CHALMERS

More effective chemical precipitation in cold surface waters

A study on calcium carbonate solubility and aluminium residue at water treatment plants

Master of Science Thesis in the Master's programme Geo and Water Engineering and Environmental Measurements and Assessment

LINA HYLT

ANDREAS TENGSTRÖM

MASTER'S THESIS 2010:35

More effective chemical precipitation in cold surface waters

A study on calcium carbonate solubility and aluminium residue at water treatment plants

Master's Thesis in the Master's programme *Geo and Water Engineering* and *Environmental Measurements and Assessments*

LINA HYLT

ANDREAS TENGSTRÖM

Department of Civil and Environmental Engineering
Division of Water and Environmental Technology

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2010

More effective chemical precipitation in cold surface waters

A study on calcium carbonate solubility and aluminium residue at water treatment plants

Master's Thesis in the *Master's programme Geo and Water Engineering* and *Environmental Measurements and Assessment*

LINA HYLT

ANDREAS TENGSTRÖM

Department of Civil and Environmental Engineering
Division of Water and Environmental Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover:
The front page picture shows the river Lyckebyån during winter, laboratory tests conducted in the Environmental Chemistry Laboratory at Chalmers University of Technology and a calcium carbonate solubility and aluminium residue plot.

More effective chemical precipitation in cold surface waters

A study on calcium carbonate solubility and aluminium residue at water treatment plants

Master's Thesis in the Master's programme *Geo and Water Engineering* and *Environmental Measurements and Assessments*

LINA HYLT, ANDREAS TENGSTRÖM

Department of Civil and Environmental Engineering

Division of Water and Environmental Technology

Chalmers University of Technology

Göteborg, Sweden 2010

ABSTRACT

This Master's Thesis has been carried out at the consulting company Norconsult AB and at Chalmers University of Technology in collaboration with Karlskrona, Kristinehamn and Lerum water treatment plants, which have similar treatment processes.

Colour and turbidity, which in many cases are caused by humic substances, need to be removed from the water, by a process called chemical precipitation, before the water can be distributed to the consumers as drinking water. Several water treatment plants in Sweden experience difficulties regarding the chemical precipitation during winter time. The experienced problems, which occur in cold water, include high aluminium residue and low calcium carbonate solubility.

The overall aim of this project is to determine what is disturbing the chemical treatment processes in water treatment plants and how high aluminium residue, after continuous filtering, is correlated to calcium carbonate solubility. The investigated chemicals include the chemical coagulants Ekoflock 70 and Ekoflock 91 and the calcium carbonate, Mikrostevns. Literature studies, raw water analyses, treatment process analyses and two laboratory tests rounds on raw water are the basis of this report. The first laboratory test round is designed to determine and verify the most important factors affecting calcium carbonate solubility, whereas the second test round how aluminium residue levels are related to various percentage of dissolved calcium carbonate.

Water temperature and pH level appears to be superior to raw water properties, regarding calcium carbonate dissolution rate and aluminium residue. However, alkalinity could have a certain influence as well. Calcium carbonate dissolution rates are slower and aluminium residue levels are higher at 0.5 °C compared to 15 °C. This is probably caused by the increased activation energy in cold water and lowered flocculation velocity, caused by increased viscosity. The pH level in the water is the most important factor for calcium carbonate dissolution rate. The dissolution rate increases as pH decreases. Optimum precipitation pH is approximately 6.0 - 6.5. pH outside this interval results in increased aluminium residue levels. Unsolved calcium carbonate particles do not seem to cause high aluminium residue levels. Instead, laboratory tests from this study indicate higher aluminium residue as a result of increased percentage of dissolved calcium carbonate. Calcium ions replacing aluminium ions might be the cause, as well as aluminium ions detaching from colloid surfaces when colloids aggregate.

Key words: calcium carbonate solubility, aluminium residue, chemical precipitation

Effektivare fällning i kalla ytvatten

En studie om kritans löslighet och aluminiumrest vid vattenreningsverk

Examensarbete inom masterprogrammen Geo and Water Engineering och Environmental Measurements and Assessments

LINA HYLT, ANDREAS TENGSTRÖM

Institutionen för bygg- och miljöteknik

Avdelningen för Vatten Miljö Teknik

Chalmers tekniska högskola

Göteborg, Sweden 2010

SAMMANFATTNING

Detta examensarbete har genomförts på konsultföretaget Norconsult AB och vid Chalmers tekniska högskola i samarbete med Karlskrona, Kristinehamn och Lerums vattenreningsverk. Dessa verk har likartade reningsprocesser, men olika råvatten.

Färg och grumlighet, mestadels orsakade av humusämnen, måste avlägsnas från råvattnet innan vattnet kan distribueras till konsumenter som dricksvatten. Denna avlägsningsprocess benämns kemisk fällning. Flera vattenreningsverk i Sverige har vintertid haft problem med den kemiska fällningen. Problemen uppträder i kallt vatten och innebär låg kritalöslighet och höga aluminiumrester.

Det övergripande målet med detta projekt är att avgöra vad som stör den kemiska fällningen i vattenreningsverken och hur problem med kritans löslighet är relaterade till höga aluminiumrester efter kontinuerlig filtrering i DynaSand-filter. Studien innefattar fällningskemikalierna Ekoflock 70 och Ekoflock 91 samt kritasorten Mikrostevns.

Målet med projektet har uppnåtts genom litteraturstudier, råvattenanalyser, studier av råvatten och processdata samt fällningsförsök med krita och ovan nämnda fällningskemikalier. I en första försöksrunda fastställs de viktigaste faktorerna som påverkar kritans löslighet, medan en andra försöksrunda försöker besvara hur höga aluminiumresthalter är relaterade till olika andel av löst krita.

Resultaten visar att vattentemperatur och pH-nivå förefaller vara överordnade råvattenkvaliteten när det gäller aluminiumresthalt samt kritans upplösningshastighet. Alkaliniteten tycks emellertid även ha en viss påverkan. Kritans upplösningshastighet är långsammare och aluminiumresthalterna högre i vatten med temperaturen 0,5 °C jämfört med 15 °C. Detta beror sannolikt på ökad aktiveringsenergi i kallt vatten och lägre flockningshastighet, som i sin tur är orsakad av ökad viskositet. Vattnets pH-värde verkar vara den enskilt viktigaste faktorn för kritans upplösningshastighet. Hastigheten ökar när pH-värdet minskar. Optimalt fällnings-pH är cirka 6,0 – 6,5. pH-nivåer utanför detta intervall leder till förhöjda aluminiumresthalter. Olösta partiklar av krita verkar inte förorsaka höga aluminiumrester. Istället tyder laboratorietester i denna studie på ökade nivåer av aluminiumrester vid större andel löst krita i vattnet. Bakomliggande orsaker till detta kan vara att positiva kalciumjoner ersätter aluminiumjoner på negativa kolloidytor, men också att aluminiumjoner lossnar från kolloidytor när kolloider bildar större aggregat.

Nyckelord: upplösning av krita, restaluminium, kemisk fällning

Contents

APPENDICES

A1 - Mikrostevns

A2 - Ekoflock 70

A3 - Ekoflock 91

B1 - DynaSand filter

B2 - Process chart Karlskrona

B3 - Process chart Kristinehamn

B4 - Process chart Lerum

C1 - Template for test round I

C2 - Template for test round II

D1 - Additional results test round I

D2 - Additional results test round II

PREFACE

The Master's Thesis comprises 30 hec and has been carried out during the spring semester in 2010. The work load has been equally divided between the authors of this report.

In this study, analysis of raw water from three municipalities in Sweden (Karlskrona, Kristinehamn and Lerum) is conducted in order to determine the reason for low calcium solubility and high level of aluminium residue during the winter. The laboratory tests are carried out from February 2010 to April 2010. The work is intended as part of a future project within the Swedish Water & Wastewater Association, SWWA, concerning the chemical precipitation at water treatment plants. The project is carried out at the consulting company Norconsult AB in Göteborg and the Department of Civil and Environmental Engineering for the Division of Water and Environment Technology, Chalmers University of Technology, Sweden. The project is financed by all involved parties as well as Nordic Water Products AB.

The project has been carried out with Associate Professor Britt-Marie Wilén and Dilip Roy as supervisors. Laboratory tests have been carried out at the laboratory of Civil and Environmental Engineering at Chalmers University of Technology. Åke Andersson, Kajsa Engblom, Dan Göthe, Anita Larsson, Eva Larsson, Stefan Lund and Mats Strand are highly appreciated for their help and collaboration with the tests. We would also like to thank laboratory engineer Mona Pålsson in particular for her expertise and guidance during the tests and our opponents Andreas Fredriksson and Jimmy Hansson, for valuable input on our report.

Göteborg, Sweden June 2010

Lina Hylt   Andreas Tengström

NOTATIONS

Abbreviations and acronyms mentioned in this report are presented in terms of units and variables.

Units

FNU	Formazin nephelometric unit
kg	Kilo gram
l	Litre
M	Molar
m^3	Cubic metre
mPas	Millie Pascal seconds
μg	Micro gram
rpm	Rounds per minute

Variables

α	Negative colloid
β	Stern layer
γ	Diffuse layer
δ	Water
COD	Chemical oxygen demand
c_b	Calcium carbonate concentration in the bulk solution
c_s	Calcium carbonate concentration at the calcite surface
c_{eq}	Calcium carbonate concentration at equilibrium
DBL	Diffusion boundary layer
EAAE	Empirical apparent activation energy
G	Velocity gradient
k'_c	Apparent chemical rate
k_c	Chemical rate
k'_T	Apparent transport rate
k_T	Transport rate
P	Power input
PAC	Polyaluminium hydroxide chloride
R	Rate of dissolution
TOC	Total organic carbon
V	Volyme of water
μ	Viscosity

1 Introduction

This Master's Thesis has been carried out at the consulting company Norconsult AB and at Chalmers University of Technology in collaboration with Karlskrona, Kristinehamn and Lerum water treatment plants as a foundation to a future project within the Swedish Water & Wastewater Association, SWWA. The Master's Thesis covers approximately 30 hec during the spring semester in 2010.

1.1 Background

Clean and safe drinking water is essential to all humans. Sweden has a history of good and safe drinking water production and distribution. However, climate change is predicted to result in increased precipitation during winter time, which could have a large impact on Swedish drinking water production. With increased precipitation follows increased levels of humic substances in the water. Colour and turbidity, which in many cases are caused by humic substances, need to be removed from the water before it can be distributed to the consumers as drinking water. In raw water from lakes and rivers, high colour and turbidity values are common and often related to the climate and surroundings of the raw water source. The most common way to remove colour and turbidity is to add precipitation chemicals. This enables the humic substances to aggregate into solid particles that are large and heavy enough to settle.

Several water treatment plants in Sweden experience difficulties regarding the chemical precipitation during winter, when surface raw water temperatures are low. The precipitation chemicals that are being used contain aluminium. The aluminium is necessary for the precipitation of humic substances in the water, but unwanted in the drinking water. The experienced problems include high aluminium residue after chemical precipitation and solids-liquid separation by means of continuous filtering in the plants. DynaSand filters are one example of such continuous filters.

In order to have a functional chemical precipitation, there must be certain pH and alkalinity levels in the water. This can be adjusted by adding carbon dioxide and calcium carbonate, which increase both pH and hardness. Using calcium carbonate to increase pH and hardness in the beginning of the treatment process appears to disturb the chemical precipitation process. However, the problems with high aluminium residue are also believed to be related to low water temperatures as well as to high colour and increased level of humic substances in the raw water.

During the past years, the water treatment plants of Karlskrona, Kristinehamn and Lerum have had contact with Norconsult AB regarding problems connected to the chemical treatment.

Karlskrona and Kristinehamn water treatment plants experience difficulties regarding the chemical treatment in winter. The calcium carbonate dissolution is frequently insufficient and aluminium residue level is often too high after the chemical floc removal in continuous filters. Both plants have tried to alter their chemical dosage without conclusive results. Lerum water treatment plant, on the other hand, has not experienced any difficulties regarding the chemical treatment. However, at Lerum full scale tests of various lime and calcium carbonate treatment has been done and therefore they possess valuable information about calcium solubility.

1.2 Aim and objective

The overall aim of this project is to determine what is disturbing the chemical treatment processes and how calcium carbonate solubility is related to high aluminium residue after continuous filtering. This aim is divided into several interim targets, including understanding the overall differences in raw water composition, studying the involved treatment plants, understanding the main mechanics of calcium carbonate dissolution and chemical precipitation. Finally, the ultimate goal is to determine how the chemical precipitation process can be optimized for best practice during the winter season.

By comparing different water treatment plants with similar process but with different raw water quality, the intention is to gain an understanding about the problems and thereby reach a solution regarding insufficient calcium carbonate solubility and high aluminium residue levels.

1.3 Method

Literature studies, raw water analysis, treatment process analysis and laboratory tests on raw water from Karlskrona, Kristinehamn and Lerum, consists the backbone of this study. Raw water analyses include studying variation in selected raw water parameters between January 2008 and April 2010. Two laboratory tests rounds are made with calcium carbonate and chemical coagulators. Prior the first test round, all three water treatment plants are studied at site, through process charts and through conversation with concerned staff.

An experimental test round constitutes a foundation to the first test round. The focus of the experimental test round is to evaluate the equipment and investigation method. The first test round is conducted early in the project in order to retrieve and analyze cold and, allegedly, problematic water. The experience from this test round is the foundation of how the second test round is designed. This includes consulting literature and concerned people. The second test round addresses how the aluminium residue is affected by different values of unsolved calcium carbonate and levels of alkalinity. Test round one and two are described in detail in Sections 4 and 5.

1.4 Delimitation

Focus lies on studying factors affecting calcium carbonate dissolution rate for one type of calcium carbonate, and aluminium residue after chemical precipitation with two types of polyaluminium hydroxide chloride (PAC). Consequently, the research is focused on calcium carbonate solubility and aluminium residue for cold compared to warm water.

The study investigates calcium carbonate solubility prior to filtration in continuous filters and aluminium residue in filtered water, immediately after filtration. The laboratory analyses are made during two occasions, the first in February-March 2010 and the second in April 2010, in order to simulate filtering conditions in the water treatment plants. Raw water from the three water treatment plants, Karlskrona, Kristinehamn and Lerum, are sampled and analyzed in laboratory.

1.5 Outline of the study

The initial stage in this report gives a general overview of the drinking water treatment process including in-depth description of the main mechanics and properties of calcium carbonate and chemical precipitation. Prerequisites for the concerned water treatments plants are discussed and the Swedish drinking water regulations, that are important for this research, are presented. The chemicals used in this study are then further presented as well as process descriptions of Karlskrona, Kristinehamn and Lerum water treatment plants. Previous full scale tests and historical raw water data and operation data are presented.

In two main sections, the results from the first and second test round are presented. The report is then summarized with accompanied discussion and conclusions. Areas for further investigations are also proposed at the end of this report.

2 Literature review

Prior this study, several experimental studies regarding residual aluminium, calcium carbonate dissolution and the use of calcium carbonate in water treatment plants, have been compiled. In this section, literature is reviewed and presented.

In 1969, Hedberg published a report in which results from full scale experiments of chemical precipitation with calcium carbonate and aluminium sulphate trials were presented. Fifteen years later, in 1984, Sjöberg & Rickard presented a detailed investigation of the temperature dependency of calcium carbonate dissolution kinetics between 1 and 62 °C and at pH 2.7 to 8.4. Furthermore, inhibiting effects on the calcium carbonate dissolution rate has been investigated by Terjesen et al. (1961), Parsiegla & Katz (2000) and Karageorgiou et al. (2007). In addition, Alkattan et al. (1998) presents an investigation and comparison of calcium carbonate and lime dissolution rates.

In 1992 Göthe & Israelsson published a literature review on the use of calcium carbonate as a hardness increaser and as an alternative to lime. In 1995 Göthe & Israelsson released their results from full scale trials with calcium carbonate at Lerum water treatment plant.

Operational experiences during 1998 and 1999 from four surface water water treatment plants in Sweden were presented by Hernebring in 2003.

2.1 Drinking water treatment

This section intends to give a general description of drinking water treatment, including common treatment processes and vocabulary. There are almost infinite ways to design a water treatment plant. The design is for example determined by economy, raw water conditions, available treatment chemicals and desired water production volume (Hammer, 1986, p. 244).

Drinking water must be aesthetically acceptable and free from colour, turbidity, odour, taste, iron, manganese and of course free from pathogens such as bacteria and viruses. Ground water, rivers and lakes are common raw water source providers. However, raw water from lakes and rivers are in general more polluted and varies in quality compared to ground water. Rivers and lakes are affected by activities in the drainage area, as well as precipitation and air temperature. Heavy rainfall may flush pollutants and organic matter into the raw water sources. During droughts, ground water influence is greater due to lack of surface run-off in the drainage area. And of course, seasonal air temperatures determine the temperature of the raw water source (Hammer, 1986, p. 242).

Producing drinking water of raw water from lakes and rivers, generally starts with a coarse bar screen, which removes the largest fractions of particles before the water is pumped into the water treatment plant. The alkalinity, hardness and pH are adjusted by e.g. calcium carbonate ($CaCO_3$), carbon dioxide (CO_2) or sodium hydroxide (NaOH). Then humic substances, such as colour and turbidity, are removed by chemical precipitation. This process is described in Section 2.3. In this study, humic substances removal occurs in continuous filters called DynaSand filters, which are described in Section 2.1.1. The water is then transported to the activated carbon filters. In activated carbon filters, adsorption removes taste and odour and humic

substances that are not removed in previous treatment steps. (Hammer, 1986, pp. 242-245)

Iron and manganese are removed from the water by oxidation. To remove pathogens, the water might be chlorinated. The water may then be adjusted to desired pH, hardness and alkalinity and finally distributed to consumers. (Avdelningen för VA-teknik, 1986, p. 7.06).

2.1.1 DynaSand filters

The information in this section originates from Nordic Water Products (2006), if nothing else is stated. Additional information about DynaSand filters are presented in appendix B1.

The DynaSand filter is a sand filter that was first introduced in 1980. It is continuously operating in the sense that almost no backwashing of clogged filters are required, in comparison to regular sand filters that regularly need to be stopped and washed. An internal backflow of water continuously cleans the sand. DynaSand filter eliminates the need for flocculation and settling tanks, since coagulation, flocculation, precipitation and filtration occur in the DynaSand filter. The coagulation chemical is added to the influent water pipe, indicated by an upper, grey arrow to the left in Figure 2.1.

In number 1 (Figure 2.1) the water is admitted through the inlet distributor and evenly distributed in the filter. The first part of the filter allows flocculation of colloids. The flocs are then removed as the water is filtered upwards through the granular sand bed.
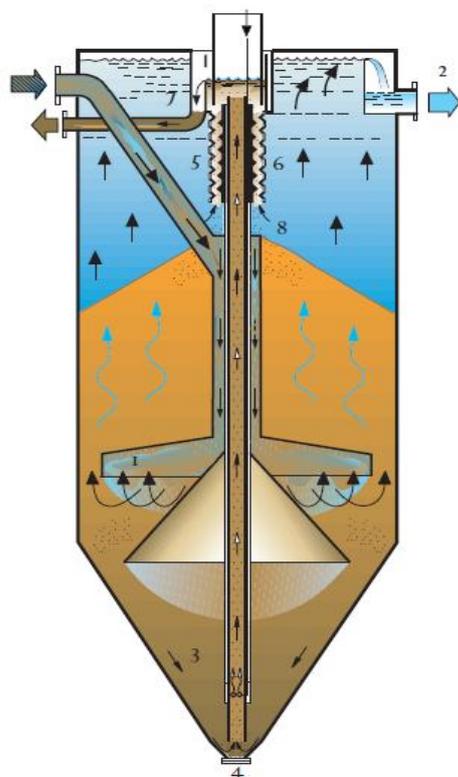
The top layer sand is slowly moving downwards, since sand and entrapped solids from the bottom layer are sucked up by an air lift pump. This results in a continuous circulation of sand.

The washing of the sand starts in the pump where turbulent flow separate sand and solids. In a sand wash (5 and 6 in Figure 2.1), solids are separated from the sand and the solids are discharged through a wash water outlet (7 in Figure 2.1). The cleaned sand, which is heavier than the pollutants, is returned to the sand bed through the sand wash outlet (8 in Figure 2.1). The treated water flows out through point 2 in Figure 2.1.

Figure 2.1 Principle of a continuous DynaSand filter (Nordic Water, 2006).

2.2 Theory and mechanics of calcium carbonate dissolution

Hydrogen carbonate (HCO_3^-) plays an important role in chemical precipitation. Higher levels of hydrogen carbonate means shorter flocculation time and lower dose of aluminium containing coagulants (Hedberg, 1969, p. 11). When calcium carbonate ($CaCO_3$) is added to water (H_2O) where hydronium ions (H_3O^+) are present, the alkalinity is increased due to the formation of hydrogen carbonate according to Eq. 1 (Hedberg, 1969, p. 13).

$$H_3O^+ + CaCO_3 \leftrightarrows HCO_3^- + Ca^{2+} + H_2O \qquad\qquad \text{Eq. 1}$$
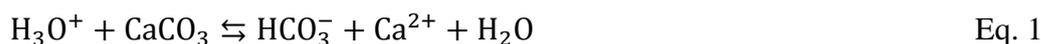
To ensure that there are sufficient amount of H_3O^+ in Eq. 1, the water treatment plants in this study add carbon dioxide (CO_2) to the incoming raw water. When added, an increase in H_3O^+ and a decrease in hydroxide ions (OH^-) occur. This means that pH is decreased due to the formation of H_3O^+. CO_2 is dissociated according to Eq. 2, Eq. 3 and Eq. 4 (Sposito, 1989, p. 38). At pH 7, water contains equal amounts of H_3O^+ and OH^-.

$$CO_2 + 2H_2O \leftrightarrows H_2O + H_2CO_3 \qquad\qquad \text{Eq. 2}$$

$$H_2CO_3 + H_2O \leftrightarrows H_3O^+ + HCO_3^- \qquad\qquad \text{Eq. 3}$$

$$HCO_3^- + H_2O \leftrightarrows H_3O^+ + CO_3^{2-} \qquad\qquad \text{Eq. 4}$$

In general, CO_2 is easily dissolved in water. However, the solubility increases as the temperature of the water decrease. At 15 °C, the carbon dioxide solubility is 2001 mg/l, while it is possible to solve 3 371 mg/l at 0 °C (Hedberg, 1969, p. 19). Göthe & Israelsson (1992, pp. 16-17) mention that the calcium carbonate dissolution rate is directly proportional to the H_3O^+ concentration in the water. For example, the dissolution rate is increased 10 times if pH is decreased one unit.

According to Göthe & Israelsson (1992, p. III) low pH value, small size fractions and long detention time are the three most important factors to obtain a high calcium carbonate dissolution rate in water. Hedberg (1969, p. 37) suggests that it is important for the calcium solubility that calcium carbonate is added at a low pH and that the pH is then continuously preserved. Water temperature is said to influence the calcium carbonate dissolution rate. This is supported by Sjöberg & Rickard (1984, p. 486) who also conclude that the calcium carbonate dissolution rate is decreasing if the water temperature is lowered. Sverdrup (1985, p. 25) on the other hand states that temperature variation have little impact on the calcium carbonate dissolution rate.

The energy input, i.e. rotation velocity of the mixing device, is considered to have high importance when determining the calcium carbonate dissolution rate. Increased rotation velocity results in a higher dissolution rate (Alkattan, Oelkers, Dandurand, & Schott, 1998, pp. 202-203).

According to Sjöberg & Rickard (1984, p. 485) the calcium carbonate dissolution rate can be divided into three regimes depending on H_3O^+ concentration and temperature of the solution. These are the H_3O^+-dependent regime, the transition regime and H_3O^+-independent regime. The regimes, which are presented Figure 2.2, are determined for a 0.7 M KCl (potassium chloride) solution. These regimes could also be applied on natural systems, as long as inhibitors of calcium carbonate dissolution rate are absent. Inhibitors that have extreme inhibitory effects on the dissolution rates are scandium, copper and phosphate (Sjöberg & Rickard, 1984, p. 492). The effects of inhibitors are investigated in Section 2.2.1.

H_3O^+-dependent regime	Transition regime	H_3O^+-independent regime
Mainly H_3O^+ diffusion into DBL $$R = k_T' \, [H_3O^+]^{0.9}$$	Moves to more acid pH at higher temperatures	Transport control increases Product diffusion out through DBL $$R = k_T \, (C_s - C_b)$$
TRANSPORT CONTROLLED	COMPLEX KINETICS Zone determined by H_3O^+ penetration trough DBL	MIXED KINETICS First order chemical reaction $$R = k_C \, (C_{eq} - C_s)$$
Mixed kinetics H_3O^+ adsorption at calcite surface $$R = k_c' \, [H_3O^+]^{0.5}$$	Moves to more alkaline pH at lower temperatures	Surface chemical control increases

Figure 2.2 Schematic illustration of calcium carbonate dissolution regimes (Sjöberg & Rickard, 1984).

As the temperature of the solution decreases, the H_3O^+-dependent regime expands to the same level as the H_3O^+-independent regime declines. The most influencing factor of the calcium carbonate dissolution rate is now the adsorption of H_3O^+ ions on the surfaces of the calcium carbonate particles. At this stage, H_3O^+ ions rapidly penetrate the diffusive boundary layer (Section 2.3) of the calcium carbonate particles. Sjöberg & Rickard (1984, p. 492) simply state that chemical reactions become limiting for the calcium carbonate dissolution rate at lower water temperatures.

If the temperature of the solution is increased, the H_3O^+-dependency declines and transport control increases. The underlying reason for this is changes in empirical apparent activation energy (EAAE), which is the smallest amount of energy that is required for a chemical reaction to occur. In Figure 2.2 the EAAE is illustrated as an arrow to the left. The EAAE increases with a lowering in temperature. The lowest activation energy determines whether the calcium carbonate dissolution rate is determined by a chemical reaction, transport rate or diffusion of H_3O^+ into the calcium carbonate diffusion boundary layer.

2.2.1 Inhibitors

Terjesen et al. (1961, pp. 281, 286) investigated the inhibiting effects of scandium and copper ions. According to the investigation, the dissolution of calcium carbonate is not affected by scandium and copper ions during the first 30 minutes of reaction time. The same study also concludes that the effect of the inhibitors increase if pH of the solution is increased. In Katz & Parsiegla (2000, p. 373) the pH dependency of the inhibitors are confirmed in solutions with pH between 7.00 and 9.25. The same study also show that pH needs to be greater than 7.6 or 8.8 (depending on copper ion concentration) to significantly inhibit the rate of dissolution of calcium carbonate. In addition, copper and scandium must have high concentrations, which is rare in raw waters.

Phosphate as inhibitor is much more efficient in the basic pH region, and a solution of pH 12 is required in order to allow all added phosphate to adsorb onto calcium carbonate particles (Karageorgiou, Paschalis, & Anastassakis, 2007, p. 448). In Figure 2.3, the effect of pH on the removal of phosphate, as it adsorb onto calcium carbonate, is displayed.

Vinson, Arvidson & Luttge (2007, pp. 118, 125) have studied inhibition, caused by dissolved manganese, on calcium carbonate dissolution. It is suggested that the inhibiting effect of manganese depends on manganese concentration, dissolved inorganic carbon concentrations and pH. Inhibiting effects on calcium carbonate dissolution rates are found in solutions with a pH greater than 8.5, hence, manganese should not be a problem in this study.
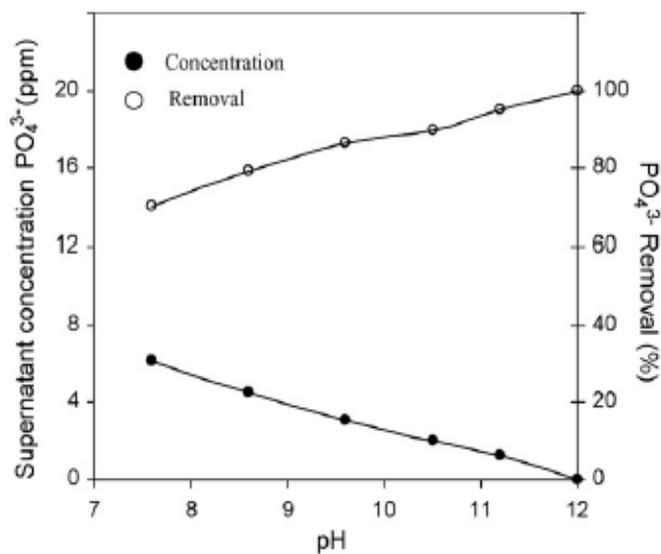
Figure 2.3 Effect of pH increase on reaction between phosphate (PO_4^{3-}) and calcium carbonate (Karageorgiou, Paschalis, & Anastassakis, 2007, p. 448).

2.3 Theory and mechanics of chemical precipitation

Raw water often contain large amount of substances that are causing colour and turbidity, such as micro organisms, clay particles and organic matter. These have the common name colloids and are either hydrophobic or hydrophilic (Hammer, 1986, p. 22). Hydrophobic particles are electrically charged, and the size and direction of the charge is determined by the ion composition. Humic substances, such as micro organisms and organic matter, and clay particles are negatively charged. In an aquatic solution hydrophobic colloids are neutral due to adsorption of positive ion on the colloids surface (Avdelningen för VA-teknik, 1986, p. 10.2). This positive layer of counter-ions is called the Stern layer, and outside it there is an additional more diffuse layer of counter-ions (Figure 2.4).
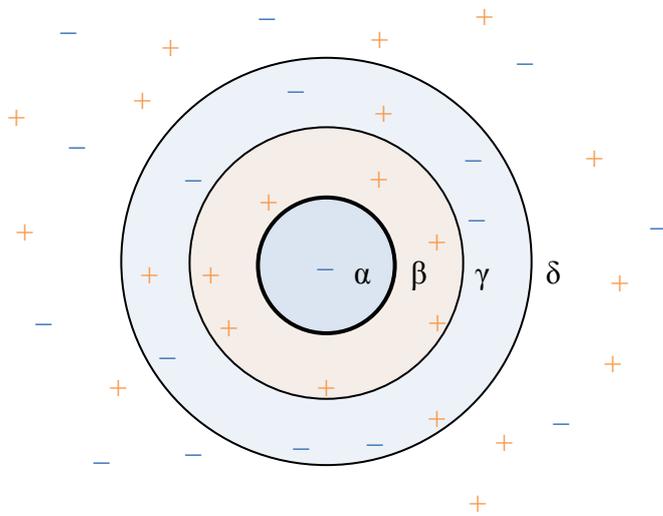
Figure 2.4 α: Negative colloid, β: Stern layer, γ: Diffuse layer, δ: Water

Between two hydrophobic colloids both attractive and repulsive forces are present. The attraction forces are caused by Van der Waals interaction due to asymmetric electron density around the colloids. Electrostatic repulsion causes colloids to remain dispersed in the water, since the repulsive forces often exceed the attraction forces (Avdelningen för VA-teknik, 1986, p. 10.04). By adding chemical coagulators, such as PAC, it is possible to cause aggregation of hydrophobic colloids by reducing the electrical forces in the stern and diffusive layers around the colloids.

When PAC, which has the general formula $[Al(OH)_xCl_{3-x}]_n$, where $0 < x < 3$ and $n \geq 2$ (Kemira Kemwater, 2003, p. 130), is added to raw water containing hydrophobic colloids, aluminium ions (Al^{3+}) are dissolved and free metal ions in water are bound to water and forming hydrated aluminium complexes (Wilén, 2008) according to Eq. 5, Eq. 6 and Eq. 7 (Kemira Kemwater, 2003, p. 125).

$$Al^{3+} + 2H_2O \leftrightarrows AlOH^{2+} + H_3O^+ \qquad\qquad \text{Eq. 5}$$

$$AlOH^{2+} + 2H_2O \leftrightarrows Al(OH)_2^+ + H_3O^+ \qquad\qquad \text{Eq. 6}$$
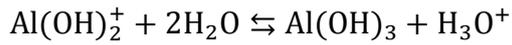
$$Al(OH)_2^+ + 2H_2O \leftrightarrows Al(OH)_3 + H_3O^+ \qquad \text{Eq. 7}$$

These reactions are completed within seconds from the addition of PAC. The reaction formula for the general PAC formula is described in Eq. 8. (Kemira Kemwater, 2003, p. 130)

$$Al(OH)_xCl_{3-x} + (3-x)H_2O \leftrightarrows Al(OH)_3 + (3-x)H_3O^+ + (3-x)Cl^- \quad \text{Eq. 8}$$
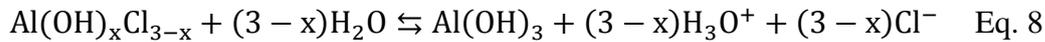
If the dose of chemical coagulant is too low, there are not enough aluminium complexes to neutralize the stern and diffuse layers (Figure 2.4) of the hydrophobic colloids. If the dosage is higher, re-stabilization of the colloids will occur since aluminium complexes cover the whole colloid surface (Figure 2.5). This means that the charge is reversed. If the dose is increased even more, a precipitation of $Al(OH)_3$ (s) is formed since its solubility constant is exceeded. This will cause sweep flocculation, which means that the particles collide and integrate with smaller particles as they settle and grow (Wilén, 2008).
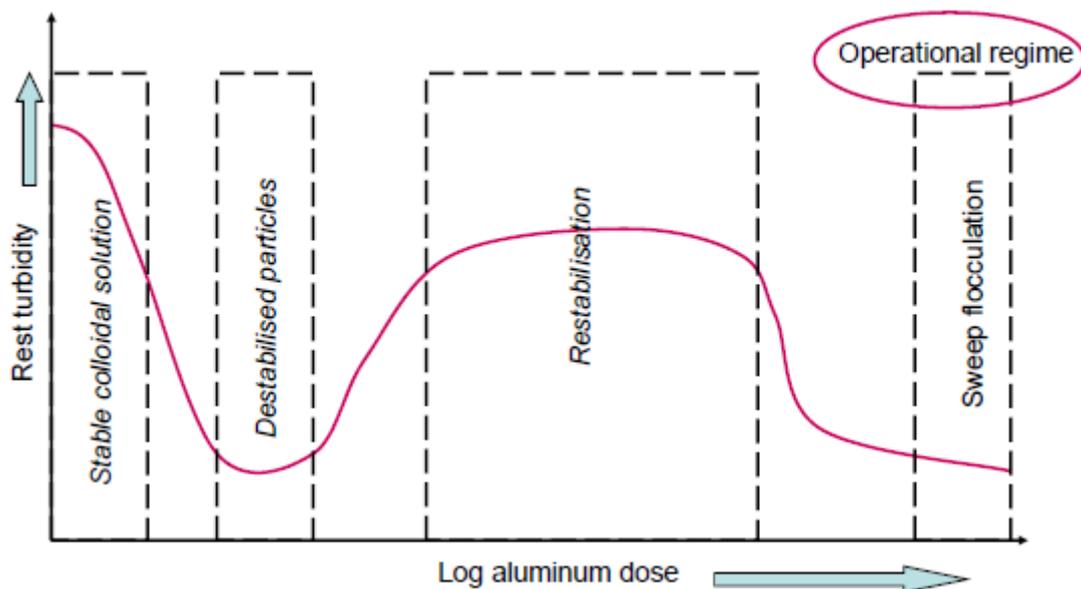
Figure 2.5 The relationship, for constant pH, of residual turbidity and dose of chemical coagulant (Wilén, 2008).

In order to have a successful coagulation and flocculation, mixing is required. During the coagulation process intensive mixing is needed in order to increase the number of particle collisions between hydrated aluminium complexes and colloid surfaces. Aluminium complexes are created when PAC is added. To describe the energy input due to mixing, the velocity gradient G [1/s] is used. G depends on the volume of water V [m^3], viscosity µ [kg/(m×s)] of the water and the power input P [kg×m^2/s^3]. The expression is described in Eq. 9.

$$G = \sqrt{\frac{P}{\mu \times V}} \qquad \text{Eq. 9}$$

Micro flocs are created through the coagulation process. In the flocculation process, larger and heavier flocs are created when micro flocs aggregate. This process require slower mixing than the coagulation process, since the flocculation need to be greater than the floc degradation. The degradation consists of two processes; breakdown of flocs due to collisions between larger particles and increased erosions on the surfaces of the flocs as they move in the liquid (Avdelningen för VA-teknik, 1986, p. 10.16).

The required dose of coagulant depends on the required flow, the type of coagulant, type of colloids in suspension, temperature, pH, chemical composition of the water and the time and velocity gradient of the mixing (Hammer, 1986, p. 22). If there is normal or high concentration of colloids, the dose of coagulant is proportional to the colloid concentration. However, at lower colloid concentrations, higher coagulant doses are needed in order to increase the number of collisions between hydrated aluminium complexes and colloids. At very high colloid concentrations, large doses of coagulant are needed in order to obtain micro flocs (Wilén, 2008). Hernebring (2003, p. 69) states that an increase in the aluminium dose always results in increased reduction of humic substances as well as a decrease aluminium residue. However, the precipitation pH has to be within reasonable boundaries. For coagulants containing aluminium, pH values of around 6.0 - 6.5 is preferred (Hernebring, 2003, p. 2).

There are several rules of thumb for determining an approximate coagulant dose. Hernebring (2003, p. 64) presents two rules of thumb, which are based on COD and colour in the raw water. Eq. 10 is based on the COD level and Eq. 11 is determined by the colour value.

$$Dosage = 0.32 \times COD_{Mn} \left[\frac{mg\ Al}{l} \right] \qquad\qquad \text{Eq. 10}$$

$$Dosage = (1.37 + 0.0064 \times colour) \left[\frac{mg\ Al}{l} \right] \qquad\qquad \text{Eq. 11}$$

In Figure 2.6, doses of aluminium sulphate between 20 mg/l and 70 mg/l are tested in order to obtain as low aluminium residue as possible after filtration. Regardless of the dose, pH 6.5 results in the lowest aluminium residue. The figure also enhance Hernebring's (2003, p. 69) statement about how increased aluminium doses, always results in lower aluminium residue, within the optimum pH range. From Figure 2.6 it is evident that 20 mg/l of aluminium sulphate results in substantially higher aluminium residue than the higher doses. For all other doses, the difference in aluminium residue at pH 6.5 is much smaller.

mg/l
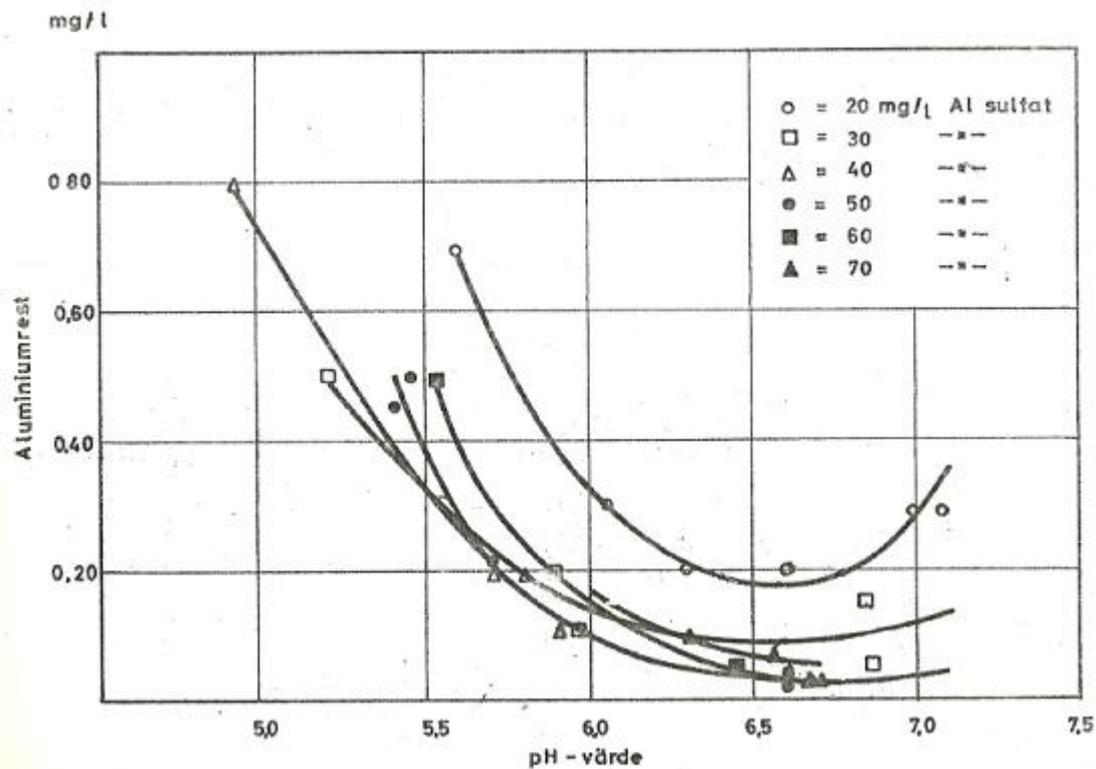
Figure 2.6 Correlation between aluminium residue and precipitation pH at different doses of aluminium sulphate (Hedberg, 1969, p. 22). pH-värde = pH, Aluminiumrest = Aluminium residue and Al sulfat = Aluminium sulphate

When PAC is added to water, free aluminium ions react with water through hydrolysis. Hydrated aluminium complexes are formed through this reaction and H_3O^+ reacts with HCO_3^- and form carbonic acid (H_2CO_3) according to Eq. 12. This causes a decrease in pH (Wilén, 2008).

$$H_3O^+ + HCO_3^- \leftrightarrows H_2CO_3 + H_2O \leftrightarrows CO_2 + 2H_2O \qquad \text{Eq. 12}$$
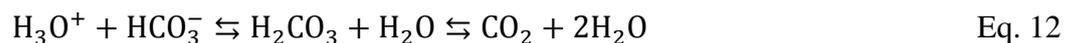
In Eq. 12, carbonic acid dissociate according to Eq. 2 – Eq. 4 (Hedberg, 1969, p. 13).

The report by Hedberg (1969, p. 23) presents precipitation trials with aluminium sulphate in raw water. The trials have been optimized by dosing CO_2 and $CaCO_3$ according to Figure 2.7. The process is compared with a corresponding process in which calcium carbonate is replaced by calcium oxide. It is concluded that dosing calcium carbonate increases the number of particles substantially. By using calcium carbonate instead of calcium oxide the density of the flocs increase while the volume of the flocs decrease. The flocs are between five to eight times heavier but approximately eight percent smaller. These factors affect the settling velocity of the flocs (Hedberg, 1969, p. 50).
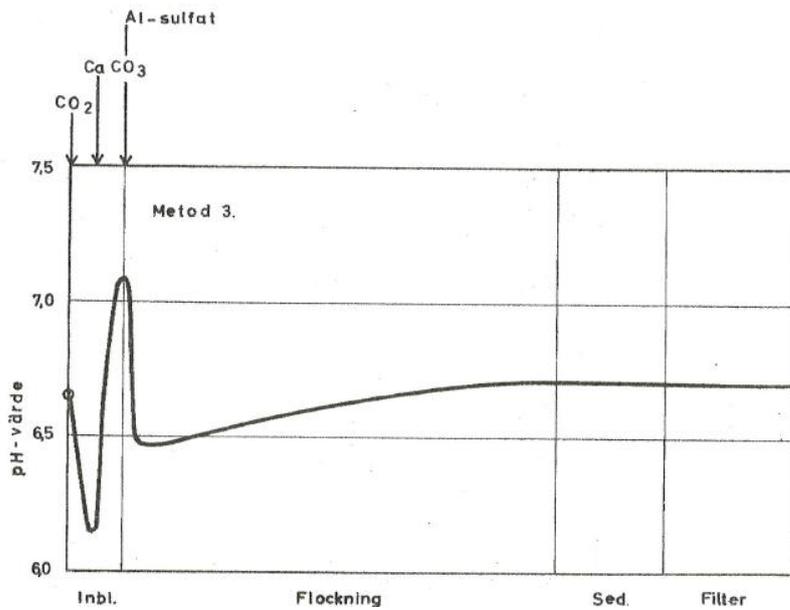
Figure 2.7 Dosing order of chemicals and how they affect pH (Hedberg, 1969). pH-värde = pH, Aluminiumrest = Aluminium residue and Al sulfat = Aluminium sulphate, Inbl. = Mixing; Flockning = Flocculation, Metod = Method

As stated in Section 2.2, the calcium carbonate dissolution rate is affected by the water temperature. Low temperature in the water results in decreased calcium carbonate dissolution rates. The effect of the temperature dependency is illustrated in the diagram in Figure 2.8 for both calcium carbonate and calcium oxide. The diagram shows an increase in residual turbidity after flocculation as the water temperature and flocculation time decrease. When comparing the 30 and 45 min flocculation curves, the temperature dependency seem to be greater for calcium carbonate than calcium oxide. When comparing residual turbidity at 2 °C and 18 °C for the different flocculation times, the curves indicate higher difference at the low temperature compared to the higher temperature. The difference is more apparent for calcium carbonate than calcium oxide.

In Figure 2.9 residual turbidity for calcium carbonate and calcium oxide is plotted against flocculation time. However, the diagram does not give any indication about the residual turbidity during the first 15 minutes of flocculation. The residue turbidity seems to differ about 30 % at 15 minutes, but only 10 % after 60 min. According to Hedberg (1969, p. 48) the flocculation velocity is proportional to the velocity gradient G, which depend on the power input and the absolute viscosity of the water. The absolute viscosity is affected by water temperature, and increase with lower temperatures. This result in a higher flocculation velocity in warmer water temperatures compared to colder water. The flocculation velocity is 15 % higher at 15 °C compared to 5 °C.
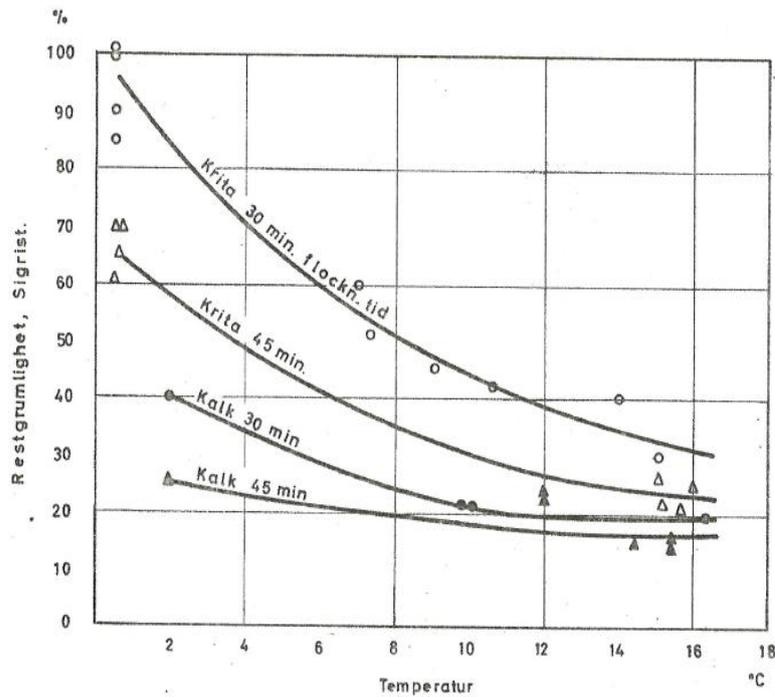
Figure 2.8 Residual turbidity related to the water temperature (Hedberg, 1969, p. 49). Restgrumlighet = Residual turbidity, Krita = Calcium carbonate, Kalk = Calcium oxide, Temperatur = Temperature
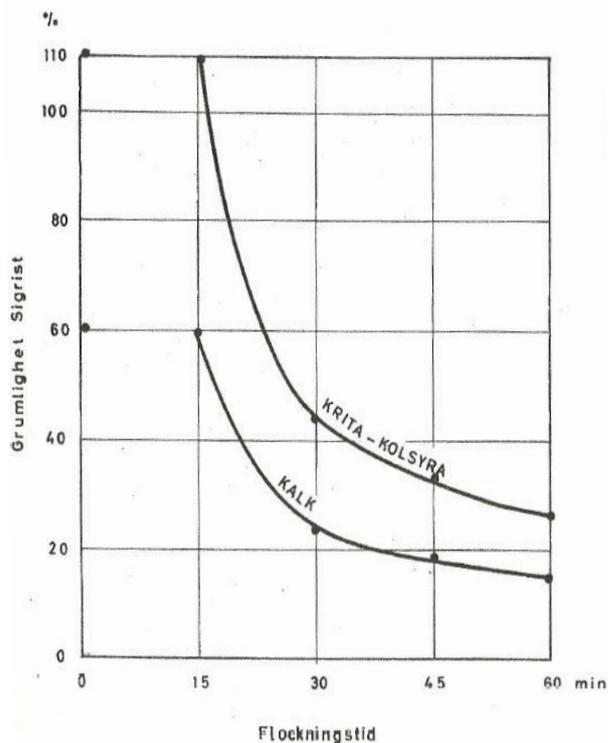
Figure 2.9 The relation between residual turbidity and detention time for flocculation for calcium carbonate and calcium oxide (Hedberg, 1969, p. 52). Grumlighet = Residual turbidity, Krita = Calcium carbonate, Kolsyra = Carbonic acid, Kalk = Lime, Flocklingstid = Flocculation time

3 Prerequisites

The water treatment plants in this study are located in cities in the southern part of Sweden (Figure 3.1). The facilities in Kristinehamn and Lerum are located outside the respective city and use lake water as raw water sources, while the water treatment plant in Karlskrona lies in the middle of the city and uses a river as raw water supply. Each treatment plant is described further in Sections 3.3 to 3.5.

The facility in Kristinehamn produces an average of 6 600 m^3 drinking water per day, Lerum about 6 500 m^3 per day and Karlskrona supply its inhabitants with 13 000 m^3 drinking water per day.

Figure 3.1 Map of the south of Sweden including the locations for the involved water treatment plants.

The three water treatment plants have had a history of using calcium carbonate to increase alkalinity, carbon dioxide as pH alternant and polyaluminium hydroxide chloride (PAC) as chemical coagulant. During the winter between 2009 and 2010, Karlskrona and Kristinehamn have removed calcium carbonate from the treatment process while Lerum still uses it. High aluminium residue is the reason why Karlskrona and Kristinehamn have removed calcium carbonate from the treatment process and replaced it with sodium hydroxide (NaOH).

The chemical coagulation, flocculation, precipitation and filtration occur in continuous filters called DynaSand filters (Section 2.1.1). The treatment process before and after the DynaSand filters differs between the facilities. However, the DynaSand filters do not appear to cause high aluminium residue values, since full scale experiments (at 5 °C raw water in the autumn of 2009) in Karlskrona demonstrate that the filters functions as intended. The experiments include turbidity measurements at different levels in the DynaSand filters. It is evident that the turbidity gradually decreases from the bottom to the top of the filter bed.

The climate varies slightly between locations of the water treatment plants. According to SMHI (a) (2009) Kristinehamn has the lowest mean temperature per year and the most number of days when the ground is snow-covered (SMHI (b), 2009). Lerum has the highest total annual mean precipitation (SMHI (c), 2009) and the least number of days with snow-cover. In Table 3.1 more precise numbers are presented for each city. In Sections 3.3.2 and 3.4.2 detailed temperature and precipitation information is presented for January 2008 to April 2010.

Table 3.1 Mean values for the normal period 1961-1990 (SMHI (a), 2009), (SMHI (b), 2009), (SMHI (c), 2009).

Water treatment plant	Annual mean temperature [°C]	Total annual mean precipitation [mm]	Mean number of days with snow-cover [days]
Karlskrona	7	500	50 days
Kristinehamn	6	600	75 days
Lerum	7	700	25 days

In Section 2.1, it is stated that the temperature and precipitation affect the properties of the raw water and thereby the treatment procedures regarding the type and dose of treatment chemicals. An important factor that affects the raw water composition is the flow of water. Karlskrona experience variations in raw water quality, depending on the time of the year. Such large variations are not to be found in the lakes of Kristinehamn and Lerum, mainly since the retention time of the water are much longer in lakes than in rivers. In Sections 3.3.2 and 3.4.2 the raw water properties for Karlskrona and Kristinehamn are displayed in diagrams. Lerum lack satisfactory raw water data and treatment operation data, hence, it is not presented.

3.1 Drinking water regulations

Drinking water treatment in Sweden is regulated by regulations given by the Swedish National Food Administration. The regulations are called SLVFS 2001:30 and contain limit values for chemical substances and microbial parameters in the drinking water. The regulations apply on drinking water distributed from water treatment plants as well as at the consumers tap. In this study, the main parameters of interest are aluminium and alkalinity.

The limit value for aluminium is 0.100 mg per litre of water. At this level, the water is said to be "suitable but with a remark". Drinking water containing aluminium values above 0.100 mg/l are not recommended to distribute. (Swedish National Food Administration, 2001)

Alkalinity, which is affected by the addition of calcium carbonate and carbon dioxide, has no limit values. However, values of 30 mg of hydrogen carbonate per litre (mg HCO_3^- per litre is a measure of alkalinity) are considered low since such levels may result in corrosion of pipes in the distribution net (Swedish Environmental Protection Agency, 2009).

Total organic carbon (TOC) has not been given a specific limit by the SLVFS 2001:30. However, TOC concentration should be as low as possible since it is a measurement of humic substances in water.

3.2 Chemicals in this study

In this study one type of calcium carbonate is used in combination with carbon dioxide. For chemical precipitation of humic substances, two types of PAC are used for colloid coagulation and flocculation. In Sections 2.2 and 2.3 the mechanics of calcium carbonate dissolution rate and chemical precipitation is presented.

3.2.1 Calcium carbonate

Calcium carbonate is a sedimentary rock which is widespread around the globe (Göthe & Israelsson, 1992, p. 3). Numerous calcium carbonate deposits originate from the remains of shells and skeletons of prehistoric sea life. The properties, such as the colour, density and crystal morphology, of calcium carbonate depend on activities that occur both before and after burial. Before burial, influence of waves and water current are critical for the formation whereas temperature, pressure and tectonic activity are decisive after burial (Cullio, 1996, p. 24).

In most commercial calcium carbonate products, calcite ($CaCO_3$) is the main or sole constituent. Calcite contain approximately 39 % calcium. Calcite is a mineral that has the following typical values:

- Refractive Index: 1.66-1.74
- Specific gravity: 2.71
- Mohs Hardness: 3 (Cullio, 1996, p. 24)
- pH: 9 – 9.7 (Göthe & Israelsson, 1992, p. 3)

Karlskrona, Kristinehamn and Lerum water treatment plants all use the calcium carbonate product Mikrostevns. It is a product that is delivered from Stevns Kridtbrud in Denmark (see product information in appendix A1). The most important properties of Mikrostevns are presented in Table 3.2.

Table 3.2 The most important properties of Mikrostevns according to product information (Appendix A1).

Description	Mikrostevns	Unit
Carbonate ($CaCO_3 + MgCO_3$)	98.8	%
$CaCO_3$	97.9	%
SiO_2	0.4	%
Fe_2O_3	0.04	%
HCl insoluble	0.6	%
Residue on a 45 μm sieve (ISO 787/7)	2	ppm
Top cut (d98%)	20	μm
Mean particle size (d50%)	2.3	μm
Particles < 2 μm	43	%
Specific surface area BET (ISO 9277)	2.2	m^2/g

3.2.2 Chemical coagulants

In this study two different precipitation chemicals have been used as chemical coagulants for colloids in the raw water. These are two types of PAC. Although they have many similarities and areas of applications, they differ slightly in composition of certain key parameters. The two chemicals are called Ekoflock 70 and Ekoflock 91, and are manufactured by the chemical company Eka Chemicals AB in Sweden.

Ekoflock 70 is being used as primary coagulant at Lerum and Karlskrona drinking water plants, while Kristinehamn use Ekoflock 91. Both contain a lot of aluminium, have low pH values and are yellowish liquids with a mild odour. In Table 3.3 the most important properties of the chemicals are compared. Ekoflock 91 contains higher amounts of aluminium and chloride, and has a higher density and viscosity. Fact sheets for Ekoflock 70 and Ekoflock 91 are found in appendix A2 and A3.

Table 3.3 Properties of the precipitation chemicals used in this study. (Appendices A2 and A3)

Product name	Ekoflock 70	Ekoflock 91
Appearance	Yellowish liquid with a mild odour	Yellowish liquid with a mild odour
pH	2.1 ± 0.3	< 2
Density	$1\ 265 \pm 25$ kg/m^3	$1\ 375 \pm 25$ kg/m^3
Viscosity	41 mPas (-20°C) <10 mPas (20°C)	145 mPas (-20°C) 42 mPas (20°C)
Aluminium	7.0 ± 0.3 weight %	9.0 ± 0.3 weight %
Chloride	14.5 ± 2.0 weight %	19.0 ± 1.5 weight %
Sulphate	<1.0 weight %	<1.0 weight %

3.3 Karlskrona water treatment plant

Approximately 43 300 consumers as well as several industries are connected to the water treatment plant in Karlskrona. The mean drinking water production is about 549 m^3 per hour (Karlskrona kommun, 2010).

Karlskrona uses a nearby river called Lyckebyån as raw water source. The quality of the water from the river varies considerably, depending on season. These variations are described in detail in Section 3.3.2.

The treatment process, which includes Mikrostevns as calcium carbonate and Ekoflock 70 as precipitation chemical, are described in a simplified way in Section 3.3.1. A complete process chart is presented in appendix B2.

During the years, several full scale trials with different chemicals and dosing points have been performed at Karlskrona water treatment plant. Some of these trials are described in Section 3.3.3.

3.3.1 Treatment process
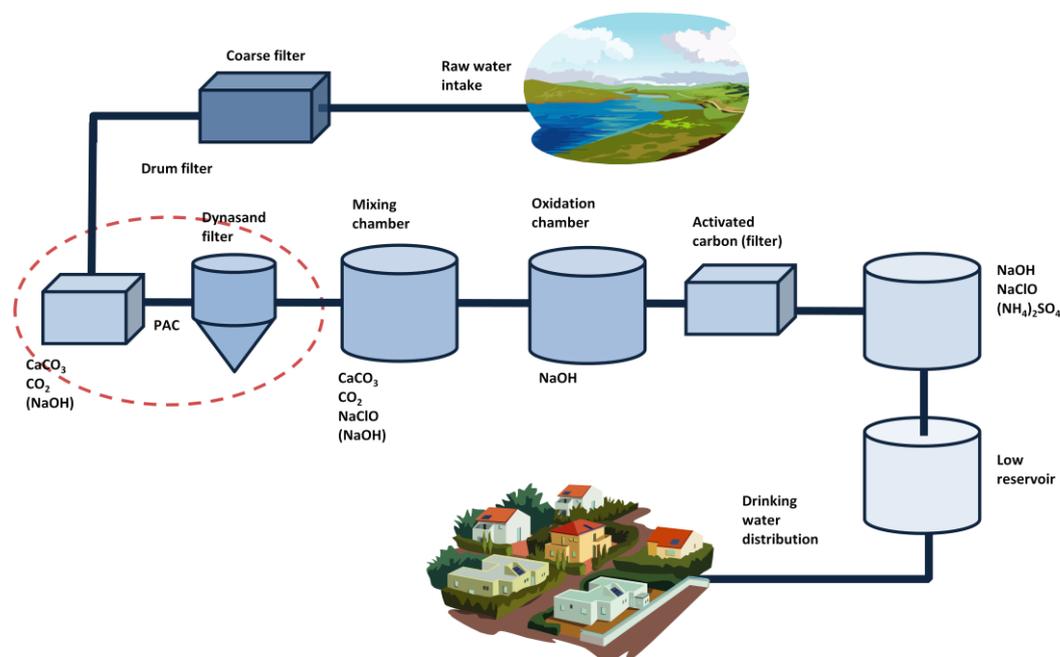
Figure 3.2 Simplified process chart of Karlskrona water treatment plant. Appendix B2 contains a complete process chart.

The treatment process of Karlskrona water treatment plant is schematically presented in Figure 3.2 and frequently discussed in this section. The area of investigation is marked with a red dashed circle and includes the treatment area close to the DynaSand filters.

The river Lyckebyån supply Karlskrona water treatment plant with raw water. The plant is located in the middle of Karlskrona and the raw water intake is approximately 150 m from the plant itself. At the intake the raw water first passes a coarse filter before it enters a drum filter, which is much finer and located in the plant. The water then enters a pool in which 30 mg calcium carbonate (Mikrostevns) is added per litre

water. The calcium carbonate is first mixed into a slurry in order to dissolve more easily in the water.

Carbon dioxide (CO_2) is added in order to dissolve the calcium carbonate and to achieve a suitable pH for the chemical precipitation process, which occur in the DynaSand filters. It is also possible to add sodium hydroxide (NaOH) at this stage. Calcium carbonate is added in order to increase alkalinity before the chemical precipitation process, and sodium hydroxide is added to provide a stable pH during the chemical precipitation. The carbon dioxide is added less than 10 seconds after the addition of calcium carbonate (Karlskrona kommun, 2010).

The detention time in the alkalinity adjustment tank is approximately 45 minutes before the precipitation chemical (ca 60 ml/l Ekoflock 70) is added to the water and pumped into the continuous DynaSand filters. There are 40 filters divided into five lines, each line has its own dosing point for precipitation chemicals. Coagulation, flocculation, precipitation and filtration takes place in the DynaSand filters according to the principle described in Section 2.1.1. In order to remove as much organic matter, iron and manganese as possible, the detention time in the DynaSand filters is about 60 minutes.

The next treatment step is a mixing chamber where calcium carbonate, carbon dioxide and sodium hypochlorite (NaClO) are mixed in order to oxidize remaining manganese in two oxidation chambers. To increase the oxidation it is possible to add sodium hydroxide. The oxidation chambers are followed by eleven activated carbon filters in which taste, odour and possible manganese particles are removed. Before the water is distributed to the consumers as drinking water, the water is adjusted to a desired pH and hardness, and disinfected by ammonium sulphate.

3.3.2 Raw water and treatment operation data

Karlskrona has an annual air mean temperature of 7 °C, totally 500 mm of precipitation per year and in general 50 days of snow-cover per year.

Between December 2009 and February 2010 Karlskrona experienced monthly air mean temperatures below the normal monthly mean values (Figure 3.3). Because of the cold air temperatures, the precipitation that came was snow. The precipitation, which is plotted in Figure 3.4, is fairly normal.
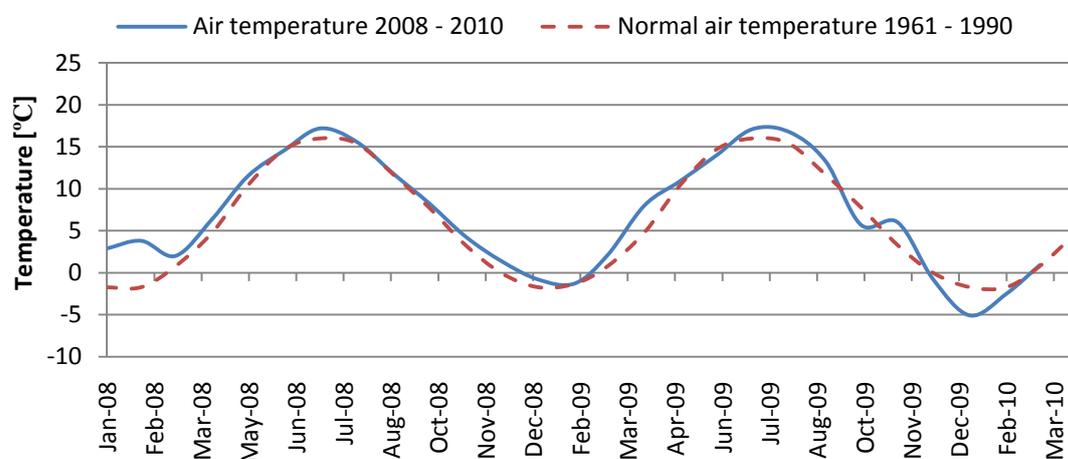
Figure 3.3 Normal and mean air temperature in Karlskrona (SMHI (a), 2009).
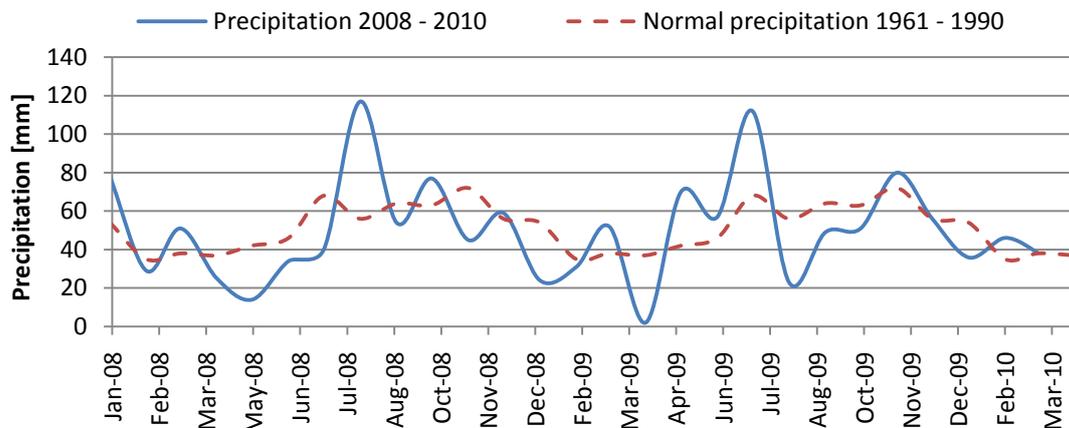
Figure 3.4 Normal and mean precipitation in Karlskrona (SMHI (c), 2009).

The cold air temperatures led to low and very stagnant water temperatures in the river Lyckebyån during the winter between 2009 and 2010 compared to the milder winter of 2008-2009 (Figure 3.5).
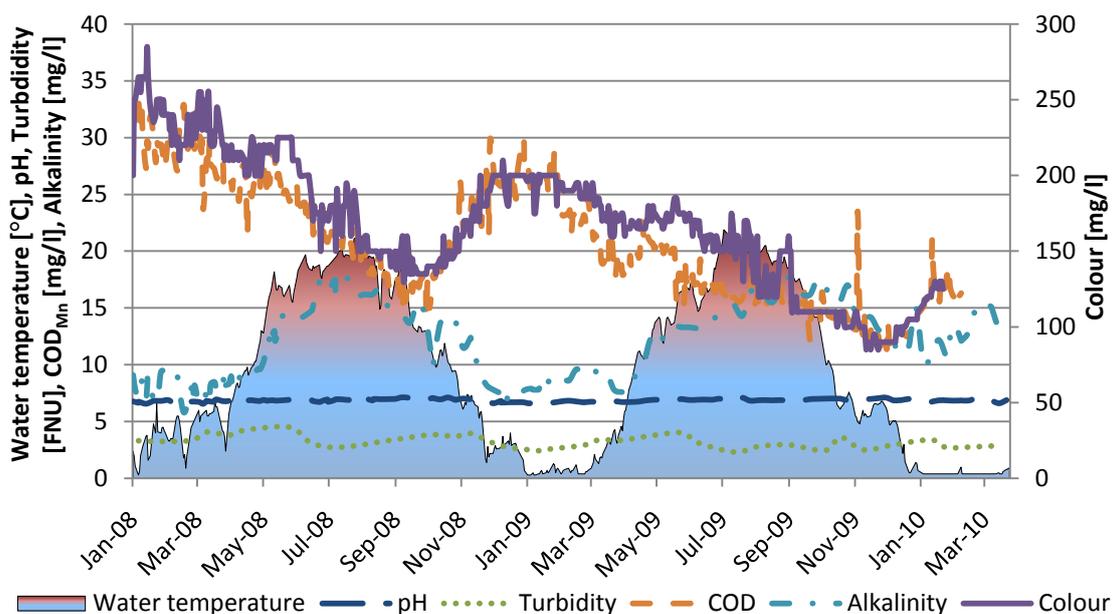
Figure 3.5 Variations in raw water from Karlskrona between January 2008 and April 2010.

In Lyckebyån, parameters such as colour, chemical oxygen demand (COD), alkalinity and water temperature generally varies depending on season (Figure 3.5). The parameters are exemplified in detail in Figure 3.6 where colour values are plotted against water temperatures. It is evident that colour, measured during the first half of the year, are higher compared to those measured during the second half, for the same water temperatures.
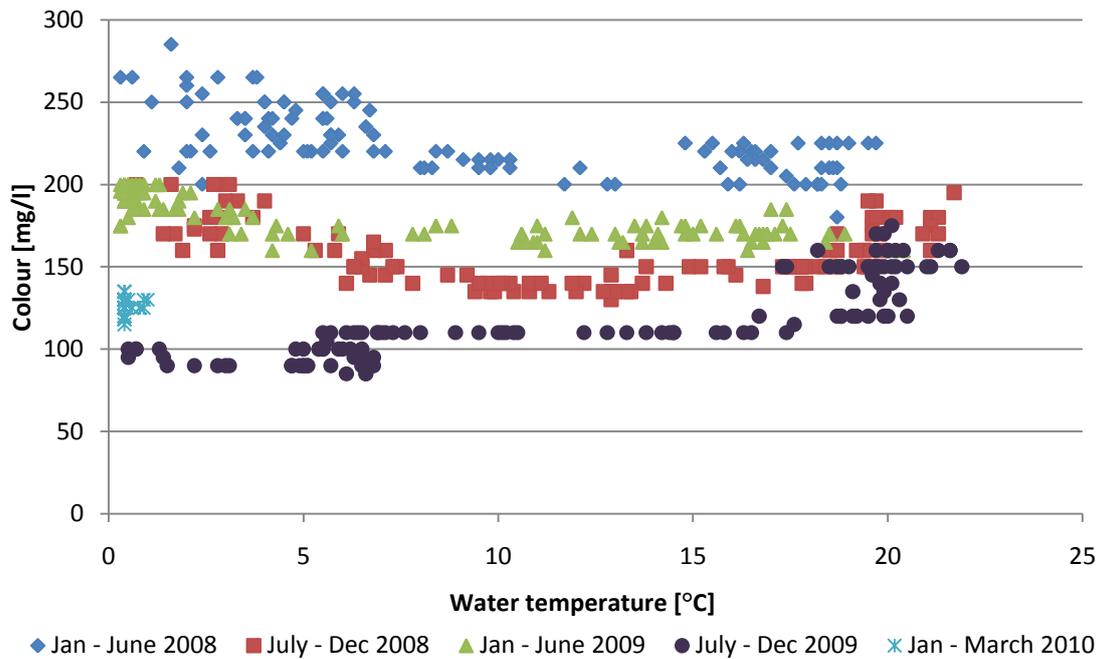
Figure 3.6 Seasonal variation in colour of raw water from Lyckebyån.

The colour variations could partly be explained by precipitation and temperature, but also from flow in the river and growth of humic substances. The winter between 2009 and 2010 were exceptionally cold and snowy, resulting in stagnant water conditions with less amount of surface run off in the drainage area. As a result of this, raw water parameters such as colour and turbidity were lower than other years and alkalinity resembled values normally observed summertime (Figure 3.5). Looking at iron and manganese content in Figure 3.7, iron seems to be fairly constant throughout the year while manganese decreases as water temperatures decline.
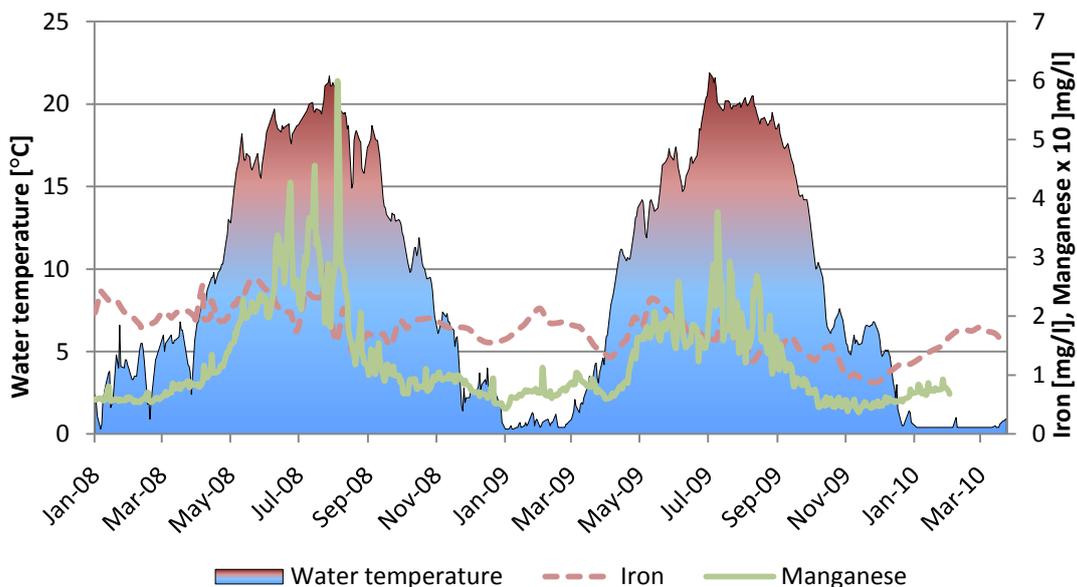
Figure 3.7 Variations in raw water from Karlskrona between January 2008 and April 2010.

In Figure 3.8 the aluminium residue measured after the DynaSand filters are presented. However, from the beginning of November 2008 the residue levels are measured further on in the process, resulting in non-representative and comparable values in this study. From Figure 3.8 it is evident that the aluminium residue levels increase as the water temperature decrease.
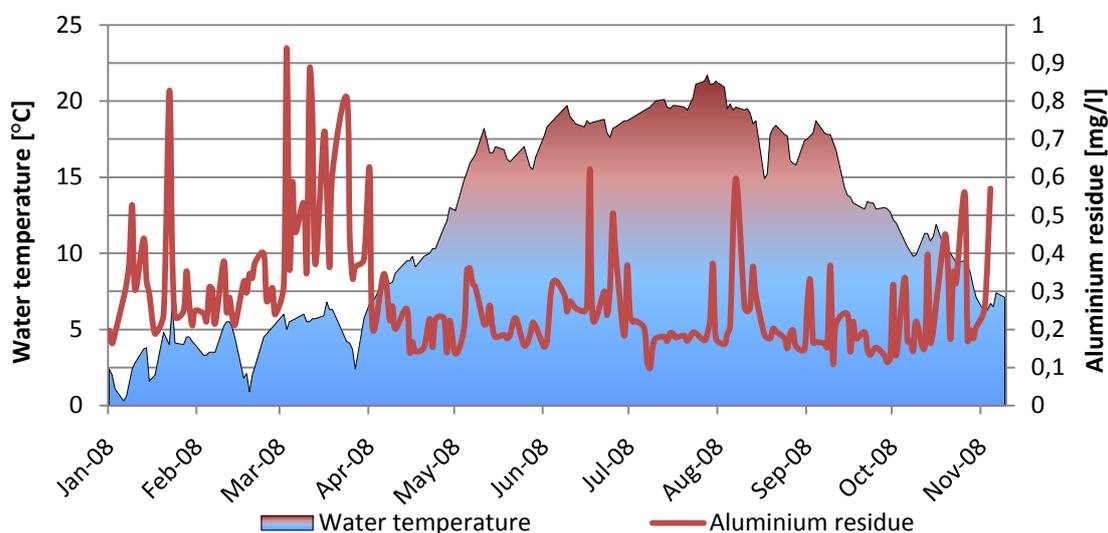
Figure 3.8 Treatment operation data from January 2008 to November 2008 in Karlskrona water treatment plant.

3.3.3   Full scale trials

In Karlskrona, full scale trials and pilot trials have been performed in order to understand the problem with high aluminium residue after the DynaSand filters. Differences in raw water composition have been analyzed, but low water temperature is the only clear correlation to the treatment result. Karlskrona speculates that cold water is the most likely trigger. Karlskrona also suspects that longer detention time in the DynaSand filters may have positive effects on the filtering process. However, moving the dosing point of precipitation chemical to an earlier stage in the process has showed no improvements to the problem. Changes in precipitation pH, different precipitation chemicals and chemical doses have been carried out without obtaining any improvements in the function of the DynaSand filters.

Figure 3.9 illustrates pilot trials, where double folded filters have been used to simulate filtering through DynaSand filters. By dosing between 90 and 130 ml/m^3 of the precipitation chemical Ekoflock 70, a curve for aluminium residue is plotted. It is clear that a higher dose of Ekoflock 70 results in a lower aluminium residue. This correlation is discussed further in Section 2.3. The pH is kept constant around 6, as well as colour around 9 mg Pt/l.
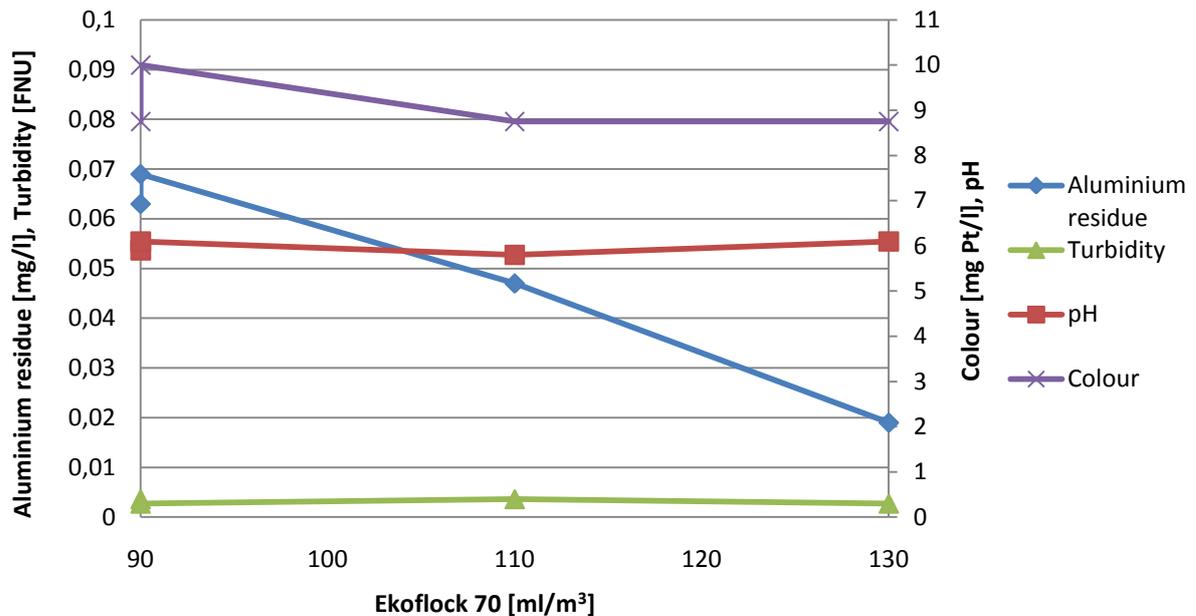
Figure 3.9 Aluminium residue is plotted against different Ekoflock 70 doses in December 2008.

By changing the precipitation pH, as in Figure 3.10, and keeping the dose of Ekoflock 70 constant at 110 ml/m^3, will result in a lowering of aluminium residue after the DynaSand filters as the pH reaches the optimum precipitation pH around 6.0 – 6.5. In Section 2.3, optimum precipitation pH has been discussed. The colour and turbidity is fairly constant regardless of Ekoflock 70 dose. Figure 3.10 shows four separate tests conducted in December 2008.
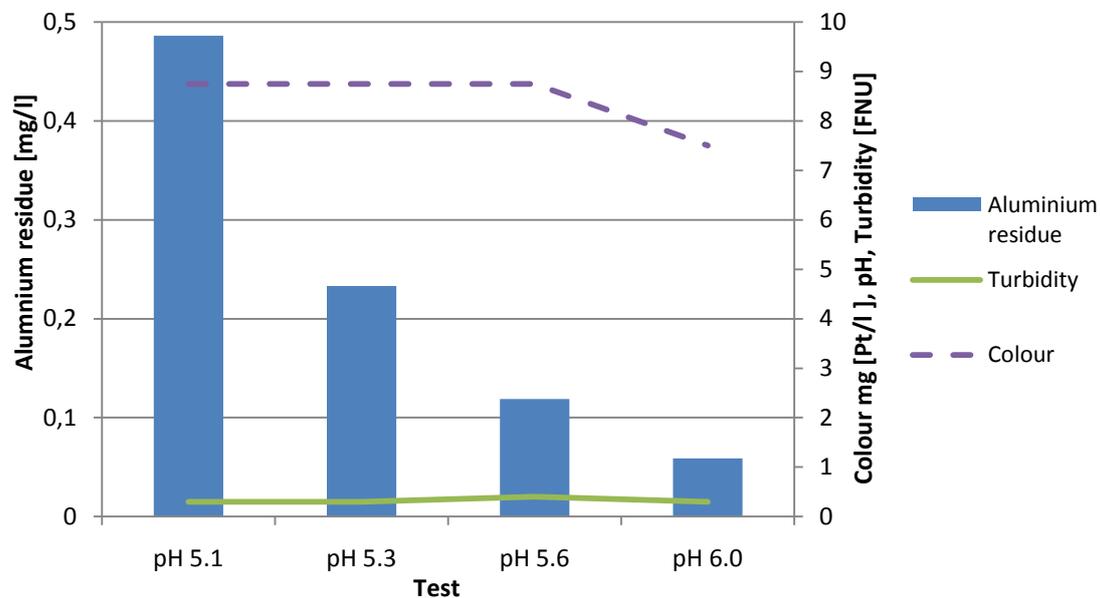
Figure 3.10 Aluminium residue plotted after dosing 110 ml/m^3 Ekoflock 70 at different pH in pilot trials in December 2008. See Figure 3.5 for raw water details in Karlskrona for December 2008.

3.4 Kristinehamn water treatment plant

The water treatment plant in Kristinehamn is located a few kilometres north of Kristinehamn in Sandköping, close to Lake Bergsjön. Approximately 20 500 consumers in Kristinehamn and surrounding neighbourhoods are connected to the water treatment plant in Kristinehamn. The water treatment plant produces about 6 600 m^3 drinking water per day which corresponds to 275 m^3 per hour.

Raw water is pumped from the nearby lake and treated at the plant and through ground infiltration. The raw water properties are described in detail in Section 3.4.2.

Several full scale trials with different dosing points and concentrations of chemicals have been performed. Some of these trials are summarized in Section 3.4.3.

3.4.1   Treatment process
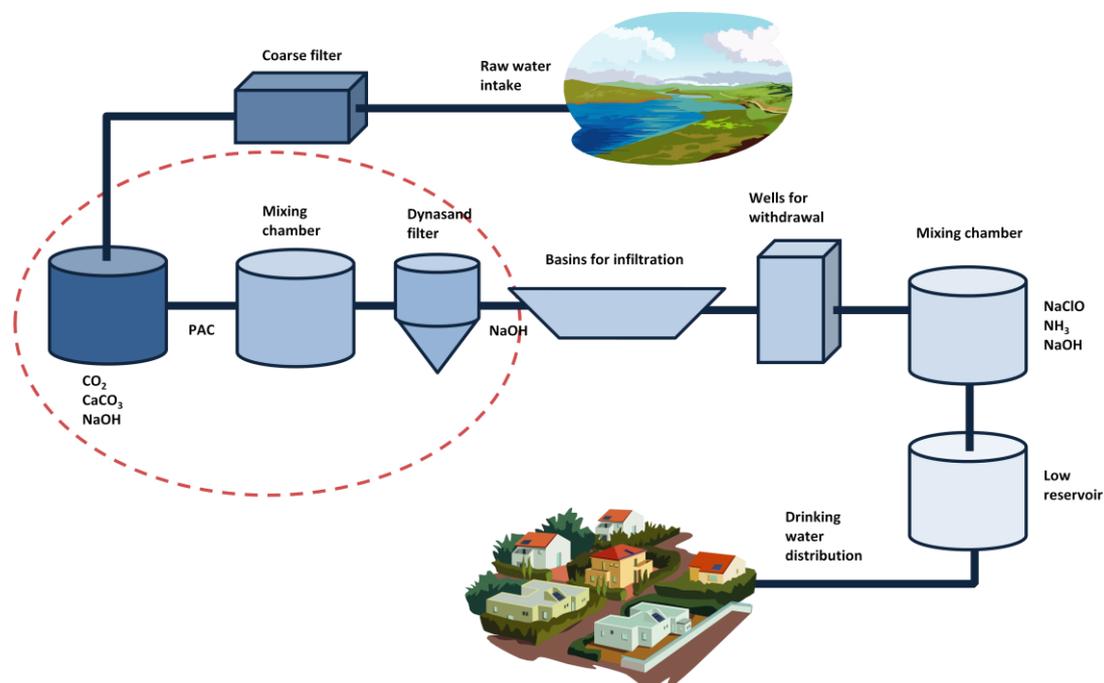
Figure 3.11 Simplified process chart of Sandköping water treatment plant in Kristinehamn. Appendix B3 contains a complete process chart.

The area of investigation for the tests rounds in Sections 4 and 5 is marked with a red dashed circle in Figure 3.11 and considers the area close to the DynaSand filters. All detention times are given by Kristinehamn water treatment plant and a detailed description of Kristinehamn water treatment plant process chart can be found in appendix B3.

Water is pumped from Lake Bergsjön and passes coarse filters and drum filters before it enters the treatment plant. 30 mg calcium carbonate (Mikrostevns) per litre water is added after first being mixed into a slurry. Carbon dioxide is added in order to solve calcium carbonate and to achieve a suitable pH for the chemical precipitation process. Calcium carbonate and carbon dioxide is dosed in the incoming raw water pipe, with 0.5 seconds in between. Sodium hydroxide, which is added in order to increase the pH of the water, is applied approximately 20 seconds after the carbonic acid. Roughly 15 seconds after sodium hydroxide is mixed in the water, the precipitation chemical

(ca 60 mg/l Ekoflock 91) is added. The water is then pumped into the DynaSand filters. There are twelve filters divided into two rows. In the DynaSand filters, coagulation, flocculation, precipitation and filtration take place according to the principle illustrated in Section 2.1.1. The detention time in the DynaSand filters is about 15 minutes.

Sodium hydroxide is then added before the water is transported to the infiltration basins. Infiltrated water can then be pumped back to the treatment plant. The next treatment step is a mixing chamber where sodium hypochlorite, ammonia and sodium hydroxide are mixed. At this point, the water is disinfected and adjusted to desired pH, alkalinity and hardness before the water is distributed to the consumers.

3.4.2 Raw water and treatment operation data

The annual mean temperature in Kristinehamn is 6 °C and the total annual mean precipitation is 600 mm. The mean number of days with snow-cover is 75 days or approximately 20 % of the year. For a normal year, the precipitation is distributed quite evenly all through the year as can be seen in Figure 3.12. From Figure 3.12, Figure 3.13 and Figure 3.16 it is clear that the winter between 2007 and 2008 was warm and damp, the winter between 2008 and 2009 was normal while the winter between 2009 and 2010 was dry and cold. Especially the winter between 2009 and 2010 was colder than normal in December and February.
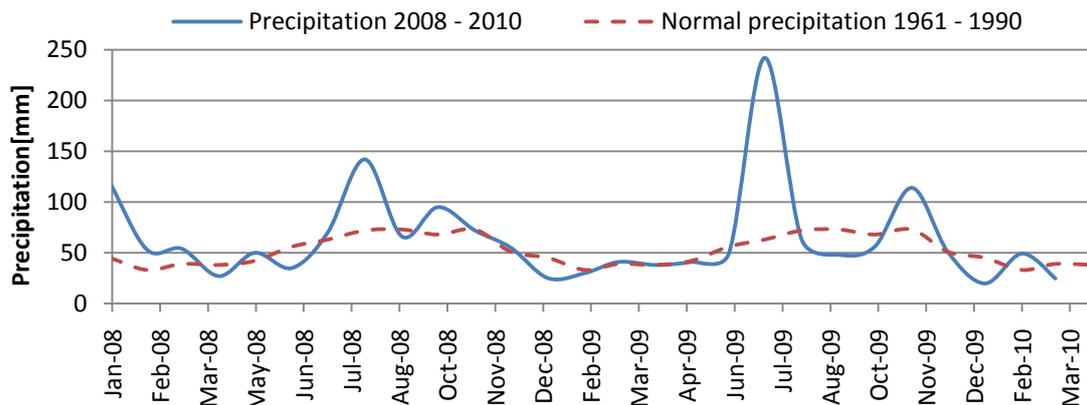
Figure 3.12 Normal and mean precipitation in Kristinehamn (SMHI (c), 2009).
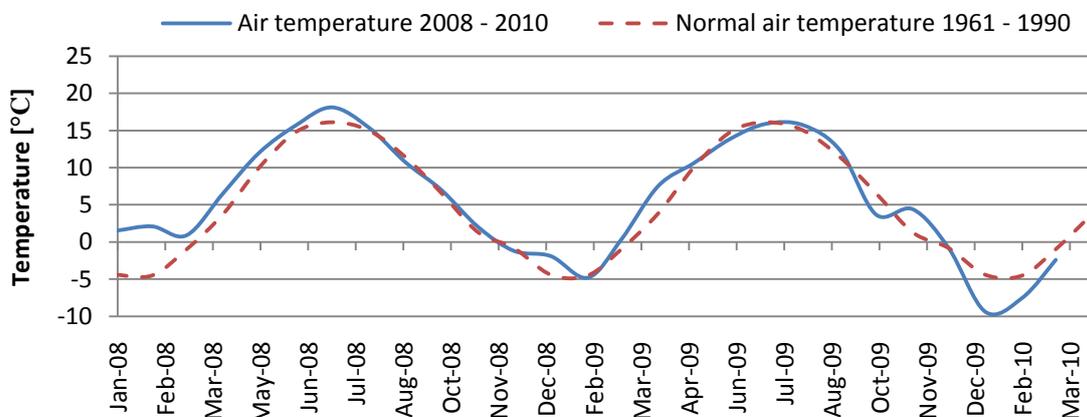
Figure 3.13 Normal and mean air temperature in Kristinehamn (SMHI (a), 2009).

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35

In Figure 3.14 and Figure 3.15 the climate's effects on the raw water properties in Kristinehamn are presented. From the figures it is evident that iron and aluminium increase during the winters, especially at the turn of 2009. This is probably caused by greater influence of ground water leakage into Lake Bergsjön due to decreased precipitation. Parameters such as colour, COD and turbidity vary throughout the year, although there is not a clear cycle as it is for Karlskrona. This is due to the fact that Kristinehamn collects raw water from a lake, which can be more stable regarding raw water conditions.
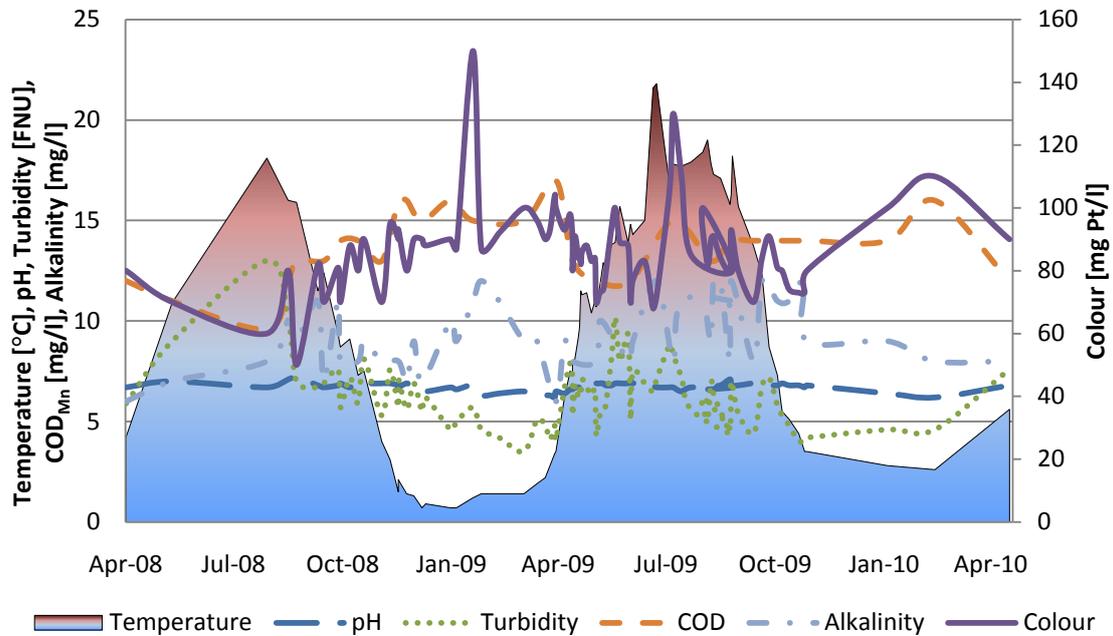
Figure 3.14 Variations in raw water from Kristinehamn between April 2008 and April 2010.
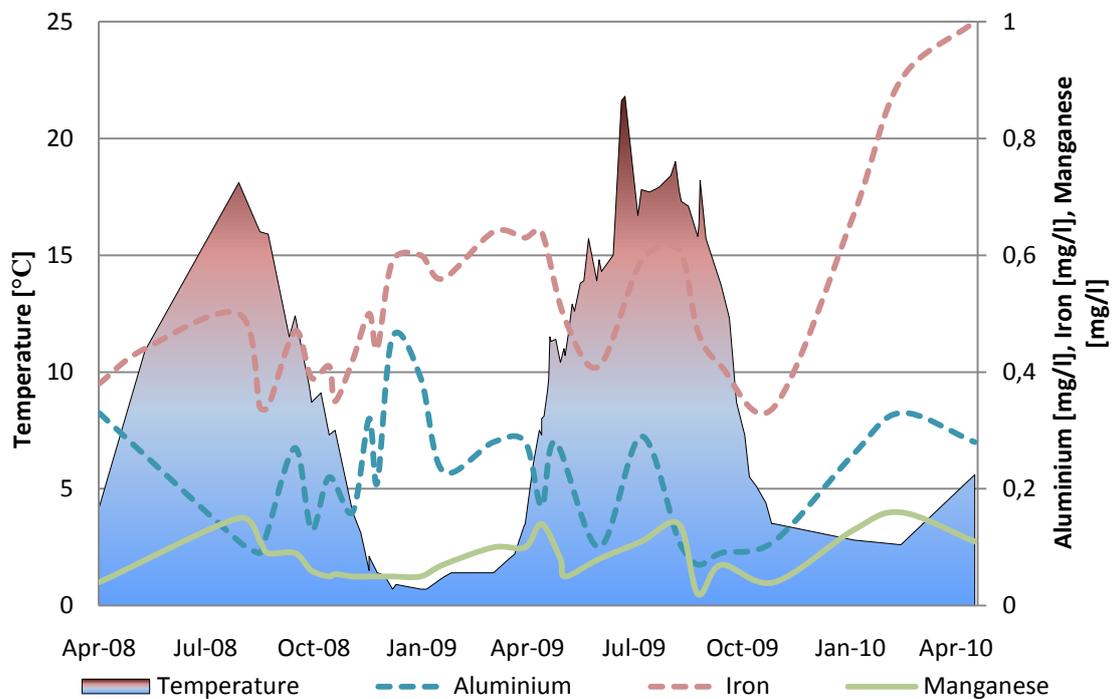
Figure 3.15 Variations in raw water from Kristinehamn between April 2008 and April 2010.

Reviewing the treatment operation data in Figure 3.16, aluminium residue increase substantially as the temperature decrease, although the dose of chemical coagulant and flocculation pH are kept fairly constant. When calcium carbonate is introduced to the treatment in December 2008, the aluminium residue level decrease below the limit value of 0.100 mg/l until January 2009 where aluminium residue values increase again. The sudden peak in colour values the same month is the probable explanation to the increased aluminium residue levels (Figure 3.14). Mean air temperatures during January 2009 were above the normal, which probably resulted in snow melting and increased surface run off in the surroundings of Lake Bergsjön.
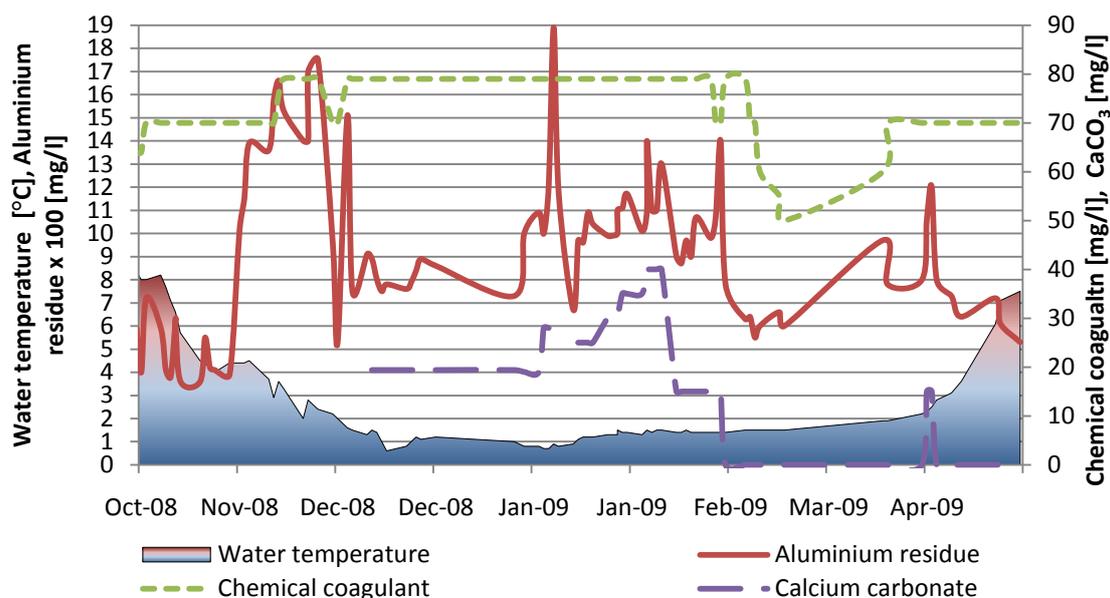
Figure 3.16 Treatment operation data from October 2009 to May 2009 in Kristinehamn water treatment plant.

3.4.3 Full scale trials

During 2009, Kristinehamn water treatment plant performed a series of dosage modifications that were closely monitored. A selection of these tests has been organized into a block diagram as presented in Figure 3.17. The values are presented based on aluminium residue and alkalinity properties. The drinking water regulations, presented in Section 3.1, have limit and guideline values for these particular parameters. In the first column (1) the alkalinity is well over 30 mg/l which is considered adequate, in the second column (2) the alkalinity is merely close to 30 mg/l and in the third column (3) the alkalinity is less than 30 mg/l. In the first row (A) the aluminium residue is beneath 0.1 mg/l which is the recommended limit for drinking water. In the second row (B), aluminium residue is 0.1 mg/l or just above it and in the third row (C) the aluminium residue is well over 0.1 mg/l.

The values that are presented are mean values for incoming raw water, including temperature (Temp), turbidity (Turb. 1), alkalinity (Alk. 1) and colour (Colour 1), as well as dosage of calcium carbonate ($CaCO_3$), carbon dioxide (CO_2) and chemical coagulant (PAC). In addition, corresponding mean values after DynaSand filtration are also presented and includes aluminium residue (Al residue), turbidity (Turb. 2), alkalinity (Alk. 2) and colour (Colour 2).

	1C		After DynaSand	
	Raw water		filtration	
Aluminium residue over 0.1 mg/l	Temp:	1.38	Al residue:	0.12
	Turb. 1:	4.67	Turb. 2:	0.28
	Alk. 1:	12.33	Alk. 2:	49.33
	Colour 1:	86.83	Colour 2:	6.33
	$CaCO_3$:	36.67		
	CO_2:	34.17		
	PAC:	79.00		

	2C		After DynaSand	
	Raw water		filtration	
	Temp:	0.80	Al residue:	0.12
	Turb. 1:	4.80	Turb. 2:	0.29
	Alk. 1:	9.00	Alk. 2:	35.00
	Colour 1:	87.00	Colour 2:	6.00
	$CaCO_3$:	32.50		
	CO_2:	25.00		
	PAC:	79.00		

	3C		After DynaSand	
	Raw water		filtration	
	Temp:	1.33	Al residue:	0.12
	Turb. 1:	4.65	Turb. 2:	0.25
	Alk. 1:	10.00	Alk. 2:	24.00
	Colour 1:	89.00	Colour 2:	4.00
	$CaCO_3$:	19.25		
	CO_2:	18.00		
	PAC:	74.50		

	1B		After DynaSand	
	Raw water		filtration	
Aluminium residue close to 0.1 mg/l	Temp:	2.60	Al residue:	0.10
	Turb. 1:	4.94	Turb. 2:	0.26
	Alk. 1:	12.00	Alk. 2:	41.78
	Colour 1:	84.33	Colour 2:	6.00
	$CaCO_3$:	31.62		
	CO_2:	27.89		
	PAC:	76.00		

	2B		After DynaSand	
	Raw water		filtration	
	Temp:	3.57	Al residue:	0.10
	Turb. 1:	4.88	Turb. 2:	0.21
	Alk. 1:	10.50	Alk. 2:	28.17
	Colour 1:	84.00	Colour2:	5.33
	$CaCO_3$:	16.83		
	CO_2:	15.17		
	PAC:	76.00		

	3B		After DynaSand	
	Raw water		filtration	
	Temp:	1.70	Al residue:	0.10
	Turb. 1:	4.53	Turb. 2:	0.21
	Alk. 1:	12.00	Alk. 2:	25.00
	Colour 1:	85.33	Colour 2:	4.67
	$CaCO_3$:	15.00		
	CO_2:	10.00		
	PAC:	76.00		

	1A		After DynaSand	
	Raw water		filtration	
Aluminium residue less than 0.1 mg/l	Temp:	15.76	Al residue:	0.07
	Turb. 1:	6.06	Turb. 2:	0.19
	Alk. 1:	11.67	Alk. 2:	42.08
	Colour 1:	84.17	Colour 2:	5.37
	$CaCO_3$:	35.00		
	CO_2:	26.25		
	PAC:	70.00		
	Alkalinity over 30 mg/l			

	2A		After DynaSand	
	Raw water		filtration	
	Temp:	14.16	Al residue:	0.06
	Turb. 1:	6.70	Turb. 2:	0.15
	Alk. 1:	9.00	Alk. 2:	30.38
	Colour 1:	81.00	Colour 2:	3.88
	$CaCO_3$:	24.25		
	CO_2:	17.75		
	PAC:	71.13		
	Alkalinity close to 30 mg/l			

	3A		After DynaSand	
	Raw water		filtration	
	Temp:	9.09	Al residue:	0.06
	Turb. 1:	6.07	Turb. 2:	0.15
	Alk. 1:	10.93	Alk. 2:	17.64
	Colour 1:	84.21	Colour 2:	3.25
	$CaCO_3$:	9.54		
	CO_2:	6.79		
	PAC:	69.57		
	Alkalinity less than 30 mg/l			

Figure 3.17 The green colour of the diagram represent regions where aluminium residue is less than 0.100 mg/l and where alkalinity is sufficient. Orange colour represent aluminium residue values close to 0.100 mg/l and almost sufficient alkalinity, whereas red colour represent aluminium residue values above 0.100 mg/l and insufficient alkalinity. Temperature is presented in °C, turbidity, alkalinity, CO_2, $CaCO_3$, Al residue in mg/l and colour in mg/l Pt.

It should be noted that the values presented in Figure 3.17 are mean values and simply meant to give an overview of the performed testes, rather than discuss the different modifications to the treatment dosage. In addition, plotting aluminium residue against alkalinity after DynaSand filtration is merely one possible combination. Part of the reason to why aluminium residue and alkalinity is chosen relates to the theories about calcium carbonate solubility affecting high aluminium residue. It may therefore appear strange that good colour reduction is found in 3C, which is supposed to be the least favourable block.

The diagram gives a clear indication that low temperature is mainly an issue for aluminium residue. It is also evident that the best result, regarding aluminium residue, is achieved for warmer water temperatures.

3.5 Lerum water treatment plant

The water treatment plant in Lerum is called Öxsjöverket, a name that originates from Lake Öxsjön which is one of the plant's raw water sources. The other source is Lake Stamsjön. Only raw water from Lake Öxsjön is analyzed.

Öxsjöverket produces approximately $6\,500$ m^3 drinking water per day to $20\,000$ consumers and industries in Lerum municipality.

The treatment process, which includes Mikrostevns as calcium carbonate and Ekoflock 70 as precipitation chemical, is described in a simplified way in Section 3.5.1. A complete process chart is presented in appendix B4.

During the 1990s, the water treatment plant in Lerum has been a place for full scale trials, where calcium carbonate has been used to increase hardness and alkalinity. Full scale trials are described in Section 3.5.2.

3.5.1   Treatment process
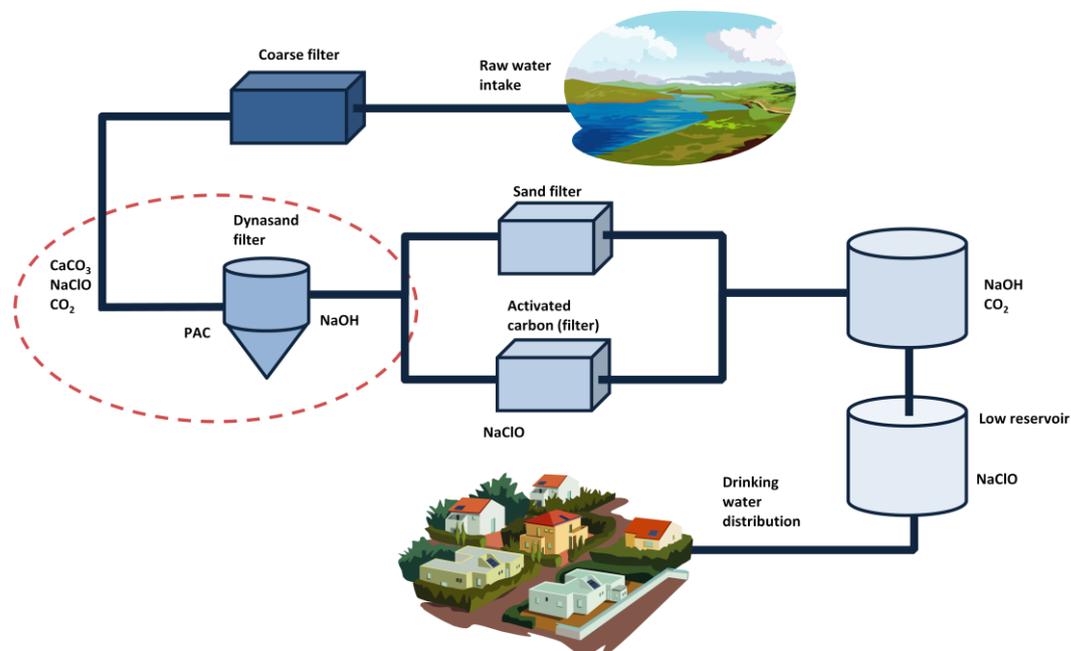
Figure 3.18 Simplified process chart of Öxsjöverket in Lerum. Appendix B4 contains a complete process chart.

Two pumping stations distribute raw water from each lake into the water treatment plant. Depending on the quality of the raw water, different proportions from each lake is mixed when the waters reach the plant. The water passes a coarse filter, which can be seen in Figure 3.18, before carbon dioxide and calcium carbonate (30 mg/l Mikrostevns) is added at the same dosing point directly to the incoming raw water pipe. After about 45 to 50 seconds the precipitation chemical (30 to 42 mg/l Ekoflock 70) is added. The dose depends on which raw water source that is used. As stated in Section 3.4.2, raw water from Lake Stamsjön generally has a lower quality and thereby requires a higher dose of precipitation chemicals.

Approximately one minute after dosing Ekoflock 70, the water reaches ten DynaSand filters. During a 30 minutes detention time, flocculation, coagulation, precipitation and filtration occur in the filters. 63 % of the filtrated water is pumped into nine rapid

activated carbon filters and 37 % of the water to eight slow sand filters. Before the water enters the filters, sodium hydroxide is added in order to increase pH. As disinfection chemical sodium hypochlorite can be dosed either on the incoming raw water pipe or in the low reservoir before the drinking water is pumped to the consumers.

3.5.2   Full scale trials

In 1995, Göthe & Israelsson published a full scale study of Öxsjöverket, where calcium carbonate was tested as an alternative to calcium hydroxide $(Ca(OH)_2)$. The trials started in the winter of 1993 and ended during the spring of 1994. The aims of the study were to investigate calcium carbonate solubility and the amount of unsolved calcium carbonate in order to determine the economical benefits of using calcium carbonate instead of hydrated lime.

Calcium carbonate (57 mg/l) of different types and fractions was dosed together with carbon dioxide directly to the incoming raw water pipe. 40 mg aluminium sulphate per liter was used as precipitation chemical. At twelve locations, between incoming raw water pipe and in a drinking water pipe on the distribution system, water samples were taken and analyzed in regards of e.g. amount of dissolved calcium and aluminium residue. In this summary of the full scale trials, only four of the locations before and after DynaSand filters are discussed. In Figure 3.19 point 1 is before any addition of chemical, point 2 after carbon dioxide, calcium carbonate and aluminium sulphate have been dosed and point 3 just before the DynaSand filters. Point 4 is just after the DynaSand filters. The detention time between point 1 and 2 are 60 seconds, 15 seconds between point 2 and 3 and 30 minutes in the DynaSand filters.
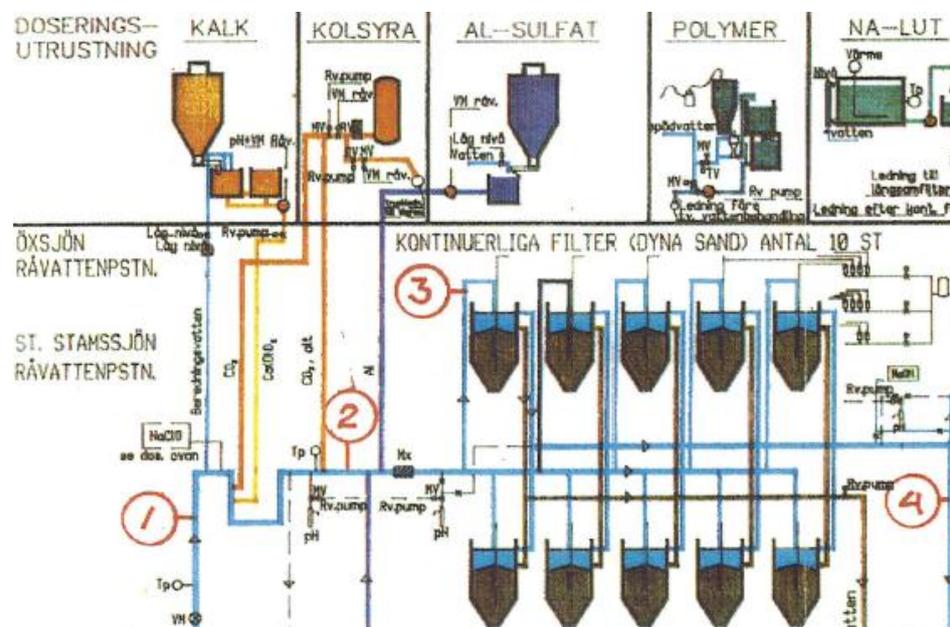
Figure 3.19 Selected parts of an old version of Öxsjöverket process chart. Circled numbers indicate four out of totally twelve locations were water samples were analyzed (Göthe & Israelsson, 1995).

In Table 3.4, variations in selected parameters, that were analyzed during the full scale trials, are presented for point 1 to 4 (Figure 3.19). Point 1 indicates the quality of raw water in the test. The raw water temperature as well as the quality of calcium carbonate that was used in the test is unknown. In point 2 there is a clear alkalinity and pH increase since a slurry of calcium carbonate is dosed. Point 3 indicates higher colour and turbidity and lower pH and alkalinity. These changes occur due to the addition of aluminium sulphate, which lowers pH and starts the coagulation and flocculation processes. In point 4, i.e. after the DynaSand filters, major decreases in colour, turbidity and COD occurs.

Table 3.4 Results in selected points from full scale tests in Öxsjöverket. The dose of calcium carbonate was 57 mg/l, which gives 17.1 mg calcium. Result data originate from Göthe & Israelsson (1995). Points 1 to 4 are marked in Figure 3.19.

Point	Colour mg/l	Turbidity FNU	COD_{Mn} (mg/l)	pH	Alkalinity HCO_3^- (mg/L)	Al residue mg/l	Ca in water	Ca solved	% solved
1	25	0.31	7	6.7	11	0.07	7	7	0,00
2	22	0.55	5	7.3	64	0.09	24	15.5	49.7
3	50	6.3	6	6.9	43	3.2	24.5	23	93.6
4	5	0.08	2	6.9	42	0.06	24	23.5	96.5

The solubility of calcium carbonate as well as aluminium residue is plotted in Figure 3.20. Immediately after point 1, the amount of dissolved calcium carbonate increases due to the addition of it. Since the amount of hydrogen carbonate (HCO_3^-) increases as calcium carbonate dissolves the alkalinity gradient follows the $CaCO_3$ until point 2 where aluminium sulphate is dosed. The aluminium sulphate lowers the pH of the water and reduces the alkalinity until the water reaches the DynaSand filters. During and after the coagulation, flocculation and precipitation have occurred in the filters, the aluminium residue levels decrease. Alkalinity, pH and solved calcium carbonate remain constant.
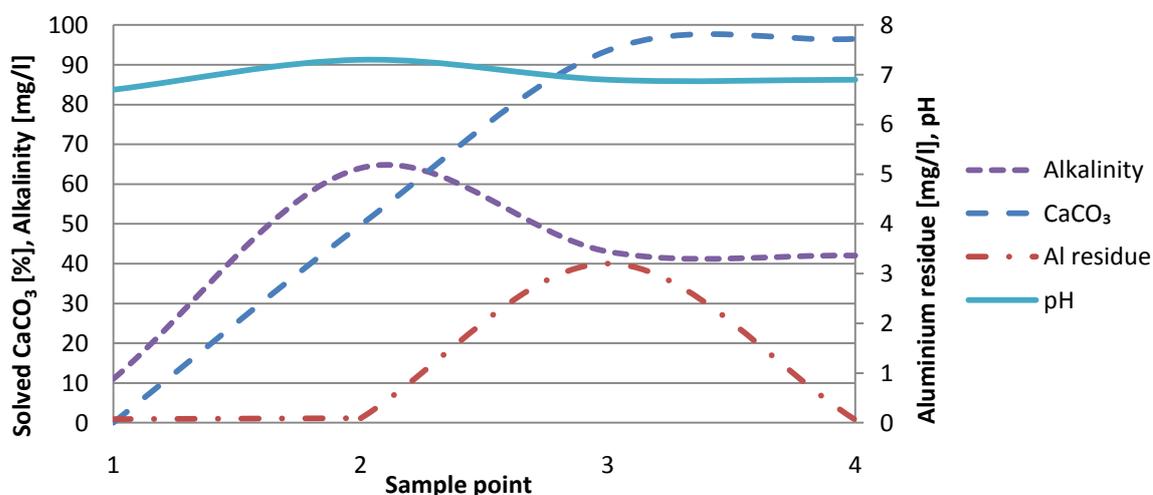
Figure 3.20 Changes in some of the measured parameters in the full scale trials in Öxsjöverket (Göthe & Israelsson, 1995).

3.6 Comparison of the treatment processes

Each water treatment plant has different treatment processes and the detention times between added chemicals vary. The most important detention times, in this report, are presented in Table 3.5.

Table 3.5 Time between chemical dosing locations and detention time in DynaSand filters in the water treatment plants. Values correspond to mean flows.

	Time between			
Water treatment plant	CO_2 and $CaCO_3$	$CaCO_3$ and Ekoflock	Ekoflock and DynaSand	Detention time in DynaSand filters
Karlskrona	<10 s	45 min	-	60 min
Kristinehamn	0.5 s	35 s	-	15 min
Lerum	0 s	45 – 50 s	60 s	30 min

4 Test round I: Calcium carbonate solubility and aluminium residue

Prior the first test round, in February 2010, an experimental test round on Lerum raw water is made. The aim of this test is to evaluate the investigation method as well as the equipment and to determine the required time and focus points for the first test round. The first test round aims to determine and verify the most important factors affecting calcium carbonate solubility. The goal is to include as many factors as possible, such as variation in water temperature, different pH, different detention times and variation in stirring speed. Since three types of raw water are used, the effects of variations in raw water parameters on calcium carbonate dissolution are examined.

The test setup is compiled in appendix C1. In one litre of raw water with the temperature of approximately 0.5 °C and 15 °C, calcium carbonate is dissolved. This is conducted for all three raw water sources. 0.5 °C represent the extreme of incoming raw water temperature during winter, while 15 °C represent a typical summer temperature. pH 5, 6 and 7 are all likely to be obtained in a water treatment plant and are therefore chosen. The desired pH values are obtained by dosing carbon dioxide before and during the tests, which was proven possible from the experimental test round. In the tests, the speed of the stirring device is set to 20 rpm, except for two additional tests where the speed is increased to 50 rpm.

The effects of calcium carbonate in combination with precipitation chemical are investigated in four tests. In two tests at the water temperatures 0.5 °C and 15 °C, 20 rpm stirring and pH 6, precipitation chemical is added after ten minutes of calcium carbonate dissolution. The aluminium residue is measured after two, four and seven minutes.

In two additional tests, the dosing process is inverted. Precipitation chemical is added resulting in a pH drop. This pH drop will hopefully create good conditions for calcium carbonate dissolution. The aluminium residue is measured after two, four and seven minutes. After eight minutes, calcium carbonate is added to the beaker and dissolved calcium carbonate is measured until 17 minutes after the start of the test. The time frame of these measurements could appear somewhat short, however, results from the experimental test round illustrate that a large quantity of calcium carbonate is dissolved during the first five minutes.

The overall idea is to observe whether the aluminium residue levels are affected if the alkalinity levels are considerably lower in the water due to the absence of hydrogen carbonate (HCO_3^-).

In Table 4.1, the raw water properties are presented for the first laboratory test round.

Table 4.1 Raw water properties of the water on which the first test round are performed.

Raw water	Karlskrona	Kristinehamn	Lerum
Colour [mg Pt/l]	125	100	19
Turbidity [FNU]	3	4.6	0.25
Alkalinity [mg/l]	15.5	9	11
Mn [mg/l]	0.091	0.13	0.2
Fe [mg/l]	1.81	0.67	0.013
Hardness [°dH]	1.5	0.79	0.037
Al [mg/l]	0.204	0.26	0.072
Ca [mg/l]	6.41	3.7	6.11
COD [mg/l]	15.5	14	N/A

According to the rules of thumb (Eq. 10 and Eq. 11) for required chemical dosage of aluminium sulphate, the concentrations that are theoretically needed in the first test round are presented in Table 4.2. The rules of thumb are re-calculated as Ekoflock doses by the knowledge of aluminium contents in Ekoflock 70 and 91 described in Table 3.3. However, the actual doses in the first test round are adapted to doses that have been used at the water treatment plants.

Table 4.2 Theoretically required doses of Ekoflock 70 and 91 on the raw waters that are displayed in Table 4.1, according to the rules of thumb.

Rule of thumb	Karlskrona Ekoflock 70 [mg/l]	Kristinehamn Ekoflock 91 [mg/l]	Lerum Ekoflock 70 [mg/l]
COD_{Mn}	71	50	N/A
Colour	134	86	37

4.1 Performance

In the first test round, raw water from Karlskrona, Kristinehamn and Lerum are examined in regard to the solubility of calcium carbonate and aluminium residue.

15 liters of raw water are collected in one litre cans at each water treatment plant. The samples are then directly transported in cooler boxes to the Environmental Chemistry Laboratory at Chalmers University of Technology. During the trials, the cans are stored at 7 °C in refrigerators.

In Figure 4.1 and Figure 4.2 the test equipment is displayed. A temperature bath containing water and ice and an additional external cooling system is used to cool the beaker. The beaker is filled with raw water and equipped with a stirring device, pH

meter and a tube with a glass stone for CO_2 addition. The pH meter measures pH and water temperature in parallell. The speed of the stirring device is adjustable.
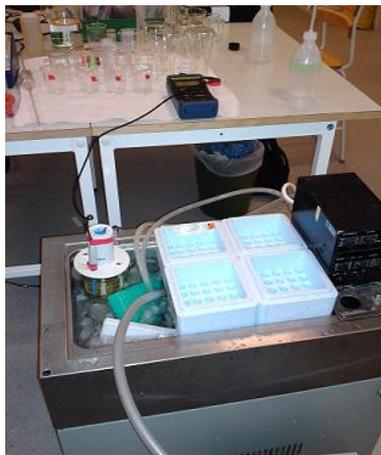
Figure 4.1 Test equipment including sample beaker, water bath, pH meter and CO_2 tube with a glass stone.

Figure 4.2 A close-up picture of the sample beaker, the stirring device pH meter in the icy water.

The calcium carbonate dissolution tests are performed according to the list below. Appendix C1 explains the test setup.

- The sample volume, 1 litre, is cooled/heated to approximately 0.5 °C and 15 °C respectively, the temperature is then kept constant

- 30 mg of calcium carbonate is added to 30 ml of water, which gives it a concentrated slurry of 1 g/l. 30 mg is chosen based on the dosage in the plants

- The stirring device is set to selected speed (e.g. 20 rpm) and kept constant throughout the entire test

- pH is adjusted to the desired value by dosing carbon dioxide from a gas-tube

- The slurry is added and carbon dioxide is dosed if necessary (in order to keep the pH stable)

- 50 ml of water is collected by a pipette after 1, 4, 7 and 10 minutes. The water is then filtered immediately through 0.45 μm filters in order to remove non-dissolved calcium and other small particles that could interfere the analyses

- The calcium concentration is measured by titration immediately after filtration, for the given duration times

- The original calcium concentration (Ca_0), the amount of added calcium (30x0.39 mg/l, since calcium carbonate contain 39 % calcium) and the calcium concentration after 1, 4, 7 and 10 minutes (Ca_1) are known which means that the calcium solubility can be calculated

- The calcium solubility is calculated according to the following equation
$$Ca_{\%solved} = \frac{Ca_1 - Ca_0}{30 \times 0.39} \times 100$$

The tests, in which the effects of calcium carbonate on aluminium residue are performed, are presented according to the list below. Table 4.3 shows dosing and measurement times for the two cases of aluminium trials.

- The sample volume, 1 litre, is cooled or heated to approximately 0.5 °C and 15 °C respectively. The temperature is then kept constant

- The coagulation chemical is dosed accordingly to Karlskrona, Lerum and Kristinehamn water treatment plants dosages

- The stirring device is set to selected speed (e.g. 20 rpm) and kept constant throughout the entire test

- The flocculation chemical is added to the container by lowering a small plastic container in the water

- 50 ml of water is collected by a pipette after 1, 4, 7 and 10 minutes

- The water is then filtered immediately in 0.45 µm filters in order to remove flocs and particles

- The aluminium residue level is measured according to the Hach-method, which is a measurement method frequently used in laboratories.

Table 4.3 In case 1, $CaCO_3$ is dosed before PAC, while in case 2, PAC is dosed before $CaCO_3$. See appendix C1 for more information.

| Case 1 – $CaCO_3$ dosed before PAC | | Case 2 – PAC is dosed before $CaCO_3$ | |
Time [min]	Activity	Time [min]	Activity
0	$CaCO_3$ dosing	0	PAC dosing
1	Measure dissolved $CaCO_3$	2	Measure Al residue
4	Measure dissolved $CaCO_3$	4	Measure Al residue
7	Measure dissolved $CaCO_3$	7	Measure Al residue
		8	$CaCO_3$ dosing
10	Measure dissolved $CaCO_3$ PAC dosing	9	Measure dissolved $CaCO_3$
12	Measure Al residue	12	Measure dissolved $CaCO_3$
14	Measure Al residue	15	Measure dissolved $CaCO_3$
17	Measure dissolved $CaCO_3$ Measure Al residue	17	Measure dissolved $CaCO_3$ Measure Al residue

4.2 Results

In this section results obtained in the first test round are presented for each of the three raw water qualities. Some of the results are presented in appendix D1.

4.2.1 Dissolution of calcium carbonate

Calcium carbonate dissolution rates are presented as function of time for different temperature and pH. From the diagrams in this section, it is evident that the calcium carbonate dissolution rates are enhanced as pH is lowered and water temperatures are increased. Apparently, a lot of calcium carbonate is dissolved in the water already after one minute of elapsed time.

Decreasing the pH with one unit, from pH 6 to pH 5, results in an increase in calcium carbonate dissolution rate of approximately 30 ± 10 percentage points, depending on which time of measurement that is compared. However, decreasing pH one unit is in reality a 10-times increase in hydronium ions. This is presented in Section 2.2.
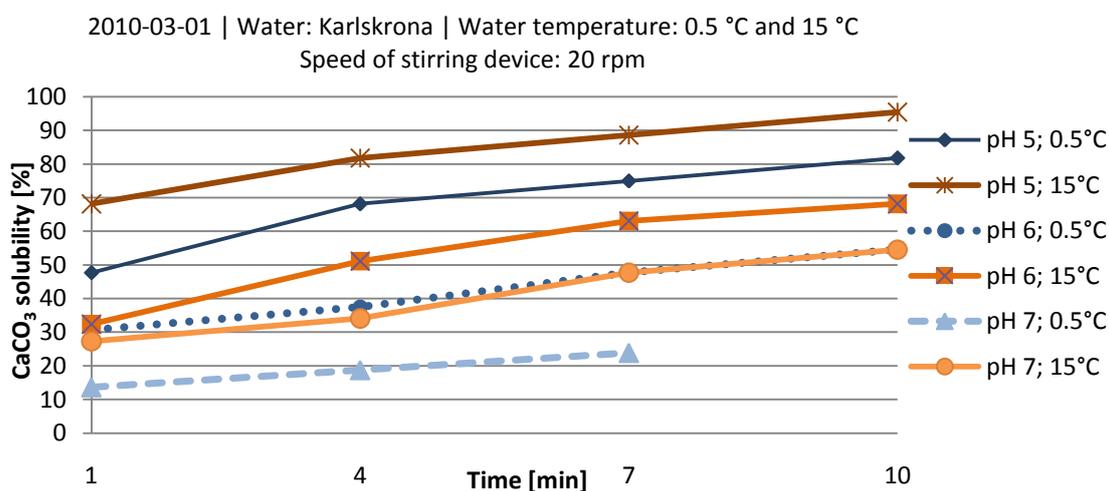
Figure 4.3 Solubility of calcium carbonate at different water temperatures and pH in Karlskrona raw water. The solubility curve for pH 7 at 0.5 °C is not complete due to test failures.

2010-02-23 | Water: Kristinehamn |Water temperature: 0.5 °C och 15 °C
Speed of stirring device: 20 rpm
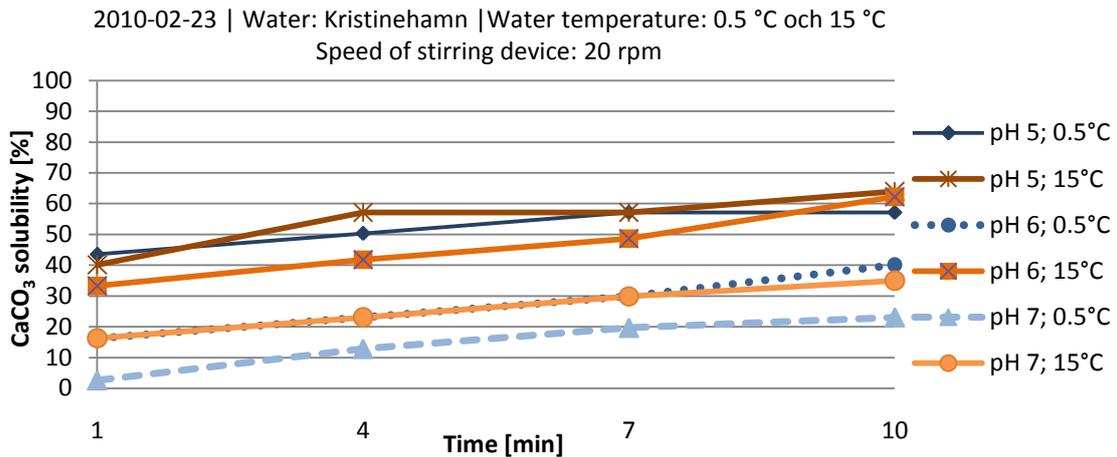
Figure 4.4 Solubility of calcium carbonate at different water temperatures and pH in Kristinehamn raw water.

2010-03-08 | Water: Lerum | Water temperature: 0.5 °C and 15 °C
Speed of stirring device: 20 rpm
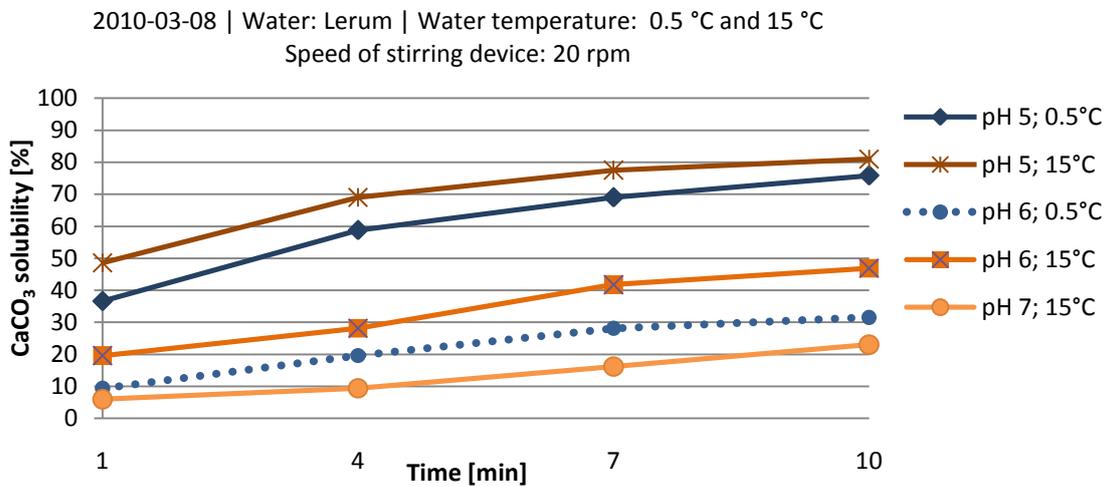
Figure 4.5 Solubility of calcium carbonate at different water temperatures and pH in Lerum raw water. The solubility curve for pH 7 at 0.5 °C is not plotted due to test failures.

4.2.2   Effect of rotation velocity on calcium carbonate solubility

Two different speeds, 20 rpm and 50 rpm, of the stirring device are tested at pH 6 at 0.5 °C and 15 °C. The effect of increased stirring speed appears to be insignificant, however this will be further discussed in Section 6. Although, there are indications of higher dissolution rates at lower stirring speeds. The variation in dissolution between 20 rpm and 50 rpm are believed to have other explanations rather than the change of speed itself.

2010-03-01 | Water: Karlskrona | Water temperature: 0.5 °C and 15 °C
Speed of stirring device: 20 and 50 rpm | pH 6
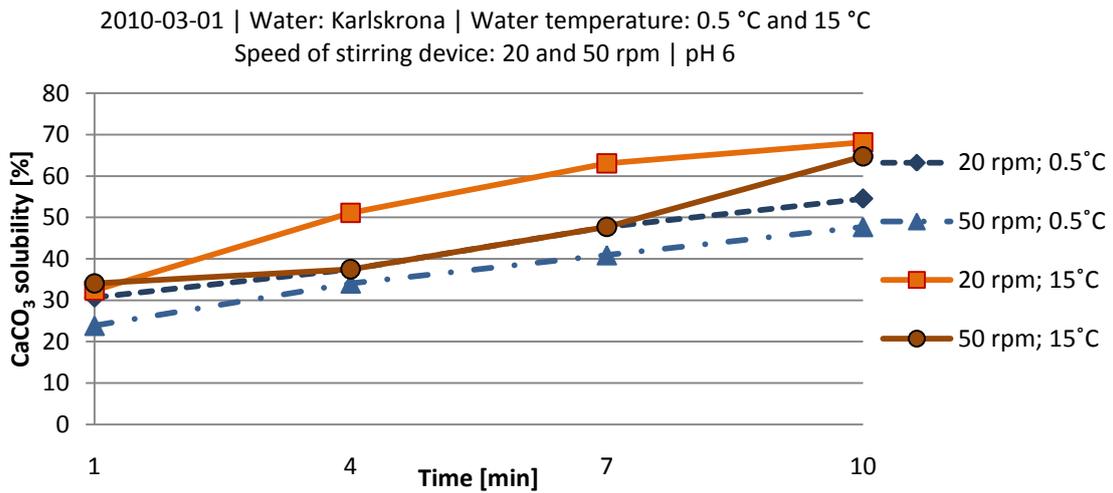
Figure 4.6 Variations in rotation velocity and its effect on calcium carbonate solubility, Karlskrona.

2010-02-23 | Water: Kristinehamn |Water temperature: 0.5 °C and 15 °C Speed of stirring device: 20 and 50 rpm | pH 6
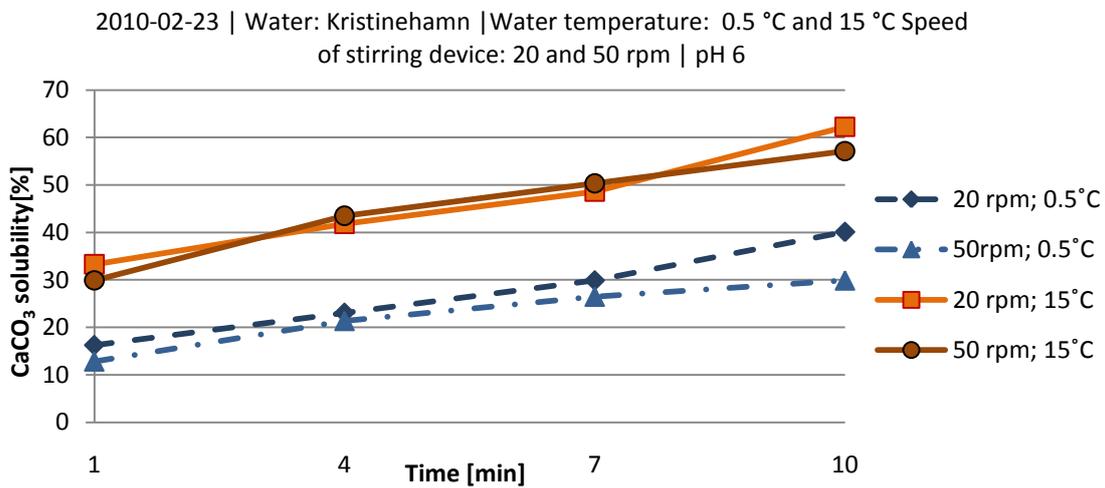
Figure 4.7 Variations in rotation velocity and its effect on calcium carbonate solubility, Kristinehamn.

2010-03-08 | Water: Lerum | Water temperature: 0.5 °C och 15 °C
Speed of stirring device: 20 and 50 rpm | pH 6
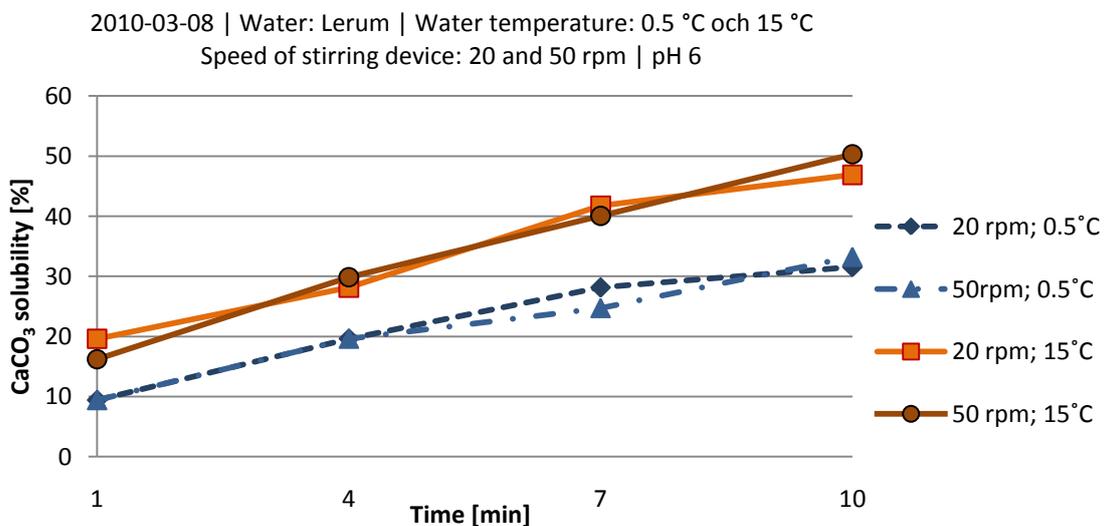
Figure 4.8 Variations in rotation velocity and its effect on calcium carbonate solubility, Lerum.

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35

4.2.3 Water temperature dependency

The effect of water temperature, between approximately 0.5 °C and 15 °C, on the calcium carbonate dissolution rate is presented in this section for Karlskrona. Similar curves for Lerum and Kristinehamn are presented in appendix D1. Linearity is assumed, since measurements are made for two temperatures only. In general, the dissolution rate increases around 1 percentage point as the water temperature increase by 1 °C, regardless of measurement time. Generally, one minute of dissolution at 15 °C corresponds to four minutes at 0.5 °C.

2010-03-01 | Water: Karlskrona | Speed of stirring device: 20 rpm | **pH 5**
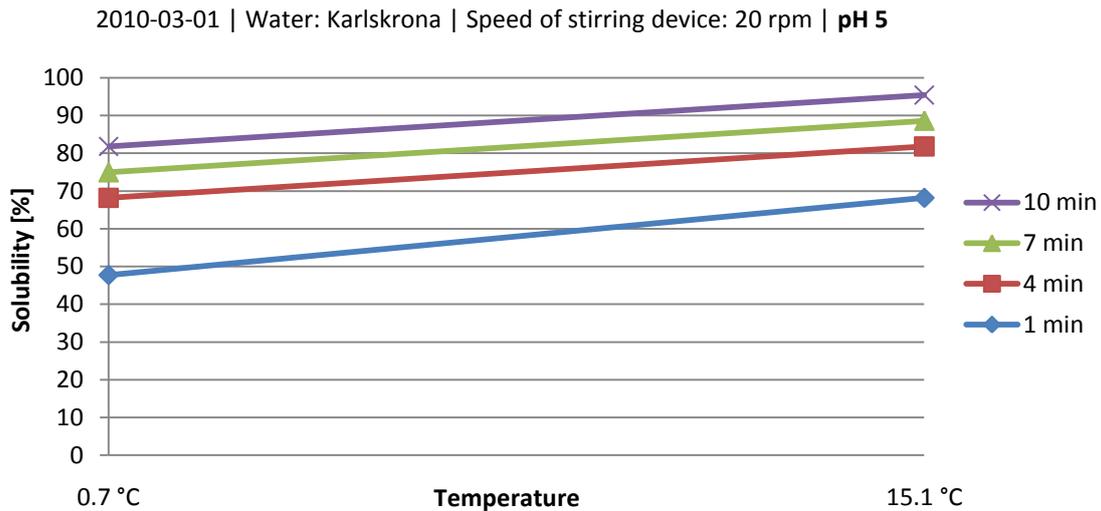
Figure 4.9 Calcium carbonate solubility as a function of water temperature at pH 5, Karlskrona.

2010-03-01 | Water: Karlskrona | Speed of stirring device: 20 rpm | **pH 6**
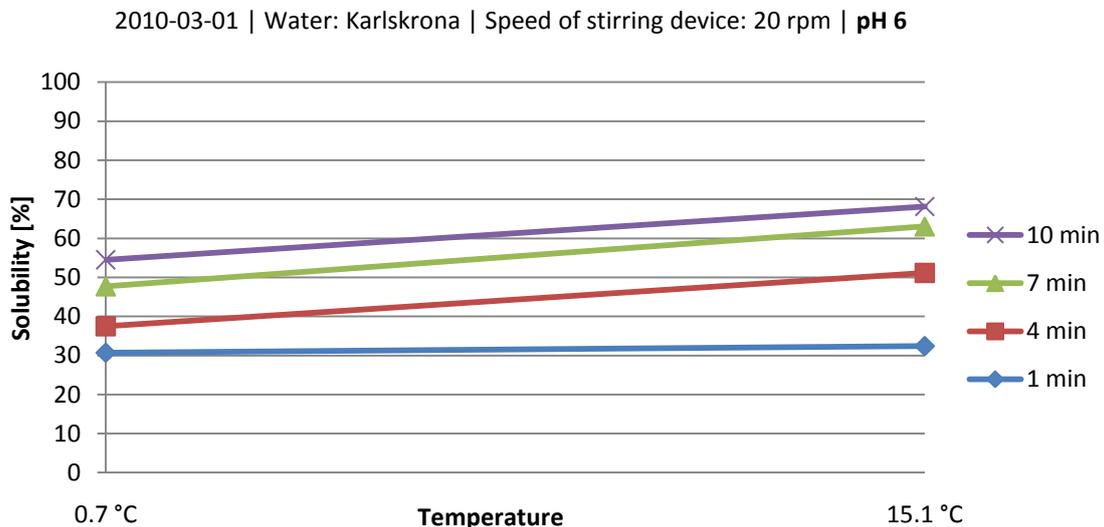
Figure 4.10 Calcium carbonate solubility as a function of water temperature at pH 6, Karlskrona.
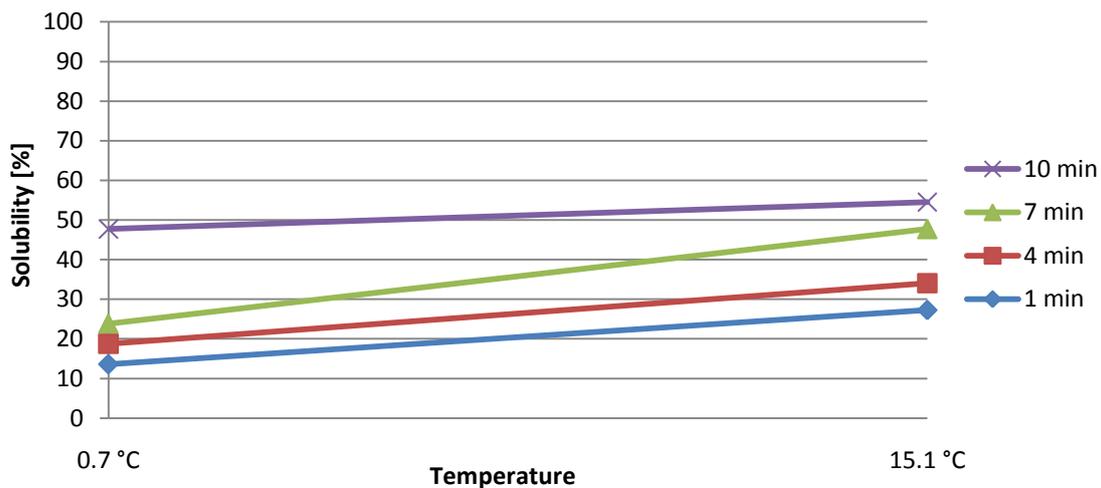
Figure 4.11 Calcium carbonate solubility as a function of water temperature at pH 7, Karlskrona.

4.2.4 Raw water quality and solubility of calcium carbonate

2010-03-15 | pH: 5 | Water temperature: 0.5 °C and 15 °C
Speed of stirring device: 20 rpm

Raw water	Karlskrona	Kristinehamn	Lerum
Colour [mg/l]	125	100	19
Turbidity [FNU]	3	4.6	0.25
Alkalinity [mg/l]	15.5	9	11
Mn [mg/l]	0.091	0.13	0.2
Fe [mg/l]	1.81	0.67	0.013
Hardness [°dH]	1.5	0.79	0.037
Al [mg/l]	0.204	0.26	0.072
Ca [mg/l]	6.41	3.7	6.11
COD [mg/l]	15.5	14	N/A
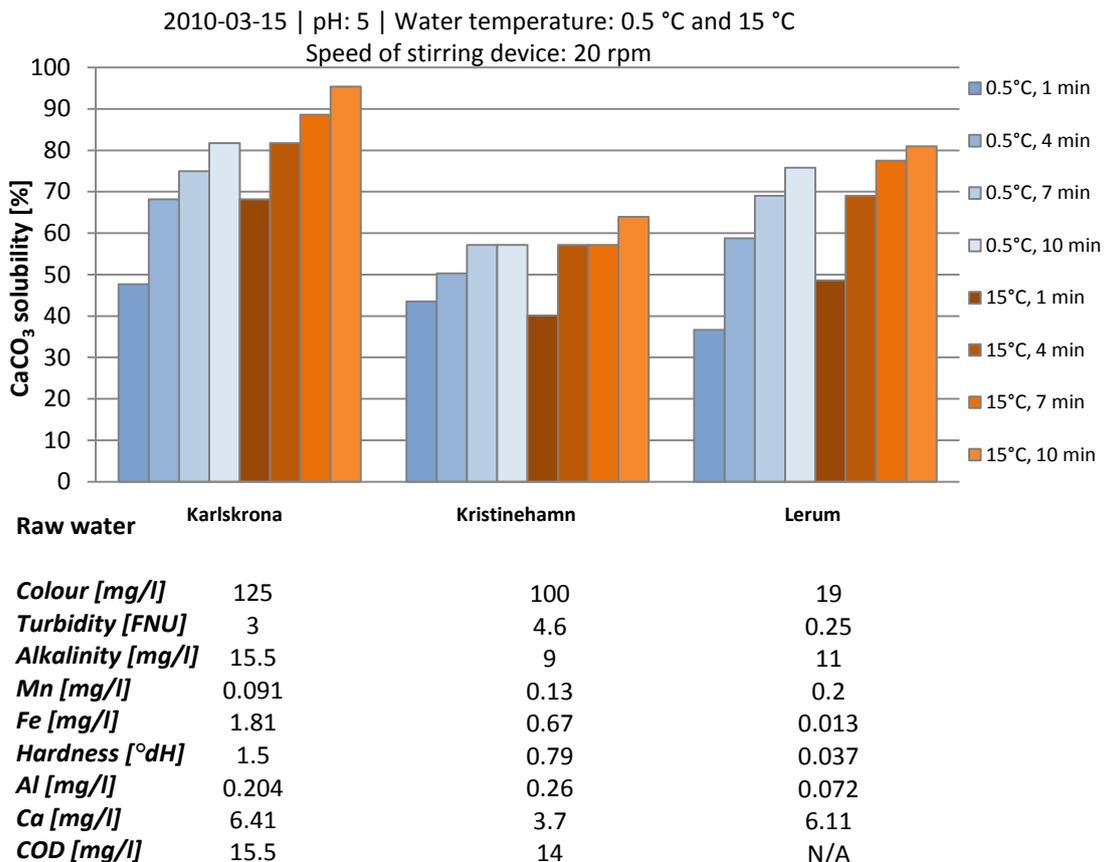
Figure 4.12 Comparison of calcium carbonate solubility at pH 5 for raw water with different properties. These are the actual properties of the water on which the calcium carbonate solubility tests were performed.

In all three raw waters, calcium carbonate from all three water treatment plants has been dissolved. For example, Lerum raw water has been tested with Mikrostevns from Karlskrona, Kristinehamn and Lerum. The comparison is performed at pH 5, 20 rpm stirring speed and at 0.5 °C. Generally, Mikrostevs from Lerum seems to dissolve slightly better in all three raw waters compared to Mikrostevns from Karlskrona and Kristinehamn.

In Karlskrona raw water, Mikrostevns solubility is almost equal during the first 10 minutes. This equality remain after 30 minutes, at least for Mikrostevns from Karlskrona and Lerum.

In Kristinehamn raw water, Mikrostevns from Lerum seems to have a higher dissolution rate during the first 10 minutes. During the whole test, Mikrostevns from Lerum dissolves better than Mikrostevns from Karlskrona. After 30 minutes there is a 10 percentage point difference between the two Mikrostevns from Karlskrona and Lerum.

In Lerum raw water, Mikrostevns from Lerum and Karlskrona dissolves faster than Mikrostevns from Kristinehamn during the first 10 minutes. After 30 minutes Mikrostevns from Lerum has solved better than Mikrostevns from Karlskrona, followed by Mikrostevns from Kristinehamn.
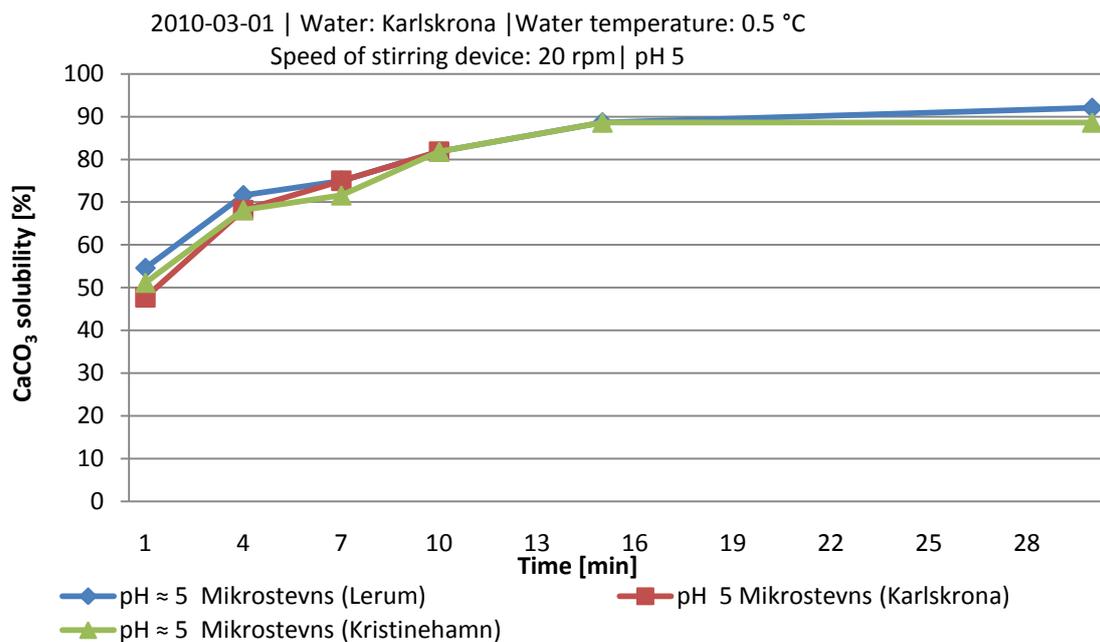
Figure 4.13 Karlskrona raw water, in which three types of calcium carbonate are dissolved. Unfortunately, Mikrostevns (Karlskrona) solubility is only measured up to 10 minutes and is therefore not as easy to compare.
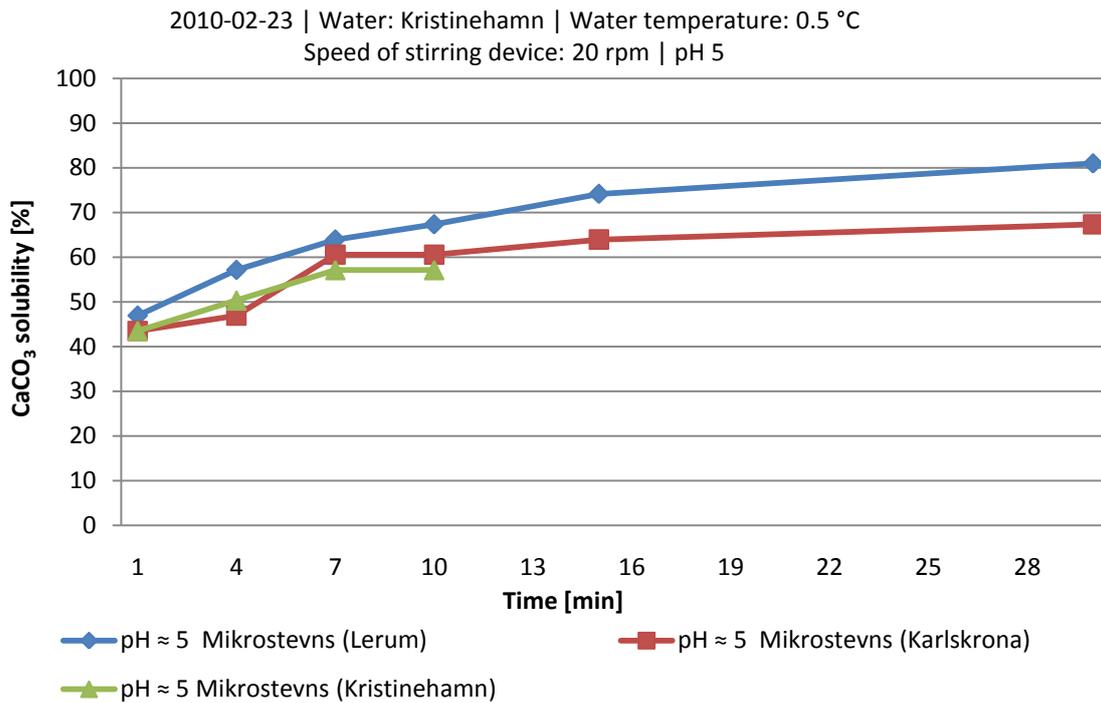
Figure 4.14 Kristinehamn raw water, in which three types of calcium carbonate are dissolved. Unfortunately, Mikrostevns (Kristinehamn) solubility is only measured up to 10 minutes and is therefore not as easy to compare.
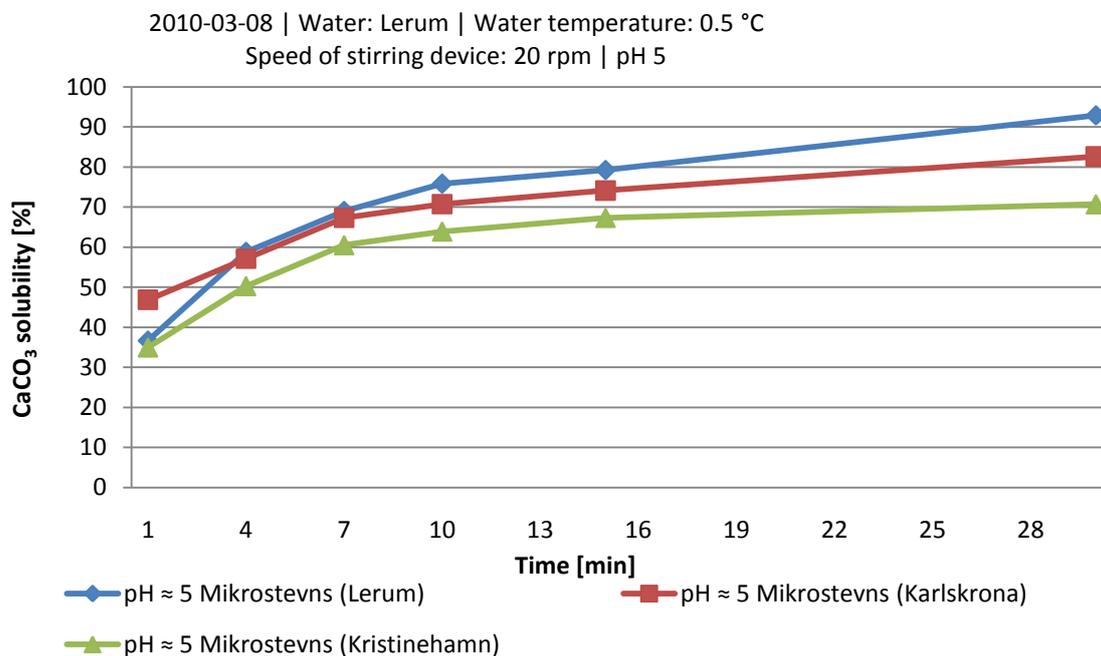
Figure 4.15 Lerum raw water, in which three types of calcium carbonate are dissolved.

4.2.5   Effect of calcium carbonate on aluminium residue

The tests, in which the effects of calcium carbonate on aluminium residue are examined, are performed in two cases illustrated in Table 4.3. To be able to plot the pH variation in the tests described in Table 4.3, the pH values have been multiplied by a factor ten.

In Figure 4.16 and Figure 4.17 from Karlskrona it is evident that:

- Case 1: Cold water results in higher aluminium residue compared to warm water.
- Case 2: Cold water results in lower aluminium residue compared to warm water. However, the final aluminium residue values are the same at 17 minutes.
- Case 1 and 2: The chemical coagulant seems affect the calcium carbonate solubility in a positive way, in warm water if dissolution after one minute in case 1 is compared to dissolution in warm water after one minute in case 2. However, by comparing the corresponding pH curves, it is possible to explain the increased calcium carbonate solubility in case 2 partly by the acidifying effect of the chemical coagulant.

In Figure 4.18 and Figure 4.19 from Kristinehamn it is evident that:

- Case 1: Cold water results in higher aluminium residue compared to warm water.
- Case 2: The aluminium residue were above 0.800 mg/l (upper measurement range for the Hach instrument were reached) during the first seven minutes in both cold and warm water. Unfortunately, due to test failures, the aluminium residue was not measured after seven minutes.

In Figure 4.20 and Figure 4.21 from Lerum it is evident that:

- Case 1: Cold water results in higher aluminium residue compared to warm water.
- Case 2: Aluminium residue in cold water starts at high concentrations, but after seven minutes a concentration of 0.01 mg/l is reached. This level is kept until 17 minutes. In warm water the aluminium residue starts at low values, then tend to increase as the time elapses. However, after 17 minutes the aluminium residue stops as the same level as cold water.
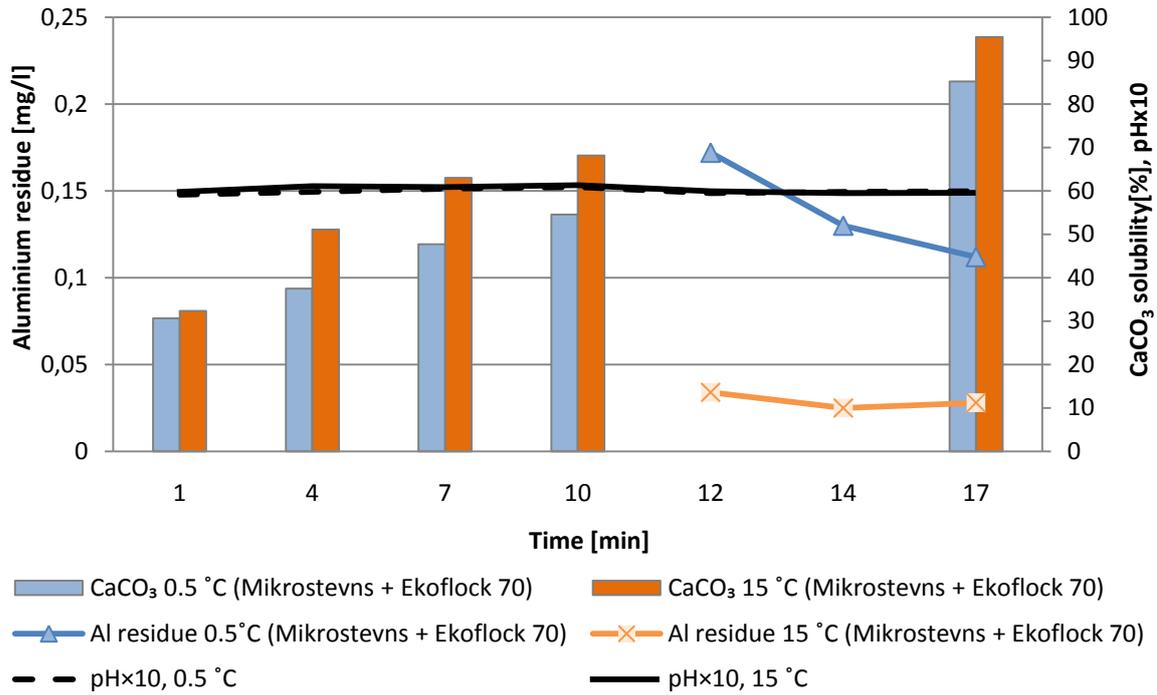
Figure 4.16 Calcium carbonate is dosed before the addition of chemical coagulant, Karlskrona.
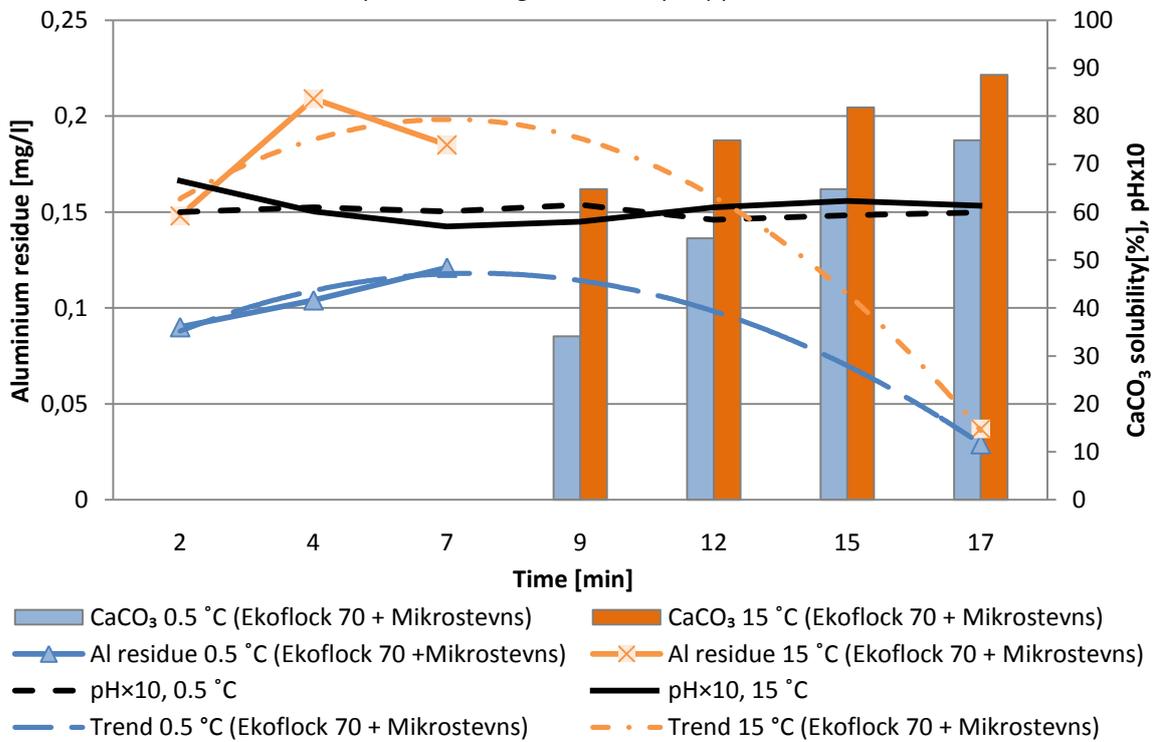
Figure 4.17 Chemical coagulant is dosed before the addition of calcium carbonate, Karlskrona.

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35
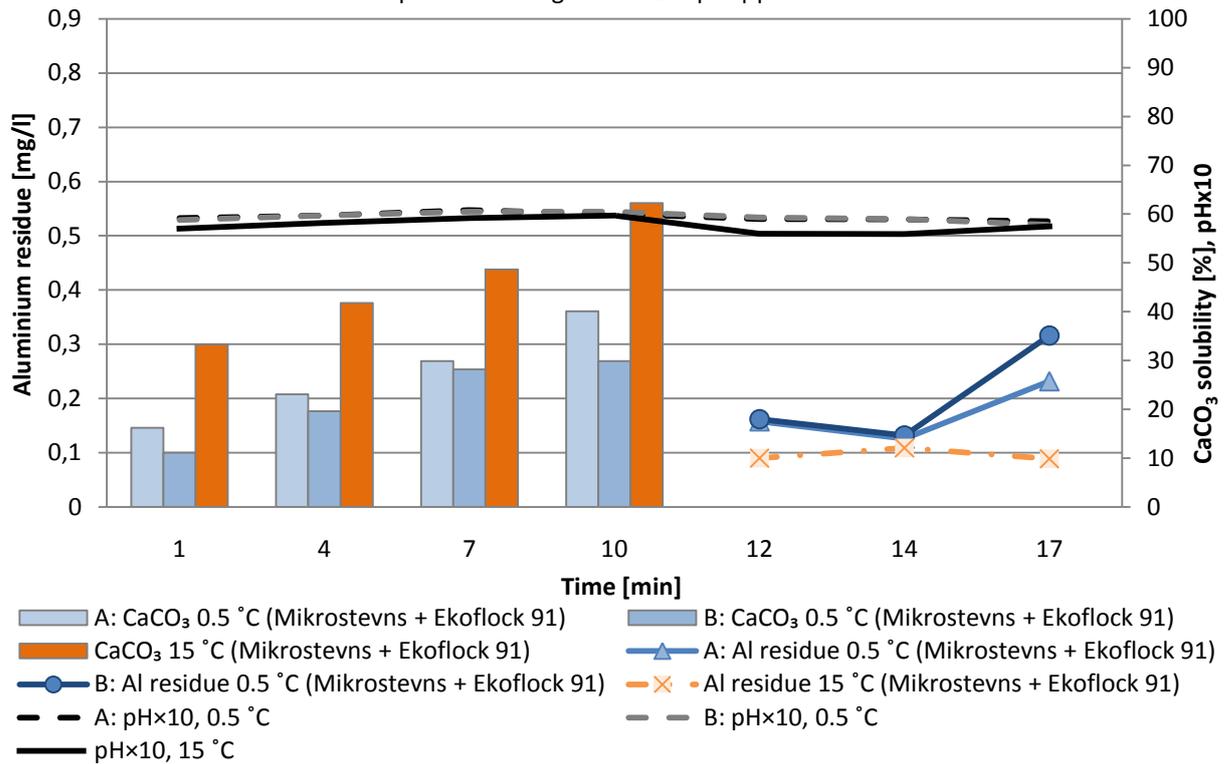
Figure 4.18 Calcium carbonate is dosed before the addition of chemical coagulant, Kristinehamn. The cold test was repeated in order to verify the accuracy of the used test method.
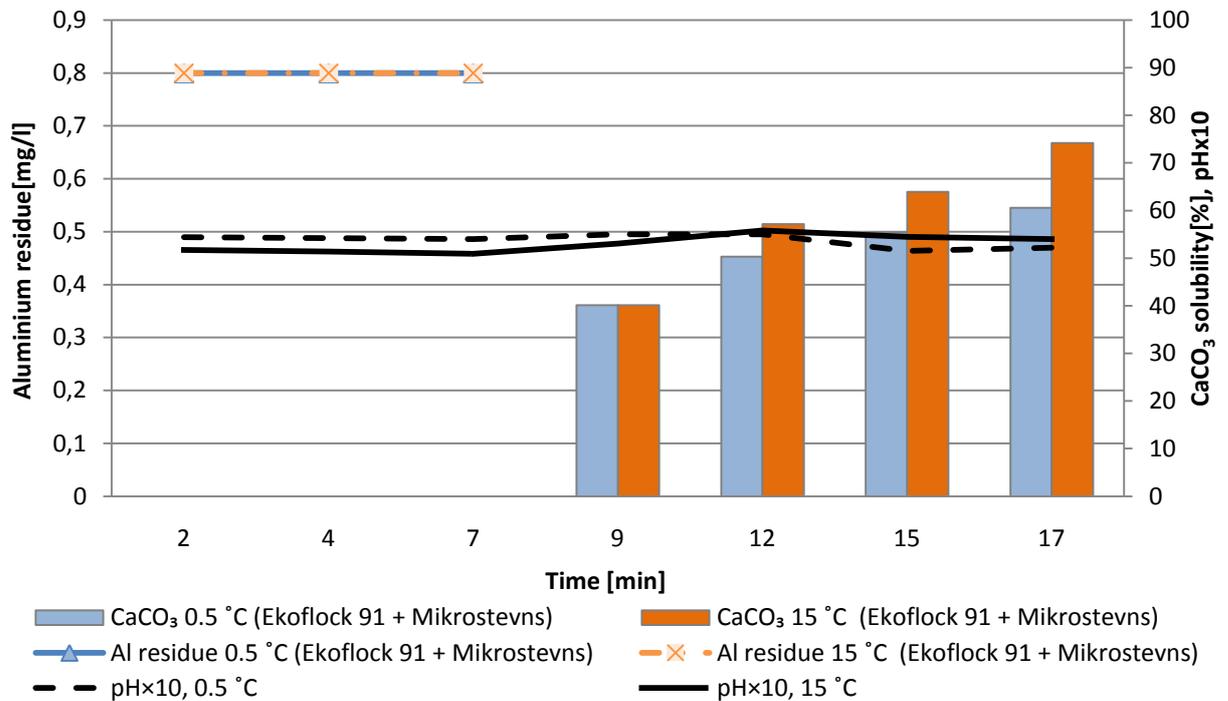
Figure 4.19 Chemical coagulant is dosed before the addition of calcium carbonate, Kristinehamn.
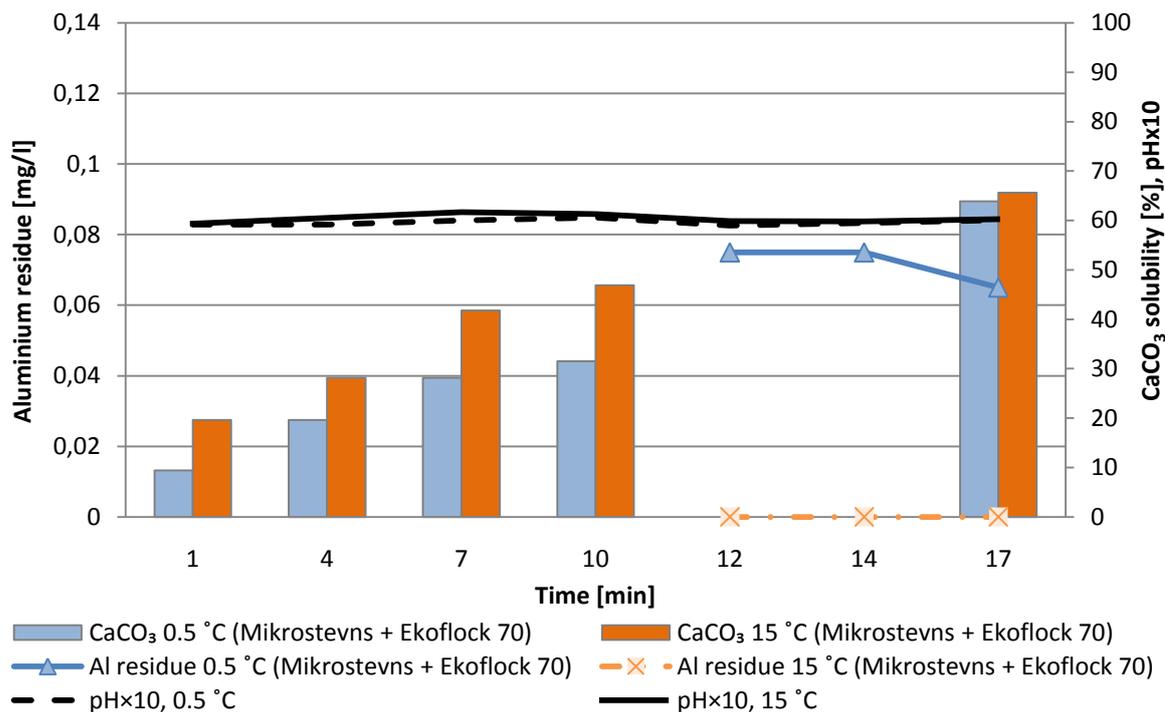
Figure 4.20 Calcium carbonate is dosed before the addition of chemical coagulant, Lerum.
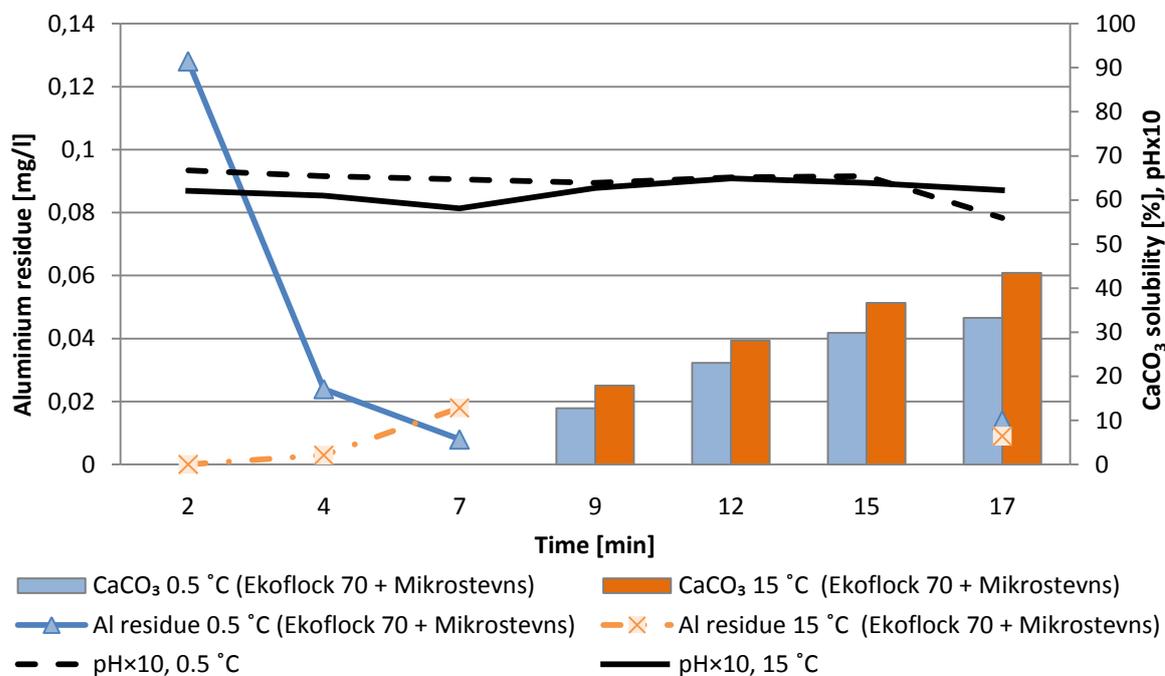
Figure 4.21 Chemical coagulant is dosed before the addition of calcium carbonate, Lerum.

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35

5 Test round II: Further aluminium residue analysis

When the involved parties in the project discussed the results from the first test round, theories and thoughts about disturbances in the flocculation process were presented. It is believed that unsolved calcium carbonate disturbs the coagulation and flocculation processes mainly in two ways. The first way could be particles of calcium carbonated attaching to humus particles, making them positively charged and repelling the positive aluminium ions. The second way occurs if not enough of the added calcium carbonate is dissolved in the water. This results in too low alkalinity levels, which disturbs the coagulation and flocculation processes. In Sections 2.2 and 2.3 it is concluded that the presence of hydrogen carbonates in the water, which is a measure of the alkalinity, affect the coagulation and flocculation processes.

The acidity of Ekoflock 70 will probably lower the pH value, which will enable increased calcium carbonate dissolution rate. However, this was partly investigated in the first test round (Figure 4.16 and Figure 4.20) and no major increase in solubility was seen after eight minutes when Ekoflock 70 was dosed. The influence of Ekoflock 70 on calcium carbonate solubility is not investigated in the second test round.

The second test round focuses on optimizing the chemical precipitation in various phases of dissolved calcium carbonate. The main goal is to assess the importance of alkalinity for aluminium residue in different raw water with different levels of total organic carbon (TOC). If TOC is measured after 15 minutes of flocculation, the TOC values probably will be indicators of the effectiveness of the chemical precipitation. By adding precipitation chemicals at different levels of solved calcium carbonate, it is possible to address how the aluminium residue level is affected by different values of unsolved calcium carbonate and levels of alkalinity. The test round investigate what percentage of dissolved calcium carbonate that is needed in order to obtain aluminium residue levels below the limit value of 0.1 mg Al per litre as well as satisfying alkalinity levels.

For easy comparison between different raw water, one type of calcium carbonate and precipitation chemical will be used in the tests. By determining the solubility of calcium carbonate at 0.5 °C and 15 °C for given values of pH and stirring velocity, it is possible to add precipitation chemicals at different percentages of solved calcium carbonate. Aluminium residue and alkalinity can then be measured. These tests investigate how the alkalinity and TOC levels in the raw water are affected after addition of chemical coagulants, at different levels of dissolved calcium carbonate. In Table 5.1 the raw water properties of the water, on which the second test round are performed, is presented.

Table 5.1 Raw water properties of the water on which the second test round are performed.

Raw water	Karlskrona	Kristinehamn	Lerum
Colour [mg/l]	140	90	21
Turbidity [FNU]	2.83	7.6	0.25
Alkalinity [mg/l]	8.4	6.1	11
Mn [mg/l]	0.069	0.11	0.016
Fe [mg/l]	0.98	1.0	0.076
Hardness [°dH]	1.2	N/A	0.86
Al [mg/l]	0.025	0.28	0.086
Ca [mg/l]	6.01	3.2	4.8
COD [mg/l]	19.7	12	3.7
TOC [mg/l]	17.4	9.7	5.7

According to the rules of thumb (Eq. 10 and Eq. 11) for required chemical dosage of aluminium sulphate, the aluminium concentrations that are theoretically needed in the second test round are presented in Table 5.2. The rules of thumb are re-calculated as Ekoflock 70 doses by the knowledge of aluminium content in Ekoflock 70, which was described in Table 3.3.

Table 5.2 Theoretically required doses of Ekoflock 70 on the raw waters that are displayed in Table 5.1, according to the rules of thumb.

Rule of thumb	Karlskrona Ekoflock 70 [mg/l]	Kristinehamn Ekoflock 70 [mg/l]	Lerum Ekoflock 70 [mg/l]
COD_{Mn}	90	55	17
Colour	147	102	39

5.1 Performance

Five tests, named case A, B, B1, B2 and B3, are made in cold and in warm water. The test round is performed according to appendix C2. The aluminium concentration, manganese content, pH, calcium concentration, TOC levels and alkalinity are examined for comparison before the test rounds.

In case A, pH is allowed to be in the interval 5.5 to 6.5. 60 mg of Ekoflock 70 is then added to the one litre beaker and sodium hydroxide is used for pH adjustment if necessary. The aluminium residue is tested after 1, 4, 7, 10 and 15 minutes. TOC is analyzed after 4 and 15 minutes. Manganese and alkalinity are measured after 15 minutes.

In case B the calcium concentration is measured after approximately 1, 4, 7, 10, 20, 30, 40, 60 and 90 minutes in order to conduct solubility charts for 30 mg per litre of

calcium carbonate. pH is adjusted by carbon dioxide and allowed to be in the interval 5.5 to 6.5.

After the solubility chart is made, case B1, B2 and B3 are performed. In case B1 Ekoflock 70 is dosed after about 30 percent calcium is dissolved. Aluminium residue is then tested after 1, 4, 7 and 15 minutes by filtering the water according to Figure 5.1. TOC is analyzed after 4 and 15 minutes. Manganese and alkalinity are measured after 15 minutes. In B2 and B3 Ekoflock 70 is dosed after about 50 and 70 percent respectively and then tested in the same manner as B1. In all cases, 30 mg of Mikrostevns and 60 mg of Ekoflock 70 are dosed. The result of dosing Ekoflock 70 is visible as brownish flocs in Figure 5.2.

Figure 5.1 A 0.45 µm cellulose filter after flocculated water has been filtered.

Figure 5.2 Flocs are visible as macro particles in a beaker during a 15 °C test with Mikrostevns and Ekoflock 70.

5.2 Results

In this section, results obtained in the second test round are presented for each of the three raw water qualities. Some of the results are presented in appendix D2.

5.2.1 Aluminium residue – case by case

In this section, curves for each case (A, B1-B3) are presented for the raw water from Karlskrona. Since there are totally 24 tests divided onto three raw waters, the test curves for Kristinehamn and Lerum are presented in appendix D2. In Figure 5.14 all cases are summarized.

For each experiment, there is a pH and temperature plot, which corresponds to the measured variations in pH and in temperature during each case.

In case A, in which no calcium carbonate is added, 60 mg of Ekoflock 70 is added at time zero, and the aluminium residue is then measured during 15 minutes. The addition of the acidic Ekoflock 70 results in a pH drop of approximately one unit during the first minute, as well as a substantial raise in aluminium concentration.

In addition, there is a small temperature increase in the beginning of flocculation, which suggests that an exothermic reaction occurs. During the 15 minute period, the decrease in TOC content, manganese concentration and alkalinity levels are measured. The values of aluminium, manganese, TOC and alkalinity at time zero represent untreated raw water values.
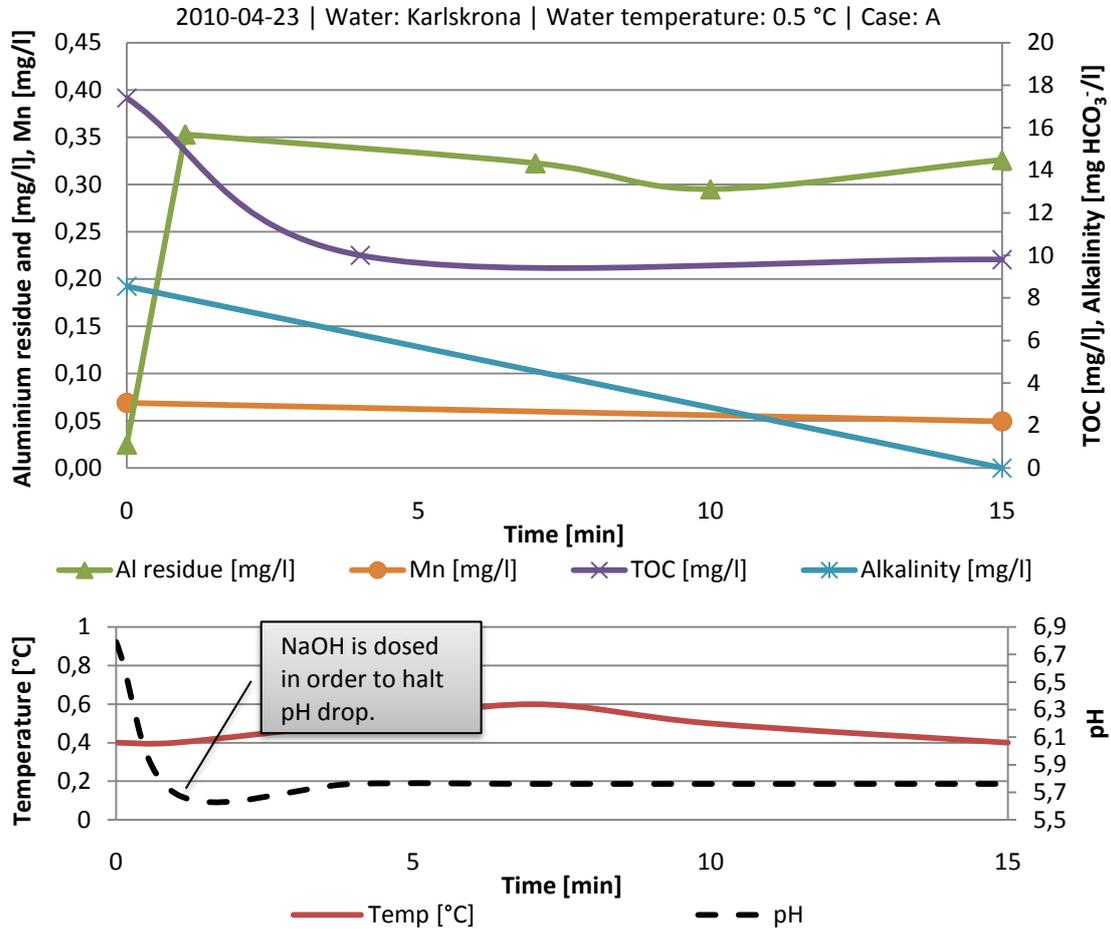
Figure 5.3 Aluminium residue in cold water without CaCO₃ addition, and corresponding pH and temperature changes.
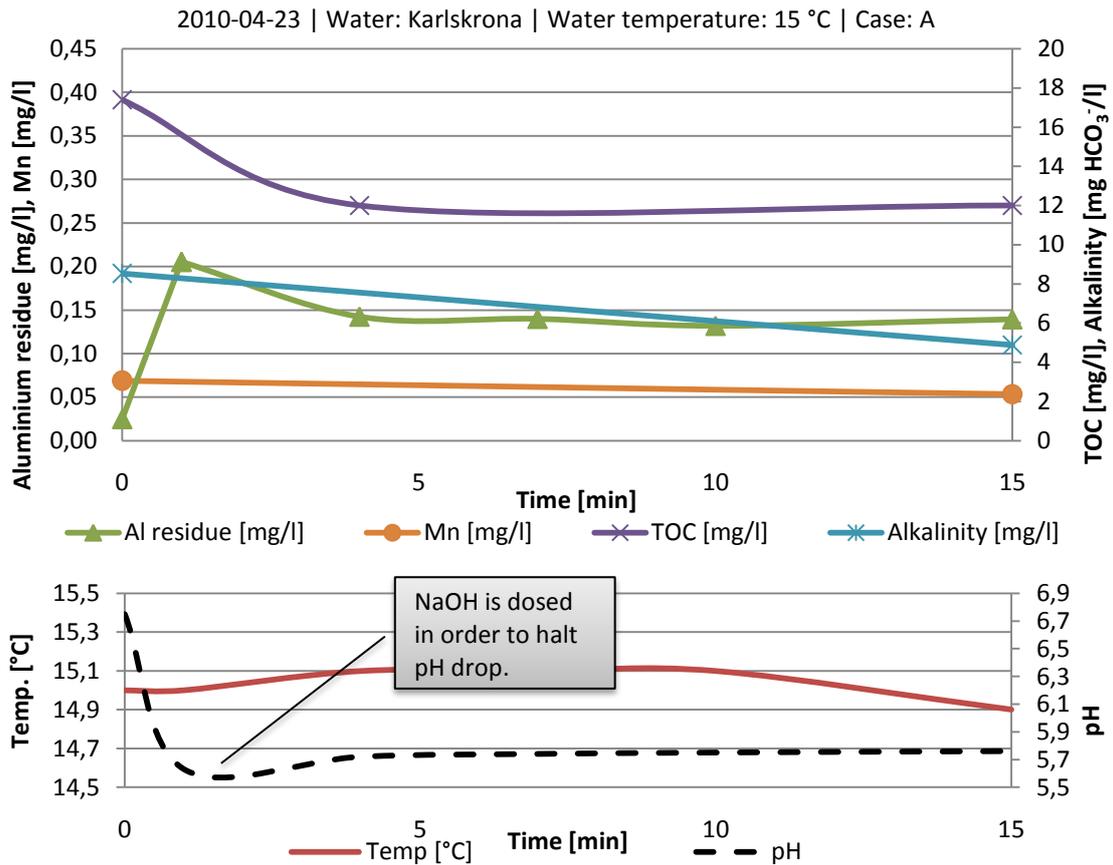
Figure 5.4 Aluminium residue in warm water without CaCO₃ addition, and corresponding pH and temperature changes.

The B cases present different percentage of dissolved calcium carbonate. As for the A cases, the properties at time zero represents the raw water. At this time point, 30 mg Mikrostevns is dissolved for a certain amount of time until a desired percentage of solved calcium carbonate is achieved. The time it takes to dissolve the desired percentage of calcium carbonate varies greatly between the cases, and is generally longer in cold water cases. The solubility curves are plotted in Figure 5.11 to Figure 5.13. As Mikrostevns is added, the alkalinity levels increase until Ekoflock 70, which "consumes" alkalinity. One minute after Ekoflock 70 addition, the aluminium levels are increased and pH value decreased. The decrease seems however just temporary, since the pH starts to increase gradually with time.

While manganese and TOC follow the same pattern, the alkalinity and aluminium residue patterns are more diverse among the different cases. The levels of mean aluminium residue are generally lower in all cases performed in 15 °C compared to 0.5 °C cases. In almost all cases there is a local aluminium residue minimum present about three to six minutes after Ekoflock 70 addition. In Figure 5.14 mean aluminium residue levels for all cases in all the three raw waters are presented.
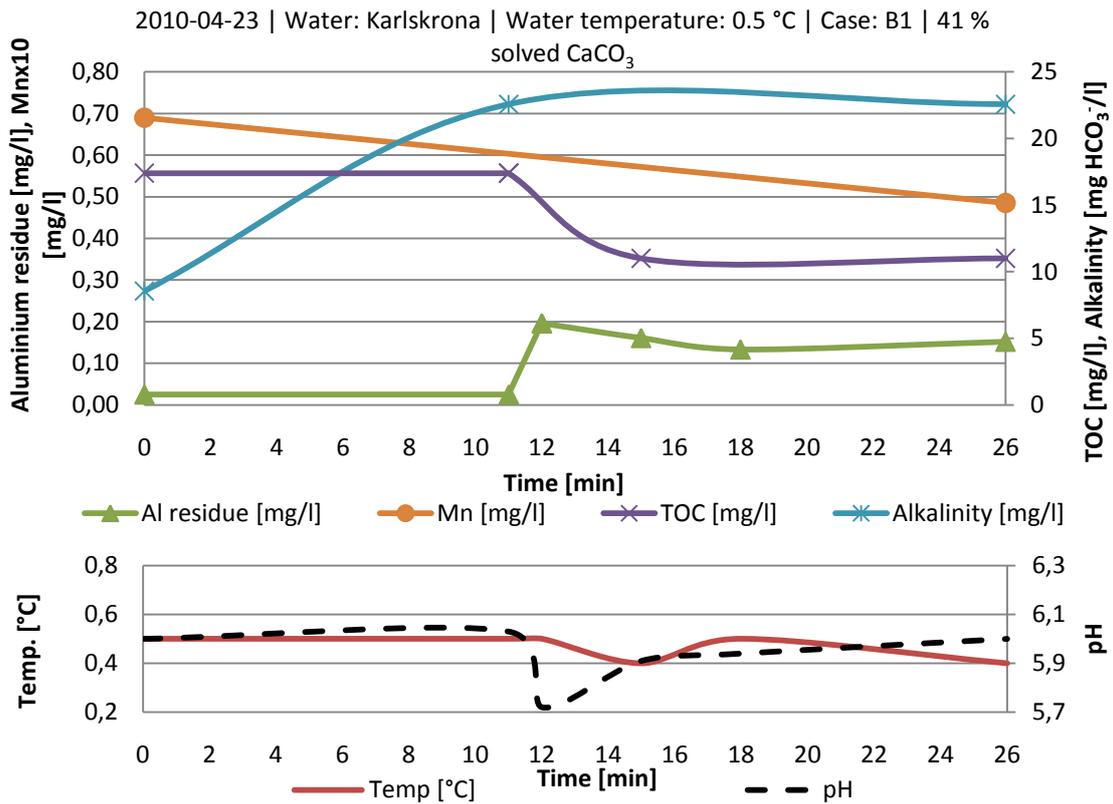
Figure 5.5 Aluminium residue in cold water after 41 % solved CaCO₃, and corresponding pH and temperature changes.
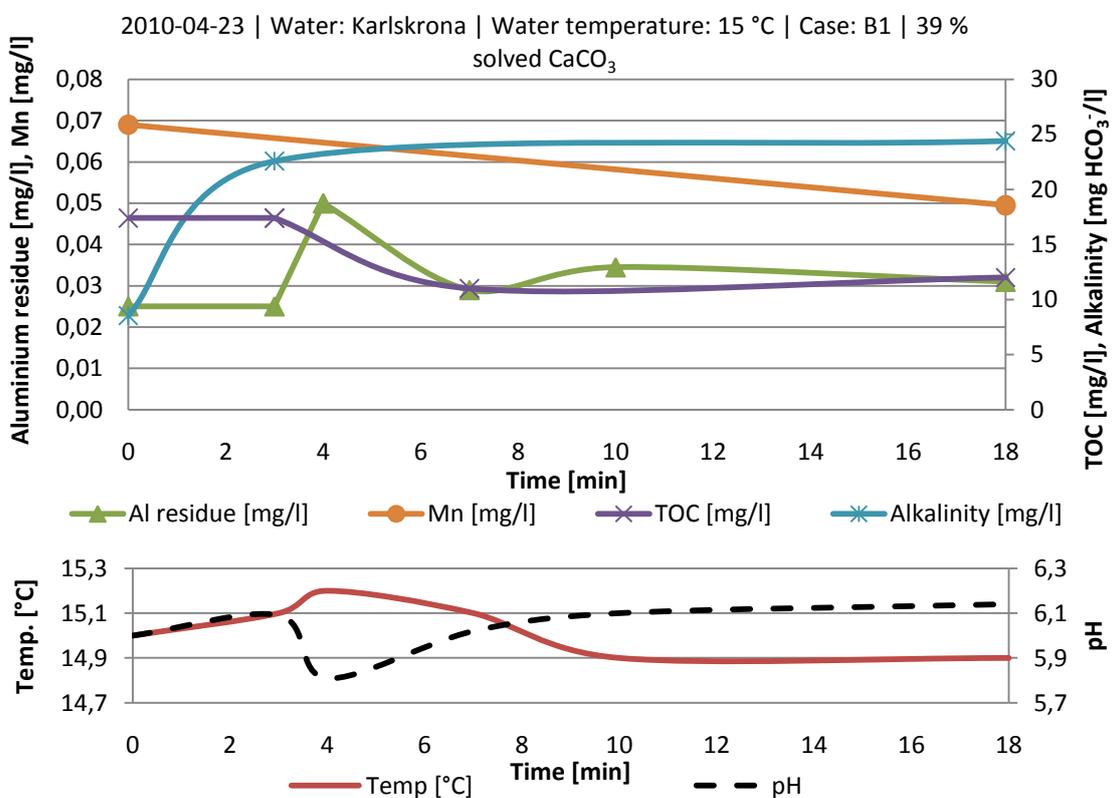
Figure 5.6 Aluminium residue in warm water after 39 % solved CaCO₃, and corresponding pH and temperature changes.

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35
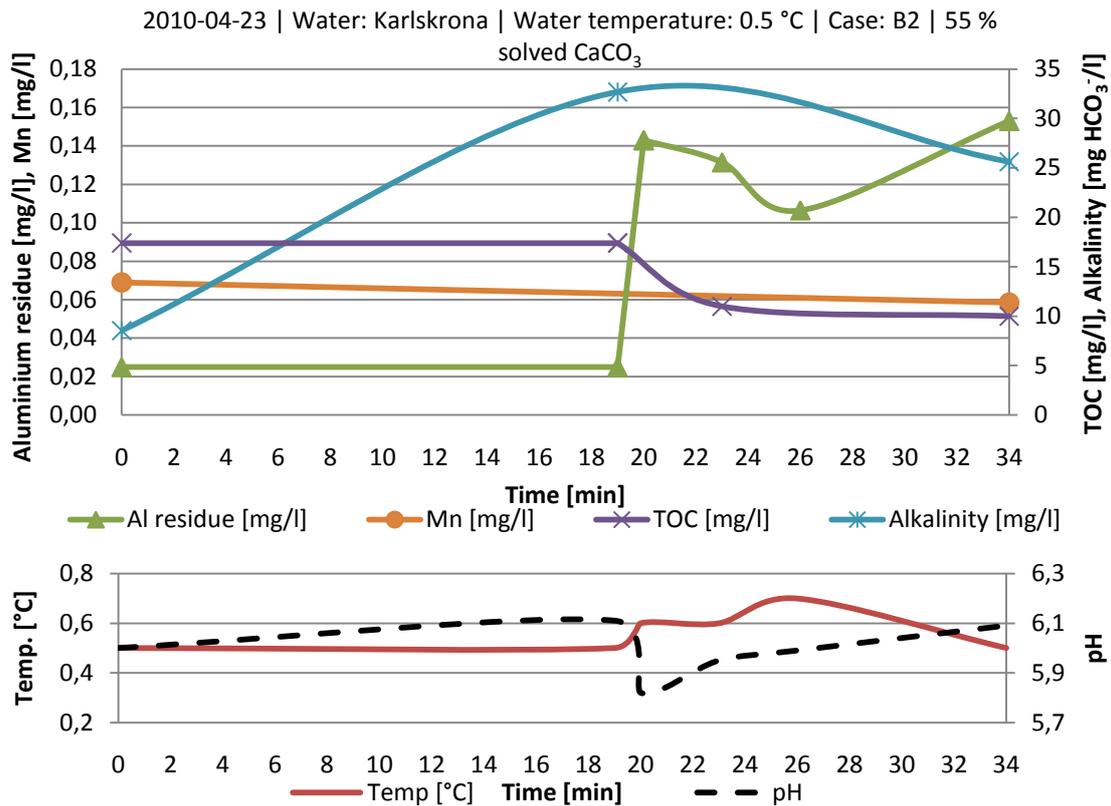
Figure 5.7 Aluminium residue in cold water after 55 % solved CaCO₃, and corresponding pH and temperature changes.
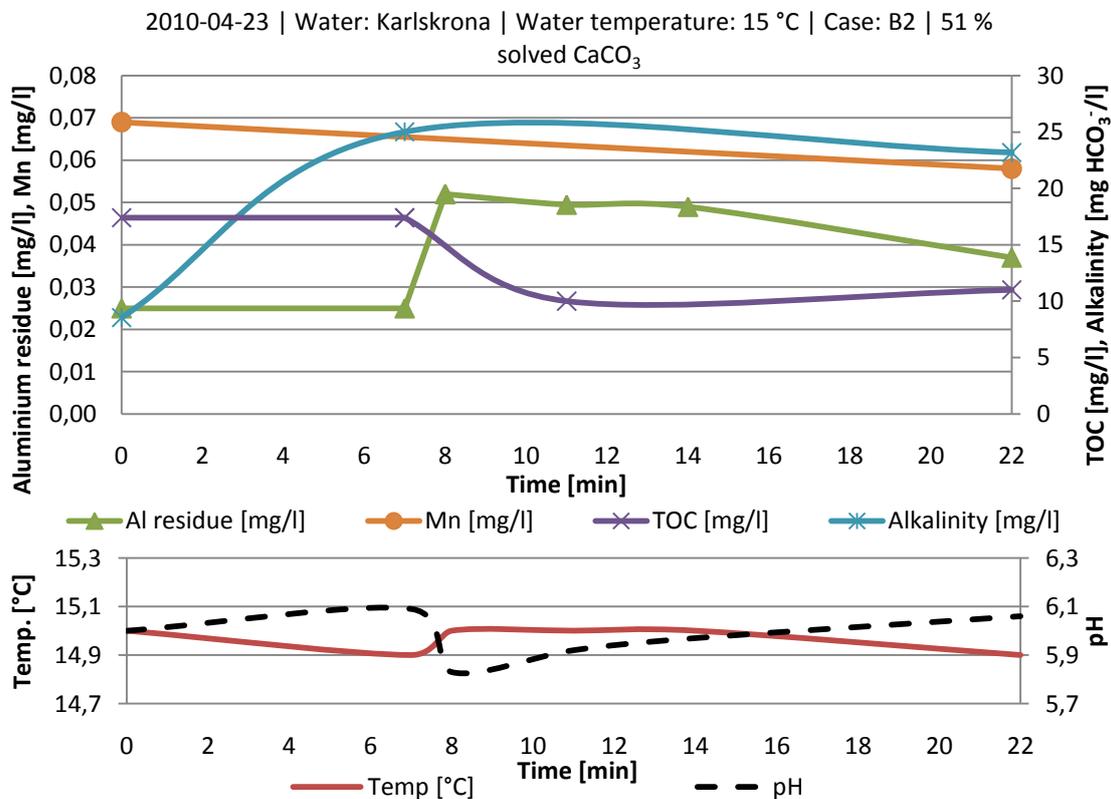
Figure 5.8 Aluminium residue in warm water after 51 % solved CaCO₃, and corresponding pH and temperature changes.
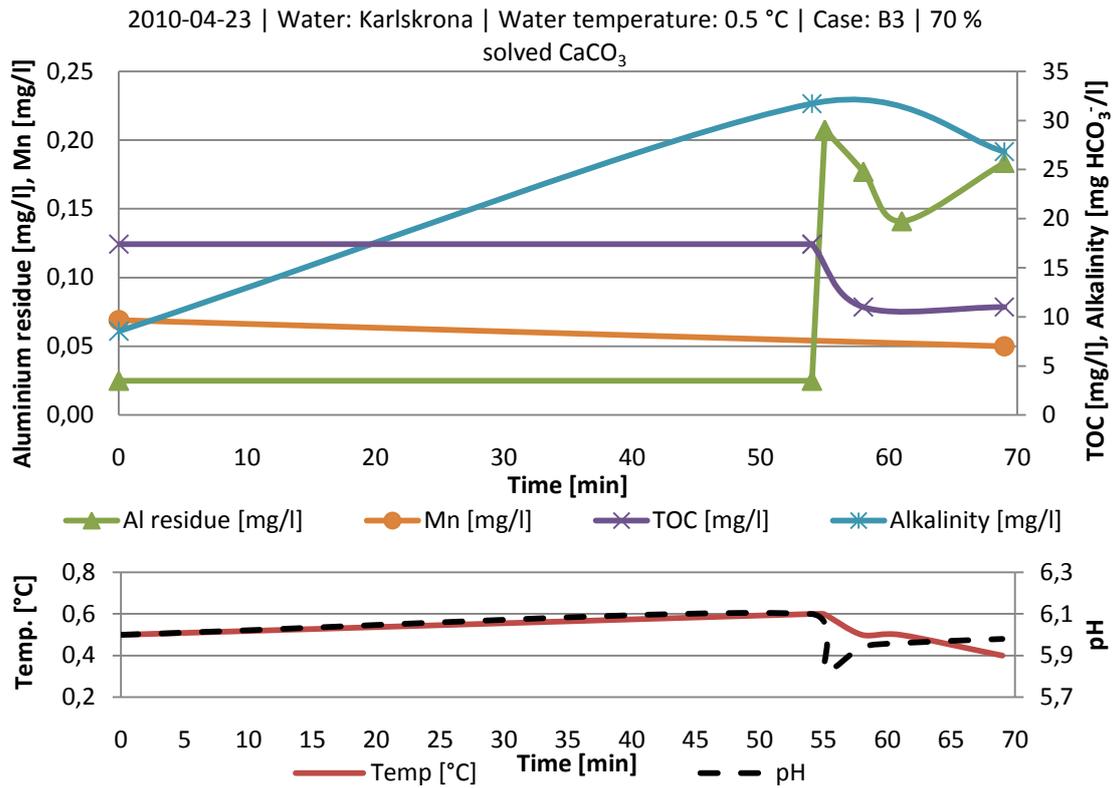
Figure 5.9 Aluminium residue in cold water after 70 % solved CaCO₃, and corresponding pH and temperature changes.
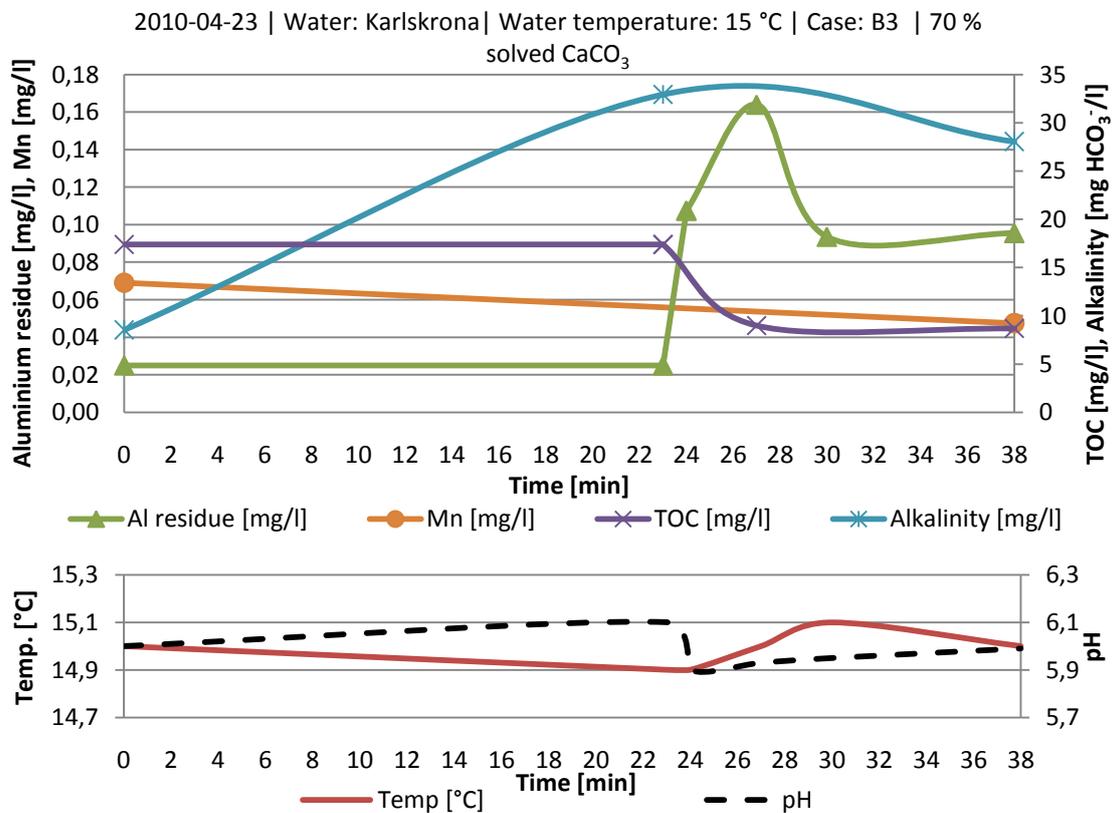
Figure 5.10 Aluminium residue in warm water after 70 % solved CaCO₃, and corresponding pH and temperature changes.

5.2.2 Mean aluminium residue at various levels of dissolved calcium carbonate

Each diagram, Figure 5.11 to Figure 5.13, contains two curves and six bars. The curves are showing the solubility of calcium carbonate at 0.5 °C and 15 °C during a 90 minute time frame. Each of the six bars symbolises the minimum, mean and maximum aluminium residue values that are obtained in cases B1, B2 and B3 for cold and warm water. The different minimum, mean and maximum values give a transparency to the tests, since the bars show the variation of aluminium residue. The aluminium residue bars are positioned on the horizontal time axis to represent the corresponding calcium carbonate solubility level on the right vertical axis.

The aluminium residue levels are generally lower in cases with raw water from Lerum, whereas Karlskrona and Kristinehamn are generally higher. Cold water results in higher aluminium residue levels compared to warm water. Since the calcium carbonate dissolution rate is lower in cold water, it takes longer time to reach the desired percentage of solved calcium. After 90 minutes, approximately 80 to 90 percent of the added calcium carbonate has been dissolved in all raw waters.
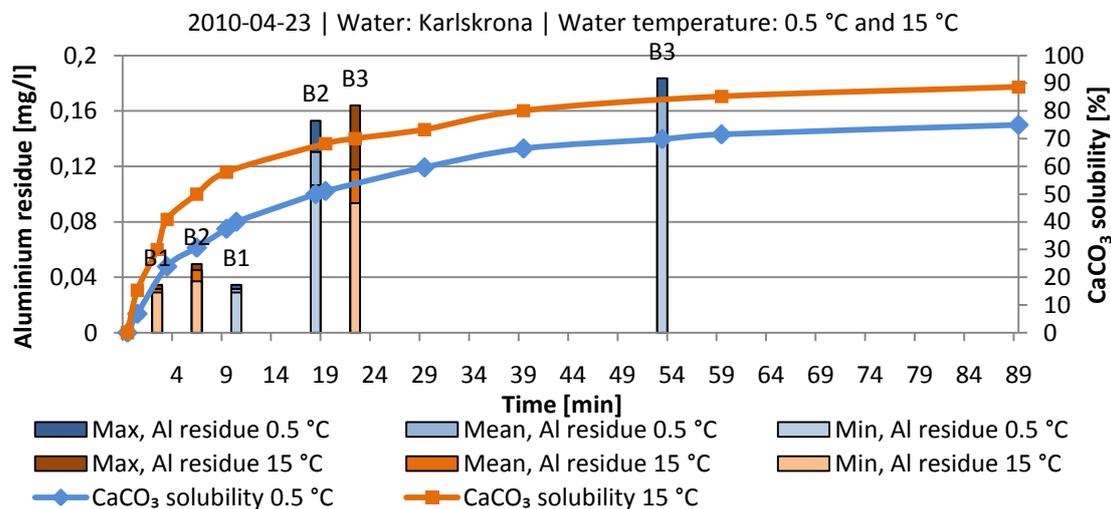
Figure 5.11 Aluminium residue at various levels of dissolved calcium carbonate in cold and warm water, Karlskrona.
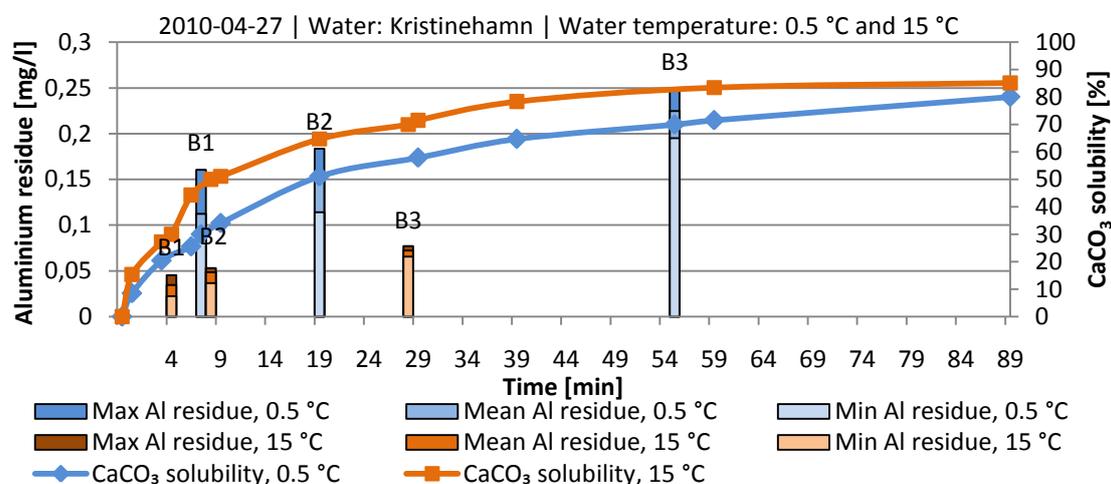
Figure 5.12 Aluminium residue at various levels of dissolved calcium carbonate in cold and warm water, Kristinehamn.
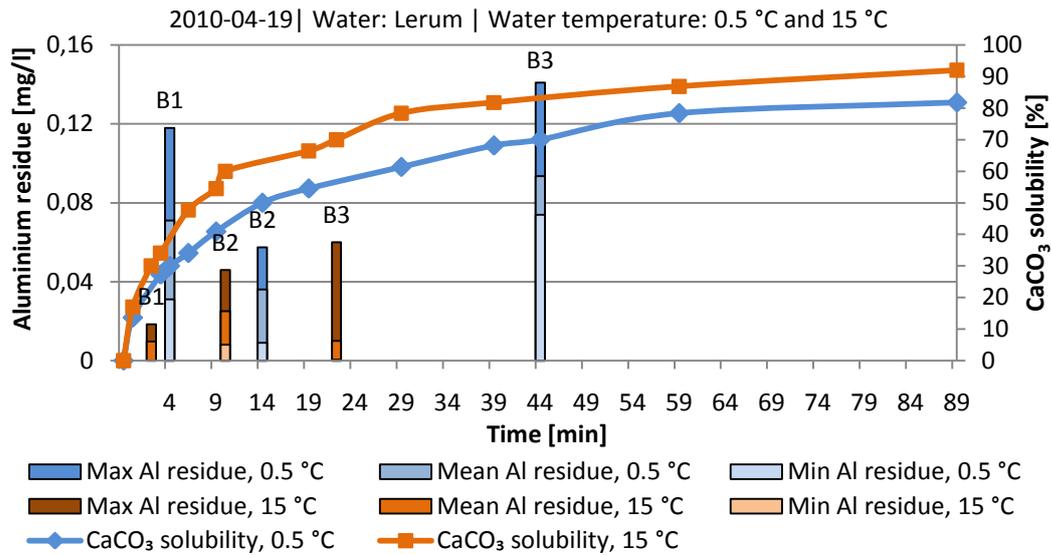
Figure 5.13 Aluminium residue at various levels of dissolved calcium carbonate in cold and warm water, Lerum.

When Figure 4.3 – Figure 4.5 are compared with Figure 5.11– Figure 5.13; it is evident that the calcium carbonate dissolution curves differ, at least during the first 10 minutes of detention time, for Karlskrona and Kristinehamn. However, Lerum has almost identical dissolution curves. The corresponding temperature and pH for all three plants are almost the same, though there is probably a slight delay before the samples are filtered in the first test round compared to the second. Yet, it appears as if there is another parameter, other than the measurement procedure, that affects the dissolution curve. One probable reason for the dissolution curve can be found by analysing the raw water. It is evident, from Table 4.1 and Table 5.1, that the alkalinity is significantly higher in Karlskrona and Kristinehamn during the first test round. In Lerum, on the other hand, there is no apparent difference in alkalinity for the two occasions.

The minimum, mean and maximum values are selected after 1, 4, 7 and 15 minutes after PAC addition. The bars in Figure 5.14 show mean aluminium residue, after Ekoflock 70 has been added, in warm and cold water in all cases for raw water from Karlskrona, Kristinehamn and Lerum. Above each bar, the mean pH value, during the 15 minute of chemical coagulant presence, is displayed respectively. It seems that higher percentage of solved calcium carbonate correlate to increased aluminium residue levels. There are also clear differences between the raw waters.
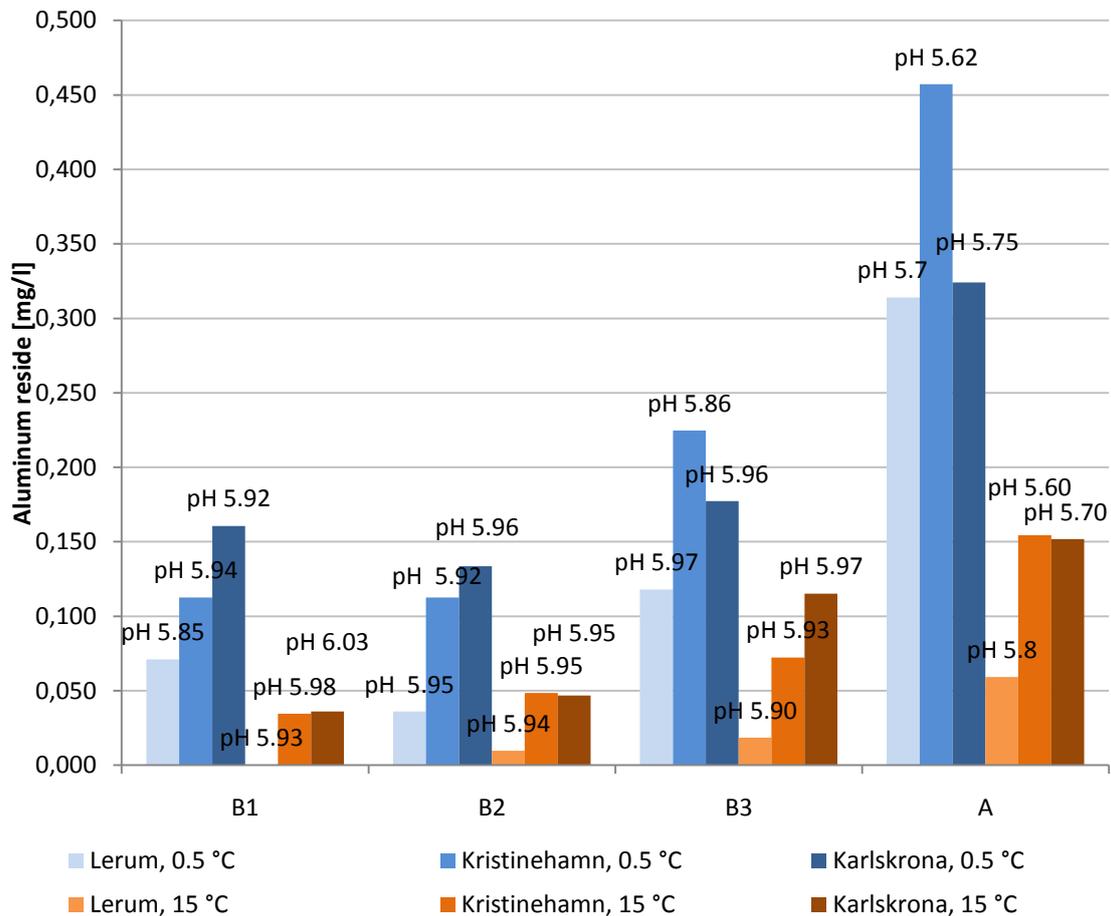
Figure 5.14 Mean aluminium residue in three scenarios of dissolved calcium carbonate and one scenario (A) without dissolved calcium carbonate. B1≈30 % solved CaCO₃, B2≈50 % solved CaCO₃, B3≈70 % solved CaCO₃.

In tables Table 5.3 and Table 5.4 mean aluminium residue values for each test are summarized and compared to each other. The purpose with the tables is to quantify the cases in which higher amount of solved calcium carbonate results in higher aluminium residue. Totally 16 out of 18 comparisons (if the A cases are excluded) show higher aluminium residue levels as the percentage of solved calcium carbonate increase.

Table 5.3 Schematic comparison of mean aluminium residue (mg/l) at 0.5 °C. The abbreviations AKa means case A, Karlskrona, B1Ka means case B1, Karlskrona etc.

	AKa = 0.32 AKr = 0.45 ALe = 0.35	B1Ka = 0.16 B1Kr = 0.11 B1Le = 0.07	B2Ka = 0.13 B2Kr = 0.15 B2Le = 0.04	B3Ka = 0.18 B3Kr = 0.22 B3Le = 0.09
AKa = 0.32 **AKr = 0.45** **ALe = 0.35**		AKa > B1Ka AKr > B1Kr ALe > B1Le	AKa > B2Ka AKr > B2Kr ALe > B2Le	AKa > B3Ka AKr > B3Kr ALe > B3Le
B1Ka = 0.16 **B1Kr = 0.11** **B1Le = 0.07**			B1Ka > B2Ka *B1Kr < B2Kr* B1Le > B2Le	*B1Ka < B3Ka* *B1Kr < B3Kr* *B1Le < B3Le*
B2Ka = 0.13 **B2Kr = 0.15** **B2Le = 0.04**				*B2Ka < B3Ka* *B2Kr < B3Kr* *B2Le < B3Le*
B3Ka = 0.18 **B3Kr = 0.22** **B3Le = 0.09**				

Table 5.4 Schematic comparison of mean aluminium residue (mg/l) at 15 °C. The abbreviations AKa means case A, Karlskrona, B1Ka means case B1, Karlskrona etc.

	AKa = 0.15 AKr = 0.15 ALe = 0.059	B1Ka = 0.036 B1Kr = 0.035 B1Le = 0.01	B2Ka = 0.047 B2Kr = 0.049 B2Le = 0.020	B3Ka = 0.115 B3Kr = 0.072 B3Le = 0.025
AKa = 0.15 **AKr = 0.15** **ALe = 0.059**		AKa > B1Ka AKr > B1Kr ALe > B1Le	AKa > B2Ka AKr > B2Kr ALe > B2Le	AKa > B3Ka AKr > B3Kr ALe > B3Le
B1Ka = 0.036 **B1Kr = 0.035** **B1Le = 0.01**			*B1Ka < B2Ka* *B1Kr < B2Kr* *B1Le < B2Le*	*B1Ka < B3Ka* *B1Kr < B3Kr* *B1Le < B3Le*
B2Ka = 0.047 **B2Kr = 0.049** **B2Le = 0.020**				*B2Ka < B3Ka* *B2Kr < B3Kr* *B2Le < B3Le*
B3Ka = 0.115 **B3Kr = 0.072** **B3Le = 0.025**				

Normal text = higher amount of dissolved calcium carbonate results in lower aluminium residue

Bold italic text = higher amount of dissolved calcium carbonate results in higher aluminium residue

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35

5.2.3 TOC reduction compared to aluminium residue

In this section, the TOC reduction in each case (A, B1, B2, B3) is plotted against the corresponding mean aluminium residue in raw water from Karlskrona, Kristinehamn and Lerum.

As illustrated in Figure 5.15, all tests performed with raw water from Kristinehamn result in TOC reductions well above 50 %, irrespectively of water temperature. However, only tests performed at 15 °C are below the aluminium limit value. According to the figure, it is evident that TOC reduction seems independent of amount of removed aluminium. Although the aluminium residues in all Lerum tests are below the limit value, the TOC reductions are below 50 %. Most of the tests performed in raw water from Karlskrona are below 50 % TOC reduction and above the aluminium limit value.
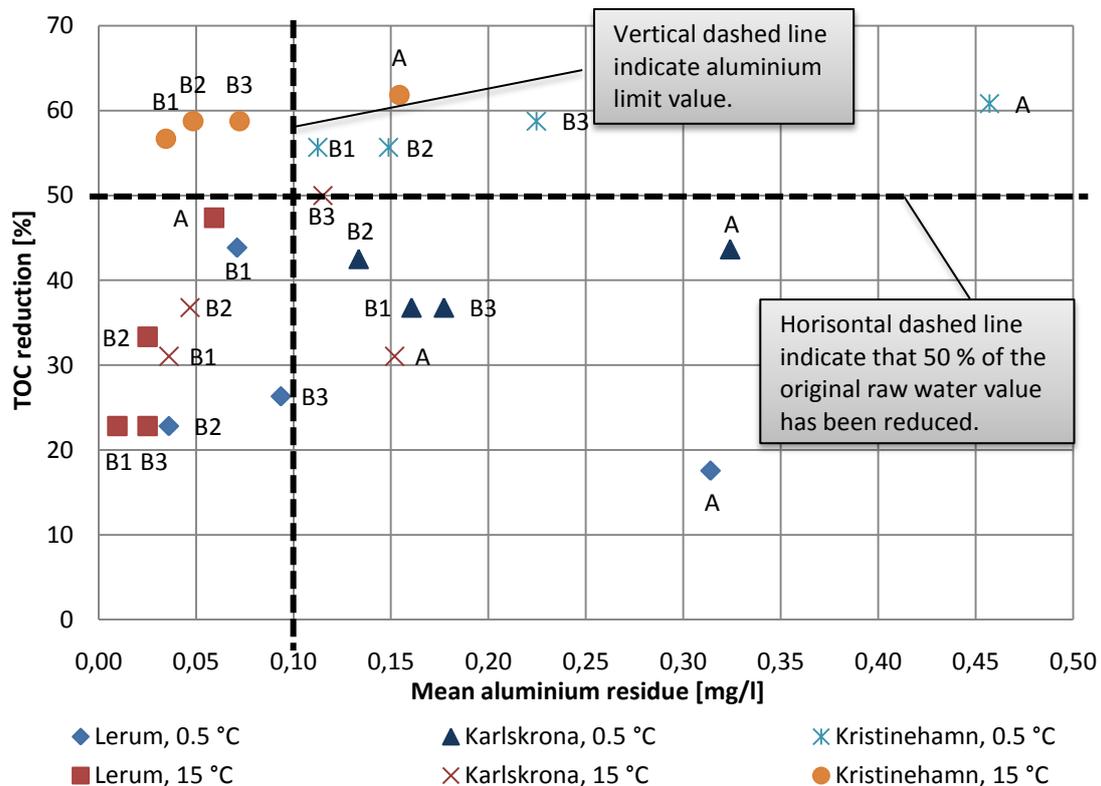
Figure 5.15 Percent of reduced TOC compared to mean aluminium residue values. The 0.100 mg aluminium per litre limit value is indicated in the figure, as well as a 50 % TOC removal border.

By plotting the final TOC values, obtained 15 minutes after the addition of Ekoflock 70, the relation looks different compared to Figure 5.15. In Figure 5.16 all tests in Kristinehamn and Lerum are reduced to around 4 mg TOC/l, while the final TOC values are around 11 mg/l for Karlskrona raw water.
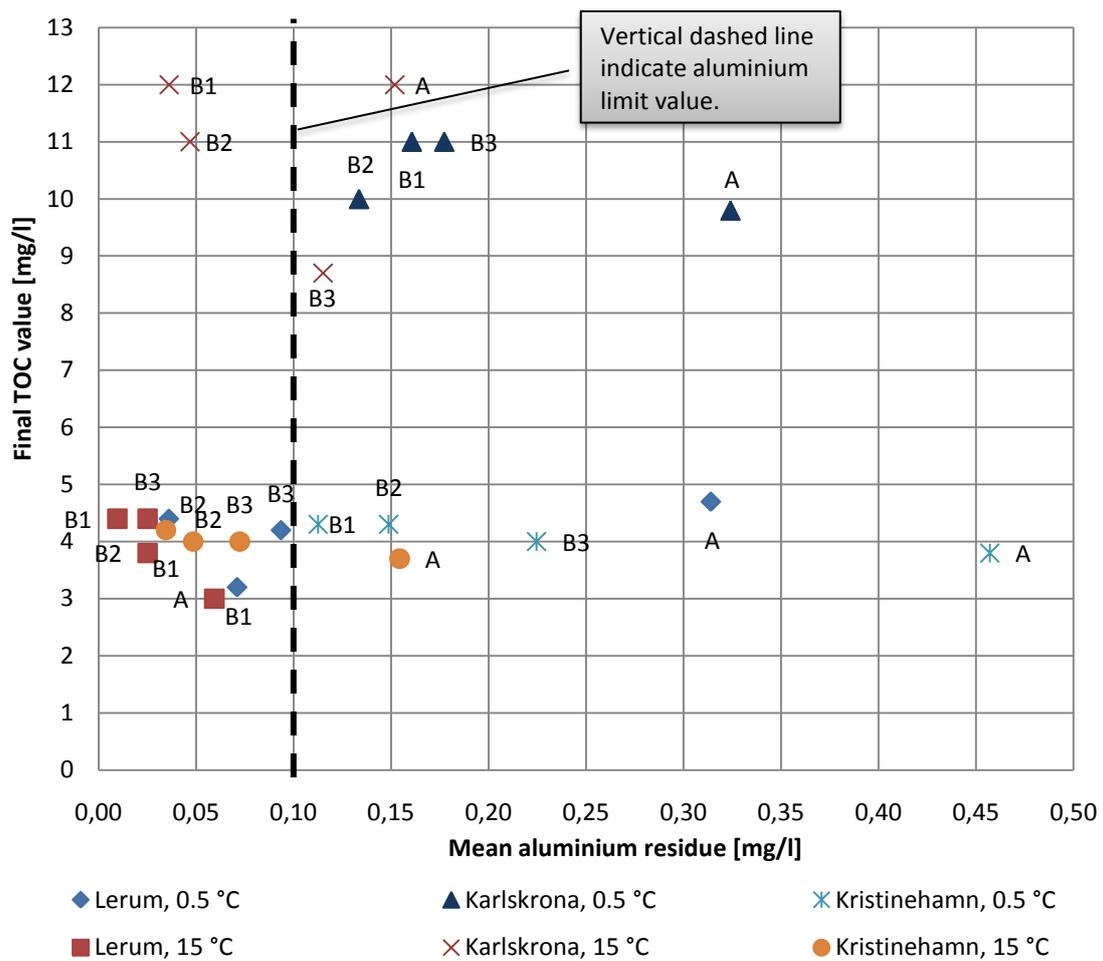
Figure 5.16 Final TOC value 15 minutes after Ekoflock 70 addition in all 24 tests in warm and cold water.

CHALMERS, *Civil and Environmental Engineering*, Master's Thesis 2010:35

6   Discussion

The problems of insufficient calcium carbonate solubility and high aluminium residues, experienced in the water treatment plants, were without difficulties repeated in the laboratory tests that were conducted in this study. As seen in Table 3.5, the time between chemical dosing and detention times in DynaSand filters varies between the three water treatment plants. The first and second test round indicate that dissolving calcium carbonate is a time consuming process, which is significantly slowed down as water temperatures decrease and as pH values increase. Insufficient amount of dissolved calcium carbonate was originally believed to cause high aluminium residue. However, the second test round indicates that partly dissolved calcium carbonate is in fact preferable compared to no or entirely dissolved calcium carbonate, which is discussed further on.

The first test round verifies the conditions which are important for calcium carbonate dissolution, that have been discussed in Section 2.2. A simplified relation-chart is presented in Figure 6.1 and represents the most important findings, regarding the factors contributing to calcium carbonate solubility and aluminium residue. The factors are presented in the text below.
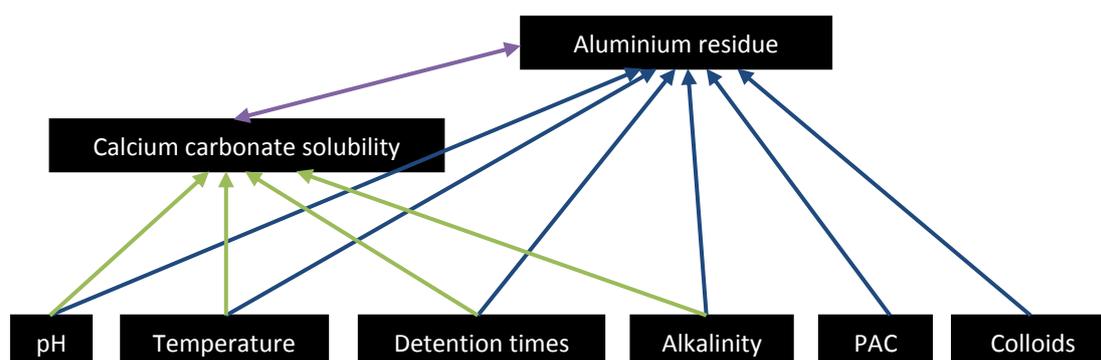
Figure 6.1 Simplified relation-chart of calcium carbonate solubility and aluminium residue, based on the results from section 4 and section 5.

pH

The connection between low pH values and high calcium carbonate dissolution rates has been confirmed both in literature and test rounds one and two. Optimum precipitation pH for coagulation chemicals containing aluminium is found at higher pH, approximately $6.0 - 6.5$, which could be one explanation to why the tests from the second test round (A cases) did not result in satisfying aluminium residue levels. This is discussed further on in this section.

Regarding the inhibiting factors on calcium carbonate dissolution, such as manganese and iron contents, it is not possible to see any effects of those in the test rounds. As stated in Section 2.2.1, the pH of the water needs to be above approximately pH 7 in order to detect any effect on calcium carbonate dissolution caused by the named inhibitors. The absence of any recognisable inhibiting effects, are probably due to the low pH values during the tests.

Temperature

The water temperature appears to be superior to raw water properties, regarding both calcium carbonate dissolution and aluminium residue. In general, the calcium carbonate dissolution rate appears to be slower and aluminium residue concentrations to be higher at 0.5 °C compared to 15 °C. At 15 °C, the calcium carbonate solubility rate increase substantially and aluminium residue levels decrease. The aluminium residue values are consequently higher in cold water, probably due to increased need of activation energy. An increase in temperature of 1 °C corresponds to an observed increase in solubility of calcium carbonate of approximately one percentage point. These temperature relations have been evident in raw water from Karlskrona, Kristinehamn and Lerum, gathered on two separate occasions, which are displayed in Table 4.1 and Table 5.1. This confirms Figure 2.2, which say that the activation energy for chemical reactions increase as the water temperature decrease.

Detention times and rotation velocity

Karlskrona and Kristinehamn water treatment plants have the longest and shortest detention times, in terms of the chemical precipitation process, yet they experience most problems of the three plants. This raises the question as to whether it is the chemical coagulants that has the most significant impact to the treatment process, rather than the detention times.

As stated in Section 2.2, the rotation velocity of the mixing device is considered to be of high importance when determining the calcium carbonate dissolution rate. On the contrary, the first test round, which compares 20 rpm to 50 rpm stirring speeds, does not demonstrate higher dissolution rate when the stirring speed is increased. Instead some cases point towards lower dissolution rates for higher stirring speeds. Although, the reason for this could derive from some disturbances, such as solid unit rotation of the water, caused by higher stirring speed. Perhaps an even greater difference in stirring speed could show the positive effects of increased energy input on calcium carbonate dissolution rates.

Alkalinity and calcium carbonate

As stated in Section 5.2.2, the alkalinity appears to affect the dissolution of calcium carbonate. Results from the first and second test round indicate that higher alkalinity is beneficial for the calcium carbonate dissolution. In addition, from Section 2.2 it is known that the properties of calcium carbonate seem to be important for its dissolution rate. Smaller fractions should increase the dissolution rate. The properties of the investigated calcium carbonate should be equal, since all water treatment plants in this study use Mikrostevns from the same distributor as calcium carbonate. However, Figure 4.13 to Figure 4.15 illustrate that e.g. Mikrostevns from Lerum dissolves slightly better in all three raw waters in this study. Mikrostevns from Kristinehamn, on the other hand, has the worst dissolution in all three raw waters. This leads to the conclusion that the quality of the calcium carbonate appears to differ from one delivery to the next since the dissolution results vary slightly. Probably, Kristinehamn received a calcium carbonate with a slightly different fraction distribution, although, the differences could also originate from the execution of the test rounds.

Unsolved particles of calcium carbonate do not indicate to be the cause of higher aluminium residue, according to the figures in Section 5.2.2. Instead, Figure 5.11 clearly shows that when approximately 30 − 50 % of the calcium carbonate is dissolved, lower aluminium residue, compared to 0 % and 70 %, is obtained. This is further described in Figure 5.14, Table 5.3 and Table 5.4, which illustrate that 16 out of 18 tests (if the A cases are excluded) display higher aluminium residue levels as the percentage of dissolved calcium carbonate increase. Different pH values, alkalinity levels and calcium ions, reacting with colloids, during the 15 minutes of chemical precipitation, could be part of the explanation to the aluminium residue results. However, Figure 5.14 show that the mean pH is slightly below pH 6 in all B cases and pH variations are small. In the A cases, on the other hand, the mean pH is approximately 5.7 and, on top of that, span over a larger pH range. As discussed in Section 2.3 the precipitation pH should lie between 6.0 and 6.5 to achieve as low aluminium residue values as possible. The considerably higher aluminium residue values in all A cases could partly relate to the lower mean pH.

From the A cases displayed in Figure 5.3 and Figure 5.4, it is possible to see that all alkalinity in the raw water is consumed. This indicates that the addition of calcium carbonate in the B cases, which result in increased alkalinity levels, are necessary to achieve low aluminium residue concentrations. Though, if the pH levels are increased in the A cases, due to sodium hydroxide addition, this would perhaps make up for the low alkalinity levels.

When comparing alkalinity development after PAC addition in case B1 to B3 for cold and warm water, an interesting pattern can be seen in almost all cases. In the B1 cases, where approximately 30 % of calcium carbonate is dissolved, alkalinity levels show almost no decreases during the 15 minutes of flocculation. In the B3 cases, major alkalinity decreases are evident when comparing alkalinity levels at the time when Ekoflock 70 is added and 15 minutes later. The alkalinity differences in the B1 and B3 cases are probably caused by the difference in percentage of dissolved calcium carbonate at the moment when Ekoflock 70 is added. In the B1 cases, the pH lowering caused by dosing Ekoflock 70, probably increases the calcium carbonate dissolution rate and thereby dissolves much of the 70 % remaining calcium carbonate. The B3 cases do not contain as much unsolved calcium carbonate, which means that it is not possible to keep a constant alkalinity level since the consumption of HCO_3^- ions are smaller than the addition of them. Eq. 1 demonstrates that calcium ions (Ca^{2+}) are released when calcium carbonate dissolves in water. It is possible that these positive ions, which increase in quantity as calcium carbonate is dissolved, attach to the negative colloids according to the principle illustrated in Figure 2.4. This would make the colloid surfaces positively charged which results in repelling forces when positive aluminium ions (Al^{3+}) are dissolved into the water due to the addition of Ekoflock 70. These free aluminium ions are then causing the increased aluminium residue.

PAC

The dose of chemical coagulant can be decided based on numerous factors, but the values of colour and COD provide a quick estimate of the chemical dose. From Table 3.3 we learn that Kristinehamn use Ekoflock 91, which contain more aluminium than Ekoflock 70. In accordance with the arguments presented in Section 2.3, higher amount of added aluminium will only cause lower aluminium residue. However, it is important that the pH remains within the optimum pH range or else the positive

effects from high PAC dosage could fail to appear. It is also important to recognise that the dosage, used in the tests, differs from the actual and theoretical dosage in the plants. Hence, the results might be somewhat misleading in the sense that the laboratory dose is optimum for one type of raw water but not for all.

The acidifying effect of the chemical coagulant provides a favourable pH range to dissolve calcium carbonate and at the same time create coagulation and flocculation. In the cases where PAC are dosed before calcium carbonate and starting at high aluminium residue levels (Section 4.2.5), the final aluminium content after 15 minutes of flocculation, are significantly lower. Repeated tests for Kristinehamn, on the contrary, demonstrate aluminium residue values above the upper measurement range, and no decrease in high aluminium residue values (Figure 4.19). The reason for this might be a substantially low precipitation pH resulting in a non-optimum precipitation process.

In cases where calcium carbonate is dosed before the chemical coagulant, the aluminium residue values are higher at 0.5 °C compared to 15 °C. This is evident in both the first and second test round.

In the second test round, when comparing Figure 4.20 from test round one with case B1 and B2 for 0.5 °C raw water from Lerum, lower aluminium residues are obtained in the second test round. The relationship between increased chemical coagulant dose and higher aluminium residue is demonstrated when comparing the first and second test round of Lerum raw water, which has similar properties of raw water quality. A lower dose of Ekoflock 70, from the first test round, resulted in a higher aluminium residue compared to a higher dose in second test round.

Aluminium residue

Lerum has had the lowest aluminium residue levels in both test rounds in this study. Lower concentrations of colour, turbidity, COD and TOC in Lerum compared to Karlskrona and Kristinehamn, are likely an explanation to this. For Lerum, the dose of 42 and 60 mg Ekoflock 70 per litre appears to be sufficient to cause collisions between hydrated aluminium complexes and colloids. This enables coagulation to occur in the destabilization region according to Figure 2.5. In the same way, raw water from Karlskrona and Kristinehamn contain a higher amount of colloids, which means that a higher aluminium dose is required to reach a suitable region for precipitation. With the chosen dosage of PAC, Karlskrona and Kristinehamn are believed to end up in the re-stabilization region, which causes high aluminium residue according to Figure 6.2.

In almost all cases in the second test round, the aluminium residue levels have increased substantially 15 minutes after Ekoflock 70 has been dosed compared to between four and seven minutes after addition, where a local minimum often is present. This phenomenon is much more evident in tests performed at 0.5 °C compared to 15 °C. Cases B3 on raw water from Kristinehamn (Appendix D2) are good examples of this difference. Starting at raw water aluminium content of 0.28 mg/l, the aluminium residue is reduced to 0.066 mg/l in the warm water case and 0.20 mg/l in the cold water case after four minutes. From here on, the aluminium residue levels increase and reach 0.072 mg/l (15 °C) and 0.24 mg/l (0.5 °C) after 15 minutes of flocculation.

During the first four minutes, aluminium ions cause aggregation of hydrophobic colloids by reducing the electrical forces in the stern and diffusive layers around the colloids, according to Section 2.3. This reduces the number of free hydrated aluminium complexes in the water, and thereby the measurable aluminium residue levels. After the local aluminium residue levels at four minutes of flocculation, it is possible that the colloids are starting to aggregate in to even larger flocs according to Figure 6.2. This aggregation causes aluminium ions to detach from the surface of some of the colloids. Some colloids now have negative surfaces, which enables those which are covered with positive aluminium ions to attach to the negative colloids and thereby taking potential places for aluminium ions. It is also possible that free positive calcium ions, due to calcium carbonate addition, may attach to these negative colloids surfaces. In cold water the water movements around each colloid are believed to be smaller, i.e. the turbidity is less. As a result of this, the aggregation of colloids into larger colloids is believed to be larger. During the laboratory tests, ocular observation of the flocs indicated no difference in flocs formed at 0.5 °C compared to 15 °C. However, it is possible that observation of flocs on microscopic level will show differences.
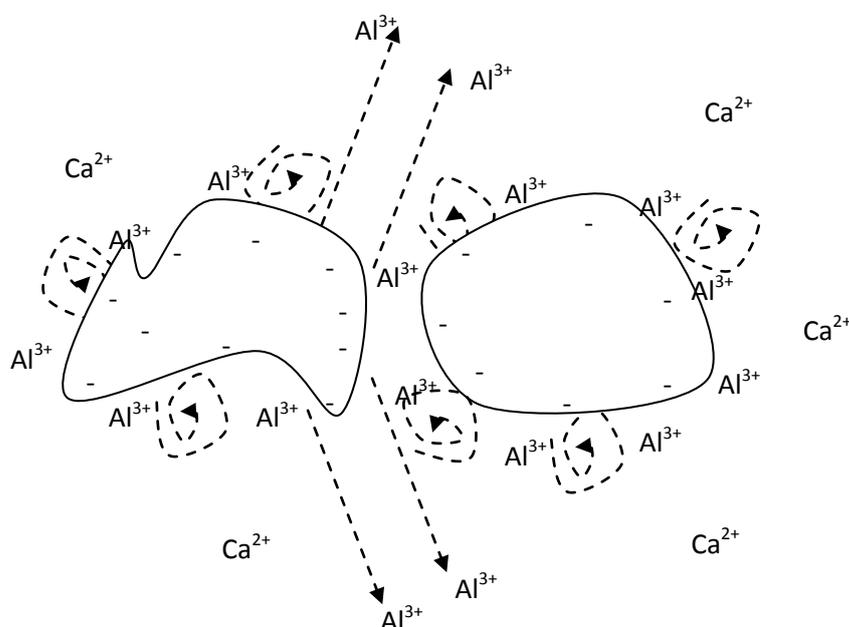
Figure 6.2 Aggregation between colloids may cause aluminium ions to detach from colloid surfaces and cause increased aluminium residue levels.

Colloids

During the first test round the raw water from Karlskrona were of unusually good quality in terms of e.g. colour and turbidity compared to the quality of previous winters (Figure 3.5). Nevertheless, calcium carbonate solubility was decreased and aluminium residue increased as laboratory tests were performed at low temperature. Since the raw water had good quality with low concentrations of humic substances, which is believed to disturb the treatment process during winters, the raw water properties are not likely to be the main probable cause in this case.

TOC is measured as an indicator on how effective the chemical coagulant and dosage of Ekoflock 70 is. Low aluminium residue values are supposed to result in high percental TOC reduction. However, the TOC reduction plots in Figure 5.15 and

Figure 5.16 indicate that TOC reduction is independent of mean aluminium residue concentrations. In 16 out of 24 tests, TOC is reduced to approximately 3 mg per litre, although Kristinehamn starts at 9.7 mg TOC per litre and Lerum at 5.7. Probably 3 mg/l represent a reduction limit for this dose of Ekoflock 70. Since both Kristinehamn and Lerum reach the same final TOC value, although having different raw water qualities, the dose of 60 mg/l seems reasonable in this perspective. Karlskrona has almost the same percental TOC reduction as Lerum, but the final TOC values are around 11 mg/l. This might relate to the high starting value of 17.4 mg/l. It is likely that a higher dose of chemical coagulant will increase the reduction of TOC in Karlskrona. However, this must verified by testing.

6.1 Elements of uncertainty

Test round one and two have been designed in collaboration with supervisors and advice and requests from the responsible people from the water treatment plants. In addition, literature has been consulted before, during and after the laboratory tests. However, since the research partly relies on sampling low quality raw water i.e. water from typical winter conditions, the first sample occasion is perceived as somewhat hurried. If more time had been given to early literature studies, it is possible that the first test round could have been made more directed.

All tests are time consuming, which means that it is not realistic to fully ensure statistical significance, by performing extensive and repeated sample taking and testing. Failed tests were not always repeated, due to shortage of time. It should be noted that the collected and analyzed raw water is only a random sample and there is a risk that the sample is not representative. In addition, the test results are sensitive to errors since only one of each test is performed for many of the scenarios. Errors also include e.g. wrong dosage, handling, computing, information, contaminated equipment and diluted samples.

7   Conclusion

In this section, the main conclusions from both the literature study and from the two laboratory test rounds are presented along with proposed areas of further investigation.

Calcium carbonate dissolution

- The pH level in the water is the most important factor for calcium carbonate dissolution rate. The dissolution rate increase as pH decrease
- Dissolution rate is lower at 0.5 °C compared to at 15 °C
- Smaller fractions of calcium carbonate are positive for the calcium carbonate dissolution rate
- The composition of calcium carbonate (Mikrostevns) appears to differ slightly from one delivery to the next, since the dissolution rates vary slightly
- The total percentage of dissolved calcium carbonate increase with longer detention times
- There is no apparent change in dissolution rate when the stirring speed is increased from 20 rpm to 50 rpm
- Inhibiting effects, caused by iron and manganese, are absent since pH is too low

Aluminium residue

- Aluminium residue levels are higher at 0.5 °C compared to 15 °C
- Higher aluminium residue levels at 0.5 °C compared to 15 °C could be a result of lowered flocculation velocity caused by increased viscosity in cold water. This means that a lower amount of the added aluminium ions in the chemical coagulant are able to attach to colloid surfaces
- Optimum precipitation pH is approximately 6.0 − 6.5. pH levels outside this interval results in increased aluminium residue
- The type of chemical coagulant is of importance for the precipitation process
- TOC reduction seems to be independent of mean aluminium residue
- During the 15 minutes of flocculation time, the lowest aluminium residue levels are obtained after four minutes of flocculation. After this, aggregation between colloids may cause aluminium ions to detach from colloid surfaces and cause aluminium residue levels to increase

Calcium carbonate, chemical coagulant and aluminium residue

- Unsolved calcium carbonate particles do not seem to cause high aluminium residue levels. Instead, laboratory tests from this study indicate higher aluminium residue as a result of increased percentage of dissolved calcium carbonate
- The water temperature and pH level appears to be superior to other raw water properties, regarding calcium carbonate dissolution rate and aluminium residue levels. However, alkalinity could have a certain influence as well
- Chemical reactions require higher activation energy at 0.5 °C compared to 15 °C, in order to occur. Slower calcium carbonate dissolution rates and higher

aluminium residue levels at 0.5 °C compared to 15 °C are probably caused by the increased activation energy
- Higher dose of chemical coagulant results in a decrease in aluminium residue. However, the precipitation pH has to be within the optimum pH range or else the positive effects from high chemical coagulant dosage will fail to appear
- Laboratory tests indicate that the lowest aluminium residue levels are achieved when both calcium carbonate and chemical coagulants are added to the raw water
- A pH drop, caused by adding chemical coagulant, will probably increase the calcium carbonate dissolution rate
- Positive calcium ions increase in quantity as calcium carbonate dissolves in water. It is possible that these ions, instead of aluminium ions, attach to negative colloids. This will increase the aluminium residue levels, since the aluminium ions are found as hydrated aluminium complexes instead of attached to colloids

7.1 Further investigation

The results from this report should be seen as indications rather than actual facts. It is important that more extensive sample taking and testing are made. This should be conducted during a longer time-span and include raw water of different qualities. New tests could include other parameters for investigation as well as different dosage, chemicals and speed of stirring device. Proposed areas of further investigations include:

- Full scale trials in water treatment plants
- Establish whether warm and cold waters require different treatment procedures
- Microscopic studies of flocs in warm and cold water

8   References

Alkattan, M., Oelkers, E. H., Dandurand, J.-L., & Schott, J. (1998). An experimental study of calcite and limestone dissolution rates. *Chemical Geology , 151* (14), 199-214.

Avdelningen för VA-teknik. (1986). *Kompendium i VA-teknik.* Institutionen för tekniks vattenresurslära, Avdelningen för VA-teknik. Lund: Lunds universtiet.

Cullio, P. A. (1996). *Industrial Minerals and Their Uses - A Handbook and Formulary.* Westwood, New Jersey, USA: Noyes Publications.

Göthe, D., & Israelsson, B. (1992). *Hårdgöring av dricksvatten med krita-kolsyra - ett alternativ till kalk-kolsyra.* Svenska vatten- och avloppsverksföreningen, VAV.

Göthe, D., & Israelsson, B. (1995). *Hårdhetshöjning av dricksvatten med krita-kolsyra - Ett alternativ till kalk-kolsyra.* Svenska vatten- och avloppsverksföreningen, VAV.

Hammer, M. J. (1986). *Water and Wastewater Technology* (Second edition ed.). Englewood Cliffs, New Jesey, USA: Prentice Hall Career & Technology.

Hedberg, T. (1969). *Optimering av den kemiska reningsprocessen samt hårdhetshöjning av mjuka ytvatten.* Göteborg: Chalmers tekniska högskola, Inst. för vattenförsörjnings- och avloppsteknik.

Hernebring, C. (2003). *Drifterfarenheter vid vattenverk med kemisk fällning under hösten/våren 1998-99.* Stockholm: Svenskt Vatten AB.

Karageorgiou, K., Paschalis, M., & Anastassakis, G. N. (2007). Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent. *Journal of Hazardous Materials , 193* (3), 447-452.

Karlskrona kommun. (2010). *Årsrapport för år 2009.* Karlskrona Vattenverk. Karlskrona: Karlskrona kommun.

Kemira Kemwater. (2003). *Konsten att rena vatten.* Helsingborg, Sweden: Kemira Kemwater.

Nordic Water. (2006). *DynaSand Clean Water.* Retrieved April 16, 2010, from Nordic Water Products: http://www.nordicwater.se

Parsiegla, K. I., & Katz, J. L. (2000). Calcite growth inhibition by copper(II): II. Effect of solution composition. *Journal of Crystal Growth , 213* (3-4), 368-380.

Sjöberg, L., & Rickard, D. (1984). Temperature dependence of calcite dissolution kinetics between 1 and 62°C at pH 2.7 to 8.4 in aqueous solutions. *Geochimica et Cosmochimica Acta , 48* (3), 485-493.

SMHI (a). (2009, July 7). *Normal årsmedeltemperatur | Temperatur | Meteorologi | Klimatdata | SMHI.* Retrieved March 26, 2010, from SMHI: http://www.smhi.se/klimatdata/meteorologi/temperatur/1.3973

SMHI (b). (2009, October 26). *Normalt antal dygn med snötäcke per år | Snö | Meteorologi | Klimatdata | SMHI.* Retrieved March 26, 2010, from SMHI: http://www.smhi.se/klimatdata/meteorologi/sno/Normalt-antal-dygn-med-snotacke-per-ar-1.7937

SMHI (c). (2009, July 13). *Normal uppmätt årsnederbörd, medelvärde 1961-1990 | Nederbörd | Meteorologi | Klimatdata | SMHI*. Retrieved March 26, 2010, from SMHI: http://www.smhi.se/klimatdata/meteorologi/nederbord/1.4160

Sposito, G. (1989). *The Chemistry of Soils.* New Work, California, USA: Oxford University Press.

Swedish Environmental Protection Agency. (2009, October 22). *Alkalinitet och försurningspåverkan*. Retrieved April 22, 2010, from Naturvårdsverket: http://www.naturvardsverket.se

Swedish National Food Administration. (2001). *Livsmedelsverkets föreskrifter om dricksvatten.* Stockholm: Swedish National Food Administration.

Sverdrup, H. U. (1985). *Calcite dissolution kinetics and lake neutralization.* Lund: Department of Chemical Engineering.

Terjesen, S. G., Erga, O., Thorsen, G., & Ve, A. (1961). Phase boundary processes as rate determining steps in reactions between solids and liquids : The inhibitory action of metal ions on the formation of calcium bicarbonate by the reaction of calcite with aqueous carbon dioxide. *Chemical Engineering Science , 14*, 277-288.

Wilén, B.-M. (2008). Lecture handouts in the course Drinking Water Engineering. *Drinking Water Production - Chemical Treatment - Chemical precipitation, coagulation, and flocculation.* Göteborg: Chalmers tekniska Högskola.

Vinson, M. D., Arvidson, R. S., & Luttge, A. (2007). Kinetic inhibition of calcite (1 0 4) dissolution by aqueous manganese(II). *Journal of Crystal Growth , 307* (1), 116-125.

PRODUCT INFORMATION

Omya
Northern Europe

Omya AB
Kalendegatan 18
SE 211 35 Malmö

Tel +46 40 20 67 00
Fax +46 40 23 65 19

www.omya.com

MIKROSTEVNS - SK

PRODUCTION PLANT:	STEVNS Kridtbrud / Denmark
SHORT DESCRIPTION OF THE PRODUCT:	High purity chalk powder. The raw chalk is washed, sieved, dried and air separated.

CHEMICAL ANALYSIS OF
THE RAW MATERIAL:

Carbonate ($CaCO_3$ + $MgCO_3$)	98.8	%
$CaCO_3$	97.9	%
SiO_2	0.4	%
Fe_2O_3	0.04	%
HCl insoluble	0.6	%

SPECIFIC PRODUCT DATA:

Fineness:

· Residue on a 45 µm sieve (ISO 787/7)	2	ppm
· Top cut (d98%)	20	µm
· Mean particle size (d50%)	2.3	µm
· Particles < 2 µm	43	%
· Specific surface area BET (ISO 9277)	2.2	m^2/g

Whiteness:

· Tappi brightness (R457, ISO 2469)	79.3	%
· Brightness (Ry, C/2°, DIN 53163)	84.4	%
Moisture ex works (ISO 787/2)	0.05	%

GENERAL PRODUCT DATA:

Loose bulk density (ISO 787/11)	0.55	g/ml
Packed bulk density (ISO 787/11)	0.75	g/ml
pH value (ISO 787/9)	9.1	
Oil absorption (ISO 787/5)	22	g/100g
DOP absorption (ISO 787/5)	28	g/100g
Conductivity (ISO 787/14)	100	µS/cm

MAIN APPLICATIONS:

PARTICLE SIZE DISTRIBUTION (Sedigraph 5100):
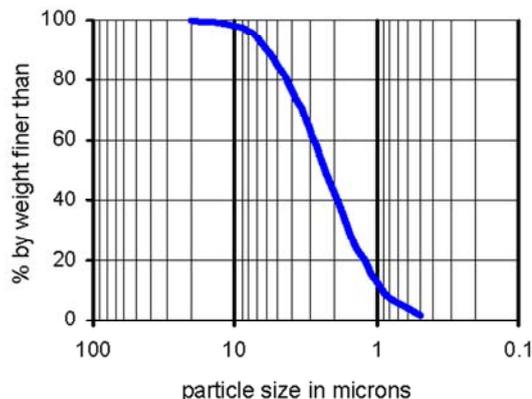
STANDARD PACKAGING:
- Bulk
- Bags (paper) of 25 kg on one-way palette of 1250 kg
- Big bags of 500 or 1000 kg on one-way palette

edition : 06.09.2005
6-PRODINFO : DKSK I52000_E
version : 000

eka

an Akzo Nobel company

Eka Facts

Ekoflock 70

Polyaluminiumhydroxikloridlösning (PAC)

Aktuellt säkerhetsdatablad är Ekoflock 50-100

Ekoflock 70 kan på grund av sin höga jonstyrka och sammansättning inte analyseras med standardiserade vattenanalysmetoder. Speciellt utarbetade och anpassade metoder krävs. Vid beräkning av pH erhålles då >3,8. Tillämpliga analyser utförda vid 20°C.

DATA		Metod
Utseende:	Gultonad vätska med svag lukt.	
pH:	2,1 ± 0,3 (Se inledning).	PA-07
Densitet:	1265 ± 25 kg/m^3	PA-08
Fryspunkt:	<-40°C	
Hållbarhet:	Minst 6 månader	
Viskositet:	41 mPas (-20°C)	
	<10 mPas (20°C)	

Analys:

			Metod
Aluminium (Al)	7,0 ± 0,3 vikt%		PA-20
Klorid (Cl)	14,5 ± 2,0 vikt%		PA-02
Sulfat (SO$_4$)	<1 vikt%		PA-03

	Medelhalt (mg/kg)	Maxhalt (mg/kg)	Detektionsgräns (mg/kg)	
Arsenik (As)	<0,5	<0,5	0,5	PA-16
Bly (Pb)	<2	<2	2	PA-14
Kadmium (Cd)	<0,1	<0,1	0,1	PA-09
Koppar (Cu)	<1	2	1	PA-12
Krom (Cr)	<1	<1	1	PA-10
Kvicksilver (Hg)	<0,03	<0,03	0,03	PA-17
Nickel (Ni)	<1	2	1	PA-13
Zink (Zn)	<2	3	2	PA-15

De angivna halterna är baserade på föregående års utfall.

De angivna detektionsgränserna avser den rutinmässigt använda analysmetodiken.

På baksidan ges en kortfattad beskrivning av de använda analysmetoderna.

Rev. date 2007-09-01-SP1

AKZO NOBEL

Appendix A2 - Ekoflock 70

ANALYSMETODER   Ekoflock 70

PA-02   <u>Analys av klorider</u>
           Kloriderna analyseras med en jonselektiv elektrod.

PA-03   <u>Analys av sulfater.</u>
           Ett bariuminnehållande reagens tillsättes till provet och den
           bildade bariumsulfaten bestämmes turbidimetriskt.

PA-07   <u>Mätning av pH samt beräkning av verkligt pH.</u>
           P g a Eka WTs höga jonstyrka och sammansättning är
           konventionellt mätt pH missvisande (för lågt). Det verkliga pH-
           värdet är framtaget m h a en korrigeringsfaktor.

PA-08   <u>Densitetsmätning.</u>
           Areometrisk bestämning av densiteten.

PA-20   <u>Analys av aluminium</u>
           Aluminium bestäms genom komplexometrisk titrering. Aluminium
           Får reagera med ett överskott av EDTA därefter tillbakatitrering
           med zinklösning.

Spårämnesanalys:

Nedanstående spårämnen analyseras i en saltsyrasur lösning m h a
Atomabsorptionsspektrometri (AAS) med bakgrundskorrektion.

PA-09   <u>Analys av Kadmium med AAS</u>
PA-10   <u>Analys av Krom med AAS</u>
PA-12   <u>Analys av Koppar med AAS</u>
PA-13   <u>Analys av Nickel med AAS</u>
PA-14   <u>Analys av Bly med AAS</u>
PA-15   <u>Analys av Zink med AAS</u>
PA-16   <u>Analys av Arsenik med AAS</u>
           Arsenik bestämmes m h a AAS-hydridgenerering.
PA-17   <u>Analys av Kvicksilver med AAS</u>
           Kvicksilver bestäms med flamlös AAS.

ÖVRIGT

Kontakta Eka Chemicals för ytterligare information angående hantering,
klassificering och märkning. Läs igenom Säkerhetsdatabladet före hantering av
produkten.

eka

an Akzo Nobel company

Ekoflock 91

Polyaluminiumhydroxikloridlösning (PAC)

Aktuellt säkerhetsdatablad är Ekoflock 50-100

Ekoflock 91 kan på grund av sin höga jonstyrka och sammansättning inte analyseras med standardiserade vattenanalysmetoder. Speciellt utarbetade och anpassade metoder krävs. Vid beräkning av pH erhålles då >2. Tillämpliga analyser utförda vid 20°C.

DATA		Metod
Utseende:	Gultonad vätska med svag lukt.	
pH:	<2 (Se inledning).	PA-07
Densitet:	1375 ± 25 kg/m^3	PA-08
Fryspunkt:	<-40°C	
Hållbarhet:	Minst 6 mån	
Viskositet:	148 mPas (-20°C)	
	44 mPas (20°C)	

Analys:

		Metod
Aluminium (Al)	$9,3 \pm 0,3$ vikt%	PA-20
Klorid (Cl)	$20,0 \pm 1,5$ vikt%	PA-02
Sulfat (SO$_4$)	<1 vikt%	PA-03

	Maxhalt (mg/kg)	Detektionsgräns (mg/kg)	
Arsenik (As)	<0,5	0,5	PA-16
Bly (Pb)	<2	2	PA-14
Kadmium (Cd)	<0,1	0,1	PA-09
Koppar (Cu)	<1	1	PA-12
Krom (Cr)	<1	1	PA-10
Kvicksilver (Hg)	<0,03	0,03	PA-17
Nickel (Ni)	<1	1	PA-13
Zink (Zn)	<2	2	PA-15

De angivna halterna är baserade på föregående års utfall.

De angivna detektionsgränserna avser den rutinmässigt använda analysmetodiken.

På baksidan ges en kortfattad beskrivning av de använda analysmetoderna.

AKZO NOBEL

Appendix A3 - Ekoflock 91

eka

an Akzo Nobel company

ANALYSMETODER   Ekoflock 91

PA-02   Analys av klorider.
             Kloriderna analyseras med en jonselektiv elektrod.

PA-03   Analys av sulfater.
             Ett bariuminnehållande reagens tillsättes till provet och den
             bildade bariumsulfaten bestämmes turbidimetriskt.

PA-07   Mätning av pH samt beräkning av verkligt pH.
             P g a Eka WTs höga jonstyrka och sammansättning är
             konventionellt mätt pH missvisande (för lågt). Det verkliga pH-
             värdet är framtaget m h a en korrigeringsfaktor.

PA-08   Densitetsmätning.
             Areometrisk bestämning av densiteten.

PA-20   Analys av aluminium
             Aluminium bestäms genom komplexometrisk titrering. Aluminium
             får reagera med ett överskott av EDTA, därefter tillbakatitrering
             med zinklösning.

Spårämnesanalys:

Nedanstående spårämnen analyseras i en saltsyrasur lösning m h a
Atomabsorptionsspektrometri (AAS) med bakgrundskorrektion.

PA-09   Analys av Kadmium med AAS.
PA-10   Analys av Krom med AAS.
PA-12   Analys av Koppar med AAS.
PA-13   Analys av Nickel med AAS.
PA-14   Analys av Bly med AAS.
PA-15   Analys av Zink med AAS.
PA-16   Analys av Arsenik med AAS.
             Arsenik bestämmes m h a AAS-hydridgenerering.
PA-17   Analys av Kvicksilver med AAS.
             Kvicksilver bestäms med flamlös AAS.

ÖVRIGT

Kontakta Eka Chemicals för ytterligare information angående hantering,
klassificering och märkning. Läs igenom Säkerhetsdatabladet före hantering av
produkten.

AKZO NOBEL

Appendix B1 - DynaSand

DynaSand® filter
– operation

The DynaSand filter is based on the counterflow principle. The water to be treated is admitted through the inlet distributor (1) in the lower section of the unit and is cleaned as it flows upwards through the sand bed, prior to discharge through the filtrate outlet (2) at the top. The sand containing the entrapped solids is conveyed from the tapered bottom section of the unit (3), by means of an airlift pump (4), to the sand washer (5) at the top. Cleaning of the sand commences in the pump itself, in which impurities are separated from the sand grains by the turbulent mixing action. The contaminated sand spills from the pump outlet into the washer labyrinth (6), in which it is washed by a small countercurrent flow of clean water. The separated solids are discharged through the wash water outlet (7), while the grains of clean sand (which are heavier) are returned to the sand bed (8). As a result, the bed is in slow, constant downward motion through the unit. Compressed air for the sand pump is provided via the control panel (9).

Thus, water purification and sand washing both take place continuously, enabling the filter to remain in service without interruption.
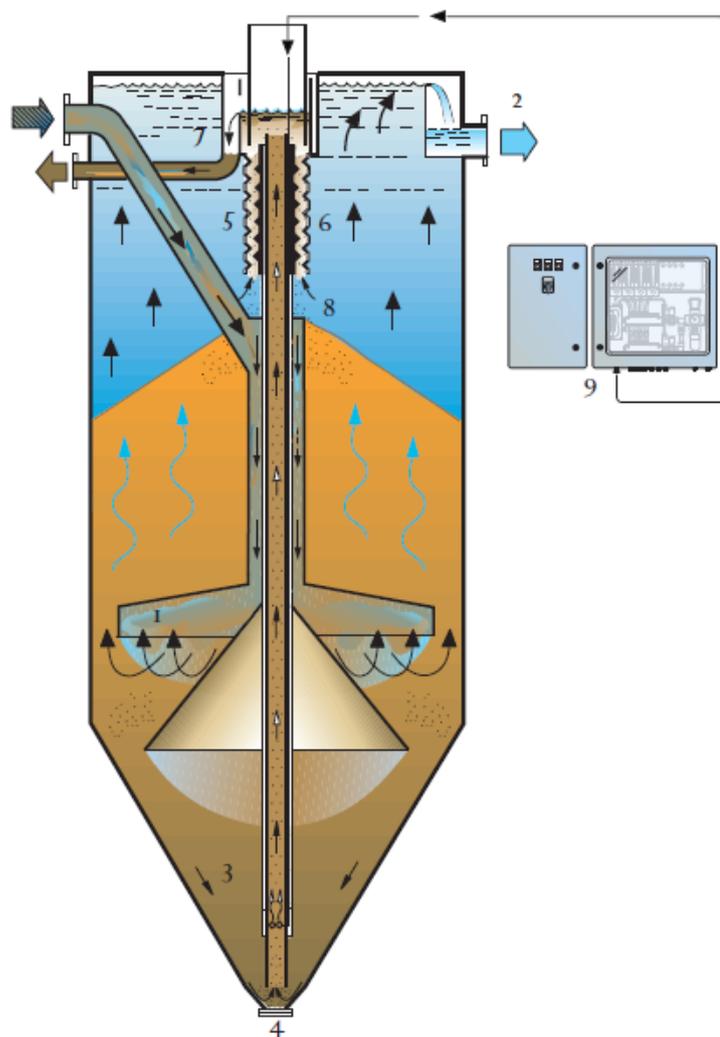
DynaSand operates continuously and requires a minimum of attention.

Mats Strand   2008-10-16

KARLSKRONA VATTENVERK

Grovfiltrering av råvattnet vid intag i Lyckebyån.

Finfiltrering av råvattnet i roterande trumfilter.

Alk.bassäng för inblandning av alk.kemikalier.

Dosering av Krita, CO_2 och ev lut.

Linjepumpstation (5 pumpar, 1 till respektive linje).

Dosering av PAC (1 dospunkt/linje).

Filtrering av bildad flock i 40 filter. (5 linjer à 8 filter).

Dosering av krita, CO_2, Na-hypoklorit och ev lut.

2 bassänger. (totalt 1400 m³)

Dosering av Lut.

Intags-filter → **Trum-filter** → **Alk.-bassäng** → **Pump-station** → **DynaSand-filter** → **Blandn.-kammare** → **Oxidations-bassänger**

Flödes-, pH-, UV-, Redox, temp.- och konduktivitetsmätning

Flödes- och pH-mätning

2 st pH-mätare och 5 st turb.-mätare

pH-mätning

pH-mätning

Flödes- och suspmätning

Dosering av polymer.

Dosering av lut, CO_2, Na-hypoklorit och ammoniumsulfat.

pH-mätning

Föravvattnat slam pumpas till Koholmen ARV.

Lamell-separator → **Kolfilter** → **Renv.-snäcka** → **Låg-reservoar** → **Dricksvatten pumpar**

Flödesmätning

Rejektvatten till Lyckebyån.

Spolvatten till Lyckebyån.

Spolning av kolfilter.

Flödes-, Tryck-, pH-, turbiditets- och kloröver-skotts mätning.

Föravvattning i 2 separatorer av tvättvatten från DynaSandfiltren.

Kolfiltrering för reduktion av lukt- och smakämnen (11 kolfilter).

Slutjustering av pH och alkalinitet samt desinfektion.

Tvådelad lågreservoar på totalt 840 m³ följd av dricksvattenpumpning till distributionsnätet via 3 varvtalsreglerade pumpar.

Vattentorn och två reservoarer (total volym 9050 m³)

Karlskrona tätort.

Lösen och Fäjö

Trummenäs

Tryckstegring Aspö.

Tryckstegring Åvägen.

Tryckstegring Allatorp.

Tryckstegring Rödeby ek med UV-dec.

Tryckstegring Dalby.

Tryck-stegring Johannes-berg.

Vatten-torn. (600 m³)

Tryckstegr. Håkantorpet

Tryckstegring Hasslö.

Hasslö.

Aspö.

Nättraby samhälle.

Allatorp.

Rödeby samhälle.

Kungsholmen och Tjurkö g:a ARV.

Tryckstegring Torhamn.

Torhamn samhälle.

Tryckstegring Sanda.

Tryckstegring Kullen.

Tryckstegring Hästkolmen.

Sanda samhälle

Ekenabben fiskhamn.

Tjurkö sommarvatten.

Kullen samhälle.

Uttorp camping.

Ytter-ön.

Hästholmen.

Östra skärgården

Appendix B3 - Kristinehamn

Appendix B4 - Lerum

LERUMS KOMMUN
ÖXSJÖNS VATTENVERK
PROCESSCHEMA

Appendix C1 - Template test round I

Test round I: The tests are made for pH 5, 6 and 7. pH is kept at the certain pH by continious CO_2 addition.

Water temperature ≈ 0.5°C | Raw water = 1 l

pH 5, 20 rpm

Time [min]	Activity
0	pH is adjusted to 5 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

pH 6, 20 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading. 60 mg PAC is then added
12	Al residue reading
14	Al residue reading
16	Al residue and $CaCO_3$ reading

pH 6, 50 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

pH 6, 20 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 60 mg PAC is then added
2	Al residue reading
4	Al residue reading
6	Al residue reading. 30 mg $CaCO_3$ is then added
7	$CaCO_3$ reading
10	$CaCO_3$ reading
13	$CaCO_3$ reading
16	$CaCO_3$ and Al residue reading

pH 7, 20 rpm

Time [min]	Activity
0	30 mg $CaCO_3$ is added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

$CaCO_3$: Water is sampled after 1,4,7 and 10 min for every test. Water samples are then filtered and the amount of solved calcium carbonate is measured. Mikrostevns is used as calcium carbonate.
Dosage: 30 mg/l and are dosed for Karlskrona, Kristinehamn and Lerum.

PAC: Water is sampled after 2,4 and 6 min for every test. Water samples are then filtered and the aluminium residue is measured. Ekoflock 91 are used for Kristinehamn and Ekoflock 70 are used for
Dosage: 60 mg/l and are dosed for Karlskrona and Kristinehamn and 42mg/l for Lerum.

Appendix C1 - Template test round I

Test round I: The tests are made for pH 5, 6 and 7. pH is kept at the certain pH by continious CO_2 addition.

Water temperature $\approx$ 15 °C | Raw water = 1 l

pH 5, 20 rpm

Time [min]	Activity
0	pH is adjusted to 5 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

pH 6, 20 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading. 60 mg PAC is then added
12	Al residue reading
14	Al residue reading
16	Al residue and $CaCO_3$ reading

pH 6, 50 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 30 mg $CaCO_3$ is then added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

pH 6, 20 rpm

Time [min]	Activity
0	pH is adjusted to 6 by the use of CO_2. 60 mg PAC is then added
2	Al residue reading
4	Al residue reading
6	Al residue reading. 30 mg $CaCO_3$ is then added
7	$CaCO_3$ reading
10	$CaCO_3$ reading
13	$CaCO_3$ reading
16	$CaCO_3$ and Al residue reading

pH 7, 20 rpm

Time [min]	Activity
0	30 mg $CaCO_3$ is added
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading

$CaCO_3$: Water is sampled after 1,4,7 and 10 min for every test. Water samples are then filtered and the amount of solved calcium carbonate is measured. Mikrostevns is used as calcium carbonate.
Dosage: 30 mg/l and are dosed for Karlskrona, Kristinehamn and Lerum.

PAC: Water is sampled after 2,4 and 6 min for every test. Water samples are then filtered and the aluminium residue is measured. Ekoflock 91 are used for Kristinehamn and Ekoflock 70 are used for
Dosage: 60 mg/l and are dosed for Karlskrona and Kristinehamn and 42mg/l for Lerum.

Appendix C2 - Template test round II

Test round II: The tests are allowed to be in the intervall of pH 5.5 to 6.5. In case B, B1, B2 and B3 pH are lowered to pH 6.00 before $CaCO_3$ is added. pH is then kept around pH 6 by continuous CO_2 addition.

Water temperature ≈ 0.5°C | Ekoflock 70 = 60 mg/l | Mikrostevns = 30 mg/l | Raw water = 1 l

Case A

Time [min]	Activity
0	60 mg PAC addition and possible dosage of NaOH to keep pH within pH 5.5 to 6.5
1	Al residue reading
4	Al residue & TOC readings
7	Al residue reading
10	Al residue reading
15	Al residue, Mn, alkalinity & TOC readings

Case B

Time [min]	Activity
0	30 mg $CaCO_3$ addition
1	$CaCO_3$ reading
4	$CaCO_3$ reading
7	$CaCO_3$ reading
10	$CaCO_3$ reading
20	$CaCO_3$ reading
30	$CaCO_3$ reading

Case B1

Time [min]	Activity
0	30 mg $CaCO_3$ addition
at 30-40% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
+1	Al residue reading
+4	Al residue & TOC readings
+7	Al residue reading
+15	Al residue, Mn, alkalinity & TOC readings

Case B2

Time [min]	Activity
0	30 mg $CaCO_3$ addition
at 50-60% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
+1	Al residue reading
+4	Al residue & TOC readings
+7	Al residue reading
+15	Al residue, Mn, alkalinity & TOC readings

Case B3

Time [min]	Activity
0	30 mg $CaCO_3$ addition
at 70-80% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
+1	Al residue reading
+4	Al residue & TOC readings
+7	Al residue reading
+15	Al residue, Mn, alkalinity & TOC readings

Appendix C2 - Template test round II

Test round II: The tests are allowed to be in the intervall of pH 5.5 to 6.5. In case B, B1, B2 and B3 pH are lowered to pH 6.00 before $CaCO_3$ is added. pH is then kept around pH 6 by continuous CO_2 addition.

Water temperature ≈ 15°C | Ekoflock 70 = 60 mg/l | Mikrostevns = 30 mg/l | Raw water = 1 l			
Case A		**Case B**	
Time [min]	**Activity**	**Time [min]**	**Activity**
0	60 mg PAC addition and possible dosage of NaOH to keep pH within pH 5.5 to 6.5	0	30 mg $CaCO_3$ addition
1	Al residue reading	1	$CaCO_3$ reading
4	Al residue & TOC readings	4	$CaCO_3$ reading
7	Al residue reading	7	$CaCO_3$ reading
10	Al residue reading	10	$CaCO_3$ reading
15	Al residue, Mn, alkalinity & TOC readings	20	$CaCO_3$ reading
		30	$CaCO_3$ reading
		Case B1	
		Time [min]	**Activity**
		0	30 mg $CaCO_3$ addition
		at 30-40% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
		+1	Al residue reading
		+4	Al residue & TOC readings
		+7	Al residue reading
		+15	Al residue, Mn, alkalinity & TOC readings
		Case B2	
		Time [min]	**Activity**
		0	30 mg $CaCO_3$ addition
		at 50-60% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
		+1	Al residue reading
		+4	Al residue & TOC readings
		+7	Al residue reading
		+15	Al residue, Mn, alkalinity & TOC readings
		Case B3	
		Time [min]	**Activity**
		0	30 mg $CaCO_3$ addition
		at 70-80% solved $CaCO_3$	$CaCO_3$ & alkalinity readings. 60 mg PAC addition
		+1	Al residue reading
		+4	Al residue & TOC readings
		+7	Al residue reading
		+15	Al residue, Mn, alkalinity & TOC readings

Appendix D1 - Additional results test round I

2010-03-08 | Water: Lerum | Speed of stirring device: 20 rpm | **pH 5**
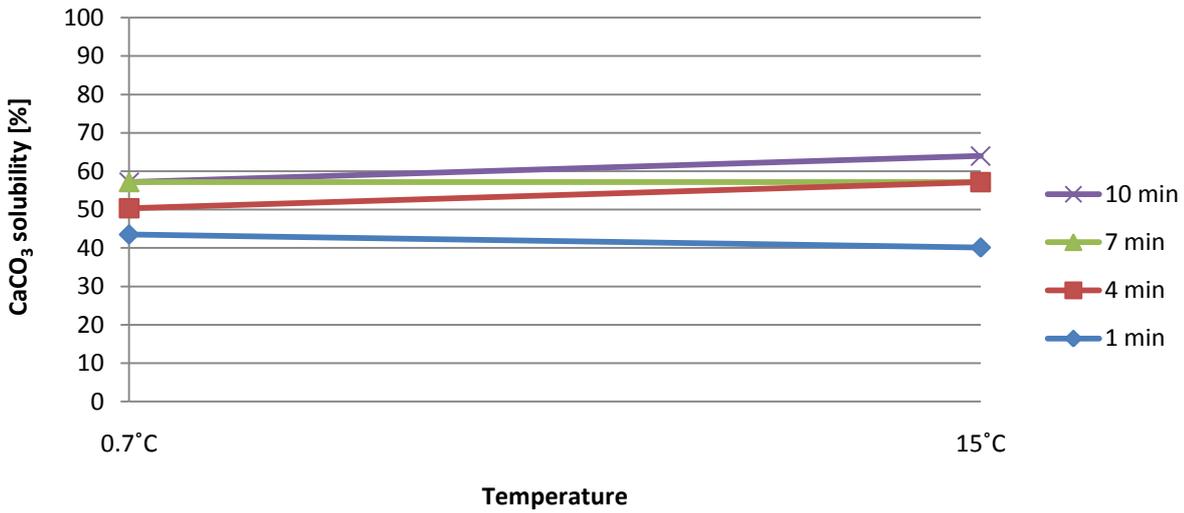
2010-03-08 | Water: Lerum | Speed of stirring device: 20 rpm | **pH 6**

2010-03-08 | Water: Lerum | Speed of stirring device: 20 rpm | **pH 7**

The test was failed, hence the look of the curves.
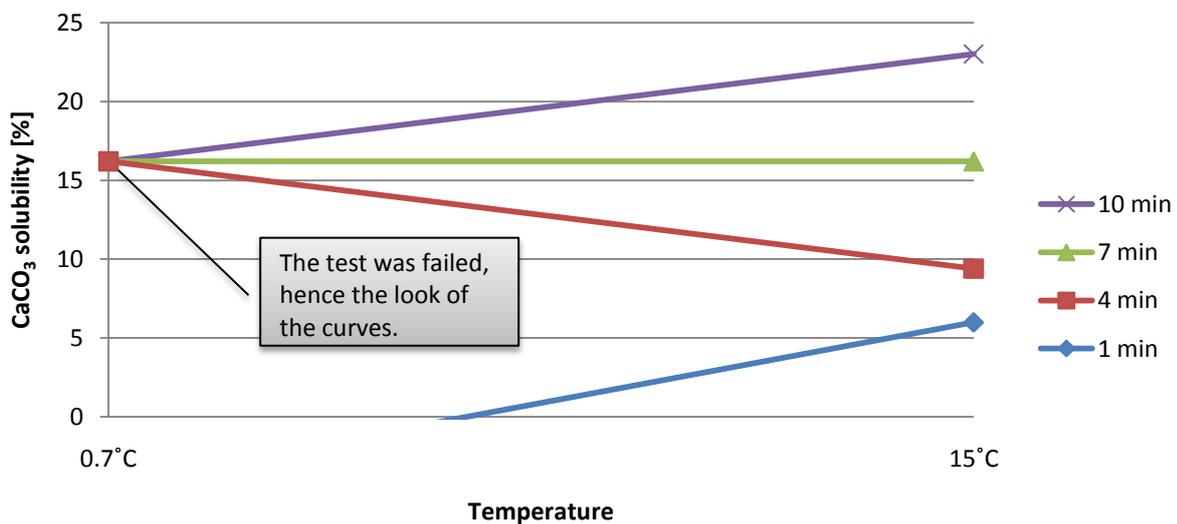
Appendix D1 - Additional results test round I

2010-02-23 | Water: Kristinehamn| Speed of stirring device: 20 rpm | **pH 5**
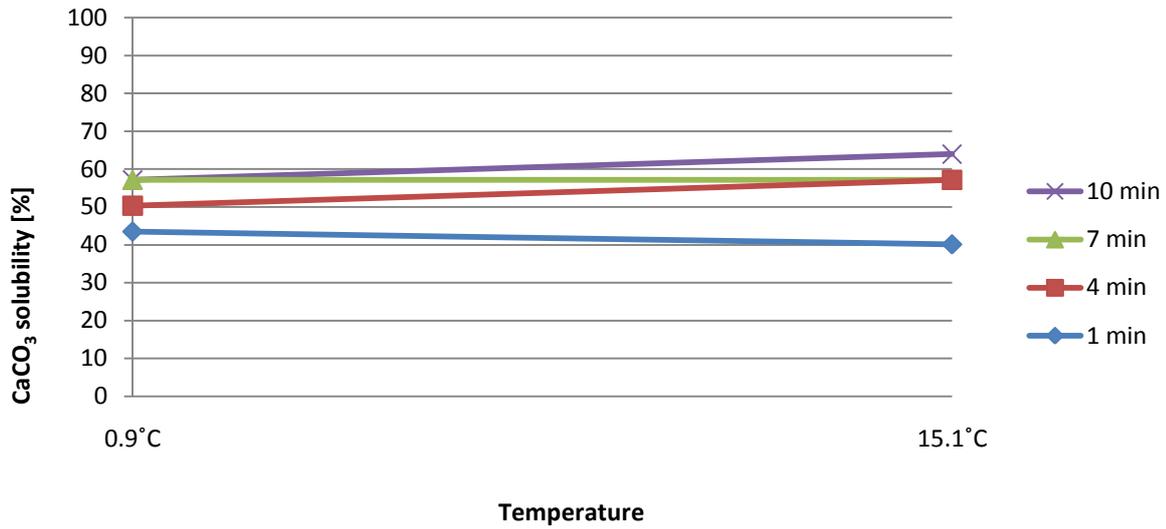
2010-02-23 | Water: Kristinehamn| Speed of stirring device: 20 rpm | **pH 6**
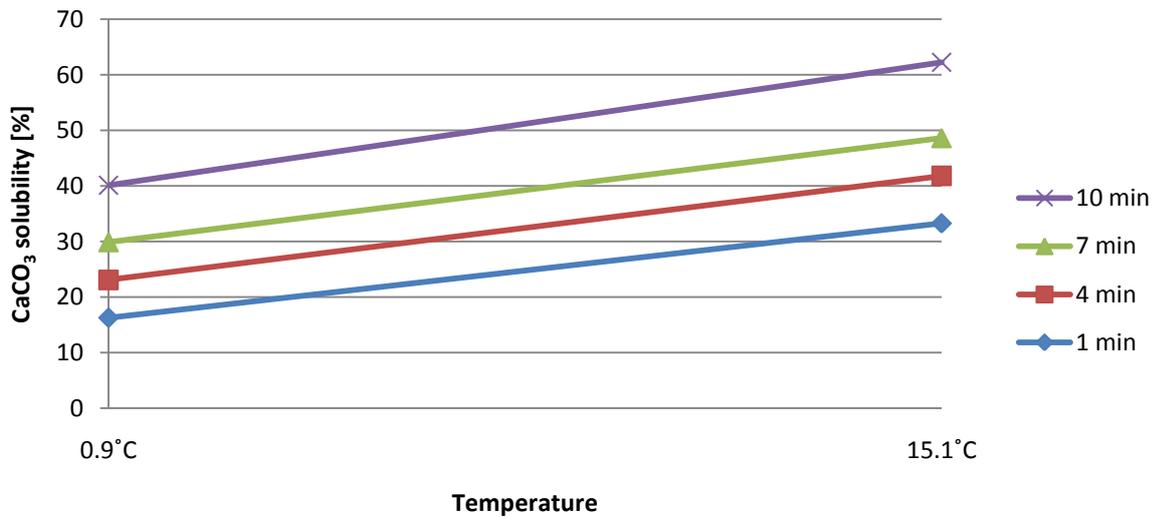
2010-02-23 | Water: Kristinehamn| Speed of stirring device: 20 rpm | **pH 7**
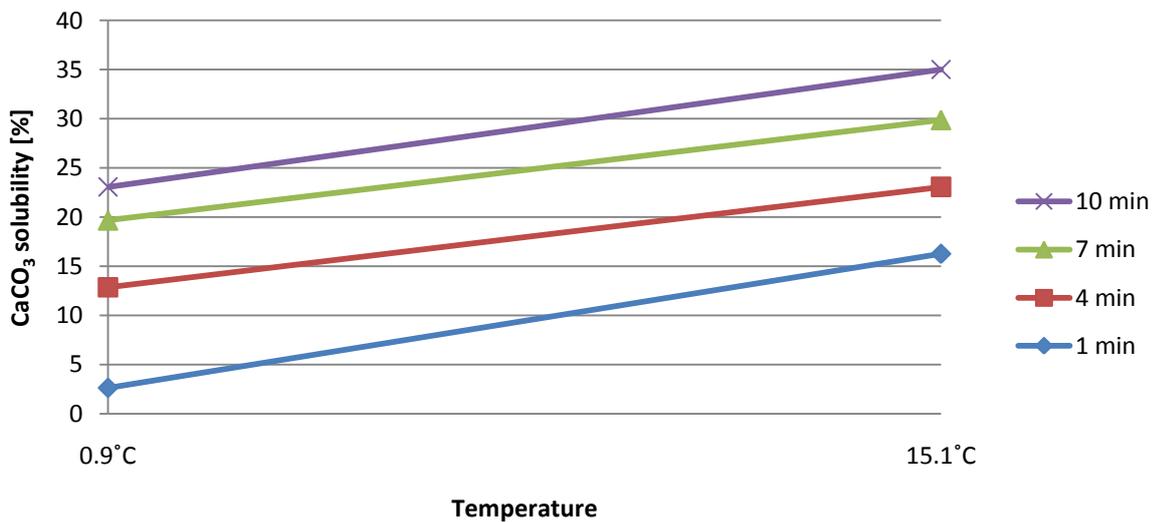
Appendix D2 - Additional results test round II

2010-04-27 | Water: Kristinehamn | Water temperature: 0.5 °C | Case: A
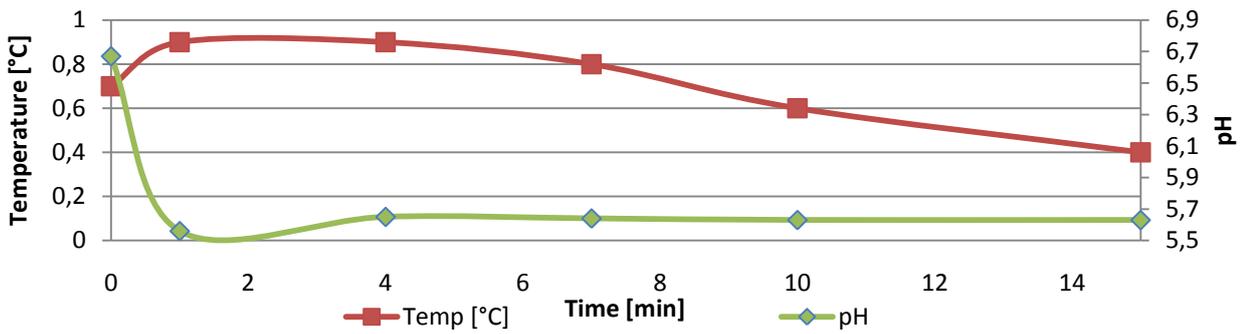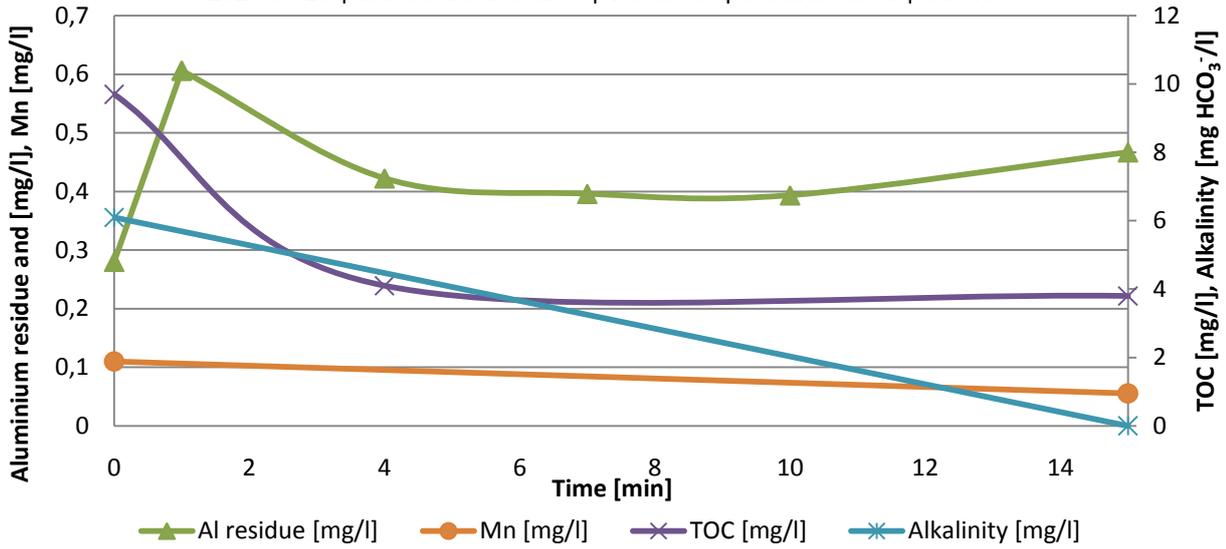
2010-04-27 | Water: Kristinehamn | Water temperature: 15 °C | Case: A
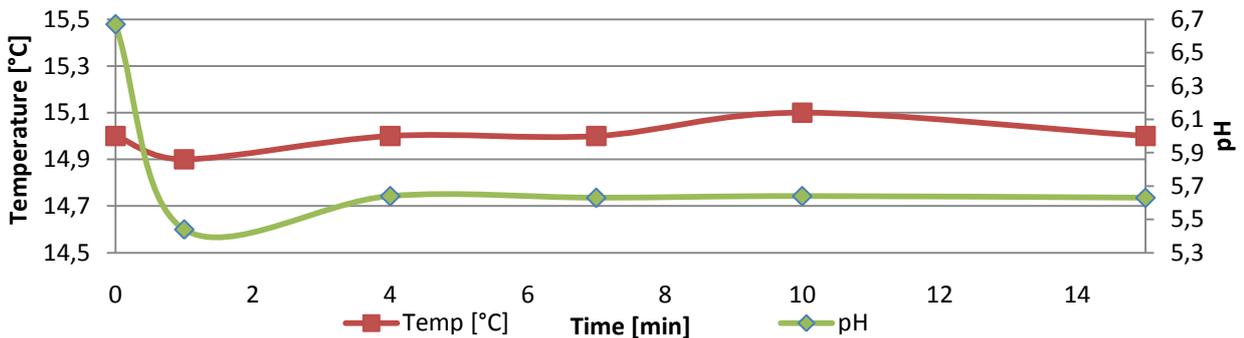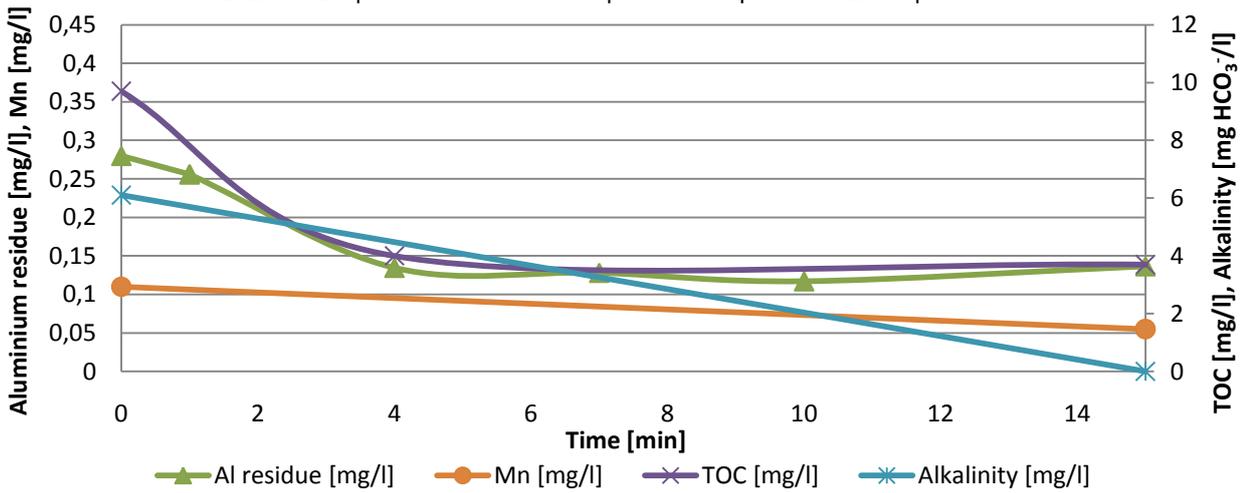
Appendix D2 - Additional results test round II

2010-04-19 | Water: Lerum | Water temperature: 0.5 °C | Case: A

2010-04-19 | Water: Lerum | Water temperature: 15 °C | Case: A
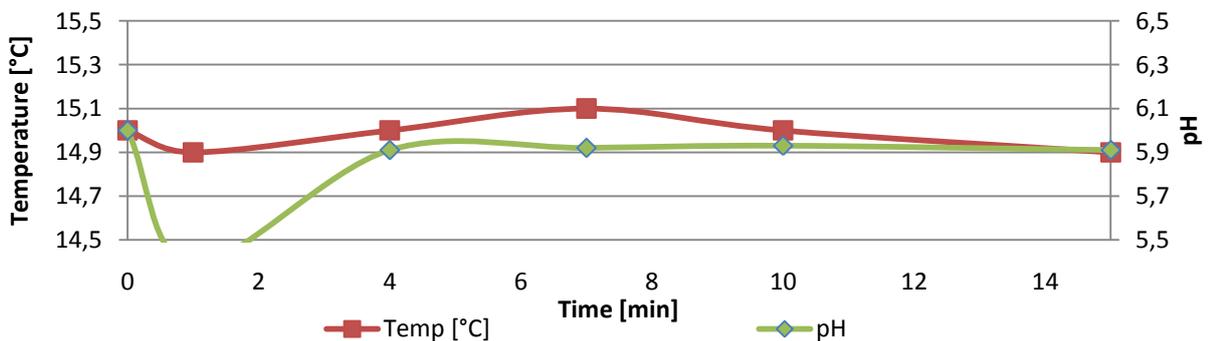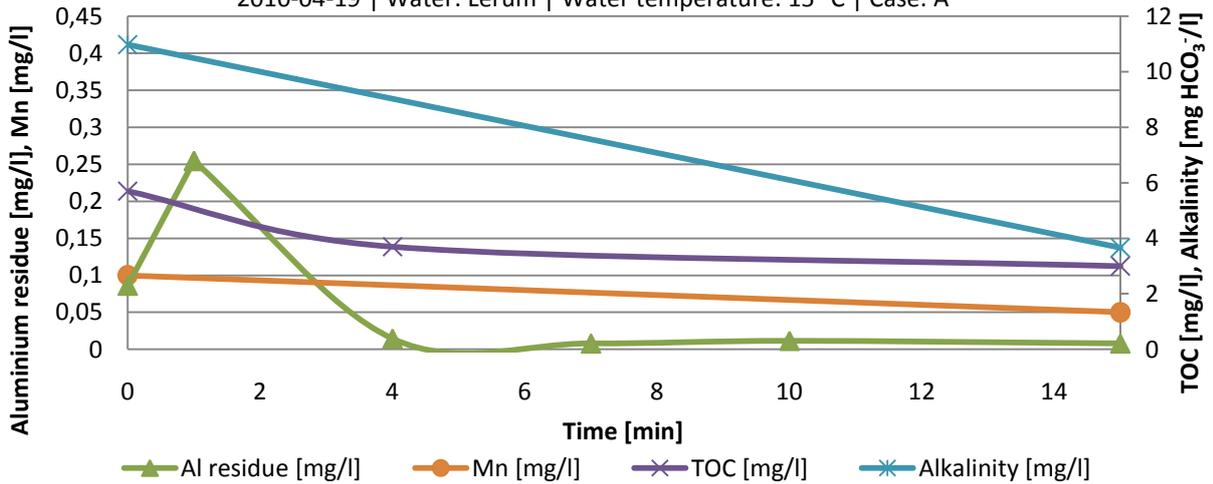
Appendix D2 - Additional results test round II

2010-04-27 | Water: Kristinehamn | Water temperature: 0.5 °C | Case: B1 | 31 % solved CaCO$_3$

2010-04-27 | Water: Kristinehamn | Water temperature: 15 °C | Case: B1 | 41 % solved CaCO$_3$
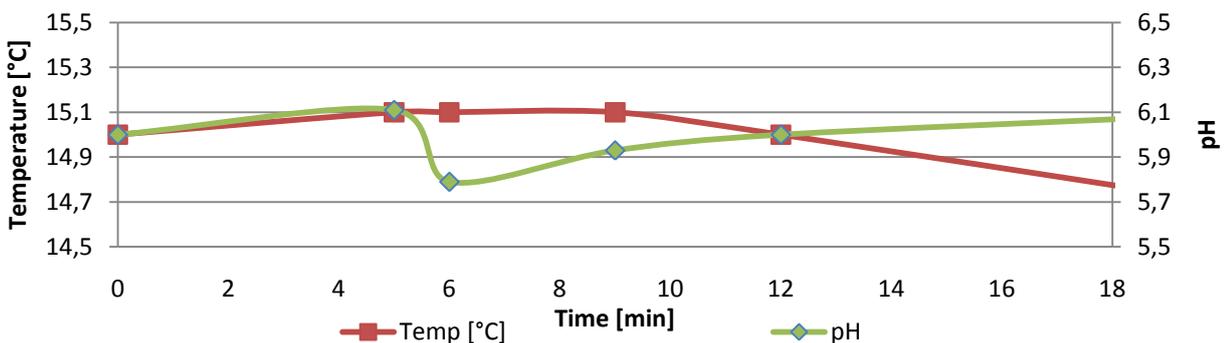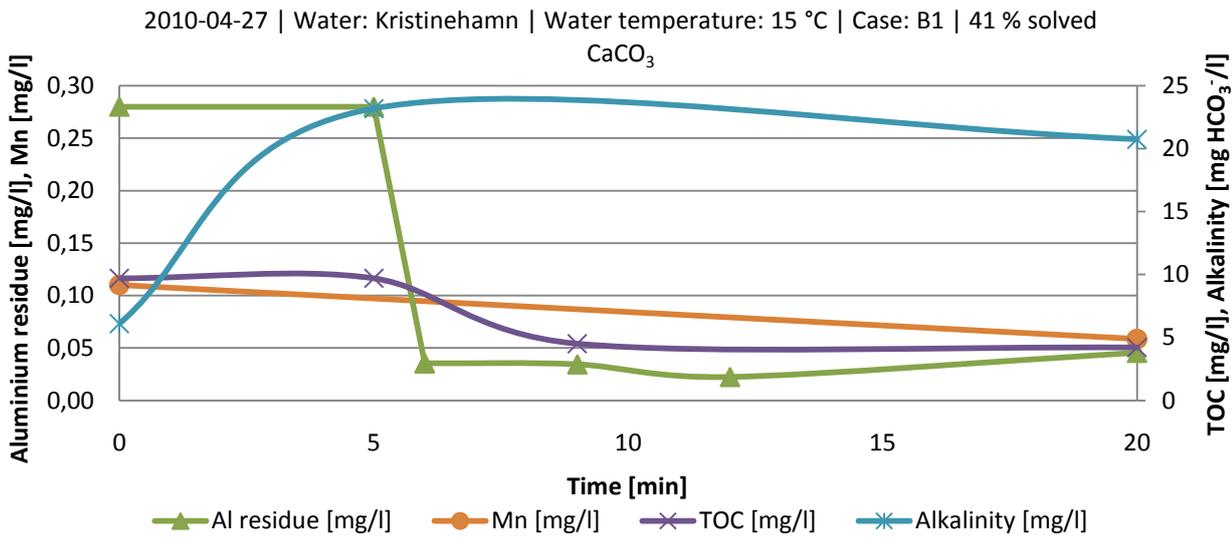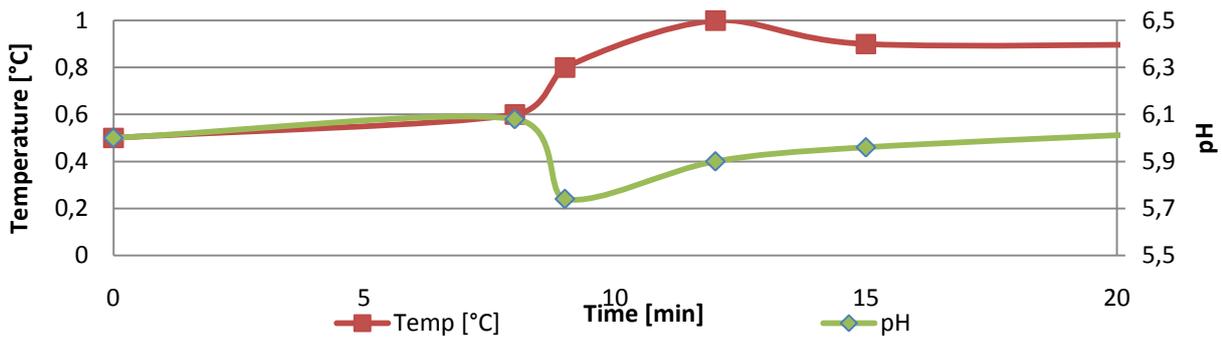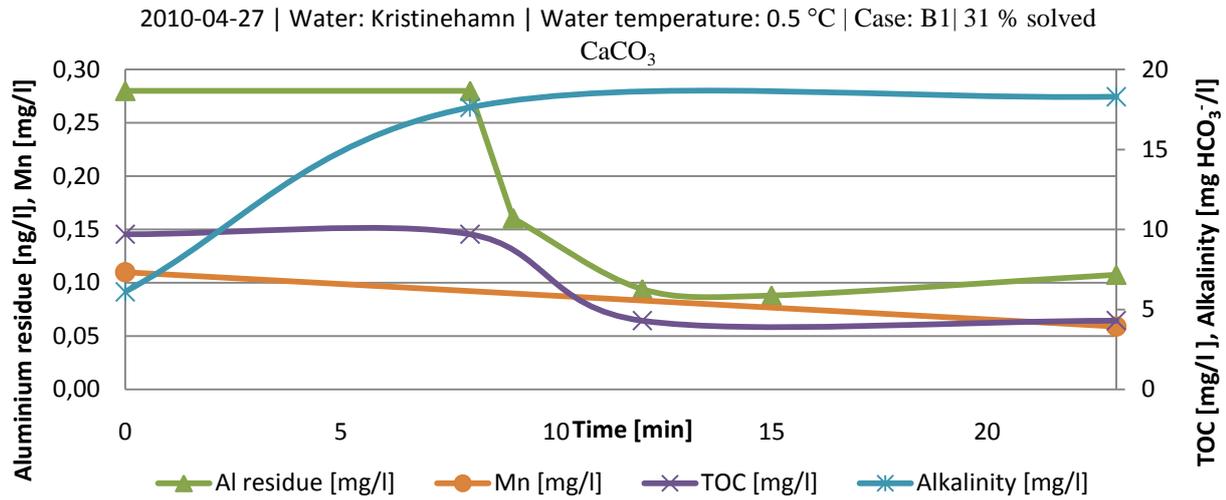
Appendix D2 - Additional results test round II

2010-04-19 | Water: Lerum | Water temperature: 0.5 °C | Case: B1| 17 % solved CaCO$_3$
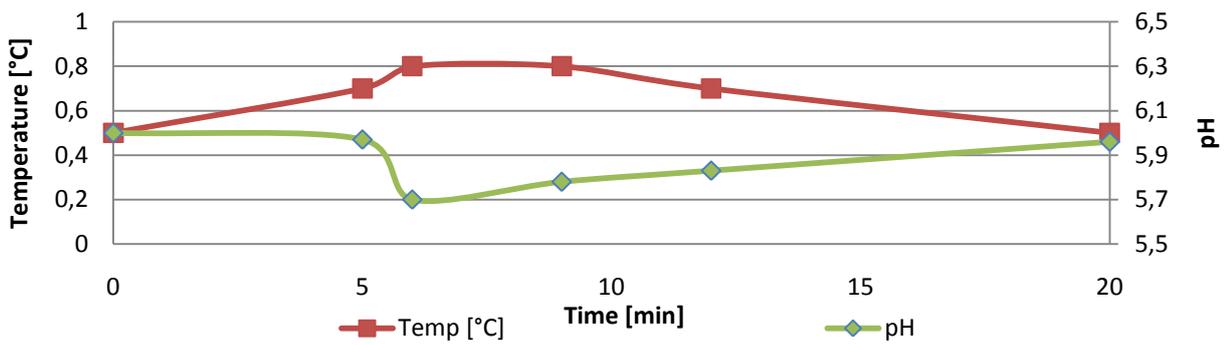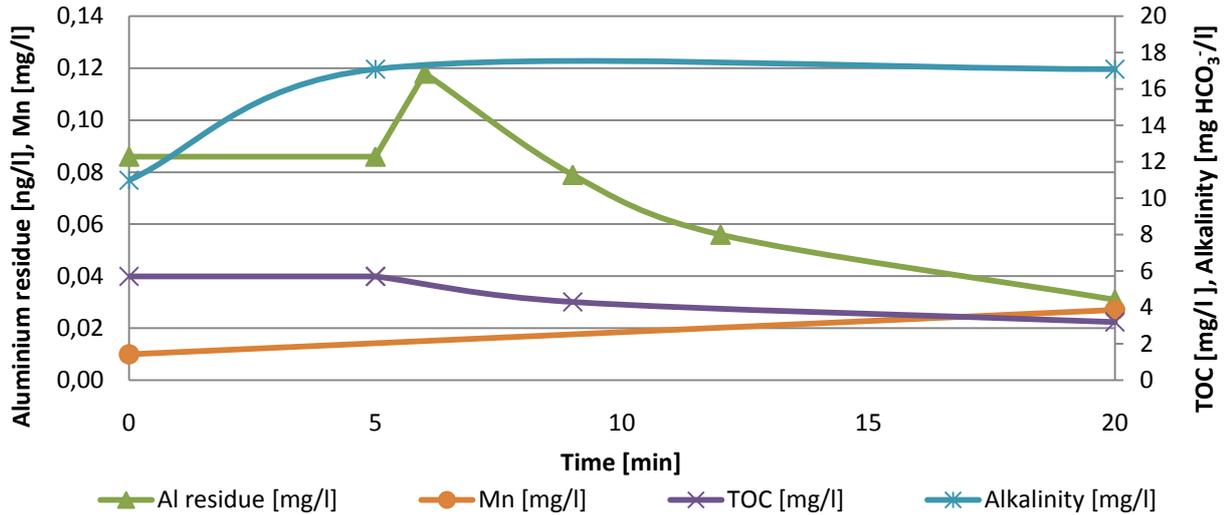
2010-04-19 | Water: Lerum | Water temperature: 15 °C | Case: B1 | 34 % solved CaCO$_3$
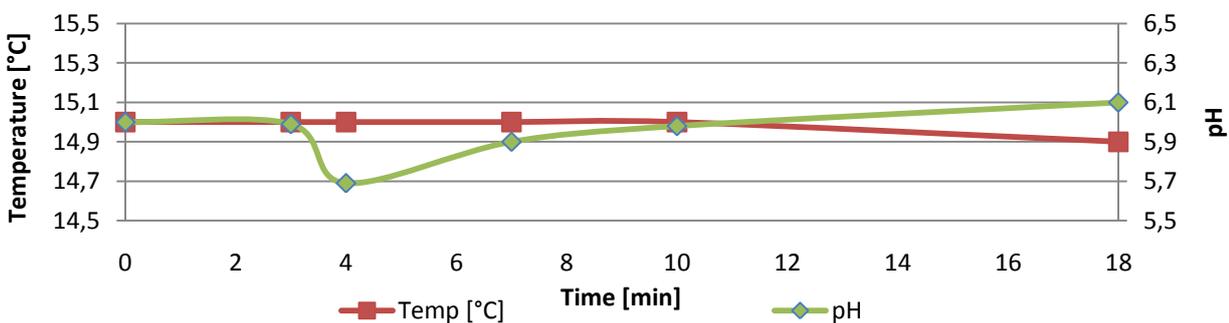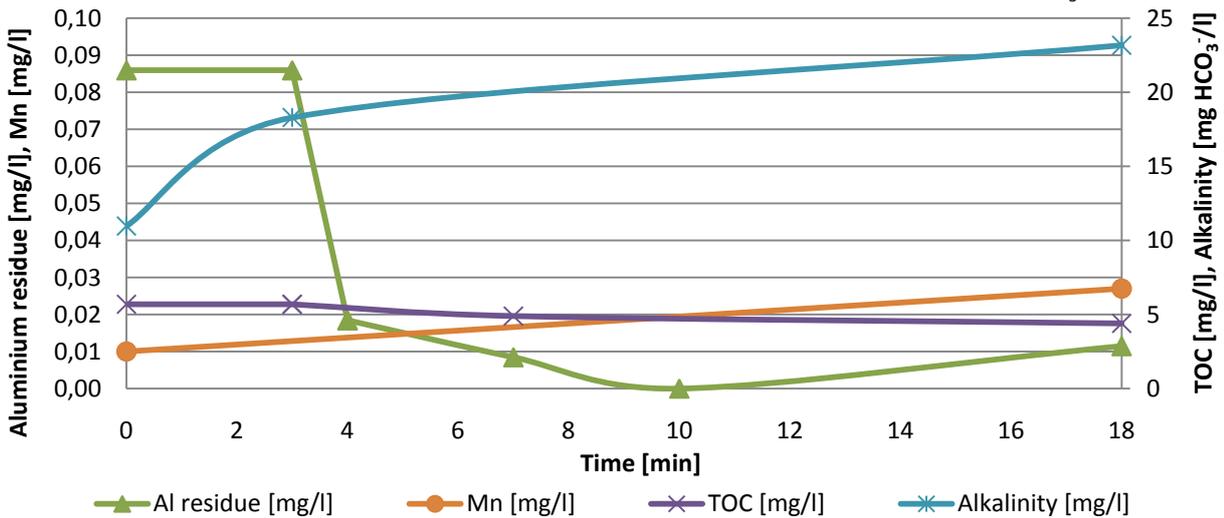
Appendix D2 - Additional results test round II

2010-04-27 | Water: Kristinehamn | Water temperature: 0.5 °C | Case: B2| 53 % solved CaCO$_3$

Al residue [mg/l] — Mn [mg/l] — TOC [mg/l] — Alkalinity [mg/l] — Assumed shape

Temp [°C] — pH
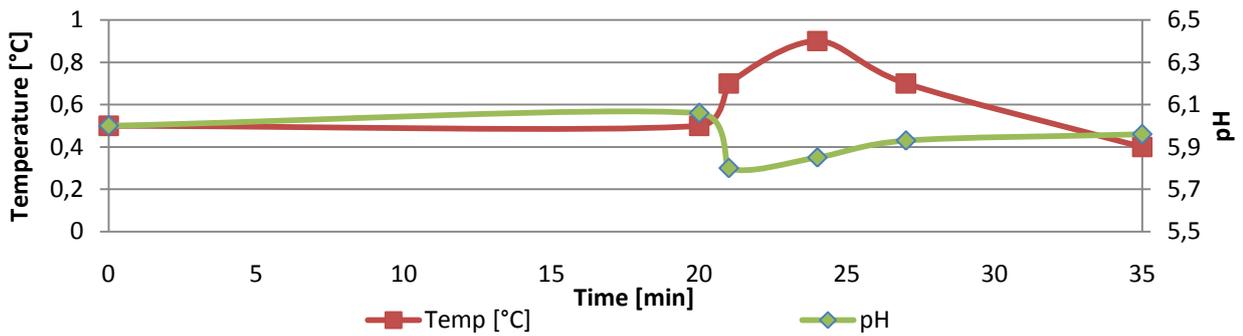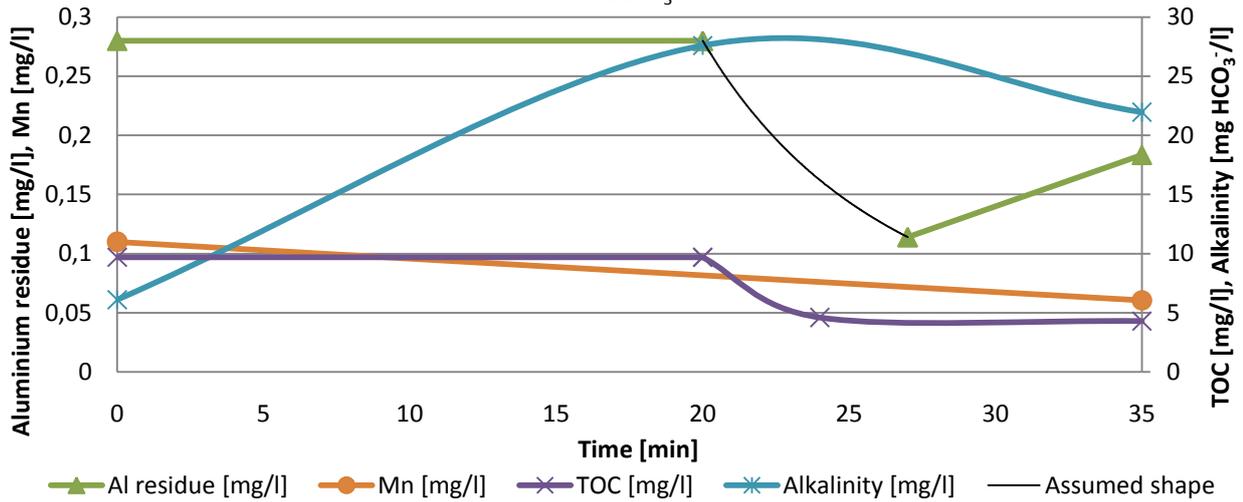
2010-04-27 | Water: Kristinehamn | Water temperature: 15 °C | Case: B2| 51 % solved CaCO$_3$
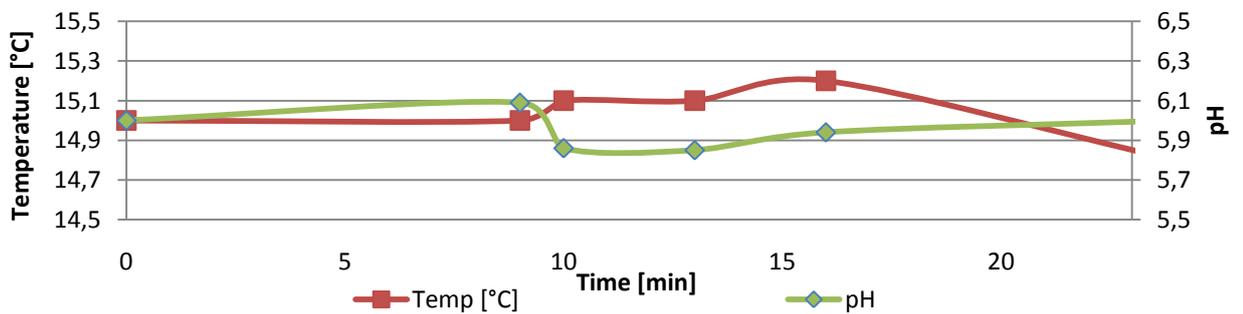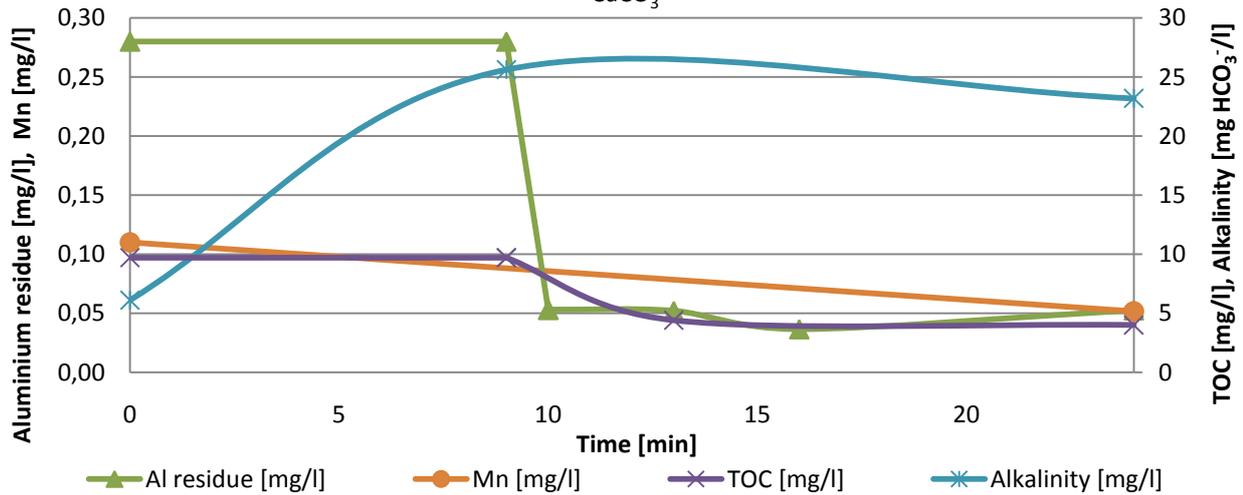
Al residue [mg/l] — Mn [mg/l] — TOC [mg/l] — Alkalinity [mg/l]

Temp [°C] — pH

Appendix D2 - Additional results test round II

2010-04-19 | Water: Lerum | Water temperature: 0.5 °C | Case: B2| 58 % solved CaCO₃
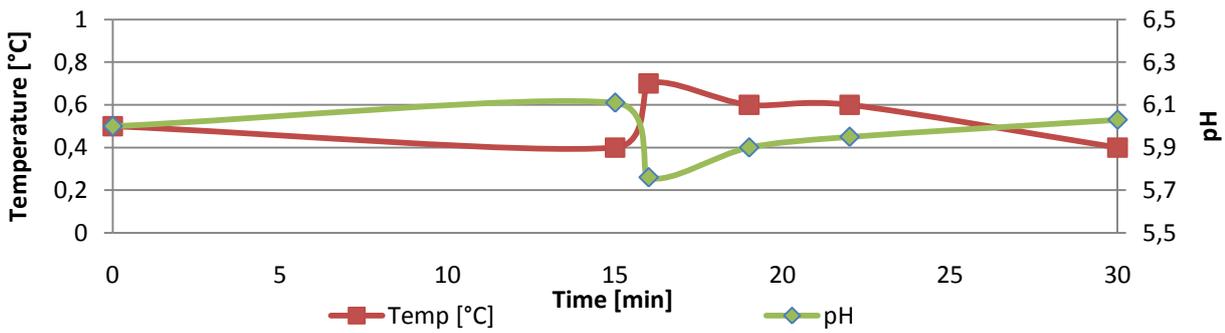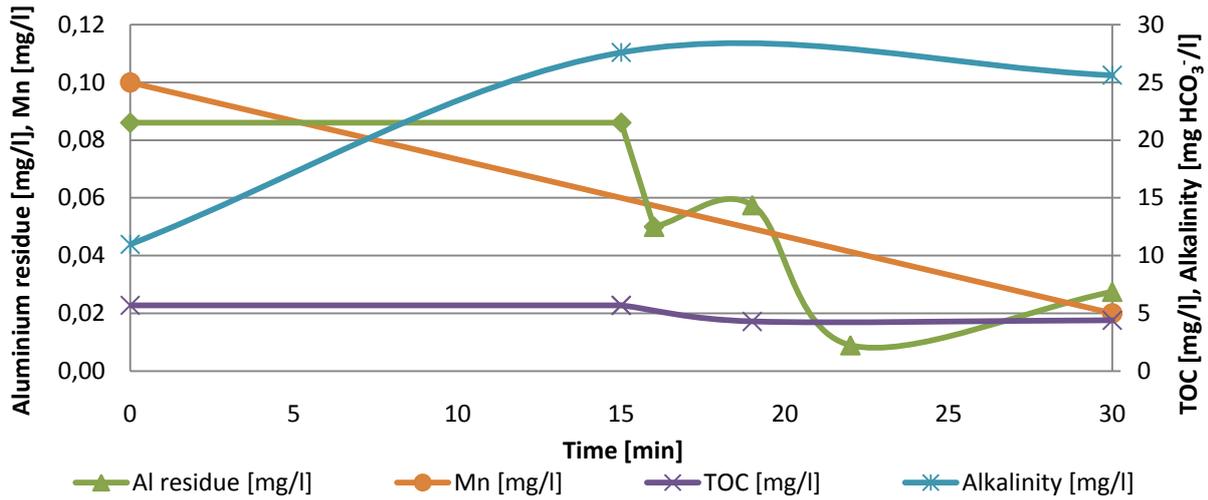
2010-04-19 | Water: Lerum | Water temperature: 15 °C | Case: B2| 56 % solved CaCO₃
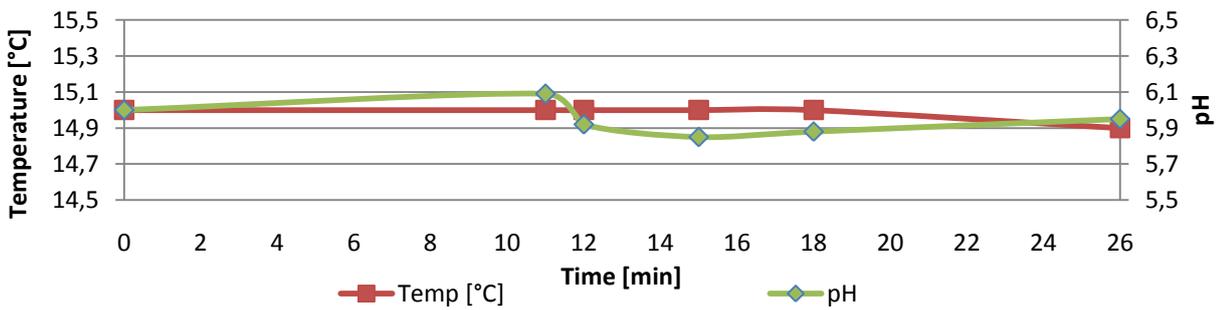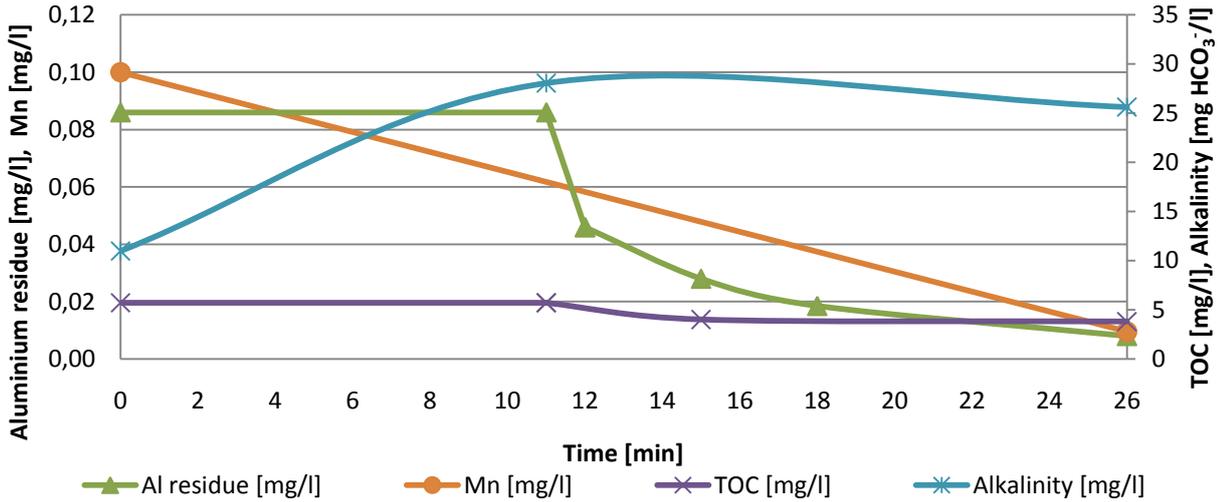
Appendix D2 - Additional results test round II
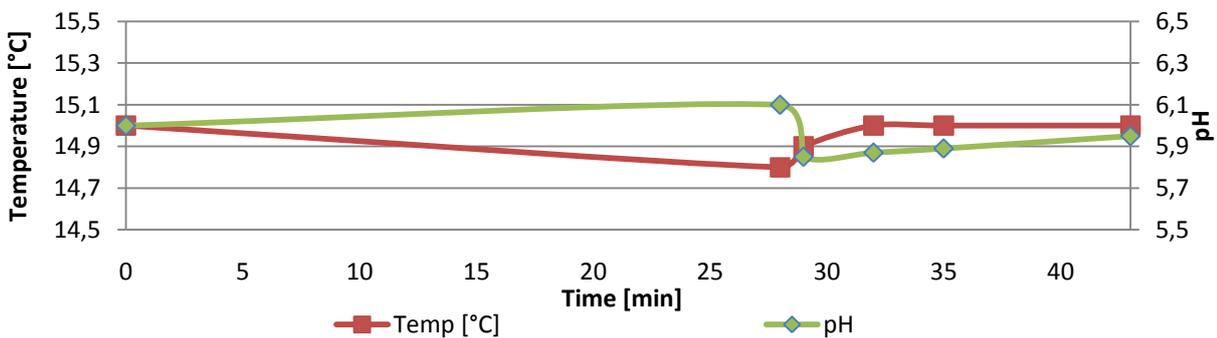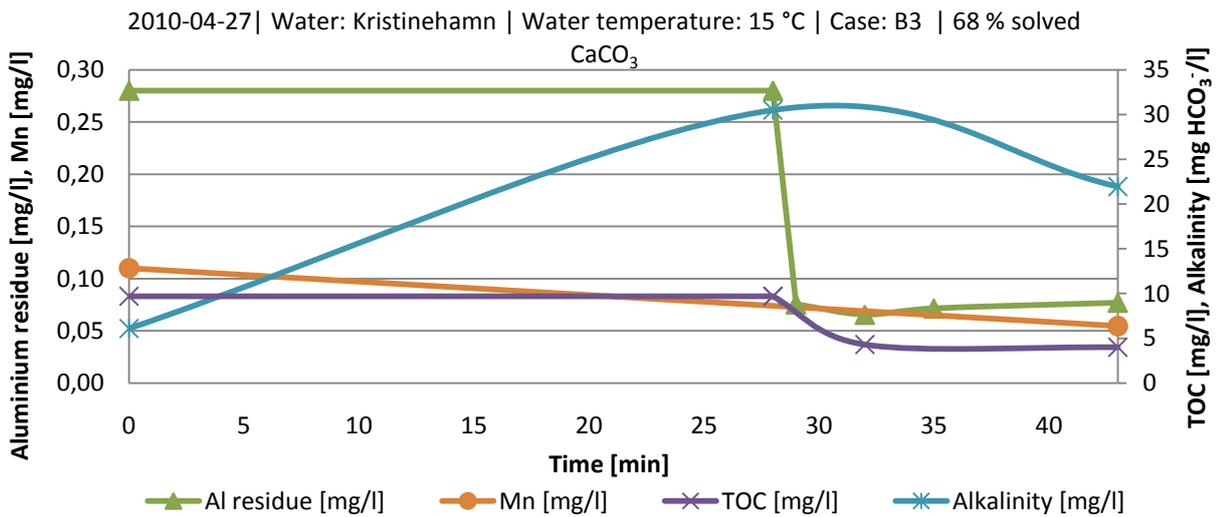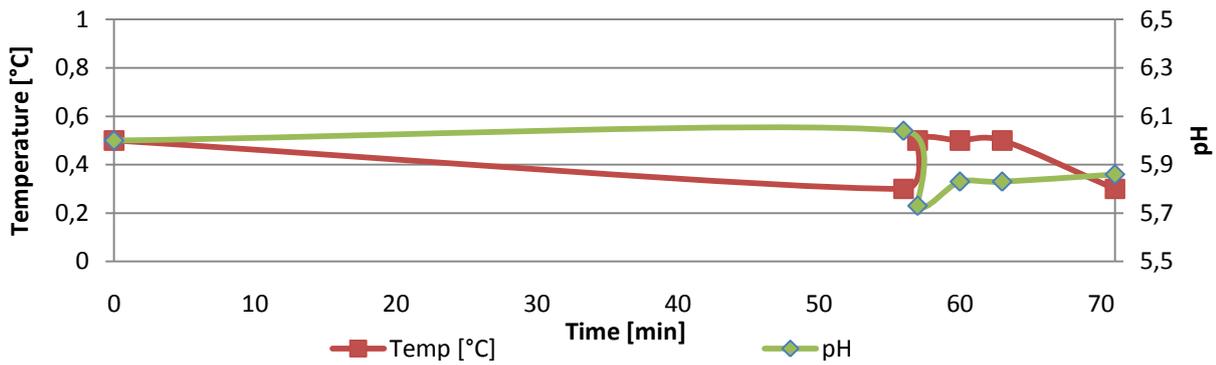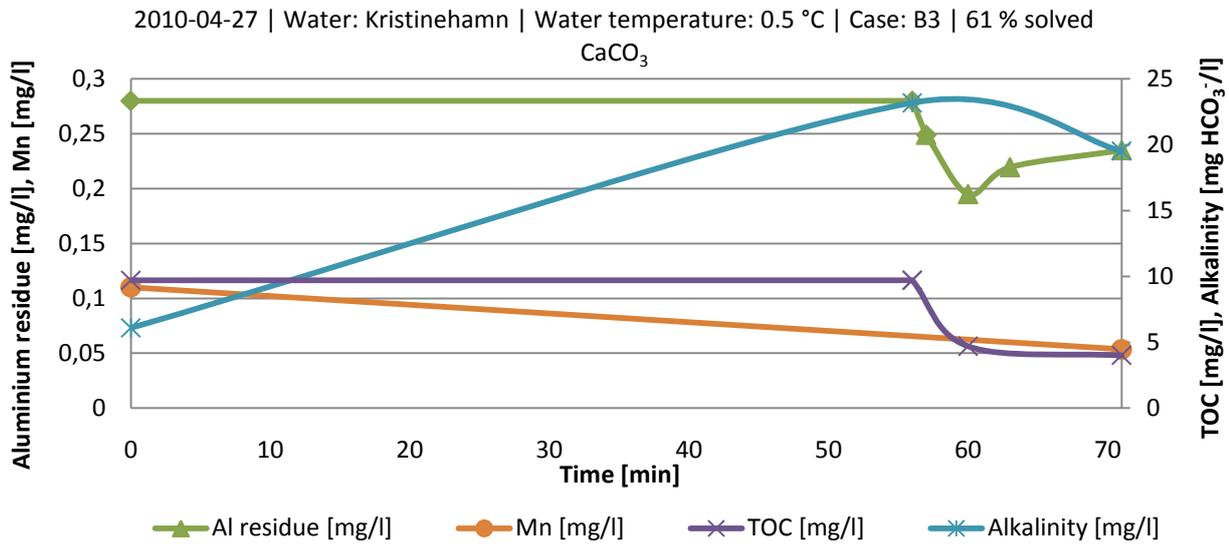
2010-04-27 | Water: Kristinehamn | Water temperature: 0.5 °C | Case: B3 | 61 % solved CaCO₃

2010-04-27 | Water: Kristinehamn | Water temperature: 15 °C | Case: B3 | 68 % solved CaCO₃

Appendix D2 - Additional results test round II

2010-04-19 | Water: Lerum | Water temperature: 0.5 °C | Case: B3 | 65 % solved CaCO$_3$
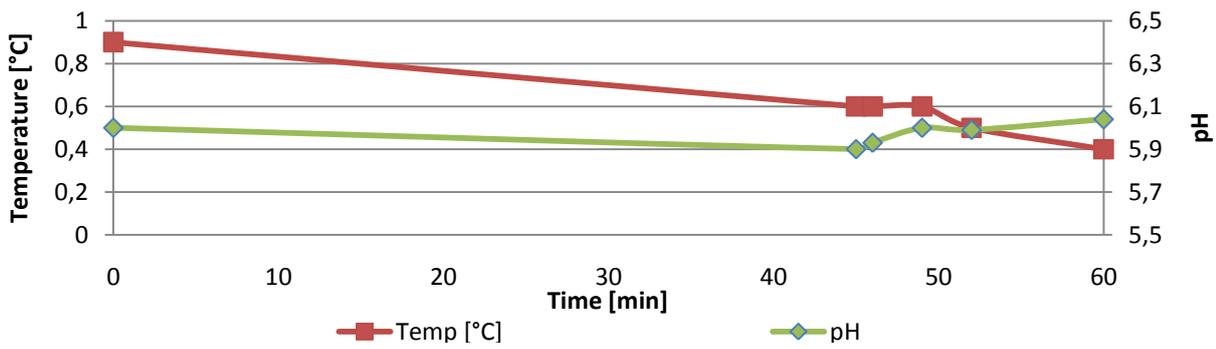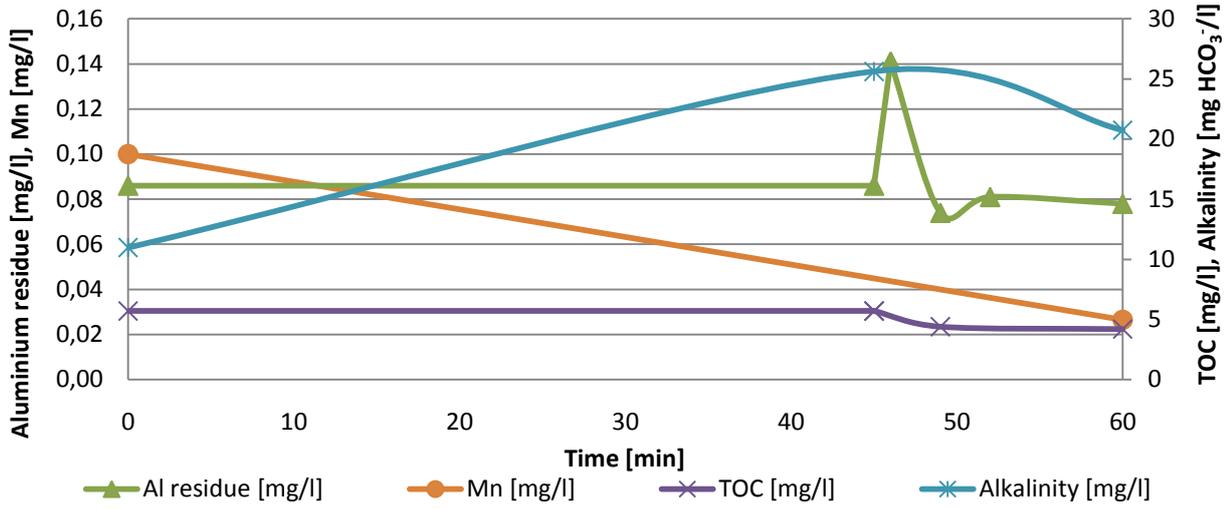
2010-04-19 | Water: Lerum | Water temperature: 15 °C | Case: B3 | 72 % solved CaCO$_3$