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Effects of ozonation/filtration on the raw water from Lake Mälaren

Effekter av ozonering/filtrering på råvattnet från sjön Mälaren

NINA LARSSON
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Abstract

Nina Larsson

This Master thesis was made to investigate the effects of ozonation and filtration on raw water from Lake Mälaren. The study was performed in lab-scale as well as in a pilot plant at Lovö waterworks, Stockholm Water Company during spring 2004.

The conventional treatment at Lovö waterworks comes with a few disadvantages, such as large consumption of chemical coagulants. The chemical consumption leads to many transports and the treatment also produces a sludge which is, in present, returned to Lake Mälaren. In 2001 a pilot plant were built at Lovö waterworks for research on new treatment processes, and ozonation followed by filtration is one of them.

Ozonation has been used in Europe for several years as disinfection at the end of the drinking water treatment process. The interests of ozonation has increased significantly in recent years and today the ozonation is used in other steps in the drinking water treatment process. Except for the disinfection, ozone has other benefits such as oxidation of iron and manganese, microflocculation, reduction of taste and odour and it is also effective to reduce the water colour. The microflocculation leads to the fact that less or no coagulants need to be used in the process.

This study started with a literature overview followed by experiments on ozonation and filtration in the pilot plant. After the first experiments the conclusions were that the ozonation and filtration did not reach the same results as Lovö waterworks. To continue, jar tests were made to see the effects of different coagulants. The result indicated that ferric sulphate together with calcium addition (pH-adjustment) was a good alternative. Thereby a lower coagulant dose could be used.

When ferric sulphate and calcium were implemented into the pilot plant, different ozone doses and ferric sulphate doses were tested. The best results occurred when an ozone dose of 6 mg O₃/l and a ferric sulphate dose of 50-60 µmol/l were used. This amount of ferric sulphate is approximately 60 % lower than that for the conventional treatment at Lovö waterworks. To produce ozone electrons are needed and energy consumption increases with approximately 66 % compared to the conventional treatment. The decrease in chemical dose and increase in energy demand gives a decrease of the total cost with 10 % compared to the conventional treatment. The results indicate that the treatment with ozonation, calcium addition and ferric sulphate as a coagulant is an alternative to the conventional treatment.

Different filters were used in the pilot plant and to improve the results a Filtralite-filter was tested instead of the GAC-filter as a bio filter. When comparing Filtralite-filter with the GAC-filter there were large differences between the filters at the beginning of the study. When the bacteria population in the Filtralite-filter had started to increase the differences became less. In the end of the experimental period the filters had similar conditions and Filtralite-filter may be a good alternative as a biofilter.

Keywords: Drinking water treatment, ozonation, filtration, chemical coagulation, pilot plant, lab-scale experiments.

Referat

Nina Larsson

Syftet med examensarbetet var att undersöka effekterna av ozonering och filtrering på råvattnet från sjön Mälaren. Studien är utförd i en pilotanläggning på Lovö vattenverk, Stockholm Vatten AB, under våren 2004.

En negativ effekt med den konventionella reningen är den stora konsumtionen av kemiska koagulanter. Kemikalieanvändningen leder till många transporter och processen producerar också ett slam som för närvarande transporteras till Mälaren. År 2001 byggdes en pilotanläggning på Lovö vattenverk för utveckling av nya processer, en av processerna är ozonering följt av olika filter.

Ozonering har använts i Europa i många år som desinfektion i slutet av dricksvattenreningsprocessen. Intresset för ozonering har ökat markant sista åren och idag används ozonet också i andra steg i processen. Förutom desinfektion har ozonet andra fördelar, som oxidation av järn och magnesium, mikroflockning, reduktion av lukt och smak samt är bra på att reducera färgen på vattnet. Mikroflockningen leder till att kemikalieanvändningen kan minska och i vissa fall tas bort helt.

Den här studien startade med en litteraturundersökning följt av försök med ozonering och filtrering i pilotanläggningen. De första undersökningarna sammanfattades med att ozonering följt av filtrering inte gav tillräckligt bra resultat och processen behöver ett komplement för att producera ett högklassigt vatten.

Undersökningen fortsatte med laboratorieanalyser för att undersöka effekterna av olika kemiska koagulanter. Resultatet visade att järnsulfat tillsammans med kalcium var ett bra alternativ och en lägre kemikaliedos kunde användas.

Efter implementering av kalcium och järnsulfat till pilotanläggningen testades olika ozondoser och olika järnsulfatdoser. Det bästa resultatet erhöles då man använde sig av en ozondos på 6 mg O₃/l och en järnsulfatdos på 50-60 µmol/l. Denna mängd av järnsulfat är ca 60 % lägre än den dos som används vid den konventionella reningen på Lovö vattenverk.

Olika filter används i pilotanläggningen och för att förbättra resultatet provades även ett Filtralite-filter som biofilter istället för GAC-filtret. Jämförelsen mellan Filtralite-filter och GAC-filter visade på stora skillnader i parametervärden i början av studietiden. När bakteriepopulationen ökade i Filtralite-filtret blev skillnaderna mindre och i slutet av undersökningstiden var parametervärdena likartade. Det slutliga resultatet indikerar att Filtralite-filter kan vara ett bra alternativ som biofilter.

Nyckelord: Dricksvattenrening, ozonering, filtration, kemisk fällning, pilotanläggning, småskaliga försök.

Department of Information Technology
Box 337
751 05 Uppsala, ISSN-1401-5765

Preface

This Master Thesis was performed at Stockholm Water Company. The study is a developing project to improve the drinking water quality in Stockholm. The task was to investigate the effect of ozonation on the raw water from Lake Mälaren and to find alternative solutions to reach a high quality drinking water.

I would like to start with an enormous “thank you” to my supervisor at Stockholm Water Company, Josefin Abrahamsson (department of environment and development) for great support, valuable advice and for introducing me to this project. Thanks to Ulf Eriksson for good advice and practical support about the ozone equipment and I also like to thank my supervisor Bengt Carlsson at the Department of Information Technology, Uppsala University.

I will thank all the staff at Lovö Waterworks that has helped me to make this project successful. I had never made this without you! Thank you for helping me with all the technical problems, for the knowledge about the treatment process and for the friendliness.

The study included chemical analyses and many hours in the laboratory at Lovö waterworks. At the laboratory I like to thank Ulla, Inga and Tessa for many advices and for helping me with the analyses.

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1 Introduction

1.1 Lovö waterworks

1.1.1 Background

Lovö waterworks is located in Ekerö municipality outside Drottningholm and together with Norsborg waterworks it supplies over one million people with drinking water in Stockholm, Huddinge, Haninge, Botkyrka, Ekerö, Lidingö, Nacka, Salem, Solna, Tyresö and Värmdö (Figure 1).

The opening of Lovö waterworks took place in 1933 and the waterworks consisted of chemical coagulation, rapid sand filter and disinfection. In 1938, slow sand filters were added due to taste and odour problems and in 1959 extensions were made to increase the capacity of the waterworks. Today Lovö waterworks produces a high quality water with a quantity of 133 000 m³/day (Stockholm water company, 2001).

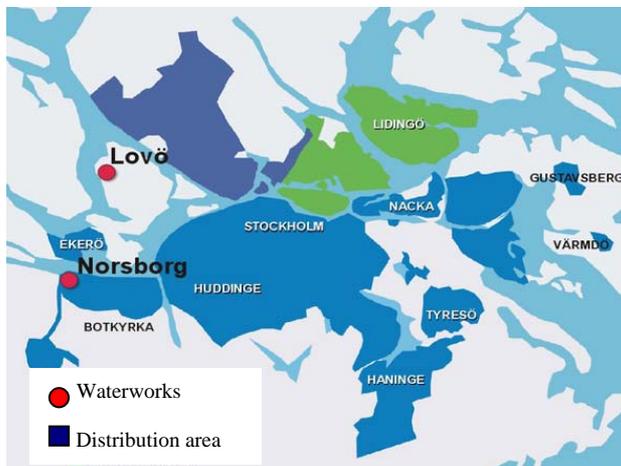


Figure 1. Lovö waterworks location and distribution area.

1.1.2 The drinking water treatment process

At Lovö waterworks the drinking water treatment process is a conventional treatment with chemical coagulation with aluminium sulphate followed by rapid sand filtration and slow sand filtration (Figure 2). The chemical treatment involves coagulation, flocculation and sedimentation and the main purpose is to remove particles and reduce natural organic matter (NOM). After sedimentation the rapid sand filter removes residual flocks. It is followed by the slow sand filter which reduces taste and odour. The treatment also includes chlorination/UV for disinfection and alkalisation to prevent corrosion in the distribution network (Stockholm Water Company, 2001).

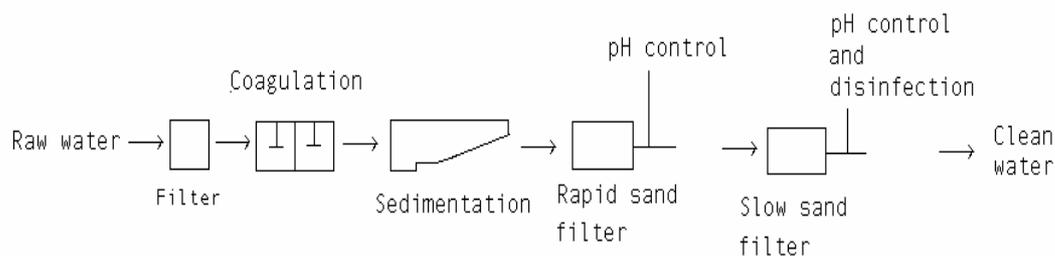


Figure 2. The treatment process for Lovö waterworks (simplified diagram).

A conventional treatment process comes with a few drawbacks, for example large amounts of chemicals are used which leads too many transports and the chemicals are also expensive. Besides, the chemical coagulation produces large volumes of sludge. Today the sludge is returned to Lake Mälaren but sludge management is being implemented and from 2005 dewatering of sludge will take place on-site and decrease the impact on the environment. After dewatering, the sludge will be used as a secondary raw material in soil production (www.stockholmvatten.se).

Due to the impacts on the environment and costs caused by the conventional treatment it is of interest to investigate other alternatives which are independent or less dependent of chemicals and still produce water of good quality. Another purpose is to increase the removal of NOM. If the concentration of NOM should increase in Lake Mälaren the chemical coagulation may not reduce the organic substance to acceptable values and a supplement to the conventional treatment is needed.

1.2 The Pilot plant

In 2001 a pilot plant was built at Lovö waterworks for investigations and research to develop new treatment processes. It was built with two systems, one reference system which is a copy of Lovö waterworks (conventional treatment) (Figure 2), and one system with ozonation (Figure 7). In this study the investigations took place in the ozonation system and the results were compared with the treatment results at Lovö waterworks.

So far studies on the ozonation, system have been made with preozonation/biofiltration without successful results. But there are possible solutions in the pilot plant yet to be investigated and analysed such as new filter medias or different ozone doses.

1.2.1 Ozonation

Ozonation followed by biofiltration has been used in Europe for several years, mainly as a disinfectant in the end of the drinking water treatment process. The interest of using ozone in drinking water treatment has increased significantly in recent years and several investigations and implementations have been made. For example, Åland waterworks has preozonation in order to use less chemicals during coagulation and also ozonation for disinfection.

Apart from disinfection, ozone has other benefits such as oxidation of humic substance, metallic ions, micropollutants, compounds causing odour and bad taste. It is an effective method for the removal of colour in the water as well (AWWA, 1996).

1.3 Lake Mälaren

Lovö waterworks is using surface water from Lake Mälaren which is one of the largest lakes in Sweden. The area is approximately 1140 km² and the volume is approximately 14 km³. The average depth is 13 meters and the deepest areas (63 meters) are in the eastern part of the Lake where Lovö waterworks is located (www.stockholmvatten.se).

The water in Lake Mälaren originates from 10 larger streams and a number of smaller streams. The catchment is approximately 22 700 km² and includes parts of Västmanland, south of Dalarna, Uppland and Närke as well as parts of Östergötland and Västergötland. (www.stockholmvatten.se)

Lake Mälaren has a raw water of good quality (Table 1) and the water has limited seasonal variation. The raw water has low turbidity (1-3,5 FNU) and colour (28 Pt) and is soft to moderate in hardness. The average pH is 7,7 and the average temperature is 7,7 °C. (Stockholm Water Company, 2001).

Table 1. Water quality at Lovö waterworks, 2001.

Substance / characteristic		Unit of measurement	Raw water average	Drinking water Average
Temperature		°C	7.7	7.7
Colour		mg Pt/l	38	5
Turbidity		FNU	3.5	0.05
Conductivity		mS/m	21,6	26.6
Chemical oxygen demand	COD _{Mn}	mg O ₂ /l	7.2	2.8
Total organic carbon	TOC	mg/l	8.2	4.4
Assimilable organic carbon	AOC	µg acetate/l	98	-
Odour		-	2.2	1.0 (none)
Taste		-	-	None
PH		-	7.7	8.5
Total hardness	° dH	-	4.3	5.4
Calcium	Ca	mg/l	25	32
Alkalinity	HCO ₃	mg/l	61	65
Iron	Fe	mg/l	0.14	< 0.02
Manganese	Mn	mg/l	0.011	< 0.001
Aluminium	Al	mg/l	0.079	0.020
Sulphate	SO ₄	mg/l	18	47
Chloride	Cl	mg/l	15	15
Chlorine Residual	Cl ₂	mg/l	-	0.27
Heterotrophic plate counts, 20°C	2 days	cfu/ml	37	< 1
Heterotrophic plate counts, 20°C	7 days	cfu/ml	110	3
Coliform bact. 35°C		cfu /100 ml	33	< 1
Escherichia Coli		cfu/100 ml	7	< 1

Source: Stockholm Water company.

2 Study description

This Master thesis was done at Lovö waterworks during spring 2004 to investigate how ozonation and filtration affect the raw water from Lake Mälaren and how ferric sulphate can be used as a coagulant at high pH-levels.

2.1 Objectives

The aim of this study was to produce a high quality drinking water with help of the treatment process in the pilot plant at Lovö waterworks. For the results to be of interest for future studies parameters that were investigated were expected to reach the same treatment results or better than the results at the Lovö waterworks (Table 2).

Table 2. The recommended values from National Food Administration and the annual mean value at Lovö waterworks are shown above.

	Unit of measurement	National Food Administration	Annual mean value at Lovö waterworks
pH	-	<7.5-9.0>	8.5
Turbidity	FNU	0.5	0.05
UV-absorbance	m ⁻¹	-	8.75
Colour	mg Pt/l	15	5
TOC	mg/l	5.5*	4.4

*The National Food Administration (Livsmedelsverket) has a recommended value of COD_{Mn} but not on TOC, both parameters measure the organic contents in a water sample. Stockholm Water Company like to replace the value for COD_{Mn} with TOC and has made an application with a recommendation value at 5,5 mg TOC/l (Abrahamsson, 2003).

The objectives were:

- Study the effects of ozonation on raw water from Lake Mälaren.
- Investigate how different filter medias affect turbidity, UV- absorbance, pH, colour and TOC.
- Study other alternatives to produce a high quality water such as different coagulants and filtermedias.

2.1 Outline of study

The study started with a literature review to obtain information regarding:

- How ozone act in water and how ozone change the water characteristics.
- The purpose of different filter media and how the filter media affects water characteristics.
- How different coagulants can be used for different treatment processes.

In the first stage the pilot plant at Lovö waterworks was used to study how ozonation and filtration may affect the raw water from Lake Mälaren. The results were further used together with the facts from the literature overview to continue the investigation.

To investigate the effects of different coagulants, jar tests were made on ozonated water from Lake Mälaren. Following, pilot scale test were made to investigate how the results from the jar tests work in a larger scale.

2.3 Hypotheses

The following initial hypotheses were made:

Ozonation

- Turbidity decreases when the ozone dose increases.
- Ozonation decreases UV-absorbance. The higher ozone dose, the lower UV-absorbance.
- pH decrease during ozonation due to high content of organic matter and moderate alkalinity.
- Ozone reduces water colour and an increase in ozone dose leads to an increase of colour removal.
- Ozonation enhances microflocculation.

Filtration

- Rapid sand filtration removes larger suspended solids from water. UV-absorbance, turbidity and colour decrease over the rapid sand filter.
- Biological filters increase turbidity removal and colour removal, decrease UV-absorbance, pH and TOC.
- Slow sand filters increase turbidity removal and colour removal and decrease pH, UV-absorbance and TOC.

Coagulation

- Coagulation followed by filtration reduces the turbidity.
- It is possible to use ferric sulphate as coagulant at high pH (pH>8.5).
- Calcium enhances coagulation.
- Turbidity decreases with increasing pH in a pH-interval of 8.5-10.8 (when using ferric sulphate as a coagulant).
- Less coagulant dose can be used when coagulation is followed by ozonation.

3 Theory

3.1 Natural Organic Matter

The water characteristics differ between different water supplies and the characteristics are affected by the environment such as the location of the catchment and the underlying bedrock.

All surface waters contain NOM in which humic substance is an important component. This humic substance is a poorly defined, heterogeneous group of non-volatile organic species that still present considerable difficulties in terms of their analysis and characterisation (Carlson, 1996).

The different water characteristics and the difficulties when analysing the substances in waters are of importance when investigating which treatment process is most suited for producing a high quality drinking water.

To measure the organic matter contents in water, different analyses can be used. Common analyses are COD_{Mn} , TOC, DOC, UV_{254} , colour, AOC and BDOC. The last two are built on biological principals and the others are chemical analysis. The organic matter is not homogenous and it is to recommend that more than one method is used when analysing the organic matter contents.

Next, a number of methods which can be used to analyse NOM are presented.

COD_{Mn}

Chemical oxygen demand, COD_{Mn} is a common measure of the organic contents in drinking water (SS 02 81 18). The definition of COD_{Mn} is as follows:

- The amount of $K_{Mn}O_4$ which, under acid circumstances, consumes of dissolved and suspended organic material ($C_aH_bO_c$) in a water sample. The result is converted into the unit $mg O_2/l$.

The method is simple and a lot cheaper than the method for TOC and the recommendation value is $4,0 mg O_2/l$ (National Food Association (SLV FS 1993:35)).

The negative effects of the preparation with $K_{Mn}O_4$ are the oxidation which is more or less complete depending on the type of organic substance. This may lead to incomplete or no oxidation of the molecules. Humic substances are complex, large molecules which can be very resistant to further degradation. This indicates that the treatment with $K_{Mn}O_4$ is not always strong enough to oxidise all humic substance in a water sample.

The benefits with the COD_{Mn} -analysis are that the results are very well documented and established in Europe. It takes some time (8 hours) to analyse a sample but the analysis is simple and the equipment is easy to use (Blomberg, 1998).

TOC

Total organic carbon, TOC, is a measure on the carbon content in the water. The principle is that organic matter oxidizes to CO_2 during combustion, addition of oxidation substrate or UV-light. The analyses are made after removal of inorganic

carbon. The method NPOC (Non-purgeable organic carbon) is designed for waters that is low to moderate in organic matter. TOC has the unit mg C/l (Blomberg, 1996).

The benefits with analysing TOC instead of analysing COD_{Mn} are as follows:

- Specific analysis for organic carbon.
- Insensitive for oxidation (chlorination).
- Less chemicals are needed.
- Possible to preserve the sample for a long time before analysis.

The disadvantage is:

- There exists no target value. This can however be compensated by the quotient of COD_{Mn}/TOC (Blomberg, 1998).

DOC

Dissolved organic carbon (DOC) is measured in the same way as TOC but the water is first filtrated through a 0,45 µm filter. DOC has the unit mg C/l. The largest part of TOC is DOC.

UV₂₅₄

Organic substances which have an aromatic structure or conjugated double bounds absorb UV-lights. UV-absorbance at 254 nm is a simple technique to measure dissolved organic matter in the water and is working well for waters with high levels with humic substances. UV₂₅₄ is common used as a surrogate-parameter for TOC and DOC. To measure UV₂₅₄ only a spectrophotometer is needed. The unit for UV-absorbance is m⁻¹.

Colour

Humic substances and metals (iron and magnesium) give natural water a colour, which varies from brown the dark-brown. The colour is determined through visual comparison between the water sample and a platinum solution.

AOC

The definition for assimilable organic carbon (AOC) is the amount of biological degradable carbon that can be converted into biomass. The parameter is used to determine the population growth of micro-organisms in the water. The micro-organisms concentration must be less than 10 µg acetate/l in out-coming water to prevent biological growth in the distribution network (van der Kooij, 1992).

BDOC

There is only a part of DOC which can be reduced by biological degradation, BDOC. The analysis of BDOC determines the amount of carbon in dissolved organic carbon that can be degraded by heterotrophic micro-organisms. The unit is mg C/l.

3.2 Conventional treatment

In this chapter conventional drinking water treatment is described and exemplified with Lovö waterworks.

3.1.1 Coagulation processes

Coagulation is commonly included in water treatment plants to promote aggregation of small particles into larger particles that can be removed by sedimentation and/or filtration. Particles that are removed by coagulation include clay- and silt-based

turbidity, natural organic matter, microbial contaminants, toxic metals, synthetic organic chemicals, iron and manganese (Pontius, 1990).

Aluminium is the most common coagulant in Sweden. It is easy to handle and apply and has been used for a long time. Common aluminium coagulants include aluminium sulphate (alum) and poly-aluminium chloride and these are most effective between pH 5,5 and 6,8 which gives a limited usefulness.

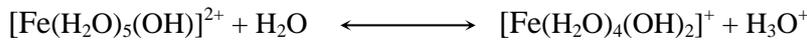
Swedish waterworks have been conservative concerning the choice of coagulant (aluminium), compared to nations such as Finland, England and Holland where ferric salts are more commonly used. Ferric salts are effective between pH 5-5,5 and pH>8,5 (Rutberg, 1998) and studies have shown that a lower ferric sulphate dose can be used in the interval pH>8,5 compared to the interval pH 5-5,5 (Qasim S.R, 1992).

Iron exists in a solution as bivalent, Fe^{2+} or trivalent, Fe^{3+} . In drinking water treatment trivalent ferric salts or aluminium salts are normally used for coagulation, for example ferric sulphate ($Fe_2(SO_4)_3$) or aluminium sulphate ($Al_2(SO_4)_3$).

When trivalent ferric salts are added to water they hydrolyse in less than a second according to:



Ferric ions are multi-protons and hence the hydrolysing proceeds to amorphous ferric hydroxide is established:



The solubility diagram for the hydrolysis of iron is shown in Figure 3.

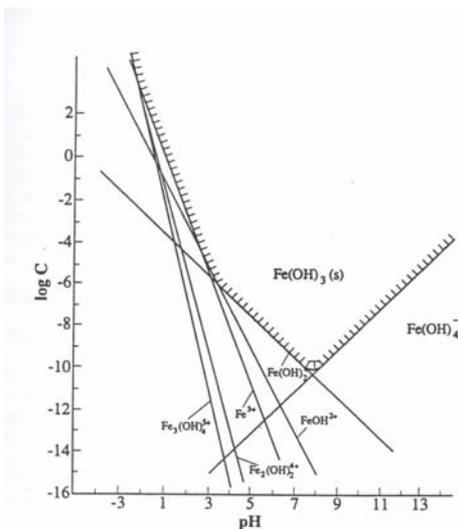


Figure 3. Solubility of iron.

The coagulation process occurs as follows:

- Reaction between coagulant and negative particles and humic substance.
- Formation of larger particles due to aggregation of particle.

The first reaction occurs rapidly after coagulant addition and the second occurs later, in the flocculation tanks. The reaction between the metallic ion and particles and organic matter forms by two destabilising processes, adsorption and sweep coagulation. Adsorption between particles with positive and negative charge leads to formation of flocks and neutralisation of the particle surface (Pontius, 1990). In the sweep coagulation particles are swept into loosely attached flocks which are tend to be weak and sensitive for mechanical disturbance (Abrahamsson, 1999)

The production of H^+ during the hydrolysis of ferric sulphate decreases the pH-level in the water. Even UV-absorbance and colour decrease when the created flocks are removed in the following filter.

At Lovö waterworks the particles are aggregated with aluminium sulphate and then removed by sedimentation followed by filtration. When using aluminium sulphate as a coagulant the optimum pH-interval are between 5,5-6,8 depending on the water characteristics (Pontius, 1990). Lovö waterworks do not have any pH-adjustment before coagulation so the coagulation occurs in the raw water pH. When adding aluminium sulphate to the water a decrease in pH occur and this decrease is caused by the production of hydrogen ions, H_3O^+ , during the hydrolyse of the aluminium sulphate. Then the addition of aluminium sulphate continue until a pH-value is achieved where aggregation of particles occur (normally around 6,7-6,8).

The average amounts of aluminium sulphate which is used at Lovö waterworks is 40 g/m^3 and for comparing this amount with a ferric sulphate dose the concentration is determined to the unit $\mu\text{mol/l}$. $Al^{3+} \mu\text{mol/l}$ is equal to $Fe^{3+} \mu\text{mol/l}$.

3.1.2 Sedimentation

Sedimentation is generally used in combination with coagulation and flocculation in order to remove flocks and decrease the filter load.

Sedimentation is particularly necessary for high-turbidity and highly coloured waters that generate substantial solids during the coagulation and flocculation processes. If filters are used instead of sedimentation in these waters the filter clogs faster and with shorter filter runs as a consequence.

Sedimentation is a solid-liquid gravity separation process. Solid particles are accumulated in the bottom of the tank due to gravity and the sedimentation is most effective when there is a laminar flow condition (Pontius, 1990).

The sedimentation at Lovö waterworks consists of six sedimentation basins with a total passing area of 4720 m^2 and $5\ 600 \text{ m}^3$ of water the basins every hour. The sedimentation process produces 800 tonnes dried sludge/year and the dried sludge contents are approximately 3-4 %.

3.1.3 Rapid sand filtration

A rapid sand filter may be used to remove suspended solids from water. The solids are removed from the water and accumulated within hollows and on the top of the filter bed. The grain size of the filter medium is of importance for the water treatment and affects the performance in two ways;

- Larger grain size causes less particle removal but also a lower rate of head loss [m/m bed depth] development.
- Smaller grain size improves particulate removal but also accelerates head loss [m/m bed depth] development and may shorten the filter runs.

The rate of head loss increases during the filter run proportionally to the solids captured by the filter.

At Lovö waterworks there are 48 rapid sand filters (in parallel) and they have a total area of 1 704 m². The average water flow through the filter is approximately 5 m/h and the average runtime is 72 hours. The backwashing is regulated by time and/or head loss (Stockholm Water Company, 2001) and maintain the desired hydraulic properties of the bed.

3.1.4 Slow sand filtration

In a slow sand filter the sand bed is designed with a uniform sand mixture of small effective-size grains. The small, uniform grain size produces a filter bed that is highly effective for capturing particulates, contains a large surface area for attachment and biological growth, and has many small pores for sedimentation.

As the water passes through the filter bed, the sand layers at, and near the surface provide an intense treatment zone where particulates are removed and bio-adsorption and biodegradation occur. Biological activity takes care of organic particles and inorganic compounds and the turbidity decreases when the biological activity increases (Pontius, 1990).

There are 16 parallel slow sand filters at Lovö waterworks, and the filters have a total area of 34 600 m². The water flow is 0.1-0.2 m/h and it takes 7-10 hours for the water to pass the filter. Two times a year (autumn and spring) the slow sand filters are cleaned to remove rests of flocks and algae in order to prevent clogging.

3.1.5 Alkalisiation

The alkalisiation is used to increase pH and in the treatment process at Lovö waterworks lime water (CaCO₃) is used for the alkalisiation. Lime water is added before the slow sand filter to increase pH to 7,8 and after the slow sand filter to increase pH to 8,5. The increases in pH are necessary for biological growth in the slow sand filter and corrosion control in the distribution network (Stockholm Water Company, 2001).

3.2. Ozonation/filtration as an alternative in drinking water treatment

3.2.1 Ozonation

Ozone is reacting fast in water, the reaction time is only about 20 to 30 minutes in distilled water at 20 C° and much shorter if contaminants are present. Ozone is produced

by oxygen radicals and the process is energy demanding. When ozone is destroyed or self destructed the ozone molecules revert back to oxygen (Eagleton, 1999).

Ozone reacts with organic and inorganic compounds in natural waters in two different ways (Figure 4);

- Direct reaction with molecular ozone.
- Indirect reaction with the radical species that are formed when ozone decomposes in water.

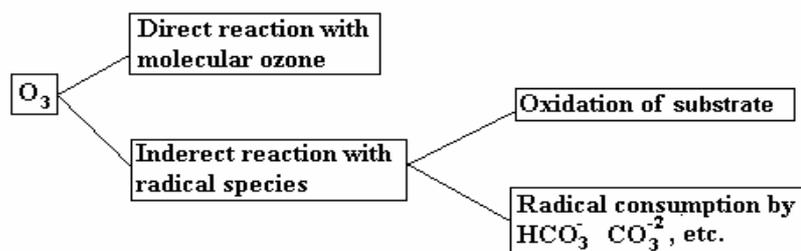


Figure 4. Ozone reaction in water.

The *direct reaction* with molecular ozone occurs in two ways due to the ozone resonance structure (Figure 5). The molecule can act as an electrophile (+) or as a nucleophile (-) which leads to a variety of products that can be produced from the reaction between ozone molecule and natural organic matter (NOM). Ozone molecules are also capable of oxidising inorganic compounds such as iron, manganese and ammonia (Becker, 1996).

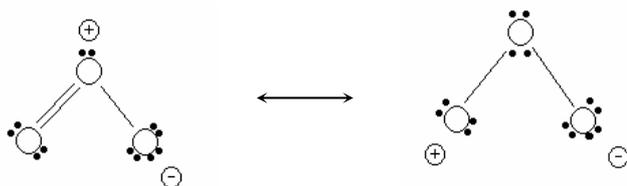
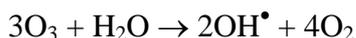


Figure 5. Resonance structure of ozone

In addition to reacting directly with compounds in water, *ozone can decompose to free radicals* and the main oxidizing decomposition product is the hydroxyl radical, OH[•] (Becker, 1996).



Hydroxyl radicals primarily react with hydrogen abstraction, additions to unsaturated bonds or by recombining with other radicals. The radical reacts rapidly and non selectively compared to direct reactions with molecular ozone (Hoigné, 1975a and 1975b). Many compounds that are inert to direct oxidation by molecular ozone may react very rapidly with the hydroxyl radical (Becker, 1996). The radical reacts with inorganic compounds such as hydroxyl ions, hydroxyl peroxide and organic compounds such as methanol and humic substances.

The oxidation of NOM by ozone enhances NOM biodegradability by reducing the size of NOM molecules and by increasing the number of low molecular weight groups like aldehydes, carboxyles and ketones the ozonation by products (OBP) (Bouwer, 1999). There are two types of by-products formed during ozonation, organic and inorganic. The organic by-products such as aldehydes and ketones are easy to remove with a biofilter. Inorganic compounds can be difficult to eliminate, for example bromate ions (EPRI, 1999).

A pH change during ozonation may occur as a result of the production of organic acids or a consumption of organic acids. The magnitude of the pH change will be determined by the balance between the two. For example, in a sample containing bicarbonate and no NOM (no TOC), the solution pH increases during ozonation as a result of consumption of organic acids and the stripping of carbon dioxide (CO₂) from the water by the oxygen carrier gas. By contrast, the pH of the solution containing NOM (TOC) decreased pH as a result of formation of new organic acids (Edwards et al, 1991).

Water with high ratios of TOC to bicarbonate would be expected to be acidified during ozonation, were as water with low ratio of TOC to bicarbonate would be expected to increase in pH (Edwards et al, 1991).

Ozone in drinking water treatment

The most common ozone applications for drinking water treatment include (EPRI, 1999):

- Primary disinfection of bacteria, viruses and cyst organisms
- Taste and odour control
- Colour destruction and removal
- Iron and manganese removal
- Microflocculation (coagulation assistance)

Disinfection

The main reason to use ozone instead of chlorine as disinfection in drinking water treatment is that chlorine causes unwanted by-products such as halogenated organic products (chloroform and trichloroacetonitrile). Also, chlorine is a weaker disinfectant and therefore ozone can be used with less contact time and at lower concentrations (WQA, 1998).

At present, no pathogen is known to survive 1,5 mg O₃/l with a contact time of 5 minutes at reasonable drinking water pH and temperatures (Eagleton, 1999). pH could be between 6 and 9 to inactivate virus with 99,9 % and the temperature has obviously no effect on the disinfection. Hence the disinfection was found to be relatively independent of temperature and pH (Katzenelson et al., 1974) (Kinman, 1975).

Taste and odour

Taste and odour-causing compounds are very resistant to oxidation but strong oxidation with ozone cause a significant decrease in both taste and odour (EPRI, 1999).

The most problematic odour compounds are 2-methylisoborneol (MIB) and geosmin. Both MIB and geosmin can be removed by slow sand filtration and carbon filtration in

conventional water treatment but the removal is more effective with ozone. MIB and geosmin removal were found to increase with increasing ozone dose with up to 96 % removal (CRC, 2003 and Tedioli et al.,1995).

Colour

Ozonation leads to a decrease in water colour which could be attributed to the breaking of the polymers of humic materials in the water. The increase in colour removal is approximately 80 % after the water has been ozonated depending on ozone dose. An increase in ozone dose leads to a decrease in colour removal (Melin et al., 2001)

Oxidation of iron and manganese

Ozone oxidises iron and manganese, ferrous (II) iron into the ferric (III) state and manganese (II) to the (III) state. The oxidized forms will precipitate as ferric hydroxide and manganese hydroxide (Pontius, 1990).

The exact chemical composition of the precipitate will depend on the nature of the water, temperature and pH. Iron oxidizes at a pH of 6-9 but manganese is more effective at a pH around 8. (EPA, 1999)

A problem with ozonation can be that ozone also oxidizes bromide ions to bromate ions. Bromate ions have shown to be an animal carcinogen and are hence suspected to be carcinogen for humans as well. The following is applicable to for water high in bromide ion contents;

- Ozonation shall occur in water with pH 6,5 or less.
- A small amount of ammonia can be added to the water prior to ozonation.
- Allowance minimal levels of dissolved ozone in the water (WQA, 1998).

The raw water from Lake Mälaren does not have any considerable bromide concentration.

Microflocculation

Coagulation assistance, also called microflocculation is a term that is used to describe several phenomena that occur when natural waters are ozonated. These phenomena include formation of new particles, spontaneous particle agglomeration without coagulant addition, improved particle removal at a given coagulant dose and a decreased optimum coagulant dose.

Possible mechanisms that cause microflocculation can be;

- Charge change from positive to negative at the particle surface and the negative particle react with a positive surface which encourages coagulation and flocculation (Eagleton. J, 1999).
- Reduction of the molecular weight of adsorbed organic matter leads to charge neutralisation or reduction of the steric layer.
- Increased concentration of oxygen functional groups may lead to the formation of organic matter-aluminium hydroxide complex.
- Increased number of carboxylic acid groups may also lead to an increase in the direct precipitation of calcium-organic matter complexes.

- Ozonation can kill lyse algae, resulting in the release of biopolymers which can act as organic polymers, resulting in charge neutralisation and bridging (Becker, 1996).

The exact mechanisms that cause microflocculation are not known and it is not likely that each one of the mechanisms can explain all of the reported phenomena.

3.2.2 Activated Carbon filtration

Biological degradation seems to be the most effective removal process for ozonation by-products (OBP) such as aldehydes, carboxyles and ketones (biodegradable fraction of the organic matter) (Melin, 2000). If ozonation is used without following biological filter, the OBP may create bacterial growth problems in the distribution network. The amount of created OBP during ozonation depends on the amount of DOC (dissolved organic content) in the water, a higher DOC concentration leads to a higher OBP concentration.

In Europe several large drinking water treatment plants use biological active carbon filter after ozonation to reduce the OBP. In Sweden there are a few plants that have ozone followed by granular activate carbon filter (GAC) for the reduction of OBP. GAC-filters can reduce organic matter with adsorption as well as biological activity. When ozonation is followed by a GAC-filter and the reduction depends on the biological activity, the filter is usually called biological active carbon filter (BAC), where the bacteria degradation is of importance.

The reduction of organic matter in the GAC-filter occurs with both adsorption and biological activity. During adsorption molecules stick together without changing the properties of the molecule. Physical and chemical characteristics of the active carbon such as specific surface pore space and chemical composition affects adsorption. Also the concentration of compounds that will adsorb, characteristics of the fluid (pH, temperature) and the effective bed contact time (EBCT) are of importance for the adsorption. Adsorption on active carbon is most effective for organic compounds with molecule weight less than 1000 Dalton (Palmer, 2000).

The biological activity in GAC-filter exists in areas where the bacteria can not be disturbed by the water flow. When organic matter adsorbs to the surface, organisms can start the biodegradation of the material. GAC-filters adsorb substrate, nutrients and oxygen which lead to an increase in effective contact time and hence faster colonisation and increasing micro-organism growth. Since adsorption increases the contact time relatively complex biodegradable organic substances can be degraded by the micro-organisms (Committee Report, 1981). During the degradation the bacteria consumes O₂ and emits CO₂ and the pH-level decrease.

The biological activity also depends on the temperature and the empty bed contact time (EBCT). The EBCT is the time it takes for the water to pass the filter. During the summer when the temperature is high, the biological activity is high and in the winter the activity is low when the temperature is low. If the biological activity is low the EBCT should be long to compensate the low biological activity (Pontius, 1990). Normally low water temperatures (around 1 C°) indicate an EBCT of 30 min to receive high biological activity (Eriksson, 1992).

Backwashing is essential to GAC-filters due to the removal of solids during backwashing. Backwashing also maintains the desired hydraulic properties of the bed as well as the possibility to control biological growth. Mud balls have been a common problem in GAC filters and therefore it is important to wash the filter continuously.

3.2.3 Filtralite

Lightweight expanded clay aggregates (Filtralite) can be used instead of carbon filter for the removal of ozonation by-products, reduction of turbidity and increased colour removal. The filter media is made by burned clay which gives the material high porosity, low density and a large specific surface area.

At Tai Po Water Treatment Works in Hong Kong, Filtralite is used in the process as a biological active filter for removal of ammonia and manganese. But the test results also showed a reduction in turbidity with 65 % which indicated that Filtralite can be a good alternative for the reduction of turbidity in the pilot plant (www.OPTIROC.com and www.filtralite.se).

Filtralite works as a GAC filter with both absorption and biological activity. For details about absorption and biological activity see chapter 3.2.2.

3.3.3 Conventional treatment versus direct filtration

Conventional treatment includes coagulation, flocculation and sedimentation followed by filtration (see chapter 3.1). This treatment is not possible to use in the pilot plant without larger rebuilding which is expensive and space demanding. The alternative is direct filtration.

In a direct filtration process settling tanks are not used and the coagulation occurs before the rapid sand filter and in the rapid sand filter. Direct filtration has become common practise in the design of new plants to treat waters low in turbidity and NOM (Pontius, 1990).

In an American Water Works Association (AWWA) Committee Report (Pontius, 1990), the following criteria as a “perfect candidate” for direct filtration is showed in Table 3.

Table 3. The figure shows the perfect candidate for the use of direct filtration.

Parameters	Units	Maximum values (AWWA)	Average mean value at Lovö waterworks
Colour	CU	40	38
Turbidity	NTU	5	3.5
Algae	asu/ml	2000	-
Iron	mg/L	0.3	0.14
Manganese	mg/l	0.05	0.011

Since the water from Lake Mälaren has a good quality and lower parameter values than the recommended values from AWWA, direct filtration could be beneficial.

3.3.4 Calcium addition

Studies from previous investigations (Becker, 2000) indicate that calcium addition can cause microfloculation in waters with certain characteristics, and when microflocs occur less coagulant can be used. The reaction occurs between the calcium and the

dissolved organic matter (DOC). Waters that were favourable are high in DOC, low in turbidity and low to moderate in hardness.

The reaction between calcium and DOC is as follows:



The complex become less negative and hence less coagulant dose is needed. Water high in hardness (high concentration of calcium) can form calcium-DOC complexes naturally and therefore, the addition of calcium it is not beneficial. Calcium addition has less effect in water low in DOC and high in turbidity due to low DOC-complex formation potential.

The reaction between calcium-DOC complex and ferric hydroxide is as follows:



3.3.5 Ekomix and Ekoflock as alternative coagulants

The coagulants Ekomix 1091 and Ekoflock 70 are manufactured by the Chemicals Dyestuffs Minerals Company, CDM. CDM produces chemicals for water treatment to industries and municipalities in Sweden.

Ekomix 1091 is a coagulant for drinking water treatment and consists of aluminium (8.1 %), iron (1,5 %), chloride (21,3 %) and sulphate (< 1,0 %). The liquid has the colour of yellow-brown and can be used in flocculation such as direct coagulation and conventional coagulation. The coagulant is adjusted for waters which are varying in water characteristics.

Ekoflock 70 has the same purpose as Ekomix 1091. It is used as a coagulant for drinking water treatment. The liquid has a yellowish colour and consists of aluminium (9,3 %) and chloride (20,0 %) (www.cdm.se).

3.4 Some previous experiences on ozonation/filtration in drinking water treatment

3.4.1 Norsborg Waterworks

Norsborg waterworks is located in Botkyrka municipality outside Stockholm and the raw water is taken from Lake Mälaren.

In a study by Seger (1998) the objective was to investigate the effect of pre-ozonation on the raw water from Lake Mälaren. The experiments were made at Norsborg waterworks.

Pre-ozonation was studied in combination with chemical coagulation, rapid sand filtration and slow sand filtration. The analyses of the water quality were measured in the raw water, after pre-ozonation, after the rapid sand filtration and after the slow sand filtration.

During a short period a lower concentration of aluminium sulphate (20 % lower) was used and the COD_{Mn} was approximately the same after the slow sand filtration

compared to the conventional treatment. But the turbidity was significant higher for the ozonation after the rapid sand filtration, even after the slow sand filtration the turbidity was higher. The chemical coagulation with aluminium sulphate does not enhance the coagulation in such way that lower coagulant doses can be used.

The ozonation improved the effect in the biological slow sand filter, measured as reduction of COD_{Mn} , UV-absorbance, TOC and DOC.

3.4.2 Minnesgårdets Waterworks

Minnesgårdets waterworks is located in Östersund (produce 18 000 m³ water/day) and the raw water is taken from Lake Storsjön. The lake has a depth of 300 meters and the water quality is high.

The treatment process at Minnesgårdets waterworks consist of alkalisation, ozonation, rapid sand filter and chlorination and is shown in Figure 6.

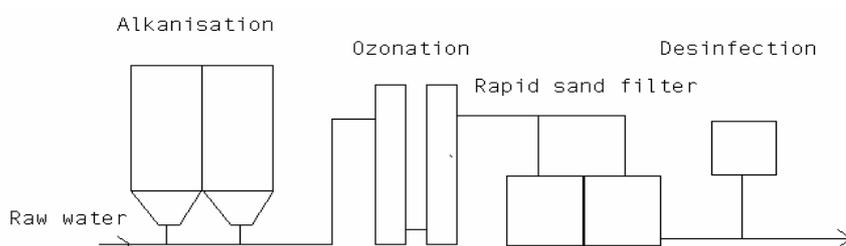


Figure 6. The process for Minnesgårdets waterworks (simplified diagram).

Minnesgårdets waterworks is one of few plants, which uses surface water and can reach recommended effluent standards without a chemical coagulant. The characteristics of the raw water are beneficial for microflocculation during ozonation. The low concentrations of DOC in the raw water cause a low concentration of ozonation by-products (OBP). Hence, active carbon filter is not necessary for the removal of OBP and the flocks can be removed by rapid sand filter (www.ostersund.se).

3.4.3 The effect of ozonation

In a pilot plant study at Hackensack, New Jersey, turbidity removal was found to increase with increasing ozone dose (Weng et al., 1986). The pilot plant results indicated that due to microflocculation the alum dosages could be reduced by 60 % and conventional sedimentation could be replaced with direct filtration. It was found that converting into pre-ozonation/direct filtration was more cost effective than expanding the existing conventional treatment facilities.

3.4.4 Removal of NOM by ozon-biofiltration

Removal of natural organic matter

In a study by Bouwer, E et al. (1999), the removal of NOM from drinking water supplies by ozone-biofiltration was investigated. Four sources of NOM were used in the study to represent a broad spectrum of NOM types that can be encountered in water treatment. The investigation was made in batch experiments and was performed with raw water or ozonated water. The results from batch experiments showed that removal of organic carbon by biodegradation was inversely proportional to the UV-absorbance

(254 nm) to TOC ratio and directly proportional to the percentage of low molecular weight material. Hence, a high UV-absorbance to TOC ratio-value leads to low biodegradation and a high percentage of low molecular weight material leads to a high biodegradation. The extent and rate of total organic carbon (TOC) removal typically increased as ozone dose increased, but the effect was highly dependent on the NOM characteristics. NOM with a higher percentage of high molecular weight material experienced the greatest enhancement in biodegradability by ozonation.

Preozonation/biofiltration

Wricke et al., (1996) made a study about NOM removal by pre-ozonation/biofiltration in a pilot plant in the region of Eastern Germany. The surface water has high levels of NOM and cause halogenated organic compounds (chloroform, trichloroacetonitrile etc.) when using chlorine for disinfection.

When using ozonation/biofiltration the result showed that ozonation caused an increase in biodegradability of dissolved organic matter (BDOC) of 25 % to 30 %. The results showed a BDOC formation maximum at 1 mg O₃/mg DOC and hence the ozonation in the pilot plant was carried out with the specific dose. 50 % of the formed BDOC was eliminated in the biofilter and the average DOC removal was 17 %.

The study also included an investigation about the effects of different DOC concentrations in the ozonation/biofiltration process. Tests were done at three different DOC concentrations and in all cases approximately 50 % of the BDOC were removed and approximately 20 % of the DOC was eliminated.

Removal of NOM and ozonation by-products

In a study by Carlson et al., (1996) removal of NOM and ozonation by-products (OBP) in biological filters in a pilot plant were investigated. Two water sources were considered;

- Horsetooth Reservoir with a turbidity of 3 NTU and DOC = 3,5 mg/l.
- Poudre River with turbidity < 1 NTU and DOC = 1,5 mg/l.

The result showed that a decrease in DOC with biofilter depth and a increase in DOC removal with EBCT for both the supplies. When looking at ozone dose the BDOC fraction of DOC increased with increasing ozone dose. Poudre River source needed a higher ozone dose to reach the same BDOC fraction level compared to Horsetooth Reservoir. Due to the higher fraction level the Poudre River also has a higher optimum ozone dose for the BDOC fraction than Horsetooth Reservoir.

3.4.5 Filtralite-filter

In a study by Melin (2000), ozonation followed by different biofilter media was studied to see if the media differ in removal of TOC, COD, turbidity, colour and UV-absorbance. The results did not show any significant difference between the filter medias and therefore Filtralite can be a good alternative as a biological filter. Another study showed that Filtralite is a good alternative for treatment of ozonated humic water as the majority of the easily biodegradable OBP was removed by the biofilter with generally over 80% removal efficiency (Melin et al., (2002)).

3.4.6 Ferric sulphate coagulation

In a study by Qasim et al, (1992), the removal of TOC and turbidity in two approaches were compared.

- Ferric sulphate coagulation under low pH (4-7,5) conditions.
- Ferric sulphate coagulation with lime softening under high pH (8,5-10,8) conditions.

Coagulation under low pH showed a optimum of TOC removal (42 %) with a Fe^{3+} concentration of 20 mg/l at a pH-level of 6,3, and the optimum turbidity removal at a Fe^{3+} concentration of 20 mg/l at a pH-level of 6,0.

The results of the experiments in high pH showed that a lower dose of Fe^{3+} could be used. For removal of 80 % of TOC only 9,5 mg/l Fe^{3+} was needed at a pH of 10,3. An optimum turbidity removal was found at a pH of 10,3 with a dose of 9,5 mg/L Fe^{3+} .

3.5 Summary

Based on the literature study presented in this chapter, the following summary can be made:

- Ozonation decreases pH in waters high in organic matter and moderate in alkalinity.
- Ozone breaks the double bounds in the molecules and increases colour removal and decrease UV-absorbance.
- Ozonation may cause microflocculation but the phenomenon is dependent on the water characteristics.
- Ozone reduces the size of the organic molecule and increases the BDOC.
- Previous investigation on the raw water from Lake Mälaren (Seger, 1998) indicates that a treatment with ozonation followed by chemical coagulation with aluminium sulphate does not enhance the coagulation in such way that a lower coagulant dose can be used.
- Coagulation with ferric sulphate occurs in the pH interval 5-5,5 and $\text{pH} > 8,5$.
- A lower ferric sulphate dose can be used when the water is pH-adjusted with $\text{Ca}(\text{OH})_2$ to a pH-level 9,5.
- The coagulants, Ekomix 1091 and Ekoflock 70 may be a alternative to traditional coagulants such as ferric sulphate and aluminium sulphate.
- Filtralite-filter may be a alternative to a GAC-filter.

4 Material and Methods

4.1 The pilot plant

The treatment process in the pilot plant begins with ozonation followed by different filter media. The treatment process for the pilot plant is shown in Figure 7.

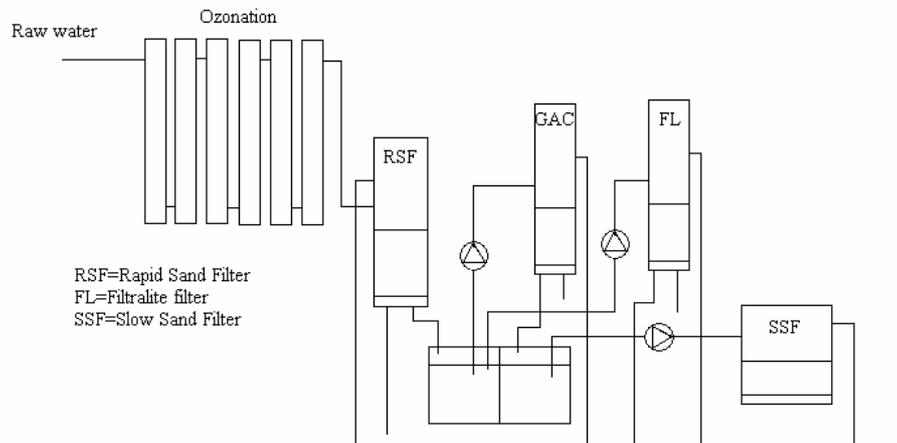


Figure 7. The treatment process for the pilot plant at Lovö waterworks (simplified diagram).

4.1.2 Ozone equipment

The ozonation consists of six columns, in three pairs, and ozone can be added in three of the columns, one in each pair (Figure 8). In this study ozone was only used in the first column and bubbles with oxygen and ozone transports through the column. The column is 4,8 meter high and has a diameter of 0,135 meter.

The water flow into the first column varied from 800 l/h to 1270 l/h. After the columns, the water was transported into a reaction tank. It is important that all the ozone molecules in the water have reacted before it enters the following rapid sand filter. A leakage of ozone can lead to health problem.

To produce ozone, an oxygen generator (Oxygen Generating System, Inc (OGSI), Model OG-15) and an ozone generator (Ozone technology, Model OT 20 – 120) were used. The oxygen generator produces pure oxygen and was connected to the ozone generator where the oxygen molecules split to atomic oxygen. The oxygen atom reacts with oxygen of other oxygen atoms to form ozone. The ozone generator has a capacity of 0-13,2 mg O₃/l (Ozone Technology manual, 1999 and Oxygen Generator manual, 1999).



Figure 8. The generators, the six ozonation columns and ozone bubbles.

4.1.2 Filters

Rapid sand filter

The rapid sand filter consists of one column with a bed depth of 0,95 meter and a diameter of 0,49 meter (Figure 9a). The water flow into the filter is the same as for the ozonation, from 800 l/h to 1270 l/h. These flows give an effective bed contact time (EBCT) of 13 minutes to 8,5 minutes and velocities from 4,3 m/h to 6,7 m/h.

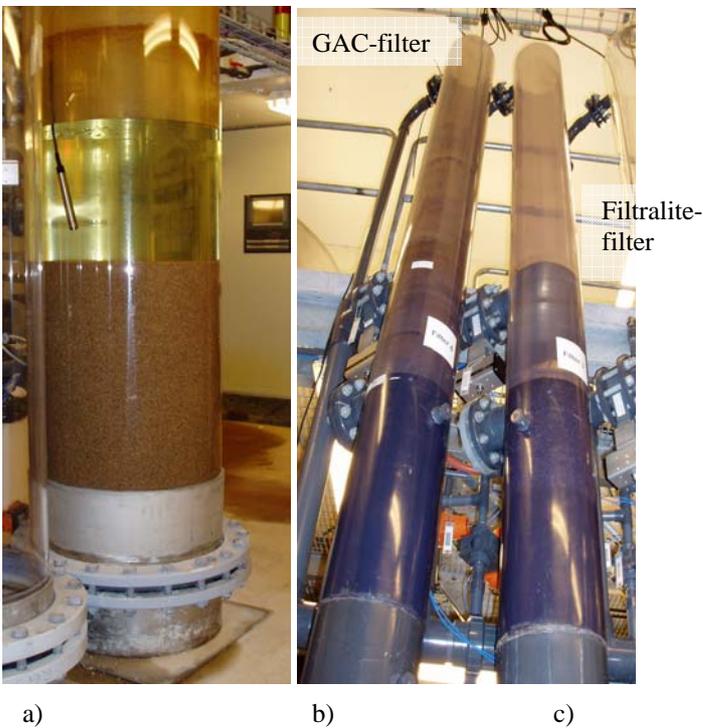


Figure 9. Rapid sand filter (a), GAC-filter (b) and Filtralite-filter (c).

GAC

The granular carbon filter has a bed depth of 1,4 meter and a diameter of 0,24 meter (Figure 9b). The water temperature was low during the study time and the biological activity in the GAC-filter was assumed to be the same. Hence, the water flow was constant at 126 l/h during the experiments. The EBCT were 30 minutes and the velocity were 2,8 m/h.

Filtralite

The Filtralite filter has a bed depth of 1,35 meter and a diameter of 0,24 meter (Figure 9c). The water flow into the column was 100 l/h, the EBCT was 30 minutes and the velocity was 2 m/h during the experiments.

Slow sand filter

The slow sand filter has a bed depth of 1,05 meter and a diameter of 1,0 meter. The water flow into the filter was 100 l/h, the EBCT was 8 hours and the velocity was 0,26 m/h during the experiments.

4.2 Chemical analysis

Analyses were made on pH, turbidity, UV-absorbance and colour in the accredited laboratory at Lovö waterworks. The water samples were collected in 100 ml plastic bottles.

To measure pH approximately 40 ml were poured into a jar and then analysed with a pH-meter. The Hach low range Model 1720C was used to measure turbidity and 20 ml of the water sample was needed.

To measure colour, a spectrophotometer was used at a wave length of 455 nm and 25 ml of the water sample was compared to a reference. For UV-absorbance a spectrophotometer was used at a wave length of 254 nm and the water was poured into a 4 cm cuvette. The result was expressed as m^{-1} .

TOC was measured with the NPOC (Non-purgeable organic carbon) method by the staff in the laboratory at Lovö waterworks.

4.3 Experiments on ozonation

To analyse the effect of ozonation on the raw water from Lake Mälaren two test series were made with following ozone doses:

- 2 mg O₃/l
- 4 mg O₃/l
- 6 mg O₃/l
- 8 mg O₃/l

The quality of the raw water and the temperature did not change significantly during the time for experiments.

Samples were collected before and after ozonation and before and after each filter to see changes during the process. The pilot plant and collection spots are shown in Figure 10 and the spots are graded from 1 to 5.

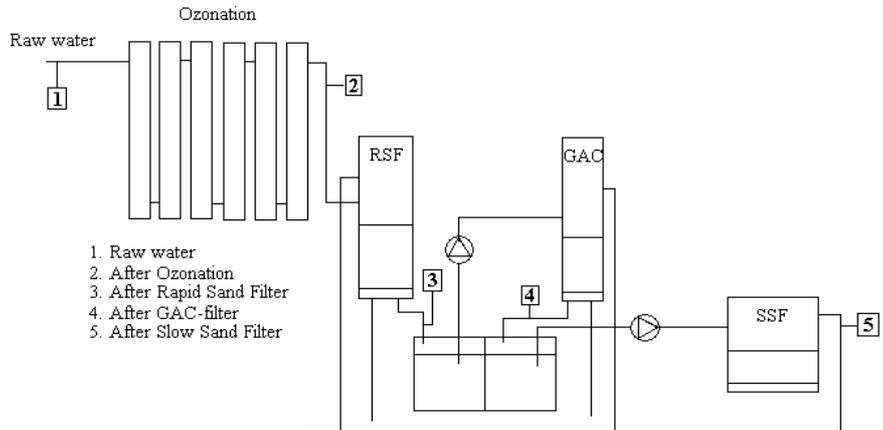


Figure 10. The pilot plant and sampling spots.

4.4 Jar tests

To investigate if a specific coagulant is an alternative for a treatment process, jar tests can be used. Jar test is an easy and fast way to measure the impacts of a coagulant and it gives a good approximation on how the coagulant will work in a larger scale.

Kemira flocculator was used. It consists of an instrumental panel and six jars (1 litre) with mixers which can work as a flocculation with rapid mixing, slow mixing and sedimentation (Figure 11).



Figure 11. The jar test equipment.

On the instrument panel the parameters (rapid mixing, slow mixing and sedimentation) can be varied, depending on time and velocity. In this study the parameters were stationary at:

- Rapid mixing - 20 seconds, 350 rpm.

- Slow mixing - 20 minutes, 40 rpm.
- Sedimentation - 10 minutes, no mixing.

These time intervals were selected in order to mimic the pilot plant, since the ozonation system does not have flocculation tanks, the flocculation occur directly before and in the rapid sand filter. That leads to a short rapid mixing time and a short slow mixing time and almost no time for sedimentation. Experiments with flocculation tanks normally take 15 minutes for rapid mixing, 20 minutes for slow mixing and 20 minutes for sedimentation.

4.4.1 Calcium and Ferric sulphate as coagulants

Jar tests were performed with ozonated water (4 mg O₃/l) from the pilot plant to see the effect of calcium and ferric sulphate addition. The aim was to increase the pH-level above 8,5 and use the aggregation effect of ferric sulphate at this level.

To investigate how the coagulation occurs and the effects of calcium addition, two equal tests were made, one with Ca(OH)₂ and the other with NaOH.

Different amounts of Ca(OH)₂ / NaOH were added to the jars to reach different pH-levels. At the same time as the flocculation was started a certain ferric sulphate dose were added. During the flocculation a reaction pH was measured one minute after addition of chemicals and after the flocculation pH, as well as turbidity, UV-absorbance and colour. Before measuring, the samples were filtrated to remove larger particles and to imitate the filtration in the pilot plant.

Since the purpose was to use less coagulant than Lovö Waterworks the ferric sulphate concentrations which were tested were lower than 134 µmol/l. The tests were made with ferric sulphate concentrations at:

- 84 µmol/l
- 100 µmol/l
- 124 µmol/l

Observations were made during the flocculation to observe differences between NaOH and lime water in for example size of the flocks or the time it takes to form flocks.

4.4.2 Ekomix 1091 and Ekoflock 70 as alternative coagulants

Jar tests were also performed with the CDM manufactured Ekomix 1091 and Ekoflock 70. The experiments were made the same way as for the ferric sulphate and calcium in chapter 4.4.1.

The tests were made with Ekomix 1091/Ekoflock 70 concentrations at:

- 100 µmol/l
- 134 µmol/l

4.5 Implementation of chemical coagulation in the pilot plant

To investigate if the results from the jar test in chapter 4.4 can be implemented on a larger scale, experiments were made in the pilot plant.

$\text{Ca}(\text{OH})_2$ was added into the pilot plant before ozonation and the ferric sulphate was added between the ozonation and the rapid sand filter (Figure 12). The first approximately 20 seconds after the ferric sulphate was added into the pipe, the water flow was turbulent, followed by slow mixing in the water above the sand in rapid sand filter. When the right dose of ferric sulphate, pH level and ozone dose had been tuned, formation of flocks occurred in the water above the filter bed. The particle accumulates in the top layer of the media and is removed by backwashing.

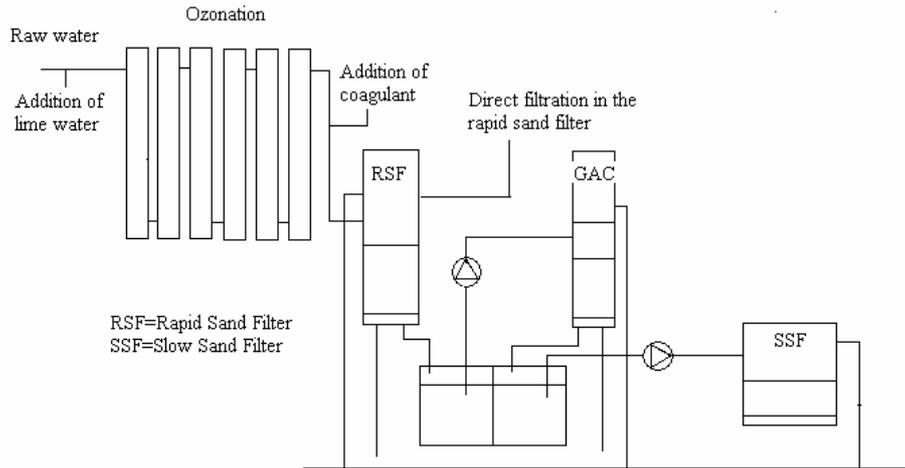


Figure 12. The treatment process with addition of calcium and chemical coagulant.

Three experiments were made with different ozone doses and these are present in following chapters.

4.5.1 First experiment on ozonation and chemical coagulants

Four experiments were made (Table 4) with an ozone dose at 2 mg O_3/l . The first test was done as a reference, without chemical coagulation. To see the effects of pH-adjustment with $\text{Ca}(\text{OH})_2$ the second experiment was made with $\text{Ca}(\text{OH})_2$ (pH=9,5) and ozonation. The following tests were made at constant pH (and $\text{Ca}(\text{OH})_2$ -concentration) and different concentrations of ferric sulphate (100-110 $\mu\text{mol}/\text{l}$ and 70-80 $\mu\text{mol}/\text{l}$).

Table 4. The four experiments were made with an ozone dose at 2 mg O_3/l .

Experiment	O_3/l	pH	Fe^{3+} dose ($\mu\text{mol}/\text{l}$)
1	2		
2	2	9.5	
3	2	9.5	100-110
4	2	9.5	70-80

To allow time for stabilization of the treatment process, each experiment was made during three days and then water samples were collected as in Figure 10. In these tests also the effects of the Filtralite-filter were analysed and samples were collected before and after the Filtralite-filter. All samples were analysed regarding to pH, turbidity, UV-absorbance and colour.

4.5.2 Second experiment on ozonation and chemical coagulants

Four experiments were made (Table 5) with an ozone dose at 6 mg O₃/l. The first experiment was done as a reference, without lime water and ferric sulphate. To see the effects of lime water the second experiments were made with lime water (pH=9,5). The following tests were made on ferric sulphate with concentrations of ferric sulphate (100-110 µmol/l and 50-60 µmol/l).

Table 5. The four experiments were made with an ozone dose at 6 mg O₃/l.

Experiment	O ₃ /l	pH	Fe ³⁺ dose (µmol/l)
1	6		
2	6	9.5	
3	6	9.5	100-110
4	6	9.5	50-60

The samples were collected and analysed as above.

4.5.3 Comparison between ozonated and un-ozonated water

To investigate the effects of ozonated water, experiments were made on ozonated water for comparison.

Three experiments were made (Table 6) to investigate the effects on water treated with ferric sulphate and calcium without ozonation. The first experiment was made with calcium, followed by two tests with different ferric sulphate concentrations (80-90 µmol/l and 110-120 µmol/l). Each experiment was made during one day to see the effects of the chemical coagulation. These experiments were not focused on the biological activity.

Table 6. Three experiments were made without ozonation.

Experiment	pH	Fe ³⁺ dose (µmol/l)
1	9.5	
2	9.5	100-110
3	9.5	80-90

4.5.4 Comparison of TOC

During the experiments with ozonation and ferric sulphate, water samples were collected to measure the TOC content in the water. The samples were collected as in Figure 10 and also before and after the Filtralite-filter. During following experiments, TOC was measured, Table 7.

Table 7. The table shows the experiments there TOC was measured.

Experiment	O ₃ /l	pH	Fe ³⁺ dose (µmol/l)
1	6	9.5	50-60
2	-	9.5	110-120
3	-	9.5	80-90
4	-	-	-

4.5.5 The pilot plant versus conventional treatment

To investigate if the results from the pilot plant can be an alternative to the conventional treatment at Lovö waterworks, a comparison was made on the parameters pH, turbidity, UV-absorbance, colour and TOC.

4.5.6 Online observations

To observe changes in pH after the rapid sand filter, turbidity after the rapid sand filter, turbidity after carbon filter and the water level in the rapid sand filter, the online computer program, CACTUS, was used. The parameters are connected to CACTUS so changes can easily be identified and analysed. These observations were made during the entire time when experiments on ferric sulphate and lime water in the pilot plant were made.

4.6 Comparison between GAC-filter and Filtralite-filter

To investigate changes over time in the Filtralite-filter and find out whether Filtralite-filter can be used instead of GAC- filter to reach better parameter values, a comparison between the two filters was made.

Experiments were made from the time the Filtralite-filter was started (2004-03-15) until the end of the project time (2004-06-21). From the beginning samples were collected before and after the GAC-filter and before and after the Filtralite to see changes in turbidity and UV-absorbance during time. These samples were used as references and to control if and when the bacterial growth started in the Filtralite filter.

At the end of the study period samples were taken as above and analyses were made on pH, turbidity, UV-absorbance, colour and TOC.

5 Results and discussion

In the first section 5.1, results from the experiments on ozonation on the raw water from Mälaren are presented and discussed. The results are presented in sub sections with the parameters pH, turbidity, UV-absorbance and colour. The exact results in form of a table are present in Appendix A.

Further investigations were made in the laboratory to see the effects of coagulants. The results from the jar tests are presented in section 5.2 and the section is subdivided into sections with calcium and ferric sulphate and alternative coagulants. The results in these sections are presented in diagrams so the exact parameter values are presented in Appendix B.

The results from the implementation of chemical coagulants in the pilot plant are present and discussed in section 5.3. This section includes results from the experiments on different ozone doses and different ferric sulphate concentrations. A section about comparisons between ozonated and un-ozonated waters is also included (Appendix C, D, E).

In section 5.4 the results from the comparison between Filtralite-filter and GAC-filter are present (Appendix F, G).

5.1 Effects of ozonation

5.1.1 pH

Figure 13a illustrates the changes in pH for different ozone doses. An increase in ozone dose leads to a decrease in pH and the treatment without ozone has the highest pH-level after filtration.

There is a decrease in pH during the ozonation depending on the formation of new organic acids which affect pH. During the rapid sand filtration, experiences normally do not indicate any pH change (Lovö waterworks), so the explanation to the decrease may be the turbulent water flow into the rapid sand filter which change the $\text{Ca(OH)}_2\text{-CO}_2$ equilibrium. An increase in CO_2 leads to a decrease in pH (Rutberg, 1998).

In the following filters the decrease in pH occurs due to the biological activity. The bacteria produces CO_2 during the biological degradation of the organic matter and the pH decrease.

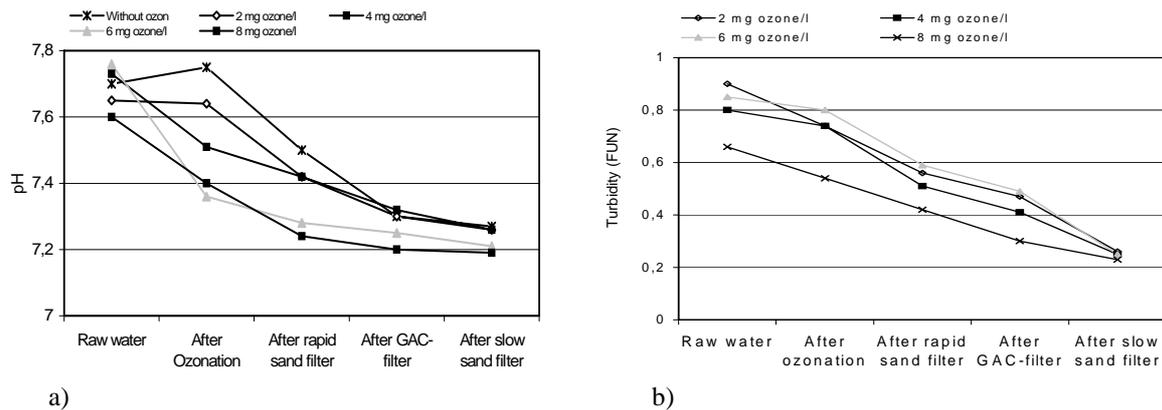


Figure 13. pH (a) and turbidity (b) versus the treatment process stages.

5.1.2 Turbidity

The turbidity decreases over the treatment process and has a value of 0,32 – 0,25 in the water from the slow sand filter. The total decrease is approximately 70 % (Figure 13b). The raw water characteristics changed during the measurements so the turbidity decreased from approximately 0,8-0,9 FNU to 0,65 FNU in the raw water but still the total decrease is approximately the same.

During the ozonation, decreases in turbidity may depend on the degradation of high molecular weight groups (Bouwer, 1999), or oxidation of substances. The microflocks caused by the ozonation as well as particles are partly removed in the rapid sand filter (Pontius, 1990) and decrease the turbidity. The biodegradable material is removed in the GAC filter and in the slow sand filter, even inorganic substances can be removed by adsorption in the filters and the turbidity decrease.

5.1.3 UV-absorbance

The UV-absorbance decreases during ozonation and is dependent on the ozone dose (Figure 14a). Increases in ozone doses lead to decreases in UV-absorbance and the highest ozone dose (8 mg O₃/l) has the largest decrease (approximately 75 %). When the water is treated with ozone the filtration does not have any significant effect on the UV-absorbance. The treatment without ozone does not change UV-absorbance significantly.

Humic matter contains double bounds that are split during ozonation, which explains the decrease in UV-absorbance. It is important to remember that the NOM concentration in the water may not decrease during ozonation even if the UV-absorbance decreases.

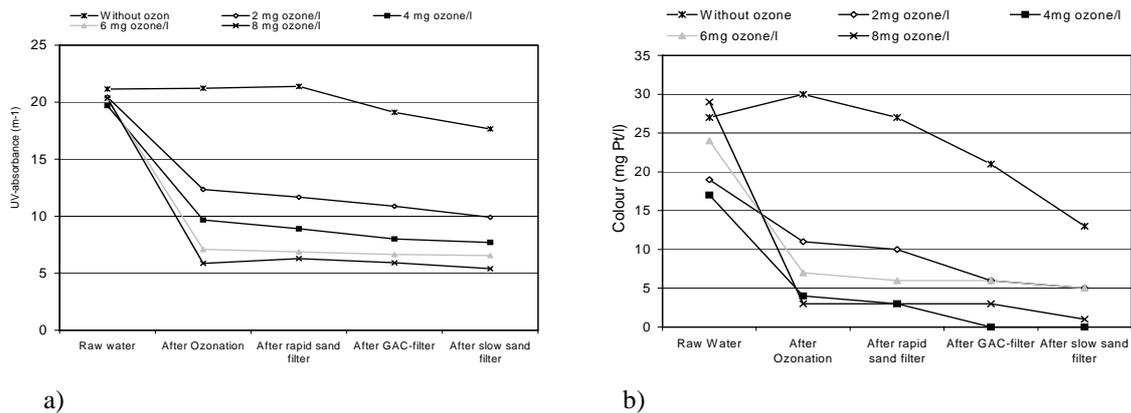


Figure 14. UV-absorbance (a) and colour (b) versus the treatment process stages.

5.1.4 Colour

The colour removal increases significantly during ozonation and an increase in ozone dose increases the colour removal. The highest ozone dose (8 mg O₃/l) removes colour to approximately 83 % during ozonation. There is a small decrease in colour over the following filters (Figure 14b).

Colour is probably caused by humic substances that have metal-complex bound into their structure. The ozone attacks carbon-carbon multiple bonds, oxidize metals and break chelates, all of which can contribute to visible colours (Pontius, 1990).

Decrease in colour during filtration and biological degradation depends on removal of particles and natural organic material.

5.1.5 Summary of section 5.1

Based on the results from section 5.1, the following summary can be made:

- The pH decreases over the treatment stages for all ozone doses. An increase in ozone dose leads to a decrease in pH.
- The increases in turbidity were independent on ozone dose, but decreased over the treatment process.
- The UV-absorbance decreases with increasing ozone dose.
- The colour decreases with increasing ozone dose.

The results showed that the treatment with ozonation and filtration did not reach the results at Lovö waterworks and a complement is needed for production of good quality drinking water.

5.2 Jar tests

The jar test experiments started at the laboratory at Lovö waterworks with water collected after ozonation in the pilot plant, but the results were not as expected. The pH-level changed quickly and there were difficulties with stabilising the process. The possible explanations may be the changes in temperature with following changes in the Ca(OH)₂-CO₂ equilibrium during the transport from the pilot plant to the laboratory.

The jar test equipment was moved to the pilot plant and all further tests were performed there. Consequently, the temperature was constant and the results became stable.

5.2.1 Calcium and ferric sulphate as coagulants

The effects of ferric sulphate on the water pH when the water was treated with calcium showed that when ferric sulphate was added to the pH-adjusted water a decrease in pH occurred. The decrease was approximately 0,5 pH-unit and was almost independent on the amount of ferric sulphate added to the water. This result does not agree with the theory, where an increase in ferric sulphate concentration decreases the pH-level. A possible explanation may be that the differences in concentration do not differ enough when using jar tests as an investigation method.

Average reduction of turbidity at different ferric sulphate doses when using pH-adjuster are shown in Figure 15. The result differed between the treatment with NaOH and the treatment with $\text{Ca}(\text{OH})_2$ and indicated a lower turbidity for the treatment with $\text{Ca}(\text{OH})_2$.

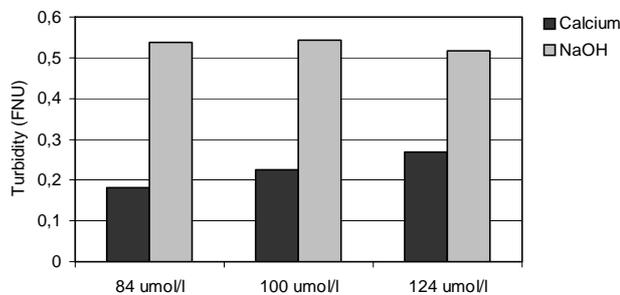


Figure 15. Comparison of turbidity between $\text{Ca}(\text{OH})_2$ and NaOH at different ferric sulphate concentrations.

In Figure 15 shows that the turbidity is not affected by the amount of dosage, but in general a higher coagulant dose gives a lower turbidity (Qasim, 1992) as for the treatment with NaOH. The explanations can be the uncertainties during the filtration where the pressure may change or that larger flocks created during flocculation may split up due to the pressure.

Since the study by Qasim (1992) showed a significant decrease in turbidity with increasing pH-values, it was of interest to see if coagulation improved the turbidity removal with increasing pH when using the ozonated water from Lake Mälaren.

When analysing the turbidity, trends could not be found for turbidity versus reaction pH at different ferric sulphate concentrations. The water was not affected in such way that turbidity decreased with increased pH. The results are uncertain due to the uncertainties during the filtration of the water sample from the flocculation.

The large decrease in pH during the treatment with ferric sulphate and that the water is not affected in such way that turbidity decreased with increasing pH leads to the fact that the pH-level needed to be more than 9,2 to cause coagulation.

The results from the experiments on UV-absorbance showed a decrease in UV-absorbance with increasing ferric sulphate dose (Figure 16a). Higher coagulant doses increase the aggregation of NOM and the flocks can easily be removed in the filter. The treatment with calcium has lower UV-absorbance values than the treatment with NaOH and the treatment with calcium seem to be beneficial.

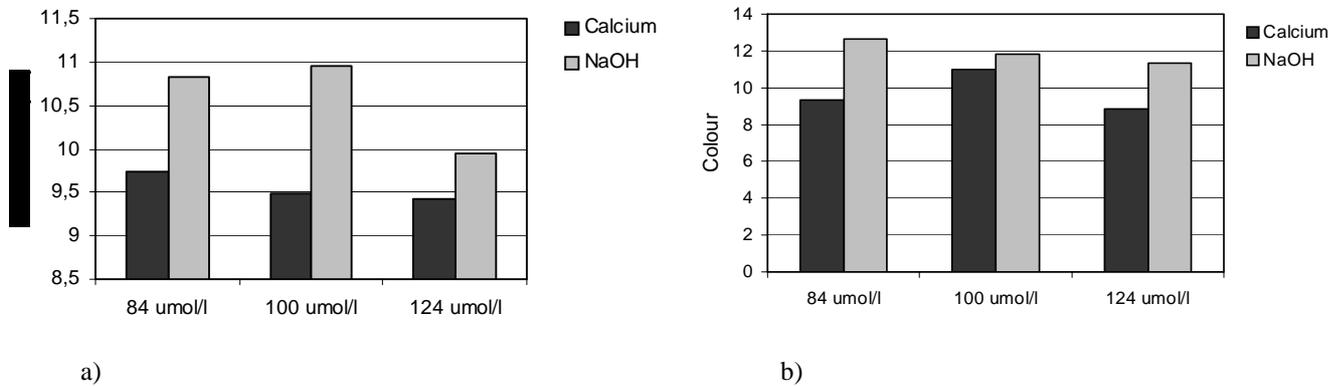


Figure 16. The average values for UV-absorbance (a) and colour (b) at different ferric sulphate concentrations.

The colour (Figure 16b) did not differ significantly between the ferric sulphate doses. In theory an increase in coagulant dose gives an increase in colour removal. Since the water has been ozonated before the treatment with ferric sulphate the colour was already low (around 10) and the addition did not have any cretin effect. The colour removal is larger for the treatment with lime water compared to the treatment with NaOH at same doses.

During the jar tests observations were made to investigate the differences between $\text{Ca}(\text{OH})_2$ and NaOH in flocculation when adding the same amount of ferric sulphate to the waters.

The results of the observation were:

- Flocculation occurred at a lower ferric sulphate dose in the jars with lime water compared to the jars with NaOH.
- The aggregation of flocks occurred more rapidly in the jars with lime water compared to the jars with NaOH.

5.2.2 Ekomix 1091 and Ekoflock 70 as alternative coagulants

The results from the jar tests with Ekomix 1091 and Ekoflock 70 indicated that the coagulants could not be used at high pH-levels and therefore no further investigations were made. Yet, the coagulants were not tested in lower pH and still can be a alternative to the coagulants in conventional water treatments.

5.2.3 Summary of section 5.2

Based on the results presented in section 5.2, the following summary can be made:

- A decrease in pH occurs approximately with 0,5 pH-units, when adding ferric sulphate to the pH-adjusted water.

- Due to the decrease in pH during the treatment with ferric sulphate the reaction pH has to be approximately 9,2 to cause aggregation.
- The turbidity, UV-absorbance and colour have significantly lower values for the water treated with Ca(OH)₂ than the waters pH-adjusted with NaOH.
- There is no correlation between turbidity and reaction pH, so an increase in pH does not cause more aggregation and does not decrease the turbidity.
- Water treated with Ca(OH)₂ seems to be a better alternative due to the more rapid flocculation at lower ferric sulphate doses and lower turbidity average.

The investigation continued with Ca(OH)₂ for pH-adjustment and ferric sulphate as a coagulant. The pH-level will be approximately 9,5 to be sure that aggregation occur.

5.3 Implementation of chemical coagulants in the pilot plant

5.3.1 First experiment on ozonation and chemical coagulants

The results from the experiments with an ozone dose at 2 mg O₃/l showed an increase in turbidity removal with increasing ferric sulphate dose which agrees with the theory. This finding is in contrast to the results from the jar tests. Higher doses enhance aggregation of particles and more flocks can be removed in the filter.

The results from the measured UV-absorbance and colour did not reach target values for the treated water. Table 8 shows the average values for the pilot plant and the average values for Lovö waterworks during the period 2004-05-03 to 2004-05-15. The average values for the pilot plant are determined from the treatment with a ferric sulphate dose at 100-110 µmol/l.

Table 8. Average values at the pilot plant for UV-absorbance and colour compared to the average values at the Lovö waterworks.

	Average values at the pilot plant	Average values at the Lovö waterworks
UV-absorbance (m ⁻¹)	11.25	8.75
Colour (mg Pt/l)	9	5

The levels of UV-absorbance and colour were deemed to high. This probably depends on the low ozone dose. Because of the unsatisfying results, no further experiments were performed at such low ozone doses.

5.3.2 Second experiment on ozonation and chemical coagulants

pH

Figure 17 a) shows the changes in pH-level during the treatment process. The addition of lime water increases the pH-level to approximately 9,5 after ozonation. The decrease over the rapid sand filter is larger for the waters treated with ferric sulphate compared to the experiments with only ozone and lime water which depends on the decrease in pH after ferric sulphate addition. The largest decrease occurred with a ferric sulphate dose at 100-110 $\mu\text{mol/l}$, this result agrees with the theory where a higher coagulant dose leads to a higher decrease in pH (Pontius, 1990). The decrease in pH during the following filters depends on the biological degradation of organic matter.

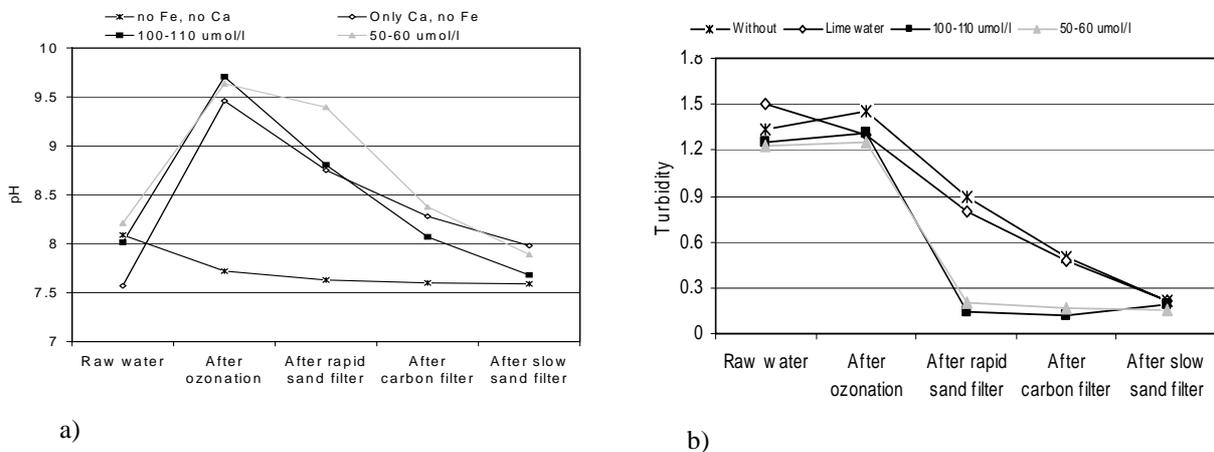


Figure 17. pH (a) and turbidity (b) versus the treatment process stages.

Turbidity

The turbidity decreased significantly over the rapid sand filter when the water was treated with ferric sulphate (Figure 17b). Yet, the decreases in turbidity between the ferric sulphate doses were similar and indicate that a lower dose can be used.

UV-absorbance

Figure 18a) shows the changes in UV-absorbance during the treatment process. The decrease in UV-absorbance over the rapid sand filter is larger for the water treated with ferric sulphate than for the water treated with ozone and lime water only. The explanation is the aggregation caused by the ferric sulphate. The coagulation occurs before the rapid sand filter and the flocks are then removed by the rapid sand filter.

There is a small decrease in UV-absorbance in the following biological filters due to the biological degradation of organic matter.

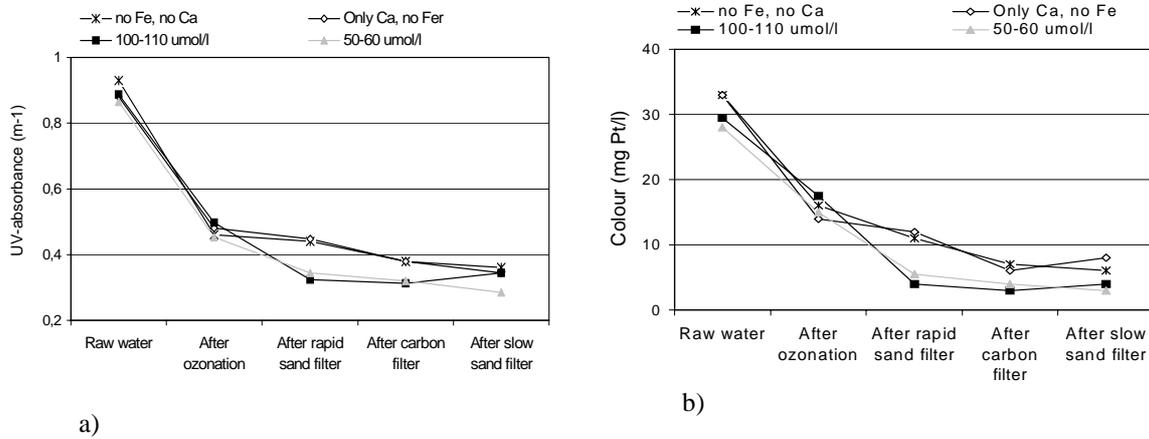


Figure 18. UV-absorbance (a) and colour (b) versus the treatment process stages.

Colour

The decrease in colour is similar for the four experiments in Figure 18b, during the ozonation. Over the rapid sand filter the waters treated with ferric sulphate has a larger decrease in colour than the waters treated with ozone and lime water.

The differences between the treatments depend on the coagulation with ferric sulphate and removal of particles in the rapid sand filter. The small decrease in colour over the carbon filter and over the slow sand filter is caused by biological degradation of the organic matter and adsorption of inorganic compounds.

The decreases are similar for the two ferric sulphate doses and this result indicates that a lower dose of ferric sulphate can be used.

5.3.3 Treatment with ferric sulphate and lime water without ozonation

As a reference for the investigations above, experiments were made on addition of ferric sulphate and calcium without ozonation.

The decreases in pH during the process are approximately the same for the treatments (Figure 19a). Over the rapid sand filter the decreases are 0,5 pH-units which is in agreement with literature data and the decreases in pH during the jar tests.

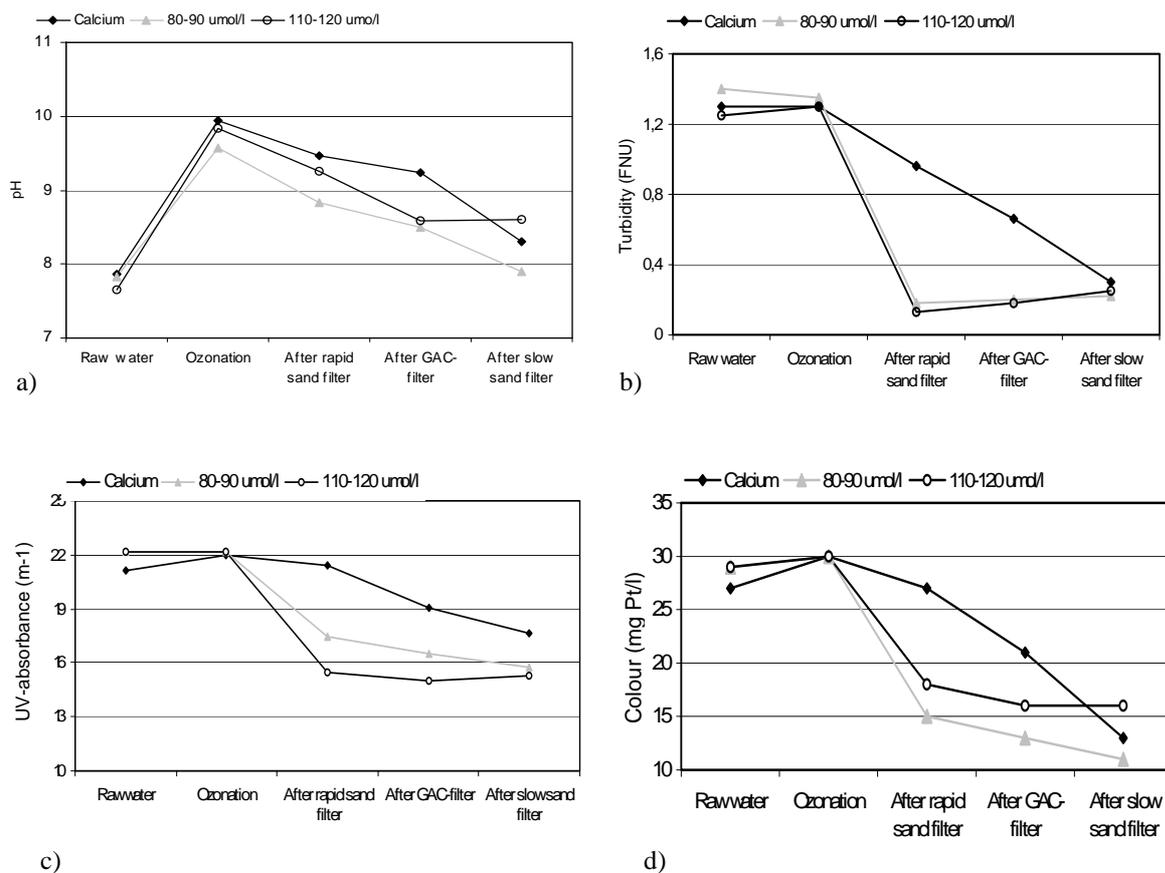


Figure 19. pH (a), turbidity (b), UV-absorbance (c) and colour (d) versus the treatment process stages.

The turbidity decreases to approximately 0,2 FNU after the rapid sand filter and do not differ significantly between the ferric sulphate concentrations. The increase during the following filters may be explained by the short time for each experiment and the biological process has no time for stabilising.

The largest decrease in UV-absorbance was obtained during the treatment with a ferric sulphate dose at 110-120 µmol/l and the treatment with lime water has the smallest decrease. Yet, the water treated with a ferric sulphate concentration at 80-90 µmol/l has the highest colour removal.

These experiments were made to investigate the effects of ozonation on coagulation and in the following chapter a comparison is made to see the differences between ozonated water and un-ozonated water.

5.3.4 Comparison between ozonated and un-ozonated waters

The comparison between ozonated water and un-ozonated water after the rapid sand filter is shown in Table 9.

Table 9. Comparison between ozonated and un-ozonated water at different ferric sulphate doses.

	Ozonated water		Un-ozonated water	
	lime water 100-110 $\mu\text{mol/l}$	lime water 50-60 $\mu\text{mol/l}$	lime water 100-110 $\mu\text{mol/l}$	lime water 80-90 $\mu\text{mol/l}$
pH	8.75	8.75	9.2	8.8
Turbidity (FUN)	0.2	0.2	0.25	0.25
UV-absorbance (m^{-1})	11	11	16	17
Colour (mg Pt/l)	5	5	17	15

Water treated with ozone has a lower turbidity than the un-ozonated water at lower ferric sulphate concentrations. The possible explanation is that the creation of microflocks during the ozonation leads to the facts that a lower ferric sulphate concentration can be used.

The water treated with ozone and a ferric sulphate dose at 50-60 $\mu\text{mol/l}$ has a UV-absorbance value at approximately 11 and the un-ozonated water (80-90 $\mu\text{mol/l}$) has a UV-absorbance at 16. Hence the un-ozonated water does not reach the same levels as for the water treated with ozone. The same result was found when measuring the colour where the water treated with ozone has values lower than 5 and the untreated water has values over 15.

5.3.4 Comparison in TOC

The changes in TOC during the treatment process are shown in Figure 20.

The largest decrease in TOC occurred when the water was treated with an ozone dose at 6 mg O_3/l and a ferric sulphate dose at 50-60 $\mu\text{mol/l}$. The lowest decrease occurred when the water where not treated at all.

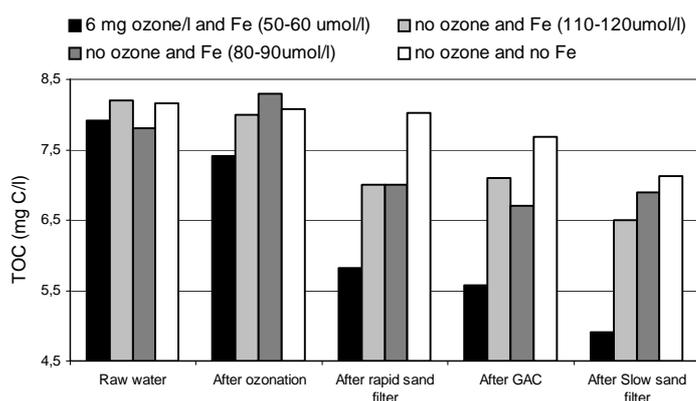


Figure 20. TOC content before and after ozonation and before and after the filters.

5.3.5 The pilot plant versus the conventional treatment

The best results from the pilot plant was obtained for the treatment with an ozone dose at 6 mg O_3/l and a ferric sulphate dose at 50-60 $\mu\text{mol/l}$ and are shown in Table 10. The results are compared with the average results at Lovö waterworks (conventional treatment) and the recommendations from the National food administration.

Table 10. The parameter values for Lovö waterworks, National Food Administration and the pilot plant.

	Unit	Results at Lovö waterworks	National Food Administration	Results from the pilot plant
pH	-	8.5	<7.5 – 9.0>	7.9
Turbidity	FNU	0.05	0.5	0.13
UV-absorbance	m ⁻¹	8.75	*	7
Colour	mg Pt/l	5	15	4
TOC	mg/l	4.4	5.5	4.9

* UV-absorbance is only used as a surrogate-parameter to TOC and COD_{Mn}, to measure organic matter content in the water and therefore there is no recommendation value from the National Food Administration.

The low pH-value from the pilot plant depends on that no pH-adjustment was made after the slow sand filter. The pH-value for the conventional treatment before distribution and pH-adjustment is lower compared to the pH-value in the pilot plant and the consumption for pH-adjustment could be less for the pilot plant.

The turbidity was higher for the pilot plant than for Lovö waterworks but still smaller than the recommended values from the National food administration. There were difficulties in stabilising the process in the pilot plant and longer test runs with stable conditions may decrease the turbidity more. Also, experience shows that turbidity removal with chemical coagulation in a pilot plant does not have as good result as the treatment in larger scale.

Both the UV-absorbance and the colour are lower for the pilot plant compared to the results from Lovö waterworks. The low values highly depend on the ozonation and a higher ozone dose would give even lower values.

The TOC content are higher for the pilot plant and the reduction of the organic matter over the GAC-filter is small compared to other studies with pre-ozonation/biofiltration stages (see chapter 7).

5.4 Comparison between Filtralite-filter and GAC-filter

The first experiment was made on turbidity and UV-absorbance and when the biological activity had increased experiments were made on pH, colour and TOC as well.

The results are presented by the difference between the GAC-filter and the Filtralite-filter ($\Delta(\text{GAC-Filtralite})$). A negative sign before the number indicate a higher value for the Filtralite-filter and a positive sign gives the GAC-filter the highest value. Hence, when there is a plus sign the GAC-filter is beneficial and when there is a negative sign the Filtralite-filter is beneficial.

5.4.1 Turbidity and UV-absorbance

Figure 21 illustrates changes in turbidity between Filtralite-filter and the GAC-filter from 2004-03-16 to 2004-06-21. The turbidity was less for the GAC-filter (negative sign) compared to the Filtralite-filter in the beginning of the treatment but changed over time. At the end of the project time there were no significant difference in turbidity between the GAC-filter and the Filtralite-filter. It took two months for the Filtralite-filter to reach similar turbidity values as the GAC-filter.

It takes some time for the bacteria-population in the Filtralite-filter to grow and settle and during this time the reducing of particles and organic matter occur with adsorption.

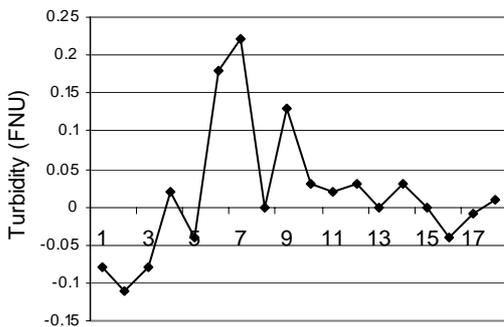


Figure 21. Δ (GAC-Filtralite) in turbidity.

The UV-absorbance (Figure 22) was lower for the GAC-filter (negative sign) in the beginning at the treatment by after approximately two month both filters had the same value. Changes were made in the end of the period (such as experiments without ozonation) and the UV-absorbance increased for the Filtralite-filter. It also seems that the Filtralite-filter is more sensitive for changes than the GAC-filter.

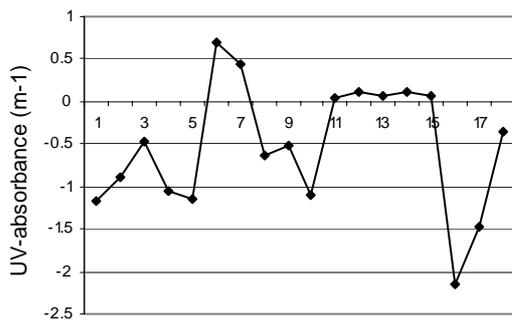


Figure 22. Δ (GAC-Filtralite) in UV-absorbance.

5.4.2 pH and colour

The changes in pH between the filters are illustrated in Figure 23 and the analyses were made during the period from 2004-05-03 to 2004-06-21. The decrease in pH over the filters depends on the biological activity. A more intensive activity leads to a larger

decrease in pH, since more CO₂ are emitted. The GAC-filter has the largest decrease in pH almost the entire time during the experiments and the possible explanation is a higher biological activity. But the difference between the filter decrease during the time and in the end of the experiments the pH-values are similar.

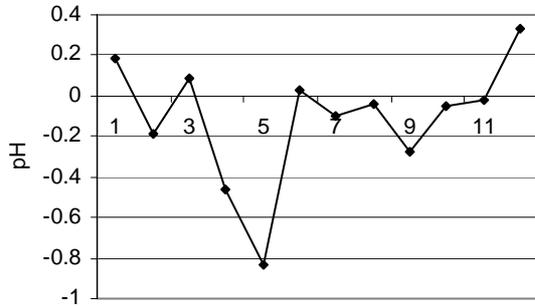


Figure 23. Δ(GAC-Filtralite) in pH.

Figure 24 shows the difference in colour between GAC-filter and Filtralite-filter. The colour removal was larger for the GAC-filter in the beginning (negative sign) and in the middle of the experiments but at the end of the study time the colour removal was more similar.

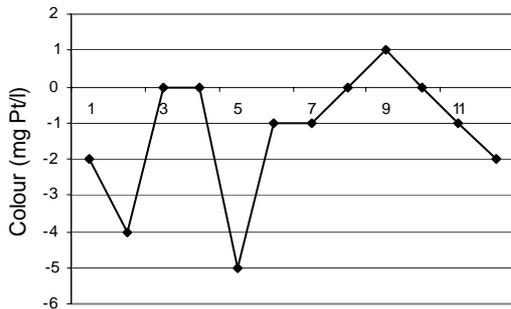


Figure 24. Δ(GAC-Filtralite) in colour.

5.4.3 TOC

The results from TOC analyses are illustrated in Figure 25. The TOC content decreases during the GAC-filtration with approximately 4 % (average during the period 2004-03-15 to 2004-06-19). Yet, the TOC concentration does not decrease during the Filtralite filtration and the water sample has the same values as after the rapid sand filter.

The decrease in TOC after 2004-05-26 depends on experiments with ferric sulphate and ozonation and the increase after 2004-06-07 depends on the treatment without ozonation.

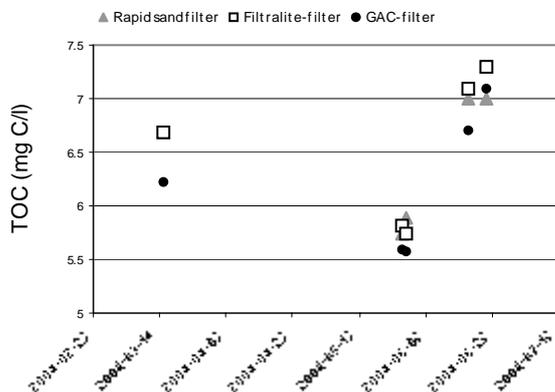


Figure 25. The difference in TOC between the GAC-filter and the Filtralite-filter.

6 Conclusions

Pre-ozonation and filtration cause changes in water characteristics. During ozonation a decrease in pH and turbidity and a significant decrease in UV-absorbance and colour occur depending on the ozone dose. The results from the experiment with pre-ozonation of the raw water from Lake Mälaren showed that the treatment did not reach the same treatment results as Lovö waterworks. Pre-ozonation followed by filtration seems not to be a good alternative without a complement to the conventional treatment at Lovö waterworks.

The results from the jar tests indicate an enhancement in microflocculation when using calcium as a coagulant. When comparing pH-adjustment with sodium hydroxide with calcium the average turbidity was 56 % lower for the water treated with calcium at the same ferric sulphate dose. The UV-absorbance was 7 % lower and the colour was 22 % lower for the water treated with calcium at the same ferric sulphate dose. The water treated with calcium also has a more rapid flocculation and the flocculation occur at lower doses of ferric sulphate. Ozonated water from Lake Mälaren has the right characteristics for a decrease in ferric sulphate dose when using calcium addition. Ferric sulphate as a coagulant and calcium as a pH-adjustment seems to be a good alternative to the treatment with aluminium sulphate.

The jar test experiments on Ekomix 1090 and Ekoflock 70 showed that these coagulants are not good alternatives to ferric sulphate at high pH-levels. Yet, the coagulants were not tested at lower pH and may be an alternative to aluminium during conventional treatment.

The results from the implementation of chemical coagulants in the pilot plant showed that a treatment with ferric sulphate (highest dose 100-110 $\mu\text{mol/l}$) and a ozone dose at 2 mg O_3/l did not reach target values for the treated water and therefore no further investigations were made on this ozone dose.

When using ferric sulphate and ozone dose at 6 mg O_3/l the result was more satisfying. A ferric sulphate dose at 50-60 $\mu\text{mol/l}$ could be used which is approximately 60 % lower than for the conventional treatment at Lovö Waterworks. The results from the pilot plant and the results from Lovö Waterworks are summarised in Table 11:

Table 11. The results from Lovö waterworks and the results from the pilot plant.

	Unit	Results at Lovö waterworks	Results from the pilot plant
pH	-	8.5	7.9
Turbidity	FNU	0.05	0.13
UV-absorbance	m^{-1}	8.75	7
Colour	mg Pt/l	5	4
TOC	mg/l	4.4	4.9

By using this low coagulant dose (50-60 $\mu\text{mol/l}$) indicates that the treatment with ozonation, calcium addition and ferric sulphate certainly can be a good alternative to the conventional treatment at Lovö waterworks.

The comparison between the GAC-filter and the Filtralite-filter showed that the Filtralite-filter could be a good alternative as a biofilter, but still, the results from this study showed better target values for the water treated with the GAC-filter. The experimental time was quite short for the biological activity in the Filtralite-filter to get stabilised, so further investigations may give other results.

7 Recommendations

The aim of this study was to produce a high quality drinking water without chemicals or with less chemicals than used at Lovö waterworks and hence to decrease the impacts on the environment. An alternative to the conventional treatment can be pre-ozonation and calcium addition followed by coagulation with ferric sulphate (pH >9,2).

To escape from large rebuilding at Lovö waterworks the alkalisation and ozonation may be placed before the conventional treatment and instead of aluminium to use ferric sulphate as a coagulant. The coagulation will occur as present, with coagulation, flocculation and sedimentation instead of direct coagulation in the rapid sand filter (Figure 26).

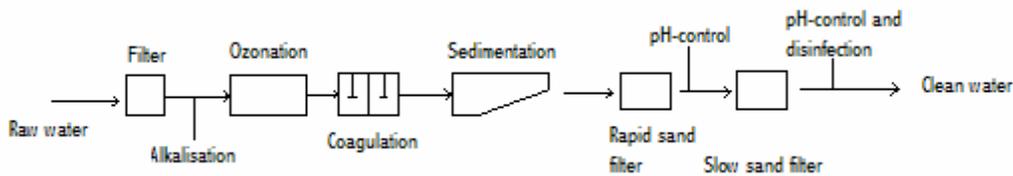


Figure 26. Alkalisation and ozonation followed by conventional treatment.

Another alternative to reach better results could be to have the biofiltration before the coagulation and rapid sand filter (Figure 27). During ozonation, the ozone breaks down high weight organic molecules to organic molecules with lower molecular weight. Today in the pilot plant these molecules are partly removed in the chemical coagulation before the rapid sand filter and less biological degradation take place in the GAC-filter. If the filters change places the biological degradation in the GAC-filter may increase and there are less material left for the coagulation. These may result in the fact that even a lower coagulant dose can be used and also a possible decrease in turbidity.

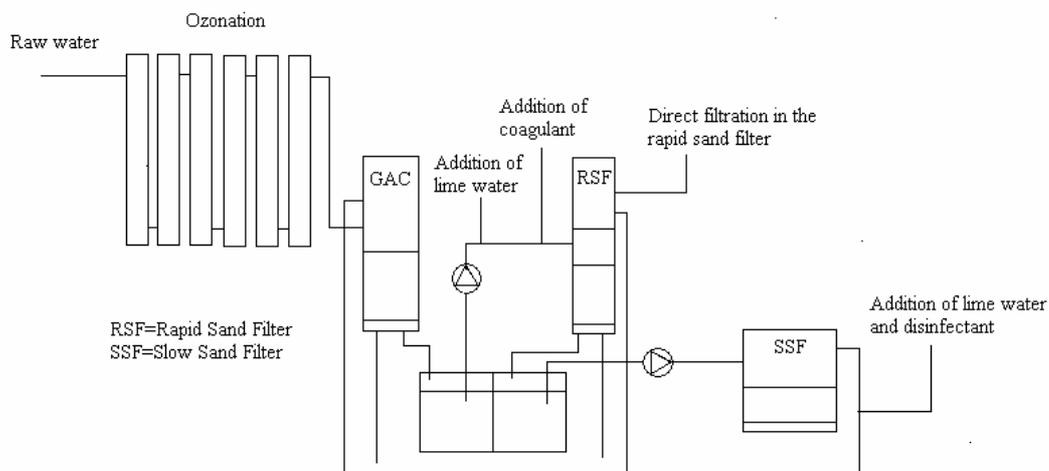


Figure 27. The treatment process with the GAC-filter before the rapid sand filter.

To have the biological filter before the rapid sand filter is more difficult and expensive to implement at Lovö waterworks and large rebuilding is needed, but if it is possible to make a significant decrease in TOC-content and turbidity with help of ozonation and the biofiltration it may be an alternative, but it is a long-term question.

The economical aspects on the treatment with alkalisation/ozonation/chemical coagulation compared to the conventional treatment are as follows.

Conventional treatment at Lovö waterworks:

Aluminium:	2000 ton/year
lime:	750 ton/year

Treatment at Lovö waterworks using the processes from the pilot plant:

Ferric sulphate:	1116 ton/year
lime:	1360 ton/year

The costs for the conventional treatment are larger, 13 %, compared to the alternative treatment with ozonation/chemical coagulation/filtration when comparing the cost for chemical coagulants.

The energy consumption for the conventional treatment at Lovö waterworks is approximately 70 Wh/m³.

Since the ozone equipment in the pilot plant is too small for larger scale experiments the energy consumption is determined from Göteborg waterworks where experiments have been made for a longer time and in a larger scale. The energy consumption for the production of ozone is 16,5 Wh/m³ for production of 1,5 g O₃/l (Engdahl, 2003). Therefore, the production of 6 mg O₃/l in the pilot plant demands 66 Wh/m³.

If using the ozonation/chemical coagulation followed by the conventional treatment, which was discussed in the beginning of this chapter, the treatment with ozonation will have an energy costs which is 94 % higher than for the conventional treatment.

The total costs (chemical coagulants + energy) showed that it is more expensive, 10 %, to use the conventional treatment and therefore the treatment with ozonation/chemical coagulation/filtration can be an alternative to the conventional treatment at Lovö Waterworks.

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Appendix

Appendix A

Experiments with different ozone doses 2, 4, 6, 8 mg O₃/l.

	pH				
	Raw water	After Ozonation	After rapid sand filter	After GAC-filter	After slow sand filter
Without ozon	7,7	7,75	7,5	7,3	7,27
2 mg ozone/l	7,65	7,64	7,42	7,3	7,26
4 mg ozone/l	7,73	7,51	7,42	7,32	7,26
6 mg ozone/l	7,76	7,36	7,28	7,25	7,21
8 mg ozone/l	7,6	7,4	7,24	7,2	7,19
	UV-absorbance (m ⁻¹)				
	Raw water	After Ozonation	After rapid sand filter	After GAC-filter	After slow sand filter
Without ozon	21,15	21,225	21,375	19,1	17,65
2 mg ozone/l	20,45	12,35	11,675	10,875	9,9
4 mg ozone/l	19,7	9,675	8,9	8	7,7
6 mg ozone/l	20,325	7,1	6,875	6,65	6,55
8 mg ozone/l	20,35	5,875	6,3	5,925	5,4
	Turbidity				
	Raw water	After Ozonation	After rapid sand filter	After GAC-filter	After slow sand filter
Without ozon	1,3	1,3	0,66	0,66	0,3
2 mg ozone/l	0,9	0,74	0,56	0,47	0,26
4 mg ozone/l	0,8	0,74	0,51	0,41	0,25
6 mg ozone/l	0,85	0,8	0,59	0,49	0,25
8 mg ozone/l	0,66	0,54	0,42	0,3	0,23
	Colour				
	Raw water	After Ozonation	After rapid sand filter	After GAC-filter	After slow sand filter
Without ozon	27	30	27	21	13
2 mg ozone/l	19	11	10	6	5
4 mg ozone/l	17	4	3	0	0
6 mg ozone/l	24	7	6	6	5
8 mg ozone/l	29	3	3	3	1

Appendix B

The results from the jar tests with ferric sulphate doses at 84 µmol/l, 100 µmol/l and 124 µmol/l and lime water.

84 umol/l ferric sulphate	Lime water (ml)	reaction pH	pH after flocculation	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
1	28	9,98	10,15	0,23	10,025	10
2	31	10,15	10,03	0,22	10,1	8
3	34	10,15	10,12	0,18	9,35	10
4	22	9,77	9,18	0,11	9,475	8
5	25	9,92	9,9	0,15	9,675	10
6	28	10,06	10,06	0,2	9,775	10
100umol/l ferric sulphate	Lime water (ml)	reaction pH	pH after flocculation	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
1	19	9,57	9,14	0,35	9,55	10
2	23	9,7	9,11	0,22	9,325	12
3	27	9,9	9,13	0,38	9,675	10
4	31	10,05	9,26	0,23	9,15	10
5	35	10,23	9,21	0,17	9,3	11
6	39	10,4	9,16		9,95	13
124 umol/l ferric sulphate	Lime water (ml)	reaction pH	pH after flocculation	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
1	19	9,34	9,11	0,25	8,575	10
2	22	9,63	9,29	0,16	8,65	10
3	25	9,77	9,76	0,2	9,25	11
4	28	10	9,96	0,7	9,5	15
5	31	10,05	9,99	0,26	8,9	15
6	33	10,13	10,05	0,3	8,75	13
Lime water	Lime water (ml)	reaction pH				
1	10	9,57				
2	14	9,71				
3	18	9,91				
4	22	10,11				
5	26	10,3				
6	30	10,44				

Appendix C

Experiment with an ozone dose at 2 mg O₃/l, ferric sulphate and lime water

Ozone dose 2 mg ozone/l

Without ferric sulphate and lime water	PH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)	Lime water	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
Raw water	7,7	1,15	23,75	28	Raw water	7,89	1,1	21,325	29
After ozonering	7,64	1,1	16,125	17	After ozonering	9,19	1,25	15,625	21
After rapid sand filter	7,67	0,8	16,4	15	After rapid sand filter	9	0,71	15,175	18
After carbon filter	7,6	0,53	13,775	10	After carbon filter	8,42	0,48	13,275	12
After slow sand filter	7,38	0,21	13,125	9	After slow sand filter	7,93	0,25	12,875	11
After filtralite	7,42	0,51	14,825	12	After filtralite	9,08	0,52	14,425	16

Lime water and a ferric sulphate dose at 110 umol/l	PH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)	Lime water and a ferric sulphate dose at 70-80 umol/l	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
Raw water	7,96	1,2	22,675	32	Raw water	7,83	1,15	22,3	30
After ozonering	9,23	1,1	18,775	20	After ozonering	9,27	1,42	16,3	25
After rapid sand filter	8,73	0,49	16,45	24	After rapid sand filter	8,52	0,49	15,425	15
After carbon filter	8,36	0,53	14,825	13	After carbon filter	7,91	0,47	13,85	13
After slow sand filter	7,82	0,22	11,825	7	After slow sand filter	7,61	0,24	11,225	12
After filtralite	8,27	0,35	14,125	13	After filtralite	8,37	0,25	13,4	13

Appendix D

Experiment with an ozone dose at 6 mg O₃/l, ferric sulphate and lime water

Ozone dose 6 mg ozone/l

	Without				Lime water			
	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
Raw water	8,09	1,34	23,25	33	Raw water	7,57	1,5	22
After ozonering	7,72	1,45	11,5	16	After ozonering	9,46	1,3	12
After rapid sand filter	7,63	0,9	11	11	After rapid sand filter	8,75	0,8	11,2
After carbon filter	7,6	0,5	9,475	7	After carbon filter	8,28	0,48	9,5
After slow sand filter	7,59	0,22	9,025	6	After slow sand filter	7,98	0,22	8,6
After filtralite	7,57	0,37	10	8	After filtralite	8,38	0,45	10,6

	Lime water and ferric sulphate dose at 100-110 umol/l				Lime water and ferric sulphate dose at 50-60 umol/l			
	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)	pH	Turbidity (FNU)	UV-absorbance (m ⁻¹)	Colour (mg Pt/l)
Raw water	8,18	1,3	22,2	27	Raw water	8,21	1,225	21,6125
After ozonering	9,91	1,41	12,425	13	After ozonering	9,635	1,25	11,3375
After rapid sand filter	8,73	0,11	8,075	0	After rapid sand filter	9,395	0,2	8,625
After carbon filter	8,23	0,11	7,825	0	After carbon filter	8,375	0,165	8,025
After slow sand filter	7,62	0,19	8,6	0	After slow sand filter	7,89	0,16	7,1125
After filtralite	8,27	0,09	7,775	0	After filtralite	8,53	0,16	7,725

Appendix E

Experiments without ozonation

	Lime water				80-90 umol/l ferric sulphate and lime water			
	pH	Turbidity (FUN)	UV-absorbance (m-1)	Colour (mg Pt/l)	pH	Turbidity (FUN)	UV-absorbance (m-1)	Colour (mg Pt/l)
Raw water	7,87	1,3	21,15	27	7,82	1,4	22,125	29
Ozonation	9,95	1,3	21,95	30	9,57	1,35	22,125	30
After rapid sand filter	9,47	0,96	21,375	27	8,83	0,18	17,475	15
After GAC-filter	9,23	0,66	19,1	21	8,5	0,2	16,525	13
After slow sand filter	8,31	0,3	17,65	13	7,9	0,22	15,725	11
After Filtralite	9,63	0,7	21,25	21	8,7	0,21	18	14

	110-120 umol/l ferric sulphate and lime water			
	pH	Turbidity (FUN)	UV-absorbance (m-1)	Colour (mg Pt/l)
Raw water	7,66	1,25	22,175	29
Ozonation	9,83	1,3	22,125	30
After rapid sand filter	9,25	0,13	15,5	18
After carbon filter	8,58	0,18	15	16
After slow sand filter	8,6	0,25	15,25	16
After Filtralite	8,25	0,17	17,25	18

Appendix F

The comparison between GAC-filter and Filtralite-filter (Turbidity and UV-absorbance)

Turbidity (FNU)				UV-absorbance (m ⁻¹)		
Date	After Rapid sand filter	After Filtralite filter	After GAC-filter	After Rapid sand filter	After Filtralite filter	After GAC-filter
2004-03-16	0,42	0,4	0,32	9,875	9,125	7,95
2004-03-18	0,45	0,44	0,33	9,625	9,625	8,725
2004-03-21	0,42	0,38	0,3	6,3	6,525	6,05
2004-05-03	0,8	0,51	0,53	16,4	14,825	13,775
2004-05-04	0,71	0,52	0,48	15,175	14,425	13,275
2004-05-05	0,49	0,35	0,53	16,45	14,125	14,825
2004-05-06	0,49	0,25	0,47	15,425	13,4	13,85
2004-05-07	0,17	0,13	0,13	12,875	11,85	11,225
2004-05-12	0,9	0,37	0,5	11	10	9,475
2004-05-13	0,8	0,45	0,48	11,2	10,6	9,5
2004-05-19	0,11	0,09	0,11	8,075	7,775	7,825
2004-05-26	0,22	0,14	0,17	8,9	8,125	8,25
2004-05-27	0,18	0,16	0,16	8,35	7,725	7,8
2004-05-28	0,22	0,14	0,17	8,9	8,125	8,25
2004-05-29	0,18	0,16	0,16	8,35	7,725	7,8
2004-06-09	0,96	0,7	0,66	21,375	21,25	19,1
2004-06-10	0,18	0,21	0,2	17,475	18	16,525
2004-06-21	0,13	0,17	0,18	16,425	16,25	15,9

Appendix G

The comparison between GAC-filter and Filtralite-filter (pH and colour)

pH				Colour (mg Pt/l)		
Date	After Rapid sand filter	After Filtralite filter	After GAC-filter	After Rapid sand filter	After Filtralite filter	After GAC-filter
2004-05-03	7,67	7,42	7,6	15	12	10
2004-05-04	9,33	9,08	8,89	18	16	12
2004-05-05	8,73	8,27	8,36	24	13	13
2004-05-06	8,52	8,37	7,91	15	13	13
2004-05-07	8,88	8,74	7,91	8	11	6
2004-05-12	7,63	7,57	7,6	11	8	7
2004-05-13	8,75	8,38	8,28	12	7	6
2004-05-19	8,73	8,27	8,23	0	0	0
2004-05-28	8,88	8,76	8,48	7	5	6
2004-06-09	9,3	9,2	9,15	27	21	21
2004-06-10	9,47	9,25	9,23	15	14	13
2004-06-21	9,25	8,25	8,58	18	18	16

Results from the TOC analysis

	6 mg Ozone/l and 50-60 µmol/l	No ozonation, no ferric sulphate	No ozonation, 80-90 µmol/l	No ozonation, 110-120 µmol/l
Raw water	7,915	8,16	7,8	8,2
After ozonation	7,41	8,08	8,3	8
After rapid sand filter	5,82	8,02	7	7
After GAC-filter	5,58	7,69	6,7	7,1
After slow sand filter	4,91	7,12	6,9	6,5
After Filtralite-filter	5,785	8,02	7,1	7,3