Mn}^{2+}$$

$$2HS^- + O_2 + 2H^+ \rightarrow 2S^0 + 2H_2O \qquad\qquad 0.48 \text{ mg } O_2/\text{mg HS}^-$$
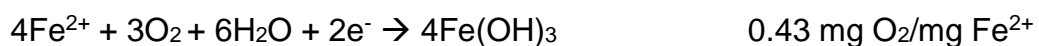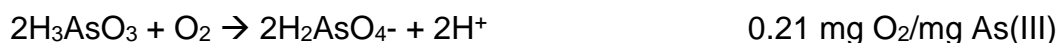
It is essential to have adequate dissolved oxygen in water, providing oxidizing capacity for arsenic oxidation process as well as extra oxygen source for other interfering reductants. According to stoichiometric oxidant demands, it is estimated that at least 1.7 mg/l dissolved oxygen should be achieved during aeration process before water is fed to filters where the majority of oxidation reactions take place.

A long series of experiments were conducted by Ghurye and Clifford (2001) to examine the effects of Empty Bed Contact Time, pH, dissolved oxygen, manganese ions Mn^{+2}, irons ion Fe^{2+}, sulfide HS^-, Total Organic Carbon and initial concentration of As(III) on oxidation rate of As(III) since these influencers could cause impacts on the oxidation process.

Those studied interfering reductants are found to have severe effects on conversion of As(III) to As(V); of which sulfide poses greatest impacts on As(III) oxidation, especially under the condition of low dissolved oxygen (as 0.1 mg/l in experiment). Though, this effect would be lessened by rising Empty Bed Contact Time, maintaining high efficiency of arsenic oxidation. When the level of oxygen saturated in water is high (as 8.2 mg/l in experiment), oxidant demands of both arsenic and interfering reductants are satisfied, gaining near-complete arsenic oxidation with short amount of time. By contrast, none of dissolved oxygen in water is utilized in arsenic oxidation process in the absence of interfering reductants. Under the range of pH level in the experiments (6.3-8.3), there is no tremendous effects on oxidation process which is nearly maximum efficiency. Similarity is also applied to temperature, although lowering pH level and rising temperature both raise oxidation efficiency few percent (Ghurye & Clifford 2001, 36-41; Ghurye & Clifford 2004, 93-95; Lowry et al. 2005, 79-80).

3.3.3 Arsenic oxidation rate

In those experiments with manganese oxide-based oxidizing media, in which manganese oxides acts as either an oxidant or a catalyst, amount/efficiency of arsenic removal were plotted in a graph as function of time, suggesting that oxidation rate of arsenite to arsenate follows first-order kinetic (Ramsay 2007, Han et al. 2011, 370; Zhang et al. 2011, 656).

$$\frac{d[As(III)]}{dt} = -k * [As(III)] \tag{2}$$

Solving the differential Equation (2) about provides an exponential function:

$$[As(III)]_t = [As(III)]_0 * e^{-k*t} \tag{3}$$

where | [As(III)] | concentration of As(III) | [µg/l]
| k | conversion rate | [min^{-1}]
| t | time | [min]

It is carefully reminded by Ramsay (2007) that k value is approximate since As(III) removal rate was influenced by both oxidation and sorption process.

The half-life of As(III) could be possibly found from Equation (3) using algorithm calculation:

$$T_{1/2} = \frac{ln2}{k} \qquad (4)$$

Ramsay (2007) has reported that k value varies among waterworks because of difference in groundwater composition. From one waterworks mentioned as an example in his study it was found that k value was 0.21 while some values gathered from other references was in range of 0.12-0.27. This means manganese oxide media requires only about 3-6 minutes to oxidize half amount of arsenite to arsenate. This assumption about arsenic oxidation with first-order rate is used throughout this thesis due to its simplicity, though there are some intricate methods as mentioned below.

Some researchers point out that oxidation process is a two-stage kinetic process, including initial very fast kinetic in the beginning followed by first-order rate with slower decrease of As(III). (Zhang et al. 2011, 657; Wu et al. 2015, 322) It is presumed by Oscarson et al. (1983) that As(III) tends to bind to oxide surfaces quickly in the first stage; while manganese oxide surfaces slowly continue to sorb As(III) in the second stage as new adsorbing surface sites are formed because of oxidation of adsorbed As(III). While Scott & Morgan (1995) has suggested that fast oxidation is caused by immediate reaction between manganese oxides and As(III), followed by coverage of produced Mn^{+2} on manganese oxide surface, discouraging adsorption and oxidation of remaining As(III) (Scott & Morgan 1995, 1904.) However, it is only an observation and presumption from experiments and no formula has been established to indicate the fast oxidation in the beginning.

On the other hand, Driehaus et al. (1995) have taken reaction sites on the surface of manganese oxides into consideration, in which formation of reaction products could restrain the oxidation ability of manganese oxides. Therefore, the

oxidation kinetics of As(III) is advised to follow a second-order rate that is representative of sharp decline of As(III) and slower oxidation rate following. In addition, molar ratio of MnO_2 and As(III) is also integrated in the formula, which complicates the situation.

4   MATERIALS AND METHODS

Different designs and processes of water treatment were examined to compare removal efficiency of critical substances, such as iron, manganese, ammonium and especially arsenic, when abstracting raw water from Boring 5 and treating it by current aeration (bubble basin) and filtration system (single manganese oxide-coated sand media). Those processes were analyzed in this thesis, consisting of (i) individual treatment of raw water from Boring 5, (ii) co-treatment with raw water either from Boring 1 or Boring 4, and (iii) individual treatment of raw water from Boring 5 in the first filter followed by addition of aerated water from Boring 1 or 4 and co-treatment in the second filter. The schemes of these studied processes are presented in the following figures:
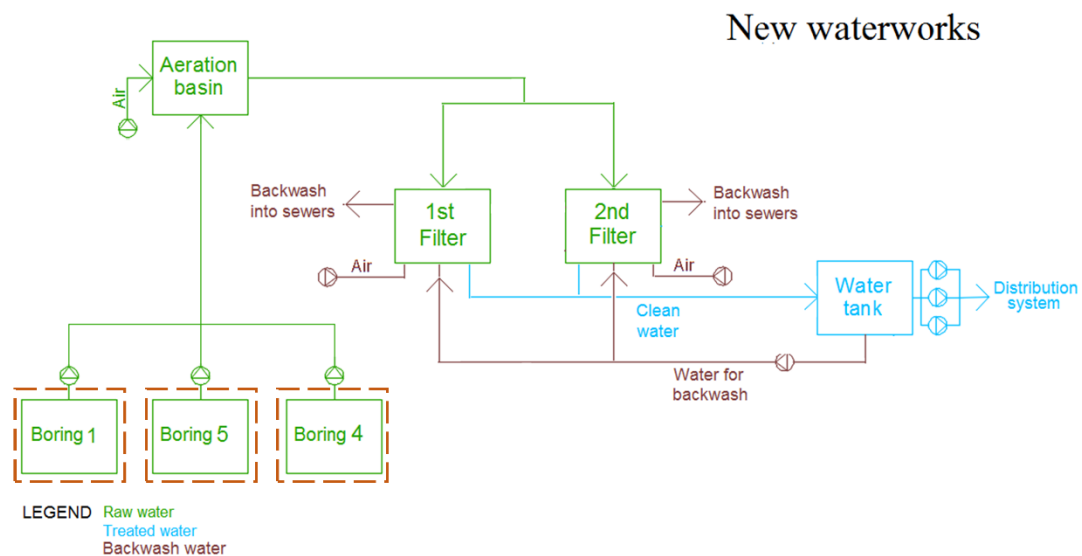
Figure 14. Individual Boring 5 raw water treatment with no changes to existing system (Design 1: arsenic co-removal with iron with original concentration)

In the process as described in Figure 14, Skovby new waterworks was assumed to function normally as it operates at present. Raw water pumps from Boring 1, 4

and 5 are triggered if the water level is low, working on alternating basis as indicated by three separate dotted rectangles. Arsenic was supposedly oxidized and removed with iron in the same raw water originated from Boring 5.
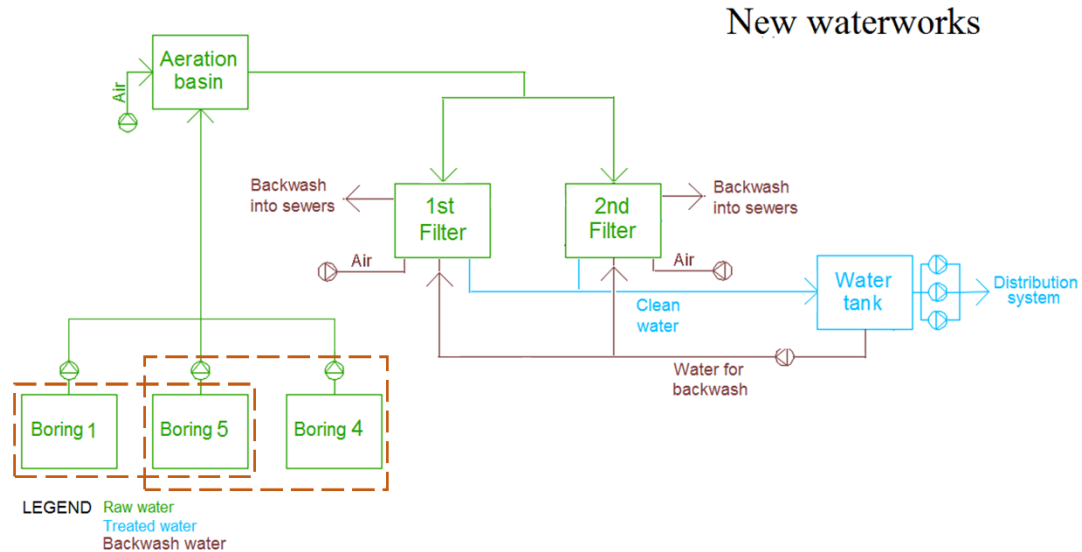
Figure 15. Co-treatment Boring 5 with Boring 1 or 4 raw water with no changes to existing system (Design 2: arsenic co-removal with iron with diluted concentration)

Figure 15 indicates that there is a minor change in the Skovby waterworks function. Raw water pumps were assumed to work in pairs instead of operating individually. The Boring 5 water pump was set up to run with one of the other water pumps as displayed by red dotted rectangles in Figure 15. In this way, the level of arsenic in Boring 5 is diluted as the arsenic contents in Boring 1 and 4 are relatively low. Arsenic underwent oxidation followed by filtration process where being co-removed with mixed iron.
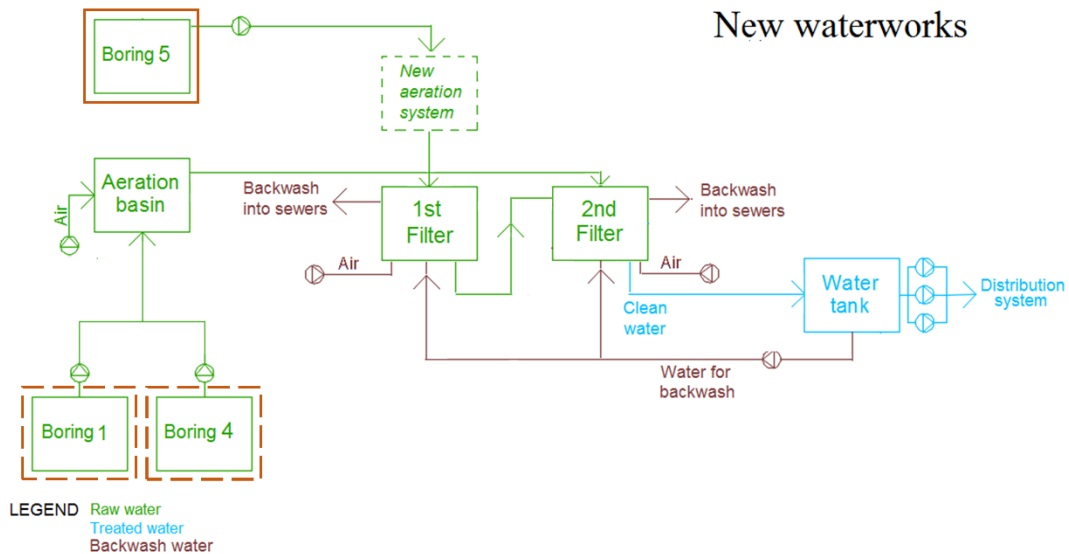
Figure 16. Individual Boring 5 raw water treatment in the first filter and continuous treatment with addition of Boring 1 or 4 aerated water in the second filter (Design 3: two-step arsenic co-removal with iron)

The process as can be seen in Figure 16 includes a number of changes. Two single filters were modified to a double filter. Raw water pump from Boring 5 were started simultaneously either with Boring 1 or Boring 4 water pump (as shown by full red rectangle for Boring 5 and dotted rectangles for Boring 1 or 4). Boring 5 raw water was then aerated in a new aeration system (as indicated by dotted green rectangle) and was introduced in the first filter where part of arsenic was removed with iron content in water from Boring 5. The first filtered water went through the second filter in the subsequent step where aerated water from Boring 1 or 4 was added.

The oxidation process of arsenic was studied in general with variation in k values to study the influence of oxidation rate on the arsenic conversion. In addition, the smallest k value was selected in the reference range to be applied for each type of the water treatment designs, as it represents the slowest oxidation process though the oxidation time might be less than that (0.12 was assigned to k value) The necessary times for complete arsenic oxidation was calculated based on Equation (3). Given oxidation time, required filtration depth for successful conversion of arsenic were estimated by Equation (5) (99% oxidation of As(III)), which was then compared against the effective height of filters to ensure that the

manganese oxide coated sand filter in new waterworks is able to convert arsenite to arsenate.

$$d = \frac{t * Q}{A} \leq h \qquad (5)$$

where

d	required filtration depth	[m]
Q	flow	[m³/h]
t	time	[min]
A	area of filter	[m²]
h	effective height of filter	[m]

The effects of interfering substances on arsenic conversion process were also discussed to gain better understanding in which ways arsenic is oxidized, either by catalysis or direct reaction with manganese oxides. Moreover, the adsorptive capacity of iron hydroxides for arsenic during adsorption/precipitation process were evaluated by taking the impacts of other competing anions for sorption sites into consideration.

As extraction rate from Boring 5 had not been defined, the maximum value for each design was estimated by increasing the flow with incremental steps in order to find the biggest amount of raw water that could be treated by the water treatment system before the concentrations of critical substances passing the limit levels. In case of raw water from Boring 5 is mixed with raw water from either Boring 1 or 4, the new concentrations of substances were calculated from Equation (6):

$$[X] = \frac{Q_{B5} * [X]_{B5} + Q_{B1/4} * [X]_{B1/4}}{Q_{B5} + Q_{B1/4}} \qquad (6)$$

where

[X]	mixed concentration of X	[mg/l or µg/l]
Q_{B5}	flow of Boring 5	[m³/h]
$Q_{B1/4}$	flow of Boring 1 or 4	[m³/h]

[X]$_{B5}$ concentration of X in Boring 5   [mg/l or µg/l]

[X]$_{B1/4}$ concentration of X in Boring 1 or 4   [mg/l or µg/l]

Regarding adsorption/coprecipitation process of arsenic by iron for different studied designs, it was assumed that arsenic was solely adsorbed on iron hydroxide. The proportion of arsenic removed out of water were estimated based on Equation (1). Consequently, the final concentration of arsenic in treated water was predicted by following equation:

$$[As]_f = (100 - \% \; As \; removal) * [As] \tag{6}$$

where   [As]$_f$ concentration of As after treatment   [µg/l]

                      [As]   concentration of As before treatment   [µg/l]

5   RESULTS AND DISCUSSION

5.1   Arsenic oxidation

The reduction in arsenic concentrations with varying oxidation rates are shown in Figure 17, in which k1 = 0.12; k2 = 0.15; k3 = 0.2; k4 = 0.27:
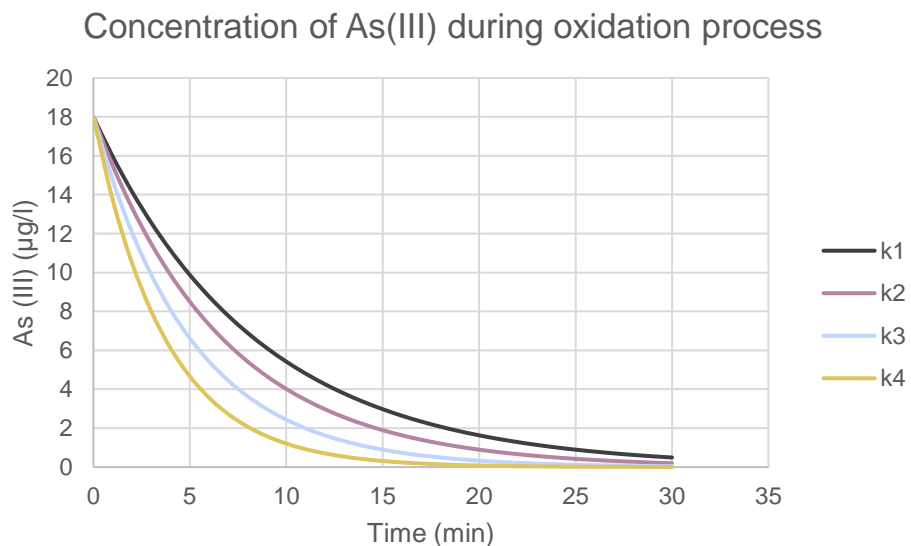
Figure 17. Concentration of As(III) against time with varying k values

It is clear that the concentrations of As(III) decreased significantly in the first 10 minutes before continuing to reduce at slower pace until nearly all As(III) is converted to As(V). Affluence of oxidizing agents like manganese oxides or dissolved oxygen could be attributed to this dramatic change in arsenic oxidation process. In the beginning, As(III) easily reacts with oxidants when water is led into filters. Alterations on manganese oxide surfaces either in case of catalyst or primary oxidant impeded the conversion of arsenic, which can be seen as slow As(III) oxidation in the latter phase.

It should be noted that the reduction curves of As(III) concentration might vary depending on the type of manganese oxides as well as preparation method, which is not considered in this study. Manganese oxides in previous studies were usually synthetic, which were made in the laboratory by using $KMnO_4$ or $Mn(NO_3)_2$ (Driehaus et al. 1995, 298; Scott & Morgan 1995, 1989, Wu et al. 2015, 320). While in this case study, manganese oxides formed around sand materials are made of oxidation of manganese ions in water. Furthermore, the initial concentrations of As(III) in laboratories studies were substantially higher than the level of arsenic in this case study with the factor of 100.

It is also suggested that bigger k value yields better conversion of arsenite to arsenate (Figure 17). The effects of interfering substances in water could be one of indicator of the differences in oxidation rate k. In fact, those substances compete with arsenic on reaction with the oxidants, which probably decreases the rate of arsenic oxidation. The concentrations of interfering substances in all four intake wells are compared with studied values in a laboratory test carried out by Ghurye & Clifford (2004) on the effects of interfering substances on arsenic oxidation (Table 6):

Table 6. Interfering substances levels in Boring 1, 4 and 5 and in an experimental study (Ghurye & Clifford 2004, 93; Geologic survey of Denmark and Greenland 2017)

Interfering substances	Ghurye & Clifford study (2004)	Boring		
		1	4	5
Sulfide (mg/l)	1-2	<0.01	<0.01	<0.05
Iron (mg/l)	0.3-2	0.297	0.417	0.84
Manganese (mg/l)	0.2	0.582	0.413	-
Total Organic Carbon (mg/l)	1.4	1.2	1.4	1.7

The most adverse interfering substance which is sulfide has the concentrations in all three borings more than 20 times less than the studied concentration. While the figures for manganese and iron are slightly higher, the levels of Total Organic Carbon are relatively equal. Nevertheless, there is high saturation of dissolved oxygen in aerated water effectively generated by aeration basin in new waterworks (10.2 mg/l of dissolved oxygen), as well as, high availability of manganese oxides coated around filter material caused by high retention on sand surfaces. High Empty Bed Contact Time in the filter also minimizes the impact of interfering substances on arsenic conversion.

Looking at these conditions, there is a high chance that the oxidation of arsenic could be achieved with high efficiency, though further laboratory experiment is recommended to gain more knowledge about this process. Ghurye & Clifford (2004) has found that the presence or absence of interfering substances would determine on how manganese oxides act in arsenic oxidation, it has not been mentioned at what concentrations of interfering substances manganese oxides could be main oxidants or catalysts or even both. In other words, there has been no defined boundary to set the role of manganese oxides in the arsenic oxidation mechanism.

Additional information about required time to convert half of arsenite to arsenate can be found in the following table below, taking variation in oxidation rates into account.

Table 7. Time for half-life oxidation of As(III) with varying k values

k-value	Half-life time (min)
0.12	5.77
0.15	4.62
0.2	3.47
0.27	2.57

Clearly, it took only less than 6 minutes for half of As(III) to be oxidized to As(V). In such favorable conditions, half-life time of As(III) could be down to approximately 3 minutes. The most critical scenarios with the most sluggish oxidation rate (k = 0.12) were tested and presented in the following sections to assess the capability of arsenic removal by different water treatment designs, especially filtration process which plays a major contribution to arsenic treatment.

5.2   Individual treatment of Boring 5 raw water (Design 1)

From calculation of arsenic removal efficiency on water treatment system – Design 1, it was found that only 48% amount of arsenic could be removed from water. This means the concentration of arsenic in the treated water was around 9 µg/l, which was still nearly two times above safety limit.

Individual treatment of raw water from Boring 5 with the existing water treatment system is not effective and unable to reduce arsenic concentration to 5 µg/l. The main reason for this ineffectiveness is low content of iron in raw water. Although it is likely that the majority of arsenic is arsenate after oxidation process, only part of it is adsorbed on iron hydroxide surfaces due to limited amount of iron. The filter column could not retain the remaining arsenic during filtration stage, allowing it to get through and end up in water storage tank with level of arsenic above Danish drinking water criteria.

The most common practice for the Skovby waterworks to overcome this situation is addition of dissolved iron content in the form of iron chloride ($FeCl_2$) or iron sulphate ($FeSO_4$) into Boring 5 raw water. It was estimated that supplementing approximately 2 mg/l extra iron to the present iron concentration would raise

arsenic removal efficiency by nearly 30%, enabling to reduce arsenic level below 5 µg/l. There is a waterworks in Denmark, named Galten waterworks, following the same procedure to treat arsenic-contaminated water. The level of arsenic in raw water is quite similar to that in the Skovby waterworks (21 µg/l), which is removed by oxidation/filtration method with addition of $FeCl_2$. (Søgaard & Madsen 2013, 239.)

This water treatment design along with addition of iron solution is beneficial in some ways. The most obvious advantage is that not so many changes are required for treatment of arsenic in Boring 5. The current water treatment system is kept intact, however, it is necessary to establish a dissolved iron storage tank and an iron dosing system prepared for iron addition into raw water. In addition, the integrated system can run automatically and additional treatment might not be needed. The cost of iron solution is quite low also.

On the other hand, there are also some disadvantages caused by adding extra iron into water. The main shortcoming is competition with other substances on reaction with oxidizing agents, especially on arsenic oxidation process. Another drawback could be an increase in frequency of backwash so as to restore filter hydraulic properties and remove any solids in filter since more waste would be produced by rising level of iron in water. The most important thing is that a permission for chemical usage in water treatment must be granted from authority and waterworks staffs must be trained to manage and handle chemicals at work.

5.3 Co-treatment of Boring 5 raw water with other raw water sources (Design 2)

Dilution of arsenic by mixing raw water from Boring 5 with another source which contains low level of arsenic showed a potential result with higher efficiency of arsenic removal. Blending Boring 5 raw water with either Boring 1 or 4 raw water lessened the concentration of arsenic in untreated water, easily achieving less than 5 µg/l of arsenic in treated water as well as satisfying other drinking water requirements of other critical substances after treatment with the existing water treatment system. The maximum abstraction flows of Boring 5 were estimated

about 20 m^3/h or 25 m^3/h when Boring 5 raw water pump operates simultaneously with Boring 1 or Boring 4 water pump respectively. Figure 18 below shows how large extraction rate of Boring 5 could be before arsenic safety level in treated water is surpassed. Since the raw water pumps from Boring 1 or 4 run with highest speed during co-water treatment, the maximum clean water production rates were estimated about 60-70 m^3/h, increasing by 40-60%.
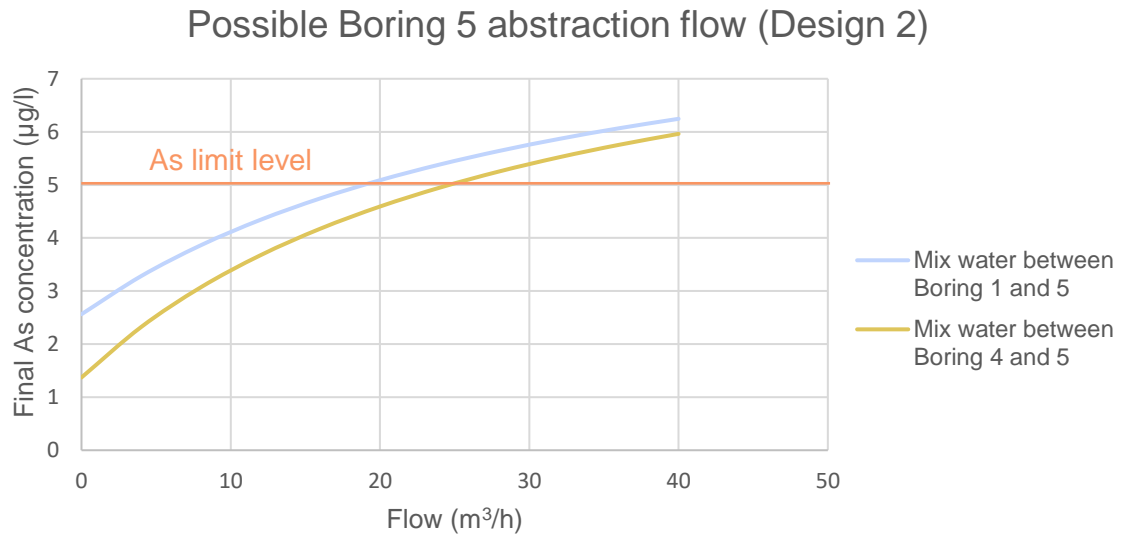

Figure 18. Concentration of arsenic in clean water after Boring 5 raw water is mixed and treated with raw water either from Boring 1 or 4 with the current water treatment system

The required depths for complete arsenic oxidation were less than the effective height of the existing filter, allowing the oxidation process enough time to convert arsenite to arsenate. The reduction in As(III) concentration during the period of filtration of water is displayed in the following chart (Figure 19):

Concentration of As(III) down through filter (Design 2)

As(III) concentration (µg/l)

Filter depth (m)

Mix water between Boring 1 and 5

Mix water between Boring 4 and 5
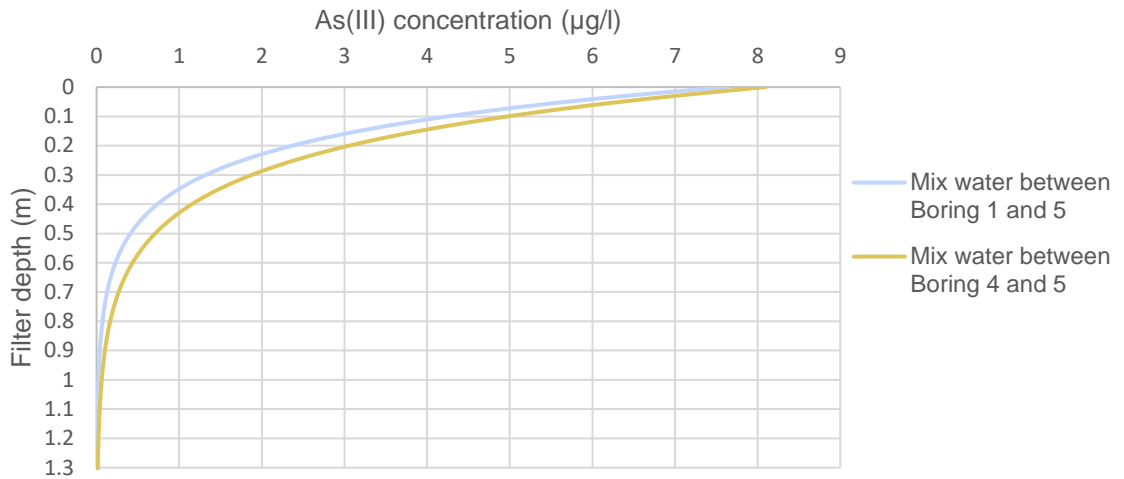
Figure 19. As(III) levels at different depths in filter (the initial concentrations of arsenic are 7.63 and 8.1 µg/l as it is diluted by mixing with raw water from Boring 1 and 4 respectively)

One can see that the concentrations of As(III) decreased rapidly in the top of the filter. After the water was filtrated through 20 cm of filter, most of arsenite has been converted into arsenate and the concentration of As(III) is below 5 µg/l. However, it is anticipated that the release of As(V) is not as fast as the reduction of As(III) because of iron hydroxides formation, attaching arsenic on surfaces and precipitating together.

There are a number of advantages provided by this water treatment design and operation. Firstly, it is possible to remove arsenic from water without addition of chemical by mixing with other low-arsenic containing water source. Secondly, no change to the existing water treatment system is required since Boring 5 raw water is treated by the same aeration and filtration system in the new waterworks at present. Finally, this solution is relatively cheap as only small amount of consultant fee is required in the beginning to plan the strategy of raw water pump.

Nonetheless, the most potential drawback of this design and operation is restriction on abstraction rate. Due to high level of arsenic in raw water, the maximum amount of abstracted water would be limit to around 20-25 m^3/h. In the long-term, extracting more water from Boring 5 is not feasible if the Skovby waterworks must supply more water to increasing number of residents in the

future unless rising the rate from other borings. It was calculated that by operating Boring 5 raw water pump at the same time with Boring 1 or 4 raw water pumps with the ratio of 1:2.6 or 1:1.6 respectively, it is possible to increase the flow rates while still ensuring the arsenic level is below 5 µg/l.

5.4 Two-step treatment of Boring 5 raw water (Design 3)

Removing arsenic in two-step process by converting the existing two single filters into a double filter could also be an option. Arsenic was co-removed by the iron content present in Boring 5 raw water initially and further by extra iron from Boring 1 or 4 raw water, presenting high efficiency of arsenic-contaminated water treatment. Other critical substances like iron, manganese or ammonium were treated effectively as well with new modification to existing water treatment system design, complying with Danish drinking water criteria. The concentrations of arsenic in treated water against potential range of Boring 5 abstraction rates with Design 3 are presented in the following graph. It should be noted that the filtration flow in the second filter is restrained up to 40 m^3/h (Jensen & Brinck 2012), thus there is a limit on the individual abstraction flow of Boring 5 as well as the total flow of Boring 1 or Boring 4 with Boring 5.
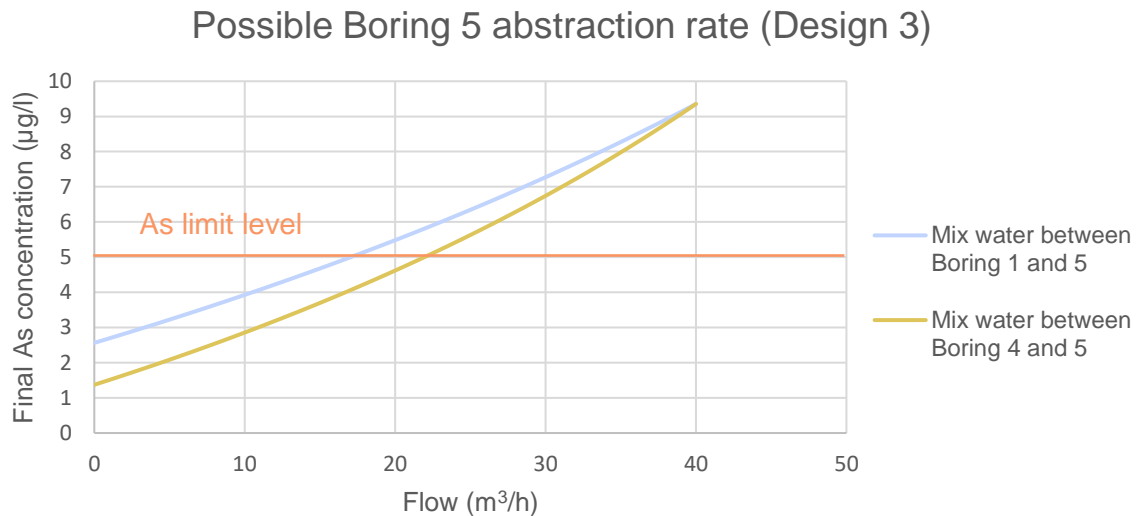
Figure 20. Concentration of arsenic in clean water after Boring 5 raw water is mixed and treated with aerated water either from Boring 1 or 4 with two-step arsenic removal process

The graph points out that the maximum allowable abstraction flows of Boring 5 could be 17 m³/h when Boring 5 raw water pump was started in pair with Boring 1 raw water pump and 22 m³/h when Boring 5 raw water pump ran at the same time with Boring 4 raw water pump. The flows of Boring 1 and 4 in both cases were 23 m³/h and 18 m³/h respectively. Although the flow rates of Boring 5 into the first filter were below the guiding minimum value, it was expected that the treatment system would still function well.

In this water treatment design and process, the complete arsenic oxidation could not be accomplished in the first filter because the required depths were more than the effective height of the existing filter. The chart below presents the drop in As(IIII) level during the oxidation process in the first filter:

Concentration of As(III) down through 1ˢᵗ filter (Design 3)
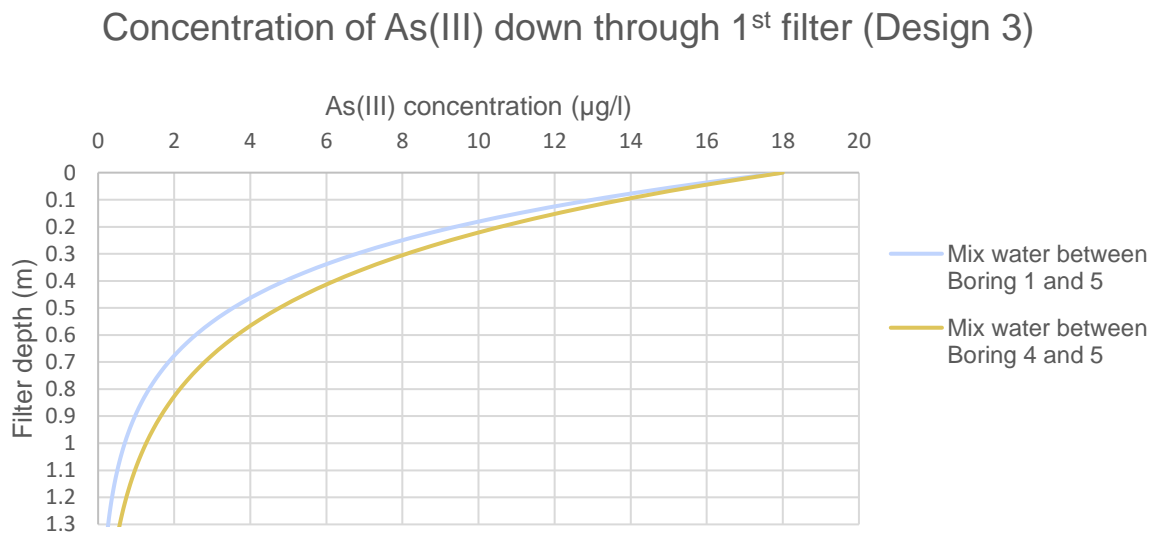
Figure 21. As(III) levels at different depths in the first filter in two-step arsenic removal

There was a significant decrease in the concentration of As(III) in the first 40 cm of the first filter. After that, the oxidation process was slower and the level of As(III) before exiting the first filter were 0.24 µg/l and 0.55 µg/l, which is equivalent to more than 97% oxidation efficiency. However, the remaining As(III) would probably be oxidized in the second filter.

Two-step arsenic removal treatment is advantageous to the Skovby waterworks. High treatment rate can be achieved by co-removing arsenic with naturally iron

content in two stages. Hence, there is no need to add iron chemical solutions into raw water or any further water treatment.

However, there are also some negatives that are worth mentioning. Establishing a new aeration system and converting single filtration to double filtration would cost an amount of money to renovate the water treatment system in addition to consultant fee for pump strategy planning as well as automatic control modification. Furthermore, the volume of clean water produced by this design is constrained, discouraging the Skovby waterworks to enhance the total water capacity of drinking water. This problem could be overcome by extending the area in the second filter, allowing bigger filtration flow as well as producing bigger water volume. It could be beneficial in the future when the number of customers consuming cleaning water from the Skovby waterworks increases.

5.5   Arsenic co-precipitation with iron

Three studied treatment designs yielded varying rates of arsenic removed. Different proportions of arsenic co-precipitated with iron particulates and later filtered out of the water treatment system are shown in Table 8:

Table 8: Percent of arsenic co-precipitated with iron during removal process

Treatment design		Percentage of arsenic adsorbed on iron particles		
		Individual treatment	Mix water of Boring 1 and 5	Mix water of Boring 4 and 5
Design 1		48%	-	-
Design 2		-	33%	39%
Design 3	1st step	-	48%	48%
	2nd step	-	16%	17%

It can be seen that nearly half amount of arsenic bound to iron particles during the arsenic removal process in Design 1. As a result, the concentration of arsenic in water was reduced around twofold (9 µg/l), though the final arsenic level was still above the threshold limit as mentioned previously. The same amount of arsenic removed was also achieved after arsenic containing water was filtrated

through the first filter in double filtration system in Design 3. However, this first filtered water was further treated with other Boring 1 or 4 aerated water in the following filter, in which more than 15% of the remaining arsenic was adsorbed and coprecipitated with newly added iron content from Boring 1 or 4 water sources.

Due to differences in the levels of iron in water as well as in the flows generated by pumping, 33% and 39% of arsenic was removed after mixing and co-treating Boring 5 raw water with Boring 1 and 4 raw water respectively.

Some competing substances that might undermine the efficiency of arsenic removal process are gathered in Table 9 with regards to their concentrations.

Table 9: Concentrations of anions competing with arsenic on adsorption to iron particles (Geologic survey of Denmark and Greenland 2017)

Competing anions	Boring		
	1	4	5
Phosphate (mg/l)	0.09	0.05	0.127
Natural Organic Matter (mg/l)	1.2	1.4	1.7
Silicate (mg/l)	Data not available		

Those numbers from Table 9 is not significant enough to have great impacts on adsorption process of arsenic on iron hydroxides. Nevertheless, it would be good if their effects are considered when determining the efficiency of arsenic removal process close to actual value. Additional chemical analysis might be necessary to provide concentrations to unknown substance silicate.

5.6   Arsenic waste management

Arsenic in raw water usually ends up in waste after treatment. This waste is in the form of liquid residual produced by filter backwashing stage. At the moment, backwash water is directly discharged into sewer system, sending to wastewater treatment plant. Treating raw water with high level of arsenic as Boring 5 raw water will lead to an increased arsenic in the backwash water. If wastewater

treatment plant is not able to manage an increasing amount of arsenic, it might be necessary to establish an onsite treatment at the Skovby waterworks. A settling basin could be a potential solution, allowing sedimentation of arsenic containing solids which is then disposed at landfill or waste management facilities.

6 CONCLUSION

To increase production capacity, it is possible for Skovby waterworks to abstract and treat raw water from new boring which contains elevated level of arsenic while achieving effluent water with high quality. Oxidation/filtration method, as known as iron and manganese removal process, is the best available treatment technique to reduce the concentration of this contaminant in the context of waterworks.

In Skovby waterworks filters, manganese oxides-coated sand plays a crucial and important role in arsenic-contaminated water treatment, particularly in arsenic oxidation process. During the transformation of arsenite to arsenate, manganese oxides could act as a catalyst for direct reaction between As(III) and dissolved oxygen in water. Manganese oxides are also considered as a primary oxidant when As(III) is oxidized to As(V) by reacting with manganese oxides through surface mechanism. Under any circumstances, the oxidation process follows first-order kinetics with half-life time of arsenic is relatively short. It takes only 3 to 6 minutes to lessen arsenic concentration by half, which usually takes place in the top of the filter. Some interfering substances, such as sulfide, iron, organic matter in water could have impacts on arsenic oxidation rate as well as determine the roles of manganese oxides in the conversion of arsenic.

Natural iron content present in Skovby waterworks water sources contribute significantly to high arsenic removal efficiency. Taking advantage of available iron amount in raw water, three studied water treatment designs and processes showed promising results. Low arsenic level under Danish drinking water criteria could be accomplished by modifying the existing filtration system to treat arsenic in two-step process or altering the current pumping strategy to co-treat raw water

of Boring 5 with either Boring 1 or 4 raw water. Individual treatment of Boring 5 raw water is also possible if chemical iron solution is added into water to rise the iron content; however, it would require permission from Danish authorities.

Several assumptions have been made during calculation to simplify the conversion of arsenic by manganese oxides as well as adsorption of arsenic on iron hydroxides. Therefore, future studies, including further experiments and bench-scale systems are recommended to gain better understanding of arsenic oxidation process as well as arsenic removal efficiency before selecting and implementing a full-scale system.

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LIST OF FIGURES

LIST OF TABLES

GROUNDWATER ANALYSIS

Table A1.1. Comprehensive groundwater analysis of intake wells and Danish potable water requirement. Sample dates of Boring 1, 2, 4 and 5 are 17/11/2015; 16/11/2016, 14/11/2014 and 14/05/2002 respectively (Geologic survey of Denmark and Greenland 2017; Ramsay)

	Boring				Water
	1	2	4	5	criteria
pH	7.7	7.6	7.4	7.84	7-8.5
Ammonium (mg/l)	**0.07**	**0.06**	0.02	**0.645**	0.05
Calcium (mg/l)	83	81.5	80.5	43.6	-
Agress.CO_2 (mg/l)	**<5**	<2	**5**	-	2
Chloride (mg/l)	31	34	29	25	250
Hydrogen sulphide (mg/l)	<0.01	<0.01	<0.01	<0.05	0.05
Fluoride (mg/l)	0.2	0.2	0.3	0.5	1.5
Hydrogen carbonate (mg/l)	214	203	219	340	-
Iron (mg/l)	**0.297**	**0.54**	**0.417**	**0.84**	0.1
Potassium (mg/l)	1.31	2.66	4.72	8.4	10
Magnesium (mg/l)	7.59	8.75	9.08	11	50
Manganese (mg/l)	**0.582**	**0.446**	**0.413**	-	0.02
Methane (mg/l)	<0.01	<0.01	<0.01	<0.01	0.01
Sodium (mg/l)	16.3	17	16.1	77	175
Nitrate (mg/l)	<0.5	<0.5	<0.5	<0.5	50
Nitrite (mg/l)	0.003	0.007	0.005	**0.012**	0.01
Oxygen content (mg/l)	1	<0.1	0.2	1.6	-
Org. Carbon NVOC (mg/l)	1.2	1.1	1.4	1.7	4
Phosphorous, Tot P(mg/l)	0.09	0.06	0.05	0.127	0.15
Sulphate (mg/l)	62	72	56	16	250
Arsenic (µg/l)	3.4	3.22	2	**18**	5
Barium (µg/l)	107	131	129	-	700
Boron (µg/l)	20	20	20	-	1000
Cobalt (µg/l)	0.32	0.21	0.23	-	-
Nickel (µg/l)	0.48	0.61	0.18	1.2	20
Total dissolved solids (mg/l)	380	380	330	350	1500

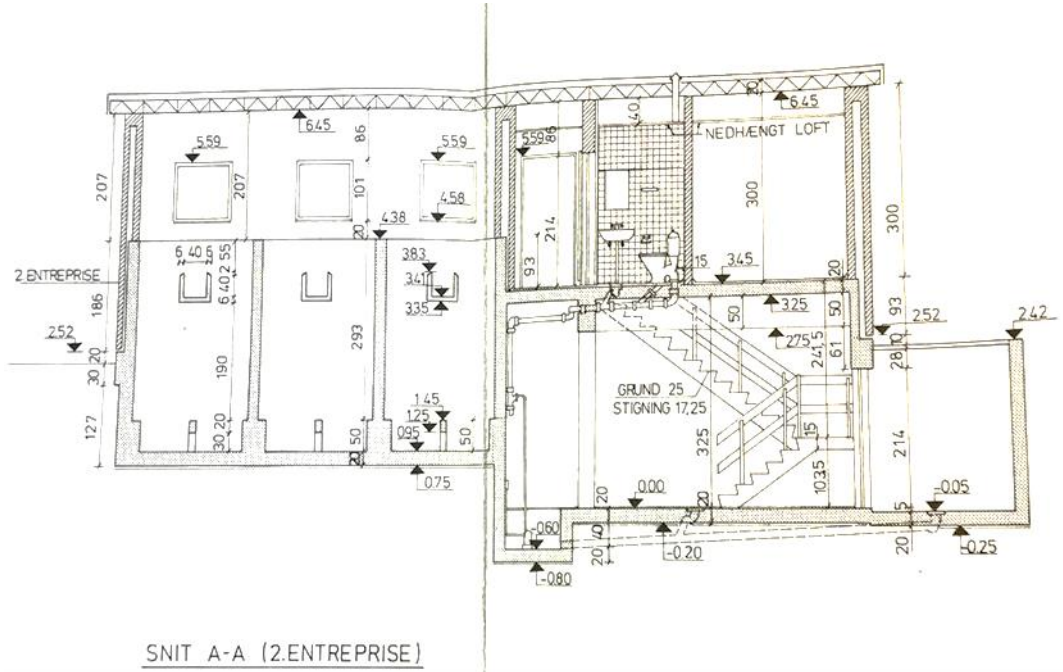**DRAWING OF FILTER IN THE NEW WATERWORKS**

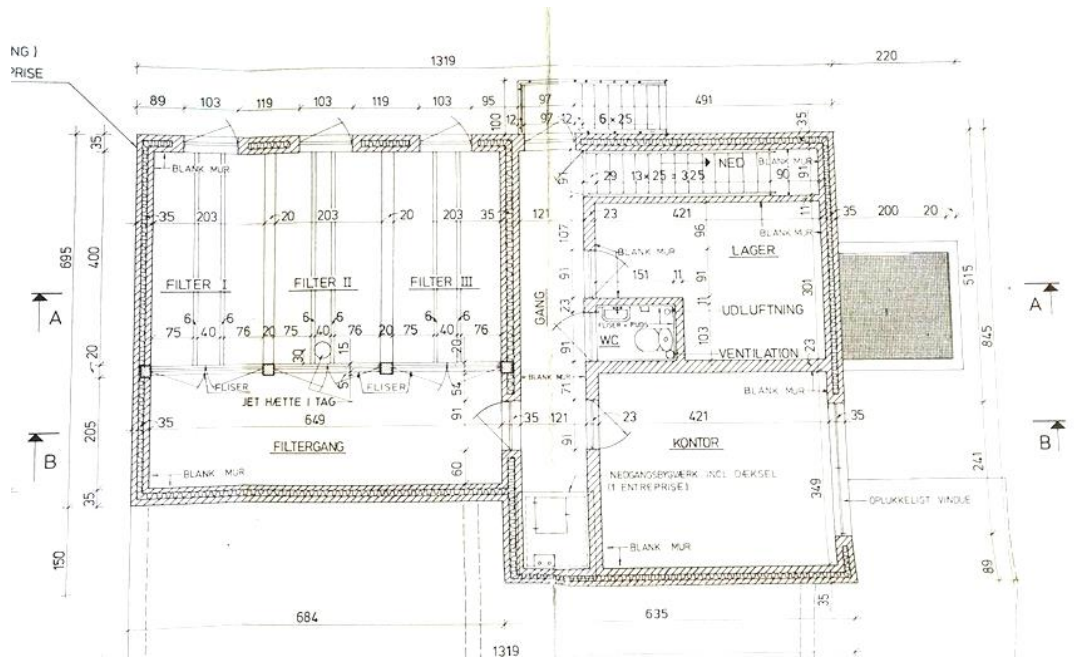Figure A2.1. Layout of filter (A-A cut) (Krüger A/S V1-38180 2016)

Figure A2.2. Layout of filter (aerial perspective) (Krüger A/S V1-38180 2016)