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Elimination of iron from groundwater for drinking water purpose, and strategic transfer of the technology to developing countries such as Ghana

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Elimination of iron from groundwater for drinking water purposes, and strategic transfer of drinking water treatment technology to developing countries such as Ghana

Ph.D. Thesis

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Abstract

Iron and manganese oxides are ubiquitous in soils and sediments. They therefore have tremendous influence on the chemistry of groundwater. To a larger extent, Fe -oxides sorb other dissolved element species and thereby control the aqueous concentrations of the sorbed species.

The traditional way to remove Fe content in groundwater for drinking water purposes is by aeration to saturation followed by precipitation of the Fe solids. However, this method is not always effective when especially, factors like high concentrations of natural organic matter (Humic substances) carbonates and silicates are present in the groundwater. Therefore, there are still gabs in the seemingly simple process of aeration filtration method for Fe removal from groundwater for drinking purposes.

An alternative way to decrease Fe in raw water is by the use of bacteria. However, in this research, the conditions under which *Gallionella ferruginea* thrive in Drinking water systems around Esbjerg municipality area, the rate at which the bacteria precipitates iron thermodynamics and the content of *Gallionella ferruginea* exopolymers were investigated. While conclusions drawn on the conditions affecting *Gallionella* in water systems were not with certainty, it was concluded that their presence increased the rate of iron precipitation 100 folds faster than the purely physic-chemical method although 1000 fold increase in Fe precipitation rate was observed by Søgaard et. al. in 2001 . Furthermore, iron precipitation process by the bacteria are energy demanding and the bacteria acquire this energy through the electrons transferred during the iron oxidative activities.

High content of silicates and natural organic matter in wells can cause the bleeding of colloidal Fe particles from wells and they may end up in the treated fresh water. As a result, the total Fe concentration in the treated drinking water may be increased to exceed the allowable limit value for drinking water. Aluminium coagulant and/or biotic method of Fe removal can effectively precipitate the colloidal particles in filters thereby reducing the net Fe content in the drinking water.

Analytical methods to characterize ferrihydrites precipitated by biotic method or purely physico-chemical method is not known. The SIMCA PCA multivariate data analysis method based on Near Infrared Spectroscopy (NIRS) was found to be an applicable tool for that purpose, so single analysis of samples from iron oxide precipitate could estimate the robustness of the ongoing process for removal of iron by either biological or purely physic-chemical means.

Ghana continues to experience rampant water shortages. This could be as a result of the monopolistic approach in the urban water sector by the government, coupled with the fact that the limited groundwater sources available, contain high concentrations of Fe, Mn, As, and other heavy metals due to severe mining activities going on in the country. The adoption of the biological method of Fe removal through the Danida Business- to –business (B2B) programme can helps Danish companies and their Ghanaian counterparts to create joint venture companies which can help to build independent and competitive companies on the Ghanaian market to sustainably produce and supply drinking water in Ghana and the rest of the continent.

Preface

This dissertation is submitted to the International Doctoral School of Science and technology, Aalborg University, Denmark for the degree of Doctor of philosophy.

The research written herein was conducted under the supervision of Associate professor Erik G. Søgaard at the University of Aalborg, Esbjerg Institute of Technology between September 2007 and August 2010.

The purpose of the thesis is to fill some of the wide gabs which exist in the knowledge of the seemingly simple process of groundwater treatment for drinking water purposes, and to strategically transfer groundwater treatment technology to a developing Country such as Ghana.

Except where acknowledged and references have been made to previous work, rendering this work, to the best of my knowledge, original. Neither this, nor any substantially similar dissertation has been, or is being, submitted for any other degree or qualification at any other university.

Daniel Anobaah Ankrah

Acknowledgement

To God be the Glory!

Supporting publications

Ankrah, D. A., and Søgaard, E. G. (2009). The applicability of iron and manganese precipitation bacteria in drinking water systems *Nanotechnology Perceptions*. 5, 3, s. 209-216. 8 s.

Ankrah, D. A., and Søgaard, E. G. (2009). A review of biological iron removal. *Thirteenth international Water technology Conference*, *(IWTC 13),* Hurghada, Egypt

Ankrah, D. A., and Søgaard, E. G. (2010). Chemometric classification of Fe precipitates from Selected water treatment plants in Denmark, Submitted to *Drinking water Engineering and Science. Delft University of Technology.*

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Chapter 1

1 Introduction

In the history of mankind, groundwater was previously abstracted mainly in desert areas where surface water was usually in short supply. Ancient civilizations especially in the Middle East used periscope-like conduits to funnel spring water from mountainous areas to towns and cities; this technology permitted the cities to spread out from the river banks. Nowadays, aquifers are tapped all over world and groundwater in increasingly becoming the primary source of drinking water for more than 1.5 billion people worldwide (Sampat, 2000).

Globally, marine water constitutes about 97 %, while 3 % is fresh water. Out of the 3 % freshwater, 79 % is stored in polar ice caps and high mountain glaciers, aquifers, and soil moisture contains 20 % and 1 % is from surface water, which is basically lakes and rivers. Besides the limited amount of fresh water availability, the intensification of climate change, coupled with increasing human population and industrial development are putting severe pressure on fresh water, resulting in concerns to seek for sustainable source of drinking water (Ian et. al., 2006).

Although hidden from view, large amount of water exist in the crevices, cracks and pores of the rocks and soils that make up the Earth's crust. As a matter of fact, groundwater constitutes 35 times the amount of water in lakes and streams. Rain that falls on the soil seeps or percolates through the interconnected pore spaces and fractures and eventually fills them.

Groundwater serves as an essential source of drinking water in many parts of the globe (see table 1.0). In Europe, especially, about 75% of the total share of drinking water comes from groundwater. Similarly, in Denmark, drinking water is based absolutely on groundwater and the government's policy is that drinking water must be from pristine groundwater source, which may only need simple treatment with aeration, pH correction and filtration, then, the water is clean enough to be released to consumers.

Table 1.0: Groundwater share of drinking water use, by region (Sampat 2000).

Region	Share of Drinking water from groundwater (%)	People served ($\times 10^6$)
Asia Pacific	32	1000 to 1200
Europe	75	200 to 500
Latin America	29	150
United states	51	135
Australia	15	3
World		1500 to 2000

Groundwater is considered to be the cleanest source of drinking water; nonetheless, Fe is usually concentrated in the percolated water, which is in contact with rocks, minerals and occasionally man-made materials like steel pipes. This makes the quality differ from one location to the other. There are localized areas in Denmark, and many other countries where Fe have degraded the water quality seriously enough to prevent usage of the water for human consumption (Ankrah and Søgaard, 2009).

Fe in groundwater should not present health hazards to consumers supplied with fresh water from groundwater for drinking purposes. However, the presence of Fe in groundwater is objectionable to the consumers as those contaminants could precipitate in fresh water distribution systems. When precipitated, Fe may cause problems of unpleasant odour, taste in drinking water and beverages, and yellow to brown stains in plumbing and laundered clothing. Additionally, Fe in distribution systems may promote growth of microorganisms, thereby forming slimy tissues several millimetres thick, which could accumulate and eventually block the distribution channels. The microorganisms could also reduce oxygen levels in the water and, where chemicals are used for disinfection, reduce the effectiveness of those chemicals.

Occurrence of Fe

Fe is the sixth most abundant element in the universe. It constitutes about 34.8% of the Earth,5% of the crust and 34 ppb in the ocean. Fe is mostly found in igneous rocks and in partially water-soluble siderite (ferrous carbonate). Fe is omnipresent in soils, sediments and groundwater, and have profound influence on the chemistry of water in aquifers and subsurface (O´ Neill, 1995).

Implementation of the drinking water directives states a series of maximum admissible concentration values for many chemical elements occurring in drinking water. However, as groundwater is used for drinking purposes with only simple treatment, many of these maximum admissible concentration values are highly relevant for groundwater protection.

One of the Danish government's policies to protect groundwater in Denmark was to classify groundwater abstraction areas, to protect valuable areas for drinking water interest (see figure 1.0)
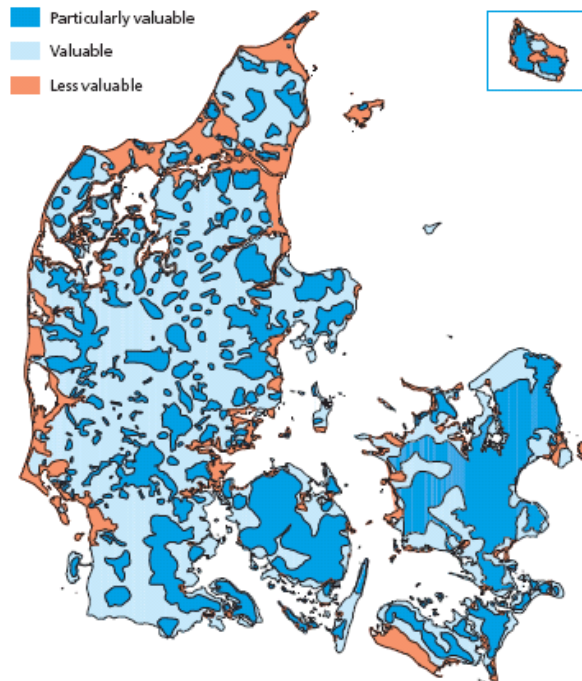
Figure 1.0: Groundwater resource in Denmark (Jens, 2010).

Similarly, the maps out areas are used to establish site-specific groundwater protection zones and associated regulations of land use to prevent groundwater pollution.

Today, Fe removal processes are known worldwide. However, there are still wide gabs in our knowledge of the ostensibly simple process of aeration, precipitation and filtration used to remove Fe from groundwater. Although two main types of Fe removal methods are known but, the characteristics of the raw water and precipitates, their identity and even the extent to which the biological Fe removal method could function in a full-scale water treatment plant in not fully known. This thesis seeks to answer some of these unknown aspects concerning water treatment plants for the removal of Fe.

1.1 Structure of the thesis

This chapter 1 provides an introduction to the research. The theoretical background is covered in Chapter 2, 3 and 4. The scope, objective and questions leading to the study are presented in Chapter 5. However, Chapter 6, 7, 8 and 9 are own studies conducted during the research period. Chapter 6 looks at biological iron removal from groundwater, considering the physico-chemical parameters, kinetics as well as thermodynamics. A case study of iron removal from groundwater at Vejers drinking water treatment plant in Esbjerg was discussed in Chapter 7. In Chapter 8, Chemometrics was used to classify iron precipitates from selected water treatment plants in Denmark. Finally, in Chapter 9, discussions of technology transfer for groundwater treatment to a developing country such as Ghana were presented. Chapter 10 presents the general conclusions drawn for the entire research.

It is worth mentioning that due to the variant nature of the research conducted during my study, the thesis has not been structured to conform to the classical style of thesis presentation. This is evident especially in Chapter 6, 7, and 8, where each study conducted has its own introduction, methodology, as well as results and discussions, and conclusions. Chapter 8 was presented as a brief introduction and the entire study can be found in supplement 2. The presentation in Chapter 9 is also different because the study was more of a Social Science than Chemical Engineering.

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Chapter 2

Drinking water treatment in Denmark

</div>

2   Introduction

In Denmark, ground water is considered as the favoured source of drinking water and it accounts for about 100 % of the drinking water supply sources. Therefore, most research and development, and technological improvements on water treatment are geared towards groundwater purification (Bjerg et. al., 2000).

This chapter, therefore gives an overview of legislation protecting drinking water standards in the EU and Denmark as well as the design of the water treatment plants basically used in Denmark to attain the required standards.

2.1   Historical background

Historically, civilization started and concentrated along areas where there was ample source of water. At that time, people knew relatively nothing about the connection between disease and drinking water. If there was water treatment at all, it was performed only for melioration of the cosmetic value and taste. In recent years, however, increasing population and improvement in scientific knowledge have resulted in many questions being raised about potability or safety of drinking water (Pontius, 1990). The drinking water standards and regulations in Denmark were developed out of a growing concern of the need to protect people from illnesses caused by contaminated drinking water. The standards have therefore developed and expanded over a period of time as knowledge of the health effect of contaminants increases and the treatment technology to remove contaminants improves (Pontius, 1990).

2.1.1   Drinking water standards in the EU and Denmark

The drinking water standards in Denmark were adopted either directly from the EU directives on drinking water or developed out of the framework of the EU directives and improved to either prevent or remove contaminants from raw water for human consumption.   The drinking water quality standards may be the same from one country to the other among the EU states but, the raw water taken from the water sources may have varying characteristics. For this reason, the design of water treatment plants in the member states vary slightly from one country to the other. Water purification is accomplished by several methods, depending on the quality of the raw water source, the philosophy of the water company as well as the availability of financial resources.

The water quality in the EU is governed by several EU directives. The implementation of the water framework directive by the EU places great importance on the usage of water resources. However, the EU directives tackle water quality standards from two perspectives which include:-

I. The raw water quality and
II. The quality of treated fresh water for drinking.

For instance, the directive 98/83/EC is enacted to protect groundwater from pollution by dangerous materials. On the other hand, the directive 80/778/EEC focuses on treated water quality for human consumption. Similar to the directive 80/778/EEC, The European Union enacted the Council Directive 98/83/EC on the quality of water intended for human consumption, adopted by the Council on 3 November 1998. This was drawn up by reviewing the parametric values of the old Drinking Water Directive of 1980, and strengthening them where necessary in accordance with the latest available scientific knowledge. This new Directive provides a sound basis for both the consumers throughout the EU and the suppliers of drinking water (Kiely, 1997). Some important parameters in the EU drinking water directive and their limit values are as shown in table 2.0

Table 2.0: EU drinking water directive parameters (Kiely, 1997).

Group description	Parameter	Maximum admissible concentration (MAC)
Organoleptic parameters	Colour	20 mg/L Pt/Co scale
	Turbidity	10 mg/L SiO_2
	Odour	Dilution of 2 at 12 ˚C
	Taste	Dilution of 2 at 12 ˚C
Physicochemical parameters	Temperature	25 ˚C
	pH	$6.5 < pH < 8.5$
	conductivity	400 µS/cm
	chlorides	250 mg/L C1
	sulphates	250 mg/L SO_4
	Calcium	100 mg/L Ca
	Magnesium	50 mg/L Mg
	Sodium	150 mg/L Na
	Potassium	12 mg/L K
	Aluminium	0.2 mg/L A1
	Total dry residues	1500 mg/L
Parameters Concerning substances undesirable in excessive amounts	Nitrates	50 mg/L NO_3
	Nitrites	0.1 mg/L NO_2
	Ammonium	0.5 mg/L NH_4
	Kjeldahl N	1 mg/L N
	Oxidizability	5 mg/L O_2
	Hydrogen sulphide	Undetectable µg/L
	Substances extractable in chloroform	No increase above background
	Hydrocarbons	10 µg/L
	Phenols	0.5 µg/L C_6H_5OH
	Boron	1000 µg/L B
	Surfactants	200 µg/L (lacryl sulphate)
	Organochlorines	1 µg/L
	Iron	200 µg/L Fe
	Manganese	50 µg/L Mn

	Copper	100 µg/L Cu
	Zinc	100 µg/L Zn
	Phosphorus	5000 µg/L P_2O_5/L
	Fluoride	1000 µg/L F
	Suspended solids	0
	Barium	100 µg/L Ba
Parameter concerning toxic substances	Arsenic	10 µg/L As
	Cadmium	5 µg/L Cd
	Cyanides	50 µg/L Cn
	Chromium	50 µg/L Cr
	Mercury	1 µg/L Hg
	Nickel	50 µg/L Ni
	Lead	50 µg/L Pb
	Antimony	10 mg/L Sb
	Selenium	10 mg/L Se
	Pesticides	0.1 µg/L
	PAHs	0.2 µg/L
Microbiological parameters	Total coliforms	PMN ≤ 1/100 mL
	Faecal coliforms	PMN ≤ 1/100 mL
	Faecal streptococci	PMN ≤ 1/100 mL
	Sulphite reducing clostridia	PMN ≤ 1/20 mL
Minimum required for softened water	Total hardness	> 60 mg/L $CaCO_3$
	Alkalinity	> 30 mg/L HCO_3
	NVOC	4 mg/L

In conformity with EU directives, the Danish government enacted into law, a bill containing an action plan which streamlined some directive into even a more stringent laws. Table 2.0 shows the limit values of few drinking water contaminants in Denmark as compared to the EU values.

It is worth noticing that the advent of the Danish legislation places much importance on drastic reduction of contaminants to levels stipulated by the legislation. In view of this, water treatment companies are increasingly looking for ways to improve the process efficiency for the removal of the contaminants, including Fe and Mn , which is the main focus in this book.

The limit value for Fe set by the World Health Organization (WHO) is 0.3 mg/l (WHO, 1996). Unlike the WHO limit values, it could be seen from table 2.0 that the EU has set a parametric value of 0.2 mg/l for Fe. However, in Denmark, several water treatment companies are targeting Fe concentration in drinking water of about 0.1 mg/l. fulfilling these rigorous standards of Fe in water supply systems demands a more efficient technology which will reduce operational cost and make judicious use of the raw water available (Kiely, 1997; Winther et. al., 2003; Drinking water, 2010)

2.2   Methods of Fe removal in filters

The removal of Fe from groundwater is a multimillion dollar industry throughout the world. The first Fe and Mn removal plant is believed to have been the one constructed at Charlottenburg, Germany in 1874. Nowadays, several methods have been documented as effective for the removal of iron and manganese from groundwater. The methods are:
• Ion exchange or zeolite softening
• Stabilization or sequestration using silicates

• Lime softening or limestone bed filtration
• Manganese greensand process
• *In situ* oxidation
• Membrane technology.

However, the predominant method used for iron removal for domestic purposes is the traditional (conventional) method known as oxidation, precipitation and filtration (OPF), which is popularly known as the purely physicochemical method (abiotic Fe removal). For this purely physicochemical method of iron removal, anoxic groundwater is mostly treated for drinking by the simple conventional process known as purely physicochemical (abiotic), in which the raw water containing soluble Fe^{2+} is oxidized by aeration followed by single (or double, depending on the groundwater quality) filtration units. Besides the physicochemical method, predominantly used in many countries, biological (biotic) iron removal, which has also been documented as a viable option for the removal of Fe from groundwater, is beginning to be given strong consideration by most water treatment engineers. Biological Fe removal technology has been applied in several water treatment plants around the globe, such as the Astrup water treatment plant near Esbjerg in Denmark, which removes up to about 20 mg/L Fe. Other places where biological Fe removal plants have been or are being built include Lomé (Togo), Barrie Ontario Ferazur (Canada), Grove, Nottingham (England) and several places in southern France; they show enormous advantages over the traditional (conventional) method of water treatment (Ankrah and Søgaard, 2009). A larger part of the research documented in this thesis is also focused on biological iron removal. Therefore, detailed information on the entire subject of biological Fe removal is documented in Chapter four.

Most of the Fe removal methods listed above are not used in Denmark except the biotic and purely physic-chemical methods. Sporadically, chemical oxidants such as ($KMnO_4$) or flocculants like $\{Al_2(SO_4)_3\}$ are used to supplement the abiotic method in cases where the groundwater is difficult to be treated but under special permission from the Danish Environmental Authorities. It is therefore important to zero in on the mechanism of the purely physic-chemical method, since it is mostly in operation in almost all water treatment plants in Denmark.

Mechanism of physicochemical iron removal in filters (abiotic iron removal)

The mechanism underlying physicochemical Fe removal is considered to be the oxidation of soluble Fe(II), leading to the formation of flocs of Fe(III) precipitates, which are subsequently removed by sand filters. This process is therefore termed "oxidation–floc formation". The chemistry can be represented as:

$$\tfrac{1}{2}O_2 + 2Fe^{2+} + 5H_2O = 4H^+ + 2Fe(OH)_3. \tag{2.0}$$

The possibility of Fe(II) being adsorbed onto the surfaces of coated filter media, followed by rapid oxidation of the Fe(II) to Fe(III) hydroxides and this is known as the "adsorptive filtration" or "chemical catalytic" mechanism. Which of these two processes predominate in filters is not yet fully known. However, it is believed that both the oxidation–floc formation mechanism as

well as the adsorptive filtration mechanism may occur concurrently during the deferrization process in sand filters. When the Fe(II) is oxidized to Fe(III), a unique characteristic of the Fe(II)/Fe(III) redox couples are that Fe(III) are susceptible to hydrolysis and precipitation. The formation of the iron or manganese precipitates then makes them susceptible to be removed by subsequent sand filtration (Ankrah and Søgaard, 2009).

2.3   Design of water treatment plants

The mechanism of the purely physico-chemical Fe removal is as enumerated above. However, modern water treatment processes provide barriers, or lines of defense, between the consumer and water born diseases. These barriers are implemented as a succession of treatment processes known as treatment process train.

As mentioned earlier, water treatment plants are designed to produce water of the desired quality by employing appropriate technology, which is cost effective and also based on the raw water quality. However, most of the raw water source for drinking water supply is abstracted from groundwater in Denmark (Bjerg et. al., 2000). Therefore, with the enactment of legislation to map out and protect the ground water sources, makes the treatment process quite simple than in most EU countries. The treatment train stages may be divided into three (3) and they are as explained below:

1. The first stage is straining: Thus fine bars of about 1 mm wide are used to screen particles such as sand and organic substances to reduce BOD_5 of decomposing organic substances. The water is then pumped from ground water into the first stage where the pH is regulated. Lime is usually added if the pH is less than 6.5. (Usually no clarification by coagulants is employed because the water abstracted from the ground normally has little or no suspended solids) (Degremant, 1991).

2. The second stage is the aeration stage. Thus raw water is exposed to or agitated with air to promote the oxidation of substances that are oxidizable such as Fe, Mn and some organic compounds.

3. The third stage that usually follows is filtration stage, commonly consisting of first and second filtration systems. The filtration stage produces water of better quality than the raw water. This is achieved by passing the influent water through a porous medium, usually sand. This removes pathogens, colloidal particulates, and organic compounds thereby enhancing the aesthetic quality of the water. The water is usually released into drinking water system from this stage. After backwashing the filter , the backwash sludge is allowed to settle in a sink. When the sink is almost full the sludge mainly ironoxides will be digged away and sent to a land fill. In Denmark it was discussd if some of the sludge could reused for some industrial purposes. Untill now, it has never been economically feasible..

Description of selected water treatment plants

Groundwater treatment in Denmark, to a larger extent, does not differ. However, water treatment engineers design the water treatment process based on the groundwater quality. Below are selected examples of Astrup, Vester Gjesing, and Vognsbøl water treatment plants in Denmark, indicating the source of their groundwater, the geology, water quality and the treatment processes adopted to treat the water at that specific water treatment plant.

2.3.1 Astrup water treatment plant

Catchment's area

Astrup waterworks treats water extracted from seven drilled wells in the community. All seven drillings are equipped with submersible pump and aboveground lockable raw water sites. The drillings are screened in intervals 75 – 125 m.u.t. and all drillings are sealed with clay plugging by penetration of the clay layer. A strict law has been made to protect all the drillings (about 200 metres radius) from effluents from wastewater or any polluted liquid that can drain into the ground water table. In addition to this, the drillings are protected against pollutants such as fertilizer, by plants planted around them in a density of about 30x30 square meters. The pumps are equipped with frequency converters and there is active field site control in the field, which implies the extraction is far more sustainable because the strain on the field area is as low as possible and large depression cone around the single drillings therefore is avoided.

Geology at Astrup WTP

The water field is placed on Esbjerg Hill Island and stretched according to the hydraulic model /45/ from drillings southeast towards Vester Nebel. The quaternary sediment is at least 150 metres thick in the area and consists of upper sediment of sand between 20 to approximately 50 metres varying with low permeable layer, which is mainly silt. Beneath the first level to an approximately depth of about 120 metres is again sand, where all drillings are screened. Most of the surrounding area is use for conversional farming (Vandforsyningsplan, 2010).

Water quality

The raw water at Astrup water treatment plant is slightly acidic with pH value of about 6.5. It has a very high Fe concentration between 5.5 and 19 mg/l and free of nitrate.   The groundwater is free of pesticides and other anthropogenic substances.

Treatment processes

Figure 2.0 shows the treatment process train at Astrup water treatment plant. Screened raw water is pumped from the wells directly into the first filtration tank, where Fe and organic substances are co-precipitated and filtered off by the sand filters. The pH of the filtrate is regulated above 6.5 to about 7.3 by the addition of CO_2 and $Ca(OH)_2$. After this, the water is aerated and channeled to second filtration tank where mostly Mn, residual Fe and organic substances as well as other impurities are filtered off from the water and released into the freshwater system. The unique characteristic at Astrup water treatment plant is that the iron is removed by a biotic method. As a result, the raw water in the first filtration is exposed slightly to atmospheric air in order to add a gradient of oxygen to only about 4 mg/l which is optimal to promote the growth of the Fe bacteria in the filters.
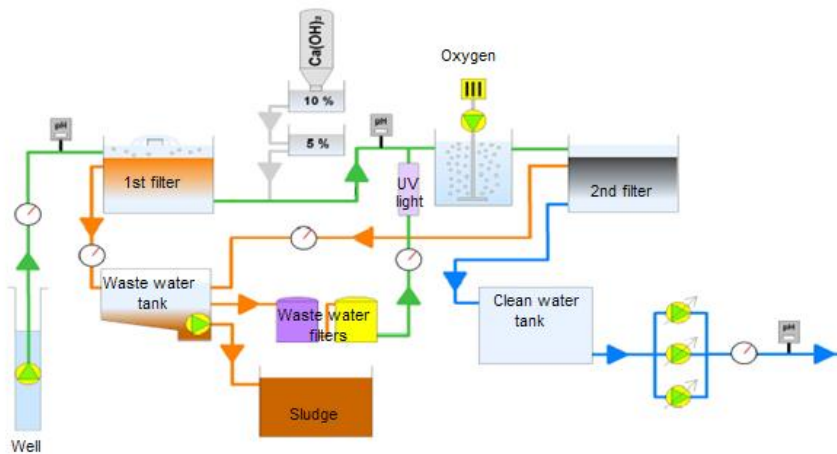
Figure 2.0 Water treatment process at Astrup water treatment plant.

The filter materials are backwashed to clean them and prevent them from being choked up with Fe/clayish precipitates and pieces of organic materials. The backwash is channelled into the wastewater sink. In the sink, the wastewater is permitted to settle and the waste water is filtered, treated with UV to control the development of pathogens and channelled back into the main treatment stream before the fully aeration step and the second filtration step.

2.3.2   Vester Gjesing drinking WTP

Well Catchment's area

Vester Gjesing waterworks treats water extracted from 6 wells placed alongside the eastern bank of Fovrfeld Bæk. Furthermore, there are other drillings in the water field, and water from these drillings are pumped for treatment at Sædding waterworks, which is connected to western Gjesing treatment plant. Approximately, 1.2 million cubic meter of water is abstracted from this field per year, of which 30 % is treated on Sædding waterworks. The drillings are conducted through a clay layer and all drillings are equipped with submerged pumps, with frequency converter given it an active field. This means that extraction is far more sustainable because the water field is put under so less strain as possible and large depression cone around the single drilling is avoided. All drillings are equipped with aboveground lockable raw water sites, about 10-metre protection zone around the drilling.

Geology

Water has been drawn from this water field for about 70 years and it is located on Esbjerg Hill Island. The surroundings of the extraction area are stretched according to the hydraulic model /45/ from drilling northeast towards Bryndum. The drillings are screened from 48 to138 m.u.t. The southern drilling has only filters at more than 100 metres in depth. The north and southern drillings have dense clay layers between 10 – 30 m.u.t including fluctuating clay and silt layer up to approximately 70 m.u.t. Again, the north and southern drillings have records of mica more than 130 m.u.t. There are no geological models present which can describe the vulnerability and potential areas with exceptional groundwater production within the specific extraction area. (Vandforsyningsplan, 2010)

Water quality

The groundwater is slightly alkaline with pH around 8. There is fairly high iron content, which varies between 4 and 12 mg/l. The groundwater is free of nitrate with low sulphate content and there have never been traces of pollution with pesticides or any other environmentally pollutants found in the water field.

Treatment processes

Figure 2.1 shows the water treatment process train at V. Gjesing water treatment plant. Contrary to Astrup water treatment plant, the raw water is pumped from the wells, screened, aerated and channelled into the first filtration tank, where iron and eventual organic substances are filtered. The pH of the water is about 7.5, which is appropriate for the precipitation of Fe, Mn and other impurities present in the water. Hence, addition of chemicals for oxidation, flocculation or chalk for pH regulation is not needed. At the second filtration tank, the water, which consists mainly of manganese, residual Fe and organic substances, are filtered off from the water. The water is then considered to be clean so it is released into fresh water tank and water distribution system. The backwash water produced as a result of washing the filter materials (beds to prevent them from being choked up) is channelled into the sink or waste water tank where the clear surface water is redirected into the main treatment line after treating it with UV to check the development of pathogens. The sludge is disposed off. Unlike Astrup WTP, the raw water is initially fully physically aerated to oxidize oxidizable elements such as iron and manganese and to strip off volatile compounds like small amounts of methane and hydrogen sulphide.
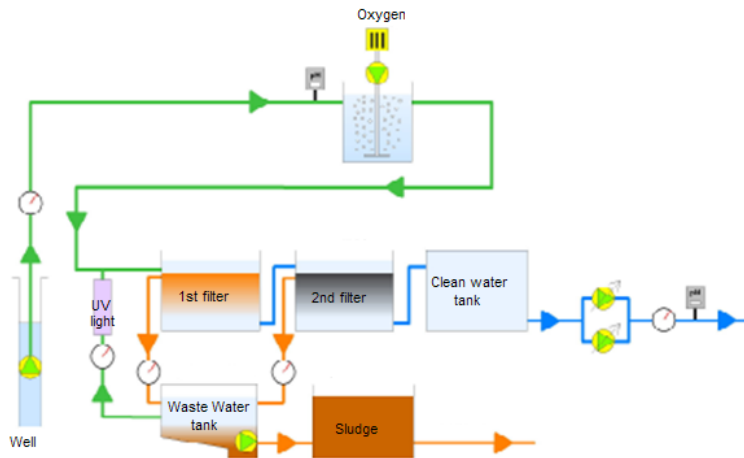
Figure 2.1: Water treatment processes at Vester Gjesing water treatment plant.

2.3.3 Vognsbøl water treatment plant

Well Catchment area

Vognsbøl WTP treats water from 10 wells solely from Sekær water field in Holsted Commune. One part of the water from Holsted is treated in Spangsbjerg water treatment plant. The raw water from Sekær is running in two 32 km long ø400 pipes to a distribution building in the immediate vicinity east of Spangsbjerg waterworks. From here it continues in one ø315 pipe to Vognsbøl waterworks. All four drillings are either fixed with aboveground lockable raw water sites or lockable well covers. The permissible water that can be extracted from the wells at Vognsbøl water works is about 30,000 cubic meters per year.

Geology of the catchment's area

Sekær water field is part of the Ribe formation. Surroundings of the extraction area are stretched according to the hydraulic model /45/ from drillings toward northeast. The drillings are screened at depth from 35 – 65 m.u.t. in quaternary melt-water sand and the surrounding environment is Municipal Park. (Vandforsyningsplan, 2010)

Treatment process

The treatment process train in Vognsbøl water treatment plant as shown in figure 2.2 is similar to that of V. Gjesing water treatment plant. The only difference between the two water treatment plants are the disinfection and recycling water tank (for re-use of backwash water) added at V. Gjesing water treatment plant but are not present in Vongsbøl water treatment plant.
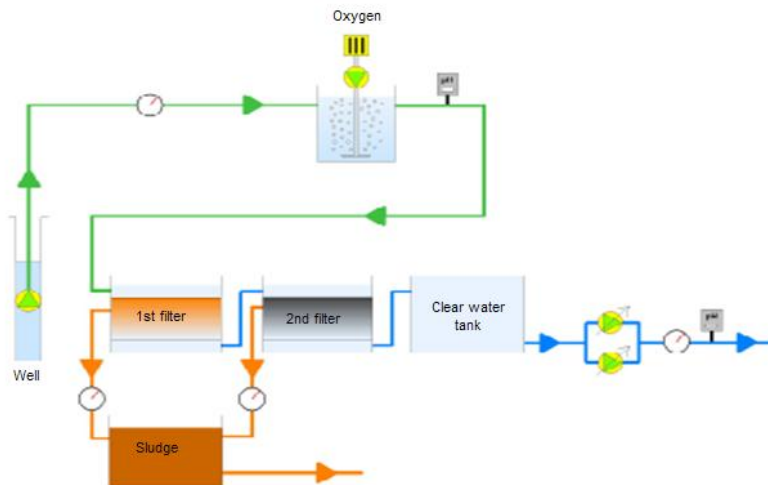
Figure 2.2: Water treatment stages at Vognsbøl water treatment plant.

2.3.4 Comparison of the selected water treatment plants

Table 2.1: compares the water quality parameters for the three water treatment plants, Astrup, V. Gjesing and Vognsbøl.

It can be seen that different levels of contaminants' concentrations exist in the raw water at the three water treatment plants. However, all the water treatment plants were able to treat or remove the contaminants to the allowable limits as indicated in table 2.0. The efficiency of the three water treatment plants can well be seen especially from their ability to remove Fe and Mn, which had very high concentrations in the raw water. But, they were both reduced to below 0.1 mg/l for Fe and 0.01 mg/l for Mn, which are the allowable limit values in Denmark.

Additionally, it can also be concluded from the process design that Vognsbøl and V. Gjesing water treatment plants are almost the same. Thus, they operate by the normal aeration- filtration or the purely physico-chemical method. This is because their raw water is first aerated to precipitate Fe and subsequently filtered by the sand filters. The simple purely physico-chemical method was enough to purify the groundwater, probably because of the optimal pH (7.5 to 8.0) , which favours purely physico-chemical method of Fe removal and also because of the fact that there were no other contaminants from natural or anthropogenic sources in the groundwater which necessitated additional treatment.

Table 2.1: Comparison of the groundwater and drinking water quality at the three WTP.

Contaminan-ts	Astrup		Vestre Gjesing		Vognsbøl	
	Raw water	Treated water	Raw water	Treated water	Raw water	Treated water
Fe (mg/l)	13	0.044	4.2	0.015	0.89	0.046
Mn (mg/l)	0.47	<0.005	0.34	<0.005	0.22	<0.005
Conductivity (mS/m)	28	32	36	37	34	36
pH	6.8	8.0	7.5	7.6	7.8	7.9
O_2 (mg/l)	0.4	10.0	0.7	9.8	0.4	10.0
NH_3 (mg/l)	0,032	<0.006	0.043	<0.006	0.13	0.010
CH_4 (mg/l)	<0,005				0.012	<0.005
Temp. (^{0}C)	8,4	9.2	8.8	9.2	6.6	11.4
Ca (mg/l)	26	-	48	-	42	49
NVOC (mg/l)	0.51	0.51	0.61	0.54	0.97	0.83

The only difference between Vognsbøl and V. Gjesing water treatment plants is that ultra-violet light at V. Gjesing to disinfect the backwash water from the waste water tank, which is re-treated for usage.

Unlike V.Gjesing and Vongsbøl, Astrup, water treatment plant removes Fe by a biological or biotic method of Fe removal. This is evident in the plant's process design at Astrup WTP, as the raw water with relatively low pH(6.8) is only slightly aerated at the first filtration stage. The slight aeration adds only a minimal amount of oxygen up to about 4 mg/l and keeps the copious amount of CO_2 in the raw water, which is required for the Fe bacterial metabolism. After the first filtration stage at Astrup water treatment plant, the water is the aerated and dosed with $Ca(OH)_2$ to give it the optimal pH required for Mn removal

With the differences in the treatment processes as well as the varying levels of contaminants in the treatment plants, the effect of the various treatment processes is interesting to note, especially on the removal of Fe.

Chapter 3

Iron precipitation

3 Introduction

Hydroxides, oxyhydroxides and oxides of Fe, hereafter collectively referred to as Fe oxides are ubiquitous in soils and sediments and have tremendous influence on the chemistry of water in aquifers and subsurface. Fe oxides may significantly sorb other dissolved species and thereby control the aqueous concentrations of these sorbed species.

The traditional physico-chemical method of Fe removal has been known for many years now. But, there are still huge gabs in the knowledge of the seemingly simple process of this method of Fe removal from groundwater for drinking purposes. This is because the chemistry of groundwater is very complex and even till date, the entire chemistry and characteristics of the Fe precipitates formed in filters media during Fe removal is not completely known.

This chapter of the thesis, however, gathers known knowledge on Fe oxides, types, structure, and subsequently focuses on the chemistry of Fe in filters.

3.1 Fe oxides

In aqueous solutions, Fe may occur in association with oxygen forming oxides or hydroxides and/or oxide –hydroxides, which are generally termed as iron oxides. These Fe oxides posses some unique characteristic features including color, low solubility and effective sorbent activities for a number of dissolve species due to their very large specific surface area. While few of the iron oxides could exist as a combination of Fe^{2+} and Fe^{3+} valent state minerals as in green rust and magnetites, most of the oxides principally exist in the Fe(III) valent states. However, in the purely bivalent state, only FeO and $Fe(OH)_2$ and Fe_2O_3 are known. See table 3.0 (Schwertmann and Cornell 2003).

Table 3.0: Types of Fe oxides **(Pedersen, 2006).**

Oxide-hydroxides and hydroxides		Oxides	
Goethite	α-FeOOH	**Hematite**	α -Fe$_2$O$_3$
Lepidocrocites	γ- FeOOH	**Magnetite**	Fe$_2$O$_3$(Fe^{II}Fe$_2^{III}$O$_4$)
Akaganeite	β- FeOOH	**Maghemite**	γ-Fe$_2$O$_3$
Schwertmannite	Fe$_{16}$O$_{16}$(OH)$_y$(SO$_4$)$_z$.nH$_2$O	-	β - Fe$_2$O$_3$
-	δ-FeOOH	-	ϵ-Fe$_2$O$_3$
Feroxyhyte	δ -FeOOH	**Wüstite**	FeO
High pressure	FeOOH		
Ferrohydrite	Fe$_5$HO$_8$.4H$_2$O		
Bernalite	Fe(OH)$_3$		
-	Fe(OH)$_2$		
Green Rust	Fex^{III}Fey^{II}(OH)$_{3x+2y-z}$(A-)$_z$; A- =Cl- ; ½SO$_4^{2-}$		

In soils and sediments, Fe oxides are ubiquitous and exert tremendous influence on the water chemistry of groundwater in aquifers. For instance, Fe is the most essential adsorbent for both macro and micro elements in groundwater because of their greater adsorbent and binding affinity (Pedersen et. al., 2005). In sedimentary rocks and soils exposed to the atmosphere, Fe mainly occur as Fe(III). Whereas in anaerobic systems, with decreasing redox potential (Eh) they occur as Fe(II), mostly ferrous sulphides, carbonates siderites and possibly, Fe(III) oxyhydroxides (Pedersen et. al., 2005).

3.1.1 Structure of Fe oxides

The structure of iron oxides consist of tightly packed arrays of cubic or hexagonally packed anions, filled with divalent or trivalent or tetravalent Fe in octahedral – Fe(O, OH)$_6$ or tetrahedral (IV)-FeO$_4$ coordination and they differ in the way they are aligned in space. The basic structural units of Fe oxides are mainly octahedral as in FeO$_6$ or tetrahedral such as FeO$_4$, and they may differ in the way they are aligned in space. Apart from schwertmannite and ferrihydrite, which are poorly crystalline, the rest may consist of nearly a well define structure exhibiting various shapes such as tablets, plates diamonds and cubes as in lepidocrocites. Apart from Fe which occupy the interstices of Fe oxides, other cations such as Al, Mn, Ni, Zn and Cu can also be present. The possibility of substitution depends on the ionic radii and the valence of the cation. Therefore, the most appropriate is the trivalent elements, and the substitution of divalent and tetravalent elements is usually less than 10 %.

The surface area, particle size and porosity of Fe oxides depend strongly on the conditions under which the crystal growth took place. For instance, high growth rate at minimal temperature values may result in poorly ordered crystal with surface area of up to several hundreds m^2g^{-1}

(Cornell and Schwertman 2003). Contrary, at high temperatures values, low surface area crystals may grow. Cornejo, in 1987, reported that heating micro porous ferrihydrites at 100 ^{0}C transformed it to a mesoporous substance with cylindrical pores due to the expulsion of water. The surface area of 2-line ferrihydrites heated, also fell from 235 to218 m^2g^{-1} (Cornejo, 1987).

To determine the structure of Fe oxides, researchers have principally used techniques such as X-ray diffraction or neutron diffraction with supplementary information coming from infra red spectroscopy, electron diffraction and high resolution electron microscopy. Fe precipitates from Water treatment plants (WTP) have often been described as XRD amorphous. Carlson and Schwertmann in 1987, characterized 67 precipitates from Finish ground water purification plants for drinking purposes with XRD. The results indicated that the Fe –rich precipitates consisted mainly of poorly ordered ferrihydrites ($5Fe_2O_3 . 9H_2O$), which had 2 - 3 "wavelike" peaks of the 6 XRD peaks from 6-line ferrihydrite corresponding to a particle size of less than 25 nm (Carlson and Schwertman, 1987; Pedersen et al., 2005).

3.1.2 The chemistry of Fe oxides

The concentration of dissolved minerals in groundwater and surface water is to a greater extent, controlled by redox reactions between the reduced form and the oxidized form of those elements. It is also governed by the pH of the water solution. Therefore, pH and redox potential are factors which tremendously affect the elements' general properties, including mobility. These factors with their influence on transformation of Fe, the existing forms in water treatment filters and speciation in groundwater are discussed in the sections below.

3.1.2.1 Transformation of Fe

The oxidation of ferrous solutions mostly form amorphous ferrihydrites or ferric hydroxides [Fe $(OH)_3 .xH_2O$], which is a general formula for an unidentifiable amorphos iron oxide mineral. Crystallization of ferric hydroxides may occur within several years in aqueous solutions with low amount of iron but, could take few hours when large amount of dissolved iron is present. However, depending on the prevailing conditions, they may be replaced by well crystallized high specific surface area and well compacted Fe(III) oxyhydroxides such as Geothites, (α-FeOOH), hematite, (α-Fe$_2$O$_3$), Lepidocrocites,(γ-FeOOH) and magnetite,(γ-Fe$_2$O$_3$). (Cornell and Schwertmann, 2003).

Transformation of Fe oxide precursor may occur either by dissolution and/or precipitation processes or via a solid state transformation of internal arrangement within the structure of the solid precursor. The possible pathways for the formation of Fe(III) oxides during soil development process are as shown in figure 3.0. However, the processes can certainly occur also in aqueous solutions containing iron, when subjected to similar environmental conditions in the soil.
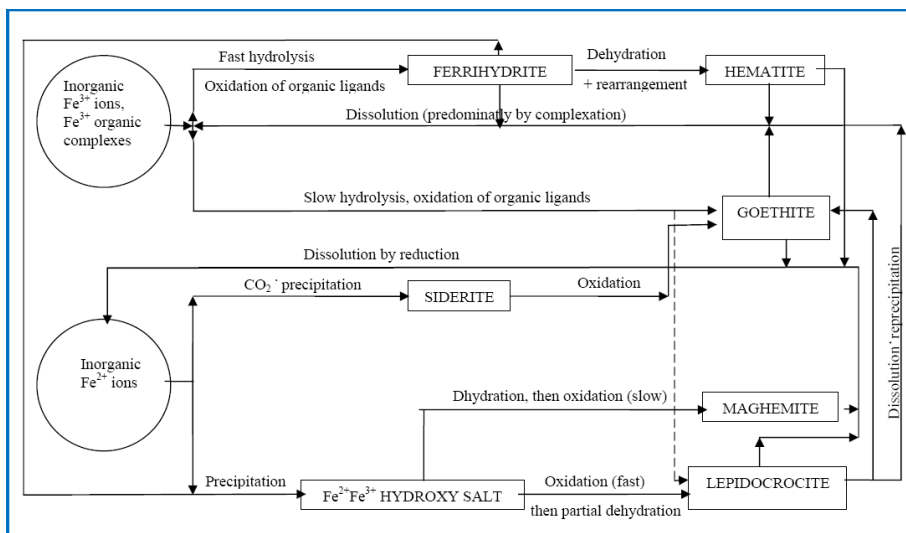
Figure 3.0: Routes of Fe(III) oxides formation in soils and water (Langmuir, 1997).

Since transformation can occur in Fe crystals, it means a less stable crystal relative to the other is first formed before transforming to a more stable one. In other words, less stable ones are formed first normally by fast precipitation before the more stable ones can be formed. The stability of some selected Fe(III) crystalline documented in terms of their solubility values are shown in table 3.1. It is therefore logical that Fe $(OH)_3$, which is a representation of ferrihydrites having the lowest solubility product of about pK_{sp} = 37 to 39 among the ferric minerals listed, could be the product of an initial rapid oxidation of ferrous aqueous solution. However, depending on the prevailing conditions, it may crystallize to form goethite or hematite or other stable Fe crystals. The existence of the less stable ferrihydrites with lower solubility products also explains the slow forming kinetics of the stable once such as goethite and hematite (Langmuire, 1997).

Table 3.1: Stability values of some important Fe(III) hydroxides (Langmuire, 1997).

Name of Fe(III) crystalline	Solubility values(pK_{sp})
Ferric hydroxides	*37-39*
Geothite	*44.1*
Maghemite	*38.8 - 40.4*
Lepidocrocite	*38.7 - 40.6*
Hematites	*43.9*

3.1.2.2 Forms of Fe in water

Iron is mainly mobilized and redistributed during weathering of the igneous and metamorphic rocks. However, the process of mobilization and redistribution occur in the form of either dissolved Fe^{2+} or solid particles of Fe(III) oxyhydroxides in an environment void of oxygen or where oxygen is present, respectively. When groundwater is abstracted to the surface or in surface water, Fe is usually found in the precipitated ferric form Fe(III) and often associated with suspended solids (Degremont, 1991).

```
                          ┌──────────────┐
                          │  Total iron  │
                          └──────────────┘
            ┌────────────────┐        ┌────────────────┐
            │ Ferrous iron   │        │  Ferric iron   │
            │  (bivalent)    │        │  (trivalent)   │
            └────────────────┘        └────────────────┘
         ┌────────┐     ┌──────────┐        ┌────────┐
         │  Free  │     │ Chelated │        │  Free  │
         └────────┘     └──────────┘        └────────┘
```

Precipitated: FeS $FeCO_3$ $Fe(OH)_2$	Dissolved: Fe^{2+} $FeOH^+$	Inorganic complexes: silicates, phosphates, sulphates, etc.	Organic complexes: humic acid, fulvic acid, tannic acid, etc.	Precipitated: $Fe(OH)_3$

Dissolved (or finely dispersed) Fe not retained on filters

Precipitated Fe retained on filters
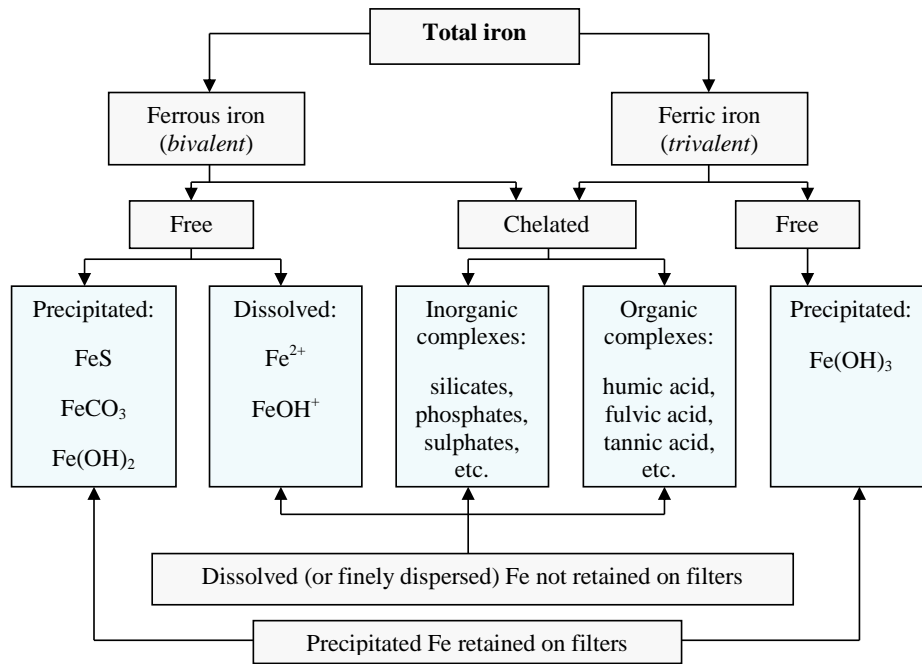
Figure 3.1: Forms of Fe in water (Degrémont, 1991, p.1202).

Figure 3.1 indicates that Fe can transform from soluble form to a non-soluble form depending on the prevailing conditions.

As seen in figure 3.1 several cases where Fe complexes with organics or inorganics exists. The organic complexes are particularly with humic substances such as fulvic, humic and tannic acid, forming peptides and chelates, while the inorganic complexes are normally formed with anions such as phosphates, sulfates and cyanides (Degremont, 1991; Moriguchi et. al., 2005) (see figure 3.1).

3.1.2.3　Fe speciation and forms in groundwater

As mentioned above the concentration of dissolved Fe in ground water is to a greater extent controlled by redox reactions between Fe^{2+} and $Fe(III)$ and governed mainly be pH (please see also figure 3.2)

Additionally, temperature, dissolved oxygen level, and the presence of other soluble ions could also affect Fe species in water. The lower the pH and temperature the longer time is required for completing the oxidation reaction. Increasing dissolved oxygen content decreases the time required for oxidation.

Changes in the oxidation state of Fe in groundwater are of great importance in understanding its properties. Fe^{2+} is the predominant species when there is lack of an electron acceptor such as oxygen (Faust and Aly, 1998). Therefore, changes in either the redox potential (E_h) which is the degree of oxidation or reduction in a system or pH (hydrogen activity) is also efficacious to determine the species present in that particular system at a point in time. The pH- E_h diagram in figure 3.2 also called the Pourbaix diagram, is an appropriate way of determining which form of Fe is stable under specific conditions of pH and E_h. The diagram contains boundaries indicating which forms of Fe/element are stable under sets of pH and E_h conditions. The Nernst equation is needed to derive the relationship between pH and redox potential and
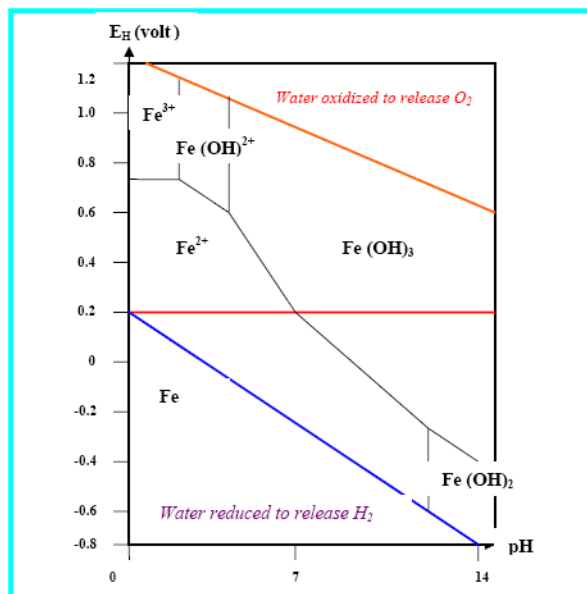
Figure 3.2: Potential-pH diagram for iron system (Sketched from Evangelou, 1998 and Degremont, 1991).

it provides a visual explanation to how pH, E_h and O_2 are mathematically related. The Nernst equation can be written as:

$$E_h = E^0 + (RT/nF)\ \ln(a_{oxidation}/\ a_{reduction}) \tag{3.0}$$

Where, E_h = redox potential, in volts, compared to standard hydrogen half-cell, which has a value of 0.0V

E^0 = Standard reduction potential at pH = 0.25 °C, at 1 atmosphere.

R = gas constant, which is equivalent to 8.314 $Jmol^{-1}K^{-1}$

T = absolute temperature in degrees Kelvin (K)

n = number of electrons transferred

F = Faraday's constant, equivalent to $96487 Cmol^{-1}$

$a_{oxidation}$. $a_{reduction}$= activity of oxidized and reduced species, respectively. However, when concentration is very small as in ideal diluted solutions, then activity can be turned into concentration in mole per Liter or partial pressures for gases.

$$\Rightarrow E_h = E^0 + (RT/nF)\ \ln \frac{a_{O_2} \times (a_{Fe^{2+}})^4}{(a_{H_2O})^2} \tag{3.1}$$

The activity of water is 1 at standard temperature, 298 K (25°C), E^0 = +1.23 V for the redox couple O_2/H_2O and partial pressure of oxygen = 0.21 atmosphere.

$$E_h = 1.23 + (8.314 \times 298.15/4 \times 96487) \times 2.303 \times \log a_{O_2} \times (a_{H^+})^4 \tag{3.2}$$

$$\Rightarrow 1.23 + 0.0148 \log a_{O_2} + 0.059 \log (a_{H^+})^4$$

But $-pH = \log a_{H^+}$

$$\Rightarrow E_h = 1.23 + 0.0148 \log 0.21 - 0.059 pH$$

$E_h = 1.22 - 0.059\ pH$ (This equation relates to water in a natural system)   (3.3)

It is worth mentioning that the equations for the oxidation and reduction of water written above are theoretical. The theoretical stability field of water in E_h and pH terms bounds all theoretical redox reactions occurring in water. The upper limit of water stability field is defined by E_h and pH values for which liquid water is in equilibrium with $O_2(g)$ at 1 bar pressure. On the other

hand, the lower limit is define by E_h and pH values for which liquid water is in equilibrium with $H_2(g)$ at 1 bar pressure.

In considering Fe in a natural system,

$Fe^{2+} = Fe^{3+} + e^-$ (E_h dependent) (3.4)

$\frac{1}{2}H_2O = 4H^+ + O_2 + e^-$ Water dissociation (3.5)
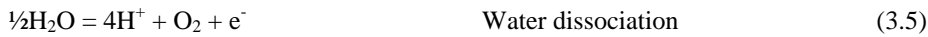
Combining the two equations,

$Fe^{2+} + H^+ + \frac{1}{4}O_2 = Fe^{3+} + \frac{1}{2}H_2O$

$Fe^{2+} + H_2O \leftrightarrows Fe(OH)_3 + e^- + 3H^+$ (Both Eh and pH dependent) (3.6)
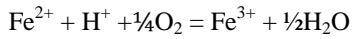
$E_h = E^0(Fe(OH)_3/Fe^{2+}) + 0.592V \log(a_{H^+}/a_{Fe^{2+}})$ (3.7)

But, $3 \log a_{H^+} = -3pH$

$\Rightarrow E^0\{Fe(OH)_3/Fe^{2+}\} - 0.592 \times 3pH$

Therefore,

$E_h = Constant - (0.0592V \times 3)pH$ (3.8)

Equation 3.6 also depicts the natural conditions by Fe- H_2O system and it could be used to show the boundaries of the regions of dominance of the various species of Fe at different pH and Eh as in figure 3.2. The activity of two iron species is equal and set to e.g. 10^{-5} at the demarcation line between two regions of individual species.

It could also be deduced from figure 3.2 that soluble Fe(II) can be transformed into precipitated forms such as $Fe(OH)_2$ or $Fe(OH)_3$ or $Fe(OH)^{2+}$ by varying the pH and redox potential of the groundwater. Most natural water may have pH values between 5.0 to 8.5 and redox potential (E_h) of about -7 to +12 (Faust and Aly, 1998 ; El Azher et. al.,2008). Thus, in groundwater where oxygen is lacking, the pH could be low and the Fe will most likely be in the reduce state. At higher pH values, which usually exist in surface water or when groundwater is abstracted, a precipitated form of Fe normally exist.

3.1.3 The mechanism of Fe removal in filters and kinetics of fe oxidation in filters.

As discussed earlier in chapter 2, several mechanisms contribute to Fe removal in filters. They are oxidation by air or by chemical means this is followed by hydrolysis of ferrihydrite, then flocculation or aggregation of hydroxide particles and finally removal of flocs. The entire mechanism is known as the traditional or purely physico-chemical method of iron removal. (Ankrah and Søgaard, 2009)

For Fe in groundwater, the kinetic investigation may however be affected by conditions such as pH, carbon dioxide, silicates and the presence of organic material. These conditions can influence the speed of a chemical reaction and also affect the reaction's mechanism and transition states. Mathematical models can describe the characteristics of the Fe oxidation in the groundwater can therefore be constructed (Stumm and Lee, 1961)

Traditionally, iron in groundwater is removed by the oxidation of the ferrous iron in the raw water to insoluble ferric hydroxide by aeration followed by precipitation. The Fe precipitate is subsequently filtered off. This can be described by the equation below:

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \tag{3.9}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \tag{3.10}$$

Combining equation (1) and (2), will give equation 3 below:

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2\tfrac{1}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+ \tag{3.11}$$
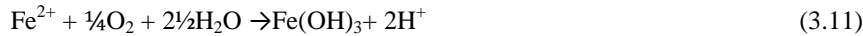
It is worth mentioning that the $Fe(OH)_3$ in the equation (3.11) is hydrolysis of Fe^{2+}. It is indicated in the equation (3.11) as the final product of ferrous iron oxidation but, it is a simplification of the reality of the oxidation of Fe in groundwater. Morgan and Stum already in 1964 proposed the expression:

$$-\frac{d\left[Fe^{2+}\right]}{dt} = k\left[Fe^{2+}\right]\left[OH^-\right]^2 po_2 \tag{3.12}$$

Integrating equation

$$-\ln\frac{\left[Fe^{2+}\right]_t}{\left[Fe^{2+}\right]_0} = k\left[OH^-\right]^2 po_2 t \tag{3.13}$$

Where, k = rate constant = 2.6×10^{13} min^{-1} atm^{-1}mole^{-2} at 20.5^{0}C

$[Fe^{2+}]_0$= Fe^{2+} concentration (mole/l)

$[Fe^{2+}]_t$= Fe^{2+} concentration at time t

$[OH^-]$= hydroxyl ion concentration (mole/l)

Therefore the time required to oxidize half of the present Fe in the water should be

$\log t_{\frac{1}{2}} = 14.318 - 2pH$ (3.14)

Studies have shown that Fe removal plants with surfaces of their filter materials coated with Fe oxide often play a key role in the oxidation and removal of Fe^{2+} in the solution (Søgaard et. al., 2001). This process is also termed as catalytic Fe removal since the Fe^{3+} coatings act as catalyst for the removal of Fe^{2+}

Apart from the homogenous oxidation of Fe^{2+} as discussed above, Fe oxygenation is greatly accelerated in the presence of surfaces. A simultaneous oxidation of iron also occur where the poorly ordered hydrous Fe oxides act as highly reactive sorbent of dissolved Fe^{2+} and other minerals in the ground water. The Fe(III) thereby form strong inner sphere complex with Fe^{2+}. The Fe(III) therefore catalyze Fe^{2+} oxidation (Barry et. al., 1994). At constant pH and O_2 concentration, the rate equation can be written as:

$R = -\dfrac{d[Fe(II)]}{dt} = (k + k' [Fe(III)]) [Fe^{2+}]$ (3.15)

Where,

k   = rate constant for the homogeneous reaction = $k_0[O_2][OH^-]^2$

k′   = rate constant for the heterogeneous reaction = $k_{so} [O_2]K/ [H^+]$

k_o and k_{so} are the real rate constants for the reactions and K is the equilibrium constant for the adsorption of Fe(II) on Fe(III) hydroxide with the numerical values:

$k_o = 2.3 \times 10^{14} \, l^3 \, mol^{-3} \, s^{-1}$

$k_{so} = 73 \, 1 \, mol^{-1}s^{-1}$ and

$K = 10^{-9.6} \, mol \, 1^{-1} \, mg^{-1}$

The effect of Fe(III) autocatalysis is pronounced at Fe(III) concentration exceeding 5-10 mg/l (Tamura et al., 1976).

Besides purely physico-chemical and chemical catalytic processes of iron precipitation, bacterial mediation in Fe removal is also known to actively precipitate Fe in filters by 1000 folds faster than that of the purely physico-chemical method (Søgaard et. al., 2001). Therefore, biotic

involvement in Fe^{2+} oxidation cannot be under estimated. The oxidation kinetics is further enhanced when Fe(III) oxides in association with bacteria intermix to form bacteriogenic Fe oxides, which consist of bacteria cells and hydrous ferric hydroxides.

In biotic oxidation, the oxidation is often attributed to a particular bacteria species. The kinetic model of the influence of bacteria is as a function of the bacterial density (or the quantity of volatile solids present) and total dissolved Fe^{2+} concentration can be written as:

$$R_4 = k_4[\text{bacterial exopolymer sites}][Fe(II)][OH^-]^2 pO_2 \tag{3.16}$$

Therefore a summary of the general rate expression including homogenous, heterogeneous, bacterial exopolymers sites and other processes not explicitly considered, can be written as:

$$R = -\frac{d\left[Fe^{2+}\right]}{dt} = \{k_0\{Fe^{2+}\} + k_1[Fe(OH)^+]$$

$$+ k_2[Fe(OH)_2]\}pO_2$$

$$+ k'_3 A[Fe^{2+}][OH^-]^2 pO_2$$

$$+ k_4[\text{Bacteria}][Fe^{2+}][OH^-]^2 pO_2$$

$$+ R_{\text{other}} \tag{3.17}$$

Where

k_0-k_2 = first order homogeneous rate constants in water, adjusted for the presence of ligands and catalysts active in the homogeneous oxidation process (s^{-1} atm^{-1})

k'_3 = overall rate constant for heterogeneous, abiotic processes (1^2 $mol^{-2}m^{-2}s^{-1}atm^{-1}$)

A = heterogeneous, abiotic surface area (m^2)

k_4 = rate constant for some bacteria, the term repeated for various strains and corrected for specific conditions (units are: 1^3 $mol^{-2}s^{-1}atm^{-1}cells^{-1}$ for bacteria measured in cells/l or 1^3 $mol^{-2}s^{-1}atm^{-1}g^{-1}$ for bacteria measured as grams volatile solids/l)

R_{other} = the oxidation rate attributable to processes not considered explicitly, such as the presence of reactive species like hydrogen peroxide ($mol\, l^{-1}s^{-1}$) (Barry et. al., 1994).

Beside the aforementioned factors which affect the velocity constant k, it is also observed that the increase in the k value is based on the mechanism of Fe removal (see table 3.2 and 3.3).

Table 3.2: Velocity constant for the precipitation of Fe(II) to Fe(III) by purely physico-chemical Fe removal (Søgaard et. al., 2001).

Examples of k values ($\times 10^{13}$ L^2. min^{-1}. atm^{-1}. mol^{-2}) from the expression of purely physico-chemical Fe^{2+} oxidation/precipitation mentioned in the text					
k value	*T /^{0}C*	*pH*	*Fe[(II)]$_o$/µM*	*Medium*	*Reference*
0.5-2.4	10.5-14.5	7.5-7.8	30-90	Ground water	Gosh et al., 1966
2.9	25	6.8	30-90	Well water	Gosh, 1974
60	?	6.25	?	Tap water	Stumm and Lee, 1961
1.9± 0.7	10	7.0	6	Oxic Lake	Davison and Seed, 1983
2.2±0.8	10	6.8-7.2	7-400	Anoxic Lake	Davison and Seed, 1983
8± 2.7	20.5	6.4-7.5	< 50	Na$_2$CO$_3$/CO$_2$	Stumm and Lee, 1961
16-21	25	6.3	< 100	Na$_2$CO$_3$/CO$_2$	Theis and Singer, 1974

Table 3.3: Velocity constant for the precipitation of Fe(II) to Fe(III) by biotic iron removal (Søgaard et. al., 2001).

k-values($\times 10^{16}$ L^2.min^{-1}. atm^{-1}. mol^{-2}) for biotic Fe^{2+} oxidation/precipitation in the biological sand filter with Fe precipitating bacteria *Gallionella ferruginea* using the kinetic expression for Fe^{2+} oxidation/precipitation mentioned in equation (3)					
k value	*T /^{0}C*	*pH*	*Fe[(II)]$_o$/µM*	*Medium*	*Reference*
3.3- 4.4	10.2-10.7	5.7-5.8	2.3	Polluted groundwater	Søgaard et. al, 2001
10- 12	10.2-10.6	5.7-5.8	21	Polluted groundwater	Søgaard et al, 2001
19- 21	10.2-10.7	5.6	52	Polluted groundwater	Søgaard et al, 2001
7.7- 13	10.3-10.9	5.7	126	Polluted groundwater	Søgaard et al, 2001

Table 3.2 depicts the velocity constant for the purely physico-chemical oxidation (homogenous oxidation), where the raw water is normally oxidized by only aeration. This was about $\times 10^{13}$ M^{-2} atm^{-1} min^{-1}

However, the k value is also known to be increased by 10 times due to chemical catalytic effects (heterogeneous oxidation).

Again, a 1000 times increase in the k value was observed by Søgaard et al 2001, when the Fe were removed from the filters by biological means (table 3.3). A plausible explanation for the sharp increase in the k value was that the iron bacteria played a catalytic effect on the velocity of the oxidation/precipitation in the biological sand filters. Thus, the bacteria exopolymers form a mesh or a network in between the pore spaces of the sand filter material, which are in contact

with the Fe in the solution. As a result, the Fe in solution either directly sorb onto the surfaces of the exopolymers or is attached to the exopolymers in a microcrystalline form (Ankrah and Søgaard, 2009).

3.1.4 Factors affecting the rate of oxidation

Several factors are known to affect the rate of Fe oxidation in water and they are as discussed below:

3.1.4.1 pH and alkalinity

The kinetic equation 3.12 depicts that the rate of Fe oxidation is dependent on the concentration of Fe^{2+}, dissolved oxygen and hydroxide ions or equally, the pH of the groundwater. Therefore, at pH of about 6 to 8.5, which normally exist in groundwater has a remarkable influence on the reaction. For every unit increase in pH, the rate also increased by 100 fold. See figure 3.3

Linearization of the experimental data by plotting the ratio of observed to initial concentrations of ferrous Fe on a logarithmic scale against time
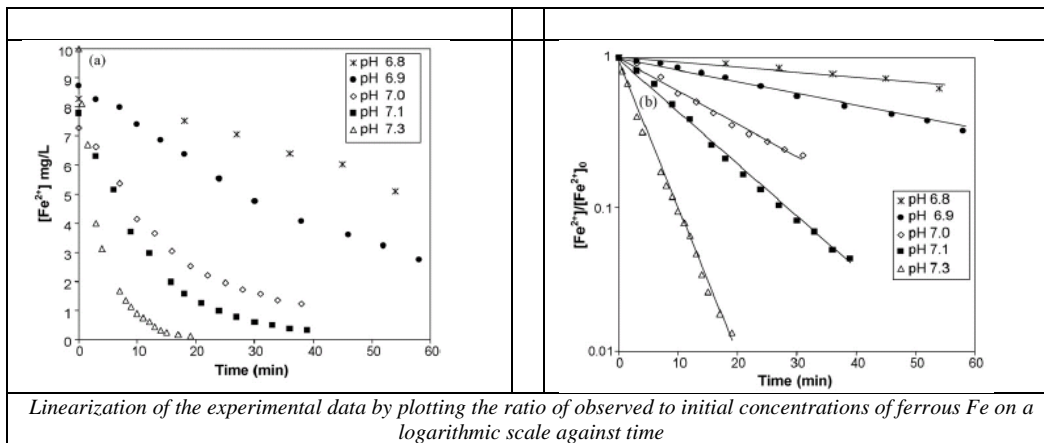
Figure 3.3: Evolution of Fe2+ concentration Vs time as a function of pH for [Fe]0 $\simeq$ 10mg/l Vs time (Azher et al., 2008).

Similarly, a correlation exists between alkalinity and the rate of oxidation. The buffer intensity (β in eq/pH) of water affects the rate of Fe oxidation at values greater than 4.0×10^{-3} eq/pH and postulated the following rate equation applies (Jobin and Ghosh, 1972).

$$-\frac{\left[Fe^{2+}\right]}{dt} = kpO_2 \left[Fe^{2+}\right]\left[OH^-\right]^2 [\beta]^n \tag{3.18}$$

Where

$$\beta = 2.3 \{[H^+]+[OH^-]+C_T [\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_2\alpha_0]\} \tag{3.19}$$

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{3.20}$$

$$\alpha_o = \frac{H_2CO_3}{CT}, \quad \alpha_1 = \frac{H_2CO_3^-}{CT} \text{ and } \alpha_2 = \frac{H_2CO_3^{2-}}{CT}$$

(The concentrations are expressed in mol/l).

Whereby, β depends on pH, temperature, alkalinity, and dissolved solids.

It was noted that the reaction proceeded at a higher rate in a solution of higher alkalinity. This is as a consequent of the CO_2 and HCO_3^- buffer system which resists the changes in acidity that occur during the oxidation reaction (Stumm and Singer, 1966)

The alkalinity of groundwater provides the buffer capacity to prevent excess pH drop during the oxidation of Fe in groundwater. In most cases, alkalinity also influences the characteristics of the Fe precipitate. Normally, at high alkalinity, (above 250 mg/l $CaCO_3$), carbonate Fe precipitates are formed rather than Fe hydroxides and a larger part of the precipitate is in the ferrous form rather than the ferric form. Contrary to the high alkalinity, at lower alkalinity values, slower oxidation and poorer floc formation of Fe precipitate occur (Snoeyink and Jenkins, 1980).

3.1.4.2 Possible catalytic effect of some elements

Oxidation is accelerated by anions such as *F^-, $H_2PO_4^-$, and HPO_4^{2-}* and lowered by others in the order *$ClO_4^->NO_3^->Cl^->H_3SiO_4>Br^->I^->SO_4^{2-}$*. For instance, silicate is an integral part of rock, especially igneous rock and clay minerals. In groundwater, silicate can be thought of as salts of an acid oxide, SiO_2, which forms silicic acid, H_4SiO_4. Therefore, the presence of silicate can interfere with Fe oxidation (Weber and Stumm, 1965). The other anions may compete with oxygen for the positions on the surfaces of the precipitated iron oxides and in that way delay the uptake of an electron from Fe(II) resulting in a slower oxidation/precipitation reaction.

Robinson et. al. in 1975, demonstrated beyond doubts that silicates can be influenced by the Fe(II) and catalyze the rate of oxidation. (see kinetic equations in 3.21 to 3.23)

In the presence of silicates at pH from 6.5 to 7.2,

$$-\frac{d\left[Fe^{2+}\right]}{dt}=k(OH^-)^2+k_{si}(H_4SiO_4)^{\frac{1}{2}}(OH^-)^{\frac{1}{2}}pO_2\left[Fe^{2+}\right]$$

(3.21)

Integrating equation 3.21,

$$-\ln\frac{d\left[Fe^{2+}\right]_t}{\left[Fe^{2+}\right]_0}=k(OH^-)^2+k_{si}(H_4SiO_4)^{\frac{1}{2}}(OH^-)^{\frac{1}{2}}pO_2t$$

(3.22)

$$t_{\frac{1}{2}}=\frac{\ln2}{\left[k(OH^-)^2+ksi(H_4SiO_4)^{\frac{1}{2}}(OH^-)^{\frac{1}{2}}\right]\times pO_2}$$

(3.23)

The above equation shows that the presence of silicates certainly interferes or slows the rate of Fe oxidation as compared to the rate of Fe oxidation without silicates. Silicate is also known to interfere with hydrolysis thereby increase nucleation and finally prevent the growth of hydrous Fe(III) oxides. This is as a result of silicic acid competition with water and hydroxides for coordination site on the Fe. At silicate levels of 7 mg/l the Fe(III) precipitates is generally amorphous (Olson and O´Melia, 1973).

3.1.4.3 Oxidation in the presence of ferrous carbonate

The mechanism underlining the oxidation of Fe^{2+} in the presence of carbonate is that the introduction of oxygen allows dissolved CO_2 over saturating the groundwater to escape, causing an increase in pH, thereby leading to over saturation of ferrous carbonates. Crystallisation of the ferrous carbonates precipitates finally occur.

$$Fe^{2+} + HCO_3^- \leftrightarrows FeCO_3(S) + H^+$$

(3.24)

In groundwater, where the rate of decomposition is rapid and oxygen is lacking. The carbon dioxide concentration will increase and alkalinity may often exceed 5×10^{-3} eq/l or in other words, there will be a decrease in pH below 7. The solubility of the total carbonic species in that groundwater is therefore dominated by the formation of ferrous carbonate and it becomes the most stable Fe specie. (Ghosh, 1966) (see figure 3.4)
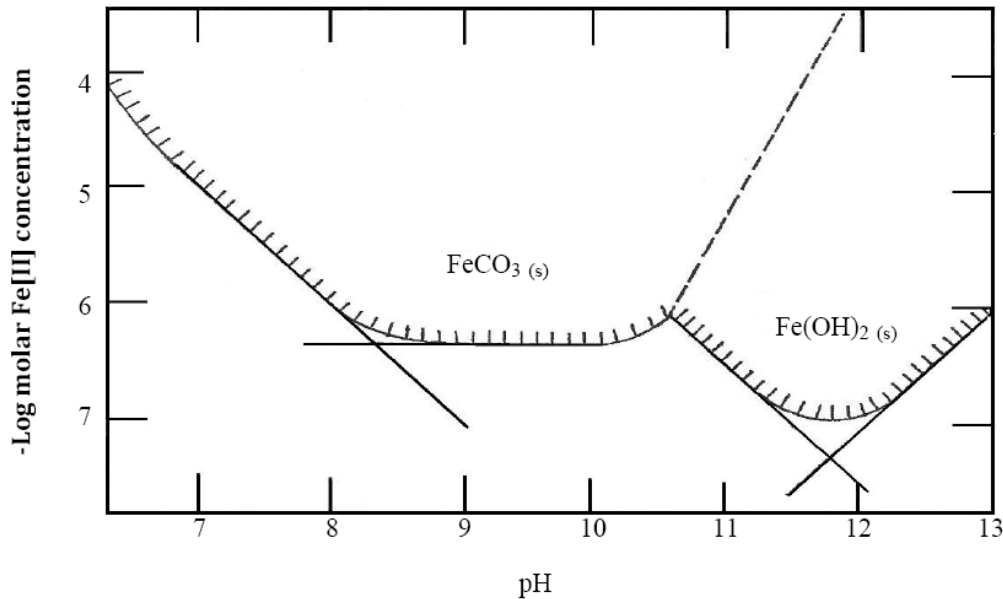
Figure 3.4: Stability of ferrous iron in water containing 10-5 of total carbonate species (Olson and Twardowski, 1974).

Also, it could be extrapolated that if Fe $(OH)_2$ is present at all, it will not be precipitated below pH values of about 9.5. This hypotheses was inferred by Olsen and Twardowski who used thermodynamic and floc filterability approach to investigate the precipitation of ferrous hydroxide, ferrous carbonate and ferric hydroxide. They indicated that it was logical to anticipate siderite or ferrous carbonate to precipitate in water treatment plants treating hard water. If that is the case, then the rate of oxidation will be very slow (Stumm and Singer, 1966; Olson and Twardowski, 1974).

3.1.4.4 Oxidation in the presence of organic matter (Humic substances)

Humic materials, being it in the dissolved or solid phase in water may carry the functional group such as carboxyl (R COOH) and hydroxyl (OH). Such groups undoubtedly could act as ligands to form complexes or coordinates and form chelates with metals such as Fe(III) (Vanloon and Duffy, 2005; Faust and Aly, 1998)

The organic materials (humic materials) can therefore act as inhibitors such that the ferrous-ferric system which is formed in the process of oxidation will intern act as an electron catalyst for the oxidation of the organic material by the oxygen (see equation 3.25 to 3.27). As a consequence, the entire rate of oxidation of Fe(II) in the water may be slowed down based on the rate at which Fe(II) is reduced by the organic matter. The reactions are as summarised:

Fe(II) +¼O$_2$ +organic = Fe(III) – organic complex $\quad\quad\quad$ (3.25)

Fe(III) – organic complex = Fe(II)± oxidized organic $\quad\quad\quad$ (3.26)

Fe(II) + ¼O$_2$ + organic = Fe(III) – organic complex $\quad\quad\quad$ (3.27)
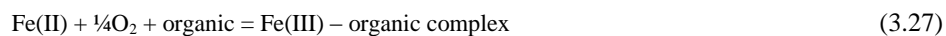
3.1.5 Hydrolysis of Fe in filters

As discussed earlier, the removal of iron from groundwater has mostly been accomplished by an oxidation reaction followed by the precipitation of a crystalline Fe, which is subsequently removed by sand filters. Therefore the filterability of the iron is remarkably affected by the sort of Fe mineral precipitated in the filters during the oxidation process.

In aqueous solutions, free metal ions are complexed with water and the metal ions are said to be hydrated. The interaction of these hydrated metal ions with acid and base is a ligand exchange reaction commonly known as hydrolysis (Jenkins and Snoeyink, 1980).

In metal ion hydrolysis, proton(s) is/are transferred from an acid to water or from water to a base. The hydrated metal cation therefore acts as the proton donor or acid. This reaction is therefore of an extreme importance in natural water since the resultant pH affects the distribution of the species in that solution

In the presence of water, an Fe(III) salt dissociates to form the purple hexa-aquo ion

$$Fe(OH)_3 + H_2O \rightarrow Fe(H_2O)_6^{3+} + 3OH^- \quad\quad\quad (3.28)$$

The electro cation induces the water ligands to deprotonates. It is a stepwise process which leads to eventual deprotonation of the entire six ligands . That is:

$Fe(H_2O)_6^{3+}$, $FeOH(H_2O)_5^{2+}$, $Fe(OH)_2(H_2O)_4^{+}$, $Fe(HO)_3$
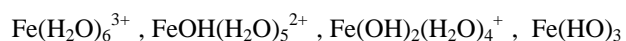
These processes normally lead to the creation of polynuclear hydroxyl complexes and ultimately lead to the formation of precipitates (Jenkins and Snoeyink, 1980).

3.1.6 Surface properties of Fe oxides

Surface speciation of Fe oxide highly affects the adsorbing capacity of cations or anions to their surfaces and it is invariably dependent on the pH of the solution. The point at which there is no charge on the surface of Fe oxides is known as the point of Zero charge(PZC). This usually ranges from pH values of 8.5 to 9.3 for pure Fe oxides without adsorbing ions. Adsorption of cations will shift the PZC to higher pH while adsorption of anions will shift the PZC to lower pH (Vanloo and Duffy, 2005). See figure 3.5
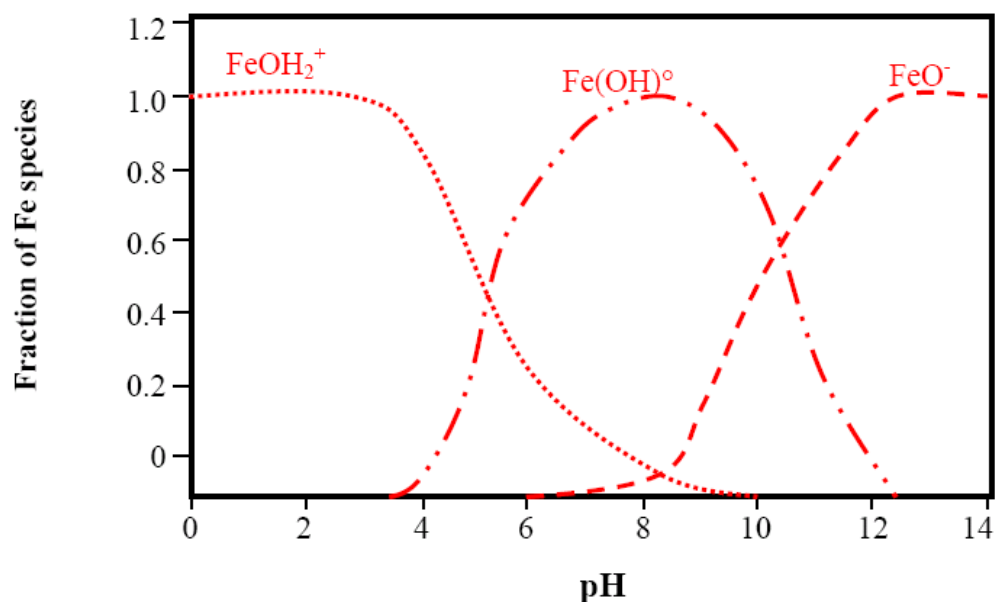
Figure 3.5: Surface speciation of Fe oxides in water.

One way of measuring the surface speciation/charge of Fe oxide, which may exist and interact with each other as colloidal particles in a solution is by measuring the Zeta potential of the solution. That is with photo electrophoresis particle mobility is measured as a function of pH under the influence of ultra violet radiation. Zeta potential is a very good index of the magnitude of the interaction between colloidal particles and it´s measurements are used to assess the stability of colloidal system (Vanloo and Duffy, 2005). The magnitude of the zeta potential gives an indication of the potential stability of the colloidal systems. If all the particles have large negative or positive zeta potential, then they will repel each other and there is dispersion stability. On the other hand, if the particle have low zeta potential value, then there is no force to prevent the particle coming together and the surface charge of the colloidal particles are said to be destabilized. In this way, the particles will coagulate/flocculate.

Chapter 4

Biological Fe removal from groundwater for drinking purposes

4   Introduction

Oxidation processes play a pivotal role in converting Fe from their soluble forms into insoluble ones. It is therefore only when the elements, initially present in their reduced forms, are successfully oxidized that they can be precipitated to enable them to be removed by sand filters. In conventional water treatment plants in Denmark, engineers usually achieve the oxidation process by aeration (see figure 4.0).

Cascading aeration method in Holstedbro WTP   *Fountain aeration process in Astrup WTP*

Figure 4.0: Cascading (Step) and fountain aeration process at Holstedbro and Astrup water treatment plants in Denmark.

The aeration methods of oxidation is typically the cheapest, safest and, hence, the traditionally preferred way of oxidizing raw water. However, in places where the groundwater contains contaminants like natural organic matter (humic substances) and higher concentrations of inorganic substances like silicates, difficulties may arise in precipitating the iron by simple aeration. This is why chemical oxidation by the addition of substances such as chlorine, potassium permanganate, hydrogen peroxide, ozone or chlorine dioxide may sometimes be required. See the equation 4.0.

$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + K^+ + 5H^+ \qquad (4.0\ )$$
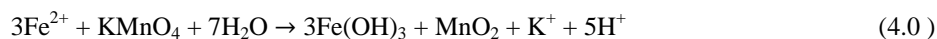
The use of chemicals in water treatment plants is always strenuously minimized due to the occurrence of unpleasant by-products of strong oxidation and the increased operational cost. In Denmark, for instance, the addition of chemical oxidants to raw water is in principle always avoided; they are used on rare occasions with specific permission and under strict supervision by the environmental authorities (Faust and Aly, 1998; Katsoyiannis et. al., 2004).

Fe oxidation by biological means is one of the most recent technologies used by water treatment engineers. It has been successfully applied as a method of Fe removal, since the microorganisms play a key role not only in oxidizing the elements but also in assisting the precipitation of Fe. The biological Fe oxidation method has been identified as catalytic in nature for the precipitation of Fe, cheaper than chemical oxidation, having a high removal capacity, and causing a rapid oxidation of soluble Fe(II) to insoluble Fe(III), which are found to be more compact or otherwise superior in nature to the precipitates formed by other treatment processes. Fe-oxidizing bacteria are generally robust and, because of the variety of species involved, one type or another develop satisfactorily and grow under a wider range of conditions in the filter materials than would be expected were only a single species involved. What is more, the Fe bacteria are known to be non-pathogenic and cause no harm or disease when ingested via water. Due to the numerous advantages that biological iron removal offers over the purely physicochemical method it has the potential to become the most favored method and there seems to be no doubt that it could revolutionize Fe removal in water treatment plants (Ankrah and Søgaard, 2009 ; Dimitrakos Michalakos, 1997).

Biological iron removal is known to overcome most of the problems associated with the application of conventional iron removal processes. Therefore, this chapter reviews pertinent literature on biological iron removal.

4.1 The effect of Fe bacterial in filter media

Ever since Fe bacteria were discovered, they are recognized increasingly as principal part of a wide range of geochemical reactions in aqueous environments. The prospects of using it to remove Fe from drinking water has been vigorously exploited by water treatment engineers, but the mechanism underlining the iron removal process by the iron bacteria is still not fully inferred. There are still controversies about whether the process of iron removal in sand filters could be either solely biological or iron oxidizing bacteria play a supplementary role in the physico-chemical iron removal process under certain conditions. The main experimental difficulty in proving autotrophy by these iron bacteria is that the organisms grow and thrive well between the pH of about 5 to 9. At these pH values, iron Fe^{2+} is physico-chemically/ non-biologically oxidized to Fe^{3+}, making it a difficult task to decide if the bacteria contributed to the oxidation of Fe^{2+}. Vayens et. al. in 2006, assessed the extent of each oxidation type(purely physico-chemical or biological) by setting-up a pilot scale trickling filter to test for iron removal from potable water. Their findings revealed that Fe removal was caused by both physico-chemical and biological reactions (Boettcher and Viswanathan, 1991). Moreover, it is now certain that the presence of biological phenomenon in the filters substantially reduces the iron concentration in the treated water by breaking the problem of the difficulty to remove Fe-organic or Fe-silicate

complexes and also increase the rate of oxidation of Fe^{2+} to Fe^{3+} (Olsen et. al., 1981; Hanert, 1992).

Metabolism of iron removal bacteria

The oxidation reaction of ferrous iron to ferric iron by biological means is similar to that of the physico-chemical reaction and it is as indicated in equation 4.1. It is known to be one of the most significant characteristics of iron oxidizing bacteria, but very little is known about the mechanism involved in initiating and perpetuating this exothermic biochemical iron oxidative processes in drinking water plants.

$$4Fe^{2+} + O_2 + 10H_2O \leftrightarrows 4\ Fe(OH)_3 + 8H^+ + Energy \qquad\qquad (4.1)$$
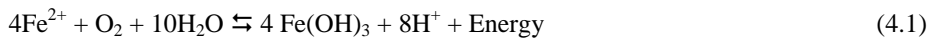
It is now certain that the iron oxidizing bacteria derive their essential energy requirements through a strictly chemolitho-trophic process (Stumm, 1992). This is an enzyme-mediated oxidation of Fe^{2+} with a concomitant fixation of carbon dioxide into an assimilable nutrient for the iron oxidizing bacteria. As a result, precipitation of Fe^{3+} salts occurs either by enzymatic action of autotrophic bacteria (intracellular) or by catalytic action of polymers excreted by the bacteria sheath (extracellular). The original source of carbon dioxide is principally from the groundwater where organic compounds in form of humic substances is transformed by anaerobic fermentation in ground water and by gravity transferred by water to e.g. 100 m deep below the ground surface. Humic substances are present in groundwater either chelated with Fe^{2+} or existing solely in the anoxic zone (Bromfield, 1956; Søgaard et. al., 2001).

Several strains of iron oxidizing bacteria may be involved in water treatment systems but in all cases, the biological oxidation process is seen as catalytic in nature, causing a rapid oxidation of soluble ferrous Fe to insoluble ferric hydroxides found to be more compact or superior to the precipitates formed from other treatment processes (Colmer et. al., 1950).

4.2   Biotic conditions for iron precipitation

A shift from abiotic to biotic precipitation is governed by the chemical and the physical properties of the water. The most important conditions for the biotic precipitation are enumerated at neutral or slightly acidic pH, a change from negative redox potential to redox potentials up to about 200-320 mV and oxygen levels changing from zero to 2-3 mg/L, together with considerable amount of CO_2. However, redox potential and pH are the main factors that determined whether biotic precipitation will take place or not. The stringent pH and Eh limits required by the iron bacteria describes them as very good example of gradient organism that develops under neither strongly reducing conditions nor in an fully oxidized milieu (Colmer et. al., 1950).

The table 4.0 below compares three of the most important iron bacteria in terms of their characteristic features as well as conditions required for their growth and development.

Table 4.0: Comparison of conditions and features of Gallionella, Leptothrix and Sphaerotilus (Bergey and Holt, 1994; Balows et. al., 1992).

	Gallionella	Leptothrix	Sphaerotilus
	Chemolithoautotrophic	Chemoheterotrophic	Chemoorganotroughs
Cell Shape and size	Kidney shape: Width: 0.5 – 0.7 µm Length: 0.8 – 1.8 µm. Gram negative cell walls	Rod Shape Width: 0.6 – 1.4 µm Length: 1.0 – 12.0 µm Gram negative cell walls	Rod shape Width: 1.2 – 2.4 µm. Length: 2.0 – 10 µm Gram negative cell walls
Sheaths/Stalk	Width: 2 nm Shape: Twisted Surface structure: Dissolves in reducing agents and weak acids	Width: 1.5 – 3 µm Shape: Hollow sometimes and straight Surface structure: Rough Detaches from the body intermittently	Width: Not specified Shape: Hollow sometimes and straight Surface structure: Smooth
Energy / Carbon Source	Carbon dioxide in form of principally HCO_3^-	Sugars, organic acids and glycerol	Carbon sources like sugars, organic acid. They also metabolize nitrogen compounds.
Type of iron produced	Ferrihydrite (Ferric hydroxide)	Ferrihydrite (Ferric hydroxide)	Ferrihydrite (Ferric hydroxide
Living conditions	Anaerobic and microaerophilic Oxygen content: 0.1 – 3 mg/l increasing Temp: About 8 – 16 ^{o}C Oxidation/Reduction Potential: negative -300 mV increasing Fe^{2+} content: 2 – 25 mg/l pH: 6 – 7.6	Slightly aerobic to aerobic Oxygen content: 1mg/l Temp: 10-40 ^{o}C Oxidation/Reduction Potential: Not specified Fe^{2+} content: Not specified pH: 7.5	Anoxic and aerobic Oxygen content: <0.1 mg/l – full saturation oxygen saturation. Temp: About: 10–40 ^{o}C Oxidation/Reduction Potential: Not specified $Fe2^+$ content: Not necessary pH: 5.4 – 9

Søgaard, et. al.,2001 Sharma, 2005, and Mouchet, 1992 described the iron oxidizing bacteria as gradient organisms. This means that they possess a unique property of causing oxidation and precipitation of soluble Fe^{2+} at conditions which straddles the theoretical boundary between the field of Fe^{2+} solubility and the formation of Fe^{3+} precipitates, as defined by the thermodynamic

analysis of the electrochemical equilibrium. See figure 4.1. They therefore thrive well under conditions that are neither completely reduced nor completely oxidized. In water treatment plants, the conditions could be manipulated and optimized by aerating or stripping off CO_2 from the ground water.
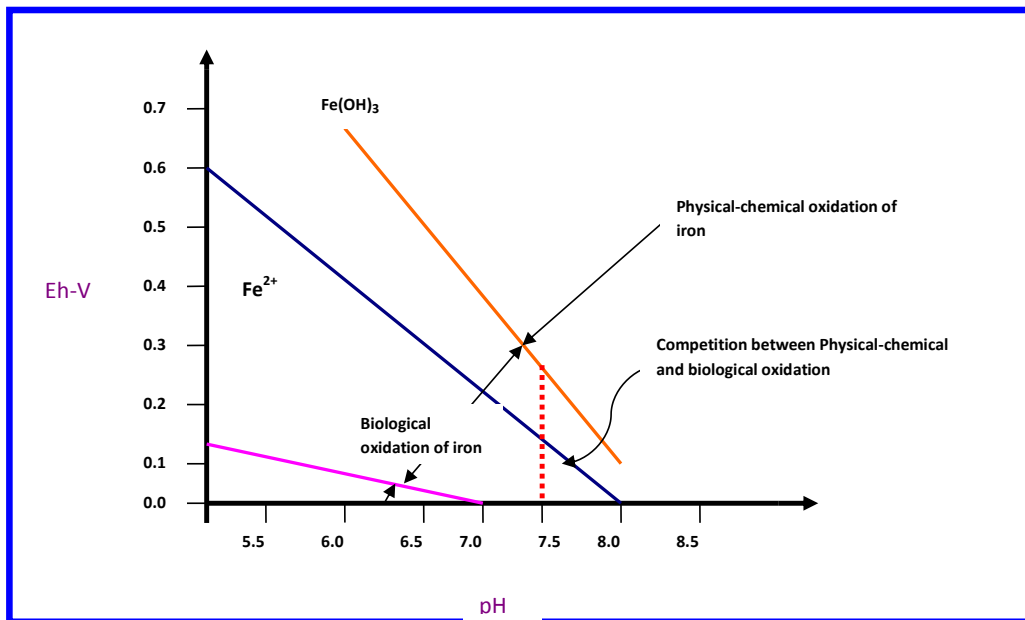
Figure 4.1: Field of activity of Fe bacteria with respect to Eh − pH (Mouchet, 1992).

4.3   Important Fe removal bacteria and their morphology

Several bacteria genera and species are found in a variety of soils and aquatic habitats associated with Fe. They require special conditions for their growth and development and as a consequence, produce extracellular polymeric substances. The required condition are mostly water, temperature, nutrient source, carbon dioxide and electron acceptor source, which in mostly ferric iron in the case of the iron oxidizing bacteria. These bacteria usually form a community encapsulated within the self developed polymeric matrix, which they produce and adhere to surfaces such as flocs of Fe particles produced in water treatment plants or in nature (Bromfield, 1974)

Microbiologists have investigated the physiology and the ultra structure of some of these unique microorganisms (Van veen et. al., 1978; Dondora, 1975; Andersen and Pedersen, 2003).   Many iron bacteria could easily be identified directly by observation under the microscope due to their distinct characteristic sheath secretion. Examples of such bacteria are of the genus S*phaerotilus eg. Sphaerotilus natans, S. dichotoma* and   *Leptothrix* group eg. *Leptothrix ochracea, L.*

lopholea, L. discophora, L. cholodnii (see figure 4.2b). Others like *Gallionella ferruginea* are recognized by their elongated helical or twisted stalks, composed of numerous intertwine micro fibrils but a non-stalk forming strain has also been reported to exist (figure 4.2a) (Pedersen and Hallbeck, 1995). Without the stalks, *Gallionella ferruginea* consist of a kidney- shaped mycoplasmodial cell body, which gives rigidity to the cell wall. On the other hand, the Eubacteria in the family Siderocapsacea, such as *Siderocapsa treubii*, S. *Major, Siderocapsa treubii* etc. might not have stalks or sheaths, making them extremely difficult to identify.

It is believed that all the above-mentioned Fe bacteria can also cause the oxidation of manganese if the concentration of manganese exceeds that of iron in the groundwater. However, there are other strains of bacteria that have a more specific manganese oxidation activity, namely Pseudomonas (e.g., *Ps. manganoxidans*); Metalogenium (e.g., *M. personatum, M. symbioticum*); and Siderobacteriales such as *Leptothrix* (e.g., *L. echinata, L. lopholes*).
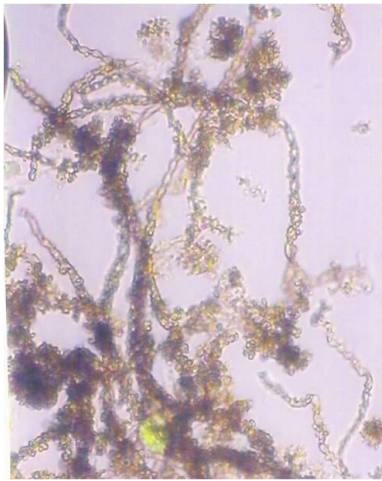
Figure 4.2a   (X40)   *Figure 4.2b   (X40)*

Figure 4.2a Light microscope image of stalks of Gallionella sp.; Figure 4.2b: Light microscope image of sheaths of Leptothrix sp. From (Ankrah et. al., 2008).

Methods like the16S ribosomal DNA sequence analyses and Generalized transducing phage(SN-T) are known to be useful tools used extensively to build up phylogenic trees, assist in the analysis of microbial communities and also identify gene sequence within single bacteria species. However, report(s) of the phylogenetic and evolutionary relationship investigations have not yet been published on sludge from an operational drinking water treatment plant (Buemer and Robinson, 2005).

4.3.1 Functions of exopolymers in sand filters

Today, the exact function of the sheath does not remain obscure. Investigations of sludge samples from filters have revealed that massive growth of bacteria sheath have profound catalytic influence on the oxidation of iron. Researchers have also argued that the sheath has nutritional and ecological consequences for the iron bacteria. This is evident in their ability to grow in slow running water low in nutrients, where the present of sheath allow the bacteria to attach themselves to solid surfaces. Furthermore, the sheath defends the organism from predators and parasites. Work done by Petersen and Hallbeck in 1995, demonstrated that G. *ferruginea* stalks gives them the unique possibility to colonize and survive in habitats with high nutrients of iron, which produces toxic oxygen radicals (e.g. O_2^-) during the chemical oxidation process. Under such conditions, the iron is normally inaccessible to the bacteria without defense system against the oxidation of iron.

4.3.2 Content of the Fe bacterial stalk

Research done by Balashov, 1970 to digest the stalk of G. *ferruginea* by proteolytic enzymes gaves the strongest conviction that the sheaths are protein in nature. Till date, although it is known that the encrustation of the sheaths of iron precipitating bacteria is protein in nature, it has however been found that besides proteins, the sheath of *Sphaerotilus natans* contain big amounts of carbohydrates and smaller amounts of lipids (Takeda et. al., 2003). Similarly, investigation conducted during this research at the Aalborg University, Esbjerg campus indicated that the exopolymers contain carbohydrates, protein and lipids. However, the content could neither be quantified nor characterized due to time constraints. A more detailed analysis of the chemical composition done by Tekeda et. al., in 2005 revealed that the sheath of Sphaerotilus natans is a complex of a polysaccharide, glycine and cystein-rich peptides. It was also indicated that the sheath polysaccharide is composed of glucose and (N-acetyl)galactosamine in an approx molecular ratios of 1:4, constituting about 70% of the sheath (Takeda et. al., 2005).

4.4 Conclusion

The purely physicochemical method for Fe oxidation and precipitation or the chemical catalytic process in sand filters may not always be effective in removing Fe contaminants from groundwater for drinking purposes. Therefore, chemical oxidants are sometimes needed to enhance the oxidation process. Biological oxidation/precipitation provides an alternative to the conventional, purely physicochemical, routes, with numerous advantages. The iron precipitating bacteria is now well known to be able to increase rates of precipitation of iron in drinking water treatment systems. A clear metabolic reason for the huge amount of work in producing iron precipitating sheaths or stalks that these bacteria perform is still uncertain. However, the bacteria could play a catalytic role by adsorbing the amorphous ferrihydrites thereby increasing the rate of iron oxidation and subsequent precipitation.

Chapter 5

5 Scope and objectives of the research

The removal of iron from groundwater has been studied since the beginning of the last century, and widely reported in literature (Morgan and Birkner, 1964 ; Ghosh et. al. 1966; Søgaard et al 2001; Zouboulis et. al. 2004; Veyenas et. al. 2006). However, it has always been that in conventional groundwater treatment plants for the removal of iron normally involves aeration of the raw water. The aeration process causes the oxidation of Fe(II) to Fe(III) and subsequently enhances the escape of carbon dioxide, thus increasing the pH . The Fe(III) hydrolyzes to form a precipitate, which sediments and is removed by filtration.

Practically, Fe(III) formation does not always proceed from the presence of only Fe(II) in groundwater and it is clear that several factors such as pH, the rate of oxidation, the presence of various dissolved compounds and carbon dioxide, exerts an influence and could potentially affect the filtration system. Therefore, many problems such as the formation of minute particles, which can easily go through filters are associated with the physico-chemical method of iron removal.

Apart from the conventional method of iron removal, Biological method has also been noted to either complement the conventional treatment or solely remove iron satisfactorily from groundwater. However, due to the ability of iron bacteria to bind to surfaces and oxidize iron and trace metals by their metabolic activities, makes them a major protagonist in Fe removal (Ferris, 2005). The bacteria are noted to actively cause oxidation of iron by reducing carbon to produce their required nutrients. By their nature as iron oxidizing bacteria, the iron oxidizing activity of some of the bacteria are partly determined by the nutrient content excreted by the cells associated with extracellular polymers (Ghiorse and Emerson, 1993).

Although investigations have been carried out on structural analysis of the sheath/stalk of *Leptothrix and Sphaerotilus*, until date, no journal has yet published investigations into the stalk of *Gallionella ferruginea*, which is predominantly found in filtration systems of drinking water treatment plants in Denmark. Chapter 6 and 7 in this thesis will therefore answer questions such as:

- What are the metabolic reasons for the iron bacteria oxidizing activities in filters of water treatment plants?
- What are the specific content of the exopolymers produced by *Gallionella ferruginea*
- What can be the causes of the high iron content in water treatment plant after the raw water has gone through the filtration system of some water treatment plants?
- What was the average size of the particles found in the treated water as a function of treatment unit?

- What could be the possible source of the particles?
- How can the problem be solved in a cheaper way as compared to the usage of chemicals which are rather expensive

Kommentar [EGS2]: Will be explained in chapter 7

The common way to assess water treatment plants if they remove iron by either purely physico-chemical or biological method is by investigation of the backwash samples by microscopy methods. However, in most cases, it is difficult to categorically conclude if the ferrihydrites are precipitated mainly in a biotic or abiotic way since the mere presence of exopolymers is not an enough evidence to mean that the water treatment plant removes iron by principally a biotic method. By finding a method to distinquish between biotic and abiotic produced iron hydroxides will give a faster and a more reliable way to characterize water treatment plants.

Pattern recognition method has been used in chemometrics to disclose and investigate complex data of physical, chemical and biological information in a wide field of research. The results obtained by previous work done by other researchers (Checa et. al., 2006; Saddler et. al., 1987) normally provide a model, which could be used to reveal the nature of similar information. Therefore, the chemometrics method was used to differentiate between data from near infrared spectroscopy analysis conducted on selected water treatment plant to provide a model that can distinguish between ferrihydrites precipitated under abiotic or biotic conditions as presented in Chapter 8.

Finally, another area which this thesis seeks to address is transferring the technology of drinking water, focusing on groundwater treatment to a developing country, such as Ghana. Globally, sustainable supply of potable water is always a vital requirement for the survival, growth and development of human civilization. Currently, it is estimated that about billion people still lack access to potable water and 2.6 billion people do not have access to basic sanitation.

Similarly, in Ghana, the intensification of climate change and increasing population is putting severe pressure on drinking water resources. The gloomy situation of lack of potable water in Ghana is further aggravated by higher concentrations of contaminants, especially iron, in groundwater, which can supplement the existing surface water sources used for drinking purposes. In fact, many wells, boreholes, and even in few cases, smaller water distribution lines have been closed down due to high concentrations of iron. However, the technology and the skills to remove iron to acceptable limits for drinking water purposes is completely lacking in the country.

Chapter 9 therefore examines water supply in Ghana, thereby focusing on the possibility for transfer the technology of groundwater treatment into the country through the DANIDA business -to- business programme.

It is worth mentioning that the proceeding Chapters after this Chapter 5 are my own studies conducted through laboratory investigations, the use of computer software, as well as trips especially to Ghana for observations, negotiations and answers to questionnaires.

Chapter 6

Biological iron removal from groundwater, considering physico-chemical parameters, kinetics, thermodynamics and content of the iron bacteria

6   Introduction

As discussed in Chapter 4, the physico-chemical method of iron removal from groundwater is typically the cheapest, safest and hence also the traditionally preferred method. However, this method may not always be effective due to the presence of other contaminants, which could potentially reduce the effect of the aeration processes. In recent years, as the usage of chemicals agents are highly encouraged to be minimized in drinking water treatment plants, engineers are working tirelessly to avoid the use of chemicals by substituting the entire purely physico-chemical process with that of the biological method which is noted to possibly over come the associated problems of iron removal with the purely physico-chemical method.

The physico-chemical iron removal method has been investigated extensively. As much as the kinetics and thermodynamic models are well developed to vividly describe the rate and behaviour of iron oxidation in filters, few similar studies have been made on biological method of iron oxidation-precipitation.

Gallionella spp. is an iron oxidizing bacteria producing exopolymers with the morphology of the stalks of combined strings and often found in filters of drinking water treatment plants in Denmark. It is the specie recognized to mainly carry out the iron oxidation in filters of drinking water treatment plants. However, the chemical content of the exopolymers *Gallionella ferruginea* has not been investigated in any international journal, and the clear metabolic reasons of the bacteria performing the oxidation- precipitation are not completely understood.

In this chapter therefore, biological oxidation of iron by the bacteria of the genus *Gallionella* was investigated for groundwater treatment, by applying a laboratory scale reactor. The content of the exopolymers of the bacterium *Gallionella spp*. was also investigated. Furthermore, the conditions, rate of oxidation of iron as compared to the purely physico-chemical method and thermodynamics of both methods were also evaluated

6.1   Experimental set-up

The reactor was set-up in the laboratory consisted of a single filtration unit to simulate groundwater water treatment plant for the investigation. The set up is as shown in figure 6.0

The system consisted of a cylindrical glass column with the dimension, 20 cm in hight and 12 cm in diameter. A transparent glass column was chosen because its transparency facilitated observation and sampling. The reactor was filled directly with filter materials with grain sizes averaged 1.2 mm, which were freshly collected from Astrup water treatment plant in Esbjerg. The plant treats groundwater by the biological methods. Supplied to the glass column, were two different sources of nutrients. The first of the nutrient contained a mixture of 0.5 g of di-potassium hydrogen phosphate H_2KPO_4 and 14.5 g of sodium bicarbonate $NaHCO_3$, which were contained in a transparent 25 litre container and 6.0 g of iron sulphate.$FeSO_4$.$7H_2O$ solution supplied from an opaque container. The second source contains ferrous sulphate

heptahydrate.FeSO$_4$.7H$_2$O. This was prepared by bubbling nitrogen gas through the tap water for about 40 minutes to strip off oxygen from the water until the content of oxygen was below 0.1 mg/l. The two sources of nutrients were pumped at the rate of about 28 ml/ min from the containers into the glass column. This was to simulate anoxic conditions as exist in groundwater but still to keep the amount of macroins as in groundwater

Water samples were collected for analyses of iron concentration, pH, oxygen and redox potential at both the influent and effluent of the reactor. The backwash samples were also investigated with microscope to identify bacterium exopolymers.
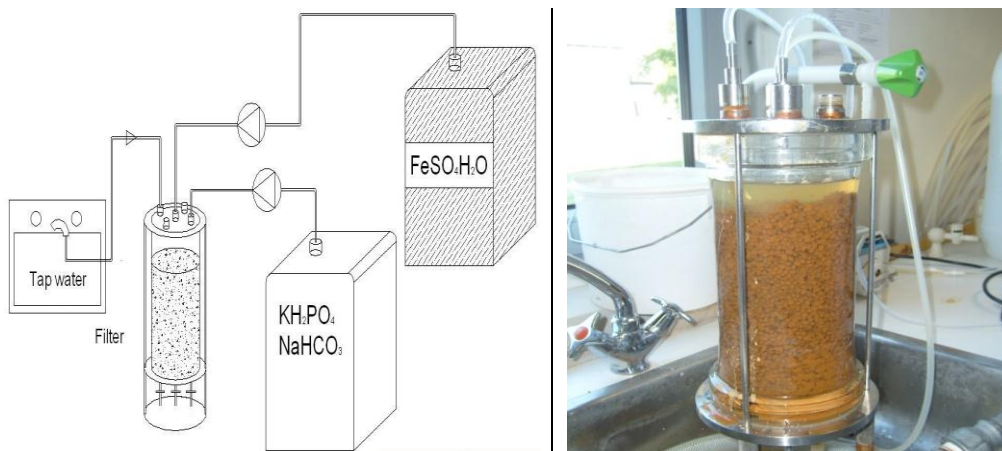
Schematic diagram of the set-up used for the experiment

Picture of the glass column used for the experiment, showing filter material and raw water

Figure 6.0 : Schematic diagram and picture of the experimental set-up for the biological reactor in the laboratory.

The pH, redox potential and conductivity were measured everyday in the treated water. Samples were collected 3 times a week and were used to measure concentration of iron. Samples from the filters were also taken to investigate the presence of the bacteria.

6.1.1 Determination of carbohydrate and protein content in Gallionella spp. exopolymers

Sampling

Three backwash samples were taken from the laboratory reactor and Astrup water treatment plant using glass sampling containers. The backwash samples were screened to ensure the

presence of bacteria exopolymers. The samples were stored under temperature of about 3 ^{0}C until analysis was performed within 24 hours.

6.1.1.1 Determination of carbohydrate content using the Anthrone method

The Anthrone colorimetric method was used to determine the carbohydrate content in the backwash samples (Trevelyan et. al., 1952). The principle of the method is based on the hydrolysis of oligosaccharide, which reacts with concentrated acids. The solution then forms complex with the added of Anthrone (10H-Anthracen-9-one). The colour intensity of the complex formed is proportional to the carbohydrate concentration.

Procedure

1.0 ml of the standard solution(1000 ppm (D (+)-glucose, $C_6H_{12}O_6$; Mol weight: 180.16: diluted 10 times to 100 ppm) and samples were displaced into a clean pyrex tubes. Four test tubes were used for each test. Thus 2 for sample provision and the other 2 serve as blank.

2.0 ml of reagent A(27.5 ml of demineralized water mixed with 472.5 ml conc. H_2SO_4 and 0.625 g Anthrone) was then added to each sample. Also, 2.0 ml of reagent B (472.5 mL conc. H_2SO_4 mixed with 27.5 ml of demineralized water) was added to the blank. All the samples prepared were then mixed with vortex mixer with a stopper in the tube. They were boiled at 100 ^{o}C in a water bath for 14 minutes, cooled down on ice for five minutes and the absorbance was measured on a spectrophotometer at a wavelength of 625 nm in a macro cuvette. See figure 6.1.
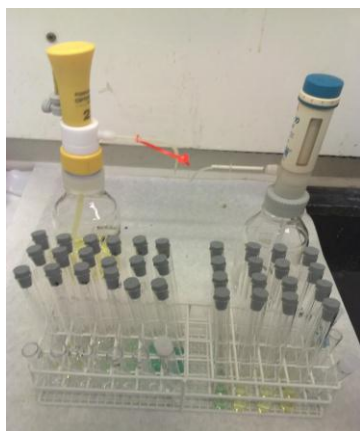
Figure 6.1: Picture showing test tubes in rags used for the determination of carbohydrate.

Calculations

A linear regression was prepared with the standard concentrations ranging from 0 to 100 ppm, and the sample concentration was extrapolated from the linear curve.

6.1.1.2 Determination of protein content using the modified Lowery method

The Lowry method was used for the determination of total protein (Lowery et. al 1951). The principle behind this method is that Cu(II) is reduced to Cu(I) during complex formation with peptides. Similarly, in an alciline solution, hydrolysis of peptide bonds reduces Cu(II) and it further promotes the subsequent reduction of phosphomolybdatephosphotungstic acid present in folin-ciocalteu´s phenol reagent. This reduction produces a blue coloration which is measured photometrically at a wavelength of 750 nm. The results depend on the absolute amino acid composition of the protein present. This means that one will obtain results using different standard protein.

Procedure

Two duplicated sets of solutions were prepared with the reagent pipes. Thus four tubes, two for each set. Cu was added to two of the measurements and the other two was without Cu. 50 µl of the standard (0.1g of bovine serum albumen to 100 ml of distilled water) was added to the tubes and the 700µl of reagents D (0.7143 g $CuSO_4 \cdot 5H_2O$ dissolved in deionized water to 50 ml. 1.4286 g Na-tartrate dissolved in deionized water to 50 ml. (L (+) Tartaric Acid) was added to the other two. The solution was then mixed on vortex mixer. 100 ml of the reagent F (5 ml Folin-Ciocalteus added 6 ml of demeneralized water) was added quickly and mixed immediately on vortex mixer. The absorbance was measured at 750 nm after 45 minutes. The zero samples/ blank was measured using water as reference. See figure 6.2.

Humic substance can interfere with the method. Therefore the standard addition method with humic substances was used to eliminate the possible interference caused by humic substances.

Calculations

Humus standard set was made by plotting concentration in ppm against blind absorbance (ABS blind). The concentration of humus in the sample was calculated by first calculating ABShumus following equation, which is derived from the first two: ABShumus = ABS total – ABSprotein Thereafter, that was put into the line equation for the standard row normally. Standard row goes through zero if the samples are measured against water
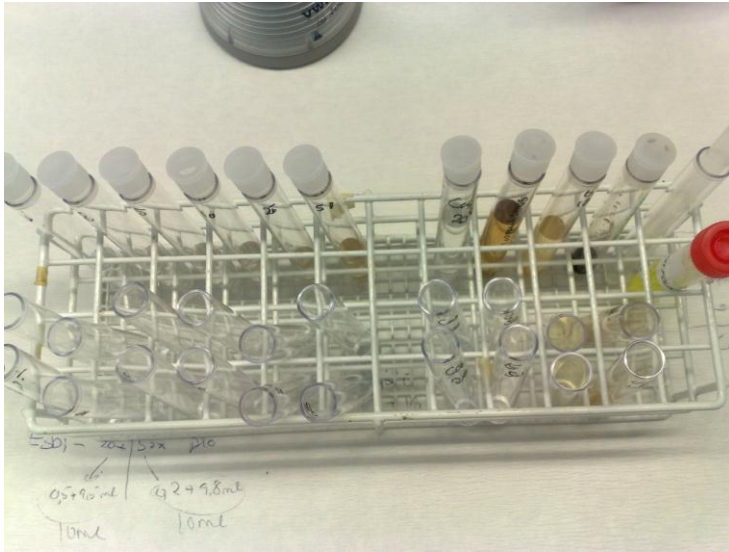
Figure 6.2: picture of test tubes in rags used for the protein experiment.

6.2 Results and discussions

The discussions for the experiments conducted in chapter 5, thermodynamic and kinetic calculations are discussed below.

6.2.1 Discussion for iron Concentration

The iron concentration measured at the outlet of the reactor over a period of time is as shown in figure 6.3. Day one to day 18 was not included in the data because the results obtained were constant just as in day 19probably because only purely physico-chemical precipitation is taking place. Also, the iron bacteria had not grown to any important level within that time period and no significant changes were observed in the measurements. However, after day 19 to day 42 the iron concentration fluctuated but eventually decreased over a period of time. Since an investigation of the backwash precipitates show that presence of bacterial exopolymers after day 19, the decrease of iron in the reactor can be attributed to purely physico-chemical iron removal supplemented by biological mediation. However, after day 36, no further decrease was observed probably because the conditions in the reactor for the iron removal were stable.
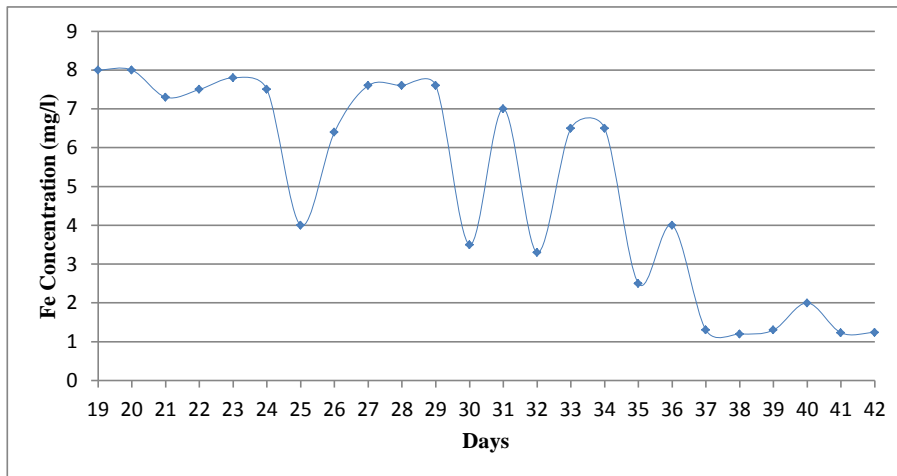
Figure 6.3: Iron concentration in the effluent water from the glass column reactor.

6.2.2 Discussion for Redox Potential

As indicated earlier in chapter 4, redox potential is one of the important parameters that effectively control the growth and development of iron bacteria. This implies that iron bacteria are sensitive to changes in redox potential and will only thrive within certain redox potential values. For this reason, the redox potential of the effluent/ outlet and the inlet water were measured. The readings were similarly taken from day 19 after the reactor was set-up since no bacterial growth was observed during the earlier days.

From figure 6.4, it could be seen that, initially, thus from day 19, a redox potential value of about -75 mV was measured at both the inlet and the outlet/effluent. . The difference in the redox potential could be attributed to some amount of oxidation of the deoxygenated $FeSO_4.7H_2O$ solution and/or as a result of the bacterial oxidation which took place in the reactor. The trend for both the inlet and the outlet redox potential fluctuated over the days except between day 29 and 34 which experienced high redox potential at the outlet. This may be due to backwashing of the filter material.

The trend of the redox potential measured in the laboratory reactor was similar to that of Astrup water treatment plant, which was measured to be -89.0 mV at the inlet but increased to 74.8 mV at the outlet. This much higher variation can be attributed to the size of the filtration system together with an increasing amount of oxygen from zero to about 4 mg/l. The redox potential measured for both Astrup drinking water treatment plant and the reactor is optimal for iron precipitation since they are similar to those in literature documented by Søgaard et. al. in 2001.
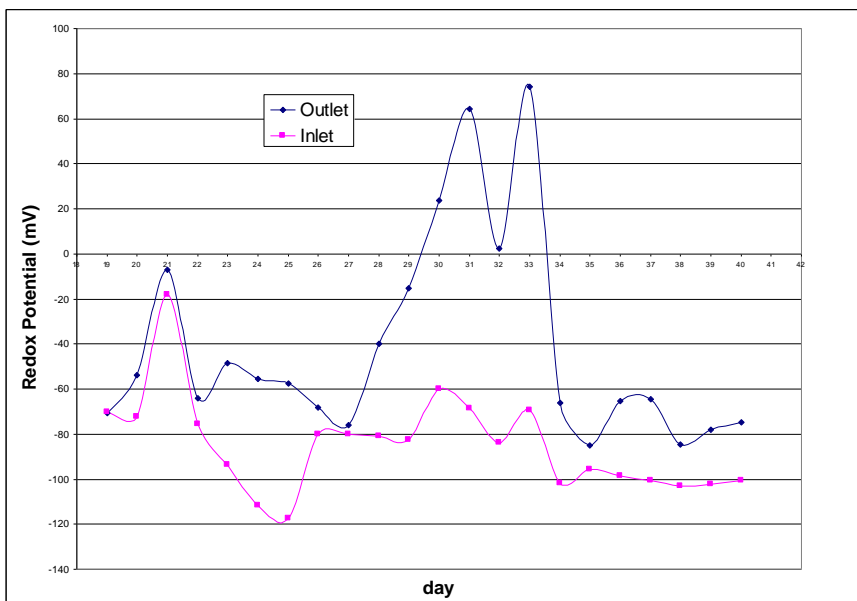
Figure 6.4: Redox potential at the input and output.

6.2.3   Discussion for pH values measured at the inlet and outlet of the reactor

The pH measurements obtained for the outlet and inlet of the reactor is as shown in figure 6.5

For the pH measurements, the reading taken earlier before the day 26 were not plotted on the graph because they showed no significant changes and also for clarification of the graph. The values shown on the graph were therefore started from the day 26 to day 40.

However, after day 26, both the inlet and the outlet pH measured were between 6.5 and 7.4 except between day 29 and 33 that gave high inlet values of about 7.9 and a corresponding outlet value of about 7.4. The high value measured is not usual and could be due to contamination from the base solution used to stabilize pH of the nutrient solution or from backwashing of the filters
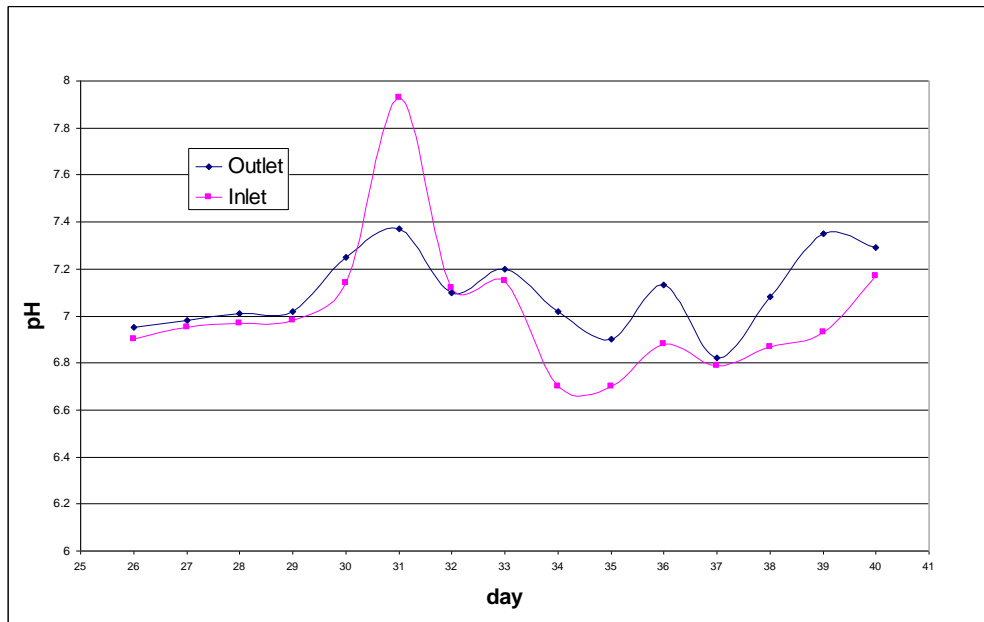
Figure 6.5: pH values at the outlet and inlet.

Throughout the duration of the experiment, the pH had a maximum of 7.4 and a minimum of 6.5 for outlet. The pH for inlet was between 7.9 and 6.6. These conditions seem to be favorable for the iron precipitating bacteria.

6.2.4 Discussions for Oxygen concentration measured at the influent and effluent of the reactor

Oxygen affects the reaction kinetics of ferrous iron precipitation and iron bacterial trophic metabolism. Therefore, oxygen concentration was measured for both the inlet and outlet of the reactor. Similarly, the initial values were not plotted due to the same reasons given under the pH measurements.
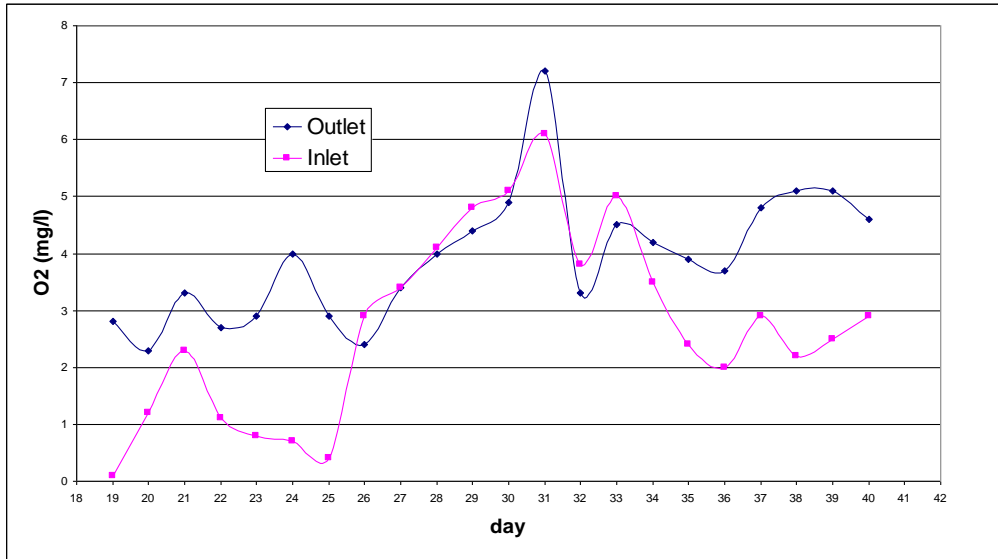
Figure 6.6: Oxygen content at the input and output.

It could be seen from figure 6.6 that the oxygen concentration in the inlet/influent water was generally lower than that of the outlet/effluent water from the reactor. The variation is due to the dissolution of atmospheric oxygen into the water during the filtration process. However, the bacteria could not scavenged the dissolved oxygen in the water. The trend continued until between day 25 and day 36, when a jump in the readings occurs. The jump could not be accounted for. However, it could be due to backwashing and/or contamination from NaOH solution used for stabilization of the inlet pH (experimental error).

Table 6.0: Comparison of the operational parameters of the lab-scale experiment with that of Astrup DWTP

Parameters	Astrup		Laboratory reactor	
	Raw water	Outlet/treated water	Raw water	Outlet/Treated water
Iron(mg/l)	13	0.04	8	1.2
Redox potential(mV)	-50	+200	-70	-60

pH	6.8	8.0	6.9	7.2
Oxygen (mg/l)	0.4	10	0	4

Table 6.0 compares the operational parameters of redox potential, pH, oxygen and iron concentration of the laboratory–scale experiment with that of Astrup drinking water treatment plant.

It could be deduced that the outlet parameters of oxygen and redox potential were lower as compared to that of Astrup DWTP. The low oxygen concentration of 4 mg/l and the negative redox potential of 60 mV at the outlet does not reflect sufficient conditions for a complete iron oxidation. If there was total oxidation of iron present due to the raw water saturation with oxygen, then the redox potential should be positive and the oxygen concentration should be about 10 mg/l at outlet of the reactor. The water was only partly aerated by help of dilution of the concentrated Fe(II) solution with tap water and not aerated separately. Therefore, the laboratory reactor only partly shows the conditions of Astrup DWTP but still it can give an expression of what is going on in the full scale filter of the DWTP. It also shows that it is possibly to let iron precipitating bacteria create their exopolymers at laboratory conditions in order to try to keep their environment anaerobically.

6.2.5   Microscope investigation of the backwash samples

Microscope investigation of the backwash samples from the reactor were taken and compared with that of Astrup WTP, where the filter materials were obtained from. Astrup WTP removes iron by biological method (see figure 6.7a and figure 6.7b).

Both figures exhibited exopolymers, which are from the stalks of *Gallionella ferruginea,* believed to be involved in and a part of the cause of iron precipitation in Astrup water treatment plant. The images from the reactor show the twisted elongated structural characteristic of *Gallionella* bacteria exopolymers more than that of Astrup water treatment plant due to mechanical actions of air and water during backwashing at Astrup water treatment plant. On the other hand, more exopolymers were found in the backwash samples from Astrup WTP due to age differences in the filter material.

It can also be seen that the *Gallionella* stalks are associated with the colloidal iron precipitates forming a mesh (network) of stalks, almost engulfing the backwash samples.
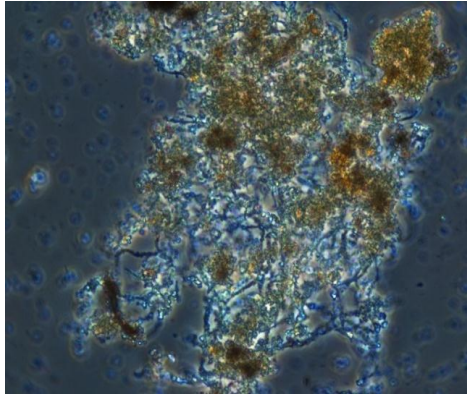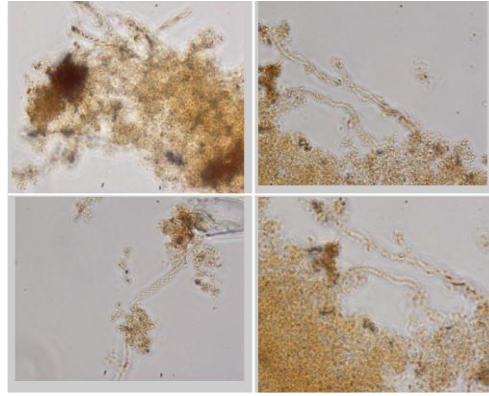
Figure 6.7a   *(X 40)*   *Figure 6.7b*   *(X 40)*

Figure 6.7: Light microscope images of iron precipitating from a biological iron removal plant in Astrup as in 6.7a, and the biological reactor set-up in the Laboratory as in 6.7b.

The exopolymers seen in figure 6.7 are the *Gallionella* cell extrusions, which localized the iron ferrihydrited precipitates to harnes the proton gradient for energy generation, since the bacteria are chemolithautotrophic. The adsorption of ferrihydrite precipitates to the exopolymers are usually attributed to alkene (C=C), aliphatic (C- C), carbonyl (C=O) and carboxylic (COOH) groups due to protein and carbohydrate content of the stalks, which form a mixture of bacterium exopolymers and iron oxide precipitate (Miot et. al. 2009). Once the biogenic iron oxides are formed, the bacteria stalks normally nucleates and iron minerals further accumulates on them. Ferrihydrites are highly reactive sorbents for dissolved metals. Therefore, it further sorb Fe^{2+}, therby oxidizing and precipitating it to Fe(III) (Dzombak and Morel 1990)

6.3   Composition of the *Gallionella spp.* exopolymers

Exopolymer contents are important since they give a reflection of bacteria identity and possible adsorptive surfce of the exopolymer produced by the bacteria. Therefore, the carbohydrate and protein content of the *Gallionella spp* in the reactor were investigated and compared to those of Astrup water treatment plant. See table 6.1.

Table 6.1: The carbohydrate and protein content of the of the backwash precipitates.

	Astrup WTP			Average	Lab. reactor			Average	Demineralize water
Carbohydrates(mg/l)	6.99	9.56	8.24	8.26	4.34	5.66	3.66	4.55	0

	Astrup WTP			Average	Lab. reactor			Average	Demineralize water
Protein (mg/l)	90.2	102.3	115.6	102.7	70.3	90.5	100.5	87.1	0

Table 6.2: The chemical composition of the sheath of *Leptothrix discophora* as in Ghiorse and Emerson, 1993.

	Concentration	reference
Carbohydrate content in Sphaerotilus-Leptotrix	34 %	Ghiorse and Emerson, 1993
Protein content in Shpaerotilus Leptothrix	24 %	Ghiorse and Emerson, 1993

Backwash samples from Astrup water treatment plant gave an average carbohydrate content of about 8.26 mg/l while an average 4.55 mg/l was measured in the reactor. The presence of carbohydrate measured in both Astrup drinking water treatment plant and in the reactor is an indication of the fact the *Gallionella spp.* bacteria metabolized carbohydrate during their metabolic activities. Also, protein concentration of 102.3 mg/l was measured in the backwash samples from Astrup water treatment plant while 87.1 mg/l was measured in the reactor. No carbohydrate or proteins were found in the demineralized water or the tap water used for the experiment in the Laboratory reactor and this was used as control for the experiment.

As much as the presence of protein in both the backwash samples of Astrup WTP and that of the reactor signify the production of protein by *Gallieonella spp.* bacteria, the protein concentration measure seem to be too high. This is because based on comparing the results with those obtained by Ghiorse and Emersen in 1993, which showed that the protein content was rather lower than the carbohydrate content in *Leptothrix* bacterium content, It was therefore expected that even if the results obtained in this study was not exactly the same as those obtained by Ghiorse and Emerson, the protein content must not be extremely high as in table 6.2.

The method used by Ghiorse and Emerson in 1993 to determine the chemical composition of the sheath of *Leptothrix* is suitable for bacteria in pure culture media. They found 34 % dry weight of carbohydrate and 24 % dry weight protein (see table 6.2). However, since it is so difficult, almost impossible to produce pure culture media of *Gallionella spp.*, the only way to carry out

the investigation was to conduct the test in the bacteria´s natural habitat which in this case was in the backwash precipitates from either the water treatment plant or the Laboratory reactor.

For this reason, the results could not be compared since similar work has not been published in any journal. However, in Ghiorse and Emerson 1993, the chemical composition of intact cellular filament and cell free sheath of *Leptothrix discophora* has been compared to that of *Sphaerotilus natan* but the results were measured in percentage by weight. Therefore, they were not compared directly with the work done in this thesis since the units were different. However, the results in this thesis could serve as the background for future experiments to be conducted on the content of *Gallionella spp.* directly in water.

6.4   Kinetic Reaction

The kinetics of iron precipitation was also investigated using results obtained from the reactor set-up.

The kinetics of iron oxidation can be represented by the expression:

$$-\frac{d\left[Fe^{2+}\right]}{dt} = k\left[Fe^{2+}\right]\left[OH^-\right]^2 pO_2 \tag{6.0}$$

By keeping [OH⁻] and pO_2 constant in equation, which is often possible in the iron precipitating part (first few centimeter) of the sand filter systems we get equation:

$$\frac{-d[Fe(II)]}{dt} = k'[Fe(II)] \tag{6.1}$$

where $k' = k[OH^-]^2 pO_2$

This equation can be integrated to give:

$$\frac{1}{t}\ln\frac{[Fe(II)]_1}{[Fe(II)]_2} = k', \text{ where} \tag{6.2}$$

$[Fe(II)]_1$ is the concentration of Fe(II) at the top of the filter and $[Fe(II)]_2$ is the concentration of Fe(III) at the outlet of the reactor

T is the resident time.

The resident time is equivalent to the volume of the sand filter, $V(m^3)$, and the discharged water in filter Q (m^3/h)

$T = V/Q$

$V = 650ml$ *(net porosity between sand grains)*

Q = 28ml/min (measured average flow)

T = 650/ 28 = 23,2 min (residence time)

$$k' = \frac{1}{t} \ln \frac{[Fe(II)]_1}{[Fe(II)]_2} = \frac{1}{23.2} \ln \frac{8.0}{0.124} = 0.180 \, \text{min}^{-1} \tag{6.3}$$

*(with the data from AAS measurements)

With $[OH^-] = 10^{-7}$ and $pO_2 = 0,084$ atm (calculated by help of Henr`s constant for oxygen and measured average value of oxygen content in laboratory reactor) for Temperature = 7,4 ^{0}C

$$k = \frac{k'}{[OH^-]^2 \times pO_2} = \frac{0.183721}{10^{-14} \times 0.084} = 2.14 \times 10^{14} \, \text{min}^{-1} \, atm^{-1} M^{-2} \tag{6.4}$$

The k value calculated to $2.14 \times 10^{14} \, \text{min}^{-1} \, atm^{-1} M^{-2}$ means that iron precioitation by biological method is faster than the physico-chemical method by a factor of 100 based on the results stated by Schwertman and Cornell in 2003, which was $1.8 \times 10^{12} \, \text{min}^{-1} \, atm^{-1} M^{-2}$.

Indeed, kinetics controls the reactions that take place at the particle/ water interface, and adsorption and desorption equilibrium tremendously control the elements pathways. Therefore, the *k* value obtained for the reactor were determined by three different pathways, thus the oxidation of Fe(II) to Fe(III) (homogenous), the catalysis of adsorption of Fe(II) to Fe(III) mineral surface (heterogenous) and biological precipitation.

The conversion of Fe(II) to Fe(III) from homogenous oxidation can be represented by the equation as in equation 6.5 below:

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2\tfrac{1}{2}H_2O \rightarrow Fe(OH)_3^o + 2H^+ \tag{6.5}$$

Therefore, at the pH averaged about 7 and oxygen concentration of about 4, which were obtained in the reactor, a homogenous oxidation of Fe(II) to Fe(III) will begin to occur. Once homogenous oxidation occurs, the ferrihydrites produced also further autocatalized Fe(II) oxidation in the solution through adsorption. This can be described by the equation:

$$Fe(III)\text{-}(OH)\text{-}Fe^{2+} \rightarrow Fe(III) - O\text{-} Fe^+ + H^+ \tag{6.6}$$
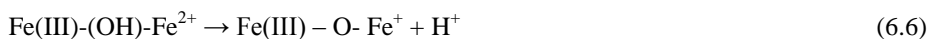
An adsorption constant with the value of about $10^{-2.98}$ is proposed by Liger et al 1999, and the active site of ferrihydrites involved in the adsorption process is normally between 2 to 16 sites nm^{-2} with an average value of about 5 sites nm^{-2} (Davis and Kent, 1990 ; Stumm, 1992).

In addition to the homogenous and heterogenous precipitation, the iron precipitation kinetic was further accelerated by the adhesive force due to the bacteria exopolymers. Unfortunately, figure on force of adhesion of *Gallionella* bacteria to ferrihydrite surfaces could not be found. However, It is certain that those three mechanisms, (homogenous, heterogeneous as well as the bacteria adhesive force) brought the k value measured to $2.14 \times 10^{14} \, min^{-1} \, atm^{-1} M^{-2}$ for the reactor, which was higher than that of the physico- chemical recorded by Schwertman and Cornell`s in 2003.

6.5 Thermodynamic analysis for the feasibility of Purely physico-chemical and biological Fe removal

This section seeks to predict the feasibility of oxidizing Fe(II) species in water by the purely physico-chemical method as compared to the biological method of iron removal. Therefore, data from the reactor set up in the laboratory were used for the calculations.

6.5.1 Biological iron precipitation

For biological Fe precipitation to occur, the iron bacteria need iron in some enzymatic processes that involve the transfer of electrons, where ferric iron may serve as a terminal electron acceptor for bacterium enzymatic process. Therefore the reaction that occurs is:

$$3H_2O + Fe^{2+} \rightarrow Fe(OH)_3(s) + 3H^+ + e^- \quad \text{oxidation of Fe} \tag{6.7}$$
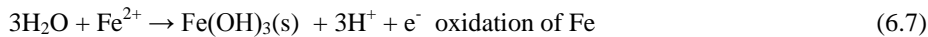
The bacteria also reduces hydrogen carbonate source to produce carbohydrate

$$4e^- + 5H^+ + HCO_3^- \leftrightarrows C(H_2O)(s) + 2H_2O \quad \text{reduction of hydrogen carbonate} \tag{6.8}$$
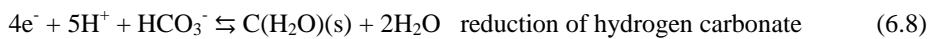
Combining the two half equations results in:.

$$HCO_3^- + 10 \, H_2O + 4Fe^{2+} \rightarrow C(H_2O) + 4Fe(OH)_3(s) + 7H^+ \tag{6.9}$$
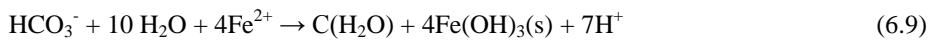
The net standard potential for equation (6.9) will be:

$$E^0 = 0.036V - 1.065V = -1.029V \tag{6.10}$$

The net negative standard potential means that the reaction is non spontaneous under standard conditions. Therefore, an external energy source is needed to trigger the reaction. The voltage was investigated under actual environmental condition at Astrup, where the water treatment plant is removing Fe by biological means.

Inserting activities based on the species from equation 6.9 into the Nernst equation, the voltage corresponding to the reaction will be written as:

$$E = E^0 - \frac{RT}{nF} \ln \frac{1 \times 1^4 \times (a_{(H^+)})^7}{a_{(HCO_3^-)} \times (a_{(Fe^{2+})})^4} > 0 \qquad (6.11)$$

The activity of the solid carbohydrate and ferric oxide are set to 1

Where:

R= Gas constant

T= absolute temperature

F= Faraday constant

n= number of electrons transferred

Substituting the numerical values for the constants and actual data from Astrup drinking water treatment plant,

R: is the gas constant; R=8.314 J/(K*mol) = 8.314*10^{-3} kJ/(K*mol)

T: The temperature of the reactor; T = 283K

n= 4

F= 96487 C/mole

For ideal diluted species in aqueous solution activity can be substituted with the corresponding concentrations

a Fe^{2+} ~ [Fe^{2+}] = 8.0 mg/l = 8.0 / 56 mmol/l = 0.00032mol/l

[H^+]= 10^{-pH} = $10^{-6,91}$ (pH = 6.91)

[HCO_3^-]= concentration of hydrogen carbonate measured as the alkalinity at the top of the filter. 3,888meqv/l = 3,888mmol/l = 0,003888mol/l

$$E = -1.029V - \frac{8.314(J/K\text{*}mole) \times 283(K)}{4 \times 96487(C/mole)} \ln \frac{1 \times 1 \times (10^{-6,9})^7}{0.00388 \times 0.00032^4} \qquad (6.12)$$

E = -0.58V (6.13)

The net potential of about -0.59V means that even if the actual concentrations of the involved species are taken into account, the bacterial activity does not by itself as a part of their metabolism, directly cause the oxidation of Fe(II). Rather, their exopolymers produced provides

surfaces which catalyze the adsorption of the Fe(II) ions or Fe(III) hydroxide which has already been oxidized by oxygen in the system. The physico-chemical method of Fe removal was therefore investigated.

6.5.2   For Physico- chemical Fe removal

$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$ half reaction for hydrogen oxidation   (6.14)

$3H_2O + Fe^{2+} \rightarrow Fe(OH)_3 + 3H^+ + e^-$ half reaction for Fe oxidation   (6.15)
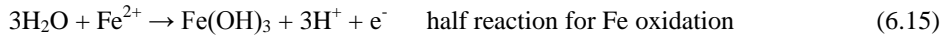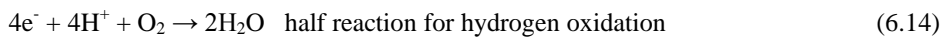
Combining the two half reactions:

$O_2 + 10H_2O + 4Fe^{2+} \rightarrow 4Fe(OH)_3 + 8H^+$ (6.16)

The net standard potential for equation 6.16 will be

$E^0 = 1.23V - 1.065V = 0.165V$ (6.17)

The net standard potential of 0.165 V means that the oxidation of Fe^{2+} can occur spontaneously in the presence of oxygen without the presence of iron bacteria.

By inserting the parameters from equation 6.16, the net potential for the physic-chemical Fe removal can be written as:

$$E = 0.165V - \frac{8.314(J/K*mole) \times 283(K)}{4 \times 96487(C/mole)} \ln \frac{1^4 \times (10^{-6.9})^8}{0.084 \times 0.00032^4}$$ (6.18)

E= 0.729V

The net potential of 0.729V implies that the reaction can occur spontaneously

The standard potential is related to the standard free energy with the equation:

$\mathit{\Delta}G^0 = - nFE^0 (volts)$ (6.19)

G= Gibbs free energy

The standard free energies were investigated for both physico-chemical and biological methods.

$\Delta G^0_1 = 4 \times 96487$ C/mole $\times 1.029V = 397$ kJ/ mole thus for biological iron removal method (6.20)

$\Delta G^0_2 = -4 \times 96487$ C/mole $\times 0.165V = -63.8$ kJ/mole for physico-chemical Fe removal   (6.21)

If these reactions could be combined, then, the bacteria could benefit from the free energy provided by the purely physico-chemical oxidation/precipitation process. The following calculation shows that the reduction of 1 mole of hydrogen carbonate into carbohydrate demands about 7 moles of reduction of Fe(II) into Fe(III)-oxides to obtain sufficient free energy for the combined reaction at standard conditions.

$$0 > \Delta G^0 = \Delta G^0_1 + n \Delta G^0_2 \Rightarrow n > 7 \qquad (6.22)$$

On the whole, the equation 6.22 implies that also about 7 times the number of electrons are needed for biological Fe removal as compared to the physico-chemical Fe removal- and this is energy demanding. If that is the case, then it means that the bacteria through their enzymatic activities trigger the fast oxidation of Fe to occur in order to gain their required energy for their metabolic processes. The Fe bacteria do not therefore directly cause the oxidation of Fe in biological iron removal.

Similarly, the potential is related to the free energy with the equation:

$$\Delta G = -nFE \qquad (6.23)$$

$$\Rightarrow \Delta G_1 \text{ (biological) = 224 kJ/mole} \qquad (6.24)$$

$$\Delta G_2 \text{ (physico-chemical) = -281 kJ/mole} \qquad (6.25)$$

By comparing the pysico-chemical iron removal to the biological iron removal method implies is as indicated below:

Thus, $\qquad \dfrac{\Delta G_2}{\Delta G_1} = (\dfrac{281}{224}) \times 100 = 125.7\%$ $\qquad (6.26)$

Equation 6.26 implies that actual all the all the oxidation of iron is carried out by the physic-chemical process instead of the biological oxidation. However, if the bacteria had contributed to the iron oxidation in the reactor at all, then they did so only by providing surfaces for the Fe^{2+} to adhere to, thereby only catalyzing the oxidation process.

6.6 Conclusion

The presence of carbohydrate and protein measured in the backwash samples from both Astrup drinking water treatment plant and the Laboratory reactor indicates that *Gallionells spp*. derive their energy source from inorganic metabolites and subsequently produce organic molecules such as protein and carbohydrates for growth and development.

Iron precipitation in filters is governed by the physic-chemical parameters such as pH and redox potential of the water. However, the results obtained could not give any meaningful trend from the pH and the redox potential measured in the Laboratory reactor over a period time.

The effect of thermodynamics and kinetics with respect to chemical reactions usually determines the distribution, fate and the abundance of chemical elements in an environment. The process of

kinetic is especially of interest since the type of iron oxide as well as the particle sizes formed is governed by the rate at which the iron was precipitated. Therefore, those two mechanisms function together to explain and predict the environmental concentrations of the species in aqueous systems. The thermodynamic calculations clearly demonstrated that the presence of the bacteria could speed up iron precipitation by 100 folds.

In biological iron removal, the bacteria does not directly cause the oxidation of Fe(II) to Fe(III). Instead, the bacteria gain energy for their growth and development from the electron transfer during the oxidation of Fe(II) to Fe(III) by the purely physic-chemical process. As a result, the bacteria avail the surfaces of their exopolymers to adhered to the Fe(III) precipitates thereby catalyzing the rate of iron precipitation.

Chapter 7

A Case study of Fe removal from groundwater at Vejers drinking Water treatment Plant

7   Introduction

As discussed in chapter two, groundwater usually contains Fe concentration above the permissible limit value for drinking purposes set by the Danish environmental Authorities. Therefore, the Fe is removed before releasing the treated water into drinking water system. Because the chemistry of groundwater is highly marked by Fe complexes and intricate species, Fe removal from groundwater can be a daunting task. The difficulty to remove Fe from groundwater could even be augmented if the groundwater contains minerals, such as silicates and humic substances (Natural organic matter) in very high concentrations. (Cameron and Liss, 1984)

In a situation where groundwater contains other minerals, which possibly form complexes with Fe, the traditional purely physico-chemical Fe removal method alone is not sufficient to remove the Fe from the groundwater to acceptable concentration.

Information gathered by Mouchet in 1992 indicated that about 75 % of the cases in which Fe is difficult being removed from groundwater to acceptable limits can be associated with complexation. Out of the 75 % cases reported due to complexation, humic substances complexing occupy about a quarter($\frac{1}{4}$) of the cases, while silicates complexing occupy predominantly three quarters($\frac{3}{4}$) of the rest of the cases (Mouchet, 1992). Furthermore, oxidation of ferrous carbonate($FeCO_3$) is extremely slow. Groundwater containing high concentration of $FeCO_3$ is always difficult to be treated by the purely physico-chemical method. This is because $FeCO_3$ cannot be oxidized to $Fe(OH)_3$ so, the $FeCO_3$ may remain in the soluble state for a long time and can end up in the fresh water system (refer to figure 3.4)(Shallenko et. al., 2006; Olsen and Twardowski, 1975).

The groundwater drinking water treatment plant at Vejers , which is located at the south-western part of Denmark, was constructed to remove Fe by the purely physico- chemical method of Fe removal. However, the concentration of Fe at the outlet of the water treatment plant (WTP) (water released into fresh water system) was about 0.2 mg/l. That concentration exceeded the allowable limits set by the Danish drinking water standards. The high concentration of Fe persisted at the outlet of the WTP even if the WTP was constructed to contain three (3) sections filtration units, which is more than the number of filtration units usually constructed in Denmark. Additionally, $KMnO_4$ at a concentration of about 1 mg/l was also added to the raw water at the third filtration stage to enhance oxidation of the Fe. A brown slimy Mn(IV) eventually forms as the end- oxidation by-product, which potentially serve as a substrate for microorganisms in the

filters. This was a unique problem in Denmark, which called for a thorough investigation into the recalcitrant Fe at Vejers drinking WTP.
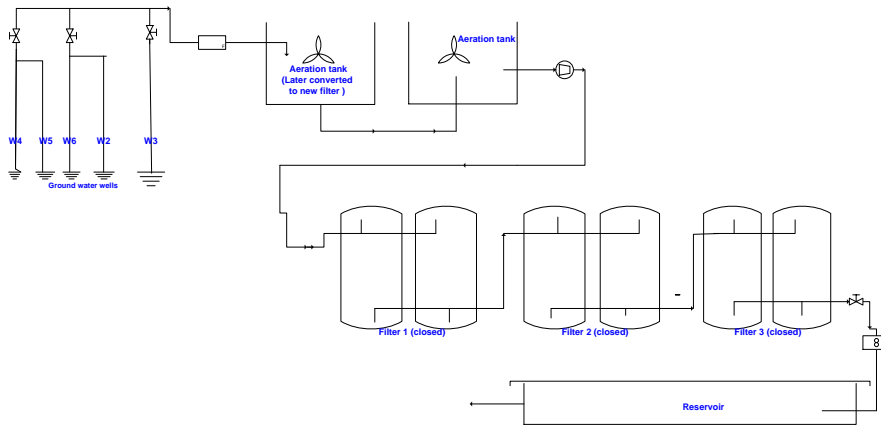
Figure 7.0: Plant design and ground water characteristics at Vejers drinking WTP.

Figure 7.0 shows the schematic process design of the water treatment plant and table 7.0 explicitly shows the raw water characteristics of each of the wells supplying raw water to the water treatment plant.

The process design of Vejers water treatment plant differs from the normal ones in Denmark, which usually consist of a single aeration tank, preceded by single or double section of sand filters for the precipitation of iron and manganese, respectively. The design of Vejers drinking WTP was uniquely in this form due to the high content of methane, ammonium, natural organic materials (NVOC) and Fe content of the raw water. (see table 7.0). The first two aeration tanks were for the stripping off of the high content of methane, ammonium and for the effective oxidation- precipitation and removal of Fe. The additional third section of the filters (filter 3) was intended for the removal of the excess natural organic material Fe and Mn, aided by the addition of potassium permanganate in between the filter 2 and filter 3.

The Vejers WTP treats water to the capacity of about 300 m^3/day, during winter seasons and the quantity increases to about 800 m^3/day during summer. The increase is because of the high influx of holiday makers to the area. The sand filter grain size for the filter 1, filter 2 and filter 3 were 0.8 mm, 0.5 mm and 0.5 mm respectively. As shown in figure 7.0, the raw water (groundwater) is abstracted from five different wells and pumped at the rate of about 30 m^3/h throughout the entire treatment process.

Table 7.0: Raw water quality of the individual wells at Vejers drinking water treatment plant.

Parameter(s)	Well 2 DGU(120-65)	Well 3 (120-59)	Well 4 (120-160)	Well 5 (120-162)	Well 6 (120-163)
pH	7.2	7.3	7.5	7.3	7.6
Oxygen (mg/l)	0.63	0.3	0.1	0.8	0.01
Temperature(0C)	8.8	8.8	8.5	8.5	8.9
Conductivity(mS/m)	40	40.8	41.3	35.6	49.9
Redox potential(mV)	-110	-80	-73	-75	-100
NVOC(mg/l)	3.5	3.3	3.9	4.0	3.9
Iron (mg/l)	6.3	8.3	3.7	6.6	7.4
Ammonium(mg/l)	1.4	1.3	1.9	1.7	1.3
sulphate(mg/l)	< 0.2	<0.2	0.88	<0.2	<0.2
Calcium(mg/l)	44.4	47.7	43.6	37.3	44.5
Aggressive CO_2(mg/l)	14.4	14.0	10	12	12
Methane (mg/l)	3.1	2.3	3.4	2.3	3.4
Nitrate(mg/l)	<0.1	<0.1	<0.1	<0.1	<0.1
Chloride(mg/l)	34	33	42	34	58
Manganese(mg/l)	0.3	0.32	0.26	0.35	0.36

Parameters after the various treatment stages

Treatment stage	Oxygen (mg/l)	pH	Si(mg/l)	NVOC (mg/l)	$CaCO_3$ (mg/l)
Aeration stage	11.0	7.8	11.01	4.0	142.0
Filter 1	11.0	7.5	10.82	2.7	135.0
Filter 2	9.7	7.4	10.82	2.7	135.0
Filter 3	10.0	7.5	10.82	2.7	135.0

7.1 Relevant techniques used for the investigations

To investigate the cause of the high concentration at Vejers drinking WTP, techniques such as Atomic absorption Spectrometer (AAS), Laser Doppler Electrophoresis (LDE), Dynamic Light Scattering (DLS), X-ray diffraction (XRD), and Fe Species Identification Kits (ISI) were used. The various techniques employed in chapter 6 are as discussed in the following sections:

7.1.1   Laser Doppler Electrophoresis (Measurement of Zeta potential relating to Electrophoritic mobility)

The creation of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region. This results to an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus, an electrical double layer builds around each particle. See figure 7.1

Stern layer

negatively charged diffuse layer

Bulk of the liquid

Positevly charged particle

ζ

Electric potential

κ -^{1} Debye length

Slipping plane

Stern plane
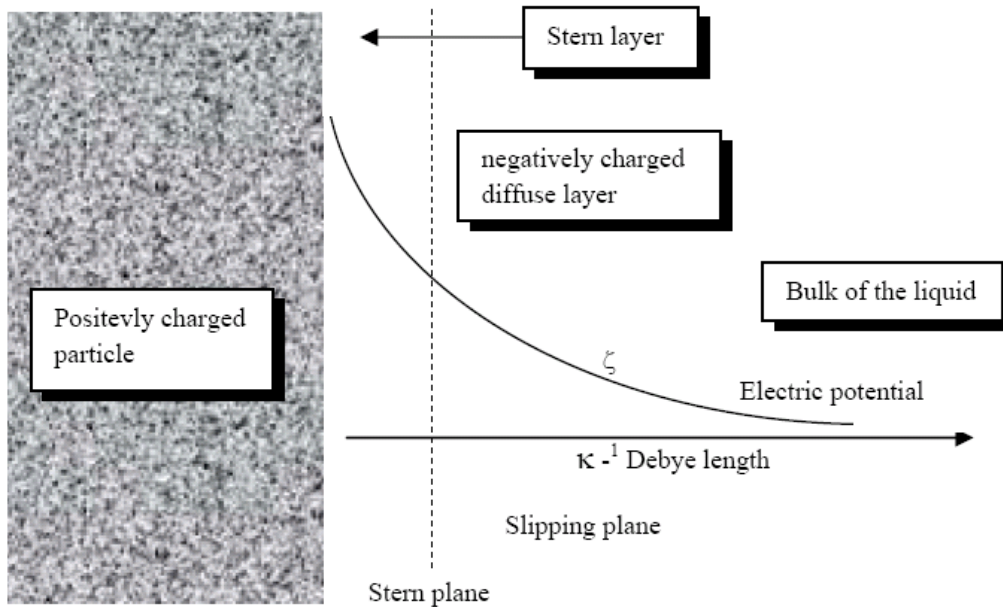
Figure 7.1: Gouy-Chapman model of the double layer (Hunter, 1993).

If an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted and they move towards oppositely charged electrode. Viscous forces acting on the particles tend to oppose the movement of the charged particles. When equilibrium is established between these two opposing forces, the particles move with constant velocity. By determining the velocity of the charged particles with respect to the moving electrolyte also known as the electrophoritic mobility of only the particle (u_E) , the Zeta potential can be calculated using the equations in 7.0.

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. On the other hand, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating

Figure 7.2 shows a schematic diagram of the Malvern Zetasizer IIc used for the experiment. The principle of operation is that two coherent rays of red light produced by splitting the output of a helium-neon laser are directed to cross at the stationary level in the capillary cell containing particulate suspensions. At the intersection, a pattern of border is formed. The particles are therefore drawn across that parttern by the applied electrical field and as they go through the light and dark strip, the amount of light dispersed also goes through similar fluctuations. The frequency of the fluctuation is proportional to the speed of the particle. The dispersed light is collected by a fast photometer and measured by a digital correlator, which converts the frequency of mobility into zeta potential.
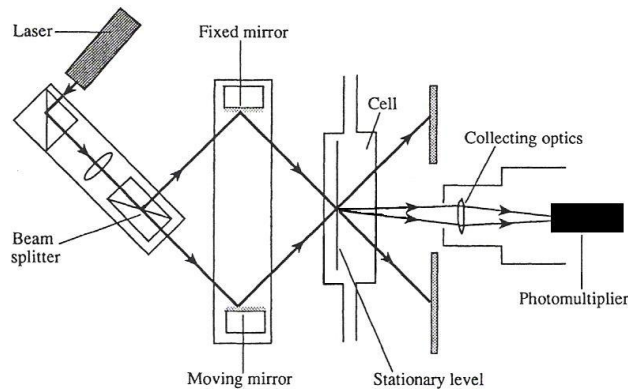
Figure 7.2: Diagrammatic representation of the Malvern Zetasizer IIc system (Hunter 1993).

The Zeta potential can therefore be calculated from the Henry equation:

$$u_E = (\frac{2\varepsilon\zeta}{3\eta})f(\kappa a) \tag{7.0}$$

Where:

u_E = velocity of particle/ Electrophoritic mobility

η = Viscosity of liquid

ζ = Zeta potential

a = particle radius

$\dfrac{1}{\kappa}$ = Double layer thickness

f = A function which varies from 1 to 1.5 as кa varies from 0 to ∞

ε = Dielectric constant

The henrys equation is a combination or modification of the Smoluchowski and Hückel equations. For very thin double layer around particle as compared to the particle radius, (that is кa >>1) then the Smoluchowski eqauation applies where the factor f becomes 1.5. On the other hand, when the double layer of the particle is very large, then, the Hückel equation is applied where the factor f becomes 1

7.1.2 Determination of streaming potential

The potential which is developed when a liquid is forced to flow through a capillary or a porous solid is known as the streaming potential. Streaming potential depend upon the presence of an electrical double layer at a solid-liquid interface. The electrical double layer is made up of ions of one charge type which are fixed to the surface of the solid and an equal number of mobile ions of the opposite charge which are distributed through the neighboring region of the liquid phase. In such a system the movement of liquid over the surface of the solid produces an electric current, because the flow of liquid causes a displacement of the mobile counterions with respect to the fixed charges on the solid surface. The applied potential necessary to reduce the net flow of electricity to zero is the streaming potential (Hunter, 1993).

Measurement
The equipment used for the experiment is shown in figure 7.3. The sample was placed in a container (1) between two filters of pore diameter of about70 μm. Ag/AgCl electrodes were placed just after the filters. The electrolyte of about 1 litre (in this experiment, which was the backwash water) was pumped under air pressure (P) of 0 to 500 mbar back and forth container 1 and 2. The direction of movement is controlled by a set of valves and vents. The instrument was controlled by computer which automatically controlled the required presure increamrnt needed for the measurements.
When a steady state has been reached, the ξ potential is calculated based on the equation described below:

$$\frac{E_s}{P} = \frac{\varepsilon\zeta}{\eta\lambda_0} \tag{7.1}$$

Where

P = differential pressure,
λ = electrical conductivity of the solution,

η = viscosity of water,

ε= relative permittivity of water, which is 80.
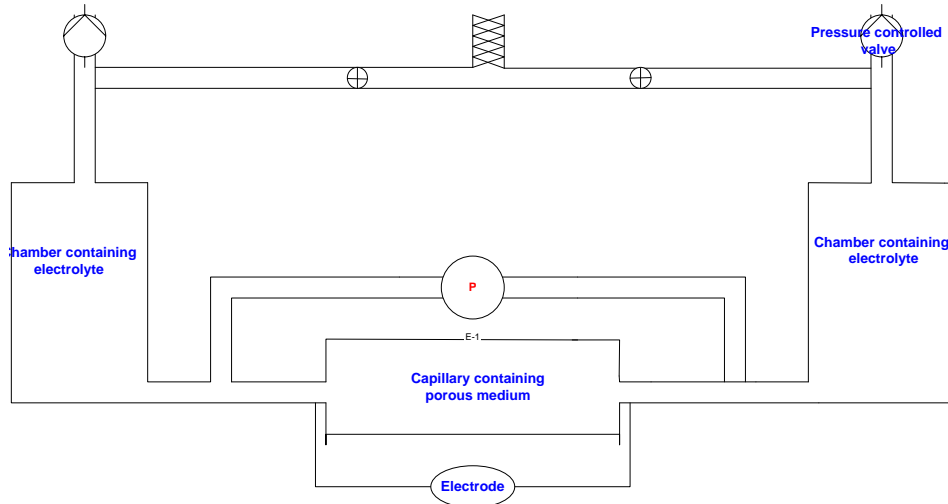
Figure 7.3: Apparatus for measuring electro-osmoses in a porous plug.

7.1.3 Determination of Fe present at the various treatment stages

The total Fe concentrations were measured with Atomic Absorption Spectrometer (AAS). In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument identifies a particular metal by focusing on a beam of atoms of metals and absorbs ultraviolet light from them when they are excited by heat at a specific wavelength through a flame and into a detector after a sample of interest is aspired into the flame. The metal to be measured in the sample absorbs some of the light, with intensity (I_o), thus reducing its intensity, (I). The instrument therefore measure the changes in intensity by comparing I to I_o and a computer data system converts the changes in intensity into absorbance, which is intern converted into the concentration of that metal present in the solution. See figure 7.4
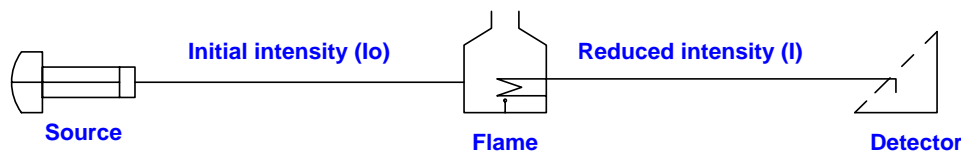
Figure 7.4: Schematic diagram of the AAS (Beaty and Kerber, 2002).

7.1.4 Determination of the Fe crystallization

This experiment was conducted to determine the crystallization of the Fe precipitates and also the size of the crystalline in the backwash samples.

The atomic planes of a crystal cause an incident beam of X-ray to interfere with one another as they leave the crystal. This phenomenon is called X-ray diffraction.

When an X-ray beam with a wavelength λ is projected onto a crystalline material at an angle θ, diffraction occurs only when the distance travelled by the ray reflected from successive planes differ by complete number n of wavelength. By varying the angle θ and plotting the angular positions and intensity of the resulting diffraction peak of radiation produce a pattern, which is characteristic of the sample (figure 7.5).

The degree of crystallization is determined by the **Bragg's equation**

$$d = n\lambda/2 \ \sin \theta \qquad\qquad\qquad (7.2)$$

Where:

d= the spaceing between the planes in the atomic lattice

n= an integer

λ= wavelength of incident wave

θ = angle between the incident ray and the scattering planes
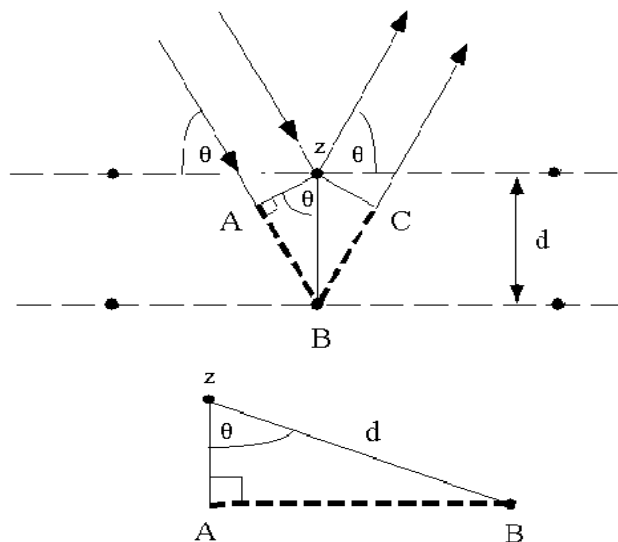
Figure 7.5: Deriving using the reflection geometry and applying trigonometry.

7.1.5 Dynamic light scattering (photon correlation spectroscopy)

When light photon hits a moving particle performing Brownian movements, the frequency of the scattered light with respect to a stationary observer will differ from the incident light frequency. The relative frequency of the incident light, which decreases or increases depending on whether the particle is moving away or towards the observer, is converted into a diffusion coefficient, which is also related to the particle radius.

The analysis was done by projecting the laser source onto colloidal suspension in water and the intensity of the scattered light were measured automatically by computer. See figure (7.6).
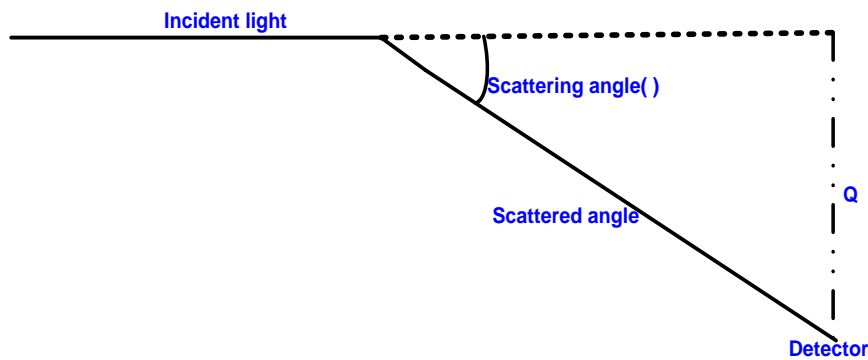
Figure 7.6: Geometry of light scattering experiment.

The intensity of the scattered light of frequency w can be represented as:

$$I_{(w)} = A \frac{DQ^2}{(\omega\text{-}\omega)^2 + (DQ^2)^2}$$

(7.3)

Where:

$$D = \frac{kT}{6\pi\eta r}$$

(7.4)

D is the particle diffusion coefficient, which is related to the particle radius by Einstein-Stokes formula represented by:

Q = magnitude of scattering vector is represented by the equation:

$$Q = \left(\frac{4\pi n_o}{\lambda_o}\right) \sin\left(\frac{\theta}{2}\right)$$

(7.5)

A = constant depending on the source of light

ω_o = frequency of incident radiation

n_o = refractive index of the medium

θ = scattering angle

T = absolute temperature of the scattering solution

λ = Wavelength of scattered light

η = Viscosity of solvent

k = Boltzmann's constant
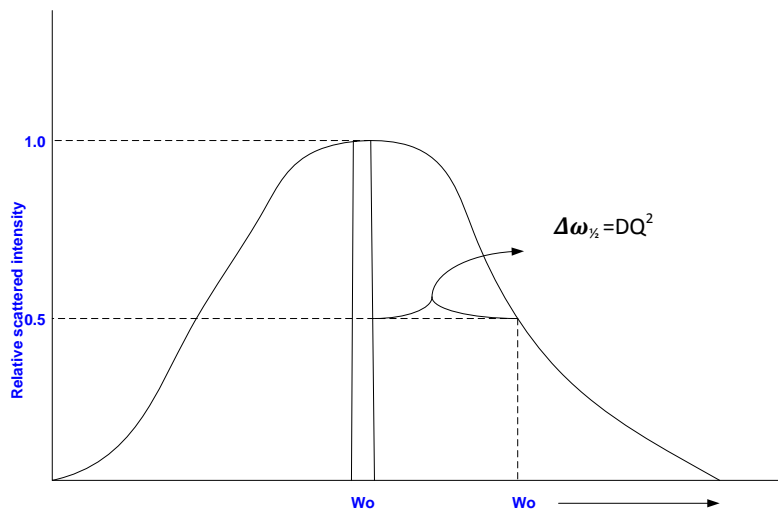
Figure 7.7: Lorentzian Doppler line broadening (Hunter, 1993).

The width of the peak at half-height is directly related to the diffusion coefficient (see figure 7.7)

$$\Delta\omega_{\frac{1}{2}}=DQ^2 \tag{7.6}$$

7.2 Results and discussions

Discussions for the investigations conducted in chapter 6 are as discussed below:

7.2.1 Investigation of the cause of the high Fe concentration at Vejers drinking WTP

As mentioned earlier, Fe in groundwater could be difficult to be removed as a result of either incomplete oxidation of the soluble Fe(II) or when the Fe present in groundwater form minute colloidal particles which go easily through the filter media. Therefore, to analyze the cause of the Fe problem in Vejers WTP, the removal of the colloidal ironoxide particles were determined at each filtration stage for filter 1, 2 and 3. The removal of the particles was investigated by first backwashing those filters (filter 1 to filter 3) carefully and measuring the Fe concentration in the filtered water after having started up water production again with cleaned filters. Fe was measured within a period of two hours as shown in figure 7.8.
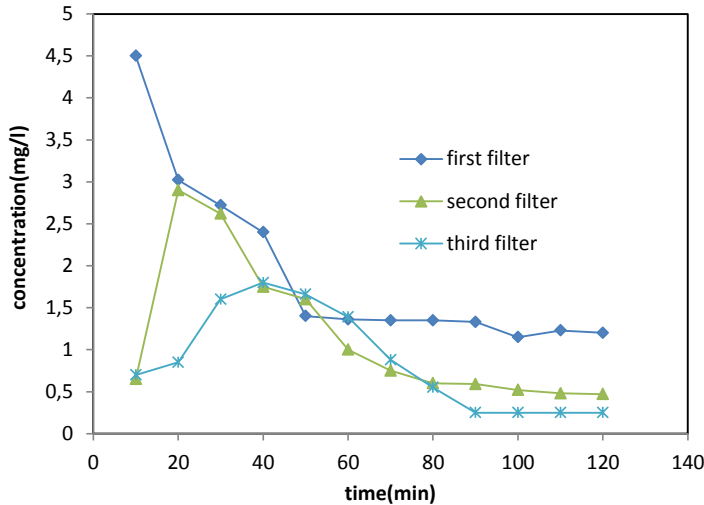
Figure 7.8: Total concentration of iron in mg/L against time (min) after filter 1, filter 2 and filter 3 measured after back washing the filter.

Table 7.1: Zeta potential of particles in water from wells, aeration tank and filter 4, and streaming potential of filter medium.

Sample identity	Zeta potential (mV)
Water sample from Well 2	-18
Water sample from Well 3	-10
Water sample from Well 4	-24
Water sample from Well 5	-23
Water sample from Well 6	-21
Water sample from Aeration stage	-16
Water sample from Filter 1	-13
Water sample from Filter 2	-14
Water sample from Filter 3	-14
Water sample from Filter 4	-14
Sample identity	**Streaming potential (mV)**
Streaming potential of Filter media	+2.8

Initially, high concentrations of Fe of about 4.5 mg/l, 2.7 mg/l and 0.7 mg/l were recorded by taken samples at the outlet of the filter 1, filter 2 and filter 3 respectively. The iron concentration after filter 2 and filter 3 then increased slightly probably because the outlet pipe still contained the previous water with settled Fe particles. Later, the Fe content began to dwindle in all the three filters to concentrations of about 1.2 mg/l after filter 1, 0.5 mg/l after filter 2 and 0.2 mg/l after filter three, and became almost constant in the respective filters. What may have happened was that due to the negative zeta potential of the Fe(III)oxide particles in the raw water, which ranged between -24 mV to – 14 mV, they may have been adsorbed to the sand filter materials. A positive streaming potential of about +2.8 mV was found for all the filters 1 to filter 3 (see table 7.1). It could be deduced from table 7.3 by using dynamic light scattering spectroscopy to measure the particle size distribution and mean particle radius in the water that the colloidal particles and other organic materials in the raw water easily passed through filter 1 and 2. However, in filter 3, most of the larger particles were removed, leaving those with mean radius of about 0.001 μm and below, which went through filters 3 and finally ended up in the fresh water systemThe results also showed that the filters 1 and 2 did not effectively remove the colloidal particles. As a consequence, those minute particles, which passed through the filters, may have been the origin of the 0.2 mg/l of iron which still remained in the drinking water. . The difference in the behavior between the three filters regarding the average diameters of removed particles is due to the different sand grain sizes used- filter 1 was about 1.2 mm while filter 2 and 3 were about 0.5 mm.

Because the minute colloidal particles could freely pass through the filters materials and end up in the drinking water, it means that the colloidal particles were not completely removed by the

filter materials. Looking at the separation from electrostatic point of view, it could be deduced that the electrostatic attractive force between the streaming potential of the filter materials and the zeta potential of the colloidal particles in the water was not substantially strong enough to retain the colloidal particles on the surfaces of the filter material. The most plausible explanation for the high concentration of Fe always observed in the drinking water seems to be some kind of already present colloidal iron particles from the water wells and less probably, a delayed or incomplete oxidation of the Fe^{2+} in the water of the water treatment plant.

7.2.2 Concentration of Species of Fe(II) and Fe(III) present across the entire treatment processes

This analysis was performed to identify the iron species present from the wells throughout to the aeration stage. The analysis was done to ascertain if the cause of the intolerable amount of iron in the drinking water was not due to delayed oxidation of Fe(II) but by colloidal Fe(III) particles. The analysis was carried out after the plant design had been reviewed to replace the initial first aeration stage by the new filter. (table 7.2 and figure 7.0)

Table 7.2: Amount of Fe(II) and Fe(III) as well as percentage constitution of Fe(II) and Fe(III) (total Fe) from groundwater to the aeration stage(water fully aerated to saturation) at vejers drinking WTP

Treatment stages	Fe(II) (mg/l)	Fe(III) (mg/l)	Fe(II)& Fe(III) (mg/l)	Percentage of Fe(III) %
Well 2	4.8	0.9	5.7	16.0
Well 3	4.6	3.4	8	43.0
Well 4	3.5	0.4	3.9	10.0
Well 5	2.8	0.4	3.2	13.0
Well 6	4.9	1.6	6.5	25.0
New filter	2.2	0.1	2.3	4.0
Aeration stage	0	2.3	2.3	100.0

It could be seen by general inspection of table 7.2 that the dominant species of Fe in all the wells were Fe(II), with well 4 having as high as about 90 % of its Fe content in the form of Fe(II) species. However, the amount disappeared completely at the aeration stage given a value of about 0 % or no Fe(II) at all. This is due to oxidation of the Fe(II) to Fe(III). The dominant Fe(II) species analyzed in the wells was not surprising, since the ground water was under anoxic or reduced conditions with low oxygen content ranging from about 0 mg/l to 0.63 mg/l and high amounts of CO_2 between 10 mg/l to 14 mg/l (see table 7.0). Surprisingly, although under anoxic conditions, not only were Fe(III) recorded, but some amount of Fe(III) also showed up in all the wells; In fact in well 3, as high as about 43 % of the total iron was in the form of Fe(III) . This is a clear indication that some of the Fe(II) had already been oxidized to Fe(III) from the wells before the raw water is pumped out for treatment. The oxidation of Fe(II) to Fe(III) must have

been influenced by several other factors such as pH of the water, the presence of dissolved minerals such as silicates which probably blocks nucleation of ferrihydrite, organic materials due to their adsorption on iron oxides in general and the presence of other inhibitors in the wells (Cornell and Schwertmann, 2003). Another probable cause of the presence of Fe(III) in the wells could be that, the process of pumping out water from the wells over a period of time may have coincidentally injected air into the wells, thereby oxidizing some of the Fe(II) to Fe(III). The measured Fe(III) may therefore represent the minute colloidal particles which passed through the sand filters unfiltered at a steady state level some time after the filters have been backwashed. Normally, the chemical catalytic oxidation of Fe(II) cannot take place if Fe(II) is already oxidized and the chemical catalytic filtration with adsorption, oxidation and co- precipitation of Fe is not very useful for colloidal particles as it is often seen where waterworks has installed precipitation tanks before the sand filtration units.

Immediately after back washing the levels were higher. High percentage of Fe(II) was measured after the new filter but this must be due to the mixture of the different raw water from the different wells. However, after the aeration stage, no Fe(II) was detected. This is a confirmation of the fact that all the Fe(II) has been oxidized to Fe(III) and that the retention time of the water in the aeration tank was high enough. If any iron remains in the water after the aeration stage at all, then it is most probable that they are in the form of minute colloidal particles and not dissolved Fe(II). If some of the Fe had already been oxidized from the well, then because of the presence of silicates, about 11.19 mg/l and natural organic matter of about 2.5 mg/l, they could tremendously affect the crystallization of the Fe precipitates in the filters.

7.2.3 XRD analysis of the Fe precipitates from the backwash sludge from filter 1 and filter 3

The X-ray diffraction spectrum of the Fe sludges from the new filter and filter 3 (Thus at the beginning of the filtration stage and at the end of the filtration stage) is as shown in figure 7.9 and 7.10. This investigation was also done to further confirm that the precipitated Fe was indeed amorphous and minute colloidal particles.
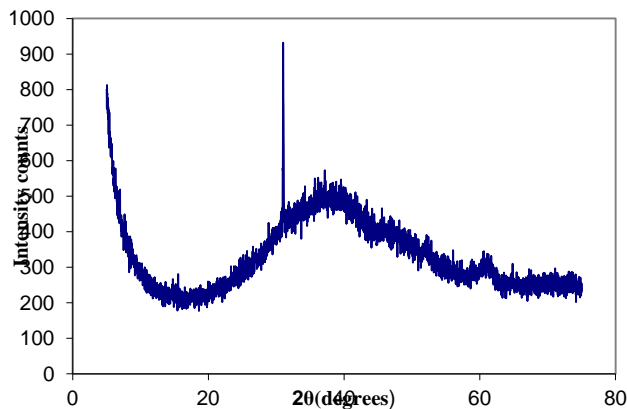
Figure 7.9: XRD measurement for the new filtration stage.
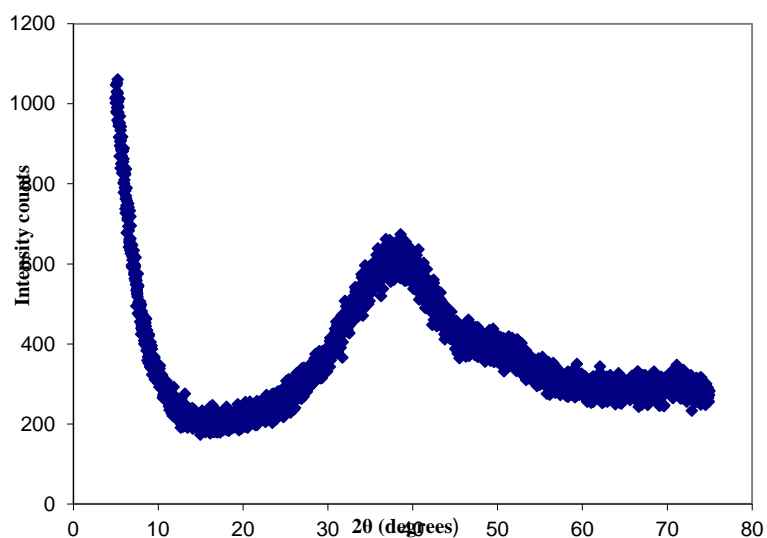
Figure 7.10 : XRD measurement for the third filtration stage.

The results from the X-ray diffractograms for both the new filter and the third filtration stage gave a 2- line ferrihydrite, and no meaningful peaks were obtained. This means that the Fe precipitates across the entire treatment process were completely amorphous ferrihydrites and no crystalline iron was precipitated in the filters. The results of the overall investigations observed conforms to what was expected due to the factors aforementioned. Therefore, it was necessary that a remedy must be found to deal with the high Fe content in the drinking water which will eventually reduce the iron concentration in the drinking water

7.3   Solutions to the recalcitrant Fe problem at Vejers Water treatment plant

Aluminium (Al) coagulants are known to be used for the destabilization of colloidal particles in drinking water treatment plants for time immemorial. Therefore, Al at a concentration of about 0.8 mg/l was initially added to the treatment process in filter 1 as an immediate temporary measure to solving the iron problem. The Al was added also with the expectation that if the cause of the refractory Fe was really due to Fe^{3+} colloidal suspensions then they could be destabilized and flocculated, making it possible to be removed by the sand filters. However, as the acceptable level of present Al in drinking water in Denmark at 0.1 mg/L can easily be exceeded and also this is not a stable solution to the problem. Therefore, biological Fe removal method was tried to oxidize and precipitate the Fe at Vejers WTP. To promote the bacterial growth, the first aeration tank was converted to new filter before the aeration tank (see figure 7.0). The results obtained from the addition of Al coagulant and the application of Fe biotic method of Fe removal to solve the Fe problem is discussed in the sections below.

7.3.1 Evaluation of the effect of Al coagulant on particle size distribution after the coagulant was added to the treatment process

The effect of Al coagulant was assessed mainly in terms of particle size distribution and the resultant mean Fe concentration after every filtration stage. (see table 5.4 and figure 7.11). The particle size distribution in table 5.4 shows that the particles radii in the raw water are distributed between 0.1 μm to 16.3 μm. After the new filter however, the particle size distribution further reduced to between 0.002 μm and 1.2 μm. On the other hand, the particle size distribution measured for the subsequent filters after the new filter (from filter 1 to filter 3) were all between 0.001 μm to about 1.0 μm. This shows that the minute particles in the water still went through the filter 1 to filter 3, without them being removed by the filters. When Al coagulant was added at the inlet of the filter 1, all the colloidal particles in the water disappeared, rendering the water almost particle free and the mean particle size and distribution were all under the detection limit.

Similarly, reduction of the colloidal particles in the water had a concomitant relationship with the concentration of Fe. See figure 7.11. It could be seen that without the addition of Al coagulant, high average concentration of iron of about 7.4 mg/l was measured in the raw water from the wells. This concentration dwindled steadily along the entire treatment process stages, keeping a mean Fe concentration of about 0.2 mg/l in the drinking water. However, when Al coagulant was added, the same trend of mean Fe concentration was measured from the raw water until filter 1. Similarly, the trend exhibited by the mean particle sizes in figure 4, there was a drastic reduction in the mean iron concentration to about 0.08 mg/l, and finally maintained only about 0.02 mg/l in the drinking water.
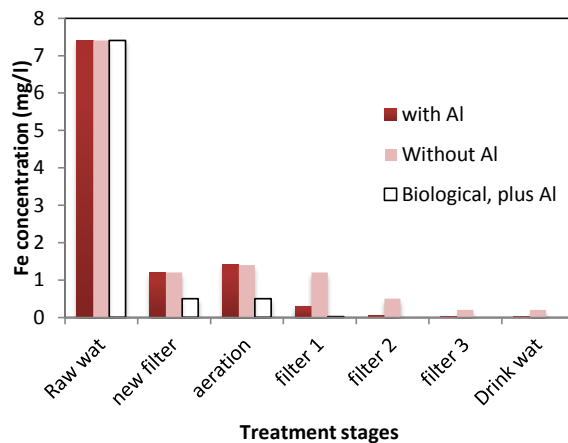
Figure 7.11: Evaluation of the effect of Al coagulant on Fe concentration without treatment, after the addition of the Al coagulant and after employing biotic method of Fe removal.

When added, the Al coagulant hydrolyses and deprotonates into various species such as $Al(OH)^{2+}$, $Al_2(OH)_2$, Al^{3+} and $Al(OH)_4^-$, with different concentration values at different pH. Especially, the Al-13 compound, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ which exist at pH between 4 and 6 just before precipitation of Al hydroxide is responsible for the coagulation effects of Al-compounds. (see figure 7.12) *Søgaard E. G., (2002)*. A sufficient pH is brought about by the alkalinity of the water provided by the hydrogen carbonate ions (HCO_3^-). The effect of the resultant solid Al hydroxide $Al(OH)_3$ (s) has a net positive charge which neutralizes the negative zeta potential on the surfaces of the suspended colloidal particles, which at the early measurements reported at table 7.1, were found to be between -14 mV and -24 mV across the various treatment stages . This enhances attraction by the long range colloidal van der Waals forces. As a result, the Al compound coagulate provided a favorable surface to adsorb and co-precipitated the colloidal particles and acted as a bridging factor in the coagulation of the particles. This made the particles possible to be removed by the sand filters. The coagulation of the colloidal particles by Al compound reflected the concentration of iron that was removed from the drinking water.
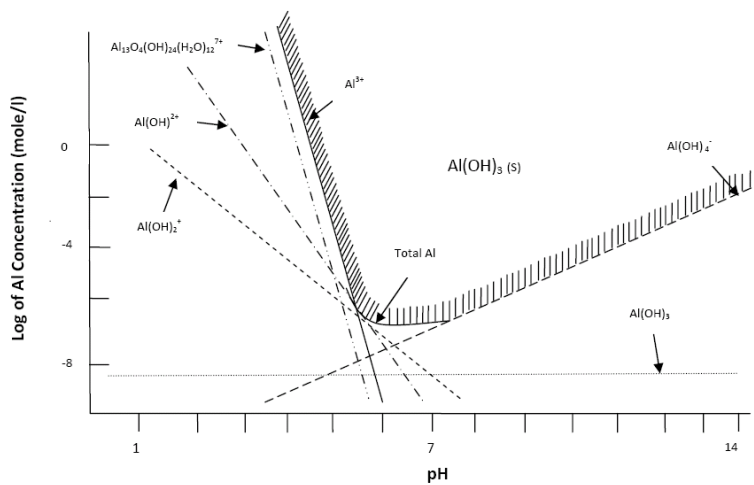
Figure 7.12: Concentration of Al species at different pH values.

7.3.2   Evaluation of the effect biological Fe removal method at Vejers WTP

To promote the growth of Fe bacteria in the new filter, the electro-chemical conditions of the raw water were optimized to favor the growth of Fe bacteria. Parameters such as pH of about 6.3 redox potential of between 30-100 mV, O_2 level of about 0.1- 1 mg/l together with copious amount of CO_2 were maintained in the new filter. After about 3 months, the bacterial growth was then confirmed by analyzing backwash samples from the new filter with the help of visible optical microscope and the image obtained is as shown in figure 7.13.
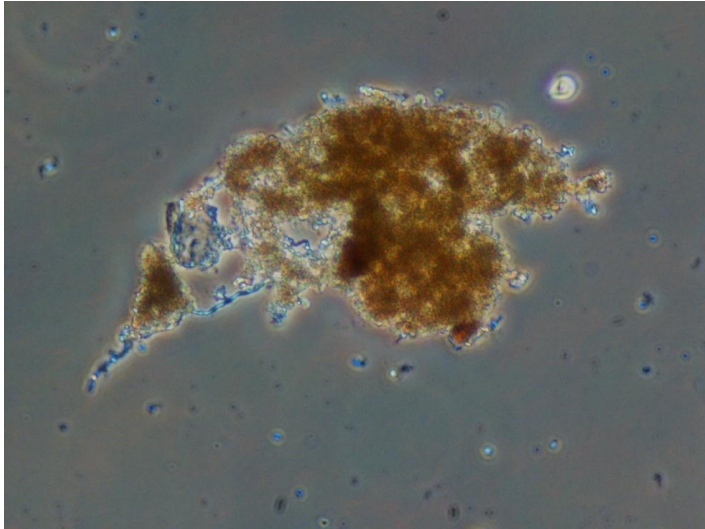
Figure 7.13: light microscope image showing exopolymers of Fe bacteria in backwash sludge sample (X 40).

It could be seen from the microscope image in figure 7.13 that the bacteria sheath/exopolymers of *Gallionella ferruginea* is adhering to the colloidal Fe particles, which partly engulfs the Fe precipitates. The bond between the exopolymers and the Fe precipitates due to complexation between Fe^{2+} and the exopolymers. - The carbohydrates in the exopolymers contain successions of hydroxyl radicals, which provide lone pair of electrons for the complexing between the exopolymers and Fe^{2+}/Fe^{3+}. The complexing effect therefore withheld some of the minute colloidal particles in the raw water.

Table 7.3: Particle size distribution before and after addition of Al coagulant, and after growth of iron bacteria .

Treatment stages	Particle size distribution (µm) before addition of Al coagulant	Particle size distribution (µm) after addition of Al coagulant	Particle size distribution (µm) after growth of iron bacteria while maintaining Al coagulant
Raw water	0.1 to 16.3	0.1 to 16.3	0.1 to 16.3
After new filter	0.002 to 1.2	0.002 to 1.2	0.002 to 1.3
After filter 1	0.001 to 1.0	Below detection	Below detection
After filter 2	0.001 to 1.0	Below detection	Below detection
After filter 3	0.001 to 1.0	Below detection	Below detection

The effect of the biotic Fe removal method was also evaluated in terms of particle size distribution, zeta potential and the resultant Fe concentration at every stage of the treatment process.

A particle size distribution of between 0.002 to 1.3 µm was measure in the water after the new filter (see table 7.3). However, the slight difference in particle size measured cannot be solely attributed to the bacteria activities. This is because, the outlets of the raw water pipes were fixed with a flat plate to enhance a gentle fall of the water into the filters, which may have also eliminated the turbulent flow of the water in the new filter. Direct fall of the water onto the surface of the filter fragmented the Fe particles previously and prevented them from forming larger particles. Also, after the growth of the bacteria in the new filter, the bacteria may have precipitated some of the Fe oxides leading to the more compact, denser and heavier particle

In the raw water, the Zeta potential, which ranged between -23 to about -14 mV(see table 7.1) reduced slighttly to about -9 mV after the new filter. This means there was a sort of charge effect from the bacterial stalk, which reversed the strong negatively zeta potential of the particles in the raw water, bringing it closer to the point of zero net charge. As a result, the iron precipitates coagulated and stuck to the stalks. This may be an evidence of the catalytic role of Fe bacteria to remove Fe from ground water.

The Fe concentration in the water at the outlet of the new filter in front of filter 1 and aeration stage measured after the growth of the bacteria exopolymers was about 0.5 mg/l. see figure 7.11. This concentration is higher than the allowable limit of 0.1 mg/l. However, there was a decrease in the concentration of iron in the water after the iron bacteria developed from about 1 mg/l to about 0.5 mg/l. Therefore, at the filter 1 in which Al was added, a drastic decrease in the residual Fe concentration to about 0.02 mg/l was measured at outlet of filter 1. This concentration was already below the allowable limit of 0.1 mg/l. Without the growth of the iron bacteria, the addition of Al could only help to remove the Fe concentration to the allowable limit after the filter 2. Undoubtedly, this means that the amount of Al added now could be reduced drastically even if it cannot yet be taken off completely from the treatment process. This will reduce the operational cost and the amount of Al that could remain in the clean water during consumption.

Besides looking at the chemistry aspects to solving the problem, mechanical solutions were also sought to the problem. Thus, the wells were properly maintained to ensure that little or no air enters them before the groundwater is pumped out for treatment. Normally, when oxidation starts from the wells then, the minute ferrihydrites can be produced right from the wells even before the groundwater is pumped out for treatment. That measure taken, ensured that oxidation of the contaminants especially Fe, does not start from the wells. Also, during the pumping process, the pumps were regulated to start up with a slower velocity until it reaches its maximum steadily velocity of about 30 m^3/h. This ensured that turbulence flow of water did not develop in the pipes and a smooth flow was ensured to avoid the particle being fragmented during the pumping process.

7.4 Conclusion

The cause of the refractory Fe present at Vejers water treatment plant was ascertained to be dispersed colloidal ferrihydrite particles in the raw water and not delayed oxidation of dissolved Fe^{2+} to insoluble Fe^{3+} oxides. The high content of silicate and natural organic matter content in the wells may have enhanced the formation of colloidal particles right away from the wells when oxygen began to be present in small amounts and along the entire treatment process. They easily passed through the filters without been filtered off and finally ended up in the fresh water system. Characterizing the iron sludge in the filters also showed that the precipitates were amorphous two line ferrihydrite and no Fe crystals were formed. By adding Al compounds in the form of coagulation agent polyaluminium chloride, the colloidal ferrihydrite coagulated, thereby enhancing their removal by the filters. An optimal removal of the colloidal iron particles was therefore obtained by the addition of the Al coagulant. However, the safer use of Al coagulant, thus maintaining it at a concentration of 0.1 mg/ is difficult due to the Al residue in the drinking water.

To avoid the use of Al, the first aeration tank was converted to a new filter, which receives raw water directly from the wells without aeration. The second aeration tank then became the first aeration tank and was followed by already existing filter units. This set up created conditions necessary for biological iron removal in the first filter.(see figure 7.0)This means that the treatment process was changed from purely physico-chemical to biological iron removal. As a result, the amount of Al added was therefore reduced and it is even expected that the Al may be taken off completely from the treatment process in the near future when the bacteria are fully developed in the near future. So instead of addition of chemicals the nature itself takes over with the new conditions for the iron oxidation/precipitating bacteria and therefore only use of limited aeration. If no extra costs to maintain the new filter with biological iron precipitation can be considered then both the environment and the economy have benefited from this change.
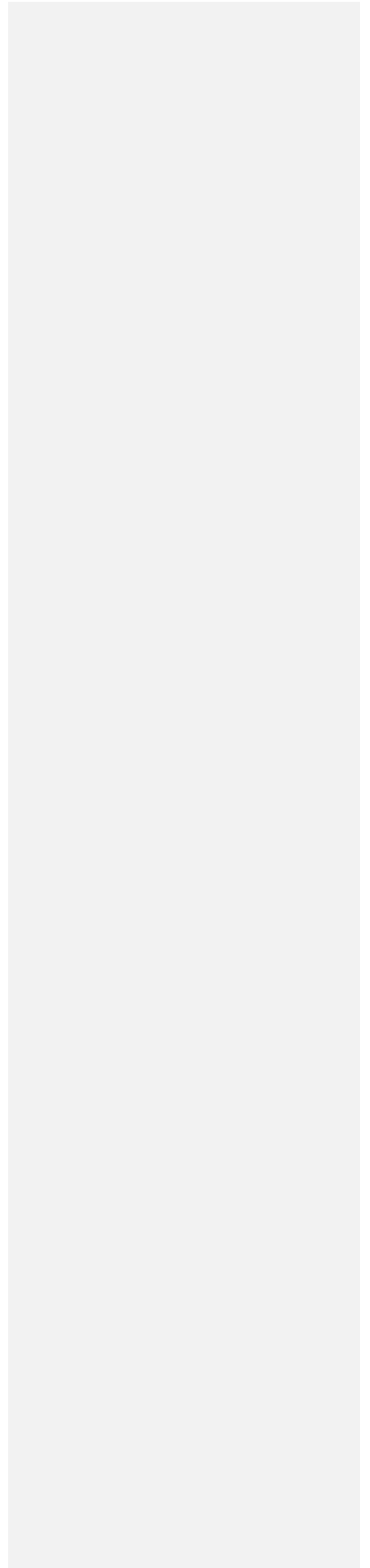
Chapter 8

Chemometric classification of Fe precipitates from selected water treatment plants in Denmark

8 Introduction

Fe in groundwater for drinking water purposes is traditionally removed by the physico-chemical method where the raw water is aerated to saturation by air. By aeration of the raw water, the Fe hydrous oxyhydroxides usually precipitate in the sand filters build for filtration of the Fe precipitates.

Besides the purely physico-chemical method of Fe removal, is the biotic method where bacteria are actively involved in the precipitation of Fe. The biological Fe removal method is found to have numerous advantages over the purely physico-chemical method. For instance, it is documented that the biologically precipitated Fe oxides enhances higher removal capacity of Fe in the raw water and also have improved filtration rate. Moreover, the particles precipitated by biological Fe removal method are compact and denser in structure and they are described as superior in nature than the corresponding a biotic precipitates.

So far, there are no known analytical methods to control the Fe oxides precipitated by biotic or abiotic method in water treatment plants. However, nowadays, pattern recognition methods have been used in chemometrics to reveal and evaluate complex parttens in a wider field of research, including Environmental, food science and in Agriculture (Esbensen, 2006).

For instance, Checa et. al. in 2006 used SIMCA to characterize proteinaceous binders in the field of cultural heritage. Also, in 1987, Saddler et al adopted SIMCA statistical package to examine biomass from representative strains of Streptomyces cyaneus and related taxa. The SIMCA approach was also useful in distinguishing between cod and haddock eggs at both stages when Vogt et al in 1986, analyses fatty acids pattern in Day-1 and Day-8 cod (Gadus morhua) and haddock (Melanogrammus aeglefinus) eggs (Vogt et. al., 1986).

In this chapter therefore, the multivariate data analysis, PCA-SIMCA is used to differentiate between biotic and abiotic Fe precipitate in selected Danish fresh water treatment plants.

8.1 Methodology

Quantitative multivariate analysis was done on ferrihydrites precipitated under biotic and abiotic conditions. The analysis was done with the help of analytical tools such as Near Infrared Spectroscopy, NIR, and visible optical microscopy were used to convert the information from the iron precipitates into raw data possible and analysed by the PCA-SIMCA software

Initially, visible optical microscopy was used to identify samples as either principally biotic or abiotic precipitated and then used to construct the PCA and SIMCA models. To create/construct the SIMCA model to distinguish between biotic and abiotic Fe precipitates, 30 biotic and 20 purely abiotic samples were used. The biotic samples were obtained from a laboratory reactor set up to grow Fe bacteria based on filter sand from the iron precipitating first filtration step of Astrup water work (Søgaard, 2000). The reactor precipitated Fe(II) solution to Fe(III)oxides. Similarly, the abiotic samples were also produced in the laboratory based on the method to prepare 2- line ferrihydrite as described in the book " Iron Oxides in the Laboratory (preparation and characterization) (Schwertman and Cornell 2003). The solution was aerated to precipitate the soluble Fe(II) to insoluble Fe(III)oxide, which was used for the investigation. Out of the entire 50 samples prepared, 40 of them (thus 25 biotic and 15 abiotic samples) were used to construct the PCA and SIMCA models. The remaining five (5) of each were samples were used for validation by using them to test the model during the construction of the SIMCA model. The chemical/abiotic objects are denoted KE while the biotic objects are denoted BIO in both the PCA and SIMCA models.

8.1.1 Near infrared spectroscopy analysis

The near infrared spectroscopy was used for the analysis of the back wash precipitates. Infra red spectroscopy is a technique used to identify chemical compounds based on how the chemical compounds in the analytes (samples) are absorbed. Normally, the near infra red spectra is absorbed by the absorption band of the chemical compounds as a result of the molecular vibration of the hydrogen bonding such as O-H, C-H and N-H. For this to occur, the monochromatic light produced by NIR radiation interacts with the sample by adsorption, reflection, refraction, diffraction and/or transmission. The data obtained from the analyses are calculated using Beer's law, which expresses the linear relationship between the molar concentrations of a substance at a particular wavelength. The Beer's equation is as indicated below (Fourth European Symposium, 2000):

$$A = -\log \frac{I}{I_o} = \log \frac{1}{T} \log \frac{1}{R} = \varepsilon \times d \times c \qquad (8.0)$$

Where,

A = absorbance

I = spectral intensity remaining after interaction

I_o = Spectral intensity of the radiation emitted by the spectrometer light source

T = transmittance

R = reflectance

ε = Molar absorptivity

d = light path length

c = sample concentration

The samples in the present investigation was measured directly as they were sampled fully hydrated in transmission mode (see picture of the NIRS in figure 8.0)

Figure 8.0: photograph of the NIRS equipment used for the analysis of the backwash precipitates.

8.2 Data processing

The data obtained from the NIRS analyses were processed using the software Unscrambler licensed by CAMO software AS in 2006. The PCA – SIMCA multivariate data analysis was done.

To predict if the samples belonged to one or more particular groups, the soft independent modelling of class anatomy (SIMCA) chemometric approach of classification was used.

The primary stage to begin SIMCA classification is Principal component Analyses (PCA) models or disjointed class-modelling. PCA analysis is used to simplify multivariate data set by transforming correlated variables into sets of independent principal components, using linear combination of the original variables (Esbensen 2006)

In PCA, individual models of the class in question are made. Subsequently, the classification stage adopts the established class model to assess which classes new objects belong to. For example, if there is an X matrix with n objects and only 3 variables, the variable space has 3 axis X1, X2 and X3. Each set of variable is treated as a swarm of data point in variable space which depicts a major trend associated among all variable plotted. This revelation of the underlining covariance structure is the key of principal component analysis. (see figure 8.1)
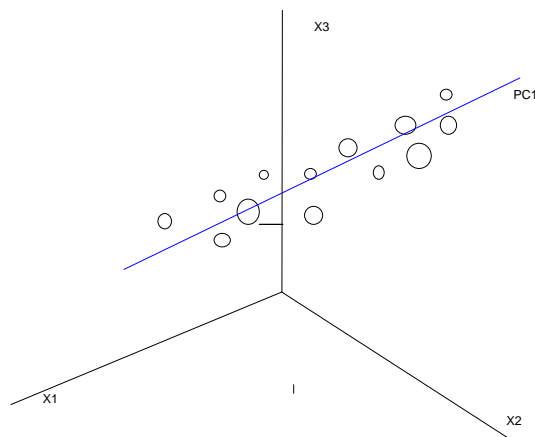
Figure 8.1: Data plotted as swarm of points in the variable space, disclosing a hidden trend.

The results from the classification stage enable the studies of the modelling and discrimination power of the individual variables.

The SIMCA approach is obtained from PCAs. It is basically based on applying separate or disjointed bilinear modeling of group data from PCA models. The principle underlining the SIMCA classification is that objects belonging to the same class show a particular pattern, which makes all the samples more similar than with respect to any other group or class. The plot in figure 8.2 shows the orthogonal (transverse) distance from all new objects to two selected models (classes) at the same time. If an object belongs to a model (class) it should fall within the membership limit - that is to the left of the vertical line or below the horizontal line in the plot. Objects that are with both lines, that is near the origin are classified as belonging to both models.
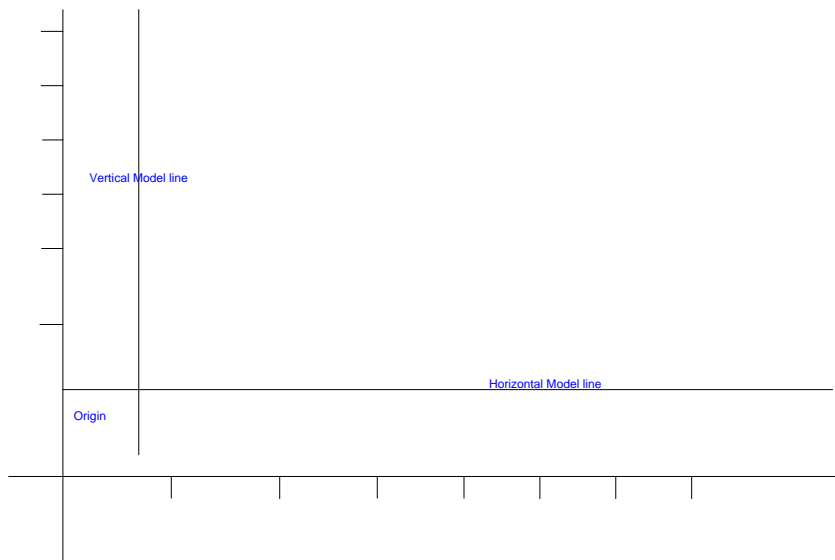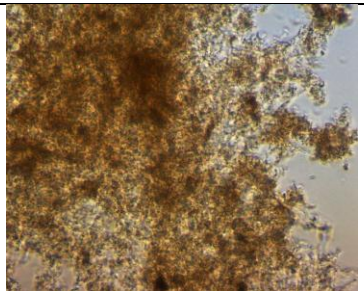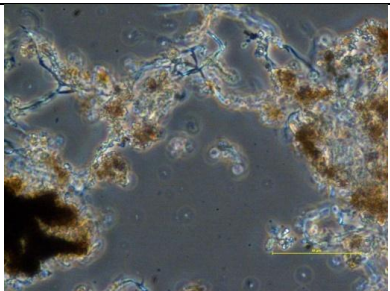
Figure 8.2: Representation of a SIMCA model plot.

SIMCA therefore uses extensive statistics to quantify model envelopes or classification species to geometrically determine if new samples lie within or outside the given model by the different distance measure from the new object to the model (Coomons plot).

Results and discussion

Microscope investigation of the backwash samples

Figure 8.3a, Backwash sample of Fe precipitate from abiotic Fe removal plant, showing loosely packed ferrihydrites.		*Figure 8.3b, Backwash sample of Fe precipitates biotic iron removal plant, showing exopolymers if Fe bacteria*

The common way to confirm if a water treatment plant operates by biological or physico-chemical iron removal methods is to investigate the backwash samples by means of microscopy, to find out if iron bacterial cells and exopolymers are present or absent. If there are no exopolymers, then the water treatment plant can be said to operate principally by purely physico-chemical method of iron removal. On the other hand, if iron exopolymers are found then it means that the water treatment plant is operating also by biological method of iron removal. Normally it is seldom to be able to observe the exopolymer generating bateria in the sampled sludge because they stick to the filter grain and also are difficult to observe without colouring their membranes. In order to classify backwash samples from water treatment plants as biotic or abiotic for this study, microscope analysis was carried out for all the backwash samples.

Figure 8.3a shows the way backwash samples from the plants or reactor which operated by principally purely physico-chemical (abiotic) methods looked like (laboratory sample). They were devoid of bacteriogenic materials and also were loosely packed with finer particles and brighter in colour.

In contrast to the purely physico-chemically precipitated iron oxides, the backwash samples from the plants which operates by biological iron removal, contained biogenic iron oxides composite materials. (see figure 8.3b) The biogenic iron oxide composite materials consisted of

intact or partly degraded exopolymers combined with amorphous ferrihydrites. By watching the precipitated sludge together with some filter sand grains it could also be seen that the exopolymers form an interconnective network inbetween the pores of the sand filter material, which are in close contact with the iron in solution. They therefore play a catalytic role in speeding up the velocity of oxidation/precipitation of iron in the biological sand filters (Sogaard et. al. 2001).

Spectra analyses of the NIRS data

Figure 8.4a, Initial PCA raw spectra	*Figure 8.4b, Reduced spectra (water peak removed)*

Figure 8.4c, Multiplicative Scattering Correction transformed spectra (water peak removed)
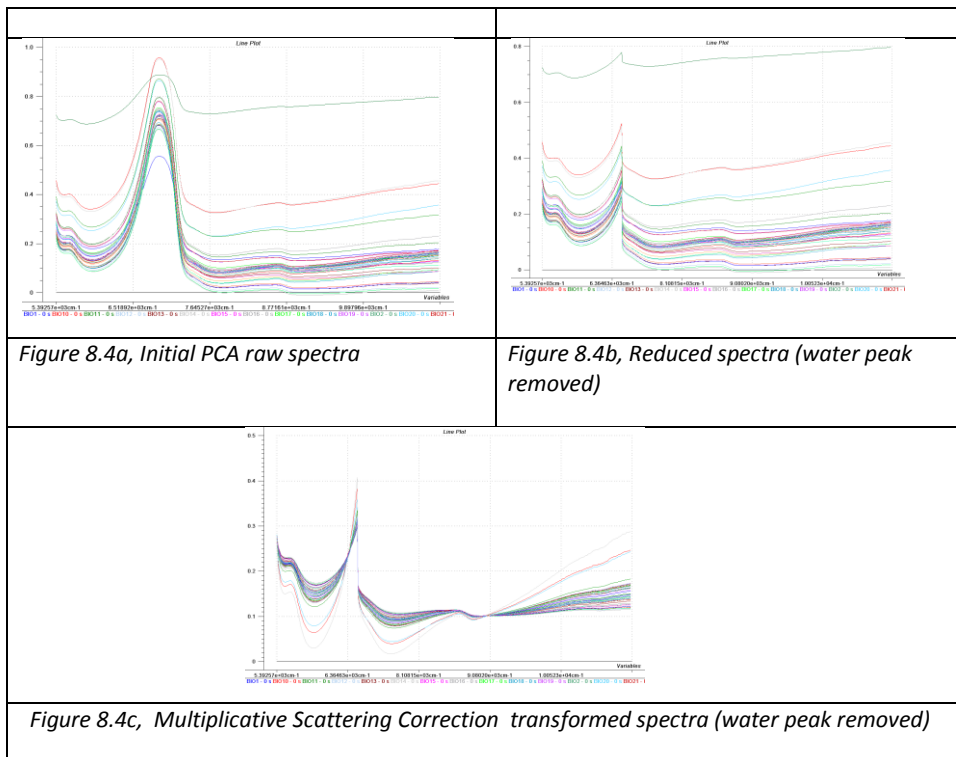
The multiplicative scattering correction (MSC) spectra for all the iron precipitates from the backwash samples used for the modeling are displayed in fig 8.4a. These spectra constituted an initial PCA of the raw data, a reduced spectra with water peak removed as in figure 8.4b and full transformed spectra after water peaks were removed is also shown in figure 8.4c.

The spectra in all cases, thus figure 8.4a, 8.4b and 8.4c seem to be smoothly arranged, lying closely to each other with a characteristic peakbetween the wavenumber of 4000 to 10000 cm-1, which corresponds to the near infrared water peak.. The water molecules which remained in the samples caused stochastic noise, thereby interfering with the spectra. The effect of the noise on the spectra was removed in order to eliminate noise factor from the results for modeling This gave the reduced spectra as shown in figure 8.4b

Backwash samples are derived from groundwater aerated and filtered through sand filters. It contain solid particles of ironoxides, eventually gas bubbles and also experienced density and amount of sample fluctuations. Therefore, to eliminate the effect of these factors, the Multivariate Scattering Correction (MSC) transformation was also done from the the reduced spectra. (see figure 8.4c)

By inspecting the the MSC transformed spectra, no distinct variation could be observed between those spectra from the spectra constituting biological iron precipitates or physico-chemical iron precipitates. However, the spectra from the MSC transformation seem to be rather more compacted/compressed without any distinct peaks but with few meanders. The few isolated spectra are possibly beoutliers.

Generally, particle size distribution, density, , particle sizes and the chemical composition are factors that determines the difference in spectra under investigation. However, by visually inspecting the spectra, none of them (not the raw one, or reduced or MSC corrected) exibitted a clear variation in shape, which could be attributed to be a difference in the abiotic or biotic backwash samples. We could therefore conclude that there is a close similarity in chemical composition, density and particle sizes of backwash precipitates from water treatment plant operating by principally either biotic or abiotic method of iron removal. The raw spectral data were therefore projected into the PCA model for analyses.

Principal Component Analysis of the raw data

Figure 8.5a, PCA analysis of BIO and KEM of raw data spectra	Figure 8.5b, PCA analysis of multiplicative Scattering Correction (full: alpha + beta) transformed spectra (water peak removed)
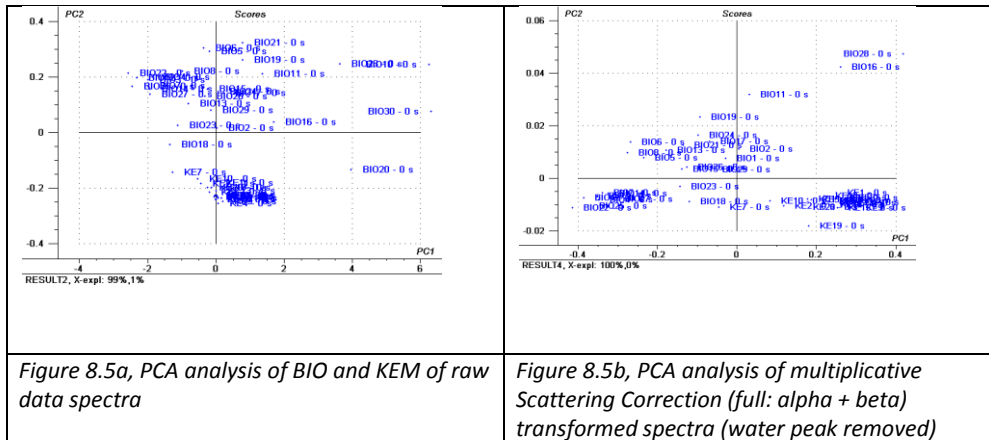
Figure 8.5a and 8.5b are score plots from Principal Component Analysis. They are two (2) pair of score vectors from objects plotted against each other. Score plots show object interrelationships. It therefore decomposes information on the object by assisting to identify trends, groups and outliers that can possibly exist in a swamp of data.

To derive the dominant patterns existing in the data from abiotic backwash iron precipitates (KE) and biotic (BIO), the raw data were displayed as two plots of principal components. The figures 8.5a show the score plots of PC1 Vs PC2 for both abiotic backwash precipitates (KE) and biotic backwash iron precipitates (BIO). It could be deduced that KE are negatively in PC2 and slightly/weak positive in PC1.They are however, grouped closely together at mostly negative PC2 and slightly positive PC1. On the other hand, BIO objects are widely/broadly spread, from positive PC1 to negative PC1 and also from strongly positive PC2 to some few with negative PC2. This trend exibited by the bio objects explains the variation and how complex and more divers the BIO samples were as compared to the KE samples. The reason for that is the way the KE samples were produced by using pure chemicals in laboratory and produce two line ferrihydrate based on a reciept of Schwertmann (1996). Contrary to this, the biological samples were produced in a laboratory flow reactor with filter material from one of the water treatment plants (Astrup), which were directly constructed for biotic iron precipitation and therefore contained the iron precipitating bacteria.

Figure 8.5b also displays score plots from Principal Component Analysis for backwash samples from KE and BIO, using the same data as in fig 8.5a. But, in figure 8.5b, the raw data were transformed to eliminate stochastic noise. It can also be seen from fig 8.5b that KE is still grouped closely together at the bottum right corner of the coordinates. Similarly, as in figure

8.5a, the BIO objects in figure 3b are broadly grouped and they seem to spread diagonally from left bottum to the right top conner of the score plots. Figure 8.5a and 8.5b clearly shows that groupings exist between the BIO and KE objects.

SIMCA Principal Component Analysis

Figure 8.6a, Astrup prediction objects projected onto chem and bio training models	*Figure 8.6b, Vr. Gjesing prediction objects projected onto chem and bio training models*
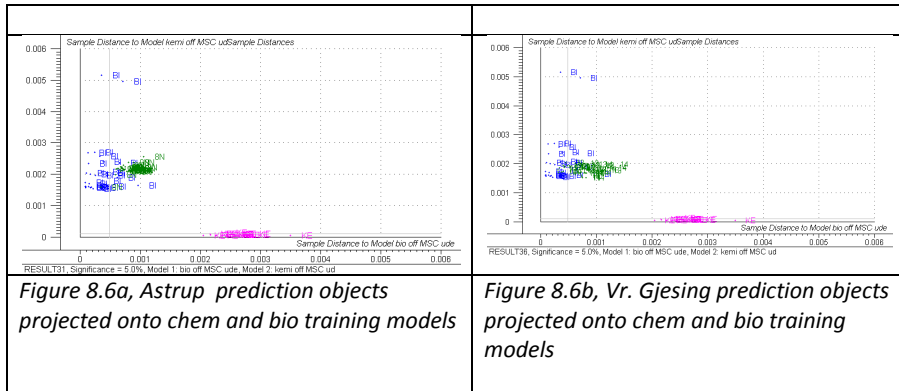
The plots above displays the coomons plots of SIMCA principal component analysis. In this method of classification, if an object belongs to a class/group, it should fall within the membership limit, which is to the left of the vertical line or below the horizontal line in the plot. Objects that lies within both model lines close to the origin belongs to both models. For easy interpretation of the results, the objects are coded in colours. Thus, the KE training set are coded in red, and in blue, while the prediction objects are coded in green.

Astrup WTP and Vr. Gjesing WTP was chosen as a start up for the modeling with the common reason that the backwash precipitate from Astrup WTP normally contained a lot of bacteria exopolymers, and therfore wasthought of as the most biotic precipitation WTP while backwash precipitates from V. Gjesing had no exopolymers at all.

Figure 8.6a, shows Astrup prediction objects projected into KE and BIO training models. The BIO training models lie to the left of the vertical model/prediction line, while the KE training models lie to the right buttom of the horizontal model/prediction line. When the predicted Astrup objects were projected into the the model, all of them fell outside both the group of the BIO training model and the KE training model. Specifically, the prediction objects from Astrup WTP lied to the top and to the right of the KE and BIO training objects respectively. This means that

Astrup WTP prediction objects did not clearly belong to the group or set of objects from neither the BIO and KE prediction objects. However, it could be seen that they lie more closely to the BIO training objects but far away from the from the KE training objects. This relationship could explain the resemblance in charateristics between the BIO training objects and that of Astrup WTP. The KE objects on the other hand may not be closely related to the the objects of Astrup WTP.

Considering figure 8.6b the V. Gjesing prediction objects were projected into the KE and BIO training models. Similar to figure 8.6a, in figure 8.6b, the BIO training model lie to the left of the model line while the KE training model lie to the right bottum of the model line. When the Vr. Gjesing prediction objects were projected into the model, all of them fell outside the group/class of both the KE and BIO training models except few of the objects which fell into the class of the BIO training. . In other words, they can be said to be more of the characteristics of the BIO training objects than of the characteristic of the KE objects. Therefore both the Vr. Gjesing and Astrup WTP objects bear no characteristic similarity to those of the KE objects since both objects lie far away from them.
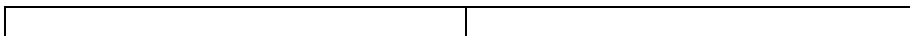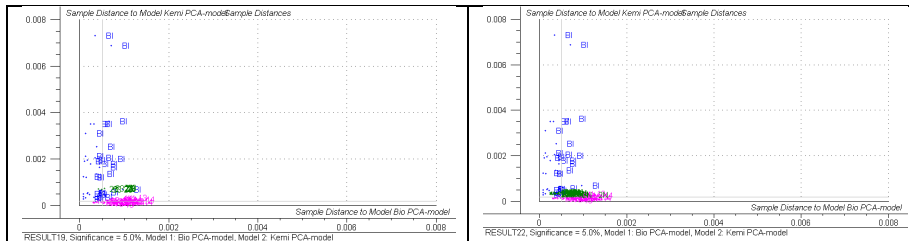
Figure 8.7a :Hjerting WTP prediction objects(in green) projected into BIO and Vr. Gjesing training sets	*Figure 8.7b: Vognsbøl WTP prediction objects(in green) projected into BIO and Vr. Gjesing training sets*
Figure 8.7C: Vojens prediction objects projected into BIO and V. Gjesing training sets	*Figure 8.7d: Ribe WTP prediction objects projected into BIO and V. Gjesing training sets*
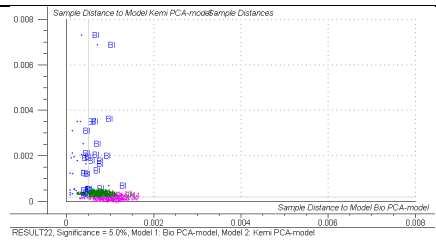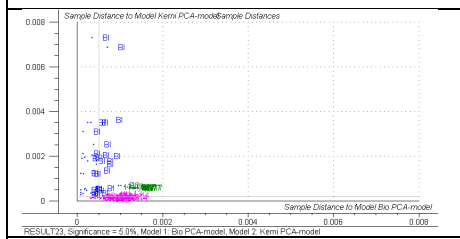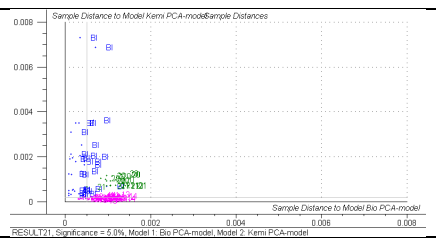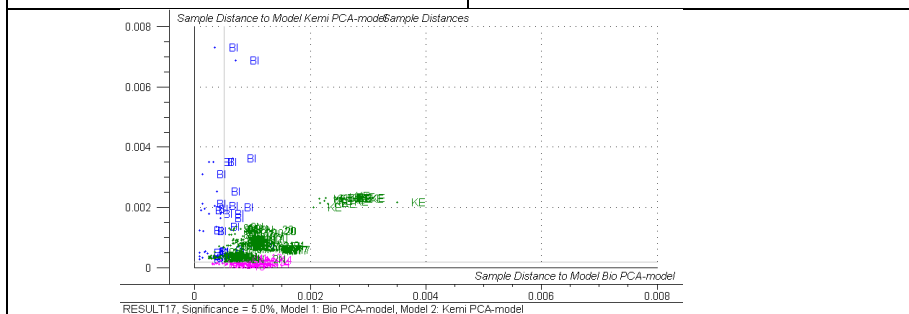
Figure 8.8: Prediction objects from 4 selected water treatment plant including, Hjerting, Vognsbøl, Vejen, Ribe, Astrup and the laboratory KE(all green) projected onto BIO(blue) and V. Gjesing(red) training models.

It is worth predicting the relationship between the BIO training objects and that of Vr. Gjesing compared to other water treatment plants since the objects from those two(2) samples were better related than that of Astrup WTP(see figure 8.6a and 8.6b). Therefore, the training objects from BIO samples and V. Gjesing were used to make a model and compared with prediction objects from four (4) selected water treatment plants, including Hjerting WTP, Vongsbøl WTP, Vejen WTP, Ribe WTP as well as the KE . The individual projections are shown in figure 8.7a to 8.7d.

However, a combination of the model projections are shown in figure 6. The training objetcs from V. Gjesing are coded in Red colour and Bio are in Blue. All the other prediction objects are are in Green.

Undoubtedly, figure 8.7a to 8.7d shows that objects from the different WTP had varying degrees of closeness to the BIO and V. Gjesing objects. However, looking at figure 8.8, it could be seen that the KE prediction objects clearly did not belong to neither the group of BIO nor V. Gjesing. This means that the KE objetcs are completely different from the group of biological and V. Gjesing. On the other hand, it could also be seen from figure 8.8 that few of the prediction objects completely belong to the class of both BIO and V. Gjesing but were mostly spread closely to the BIO or V. Gjesing objects. This could be due to the fact that they may have undergone the same method of Fe precipitation but they have a slightly different element constitution due to different levels of manganese precipitation or addition of chalk

Near infrared spectral analyses are normally decoded based on the changes in chemical composition and /or particle size distribution of the samples under investigation. Furthermore, 2-line ferrihydrites $(5Fe_2O_3 . 9H_2O)$ usually dominates the Fe precipitates at circumneutral pH, at which Fe is normally precipitated in water treatment plants. However, after the precipitation, the poorly ordered ferrihydrites could be partially re-ordered depending on its presence on exopolymers or in sludge that is precipitated in a chemical catalytic way by absorption to existing ironoxide coating on the sand grains in the filter

By help of the created model it could be possibly to see eventual changes in the conditions of Fe(II) oxidation/precipitation from the involved WTP's and also from the reactor and the WTP that the model was based on without performing further analysis. In that way some changes can easily be seen e.g. if a biofilter is so much disturbed by incoming raw water with higher Eh than normal from one of the wells due to intensively pumping or a normally abiotic iron precipitating chemical catalytic filter suddenly start to precipitate iron in a biological way due to reduction in level of airation or a suddenly decrease in raw water rH2.

8.3 Conclusion

Multivariate data analysis and near infrared spectroscopy can be used to distinguish between backwash samples of iron precipitates from sand filters at different water treatment plants. A model created partly by objects (samples) from a laboratory reactor which precipitates Fe(II) in a biological way and samples partly from a water treatment plant which oxidize and precipitates its Fe(II) in an almost purely chemical catalytic way can make up a training model to investigate samples from other WTPs. Iron precipitates from different WTPs look very similar because they are all in principally poorly ordered ferrihydrate. The investigated samples, however, showed relations to both types of precipitates but could also be distinguished from each other and from the objects from the training model.

Changes in conditions for iron precipitation in either a biotic or an abiotic direction on WTPs is based on the model of the created multivariate data analysis and NIRS is expected to be observed by solely a NIRS analysis without further investigation. Likewise, stability in the same conditions will also be confirmed by help of the same model and methodology.

Chapter 9

Sustainable groundwater treatment technology transfer to a developing Country such as Ghana, through the Danida Business to Business (B2B) Programme.

9 Introduction

In order to achieve the target set by the Millennium Development Goal 7 (MDG7), Ghana and most developing nation's water and sanitation services have been opened to private sector participation in the past 15 years. However, much has not been achieved due to issues relating to technology transfer, low tariffs, water quality and stakeholder ownership (Osumanu, 2008).

It has been recognized that groundwater is not only feasible, but also the most cost effective source of potable water for scattered and remote communities. Although groundwater is highly used in the communities and towns in Ghana, it is estimated that over 40 % of drilled wells are either abandoned after drilling the wells or rejected by the intended beneficiaries for the common of very high levels of iron(Fe) (>0.3 mg/L) and manganese (Mn)(0.1 mg/L). Furthermore, due to high levels of Fe and Mn in Ghanaian groundwater, over 60 % of the groundwater drilled is used only for purposes other than drinking, cooking or laundry(ref). Other contaminants plaguing water delivery process in Ghana includes fluoride (F), arsenic (As), heavy metals due to acid mine drainage and chlorides found in the Northern/Upper regions, mining areas and the coastal belt respectively (Corporate brochure 2004).

The Danida Business to Business programme is an initiative from the Danish government geared towards contributing to poverty alleviation in developing countries, by promoting socio-economic growth and development. The main strategy to achieve the objective of this initiative is to promote technology transfer and know-how from Danish Companies to the beneficiary country of the support. By way of economic support and advisory role, the B2B programme promotes the establishment of long term sustainable and commercially viable business ventures through the creation of partnerships. As a consequence of the partnership, a win-win situation is created, where the Danish companies gain access to new market, new products to trade in and production prospects. On the other hand, the beneficiary companies in the developing countries benefit through gaining access to new technologies and know-how.

This chapter therefore assesses the situation in the drinking water sector in Ghana and thereby focuses on the possibility and viability to sustainably transfer the water treatment technology acquired during my Ph.D. studies through the Danida Business to Business programme to a developing country such as Ghana.

The ultimate aim of the technology transfer is to use Ghana as a platform to build sustainable joint venture Ghanaian drinking water treatment Company that will serve Ghana and the entire West African communities.

9.1 Background

For many countries in the developing world, gaining access to clean and affordable water is a difficult daily struggle. Access to treated water is available to only 62 to 70 % in the urban areas and 35 to 40 percent in rural areas (UNDP, 2003). Moreover, only about 40 percent of the people in the urban areas have a tap water that is flowing and 70 % of the poor in the rural areas do not have pipe water. To deal with the crisis of drinking water supply, a number of policy reviews and institutional re-structuring have been carried out over the past two decades by the government of Ghana. The result, among others, was the creation of the Ghana Water Company Ltd and the Community Water and Sanitation Agency (CWSA) as two autonomous entities out of the former Ghana Water and Sewage Cooperation (GWSC), each with a specific mandate. Also, steps have been taken, since, to encourage private sector participation in the delivery of water and sanitation services. These efforts, notwithstanding, there is still a big gap between water supply and demand, and the entire country continues to experience water shortage at an alarming rate, which requires serious attention (UNDP, 2003).

9.1.1   Information on Ghana

Ghana is situated in West African and it's known to have one of the most thriving democracies on the African continent. In the light of this, Ghana is often referred to as an "Island of peace" among one of the most lawless regions on the planet.

Figure 9.0: Map of Ghana showing the ten (10) administrative capitals (U.S. Central Intelligence Agency, 2010).

Ghana is located within Latitude 4^0 30´ N and 11^0 0´ N of the equator and longitude 1^0 10´ E and 4^0 30´ W. Ghana shears border with Togo to the east, La Cote d´voire to the west, Burkina Faso to the north and the Gulf of Guinea to the South. Ghana covers a land area size of about 238.500 square kilometers and it is divided into 10 administrative regions with a population of about 23 million inhabitants joined together from over 100 ethnic groups, each with its own language. However, they have all adopted English as their language since the British colonial rule (Tamakloe, 2010). See figure 9.0.

9.1.2   Socio-economic characteristics

The Ghana economy is among the top 10 performers in Africa during the last decade. IMF reports indicated that the economy grew by 5 to 6 percent projected for 2010. In 2009, GDP grew by 4.7 % and GDP per capital is about US$ 1,500. In terms of contribution of sector to GDP, Agriculture leads by 37.5%, services occupy about 37.3 % and Industry 25.3%. In the year 2010, unemployment stands at 11% and about 28.5% of the population lives below the poverty line (U.S. Central Intelligence agency, 2010).

Ghana's economy still depends on international finance and technical assistance, with Gold, Cocoa production and timber as the major foreign exchange. However, recently, non-traditional crops such as Cashew, pineapples, peanuts, Cassava and fish are also exported.

9.1.3   Physical Characteristics

Generally, Ghana is considered to be a low land country. Geographically, the country is divided into 5 regions. That is, the coastline areas in the south, the Northern belts, the South central, South-west and the Central part. The coastlines consist of sandy shores and are joined by steams and rivers. On the other hand, the south central and the south western part consist of forest plateau including the Kwahu plateau, The Togo Akwapim ranges as well as the Ashanti highlands. The Northern belt also consists of high plains and the central part is made up of the Volta basin which has the largest artificial lake in the world known as the Volta Lake (Asomaning, 1991).

Ghana experiences a tropical climate with temperatures values ranging from 28 ^{0}C to about 33 ^{0}C. Mean maximum annual rainfall in the south west is about 2,150 mm and 800 mm in the south- east, and about 1000 mm in the North of the Country (Asomaning, 1991).

9.1.4   Geochemical background in connection with groundwater in Ghana

Figure 9.1: shows the geological map of Ghana. The south west and the north-west plateau consist of the oldest crystalline rocks of the Birimian and Tarkwaian formations with granite intrusions.
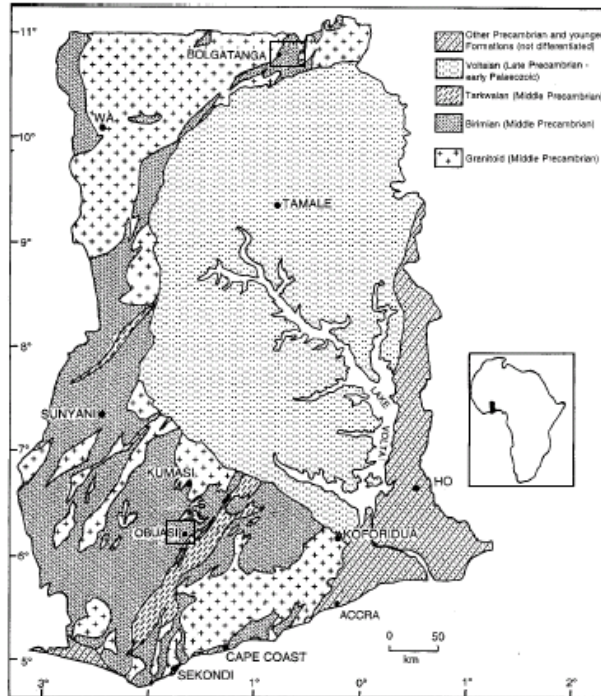
Figure 9.1: Geological map of Ghana (Kesse, 1995).

On the other hand, the South-eastern Ghana, which encompasses the Akwapim- Togo Hill range is also made up of a sequencial mixture of metamorphosed sedimentary and igneous rocks. Furthermore, the central and eastern part of Ghana, which is covered by the Volta basin is made up of consolidated sandstones, mudstone and limestone of the Voltain formation. The coastal belts is made up of younger sediments which are made up of wind-blown, river-borne beach or marine deposits of clay, sand and gravel, predominantly unconsolidated with mixed age. Major episodes of mineralization have produced mineral deposits, many of which are gold-bearing, diamond bauxite, manganese and many other of significant economic values (Kesse, 1995).

9.1.4.1 Groundwater quality

The geology of a location highly affects the groundwater quality. Throughout the country, groundwater mainly consist of low salinity and it is usually acidic with pH below 6.5 and low value of total hardness. However, in areas composed of lime stones and at the coastal areas, the pH of groundwater is high, > 7 and saline at the coast where the sea water intrude into groundwater.

As much as the elemental composition of groundwater may differ from one geographical area to the other, research conducted by Schafer et. al. in 2008 on surface and groundwater in Ghana identified problems with pH ranging from 3.69 to 8.8, conductivity between 10 to 45, 000 and

turbidity of about 0 to > 542 NTU. However, a summary of the potential groundwater problems in Ghana according to the specific geological areas and locations is as shown in table 9.0.

Table 9.0: Typical groundwater characteristics in Ghana.

pollutants	Potential problem	geology	Location
Iron (Fe)	Excess, often significant	All aquifers	Many locations
Manganese (Mn)	Excess	All aquifers	Several locations
Flouride (F)	Excess (up to about 4 mg/l)	Granites and some Birimian rocks	Upper regions
Iodine(I)	Deficient (less than 0.005 mg/l)	Birimian rocks, granites, and voltain	Northern Ghana, especially Upper regions
Arsenic(As)	Excess (>0.01 mg/l)	Birimian	Especially south-western Ghana(gold belt)

It could be seen from table 9.0 that Fe, Mn, F and As are the major problematic pollutants in Ghana. However, nowadays, with the intensification of mining activities by several multinational companies, high concentrations of cyanide and copper are found in both groundwater and surface water at areas where the mining activities are very intensive. (Schafer et. al. 2010)

9.2   Problems associated with the water sector in Ghana

The intensification of climate change and the increasing population in Ghana, is putting severe pressure on drinking water resources and water supply in Ghana.

The gloomy situation of lack of potable water is further worsened by higher concentrations of iron, manganese and salinity in ground water for drinking purposes, especially along the coastal areas. Higher concentrations of fluoride have also been identified in groundwater in the Upper-east region, causing severe health problems to the inhabitants. The contaminants in ground water, coupled with afore mentioned problems limit the sources of potable water in the entire country. Furthermore, for health reasons and the increasing consciousness of global environmental protection, calls for efficient and environmentally friendly methods to treat groundwater water to acceptable standards.

Many Wells, boreholes, and even in some cases, smaller water treatment plants have been closed down due to higher concentrations of iron, Manganese and/fluoride. However, The technology and the skills to remove the contaminants to acceptable limits for drinking water purposes is completely lacking in the country.

It is perceived that investments in water supply and sanitation would require injections of large amounts of capital (Brocklehurst and Janssen, 2004). It's evidently clear that, sometimes capital is required, but other problems has to do with lack of proper supervision, appropriate technology transfer, genuine involvement of stakeholders and the community ownership of the water project. Part of the problem is derived from the fact that, water sector privatization in Ghana was adopted not out of a sense of opportunity, but rather out of desperation. As a result there was no research-based technology in the sector and that lead to the drilling of bore holes which were never used by the people due to poor quality. The other part of the problem also, has to do with the legal challenges. Section II, Subsection I (e) of the Water and Sanitation Policy of Ghana requires the development of a strong legislative and regulatory framework and capacity for supervising environmental sanitation activities and enforcing standards (Ghana, 1993:2). Fifteen years after drafting the policy no such legislative and regulatory framework has been developed (Osmanu, 2008). The rationale behind involving the private sector is to cut the size of the public sector in search of new technologies and expertise and gain access to increased capital and greater economic efficiency to improve operations and generate revenue (Osumanu, 2008)

The general assessment of private sector participation in water provision in Sub-Saharan Africa has produced mixed results. While those of countries such as Cote d'Ivoire, Guinea, and Senegal have chalked relative success, this cannot be said of countries like Gambia, Uganda, Kenya, and other countries. A number of contracts in these countries including Ghana have to be terminated after a few years of operation. In Ghana though there has been some problems, many people have accepted private sector participation in urban infrastructure provision more beneficial (White and Bhatia 1998; Briscoe, 1999; Nkrumah 2004). What is required now is need for technologies to make every water available portable, acceptable and usable.

9.3   Organizational structure and function of the institutions in the water sector in Ghana

The political structure may have also contributed to the water and sanitation delivery problem in Ghana. The fact is that, this sector comes under four different important ministries in Ghana, thereby bringing about some conflict of interest. They are the Ministry of Local Government and Rural development, The Ministry of Water resource and Housing, The Ministry of health and the Ministry of Science and Technology.

The Ministry of Local Government and Rural Development (MLGRD) sets the policy framework for the development of local communities and oversees the performance of local administrations – Metropolitan, Municipal and District Assemblies. On the other hand, the Ministry of Water Resources, Works and Housing (MWRWH) is also the leading government institution responsible for water and accordingly formulates policies for the sector. This Ministry is responsible for formulation of strategies, resource mobilization, co-ordination of budgets, monitoring and evaluation as well as facilitating inter-sectoral and sub sector coordination in the water sector. The Ministry of Health formulates the national health policy and provides strategies for health delivery through preventive and curative methods. It supports the Water and Sanitation Sector(WSS sector) by playing active roles in guinea worm eradication, personal and environmental sanitation. Finally, the Environmental Protection Agency (EPA)

established under the ministry of science, by an act of Parliament, regulates and enforces environmental quality laws, including policies and regulations pertaining to pollution control of water resources.

Figure 9.2 is an annotated diagram of the organizational structure and functions of the drinking water sector in Ghana. It is however, worth mentioning that the Ministry of Science and technology and the Ministry of health were not included in the diagram because they are not directly involved in water production and delivery in the Country
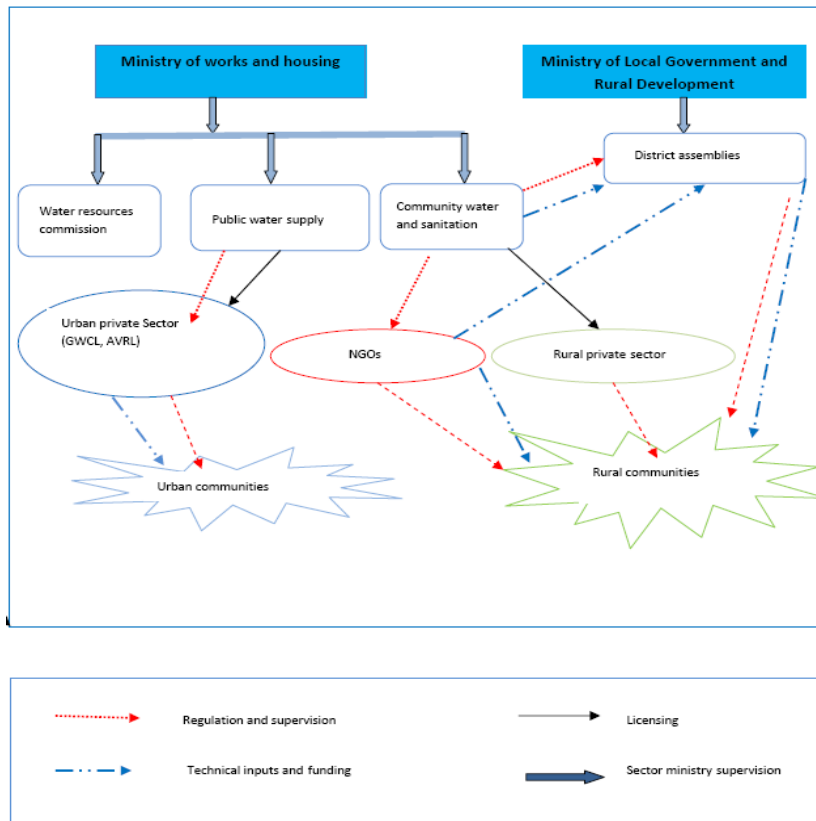
Figure 9.2: Annotated diagram of the organizational structure and functions of the drinking water sector in Ghana.

The organizational systems interlocks, but two distinct approaches by the private sector involvement in the drinking water supply sector are followed in Ghana. These are the urban private or urban area public utility and the rural private sector.

In the urban private sector, the Ghana water company Ltd., is responsible for providing, distributing and conserving water for domestic, public and industrial purposes. Furthermore, the company has been mandated to establish, operate and control sewage system in Ghana. Since 2006, it may be the only private operator. Aqua vitens Rand Ltd, (AVRL) which is a joint venture of the Dutch Vitens Rand water services, has been awarded a 5 year contract to assist The Ghana water company Ltd and their contract may come to an end by the year 2010. This seems to be a sort of monopolistic approach adopted by the government in the urban sector.

The district assemblies use the Community Water and Sanitation Agency (CWSA) and local expertise from the private sector. This sector may be an example of the private sector investment (PSI) and it is widely open to investors, but it is speculated that this sector is not attractive to investors. Therefore, the CWSA seeks to provide financial support to the rural sector by soliciting for funds from agencies and organizations such as The World Bank, (IMF), Canadian international Development agency, CIDA, Danish international Development Agency, (DANIDA), African development Bank (ADB), JICA, EU and some religious bodies, etc.

The above structure depicts that any partnership in the water sector should work together with the CWSA, GWCL and foreign donor agencies to improve on the water situation in Ghana.

9.4 Existing technologies for water treatment in Ghana

Water supply in Ghana was previously categorized based on population- Thus rural and urban. However, nowadays, it is classified into urban water supply or community water supply based on the service delivery approach. The urban water supply is provided by the Ghana water Company Limited (GWCL). The GWCL constitute about 86 urban systems while the rest of the Country are catered for under the community water supply. This basic classification therefore affects the type of technology used for water supply in Ghana.

The 86 urban water systems manned by the GWCL ranges from the capacity of about 216 m^3/day to about178000 m^3/day. The source of water is mainly surface water from lakes and rivers. The raw water is pumped into a settling tank where aluminium coagulant is added to coagulate minute particles and allow the bigger flocculants to settle under gravity. The water is then pumped through sand filters, disinfected with chlorine and the water is released to consumers. Figure 9.3 shows a simple surface water treatment plant at Begoro in the Eastern region of Ghana.

Dammed water from the stream

Pump, pumping the water from the dam to the filters

Sand filtration tank

Water distribution tank

Figure 9.3: Surface water treatment plant at Begoro in the Eastern Region of Ghana.

In the case of Community water and Sanitation Agency (CWSA), they mostly provide boreholes or mechanized wells to supply groundwater. Therefore, in almost all the cases, the groundwater is not treated at all to remove the contaminants before they are used. This is not because of lack of contaminants in the groundwater but because they lack the appropriate technology to treat the groundwater.

Out of the 86 urban systems catered for by the GWCL, the rest of the nation is expected to be covered under the Community water system. Nevertheless, the community water system is able to cover only about 70 % of the communities, which they are expected to provide water service for. This leave about 30 % who resort to using untreated flowing rivers, pond and hand dug well as their source of domestic water consumption. See figure 9.4. In some case, those rural people use cloths or ceramic pots to filter the water manually before consumption.

Figure 9.4 Pictures of sources of drinking water in the rural areas in Ghana. Figure A is a pond, B is a borehole and C is a hand dug well (Schafer et. al,. 2010).

9.5 Needed/suggested technology to be transferred for the concept of business cooperation for the water sector in Ghana (Focus of the B2B)

As mentioned earlier in the introductory chapter, access to potable water continues to be a difficult struggle for most Ghanaians. However, among others things, lack of technological know-how to locate the source of good quality groundwater and surface water sources, the expertise to remove natural contaminants (Fe, Mn, As, F and natural organic matter NOM) from the raw water and lack of state –of- the- art laboratory to test for the water quality are serious issues plaguing the water delivery process in the entire country.

Therefore, business cooperation in the water sector must focus on drilling of water wells, provision of consultancy services in the field of drinking water and construction of water treatment plants with efficient process design to treat both groundwater and surface water for domestic and industrial use, geological survey, and mobile laboratories for water quality analyses. To effectively deal with the water crises, the cooperation must seek to focus on the production of drinking water, since the intensification of climate change and increasing Ghanaian population is exerting severe pressure on water resource in Ghana. Therefore, a water treatment company in the water market may solve the water problem by building water treatment units which will remove the contaminants from groundwater by the conventional physico-chemical process or by biological method (the use of iron precipitating bacteria). One focus could be where, recalcitrant colloidal ferrihydrites are present, a tailored treatment before releasing the water into drinking water system. The promotion of iron bacterial growth is also expected to be as a catalyst for Fe and Mn oxidation/precipitation to co-precipitate with other

potential contaminants such as heavy metals and natural organic matter to facilitate their removal.
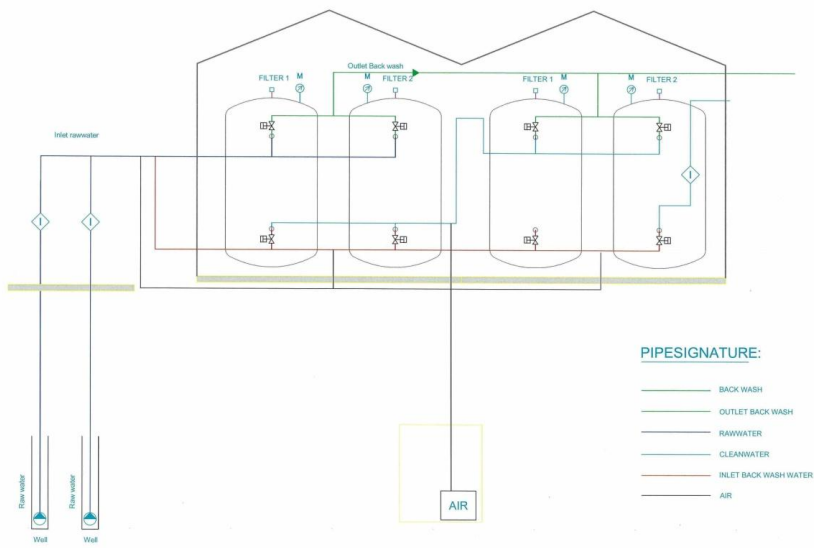
Figure 9.5: Schematic diagram of proposed groundwater treatment plant in Ghana.

Figure 9.6: Picture of the model plants to be constructed in Ghana, exhibiting two filter vessels connected in series for double filtration.

There are several designs and types of water treatment plants that can be built, ranging from mobile to stationary ones for the treatment of raw water from both surface and groundwater sources.

The plants units may typically consist of a pre-treatment unit for the production of iron bacteria to remove iron. The pre-treatment unit will be preceded by an aeration stage to strip off objectionable odour and gasses such as methane (CH_4), hydrogen sulphide (H_2S) and ammonia (NH_3) and the water will then be pumped through a second filtration stage to remove residual iron and manganese. Addition of chemicals will strictly be avoided. Mobile water quality analyses laboratory will also be constructed to monitor the water quality and ensure that the water produced meets the quality standards set by the CWSA and the Ghana standard board

To reduce cost, all the construction must be done in by a factory in Ghana, so as to make them affordable, but it will produce safer and sustainable drinking water for the Ghanaian society. see figure 9.5 and 9.6

9.5.1   Unique features of the plants to be constructed in Ghana

* Operates full scale by biological iron removal method to remove contaminats such as Fe, Mn, As, organic materials and also take off objectionable gasses such as NH_3, H_2S and CH_4.

* No chemical agent for oxidation or disinfection may be required. This will give a low operational cost and avoid chemical residues in drinking water.

- The vessels are made up of hot galvanized iron with a long term lifespan of about 85 years.

- No internal dissolution of hot galvanized iron into drinking water system as in the case of the usage of materials such as polyethylene or glass fibers.

- The plants could be installed to operate either manually or fully automated and also constructed at different capacities ranging from single household to an entire city of any population.

9.6   Processes followed to building a joint venture company in Ghana.

The exact processes followed before gotten to the pilot stage of the project were very cumbersome. It entailed a great deal of cultural, political, social and even in some cases, religious considerations. It is worth noticing that this part alone involved taken over 10 consecutive trip or travelling from Denmark to Ghana, over the three year period of my Ph.D. programme. The trips were for intense negotiations and presentations to opinion leaders, chiefs politicians, the two main public drinking water supplying companies (GWCL and CWSA) as well as our current business partners in Ghana.   Therefore, I have carefully involved the general issue which may not be sensitive for the companies sponsoring the project. In the nutshell, the project is at the pilot phase, where a joint-venture company has been established in Ghana and has received the mandate to do business. Also, GWCL and CWSA supported the Joint venture Company both in kind and in cash, to build the demonstration plants at Agona Nkwanta and Begoro. DNIDA has also approved our application for a support of five million Danish kroners (5,000,000 DKK) to continue the project.

9.7   Financial evaluations

Also under financial evaluations, the information is kept out. However, the joint venture company will be manned by a joint capital contributed by the members and DANIDA for 3 years period, after which the company will begin to make profit and ran on its own.

9.8   Legal aspects

This legal aspect looks at acceptable procedures to followed in order to set-up or establish a company in Ghana. To ensure that a joint venture company is encouraged, promoted, facilitated and maintain records for technological transfers in all sectors of the economy the Company registered with the Ghana investment promotion council. The parties involved in the joint venture agreement consulted and employ legal adviser(s) to assist in establishing the joint venture company. For registration at the Accountant generals department, the partners ensured that they provided the purpose of the Joint Venture Company (J/V), budget, concept for business cooperation, and staffs organization.

The laws on foreign investments in Ghana permits that foreign investors could establish a company in Ghana either wholly or as a joint venture, consisting of foreign partner(s) and/or local partner(s). When foreign investors, invest in a joint venture Company in Ghana, it is mandatory that the local partners hold a minimum of 10 % ownership. However, the entire laws enshrined in the Ghanaian Companies code 1963, act179 were strictly followed to register the Joint venture company and it will also be adopted throughout the companies existence in Ghana.

9.9 Environmental issues

The very visible and tangible impact of some industries in the last few decades and the increasing pool of sophisticated knowledge, both in the professional and public spheres, has led to increased pressures upon organizations to become environmentally friendly. Until comparatively recently, it might have been ignored these pressures. There is now a broad range of powerful forces, which makes this an increasing unattractive option for an organization. It has thus become necessary for organizations to take and adapt to these forces whilst ensuring that their growth and profitability are maintained. The environmental issues to be considered are categorized into external environment and occupational health and safety and they are as discussed below:

9.9.1   External environment

The joint venture will liaise closely with the Environmental Protection Agency (EPA) of Ghana once all the details about site design, construction and production-related activities are well defined. It is hoped that such consultations would determine whether the scale of operations would warrant obtaining an environmental permit from the EPA. Prior assessment of the environmental impact of the operations at the production site, and preparation of an environmental management plan (EMP) will be done.

In spite of the outcome of consultations with the EPA, the J/V remains conscious of the need to take measures to mitigate the impacts of its operations on the immediate environment of the production site and beyond. Specifically, the impact on air, water, land, flora/fauna, health and safety of workers, and the socio-economic conditions of neighbouring communities will closely be monitored at the beginning of the project and also during production phase. Should it become necessary, the J/V will be willing to cooperate with relevant agencies to establish and implement appropriate standards and guidelines to ensure an acceptable level of public health, and environmental protection.

9.9.2   Occupational health and safety

The joint venture company will adheres firmly to environmental health and safety regulations and procedure in whatever project it carries out in Ghana and elsewhere in the world. It is

therefore a matter of certainty that the joint venture company will implement health and safety measures at all times. However, the health and safety practices to be adopted are categorized into

- Health and safety at project implementation phase and

- Health and safety at everyday operations.

The Environmental Health and Safety measures will be documented as a complete manual distributed to all workers of the company. All employees are to be taken through special trainings on Environmental and Social safeguards. Periodically, refresher courses shall be given to the workers to keep them abreast with environmental issues. Measures to be taken will include the following:

- Application of risk control measures to avoid hazards and accidents on working conditions and practices carried out by employees.

- Provision of education and training programmes for all employees so as to ensure that they adhere strictly to rules and regulations for working procedures and activities carried out by the company.

- Outlining a clear contingency plan to handle emergency situations to the employees and the general public.

- Efficient and effective system for accident reporting and recording.

- Ensure protection against any form of danger or harm at all times at work

- Provision of safe working environment

- Execution of activities that are without causing any harm to the employees, the general public or to the environment

- Compliance of health and safety rules by all parties

- Participation of all parties with respect to health and safety issues

- Hazards from the handling of heavy equipment, including noise, stress, lifting heavy materials etc
- Adequate sanitary facilities should be available for workers and open free range defecation and urinating should not be tolerated
- Adequate protection and signaling of work sites with clear marking of the safety border on the works perimeter
- Prohibition of access to work sites by any persons not having a 'permit to work', in particular were it concerns areas marked as 'restricted'.
- The use of personal protection equipment by employees
- The use of hearing protection equipment when working under noisy conditions
- Adequate medical testing and insurance for all employees
- Medical emergency evacuation plans for different types of incidents and injures that might occur
- Provision of adequate waste and material storage facilities. Access to such   facilities should be restricted

Basic rules with regard to protection of public health, including most importantly hygiene and disease in cholera, river blindness, guinea worm infestations and (HIV)

9.10 Corporate Social Responsibility

The joint venture company wish to keep a high status as to their corporate social responsibility. At any city or town that the company will be established, the partners expect to be able to create good working environment for its staff and in addition educate the staff to a high technical level to be able to create a good working atmosphere.

Besides that the joint venture company wish to involve themselves into the public sector and contribute to raising the hygienic standard in areas that they will provide water treatment plants, by providing potable water to the consumers.

A stable public development is closely connected to the possibility of obtaining clean water. Therefore, a water distribution that is well functioning is of great importance to general public health and especially in keeping the rate of disease prevalence low and at the same time eases the daily work for women and especially mothers with small children to go out and hunt for water.

Simple plants (Low-tech plants) will provide the local communities with the opportunity to service, repair and perhaps even build and sell equivalent plants once the technology is grasped.

It is imperative that the consumers understand the importance of keeping the waterworks clean and avoid that the area surrounding the works and wells being contaminated. This means that faucets, washing areas and cattle/farm animals should not be found in the vicinity of the wells/borings.

9.11 Development objectives and impacts

The joint venture company expect to contribute to development of the nation Ghana as a whole. Therefore, developmental impact of the project is of paramount interest. The developmental issues will therefore be looked at in terms of its commercial impact, social impact, environmental impact, technological impact as well as the spin-off effect or positive externalities to the society.

9.11.1 Commercial impact

Providing efficient technological solutions for solving water problems in Ghana based on Danish technologies and Ghanaian standards at affordable price levels is expected to have a strong commercial impact. With the current labor cost in Ghana, training the staff to handle the project properly will mean the production can gain high demand both locally and abroad. This will eventually increase revenue and later increase the number of employees.

9.11.2 Environmental impact

Many water-borne diseases and water related diseases are on the rise in Ghana due to poor domestic environment. Nevertheless, there has been some overall gain in health over the past 30 years. Life expectancy at birth has improved from 45 years in 1984 to 55 years in 2000
Therefore, by setting up the Company to provide potable water for the nation will go a long way to reduce water borne diseases, improve domestic environment and eventually trigger development in the entire nation (Tamakloe, 2010).

9.11.3 Social impact

The environmental problems in Ghana are enormous. There has been an increasing poverty in Ghana in the 1990s, which has impacted negatively on the environmental. Illiteracy coupled with lack of awareness of environmental issues and legislation has also contributed enormously to environmental problems in the country. The Company will therefore increase employment opportunities in the country and the employees will create awareness on the effects and benefits of improve environment in a society.

9.11.4 Technological impact

Presently, the available technology for drinking water treatment in Ghana is based on the old foreign methods for treating only surface water. Even so, there is no available local company that can entirely construct a treatment plant on its own without consulting foreign companies. Additionally, knowledge on the treatment of groundwater is lacking and most of the groundwater abstracted is consumed untreated. The joint venture company will get access to new technology, which will provide more competitive solutions to water problems.

9.11.5 Spin-off effect

Currently, countries in the entire West African sub-region have similar problems with drinking water. Therefore, with the creation of the joint venture company, once it is up and running, it will extend its business to other countries. There is therefore the likelihood cause development in the entire West African sub-region.

9.12 The Future Market Outlook

The market outlook is projected within the context of the CWSA strategic plan for the delivery of community water systems from 2010 onwards. At the end of 2008 the national rural water coverage was estimated at 57% while urban coverage stood at 59%. To further close the deficit of almost 43% for rural water supply, CWSA plans to develop additional 15,964 boreholes and 1,826 Standing Water Pipes) STWPs by 2015. A sizeable number of these new schemes will be in the regions with high incidence of Fe and Mn.
Based on a historical contamination rate of about 15%, it is estimated that about 2,700 water purification plants will be needed over the next 5 years for the rural water schemes alone.
Ghana Water Company has quite a number of schemes which have iron and manganese problems. They provide another market for the product we are putting on the market. They have

also indicated the willingness to consider our product in the future once they are convinced that it will provide the solution to their problems (cooperate brochure, 2004).

Project as such may not only target to sells in Ghana market but also in the neighbouring ECOWAS states. Out of the ECOWAS states, Liberia and Sierra Leone are the key target markets because of the huge re-construction in various sectors to revive those countries from the ravages of their recent civil wars. There is also a huge market in Nigeria with a population of over 150 million people due to the magnitude of the Fe and Mn problem. Rehabilitation and expansion of potable water supply in these countries place high on their economic and social resuscitation agenda, which offer significant opportunities for the Ghanaian- Danish partnership in the water sector in Ghana.

9.13 Competitive advantages of the partnership

In comparison with the competing firms, the partnership is expected to have the following competitive advantages:

- Competitive price for the products (less than half price of similar product made in Denmark of from other foreign countries),

- Provision of after sales services to contract,

- Available water treatment experts (trained) to analyse and recommend treatment based on specific problems. This will also provide quick access to solutions.

- Local manufacturing set-up which will facilitate real-time demonstration of the technology and training of local technicians in installation and maintenance to avail to the communities effective after sales services.
- Possibility of adapting products or designing specific products to suit the needs of specific community water quality challenges.
- Possibility of facilitating the arrangement of financing for the products for the communities without sufficient funds for the purchase of the water purification plants.
- Closeness to the Ghana government, local government agencies, Ghana Water Company, CWSA, consultants and contractors, and private sector operators, which will make it easy to promote the products to court high patronage.

It is therefore expected, that it will be very hard for any competitor to meet the product mix of the partners, as the partners have top quality products of own production, design and installation experience, local experience, local dealer for support, large network and well established organizations with good marketing support.

Based on the above, a partnership will be considered to be in a very strong position to build sustainable and viable business cooperation in Ghana.

9.14 Conclusion

The potential in introducing water treatment package plants in Ghana is seen to be great, but it is also a very challenging task to be a first-mover. The market for the products in the water sector is not yet matured at all but, is under development.

There is little or no doubt at all that a Danida Business to Business support to create a joint venture company between Ghanaian and Danish partners is sustainable and will prove its efficiency and competitiveness on the Ghanaian market

At present, the market in the water sector in Ghana looks very promising but uncertain. Therefore, the Danida support is essential in order to become successful in Ghana. Without Danida support, the parties may not be able to enter into this kind of cooperation as there are numerous uncertainties. However, the water treatment solutions to be introduced by the partnership will contribute directly to the improvement of the health and sanitation situation by delivering high quality drinking water.

Such partnerships, when properly created, will create new employment opportunities within the field of production, sales and installation of water treatment plants. The B2B-programme therefore contributes to this development to a large extent.

In conclusion, establishment of the proposed partnership will contribute to improve socio-economic growth and development in Ghana and at the same time create a good business opportunity for the partners.

Chapter 10

10 General conclusions

There are limited amount of fresh water available globally. Moreover, the situation is worsened by the intensification of drought, coupled with increasing human population and industrial development. Although groundwater continue to be the preferred source of drinking water, it normally contains high levels of natural contaminants such as Fe above the allowable limit values, which necessitates their removal before releasing the drinking water for consumption.

Nowadays, there is also the realization of the relationship between water quality and possible health effects on consumers. As a result, Environmental authorities are setting up stringent drinking water standards through legislations to protect consumers. Furthermore, scientists are also every now and then, coming up with several technologies to clean raw water and make it safe for consumption. All those measures are being taken with the common reason of ensuring sustainable water production and also prevent disease outbreak through drinking unsafe water. Nevertheless, there are still gabs to be filled in the seemingly simple process used to remove the habitual Fe from groundwater designated for drinking purposes.

In this thesis the following questions were raised and tried to be answered:

- What are the metabolic reasons for the iron bacteria oxidizing activities in filters of water treatment plants?
- What are the specific content of the exopolymers produced by *Gallionella ferruginea*
- What can be the causes of the high iron content in water treatment plant after the raw water has gone through the filtration system of some water treatment plants?
- What was the average size of the particles found in the treated water as a function of treatment unit?
- What could be the possible source of the particles?
- How can the problem be solved in a cheaper way as compared to the usage of chemicals which are rather expensive?
- Is it possibly by help of multivariate data analysis to develop a method to find out in a fast way if a biological iron precipitating filter has changed its level of oxidation and precipitation of Fe(II) from groundwater compared to purely physico-chemical precipitation?

The bacteria acquire energy for their metabolic activities through electrons transferred during the iron oxidation process. This implies that in filters, the bacteria do not directly cause oxidation of iron. This was evident when the value of about 125 % of free energy was obtained by comparing the exergonic physico-chemical method to the endergonic biological method in the reactor set up

in the laboratory. The 125% value obtained is a clear indication that all the oxidation of iron is first of all carried out by the physico-chemical process instead of biological process. However, if the bacteria contributed in anyway to the iron precipitation process at all, they did so only by providing surfaces to mechanically entrap and enmesh the formed tiny iron precipitates.The energy came from the simultaneous physic-chemical precipitation.

We found that the exopolymers of *Gallionella ferrogenia* contained mainly carbohydrates and proteins as in other exopolymers of iron precipitating bacteria.

The purely physico-chemical method of iron removal may not in all cases be effective against the removal of Fe from groundwater for drinking water purposes. Consequently, the biological method of iron removal can be useful instead of the addition of chemicals. This could be found from the investigations and change of the setup at Vejers DWTP. The development of bacterial exopolymers in filters seemed to provide ample surfaces, which had the capability of adsorbing minute colloidal Fe particles and remove them from the raw water during the treatment process. However, also the pumping system was optimized in order to avoid the production of the small minute size particles. The particles were already produced in the wells during pumping. The particles produced had the size of 1μm down to nm range.

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Although ferrihydrites precipitated by biological method of Fe removal are known to be denser and compact than those precipitated under purely physic-chemical method, till date, there is no known analytical methods to characterize and distinguish sludge. SIMCA method is a chemometric approach of classification, which can be used to predict if samples belong to one or particular groups.

The near infra-red spectra obtained from both the biologically precipitated ferrihydrites and the physic-chemically precipitated ferrihydrites seem to be the same or look alike when viewed by the naked eyes. However, by performing PCA analyses of the raw data provided a parttern which clearly distinguished the backwash precipitates into physic-chemically precipitated ferrihydrites and biologically precipitated ferrihydrites on score plots of PV1 Verses PC2. The SIMCA –PCA multivariate data analysis together with NIRS seem to be able to solve that problem

The water crises in Ghana can be very alarming. In the urban areas where surface water is solely depended on, the water sources regularly dry up during the dry season. Also, in the rural areas where groundwater is usually used, the groundwater normally contains high levels of contaminants such as Fe, Mn, F and heavy metals. The biological method of Fe and Mn removal can therefore be used to control those contaminants. Furthermore, besides the technology aspects of water treatment, the water crises could also be attributed to the sort of monopolistic approach adopted by the government in the urban water sector. However, by privatizing the urban water supplying sector will trigger more reliable companies to compete in the market, which will lead to efficient production and supply of water in the country.
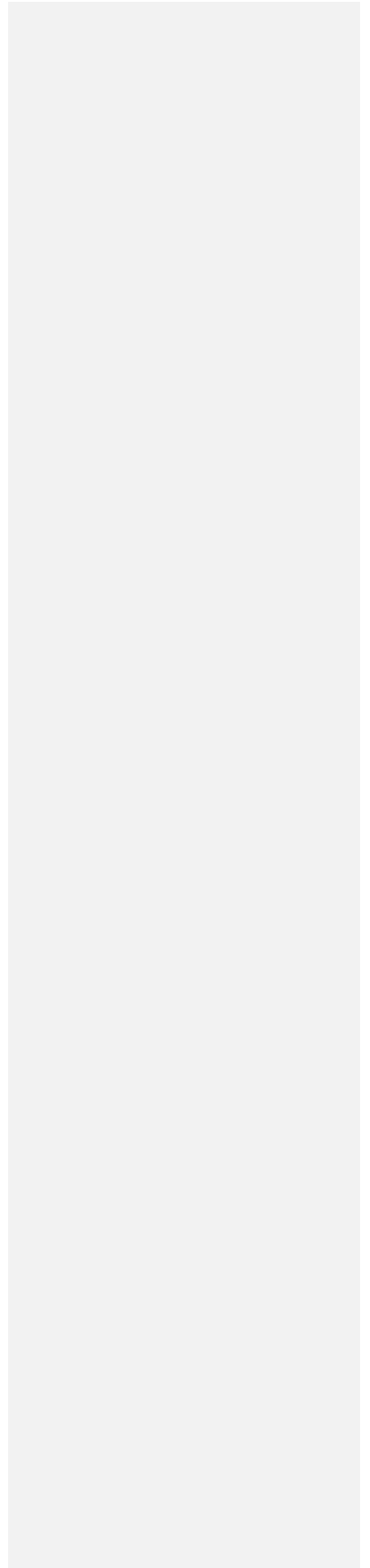
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Supplement 1

Supplement 2

Supplement 3