



PRECIPITATION OF IMPURITIES FROM BRINE

Lappeenranta–Lahti University of Technology LUT

Master's Degree Programme in Chemical and Process Engineering, Master's thesis

2021

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ABSTRACT

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Precipitation of impurities from brine

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60 pages, 44 figures, 6 tables and 4 appendices

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Keywords: sodium chlorate, brine, impurities, precipitation

The pulp and paper industries use chlorine dioxide, ClO_2 , for bleaching. It is produced mainly from bulk chemical sodium chlorate, NaClO_3 . Production of sodium chlorate is performed by electrolysis of brine. Impurities that enter the chlorate process can contaminate the cell liquor and affect electrolyzer operation and performance. Impurities impact chlorate cell anodes and cathodes, reducing operating efficiencies and increasing operating voltages.

The aim of literature part of this thesis was to review the main impurities in the chlorate cell liquor, which influence the most to the energy consumption and the conditions where those impurities precipitate and how these impurities could be precipitated.

The purpose of experimental work was to examine the precipitation conditions of brine impurities used for sodium chlorate manufacturing. The impurities were precipitated and filtered by specially designed experimental apparatus. The experimental apparatus consists of two similar precipitation and filtering stages. The brine and deposit samples were analyzed by using ICP-device (Inductively coupled plasma). Brine impurities were precipitated in two different pH levels and by using precipitants such as sodium carbonate and ferric chloride.

From the ICP-results could be observed that the major impurities in the brine are aluminium, calcium, magnesium, iron, phosphorus and silicon. It could be also noticed that sulphates seem to accumulate to the brine and this causes the solubility of sodium chloride to reduce. The results from the first two trial points had some positive trends. Aluminium, calcium, silicates and phosphates levels seem to lower after precipitation stages. Lower pH alone in the impurity precipitating seems to have minor effect on removing impurities from the brine. Ferric(III)chloride appears to precipitate phosphates and some silicates from the brine. Sodium carbonate addition had a minor impact on decreasing calcium and magnesium levels in the brine. The combination of sodium carbonate and ferric(III)chloride addition did not give any further information which impurities that combination would precipitate more.

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Natriumkloraaatti, NaClO_3 on bulkkikemikaali jota käytetään pääasiassa selluloosan valkaisuun käytetyn klooridioksidin, ClO_2 , raaka-aineena.

Natriumkloraaattia valmistetaan suolaliuoksen elektrolyysillä. Epäpuhtaudet klooraattiprosessissa voivat saastuttaa kennoliuoksen ja vaikuttaa näin ollen elektrolyysi reaktorin käyttöön ja toimintaan. Epäpuhtaudet vaikuttavat klooraattikennon anodeihin ja katodeihin pienentämällä näiden toiminnan tehokkuutta sekä lisäämällä näiden käyttöjännitteitä.

Kirjallisen osan tavoitteena oli selvittää energian kulutuksen kannalta tärkeimmät kennoliuoksen epäpuhtaudet sekä olosuhteet, joissa nämä epäpuhtaudet saostuvat ja selvittää miten näitä epäpuhtauksia voitaisiin saostaa. Kokeellisen osan tarkoituksena oli selvittää käytetyn suolaliuoksen epäpuhtaudet ja keinoja niiden saostamiseen. Epäpuhtauksia suodatettiin työtä varten rakennetulla koelaitteistolla. Koelaitteisto koostui kahdesta samanlaisesta saostus- ja suodatusvaiheesta. Suolaliuos- ja sakkänäytteet analysoitiin käyttäen ICP-laitetta (Inductively Coupled Plasma). Epäpuhtauksia saostettiin kahdessa eri pH tasossa ja käyttäen saostajina natriumkarbonaattia sekä rautakloridia.

ICP-tuloksien perusteella suolaliuoksen pääasialliset epäpuhtaudet ovat alumiini, kalsium, magnesium, rauta, fosfori ja pii. Lisäksi havaittiin sulfaattien kertyvän suolaliuokseen ja näin ollen vähentävän suolan liukoisuutta. Kahden ensimmäisen koepisteen perusteella havainnointiin, että alumiini, kalsium, silikaatti ja fosfaatti tasot vähenivät saostusvaiheiden jälkeen. Alemman pH tason yksinään ei havaittu vähentävän epäpuhtauksien määrää suolaliuoksessa. Rautakloridin havaittiin saostavan hyvin fosfaatteja ja silikaatteja. Natriumkarbonaatilla sen sijaan ei näyttänyt olevan suurta vaikutusta kalsium ja magnesium tasojen pienentämisessä. Myöskään natriumkarbonaatin ja rautakloridin yhteisvaikutuksella ei saatu lisätietoja siitä, miten niiden yhdistelmä saostaisi epäpuhtauksia paremmin.

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Imatra, December 2021

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1 INTRODUCTION

The pulp and paper industries use chlorine dioxide, ClO_2 , for bleaching. It is produced mainly from bulk chemical sodium chlorate, NaClO_3 . Sodium chlorate is used also in weed control, production of potassium chlorate and sodium chlorite and several other smaller applications.

Production of sodium chlorate is performed by electrolysis. This process uses salt, water and electricity as its feedstock. The end products are sodium chlorate and hydrogen gas. The sodium chlorate is produced continuously in specially designed cells. The electrolytic cells consists of anodes, which are made of titanium and covered with a noble metal coating and of cathodes which are generally made of steel. The formation of hydrogen takes place at the cathode and chlorine is formed at the anode. The hydrogen gas is separated from the liquid phase and chlorine, due to the pH conditions, remains in solution forming hypochlorous acid and hypochlorite ions. The liquor is continuously circulated between the cells and the reaction tanks.

Impurities that enter the chlorate process can contaminate the cell liquor and affect electrolyzer operation and performance. In unseparated systems like chlorate cell technology, the need to reduce the interelectrode gap to save power and the trend toward closed loop systems requires the reduction of electrolyte impurities. Impurities impact chlorate cell anodes through the classical failure modes of coating loss, passivation and blinding deposits. The impurities of brine can also deposit on the cathodes, reducing operating efficiencies and increasing operating voltages.

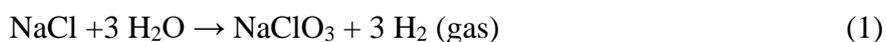
Typical brine contains various amounts of magnesium, calcium, iron, silica, sulphate, aluminium, fluoride, phosphates, barium and strontium. They can be grouped to: cationic impurities such as Ca^{2+} and Mg^{2+} , anionic impurities such as sulphate and fluoride, and non-ionic impurities such as aluminium and silica. These impurities can be precipitated with chemicals such as sodium hydroxide, sodium carbonate and calcium chloride, and can be filtered off together with the salt insolubles. Silicon can be removed by addition of magnesium ion to form insoluble magnesium silicate or by precipitating with iron compounds. Removal of phosphates can also be achieved by addition of iron compounds. The ion

exchange is the option for a secondary brine purification. The formation of calcium and magnesium “fur” on the cathodes is unavoidable even with ion exchange brine purification. Therefore, it is economical to shut down the plant occasionally, empty the cells and the reactors and acid wash the system with HCl. This restores the cathodes to a clean condition and significantly reduces cell voltages.

The aim of literature part of this thesis is to review the main impurities in the chlorate cell liquor, which influence the most to the energy consumption and the conditions where those impurities precipitate. First the principles and chemistry of sodium chlorate production are reviewed to give enough theoretical background to the next chapters. In experimental part the main purpose is to find the most suitable conditions for impurity removal by precipitating.

2 CHLORATE CELL CHEMISTRY

The overall equation for the reaction involving sodium chloride to produce sodium chlorate is given by deceptively simple reaction 1.



However, there are several reaction steps in this process along with a number of side reactions. Present in the cell are sodium, chloride, and chlorate ions, plus hypochlorite, hypochlorous acid, oxygen, hydroxide, protons and dichromate. All of these except sodium and dichromate are products and/or reactants in the chlorate process. The interaction of these species with each other and with the electrodes, both anode and cathode, is responsible for the side reactions that result in by-products and in a loss of efficiency. /1/

A step-by-step view of the formation of chlorate starts at the anode where the chloride ion is oxidized to produce chlorine. This is the same reaction (2) that occurs in chlor-alkali cells.



The sole function of the anode is to produce the chlorine at a low overall potential. The rest of the chlorate production process depends then on solution chemistry. As shown in Fig. 1, the chloride ion is oxidized at the anode to produce chlorine atoms which recombine to form chloride molecules. The chlorine molecules leave the anode surface to further react in the solution. The important feature of this part of the process to keep in mind is that the chlorine production is a surface reaction and substances adsorbed or deposited on the anode surface can interfere with this process, resulting in higher potentials, decreased efficiency and premature failure of the anode. /1/

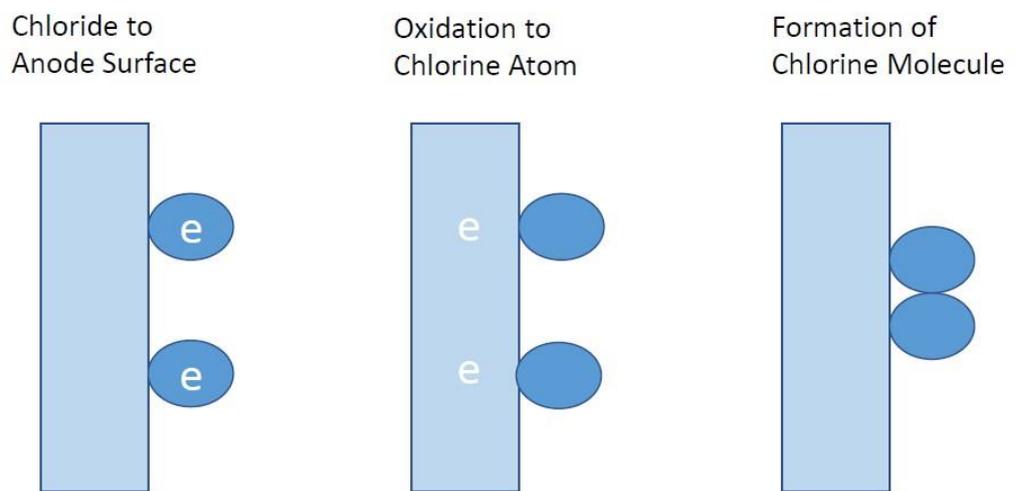
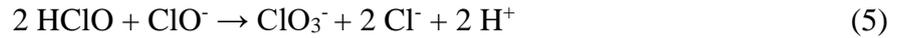


Fig. 1 Schematic of chlorine evolution mechanism according to /1/

Once the chlorine molecule is produced and leaves the anode surface it is ready to produce hypochlorite (reaction 3) which is in equilibrium with hypochlorous acid (reaction 4). /1/



It is the hypochlorite species which then actually forms the chlorate molecule through the reaction of two moles of hypochlorous acid with one mole of hypochlorite according to reaction (5). This reaction is enhanced by higher temperatures typically 60-80°C and by allowing a sufficient residence time for the reaction to proceed to completion. Reaction rate is optimum at a pH of 6-7 /2/.

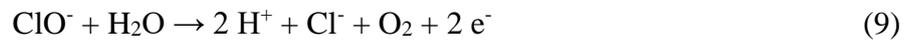
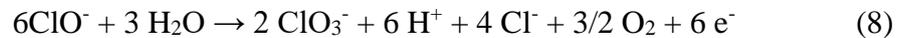


At the cathode, the principal reaction (6) is the reduction of water to hydrogen and the formation of hydroxide ions



The hydroxide ions are essentially consumed by the hydrolysis reaction of the chlorine while the hydrogen is the principal by-product. The key improvement opportunity for cathodes lies in decreasing the overall potential for reaction 6.

Besides these reactions in the chlorate cell there are a number of side or parasitic reactions, both chemical and electrochemical, that can occur which can decrease the efficiency of the process and produce by-products. The parasitic reactions involving the anode are



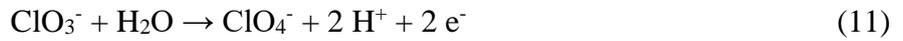
Reaction 7 is simple water oxidation. This reaction is usually relatively scarce, but becomes more significant as the chloride concentration drops. Also if the electrolyte feed is impeded the amount of chloride reaching the anode surface will be decreased and the oxidation of water will increase.

Reactions 8 and 9 will decrease the current efficiency of the process by destroying the hypochlorite previously made. These reactions are also a source of oxygen in the cell gas. /3/

In the electrolyte itself, the hypochlorite can undergo a decomposition reaction (10) which again will decrease the efficiency of the process and also produce oxygen.



One other reaction to be considered is the oxidation of chlorate to perchlorate. While this reaction (11) does not produce oxygen it does represent a side reaction that has become more significant with the recent trend towards closed loop systems.

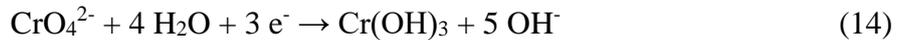


At the cathode, the principal parasitic reaction (12) also involves the hypochlorite ion. Like wise, the chlorate molecule can also be reduced as in reaction (13). Both of these represent a loss of efficiency, but do not produce oxygen. /1/



2.1 Chromate addition

Chromate is added to chlorate electrolyte to form a thin film of chromium hydroxide on the cathode as seen in reaction 14.



This thin chromium hydroxide film prevents its own growth as well as the parasitic reactions (reactions 12 and 13), while still allowing the hydrogen evolution to proceed on the cathode /3/. The thickness and growth rate of the film depends on such factors as the cathode material, the electrode potential and the chromate concentration.

An additional positive effect of chromate is the enhanced buffer capacity in the pH range 5-7, where formation of chlorate (reaction 5) has its highest rate. Chromate buffers according to reactions 15 and 16. /2/



3 SODIUM CHLORATE PRODUCTION

3.1 Introduction

Sodium chlorate is produced from sodium chloride and purified water in undivided electrochemical cells. A low concentration of sodium dichromate in the range 2-6 g/l is added to improve the current efficiency /4/. The process is carried out in specific pH and temperature conditions. The process is continuous and it has a high degree of closure. The by-product of the electrolysis is hydrogen which can be utilized as a fuel. Most of the industrial electrolyte cells are monopolar cells, constructed of titanium and steel /4/.

A typical process of sodium chlorate production consists of the following steps, brine production, brine purification, electrolysis, crystallisation and drying or dissolving. Typical process is given in the block diagram in Fig. 2. Evaporation can be used at brine purification stage where it concentrates the brine to remove sulfate ions.

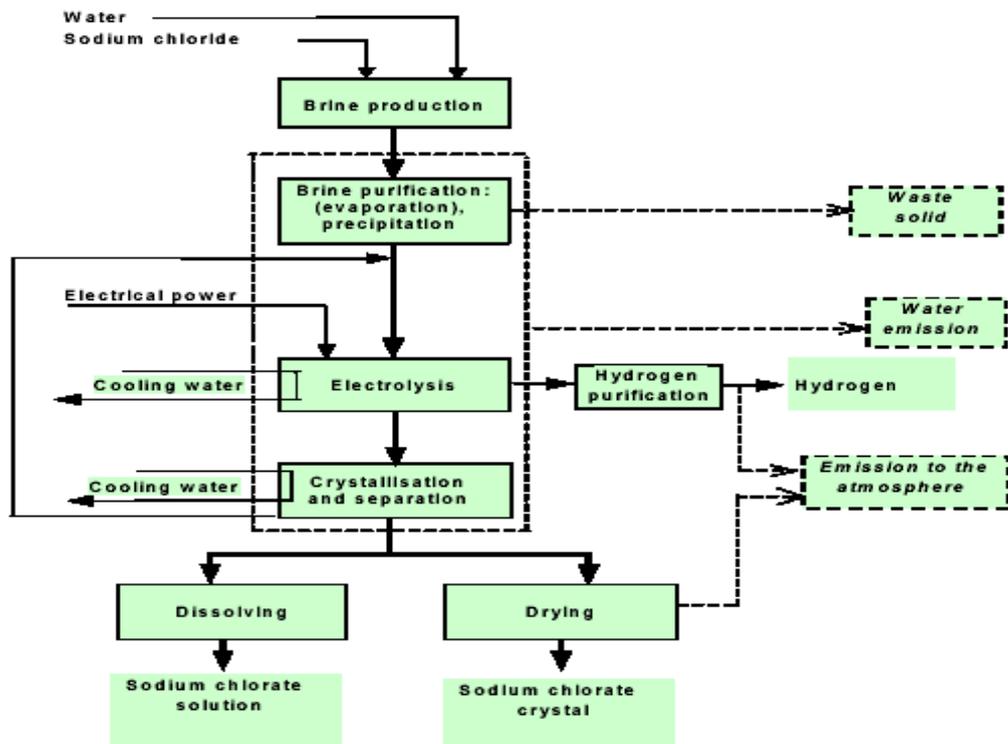


Fig. 2 Sodium chlorate production, block diagram. /5/

3.2 Brine production and purification

Saturated sodium chloride brine is prepared by dissolving the solid sodium chloride salt in hot process or softened water in a saturation tank. The quality of the sodium chloride depends on its origin and availability. Brine quality should be very clean for the electrolytic process.. The impurities can be precipitated with chemicals and removed by filtration together with the salt insolubles. A secondary purification of the brine may be achieved by ion exchange. /4/

3.3 Electrolysis

Hydrochloric acid and dichromate are added to the purified brine in order to get proper conditions for promoting sodium chlorate formation and to avoid side reactions during electrolysis. Then brine is led into a set of electrolysis cells and reaction tanks. As a whole, electrolysis is carried out in a controlled range of temperature between 60-80°C and pH 6,0-6,5. The electrode gap is typically around 3mm and with current densities in the range 2-3 kA/m² /6/. The formation of hydrogen gas takes place at the cathode and at anode chlorine is formed. The hydrogen gas is separated from the liquid phase and chlorine, due to the pH conditions, remains in solution forming hypochlorous acid and hypochlorite ions. The liquor (the solution from cells) is continuously circulated between the cells and the reaction tanks. In the cells and in the reaction tanks, sodium chlorate is formed to the following overall reaction 17. /4/



The hydrogen coming from the electrolysis cells contains impurities like chlorine and oxygen. For safety reasons the oxygen content must be controlled. The production of oxygen can be minimised by controlling and optimizing the process parameters. Chlorine is removed from hydrogen by using reducing agents or in scrubbers with sodium hydroxide. The heat energy generated in the cells is taken away by cooling the circulated liquor. The liquors coming from electrolysis are stored in tanks for finishing the transformation of hypochlorite into chlorate. NaOH- solution is used for pH control. Small quantities of sodium hypochlorite

remain in the liquor after this stage. Corrosion problems can be avoided before the next steps by using e.g hydrogen peroxide H_2O_2 as a reducing agent. /5/

3.4 Crystallisation

Sodium chlorate is recovered from the liquors by concentration in a crystallisation unit using heat and vacuum or by lowering the temperature of liquors using refrigerating systems after an intermediate step of concentration by vacuum evaporation. Sodium chlorate crystals are separated and washed by filtration. The mother liquor and the washing liquid, containing sodium chloride, sodium chlorate and sodium dichromate, are recycled back to the main loop. /4/

3.5 Drying

The sodium chlorate crystals are dried with warm air in a dryer. Fluidised bed dryers are commonly used with an air temperature of around 150°C. The drying process generates an emission of sodium chlorate particles. This emission is reduced by using scrubbers, filters and other clean-up systems.

Sodium chlorate can be stored and delivered as crystals in bulk or upon requirements as a water solution. /4/

3.6 Electrolyte cell configurations

Sodium chlorate cells can be categorised to monopolar and bipolar cells. Monopolar and bipolar cells differ by the construction materials. Monopolar cells can be built entirely of such metals as steel and titanium. Bipolar cells must be built of plastic materials or metal sections that are carefully insulated from each other, because of the several unit cells within one electrolyzer vessel.

The principle of monopolar cells is that every part of an electrode placed into a cell has only one polarity, either negative (cathodic) or positive (anodic). Monopolar cells have several numbers of interleaved cathodes and anodes to provide large surface areas, thereby allowing very high cell currents. However, the cell voltage is restricted to that of one unit cell, which is between 2,75-3,5 V. Two variations of the monopolar cell are seen in Fig. 3. The simple monopolar cell in which only straight-through liquor circulation is desired, is used for

example by Krebs /6/. The other variation of the monopolar cell with two cathodes per anode is used by Ugine-Kuhlman and Pennwalt /6/. This variation allows some internal circulation within the cell. Other interesting feature is that cathodes in this configuration may be slotted or perforated. Slotting and perforating increases turbulence on the cathode face and also reduces H₂ blistering of steel. Increased turbulence has the beneficial effect of decreasing the thickness of calcium and magnesium deposits.

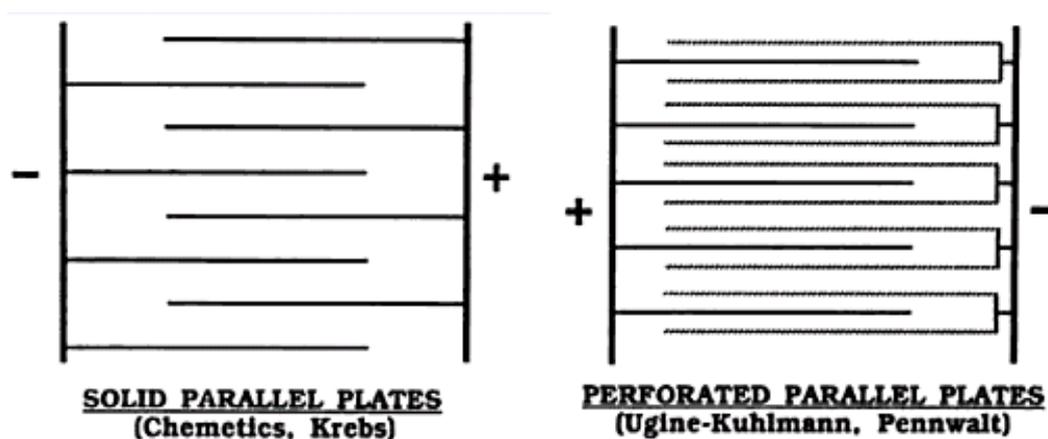


Fig. 3 Electrode configurations for monopolar cells. /6/

The principle of bipolar cells is that apart from the two leads that bring the current into and out of the cell, all other electrodes placed between these leads have a negative polarity at one end or on one face and a positive polarity at the other end or on the other face. Fig. 4 illustrates the major configurations of bipolar cells. The plate bipolar cell is the arrangement used in most graphite electrode cells. /6/

The monopolar cells are mainly used in Finland. Cell voltage is normally ~3 V, current efficiency 90-96%, temperature 80-85%, pH 6-7 and sodium chlorate's maximum concentration 650 g/l /7/. Cells are connected in series. Kemira Chemicals uses horizontal monopolar cells, which it has devised by itself. /6/

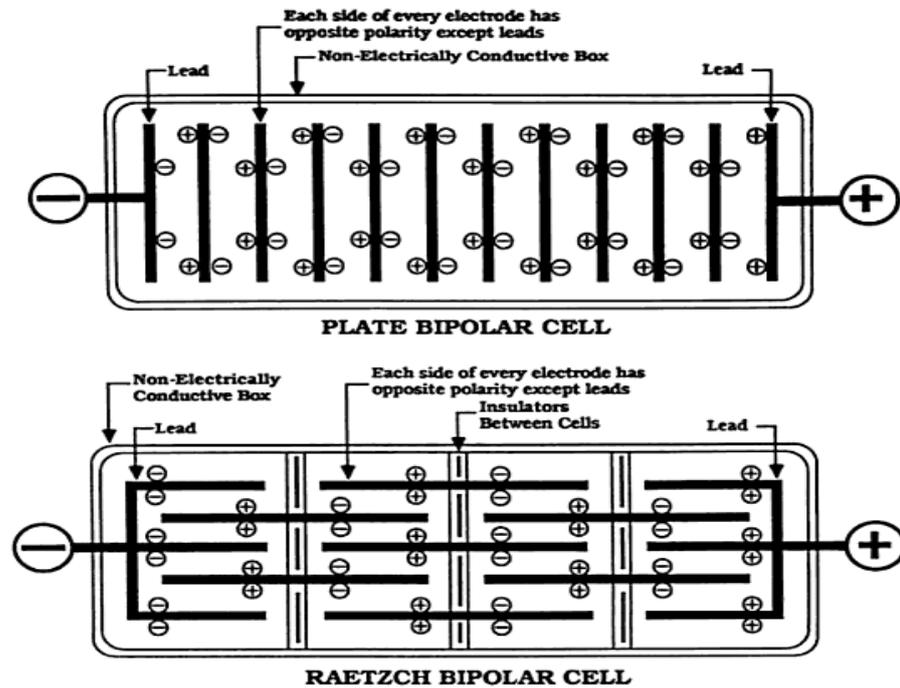


Fig. 4 Electrode configurations for bipolar cells. /6/

3.7 Materials of cell construction

Steel surfaces are cathodically protected during normal operation and also during shutdown conditions with the aid of relatively low current cathodic protection rectifiers that supply a current of about $15\text{-}75\text{ A/m}^2$. /6/

The steel for cathodes must be a relatively pure low-carbon grade and free of inclusions to minimize problems of hydrogen blistering. Severe hydrogen blistering can result in contact between the anode and the cathode, thereby electrically shorting the cell. Most industrial cathodes are therefore perforated to further reduce the incidence of blistering.

The titanium anodes are today almost always coated with ruthenium oxides, which are commonly called dimensionally stable anodes, DSAs. In Fig. 5 is illustrated the structure of DSA. These DSAs anodes have lots of benefits, such as high current density and efficiency and dimensional stability, as the name says. However, these anodes are sensitive to some cell operating conditions and the presence of such impurities as Mn^{2+} , Ba^{2+} , F^- and Si in combination with Fe, Al and Mg, organic substances and high concentrations of SO_4^{2-} . High concentrations of these impurities result in poor anode performance and sometimes degradation of the coatings, with significantly shortened life. /6 /

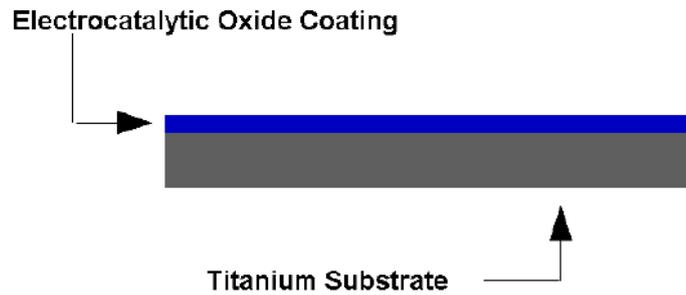


Fig. 5 Dimensional stable anode structure. /8/

4 ELECTROLYTE IMPURITIES IN CHLORATE CELLS

The control of brine quality has received major attention over the years. In unseparated systems like chlorate cell technology, the need to reduce the interelectrode gap to save power and the trend toward closed loop systems has required the reduction of electrolyte impurities. /9/

Impurities that enter the chlorate process can contaminate the cell liquor and effect electrolyzer operation and performance. It is well known that there are impurities which result in increased oxygen levels in the cell gas. There are other impurities which effect anode and/or cathode performance resulting in an increase in cell voltage. The major impurities of brine are calcium and magnesium. Both of these deposit on the cathodes of the electrolytic cells. It is essential to remove calcium and magnesium as completely as possible. Failure to remove these impurities results in increasing cell voltage because of the growth of a cathodic calcium and magnesium deposit, which adds to the cathode layer resistance.

Organics have been linked to temporary cell liquor foaming problems. Salt, water used to dissolve salt or chemicals added to process can contain organic components. /10/

Possible main effects on electrolyzer operation caused by excessive levels of cell liquor impurities are listed in Table I.

Table I Main effects on electrolyzer operation caused by brine impurities. /10/

Brine impurities	Possible effects on electrolyzer operation
Sodium sulphate, Na₂SO₄	-Co-crystallization of NaClO ₃ and Na ₂ SO ₄ between the electrodes. - Increase in cell voltage. Reduction in cell liquor circulation through a cell with oxygen level increase in the cell gas. Increase in tendency for foaming. -Very high SO ₄ levels can increase anode coating wear rate.
Aluminium, Al	-Forms insoluble compounds with Ca and Si. -Aluminium is amphoteric, and it can be present as the cation Al ³⁺ or as the anion AlO ₂ ⁻ . In neutral solutions it is present as Al(OH) ₃ or as a fairly insoluble form as Al ₂ O ₃ ·3H ₂ O.
Fluoride, F	-In high enough concentrations can form HF acid which can dissolve ruthenium or titanium component of anode and titanium substrate
Silica, S	-Hard deposits or scale (silicates) formed on electrodes and other cell room equipment. Possible increase in cell voltage -At pH > 10 silica is in soluble form HSiO ₃ ⁻ or SiO ₃ ⁻ , and below pH 10, it is SiO ₂ or H ₂ SiO ₃ .
Iron, Fe	-Iron compounds can deposit on the anode. No effect on cell voltage, except iron phosphates. -Can act as a catalyst to cause decomposition of sodium hypochlorite to oxygen. More effective catalyst at 80°C than 60°C and in presence of other catalyst – Ni, Cu, Ru, etc
Magnesium, Mg	-Normally enters chlorate system if brine treatment is inadequate. Can enter with plant water or HCl. Mg compounds can deposit on cathodes leading to an increase in cell voltage. Scale has a high resistance.
Calcium, Ca	-Calcium enters with brine, especially if there is no secondary brine treatment. Can enter with plant water or HCl. Ca compounds deposit on the cathode. - Cause a rise in cell voltage. Scale has a high resistance.
Nickel, Ni	-Can cause catalytic decomposition of “hypo” to oxygen. More effective at 80°C than 60°C. Normally enters with brine or HCl.
Copper, Cu or Cobalt, Co	-Effective catalyst to decompose hypochlorite.
Barium, Ba or Strontium, Sr	-Precipitate as BaSO ₄ or SrSO ₄ if the solubility limits are exceeded. -Can precipitate on top and within anode coating. Coating adhesion can be lost. Can cause increased cell voltage.
Manganese, Mn	-Can be oxidized to manganate which can deposit on anodes. -Can lead to increased cell voltage.
Platinum, Pt	-Catalyst that can decompose hypochlorite to oxygen.
Ruthenium, Ru	-Catalyst that can decompose hypochlorite to oxygen. -Comes from loose coating during initial period of operation.
Vanadium, V	-Can be oxidized to vanadate which can deposit on anodes. -Can lead to increased cell voltage. -Can cause catalytic decomposition of hypochlorite to oxygen.
Suspended solids	-Can build up in between electrodes and in vessels and piping. -Excessive amounts can lead to cell blockages, reduction in electrolyte flow and consequent localized or widespread anode coating damage (caused by low NaCl levels or high O ₂ levels).
Phosphates, PO₄	-May be beneficial in reducing the amount of electrode scale. -Higher levels can lead to FePO ₄ deposition on anodes with subsequent cell voltage rise.

The solubility products of substances that might precipitate in a brine are listed in Table II. The solubility products are presented in literature data for the substances in water near room temperature and it should be noted that the in concentrated brine the solubility behavior might be different. /11/

Table II Representative solubility product constants/11,12/.

Substance	Solubility product constant, K_{sp} at 25°C
MgCO ₃	6.8 x 10 ⁻⁶
CaCO ₃	3.4 x 10 ⁻⁹
SrCO ₃	5.6 x 10 ⁻¹⁰
BaCO ₃	2.6 x 10 ⁻⁹
CaSO ₄	4.9 x 10 ⁻⁵
BaSO ₄	1.1 x 10 ⁻¹⁰
Mg(OH) ₂	5.6 x 10 ⁻¹²
Ca(OH) ₂	5.0 x 10 ⁻⁶
Sr(OH) ₂	1 x 10 ⁻⁴
Ba(OH) ₂	5 x 10 ⁻³
Fe(OH) ₂	4.9 x 10 ⁻¹⁷
Fe(OH) ₃	2.8 x 10 ⁻³⁹
FePO ₄ · 2H ₂ O	9.9 x 10 ⁻¹⁶
Mn(OH) ₂	5.6 x 10 ⁻¹²
Ni(OH) ₂	5.5 x 10 ⁻¹⁶
Ba(IO ₃) ₂	4.0 x 10 ⁻⁹
Mg ₃ (PO ₄) ₂	1.0 x 10 ⁻²⁴

Also following guidelines for cell liquor impurities is shown in Table III. /10/

Table III Maximum concentrations of cell liquor impurities /10/

Brine impurities	Max. concentration, mg/l
Na ₂ SO ₄	20000
F	25
Si	5
Fe	15
Mg	1
Ca	1
Ni	1
Cu	1
Co	0.05
Sr	1
Ir	0.05
Ba	0.1
Mn	0.1
Rh	0.5
Pt	0.1
Ru	0.1
V	0.5
Suspended solids	10
Phosphates	10

4.1 Impurity effects on electrodes

DSA (dimensionally stable anodes) service life and performance are greatly influenced on occasion by the impurities present in chlorate cell electrolytes. Impurities impact chlorate cell anodes through the classical failure modes of coating loss, passivation and blinding deposits. With cathodes, reduced operating efficiencies and increased operating voltages are observed in cell performance caused by deposits /8/. Impurities that result in precipitation within the cell compartments can cause a loss of flow within the electrolyzer or locally between anodes and cathodes in unseparated systems.

There are four ways to interrupt the electrical circuit between the metal substrate of the electrode and the electrolyte. The interface between the catalyst and the substrate can become non-conductive preventing electron flow from the catalyst to the substrate (passivation). Secondly, the catalyst can be lost in service exposing the valve metal substrate, which oxidizes and cannot accept electrons from solution without the presence of the catalyst (coating loss). Thirdly, the substrate can be chemically attacked at the coating interface, resulting in loss of adhesion of the coating (substrate attack). And finally, a foreign material can deposit on the surface of the catalyst effectively isolating the catalyst from the solution (blinding deposits). Impurities in the electrolyte impact directly and indirectly on each of these failure mechanisms. /8/

4.2 Failure mechanisms

The following paragraphs deal with more specific details of failure mechanisms of anodes.

4.2.1 Passivation

Substrate passivation can be defined as the growth of a non-conductive oxide barrier between the DSA catalyst and the valve metal substrate as illustrated in Fig. 6.

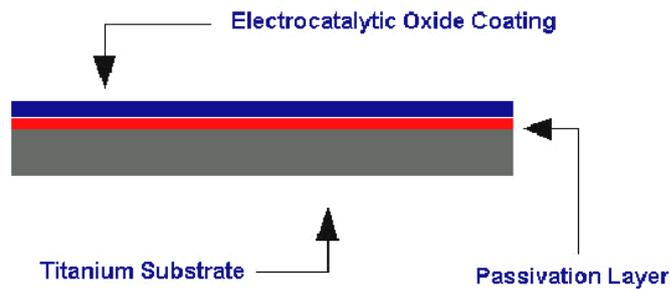


Fig. 6 Substrate passivation of dimensional stable anode. /8/

This is the primary failure mode for anodes designed for use in oxygen evolving applications such as electrogalvanizing. Passivation failures in chlor-alkali service have been rare but are observed in diaphragm and membrane cells /9/. Passivation effects are more prevalent in chlorate systems because of the characteristically small inter-electrode gap and the increase of concentration of impurities over time because of the closed loop systems /8/.

Impurities do not directly interact with the DSA to cause passivation failure but rather create conditions in which chloride ion is prevented from reaching the electrode surface in sufficient quantity to support the current passage. Water electrolysis takes over as the dominant reaction resulting in passivation. Any elements that can precipitate in sufficient quantity to block flow can lead to passivation effects. Historically Al, Ba, Ca, Mg, Si, Sr and Ti compounds have been contributors, but attention to brine quality over the years has minimized this source of passivation failure throughout the industry. /8/

4.2.2 Coating wear

Brine impurities directly and indirectly affect the catalyst wear mechanism. Normal performance is characterized in Fig. 7. Typically a 10-15% initial loss of catalyst is observed over the first six months to a year of operation /9/, followed by a gradual wear with time throughout the useful life of the coating. No change in voltage performance is expected until below 20% of original loadings is present. As wear continues, a gradual increase in operating voltage will be observed as wear exposes uncoated areas of the substrate as seen in Fig. 8. Current will shift to remaining active areas, locally increasing current density and observed operating voltage. /8/

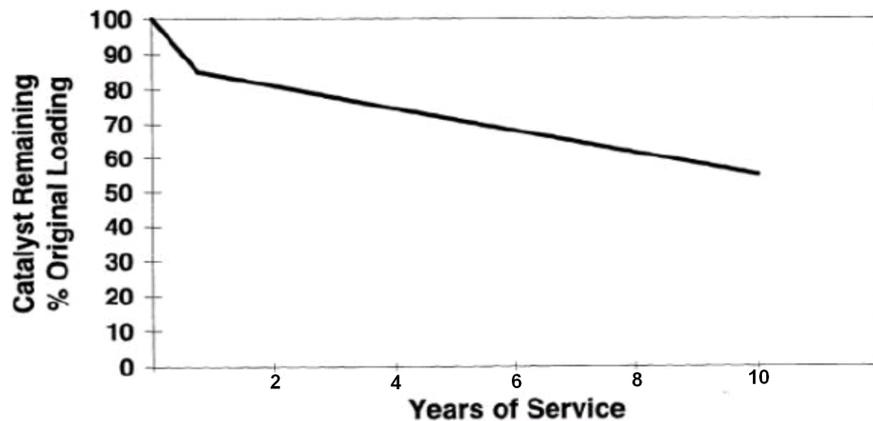


Fig. 7 Normal coating wear rate for chlorate dimensional stable anode. /8/

Wear accelerating impurities can be characterized into two groups. Those that attack the DSA directly when present in the electrolyte and those which have a secondary role by interacting with another part of the system causing subsequent effects on the DSA. These secondary impact materials are:

- calcium
- magnesium
- aluminium
- silica
- titanium oxides
- titanium hydrides
- suspended solids
- heavy metals

These materials directly impact on cathodes allowing the alkaline condition of the cathode region reach the DSA surface, directly attacking the coating matrix. In chlorate systems, hardness scales can grow from cathode surfaces to bridge the gap between anode and cathodes. The porous nature of these deposits works like a sponge, allowing caustic to directly attack the DSA matrix. Aluminium and silica are frequently found within these hardness deposits adding to the growth rate above that expected from hardness values alone. /9/

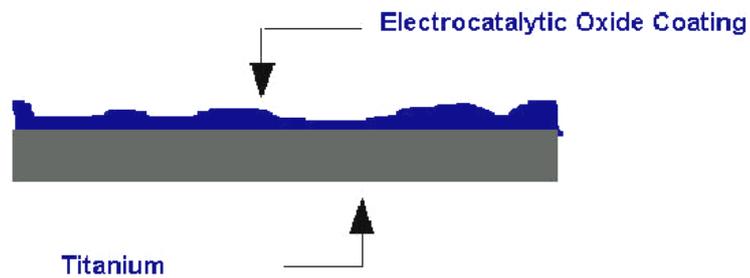


Fig. 8 Coating wear. /8/

4.2.3 Substrate attack

Fluoride ion directly attacks the titanium at the coating and substrate interface. The corrosion resistance of DSA depends on the stability of the oxide film /9/. Fluoride ion can penetrate this film, destabilizing the titanium surface. Titanium dissolution results in loss of catalyst. Substrate attack method is illustrated in Fig. 9. The symptoms of fluoride attack are characteristic of wear from titanium instability. /8/

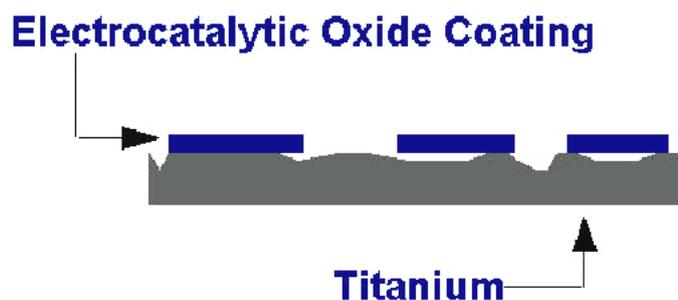


Fig. 9 Substrate attack. /8/

4.2.4 Blinding deposits

The most frequently encountered effect of brine impurities on DSA performance is the formation of blinding deposits. Both organic and inorganic deposits have been encountered over the years. The inorganic deposits can be the result of chemical precipitation when solubility product limits are exceeded as in the case of BaSO_4 or may be electrochemically oxidized to the anode. /9/

In general, these deposits form by both electrochemical and electrophoretic processes. As they form, they alter the current distributions within the cell and can result in locally high current densities in non-blinded regions. The first indication of a problem is usually raising cell potentials. Inorganic deposits are normally visible on inspection. Surface deposit effect can be seen in Fig. 10. Most common inorganic deposits are barium sulphate, phosphates, tin, iron, silicon and titanium in systems where Ti cathodes are used. /8/

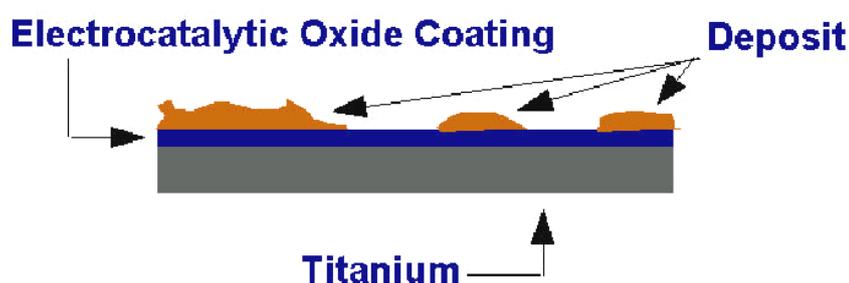


Fig. 10 Surface deposits. /8/

5 IMPURITY SOURCES IN THE CHLORATE PROCESS

Brine impurities originate from various sources and their effects on cell performance vary. The contaminants can be brought into the brine system by salt, by chemicals used in brine purification steps, by water for dissolving salt, from materials of tanks, pipework and cell components or by the process itself, and which the main source of these impurities is salt. The impurities in the salt depend on the origin of the raw material. Rock salt, vacuum salt, sea salt, brine from well mining or salt from waste incinerators serve as supplies of NaCl. Impurities can also enter the chlorate process from the water which is used to make brine, so the water should be treated before use to remove cations and silica. The more varied the sources are, the more diverse the impurities./13/

Combinations of different impurities and their interactions must also be considered. The elements of hardness, magnesium and calcium are the main impurities in salt. Salt is also the source of barium and strontium and additionally brine treatment chemicals.

Iron is a common impurity in plants that receive salt in bulk. Potassium ferrocyanide is added to the salt to prevent caking. Iron can also be dissolved from process equipment.

Sulphate is the principal anionic impurity in brine, usually present in gram-per-litre quantities. The other significant anionic impurity is fluoride. Fluoride does not cause problems even at the 50 ppm level, though precipitation of iron fluoride will occur if iron is present in the solution and as mentioned earlier, fluoride can damage anode coatings.

Silica by itself does not cause difficulty in the chlorate cell, but has synergistic effects when calcium and aluminium are present. Silica is considered to be difficult to remove from brine. Usually the silica containing salt is in the form of clay or sand. Silicas are quite insoluble but it is possible for silica to accumulate beyond its specified limits in the brine. Other sources include brine filter beds, filter aids, atmospheric contamination, concrete salt storage pads and process water.

Aluminium isn't very harmful impurity, but with calcium and silica it forms insoluble combinations. With silicates aluminium forms aluminosilicates. The sources of aluminium and silica are quite same /14/.

Experience in a commercial chlorate system has raised a concern over the effect of phosphates on anode performance in chlorate applications. /8/

Phosphates enter the chlorate process from salt and brine and also from hydrogen peroxide. Phosphates interact strongly with iron oxides/hydroxides by adsorbing on their surface and can precipitate with dissolved iron species to form iron phosphates. /14/

Impurity balance is the sum of incoming and outgoing material streams. From Fig. 11 we can observe these streams and the principle, how impurity balance is characterized.

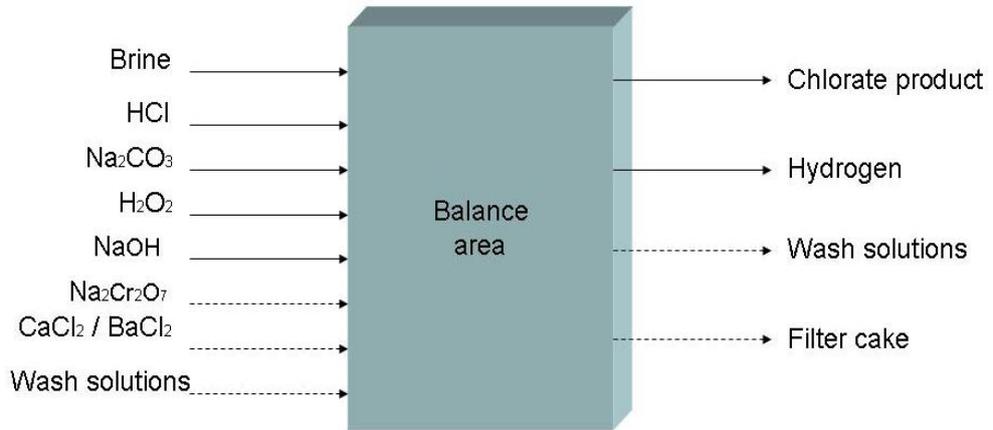


Fig. 11 Impurity balance-incoming and outgoing streams. The streams with dotted arrows are not continuous. /15/

6 REMOVAL METHODS FOR IMPURITIES

6.1 Brine treatment

Fig. 12 shows one example of block flow diagram for primary brine treatment. Sodium carbonate and sodium hydroxide are added to the brine so that metal hydroxides and carbonates can be precipitated. The produced brine are led straight to chlorate cells or brine can go to secondary brine treatment, ion exchange.

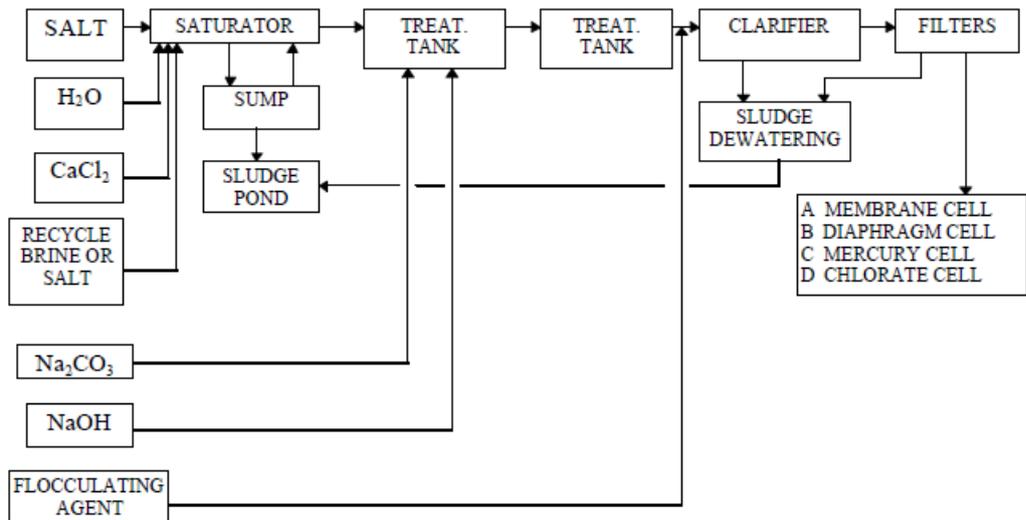
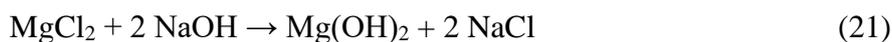


Fig. 12 Primary brine treatment block flow diagram. /17/

The aim of brine treatment is to remove contaminants that harmfully affect electrodes, separators, cell performance or product quality. The main elements to be removed are calcium and magnesium. Because of all salt is contaminated with sulphate salts, the treated brine solution contains sulphate, which cannot be removed by normal brine treatment. In closed systems, too much sulphate accumulates and must be removed. The brine purification is usually started with primary or chemical treatment which removes calcium and magnesium. It consists of the additions of chemicals to precipitate the cations as hydroxides and carbonates. Sodium carbonate and sodium hydroxide are typically used. The reactions that cause precipitation are /17/:



Reactions 18 and 19 produce Na_2SO_4 when CaSO_4 and MgSO_4 are converted to carbonates. While Ca and Mg are removed by precipitation, Na_2SO_4 accumulates and reduces the solubility of NaCl as shown in Fig. 13. Therefore, the sulphate content of the brine should be kept low.

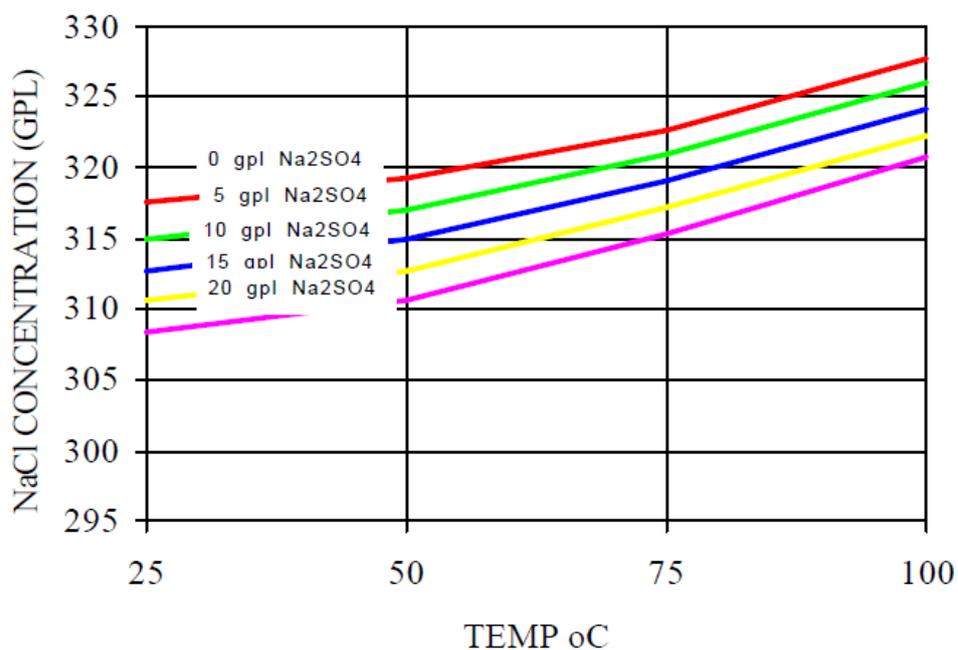


Fig. 13 Solubility of NaCl in system NaCl-Na₂SO₄-water. /17/

Reactions 18 through 22 are quite slow and generate precipitate with wide ranging settling characteristics. Affected factors to the reactions and precipitate formed are:

- Solubility of precipitate
- Temperature
- Time
- Chemical excess
- Agitation
- Ca/Mg ratio
- Flocculating aids
- Order of chemical addition

6.1.1 Solubility of precipitate

The addition of NaOH to the brine causes the formation of Mg(OH)₂ by reaction 21. Excess NaOH reduces the solubility of Mg(OH)₂. The solubility of Mg(OH)₂ in saturated brine versus NaOH concentration is shown in Fig. 14. It shows the Mg solubility is nearly zero at 0.1 g/l NaOH.

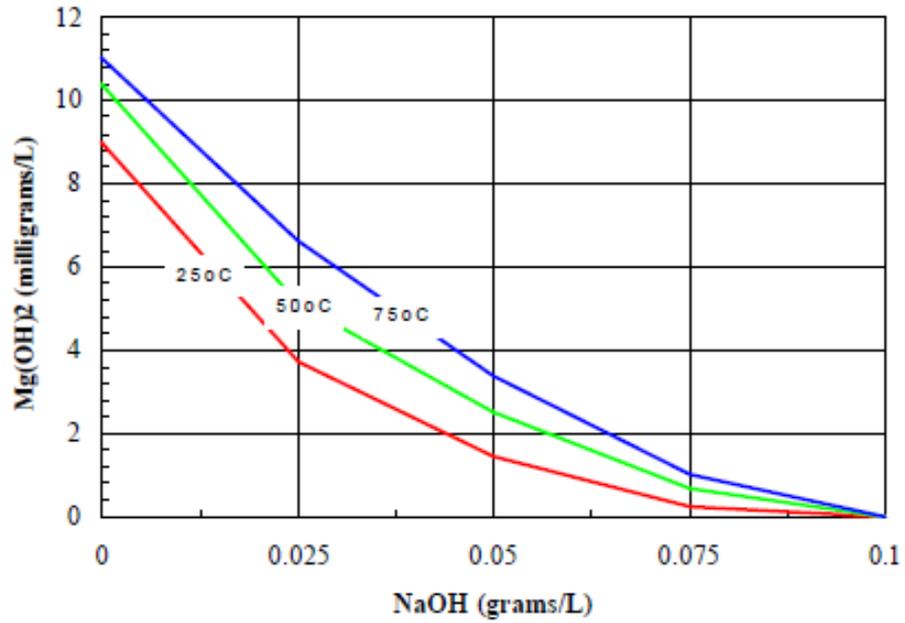


Fig. 14 Concentration of Mg vs. NaOH concentration in saturated brine. /17/

CaCO₃ is produced by reaction of CaSO₄ with Na₂CO₃ by reaction 18 and excess Na₂CO₃ reduces CaCO₃ solubility. Fig. 15 shows the solubility of CaCO₃ versus Na₂CO₃ concentration in brine. It shows the CaCO₃ solubility stabilizing at about 2 mg/l CaCO₃ between 0,5 and 0,7 g/l Na₂CO₃. These solubility limits help determine the recommended additional chemicals /17/

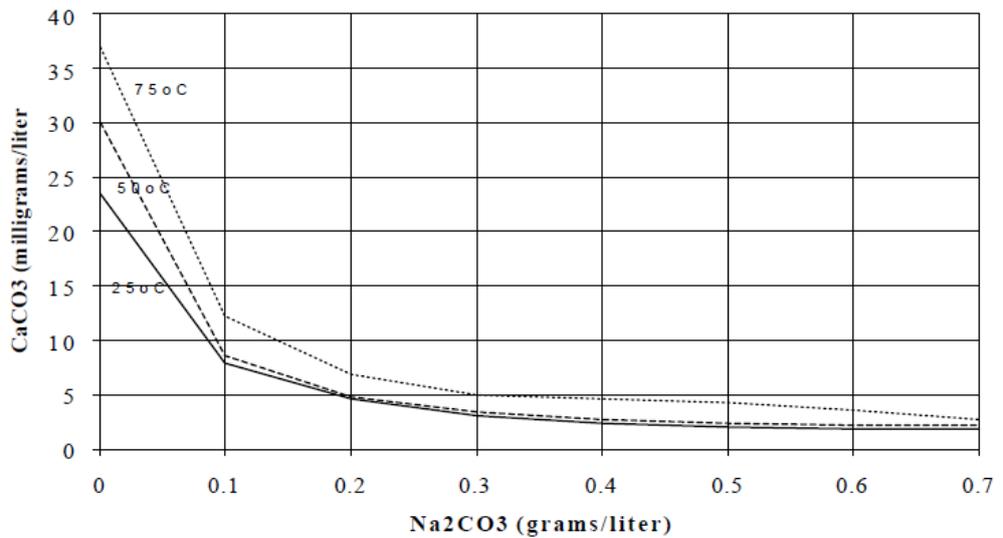


Fig. 15 Concentration of CaCO₃ vs. Na₂CO₃ in saturated brine. /17/

6.1.2 Temperature, time and chemical excess

Using only stoichiometric quantities, reactions 18 through 22 can take several hours. With excess chemical addition and proper temperature, reactions can be nearly complete in a few minutes. At 20°C, 20 to 40 minutes is required while at 60°C reactions are essentially complete in 2 to 5 minutes. Higher temperatures also increase crystal size and settling rate. Excess chemicals also reduce contaminant solubility. /17/

6.1.3 Agitation

Proper agitation is critical. The chemicals must be initially mixed into the brine thoroughly for uniform reactions and floc formation. Too much mixing can break the floc resulting in very long settling times and poor brine quality. No mixing is desired during flocculation. Because of that agitation should be mild, just enough to keep the treating chemicals well mixed. /17/

6.1.4 Ca/Mg ratio and flocculating aids

The objective of primary treatment is to produce a flocculant precipitate that will settle at about 38 cm/h or faster and produce brine with 10 ppm suspended solids or less. Generally, this can be reached without addition of flocculating agents. Brines with low or high Ca/Mg ratios (less than 4 or greater than 16) will probably require a need for the use of a flocculating aid. /17/

6.1.5 Order of chemical addition

There is disagreement about the order in which the NaOH, Na₂CO₃ and flocculating agent should be added to brine. It is recommended to add all the chemicals together or to separate addition points. NaOH should not be added before the Na₂CO₃ because once the metal hydroxides are formed and broken up without calcium carbonate, it is difficult to get them to settle. /17/

6.2 Precipitation methods for significant impurities

The significant impurities of brine are iron, fluoride, silicates, phosphates and aluminium. The precipitation of each impurity is presented more detailed in next paragraphs.

6.2.1 Iron

Iron concentrations should be in the low ppb range after primary brine treatment. Two possible approaches to lower the concentration of iron contaminants are precipitation as oxides or hydroxides and ion exchange. Oxides can be removed by adding NaOCl to the brine at a pH of 10-12, followed by filtration. Addition of NaOH precipitates iron hydroxide. Formed insoluble precipitate is Fe(OH)₃ which requires relatively low pH for precipitation. /11/



6.2.2 Fluoride

Fluoride adversely affects both the anode coating and the titanium substrate. Fluoride can easily be precipitated as an insoluble fluoroapatite, Ca₃(PO₄)₂ · CaF₂ by the addition of Na₃PO₄ and CaCl₂ during primary brine treatment, followed by the additions of soda ash or caustic soda. Reaction described in reaction 24.



Studies with chlorate cell liquors have shown that 20% excess CaCl₂ and 10% excess Na₃PO₄ are required for effective removal of fluoride ion. Further reductions can be achieved by sodium carbonate addition to remove the excess calcium ion, when the precipitated CaCO₃ removes additional amounts of fluoride. /11/

6.2.3 Silicates

Silica, when present in brine, may be in either a soluble or a colloidal form. The soluble form at $\text{pH} > 10$ is HSiO_3^- or SiO_3^{2-} and below $\text{pH} 10$ it is SiO_2 or H_2SiO_3 . At $\text{pH} > 10$, silica can be removed by the addition of a soluble magnesium compound followed by NaOH addition /11/. The addition of insoluble magnesium oxide may also be used to lower the silica level, but it is not as effective as the addition of a soluble magnesium species such as the chloride.

The addition of magnesium ion to a solution containing silica is the standard process for production of insoluble magnesium silicate. The reaction (25) for the formation of the metalsilicate is /11/:



The magnesium silicate, once formed at high magnesium ion concentration, is probably absorbed by the $\text{Mg}(\text{OH})_2$ precipitate and is slow to redissolve. /17/ Figure 16 shows the effect of adding soluble magnesium to the silicate containing brine stream in stoichiometric excess. Fig. 16 tests were conducted with saturated brine; reaction time was 30 minutes, the pH of the brine was maintained at 11 and temperature was maintained at 22°C for precipitating the magnesium silicates.

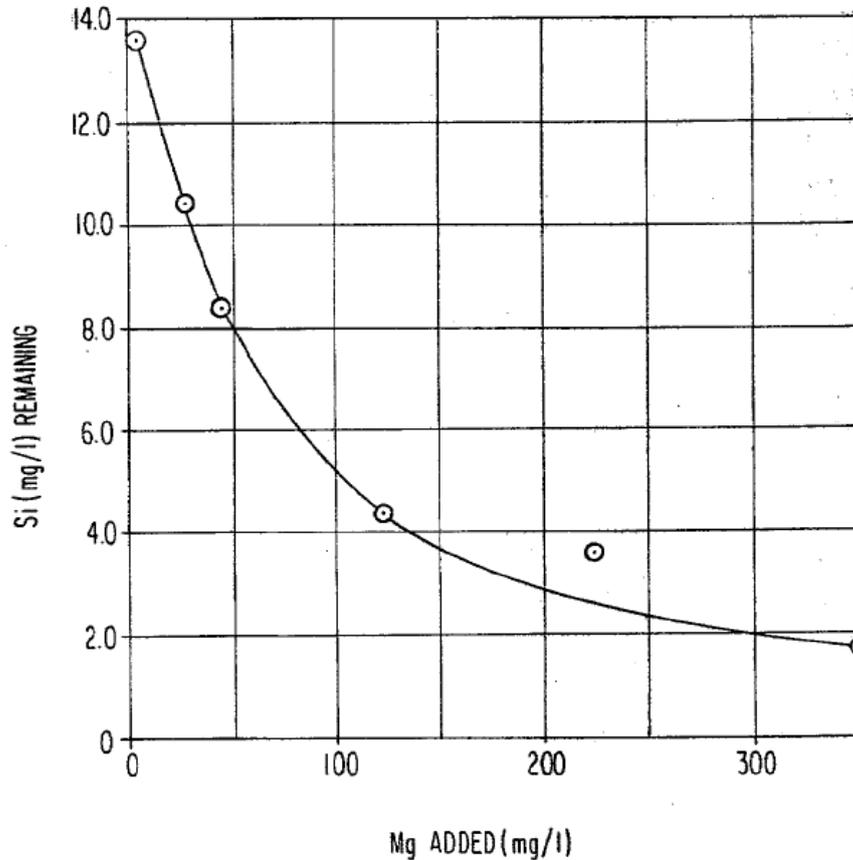


Fig. 16 Effect of added Mg on silica concentration in brine. /17/

Fig. 17 illustrates a graph of the concentration of silicates remaining in the brine after treatment and purification as a function of pH in the precipitation step. Measurements were made using brine that had been treated with excess soluble magnesium and then treated with 1 g/l excess of sodium carbonate and 0,3 g/l excess of sodium hydroxide. The treated brine was allowed to stand for 30 minutes and then filtered at 22°C through a filter having average pore sizes of approximately 0,2 microns. Slightly more than 10 ppm Si remained in the brine when precipitation of the magnesium silicates was undertaken at a pH of 10. The brine contained about 1,0 ppm Si when precipitation was conducted at a pH of 11. The decrease in Si content begins to level off at a pH of about 11. Long settling times maximize the amounts of magnesium silicates that are precipitated and separated. /17/

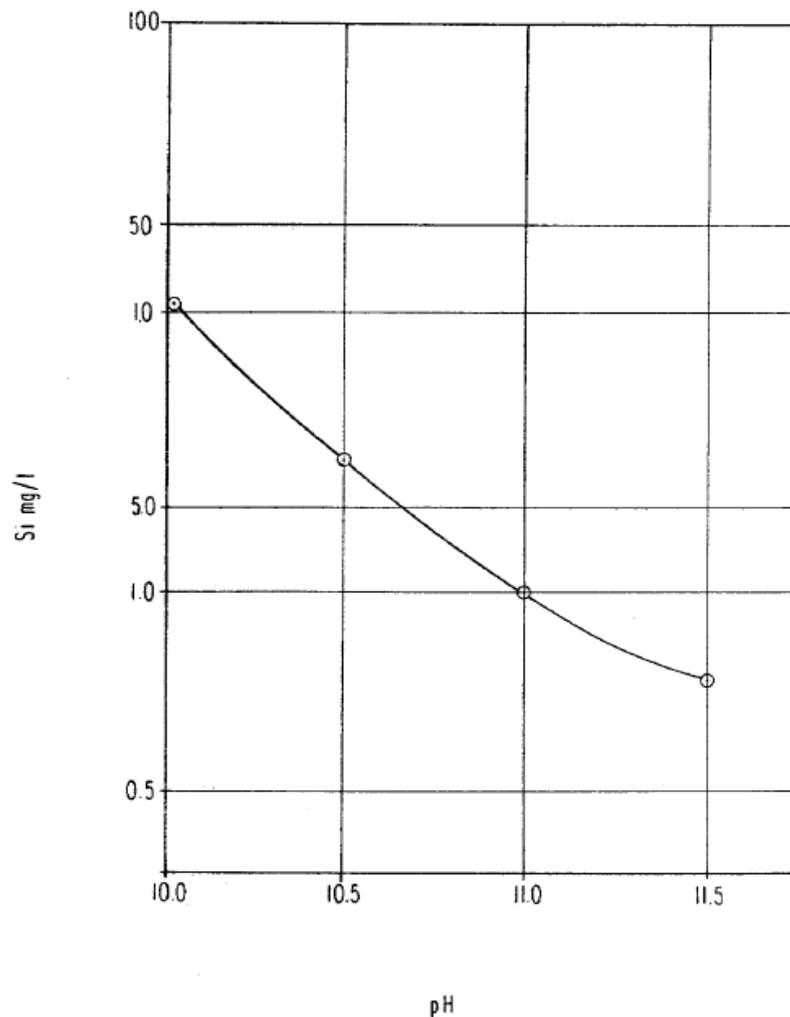


Fig. 17 Concentration of silicates vs. pH in brine. /17/

There are several patents including silicon removal from brine. Couple of these patents is observed above.

United States Patent 6627085 (30.9.2003) introduces process which produces a brine with low silicon content /18/. The new brine treatment process can be carried out at a narrow 9.0-9.9 pH range, at 60°C, with 2 hours residence time. This removes silicon to < 1 ppm, magnesium to < 0.1 ppm and calcium to < 2 ppm. It has been found in this patent that if NaOH addition is reduced to maintain an excess level of 0-70 ppm, the silicon could be reduced to less than 1 ppm.

United States Patent 4946565 (7.8.1990) claims that impurities of silicon can be removed by precipitation with iron ions /19/. Preferably, Fe(II) and/or Fe(III) can be employed as the iron ions. The iron ions can be added either to the electrolyte or to an aqueous solution of the alkali metal chloride.

When iron ions are added to the brine or electrolyte, the iron ions combine with the silicon impurity. The complex is precipitated from the brine or electrolyte and can easily be filtered off. As the iron ion both Fe(II) and Fe(III) can be used separately or together. However, Fe(II) is preferred because it forms a very strong insoluble complex, Fe_2SiO_4 with silicon contamination, while Fe(III) forms a weaker complex.



Iron can be added as a salt. Any iron salts in which the anion does not disturb the electrolysis can be used. It is preferred to use iron chlorides as the source of iron, for example Cl^- can be used in the electrolysis process as the raw material for chlorate production. The iron salt is added in amount which is effective on providing the desired elimination of silicon. It is suitable to use a stoichiometric excess of iron. Most preferred ratio of iron to silicon is 5:1, expressed as mole Fe to mole Si. The brine is strongly agitated and the pH is adjusted to about 9. The iron salt is dosed depending on the content of Si in the solution. The temperature in this purification process is preferably 40-60°C.

The present process can easily be combined with the known processes of purification for removing contaminations of magnesium and calcium. The content of Si in the brine and electrolyte can be reduced by over 90% by this process. /19/

In the other hand United States Patent number 5356610 (8.10.1994) introduces the following removal method for calcium and silicon compounds /20/.

The method comprises adding carbonate ions and an iron containing compound to the liquor for precipitating calcium carbonate and forming and precipitating a complex of iron ions and a silicon compound and subsequently co-separating the precipitates from the thus purified liquor. FeCl_2 is the preferred compound. The advantage of the present method is besides the comparatively low investment and energy costs, also the large flexibility as regards the amount of calcium and silicon that can be removed from the chlorate process. The co-separation step is also cost saving and contrary to what be expected, improves the separation effect. This is due to the interaction between the precipitates of calcium carbonate and

iron-silicon compound, which gives a co-precipitate with larger size and reduced tendency to clog the filters. This also makes it possible to separate e.g. calcium fluoride crystals which are small and therefore normally difficult to remove from liquor.

In the precipitation of calcium carbonate and complex of iron ions and silicon compound, the pH of the liquor should be alkaline, preferably in the range of from 8 to 11. It is especially preferred to first add carbonate ions and then an iron-containing compound at approximately the same pH, whereupon the pH is adjusted for precipitating magnesium hydroxide and more calcium carbonate. For precipitating magnesium hydroxide, the pH of the liquor is adjusted from 10 to 12,5.

6.2.4 Phosphates

Phosphate can be removed from aqueous streams by addition of precipitant, from which aluminium, iron and calcium salts are the most used /21/. The main factors to consider in the precipitation of phosphorous are the selection of the coagulant, its dose and pH. Phosphorous removal using calcium chloride works best when pH is above 10. Traditionally aluminium chloride, alum and poly-aluminium chloride are used to remove phosphorous. Ferric chloride FeCl_3 is the preferred iron salt to remove phosphorous. Iron salts are the most promising in the practical application of phosphorous removal because of their relatively low cost and high phosphorous removal efficiency. Iron phosphate precipitates best at pH range 6-7. The basic reaction to form FePO_4 is expressed in reaction /21/.



6.2.5 Aluminium

Aluminium is amphoteric, so in acidic solutions it is present as the cation Al^{3+} and in basic solutions as the anion AlO_2^- . In neutral solutions, aluminium is present as a fairly insoluble compound $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$. It can be precipitated as the hydroxide by addition of OH^- , but it will remain in solution above the 100 ppb limit if the pH exceeds 8,5. When salt is dissolved at low pH, the aluminium

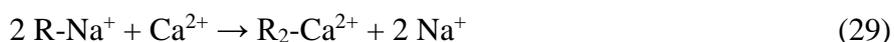
levels in raw brine are much higher than when the salt is dissolved at pH 8 or 9. Thus when salt is dissolved at nearly neutral pH, the solubility of aluminium is suppressed, resulting in Al levels for 100-200 ppb after primary brine treatment. Further lowering to ppb levels can be achieved by MgCl_2 addition. The aluminium, most likely as colloidal $\text{Al}(\text{OH})_3$ or hydrated Al_2O_3 , is removed by adsorption on the $\text{Mg}(\text{OH})_2$ particles or as complex Mg-Al hydroxide. /17/



6.3 Ion exchange

Secondary brine treatment using ion exchange is capable for reducing the calcium, magnesium, and many other cations in the chemically purified brine from about 1-5 ppm to less than 20 ppb. Purified brine, still at ambient temperature, then flows continuously to the next stage of the process, the electrolytic cells.

Ion exchange resins used for brine treatment are generally composed of an organic polymer base with active ion-exchange sites that have affinity for various cations. The resin R^- in the sodium form is contacted with the brine, containing impurities such as Ca^{2+} , usually by downward flow through the resin bed. As the solution contacts the resin, the ions to be removed exchange with the mobile ion in the resin, as in reaction (29):



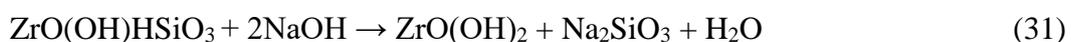
Ion exchange resins also remove other cations, such as Ba^{2+} , Sr^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} . The typical relative affinity of the resins for various cations is shown below in decreasing order:



The exchange capacity is a function of operating pH, feed brine, Ca concentration, flow rate temperature and the backwash flow rate. The ion exchange resin is regenerated periodically by an HCl acid flush followed by a NaOH treatment. It is

essential that the feed brine to the ion-exchange column be free of active chlorine, which deteriorates the resin and free of insoluble solids, both of which result in ineffective utilization of resin capacity and increased regeneration costs. /22/

Recently, a novel ion exchange material based on $ZrO(OH)_2$ has been developed. This has been shown to remove sulphate, iodide and silicate from brines. For example mechanism proposed for the removal of silica is shown in following reactions. /18/



6.4 Impurity removal by washing

Impurities can be removed also by mechanical means. As scale and other impurities accumulates on chlorate cell electrodes, the cell voltages increase with time. Acid cleaning the cells removes the electrode deposits and decreases cell voltage back to normal values. The cells can be washed with 10% max. inhibited HCl. Organic phosphates are used as inhibitors. The inhibitor is added to acid wash before use. Alternatively not inhibited HCl can be used, but its use is slightly questionable because of the increase of steel corrosion and shortened lifetime of steel cathodes /23/. Depending upon the amount of impurities entering the chlorate liquor circuit, the frequency of acid washing typically varies from three of four times per year to once every two years. A typical acid wash will require 24 hours or longer total plant shutdown. /24/

Some deposits, such as iron phosphates and Al or Si based compounds, usually require an additional cleaning in 0,5 – 2,0 % NaOH, at elevated temperatures and times, to be completely removed /6/.

EXPERIMENTAL PART

7 INTRODUCTION TO EXPERIMENTAL PART

The purpose of experimental part was to examine the precipitation conditions of brine impurities used for sodium chlorate manufacturing. The impurities were precipitated and filtered by specially designed experimental apparatus.

The brine and deposit samples were analyzed by using ICP-device (Inductively coupled plasma). Brine impurities were precipitated in two different pH levels and by using precipitants such as sodium carbonate and ferric chloride.

8 DESCRIPTION OF THE EXPERIMENTAL APPARATUS

The principle of the equipment is shown in figure 18. More detailed piping and instrumentation diagrams are in Appendix I & II. The brine enters the system through flow meter (Kytola Instruments) at the rate of 2 l/min. The apparatus consists of two almost similar stages. First stage consists of 1 m³ flocculation tank with mixer (Bonfiglioli Vectron) and surface gauge (Flowsolve Gestra NRGT). Surface level at first stage was set to 0,65 m³. Mixer was set to operate at frequency of 571 rpm. After flocculation tank are magnetic pump (Iwaki Magnet Pump with frequency transformer) which pumps the solution through the filters to the second stage. Filters function was to collect precipitate from the brine. Filters are custom made with polytetrafluoroethylene (PTFE) felt filter patented by GORE™ High Durability Membrane technology. The membrane efficiency of filter fabrics were 0,5 – 1,0 microns. The first stage also includes dosing pump (Iwaki Metering pump) for sodium carbonate addition. The pH was measured from the incoming brine and after the first stage (Polymetron 9100 Hach Ultra).

The second stage consists of similar 1 m³ flocculation tank with mixer, surface gauge, magnetic pump and filters as in the first stage. Surface level at second stage was first set to 0,65 m³ and later lowered to 0,5 m³. There are also two similar dosing pumps for hydrochloric acid and ferric(III)chloride. The pH in second stage is measured from the flocculation tank. After second stage the

solution are pumped to the pumping tank and further back to the brine storage tank. Fig. 18 illustrates a reduced block diagram of the experimental apparatus.

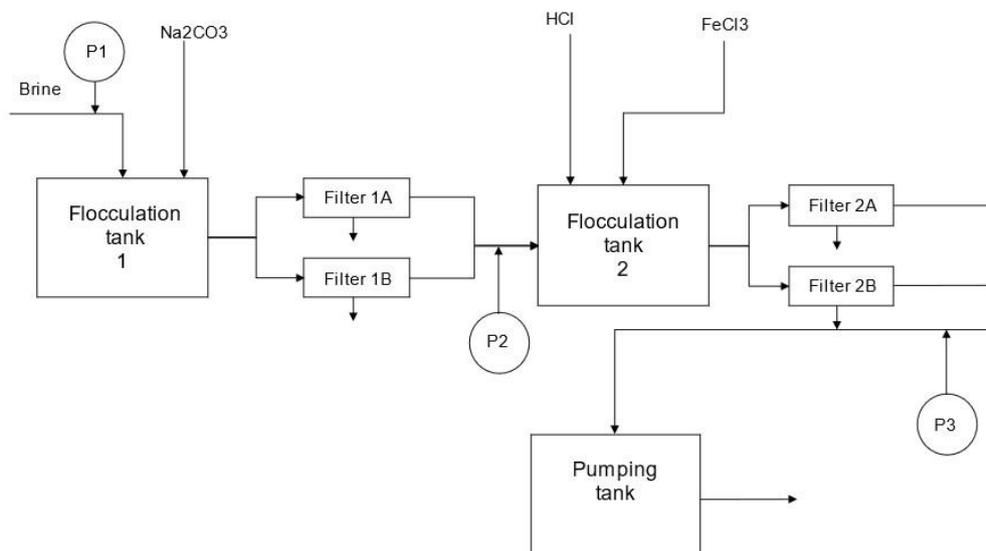


Fig. 18 Block diagram of the experimental apparatus, where P1 is sample point 1, P2 is sample point 2 and P3 is sample point 3.

9 ANALYSIS METHODS

The brine and deposit samples were analyzed by using ICP-device (Inductively coupled plasma).

9.1 Inductively Coupled Plasma (ICP)

Inductively coupled plasma (ICP) is an atomic emission technique by which one can evaluate a considerable number of elements from the sample. Plasma used in technique is a gas, which is in a high temperature and it is determined as an ionized gas, which comprises of ions, electrons and neutral particles. Plasma's operation temperature is between 7000 and 15000 K. Energy for the plasma is transmitted by an induction. High temperature scatters components of sample into atoms and ions and these particles can excite into higher energy levels. When a particle returns from an excited state to a normal level, it emits light. Due to this

light wavelength, elements can be identified and element's amount in the sample can be described. /25/

Source of information embodies three silica quartz tubes, which are unlatched pipes at the top as seen in Fig. 19. The sample is converted into an aerosol, which the support gas transports through the central pipe. For ICP, the argon stream is used as the transporter gas. Alternating current with a frequency of about 27 MHz for the needed excitation is fed by two or three turns of a metal induction tube. The inhibited plasma gas is self-sustaining and it both stabilizes and also thermally isolates the instrumentation. /25/

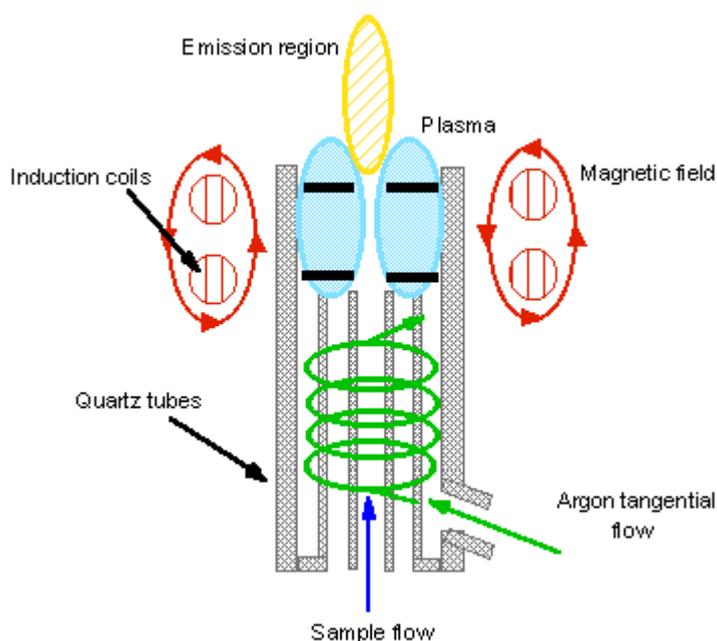


Fig. 19 Schematic of an ICP-torch. /26/

10 EXPERIMENTAL PLAN

Experimental plan with variable values are presented in Table IV. pH at the first stage was not adjusted. The trial points were selected according to Kemira's proposal. Experimental plan with variable values is presented in Table IV. pH at the first stage was not adjusted. Trial points 7 and 8 are parallel, so to see how the parallel measurements differ.

Table IV Trial points 1-8 in ambient temperature, pH at first stage ~9-10.

Trial point	Brine, l/min	Na ₂ CO ₃ 20g/l, ml/min	FeCl ₃ 20g/l, ml/min	pH at second stage	Filter fabric at 1.stage, microns	Filter fabric at 2. stage, microns	Residence time at 1.stage, min	Residence time at 2.stage, min
1	2	-	-	8	0.5	0.5	325	325
2	2	-	-	7	0.5	0.5	325	325
3	2	-	-	7	0.5	0.5	325	250
4	2	-	2	7	0.5	0.5	325	250
5	2	1	-	7	0.5	0.5	325	250
6	2	1	-	7	0.5	1.0	325	250
7	2	1	2	7	0.5	1.0	325	250
8	2	1	2	7	0.5	1.0	325	250

Samples of liquid solution and precipitates were taken during each trial points. Solution samples were taken from three different points; incoming brine (P1), after first stage (P2) and after second stage (P3). Precipitates were taken from filters at both stages (S1/S2) if enough precipitate had formed during that specific trial point. At second stage pH was lowered by 15 % HCl addition.

Both solution and precipitate samples were analyzed by inductively coupled plasma-device.

11 RESULTS AND DISCUSSION

The results from each trial point are listed below and detailed results are listed in Appendix III. Fig. 20 illustrates how the impurity levels of the major elements found in incoming brine changed during the trials.

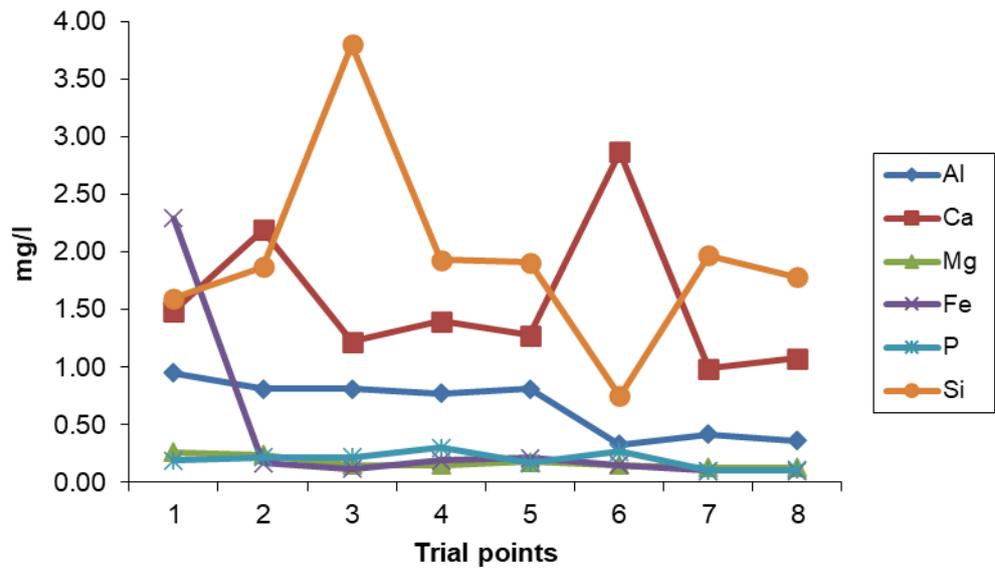


Fig. 20 The major impurities in the incoming brine during the trial points. Trial points 7 and 8 are parallel.

From Fig. 20 can be seen how the amounts of calcium and silicon in the incoming brine have changed quite much between the different trial points. On this basis, the analysis of silicon in particular could be expected to be difficult. The high level of iron in the first trial point is a result of a power failure in the chlorate production. Power failure causes a phenomenon which makes the accumulated impurities from chlorate cells disconnect and move forward in the process cycle.

11.1 Precipitation with two different pH levels

The pH level in first stage was 9-10 and the pH in the second stage was adjusted to 8. Fig. 21 shows the main impurities in the first trial point. Liquid samples were taken from incoming brine, after first stage and after second stage. Deposits from filter in first stage are observed in Fig. 22.

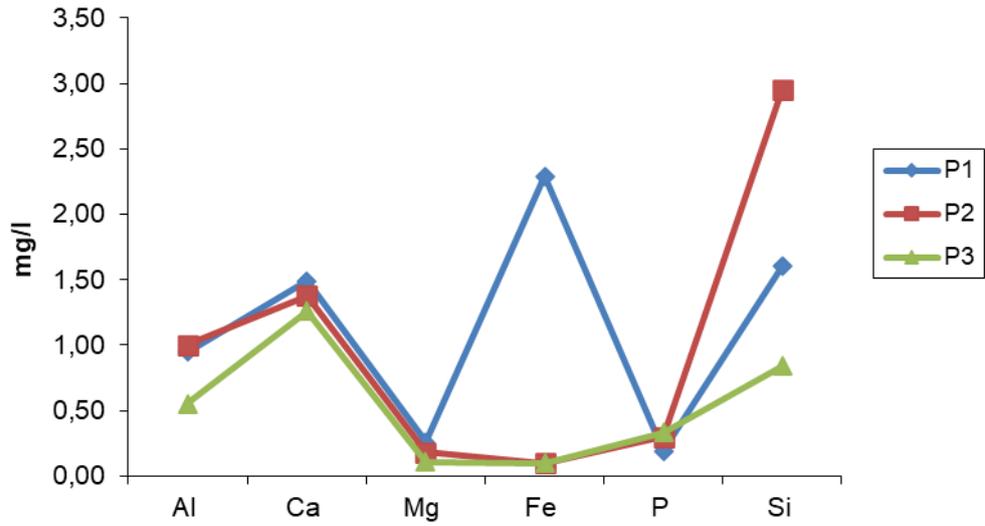


Fig. 21 Trial point 1. The main impurity components and their levels from incoming brine (P1), after first (P2) and second stage (P3). pH at second stage is 8. Filter fabric efficiency at first and second stage 0.5 microns.

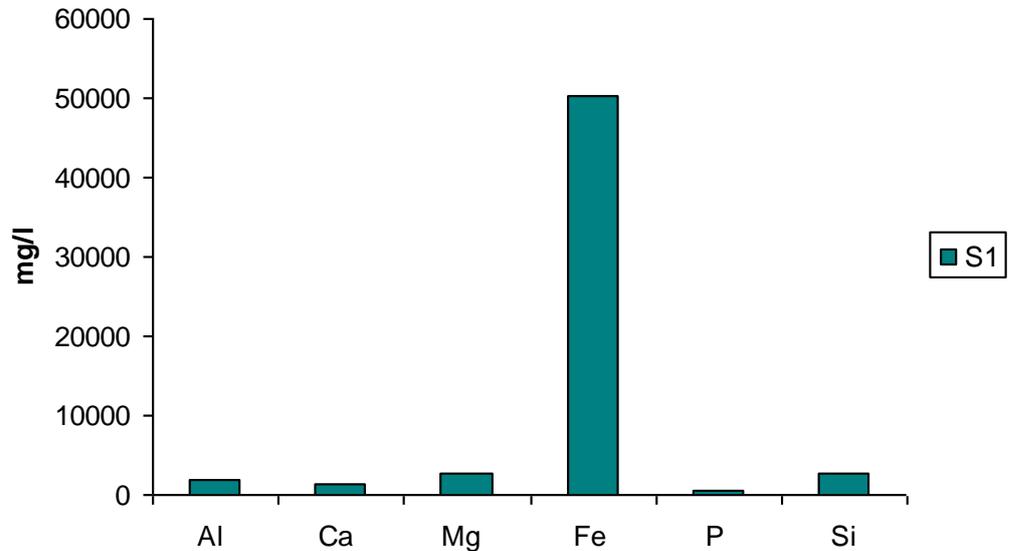


Fig. 22 Diagram of the deposits from first stage filter (S1). Filter fabric efficiency 0.5 microns.

From the ICP-results it can be observed that the major impurities in the brine are aluminium, calcium, magnesium, iron, phosphorus and silicon. Some other elements had also high value, but these elements are not determined as a very harmful impurity. There was a power failure in the chlorate production during the first trial point. This is the most probable reason for the high iron quantity in the

incoming brine and deposit from the filter. Phosphorus and silicon amounts in liquid samples seem not to follow up any rational explanation. pH reduction to level 8 at second stage seems to have minor impact on lowering the impurity levels.

Fig. 23 shows a diagram for the second trial point and fig. 24 shows a diagram for the third trial point. Conditions were the same for both as in the first trial point, except pH at second stage was settled to 7. These two trial points differ only for that the delay at 2.stage is shorter at trial point 3 than trial point 2. Liquid samples were taken from both trial points. Deposit samples for second trial point are illustrated in Fig. 25.

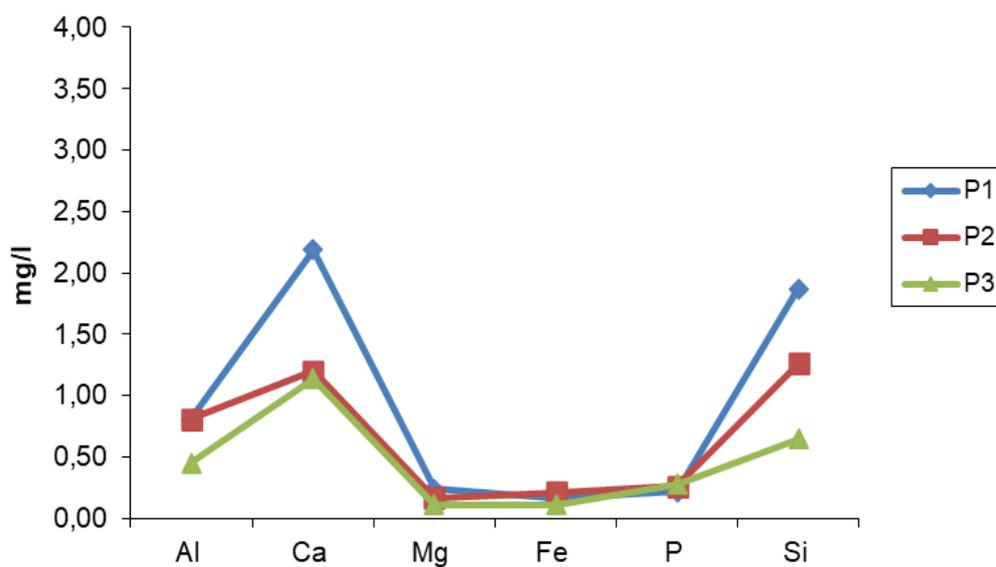


Fig. 23 Trial point 2. Impurity levels from incoming brine (P1), after first (P2) and second stage (P3). pH at second stage is 7. Filter fabric efficiency at first and second stage 0.5 microns.

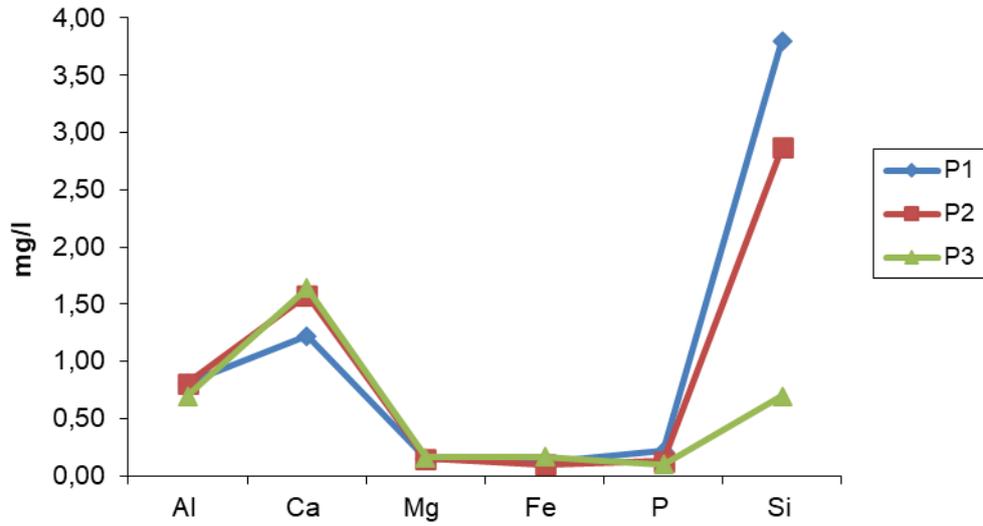


Fig. 24 Trial point 3. Impurity levels from incoming brine(P1), after first (P2) and second stage (P3). pH at second stage is 7. Filter fabric efficiency at first and second stage 0.5 microns.

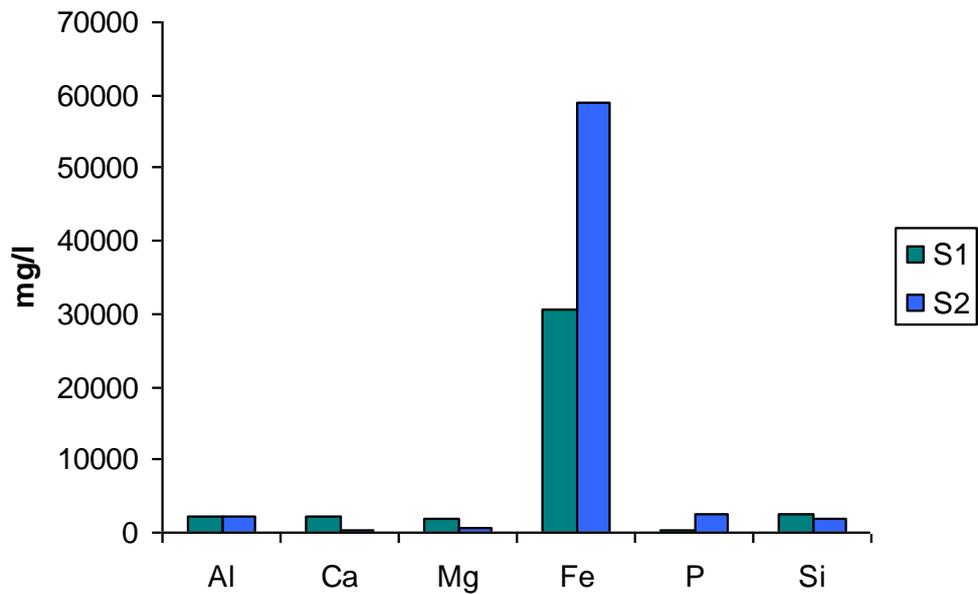


Fig. 25 Trial point 2. Deposit levels from first stage filter (S1) and second stage filter (S2). pH at first stage is ~9-10 and at second stage 7. Filter fabric efficiency at both stages 0.5 microns.

From the figures above can be noticed that most of the impurities detected seem to decrease by filtering, especially silicon levels. There are some inconsistencies in calcium and phosphorus levels between parallel samples. More parallel experiments are needed to determine how these impurity levels behave. Fig. 25 shows well that lower pH level precipitates more iron than higher pH.

11.2 Precipitation with ferric chloride addition

Ferric(III)chloride was added to second stage at the rate of 2 ml/min. The addition of ferric(III)chloride to flocculation tank should precipitate iron-silicon and iron-phosphate compounds, according to reactions 32 and 33, which should deposit on the filter. Fig. 26 and 27 show the gotten results for this precipitation trial.

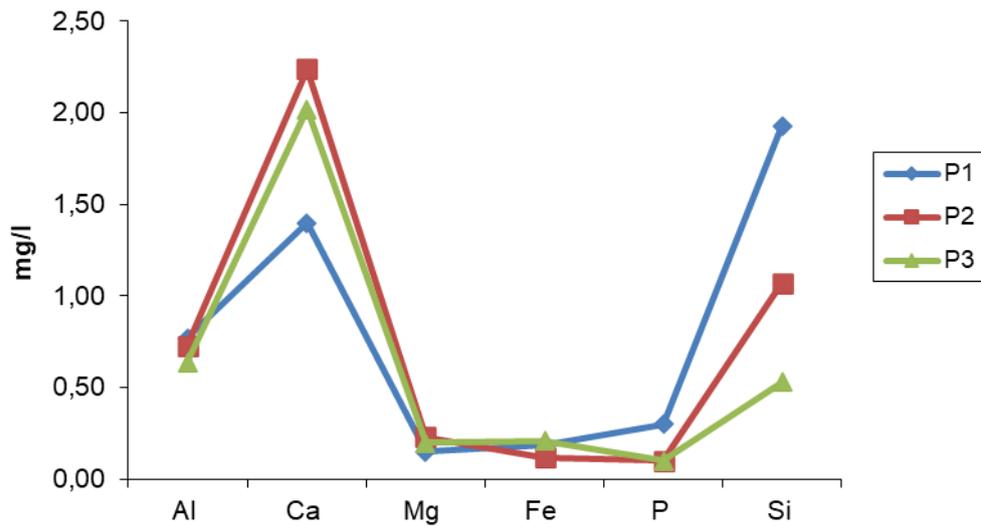
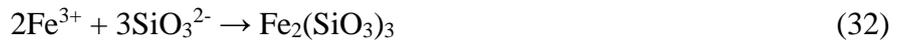


Fig. 26 Trial point 4. Impurity levels of different components from incoming brine (P1), after first (P2) and second stage (P3). Ferric(III)chloride addition and pH 7 at second stage. Filter fabric efficiency at first and second stage 0.5 microns.

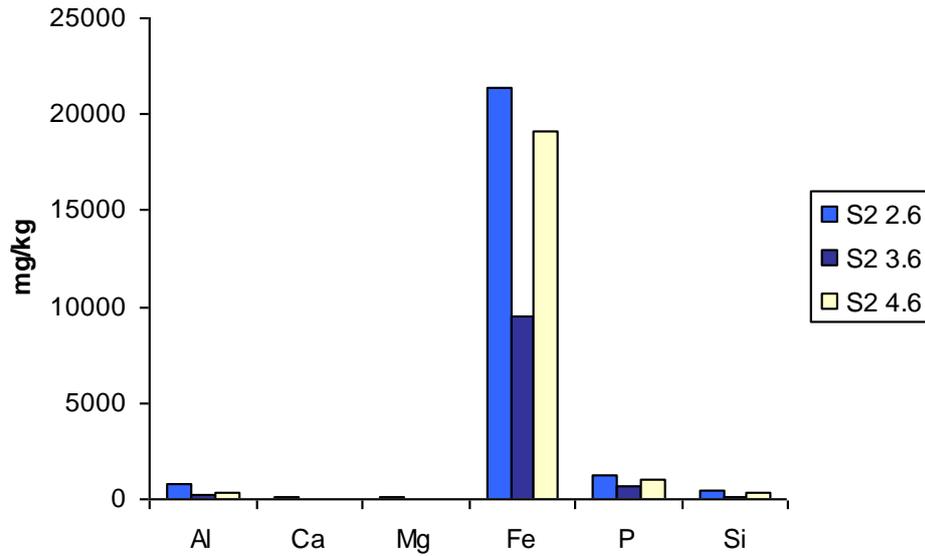
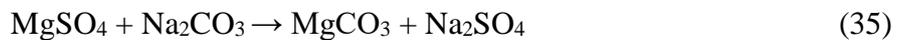


Fig. 27 Trial point 4. Deposit samples from second stage filter (S2). Ferric(III)chloride addition and pH 7 at second stage. Filter fabric efficiency 0.5 microns. The samples were taken on three consecutive days in June.

Silicon and phosphorus levels seem to decrease in the brine after second stage filtering when ferric(III)chloride is added. Iron levels are high in the precipitates as can be assumed. Iron ion most likely forms complexes with both silicates and phosphates. Iron phosphate precipitates best at pH range 6 to 7 according to the literature. /19/

11.3 Precipitation with sodium carbonate addition

Precipitation with sodium carbonate was executed by adding sodium carbonate at the rate of 1 ml/min to the flocculation tank. According to the literature sodium carbonate should convert calcium and magnesium sulphates to carbonates according to reactions 34 and 35 and which are removed by precipitation /14/. Fig. 28 and 29 illustrate the results from liquid samples in two parallel experiments.



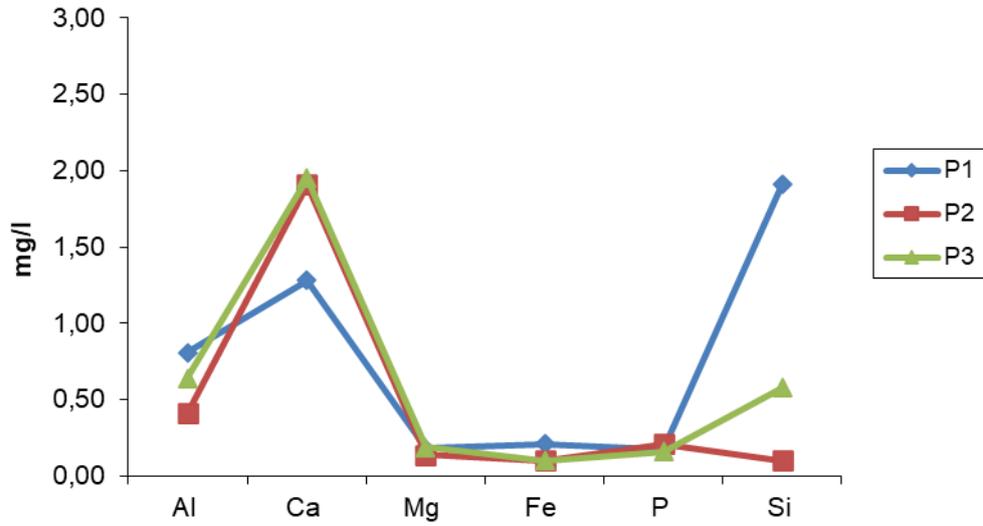


Fig. 28 Trial point 5. Impurity levels of different components from incoming brine (P1), after first (P2) and second stage (P3). Sodium carbonate addition at first stage, pH at second stage is 7. Filter fabric efficiency at first and second stage 0.5 microns.

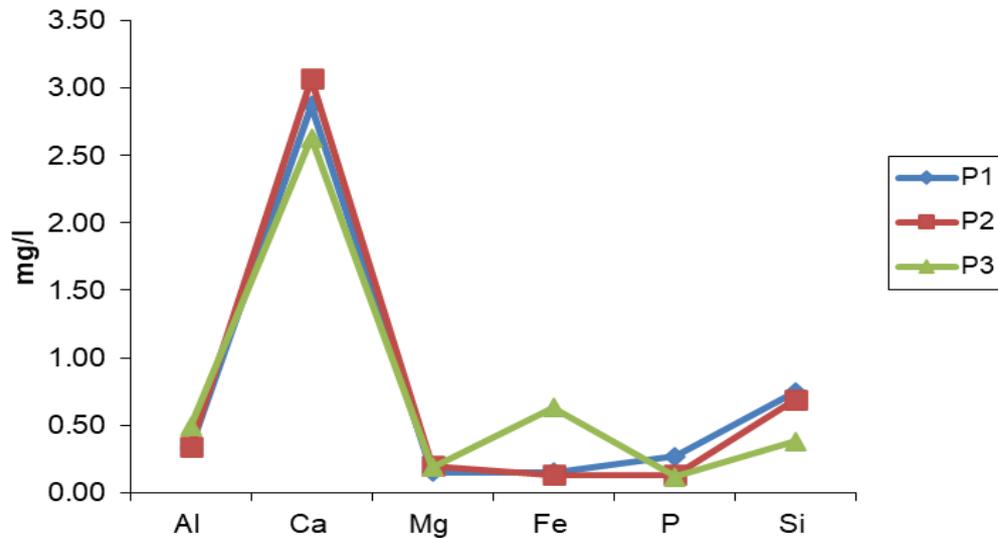


Fig. 29 Trial point 6. Impurity levels of different components from incoming brine (P1), after first (P2) and second stage (P3). Sodium carbonate addition at first stage, pH at second stage is 7. Filter fabric efficiency at first stage 0.5 microns and at second stage 1.0 microns.

As can be seen from the figures above, there is quite big variations between parallel results. Calcium and magnesium levels should decrease in first stage compared to incoming brine because of the sodium carbonate addition. However opposite effect is happened according to achieved results.

Fig. 30 and 31 demonstrate the precipitate samples from sodium carbonate trials. In trial point 5, for sodium carbonate addition, there were not enough deposits in the first stage filter. After longer precipitation time some deposit formed to the filter and samples were taken.

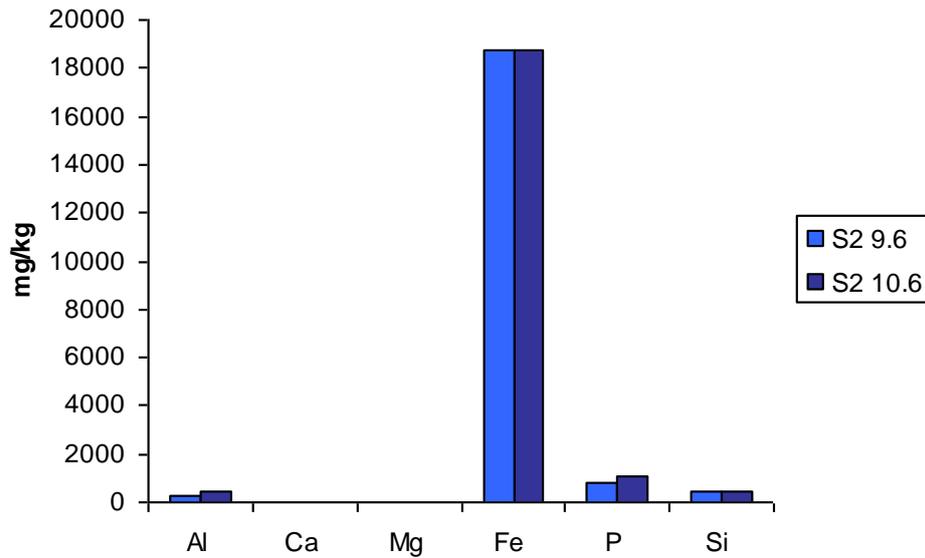


Fig. 30 Trial point 5. Deposit samples from second stage filter (S2). Sodium carbonate addition at first stage, pH at second stage is 7. Filter fabric efficiency 1.0 microns.

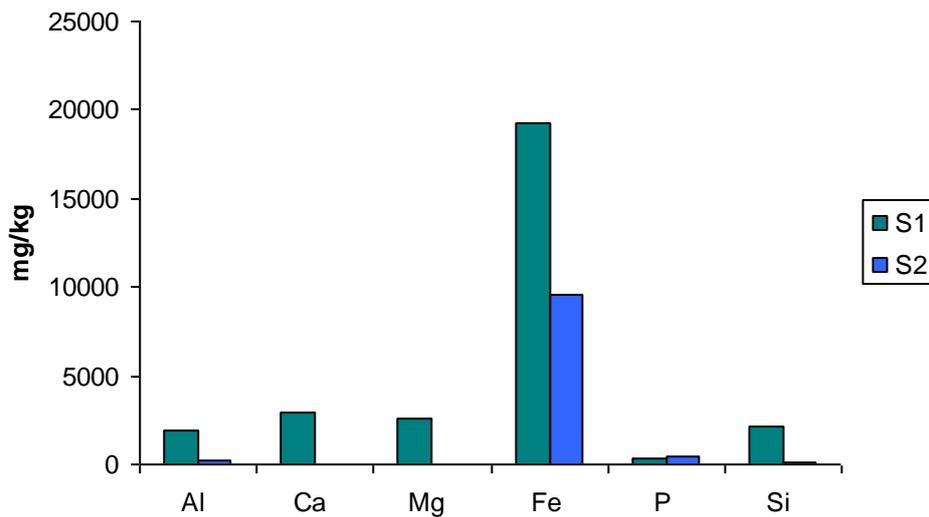


Fig. 31 Trial point 6. Deposit samples from first (S1) and second stage (S2) filters. Sodium carbonate addition at first stage, pH at second stage is 7. Filter fabric efficiency at first stage 0.5 microns and at second stage 1.0 microns.

Parallel samples from second stage show that deposit levels for impurities are quite similar in different samples as seen in Fig. 30. From Fig. 31 it can be observed that most of the impurities precipitate at the first stage. Aluminium, calcium, magnesium and silicon seem to precipitate mostly at the first stage of filtering. Iron levels are again much higher than any other element. Main reason for this is probably the dissolved iron particles in the system, which comes from process equipment and also from the used salt itself.

11.4 Precipitation with sodium carbonate and ferric chloride addition

The addition of sodium carbonate and ferric(III)chloride should together precipitate even more impurities out of the liquid than using only one alternative addition.

As mentioned before, sodium carbonate precipitates calcium and magnesium carbonates and ferric(III)chloride precipitates with both silicates and phosphates. Sodium carbonate was added at the rate of 1 ml/min at first stage and ferric(III)chloride was added at the rate of 2 ml/min at second stage. Fig. 32 to 34 illustrates the results from parallel trial points 7 and 8.

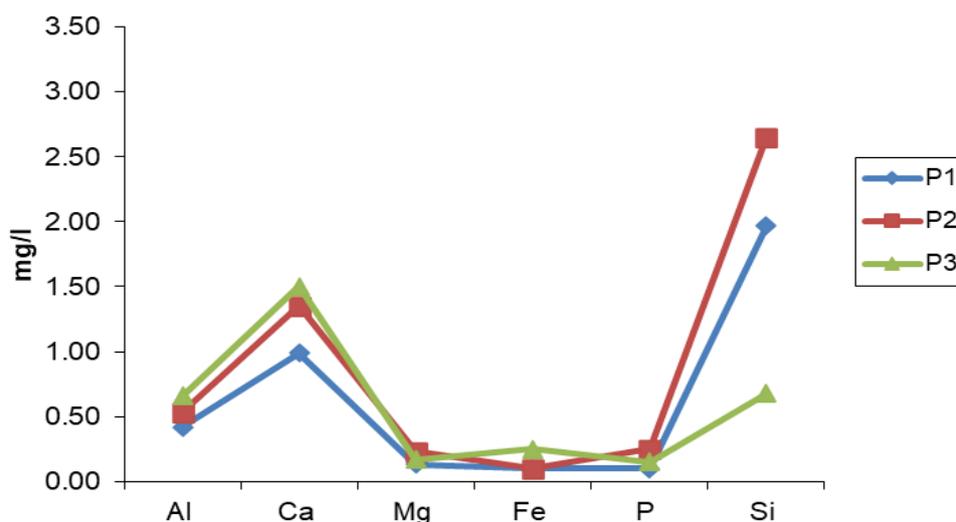


Fig. 32 Trial point 7. Impurity levels of different components from incoming brine (P1), after first (P2) and second stage (P3). Sodium carbonate addition at first stage and ferric(III) chloride addition and pH 7 at second stage. Filter fabric efficiency at first stage 0.5 microns and at second stage 1.0 microns.

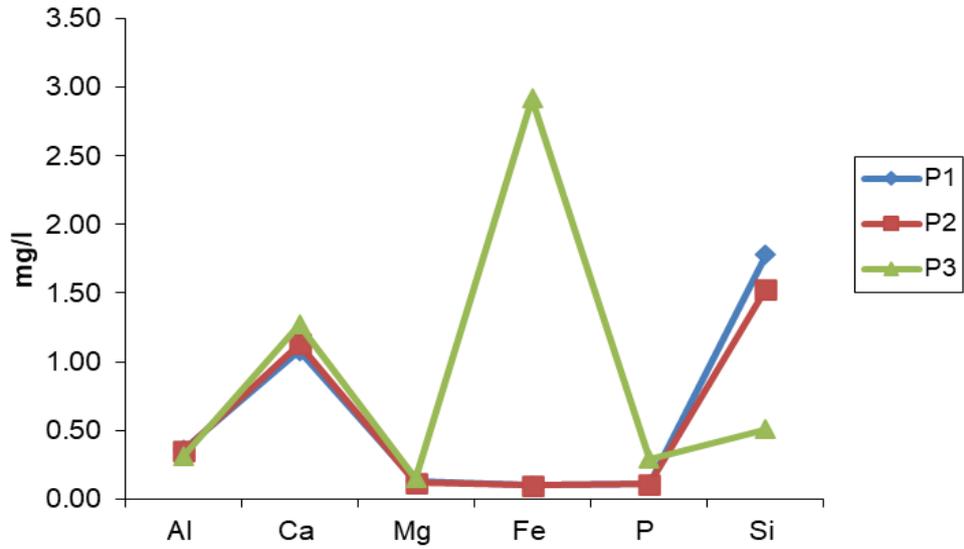


Fig. 33 Trial point 8. Impurity levels of different components from incoming brine (P1), after first (P2) and second stage (P3). Sodium carbonate addition at first stage and ferric(III)chloride addition and pH 7 at second stage. Filter fabric efficiency at first stage 0.5 microns and at second stage 1.0 microns.

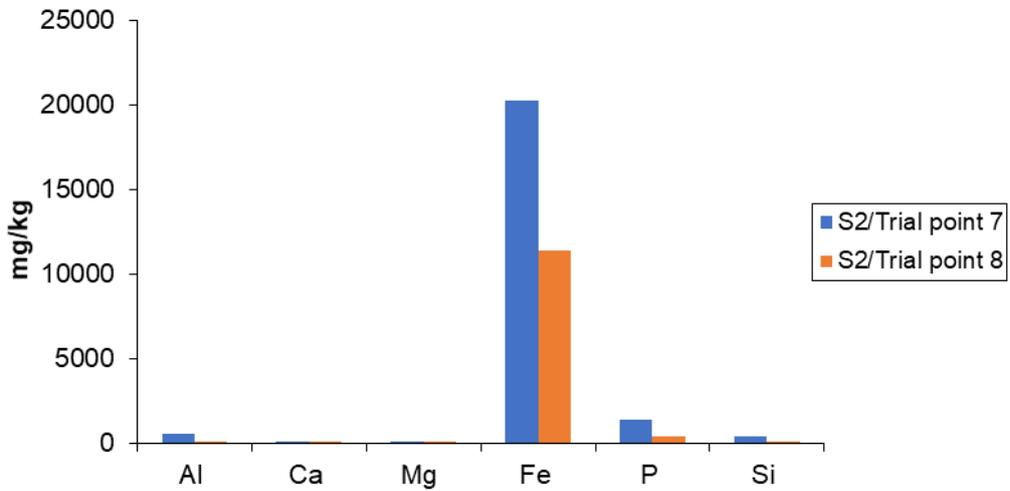


Fig. 34 Deposit samples from second stage filter (S2). Sodium carbonate addition at first stage and ferric(III)chloride addition and pH 7 at second stage. Filter fabric efficiency 1.0 microns.

Addition of sodium carbonate didn't have expected effect on the brine samples. Changing the amount of sodium carbonate addition needs to be considered. Silicon level has again decreased after the second stage filtering. Deposits mostly consist of iron together with some aluminium, phosphorus and silicon. Precipitate samples reveal the fact that calcium and magnesium are precipitated at the first

stage. This is however opposite to the results obtained from the brine samples. The high increase of the iron level in Fig. 33 is explained by the ferric(III)chloride addition in the second stage.

11.5 Sulphates

From Fig. 34 can be seen how sodium sulphate, Na_2SO_4 , levels have changed during the trial points. Sulphate seems to accumulate in the brine. According to literature this reduces the solubility of NaCl /16/ and in this case it can be the main reason for the high amounts of NaCl found in the filter deposits.

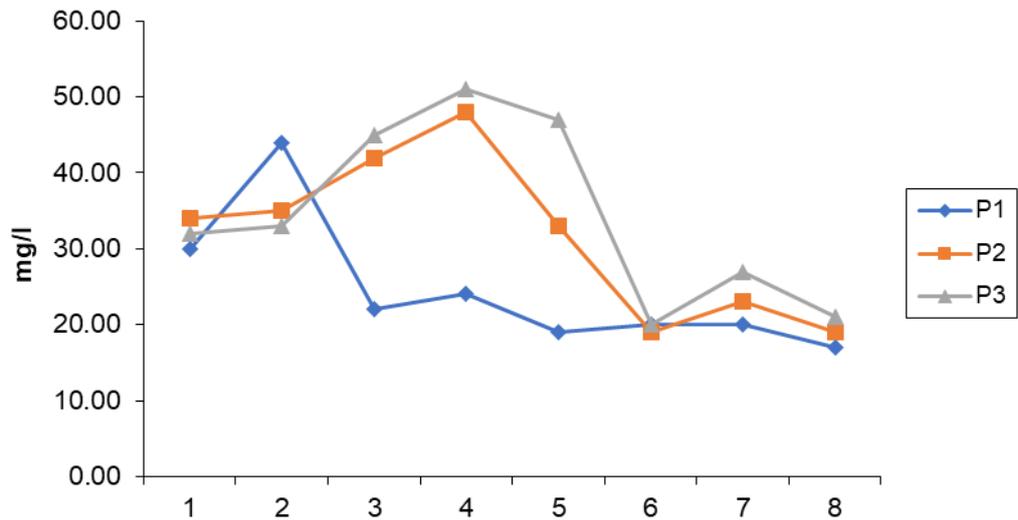


Fig. 35 Sodium sulphate levels from incoming brine (P1), after first (P2) and second stage (P3) in different trial points.

11.6 Precipitate solubility of brine impurities

As mentioned before the major impurities in the brine are aluminium, calcium, magnesium, iron, phosphorus and silicon. Table V shows the main precipitates of these impurities and their solubilities. From table V can be seen that all precipitates are quite insoluble, excluding chlorides which are all soluble in water.

Table V Solubility chart for major precipitates. W is soluble in water, A is insoluble in water but soluble in acids, w is sparingly soluble in water but soluble in acids and I is insoluble in water and acids. /27/

	Al ³⁺	Ca ²⁺	Mg ²⁺	Fe ²⁺ / Fe ³⁺
Carbonate, CO ₃ ²⁻	-	CaCO ₃ w	MgCO ₃ w	FeCO ₃ / - w
Chloride, Cl ⁻	AlCl ₃ W	CaCl ₂ W	MgCl ₂ W	FeCl ₂ / FeCl ₃ W W
Phosphate, PO ₄ ³⁻	AlPO ₄ A	Ca ₃ (PO ₄) ₂ w	Mg ₂ (PO ₄) ₂ w	Fe ₃ (PO ₄) ₂ / FePO ₄ w A
Silicate, SiO ₃ ²⁻	Al ₂ (SiO ₃) ₃ I	CaSiO ₃ w	MgSiO ₃ A	FeSiO ₃ / Fe ₂ (SiO ₃) ₃ w w
Sulfate, SO ₄ ²⁻	Al ₂ (SO ₄) ₃ W	CaSO ₄ w	MgSO ₄ W	FeSO ₄ / Fe(SO ₄) ₃ W w

11.7 SEM-results

The scanning electron microscope, SEM, analyses were made at the Lappeenranta University of Technology. Filter fabrics were analyzed by using the SEM-device to find out which causes the filter fabrics to block so rapidly at the second stage. Visually could be seen that the fabrics were covered by undefined deposit, but more detailed analysis was needed. Table VI shows the SEM-results and Fig. 35 to 43 present the scanned pictures of the filter deposits. In Appendix IV is presented the specific results for the SEM-analyzes. Different magnifications were used to find out general picture of the contents and also detailed picture of filter fabric's texture and material.

Table VI SEM-results with different magnifications in weight-%.

Magnification	C %	N %	O %	F %	Na %	Al %	Cl %	K %	Cu %
55x	7.33	-	2.79	27.92	24.82	0.33	36.10	-	0.72
120x	7.15	-	2.65	31.70	23.72	0.26	33.69	-	0.83
1300x	7.27	1.72	3.78	28.82	24.15	0.23	33.34	-	0.70
1300bx	11.01	1.40	3.88	50.70	12.69	0.28	18.76	0.33	0.95

From Table VI can be seen that the concentrations of the various components vary between different magnifications. The filter deposits were unevenly divided to filter fabrics, so the magnifications are taken from certain points of the filter fabric.

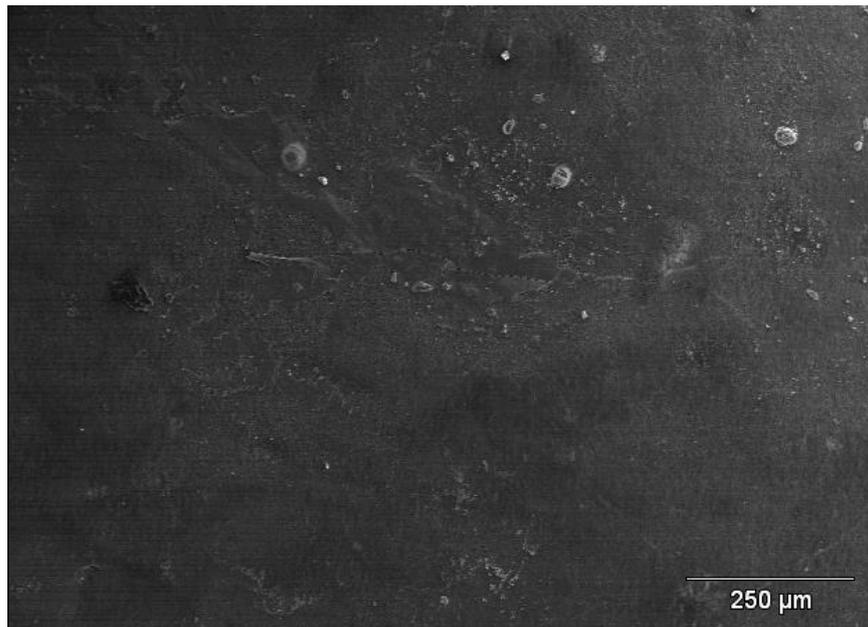


Fig. 36 SEM-picture of PTFE-filter with 55x magnification.

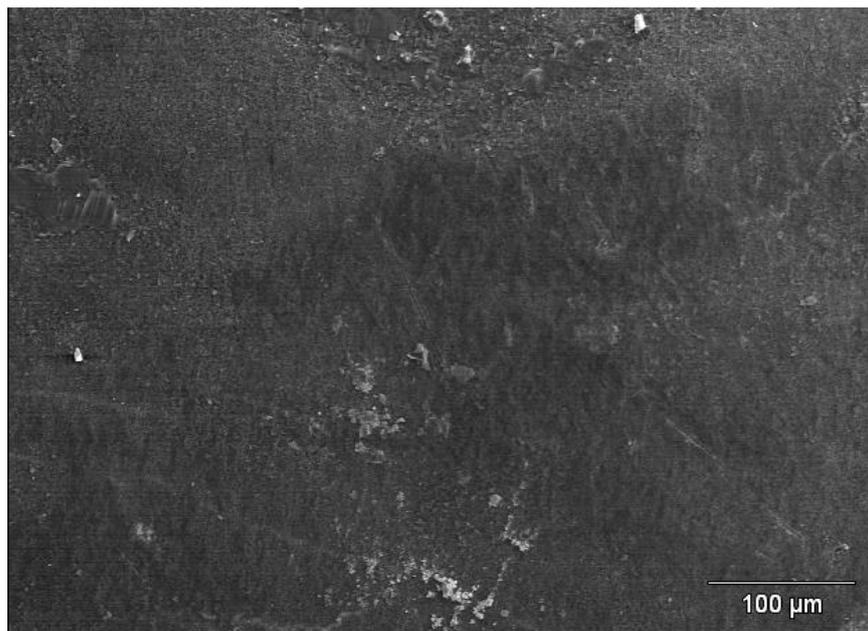


Fig. 37 SEM-picture of PTFE-filter with 120x magnification.

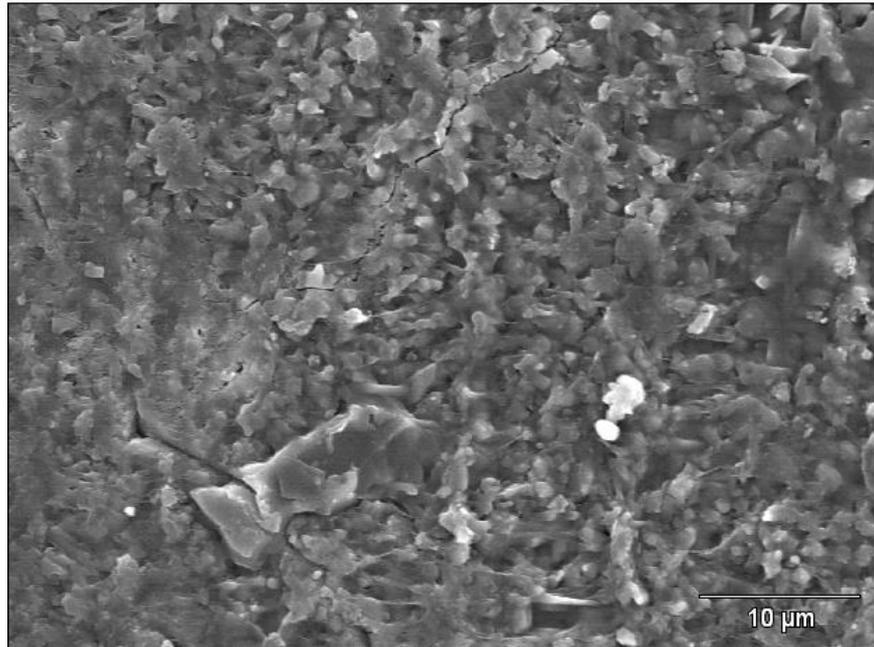


Fig. 38 SEM-picture of PTFE-filter with 1300x magnification.

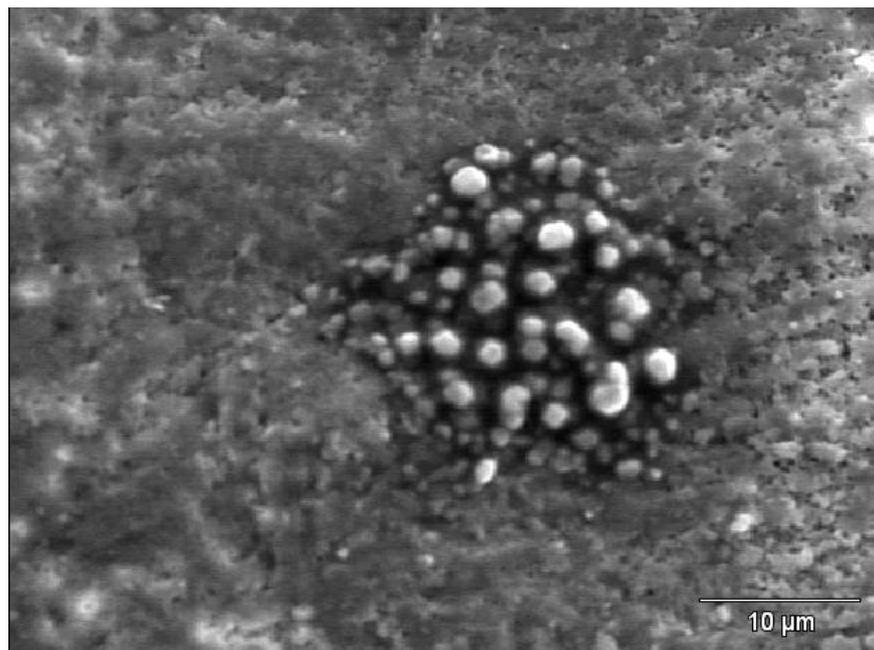


Fig. 39 SEM-picture of PTFE-filter with 1300x magnification.

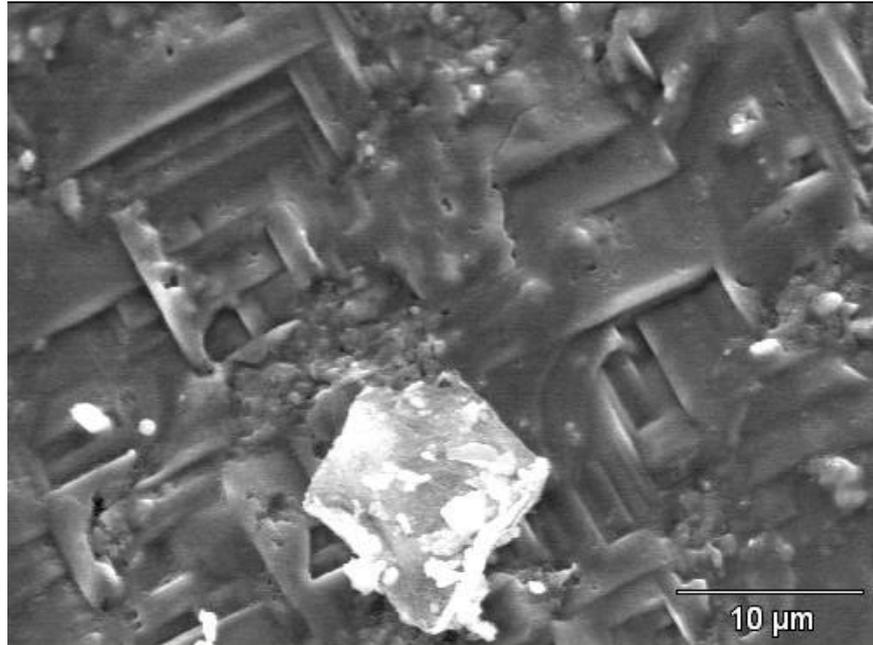


Fig. 40 SEM-picture of PTFE-filter with 1500x magnification.

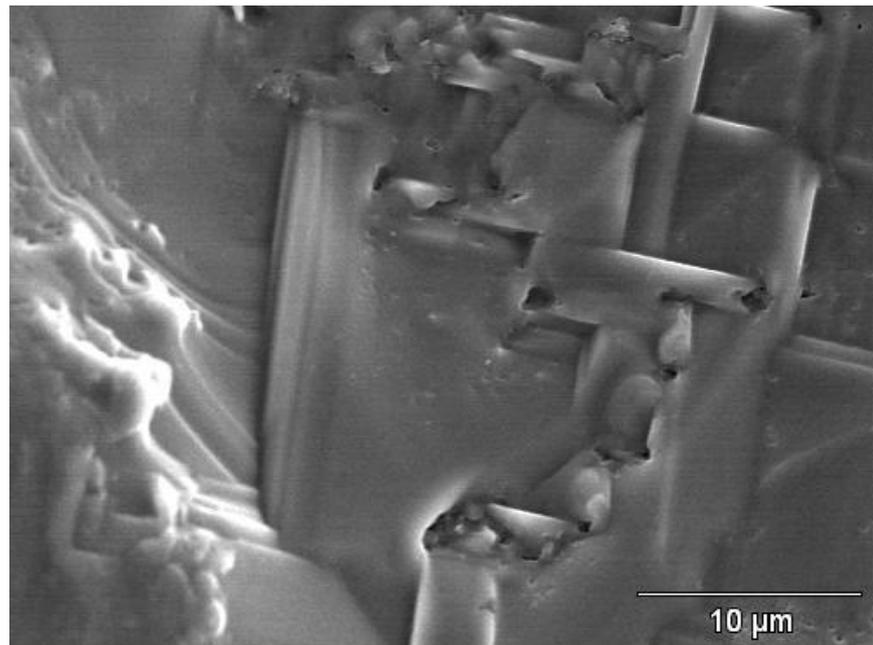


Fig. 41 SEM-picture of PTFE-filter with 1800x magnification.

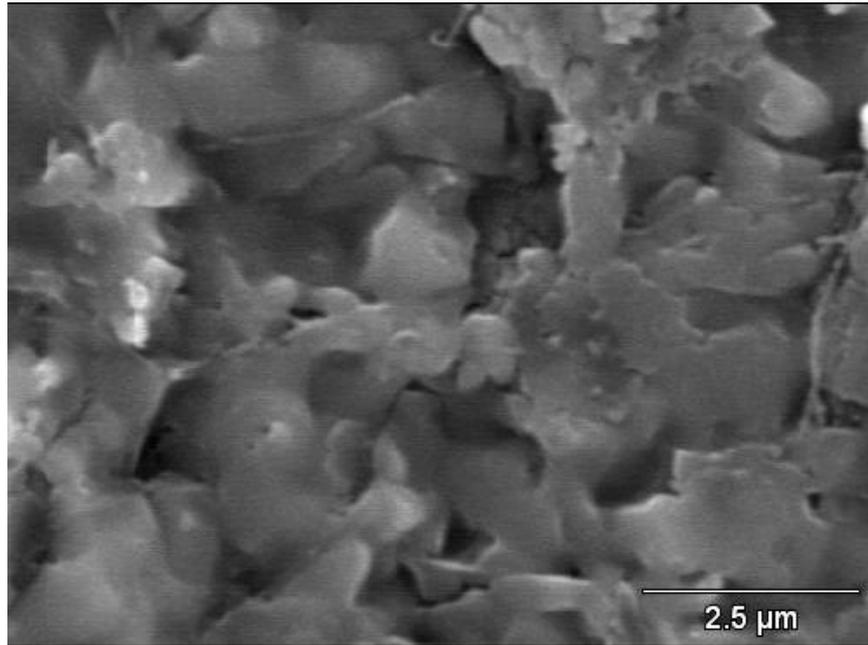


Fig. 42 SEM-picture of PTFE-filter with 7000x magnification.

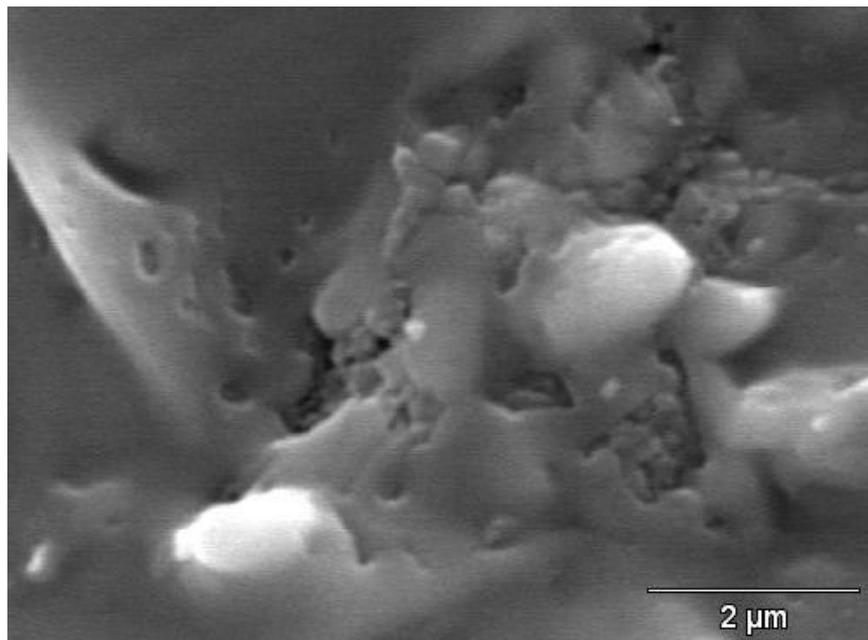


Fig. 43 SEM-picture of PTFE-filter with 8500x magnification.

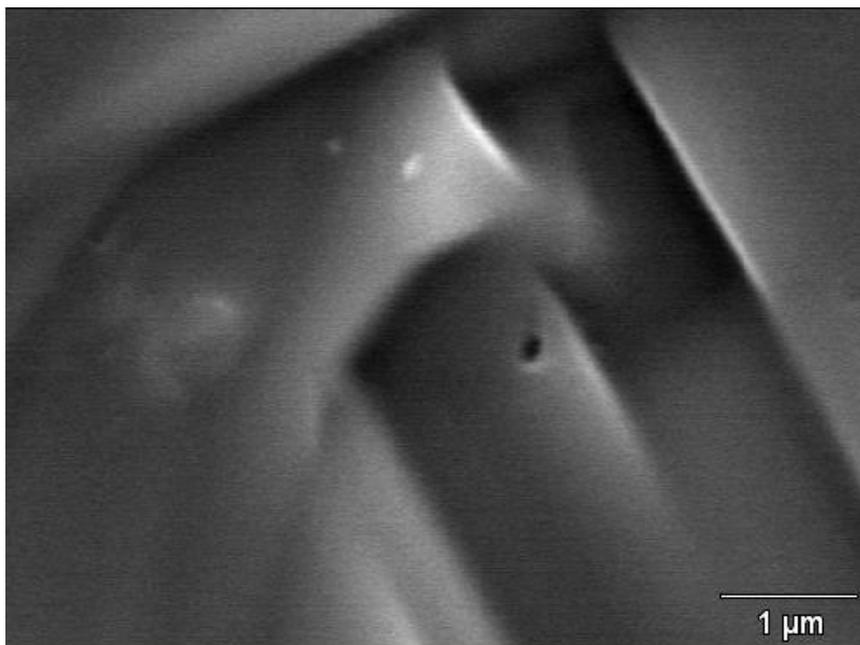


Fig. 44 SEM-picture of PTFE-filter with 11000x magnification.

When observing the SEM-results, it can be seen that the major elements found at the filter deposit are sodium, chlorine and fluoride. These elements are most likely in the form of sodium chloride, salt.

On the basis of these results can be assumed that cause for the filter fabric blockages are too saturated brine. The fluoride comes from the incoming brine and also from the filter fabric, polytetrafluoroethylene, PTFE. The filter fabric seemed not to withstand the pH level lowering to pH 6.

12 Conclusions and further developments

The main motivation for this investigation was to find out suitable conditions for impurity removal by precipitating. In some trial points impurity levels after first stage were for some reason higher than in incoming brine. Reason for this could be inaccuracy either in sample analyzes or sampling.

The rapid blockage of the filter fabrics at the second stage caused problems. Changing the membrane efficiency of filter fabric from 0.5 microns to 1 microns had some influence on improving filtering. SEM-results revealed that sodium chloride was the main reason of filter fabric blockage. pH could not be lowered more than to pH 7 because of the quick decomposition of filter fabrics at lower pH.

From the ICP-results it could be observed that the major impurities in the brine are aluminium, calcium, magnesium, iron, phosphorus and silicon. Sulphates accumulate to the brine and this causes the solubility of sodium chloride to reduce. These found impurities are most likely in form of salts and precipitates in brine, mainly Ca and Mg chlorides and sulphates and also silicates, phosphates, which are all harmful in the chlorate process.

The results from the two trial points after reference point, gave indication of reduced levels of aluminium, calcium, silicates and phosphates after precipitation stages.

Lower pH alone in the impurity precipitating seems to have minor effect on removing impurities from the brine. The two added compounds, first the ferric(III)chloride, was used to solve out its ability to precipitate phosphates, such as FePO_4 , and the second, sodium carbonate was used to precipitate calcium and magnesium from the brine. With ferric(III)chloride addition, lower pH level is preferred because iron phosphates precipitate best at pH range 6 to 7. However if iron is used for removing silicon, the pH should be adjusted to about 9 [17]. Sodium carbonate addition had a minor impact on decreasing calcium and magnesium levels in the brine. The sodium carbonate was intended to precipitate CaCO_3 and MgCO_3 , which both are quite insoluble compounds. The combination of sodium carbonate and ferric(III)chloride addition did not give any further improvement. Ferric(III)chloride appears to precipitate phosphates and some silicates from the brine. According to the literature this fact corresponds well to the results from earlier studies [19; 21]. The precipitants which are formed, both FePO_4 and $\text{Fe}_2(\text{SiO}_3)_3$ are sparingly soluble in water. It could be interesting to explore if the ferric(III)chloride precipitates silicates better at higher pH, so it could be valuable to try out which effects the ferric(III)chloride addition at first stage precipitation could achieve.

Because of short, disturbance-free operating time, no definite conclusions can be drawn based on the results. For further investigation much more parallel studies of different trial points are needed to find out which conditions are the best for removing impurities from brine. Other precipitants than ferric(III)chloride and different filter fabric materials should be tested to find out which suits the best for this purpose to precipitate impurities from brine.

Some development of the test apparatus should be considered. The filters are quite time-consuming to strip down to collect the deposit samples, so faster way to open and close the filters could be practical. Also the retention of salt to the system should be reduced by some means, for example coarse filters before the finer filters.

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APPENDICES

Appendix I	The pipe and instrumentation diagram
Appendix II	Pictures of the experimental apparatus
Appendix III	ICP-results
Appendix IV	SEM-result

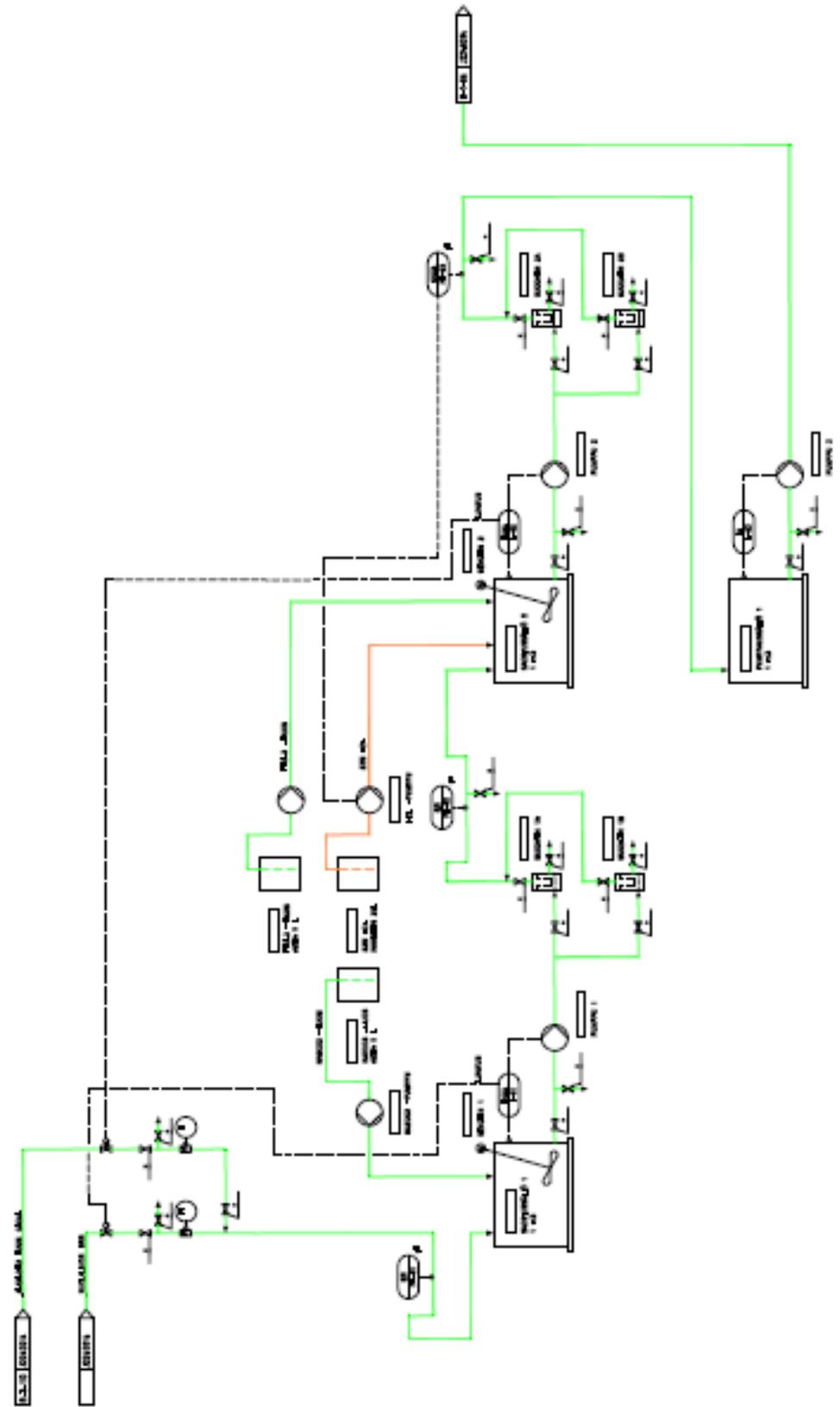


Fig. 1 Pipe and instrumentation diagram of the experimental apparatus.



Fig. 1 Custom made filters.

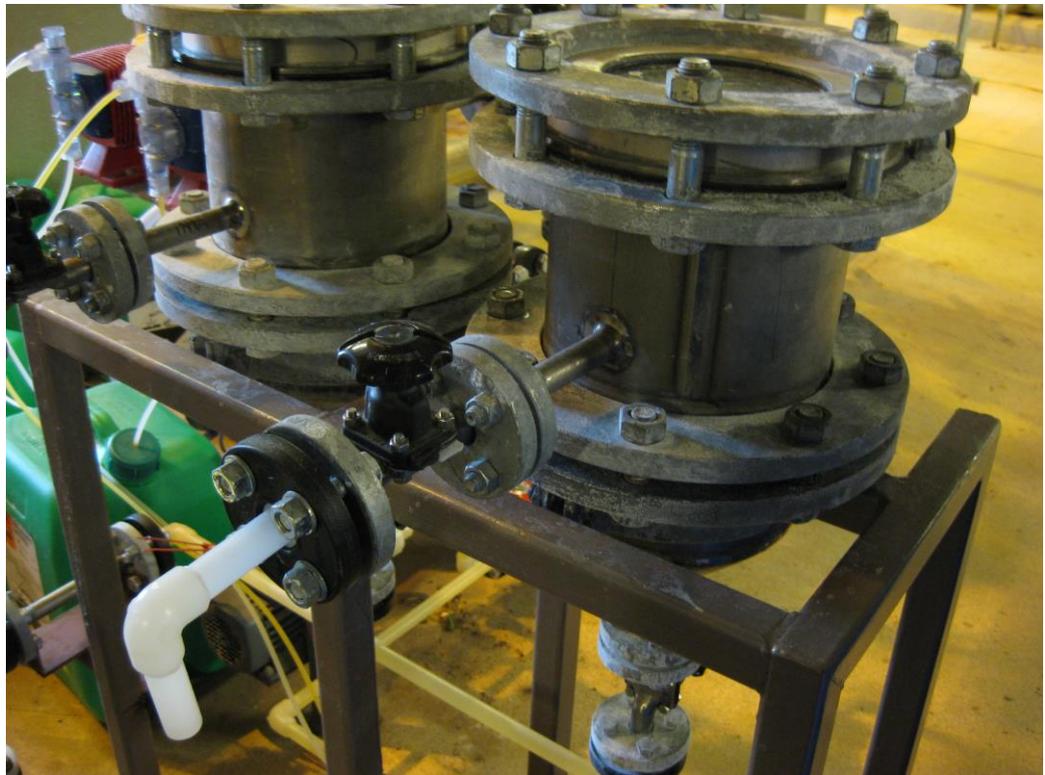


Fig. 2 Custom made filters.

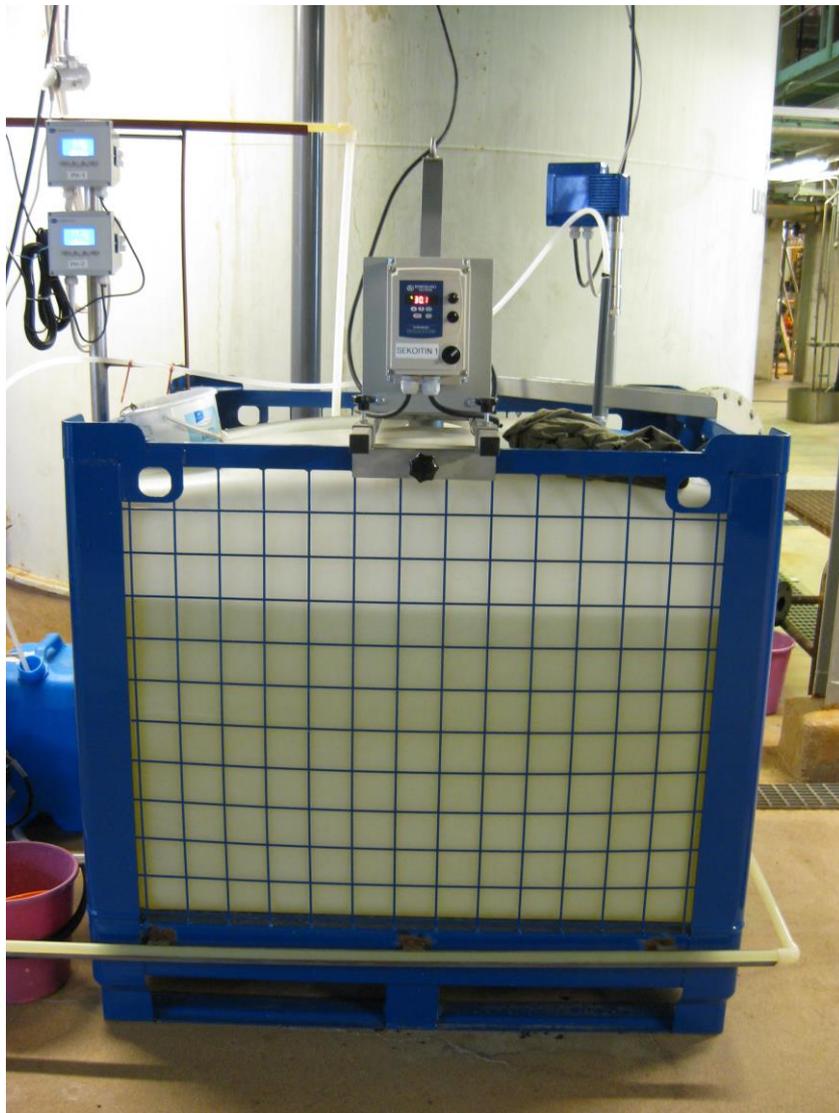


Fig. 3 Flocculation tank.

Table I ICP-result for trial point 1.

Trial point 1	14.5.2010	14.5.2010	14.5.2010	19.5.2010
	P1	P2	P3	S1 A+B
	mg/l	mg/l	mg/l	mg/l
Al 396.152	0,95	1,00	0,55	1881,54
As 188.980	<0,10	<0,10	<0,10	1,32
Be 313.042	<0,10	<0,10	<0,10	<0,10
Ca 396.847	1,49	1,38	1,26	1360,79
Cd 226.502	<0,10	<0,10	<0,10	8,57
Co 238.892	<0,10	<0,10	<0,10	<0,10
Cr 276.653	54,38	60,00	54,96	462,41
Cu 224.700	<0,10	<0,10	<0,10	103,81
Fe 238.204	2,29	<0,10	<0,10	50223,10
Mg 279.553	0,26	0,18	0,11	2638,21
Mn 257.610	<0,10	<0,10	<0,10	242,04
Mo 202.032	<0,10	<0,10	<0,10	9,02
Ni 216.555	<0,10	<0,10	<0,10	128,64
P 214.914	0,19	0,30	0,33	498,23
PO4	0,58	0,92	1,01	-
Pb 182.143	0,38	0,43	0,41	13,80
S 181.972	68,97	78,73	74,23	83,30
Na2SO4	30,00	34,00	32,00	-
Sb 217.582	0,10	0,12	0,11	0,76
Se 196.026	0,27	0,31	0,30	<0,10
Si 251.611	1,60	2,95	0,84	2689,88
Sn 189.925	<0,10	<0,10	<0,10	6,28
Sr 407.771	<0,10	<0,10	<0,10	16,16
Ti 336.122	<0,10	<0,10	<0,10	352,69
Tl 276.789	<0,10	0,15	0,13	<0,10
V 326.769	<0,10	<0,10	<0,10	23,59
Zn 213.857	0,22	0,24	0,35	268,56

Table II ICP-results for trial point 2.

Trial point 2	24.5.2010	24.5.2010	24.5.2010	26.5.2010	26.5.2010
	P1	P2	P3	S2A	S1B
	mg/l	mg/l	mg/l	mg/l	mg/l
Al 396.152	0,81	0,81	0,45	2051,62	2268,77
As 188.980	<0,10	<0,10	<0,10	4,31	0,40
Be 313.042	<0,10	<0,10	<0,10	<0,10	<0,10
Ca 396.847	2,19	1,20	1,14	419,08	2145,76
Cd 226.502	<0,10	<0,10	<0,10	9,90	5,09
Co 238.892	<0,10	<0,10	<0,10	<0,10	<0,10
Cr 276.653	68,10	65,69	63,34	1239,02	428,04
Cu 224.700	<0,10	<0,10	<0,10	54,14	67,15
Fe 238.204	0,17	0,21	0,11	58954,41	30727,90
Mg 279.553	0,24	0,17	0,11	662,94	1822,07
Mn 257.610	<0,10	<0,10	<0,10	179,01	202,37
Mo 202.032	<0,10	<0,10	<0,10	9,94	5,92
Ni 216.555	<0,10	<0,10	<0,10	220,21	103,45
P 214.914	0,22	0,26	0,28	2564,36	441,06
PO4	0,67	0,79	0,85	-	-
Pb 182.143	0,32	0,38	0,28	9,69	9,17
S 181.972	100,77	80,31	76,58	71,73	64,17
Na2SO4	44,00	35,00	33,00	-	-
Sb 217.582	0,13	0,13	<0,1	0,64	0,31
Se 196.026	0,29	0,33	0,35	<0,10	<0,10
Si 251.611	1,87	1,26	0,65	1828,22	2611,81
Sn 189.925	<0,10	<0,10	<0,10	16,56	3,22
Sr 407.771	<0,10	<0,10	<0,10	3,59	14,23
Ti 336.122	<0,10	<0,10	<0,10	205,81	416,90
Tl 276.789	<0,10	<0,10	0,12	<0,10	<0,10
V 326.769	<0,10	<0,10	<0,10	48,23	20,03
Zn 213.857	0,23	0,26	0,36	50,23	224,49

Table III ICP-results for trial point 3.

Trial point 3	1.6.2010	1.6.2010	1.6.2010	2.6.2010
	P1	P2	P3	S2 A+B
	mg/l	mg/l	mg/l	mg/l
Al 396.152	0,81	0,81	0,70	740
As 188.980	<0,10	<0,10	<0,10	1,02
Be 313.042	<0,10	<0,10	<0,10	<0,10
Ca 396.847	1,22	1,58	1,64	82,9
Cd 226.502	<0,10	<0,10	<0,10	3,53
Co 238.892	<0,10	<0,10	<0,10	<0,10
Cr 276.653	28	32	36	429
Cu 224.700	<0,10	<0,10	<0,10	18,0
Fe 238.204	0,12	<0,10	0,17	21357
Mg 279.553	0,15	0,15	0,16	68,7
Mn 257.610	<0,10	<0,10	<0,10	100
Mo 202.032	<0,10	<0,10	<0,10	5,40
Ni 216.555	<0,10	<0,10	<0,10	78,2
P 214.914	0,22	0,13	<0,10	1245
PO4	0,67	0,39	0,30	-
Pb 182.143	0,43	0,32	0,29	19,7
S 181.972	51,9	96,1	101,6	74,5
Na2SO4	22,00	42,00	45,00	-
Sb 217.582	<0,10	<0,10	<0,10	0,28
Se 196.026	0,31	0,31	0,29	<0,10
Si 251.611	3,80	2,87	0,70	478
Sn 189.925	<0,10	<0,10	<0,10	9,30
Sr 407.771	<0,10	<0,10	<0,10	0,73
Ti 336.122	<0,10	<0,10	<0,10	34,5
Tl 276.789	0,17	0,12	<0,10	<0,10
V 326.769	<0,10	<0,10	<0,10	17,7
Zn 213.857	0,21	0,20	0,24	45,2

Table IV ICP-results for trial point 4.

Trial point 4	4.6.2010	4.6.2010	4.6.2010	3.6.2010	4.6.2010
	P1	P2	P3	S2A+B	S2A+B
	mg/l	mg/l	mg/l	mg/l	mg/kg
Al 396.152	0,77	0,73	0,64	275	325
As 188.980	<0,10	<0,10	<0,10	0,30	0,25
Be 313.042	<0,10	<0,10	<0,10	<0,10	<0,10
Ca 396.847	1,40	2,24	2,02	18	34
Cd 226.502	<0,10	<0,10	<0,10	1,6	3,5
Co 238.892	<0,10	<0,10	<0,10	<0,10	<0,10
Cr 276.653	36,43	31,12	32,31	170,70	270,41
Cu 224.700	<0,10	<0,10	<0,10	6,49	13,24
Fe 238.204	0,19	0,12	0,21	9448	19119
Mg 279.553	0,15	0,23	0,20	4,74	4,52
Mn 257.610	<0,10	<0,10	<0,10	24	25
Mo 202.032	<0,10	<0,10	<0,10	1,91	2,54
Ni 216.555	<0,10	<0,10	<0,10	18	42
P 214.914	0,30	<0,10	<0,10	722	990
PO4	0,92	0,30	0,30	-	-
Pb 182.143	0,28	0,28	0,25	2,30	0,85
S 181.972	54,99	110,46	117,04	56	94
Na2SO4	24,00	48,00	51,00	-	-
Sb 217.582	<0,10	<0,10	<0,10	<0,10	<0,10
Se 196.026	0,29	0,27	0,26	<0,10	<0,10
Si 251.611	1,93	1,07	0,53	136	315
Sn 189.925	<0,10	<0,10	<0,10	1,84	2,08
Sr 407.771	<0,10	<0,10	<0,10	0,20	0,43
Ti 336.122	<0,10	<0,10	<0,10	2,10	2,82
Tl 276.789	0,12	<0,10	0,12	<0,10	<0,10
V 326.769	<0,10	<0,10	<0,10	5,26	5,83
Zn 213.857	0,22	0,25	0,24	6,02	19,57

Table V ICP-results for trial point 5.

Trial point 5	9.6.2010	9.6.2010	9.6.2010	9.6.2010	10.6.2010
	P1	P2	P3	S2A+B	S2A+B
	mg/l	mg/l	mg/l	mg/l	mg/kg
Al 396.152	0,81	0,41	0,64	266	443
As 188.980	<0,10	<0,10	<0,10	0,20	1,09
Be 313.042	<0,10	<0,10	<0,10	<0,10	<0,10
Ca 396.847	1,28	1,91	1,95	40,39	30,82
Cd 226.502	<0,10	<0,10	<0,10	3,63	3,69
Co 238.892	<0,10	<0,10	<0,10	<0,10	<0,10
Cr 276.653	31,31	26,96	31,17	237	196
Cu 224.700	<0,10	<0,10	<0,10	22,56	21,91
Fe 238.204	0,21	<0,10	<0,10	18737	18737
Mg 279.553	0,18	0,14	0,19	11,13	6,54
Mn 257.610	<0,10	<0,10	<0,10	74,22	89,28
Mo 202.032	<0,10	<0,10	<0,10	3,92	3,87
Ni 216.555	<0,10	<0,10	<0,10	100,72	88,78
P 214.914	0,17	0,21	0,16	828	1119
PO4	0,52	0,38	0,49	-	-
Pb 182.143	0,33	81,20	0,25	1,20	3,99
S 181.972	44,35	<0,10	108,02	87,6	76,9
Na2SO4	19,00	33,00	47,00	-	-
Sb 217.582	<0,10	0,68	0,10	0,13	<0,10
Se 196.026	0,27	<0,10	0,31	<0,10	<0,10
Si 251.611	1,91	<0,10	0,58	468	445
Sn 189.925	<0,10	<0,10	<0,10	2,12	3,22
Sr 407.771	<0,10	<0,10	<0,10	0,61	0,48
Ti 336.122	<0,10	<0,10	<0,10	3,79	4,42
Tl 276.789	0,11	0,12	0,15	<0,10	<0,10
V 326.769	<0,10	<0,10	<0,10	6,38	10,07
Zn 213.857	0,20	0,37	0,25	9,70	13,18

Table VI ICP-results for trial point 6.

Trial point 6	15.6.2010	15.6.2010	15.6.2010	16.6.2010	16.6.2010
	P1	P2	P3	S2A+B	S1B
	mg/l	mg/l	mg/l	mg/l	mg/kg
Al 396.152	0,33	0,34	0,49	175,5	1859
As 188.980	<0,10	<0,10	<0,10	0,97	0,27
Be 313.042	<0,10	<0,10	<0,10	<0,10	<0,10
Ca 396.847	2,87	3,07	2,63	34,09	2943
Cd 226.502	<0,10	<0,10	<0,10	1,63	4,41
Co 238.892	<0,10	<0,10	<0,10	<0,10	<0,10
Cr 276.653	27,66	24,76	23,79	297,6	232,6
Cu 224.700	<0,10	<0,10	<0,10	15,06	166,5
Fe 238.204	0,15	0,13	0,63	9578	19234
Mg 279.553	0,15	0,20	0,19	11,00	2562
Mn 257.610	<0,10	<0,10	<0,10	46,53	218,55
Mo 202.032	<0,10	<0,10	<0,10	21,88	10,61
Ni 216.555	<0,10	<0,10	<0,10	69,30	125,8
P 214.914	0,27	0,13	0,12	405,4	323,1
PO4	0,82	0,39	0,36	-	-
Pb 182.143	0,29	0,35	0,31	2,08	34,82
S 181.972	47,16	43,29	45,33	67,54	170,2
Na2SO4	20,00	19,00	20,00	-	-
Sb 217.582	<0,10	<0,10	<0,10	0,43	1,71
Se 196.026	0,23	0,26	0,22	<0,10	<0,10
Si 251.611	0,75	0,69	0,38	164,7	2130
Sn 189.925	<0,10	<0,10	<0,10	2,91	3,80
Sr 407.771	<0,10	<0,10	<0,10	0,37	98,17
Ti 336.122	<0,10	<0,10	<0,10	5,39	223,9
Tl 276.789	<0,10	<0,10	<0,10	<0,10	<0,10
V 326.769	<0,10	<0,10	<0,10	15,07	15,31
Zn 213.857	0,29	0,27	0,17	26,78	848,4

Table VII ICP-results for trial point 7.

Trial point 7	11.6.2010	11.6.2010	11.6.2010	11.6.2010
	P1	P2	P3	S2 A+B
	mg/l	mg/l	mg/l	mg/l
Al 396.152	0,42	0,53	0,66	569
As 188.980	<0,10	<0,10	<0,10	1,44
Be 313.042	<0,10	<0,10	<0,10	<0,10
Ca 396.847	0,99	1,35	1,50	33,70
Cd 226.502	<0,10	<0,10	<0,10	4,06
Co 238.892	<0,10	<0,10	<0,10	<0,10
Cr 276.653	24,23	24,83	25,05	203
Cu 224.700	<0,10	<0,10	<0,10	21,52
Fe 238.204	<0,10	<0,10	0,25	20261
Mg 279.553	0,13	0,23	0,17	10,08
Mn 257.610	<0,10	<0,10	<0,10	63,54
Mo 202.032	<0,10	<0,10	<0,10	2,97
Ni 216.555	<0,10	<0,10	<0,10	94,47
P 214.914	<0,10	0,25	0,15	1386
PO4	0,30	0,76	0,46	-
Pb 182.143	0,24	0,28	0,23	3,93
S 181.972	45,15	52,64	62,85	59,1
Na2SO4	20,00	23,00	27,00	-
Sb 217.582	<0,10	<0,10	0,10	<0,10
Se 196.026	0,30	0,30	0,30	<0,10
Si 251.611	1,97	2,65	0,68	413
Sn 189.925	<0,10	<0,10	<0,10	4,12
Sr 407.771	<0,10	<0,10	<0,10	0,52
Ti 336.122	<0,10	<0,10	<0,10	5,07
Tl 276.789	0,13	0,15	0,12	<0,10
V 326.769	<0,10	<0,10	<0,10	12,05
Zn 213.857	0,36	0,38	0,24	31,85

Table VIII ICP-results for trial point 8.

Trial point 8	18.6.2010	18.6.2010	18.6.2010	18.6.2010
	P1	P2	P3	S2 A+B
	mg/l	mg/l	mg/l	mg/l
Al 396.152	0,36	0,35	0,31	147,5
As 188.980	<0,10	<0,10	<0,10	0,36
Be 313.042	<0,10	<0,10	<0,10	<0,10
Ca 396.847	1,08	1,13	1,27	25,05
Cd 226.502	<0,10	<0,10	<0,10	2,05
Co 238.892	<0,10	<0,10	<0,10	<0,10
Cr 276.653	25,66	22,97	22,65	185,2
Cu 224.700	<0,10	<0,10	<0,10	12,38
Fe 238.204	<0,10	<0,10	2,92	11399
Mg 279.553	0,13	0,12	0,15	4,80
Mn 257.610	<0,10	<0,10	<0,10	19,60
Mo 202.032	<0,10	<0,10	<0,10	9,44
Ni 216.555	<0,10	<0,10	<0,10	51,23
P 214.914	0,11	0,11	0,29	394,2
PO4	0,33	0,33	0,89	-
Pb 182.143	0,29	0,31	0,34	<0,10
S 181.972	40,09	44,80	49,46	45,31
Na2SO4	17,00	19,00	21,00	-
Sb 217.582	<0,10	<0,10	<0,10	0,22
Se 196.026	0,23	0,27	0,25	<0,10
Si 251.611	1,78	1,53	0,51	121,3
Sn 189.925	<0,10	<0,10	<0,10	1,55
Sr 407.771	<0,10	<0,10	<0,10	0,43
Ti 336.122	<0,10	<0,10	<0,10	2,66
Tl 276.789	<0,10	0,11	0,12	<0,10
V 326.769	<0,10	<0,10	<0,10	9,25
Zn 213.857	0,27	0,27	0,25	68,90

Table VIII The major impurities in the incoming brine during the trial points.

	1	2	3	4	5	6	7	8
	mg/l							
Al	0,95	0,81	0,81	0,77	0,81	0,33	0,42	0,36
Ca	1,49	2,19	1,22	1,40	1,28	2,87	0,99	1,08
Mg	0,26	0,24	0,15	0,15	0,18	0,15	0,13	0,13
Fe	2,29	0,17	0,12	0,19	0,21	0,15	<0,10	<0,10
P	0,19	0,22	0,22	0,30	0,17	0,27	<0,10	0,11
Si	1,60	1,87	3,80	1,93	1,91	0,75	1,97	1,78

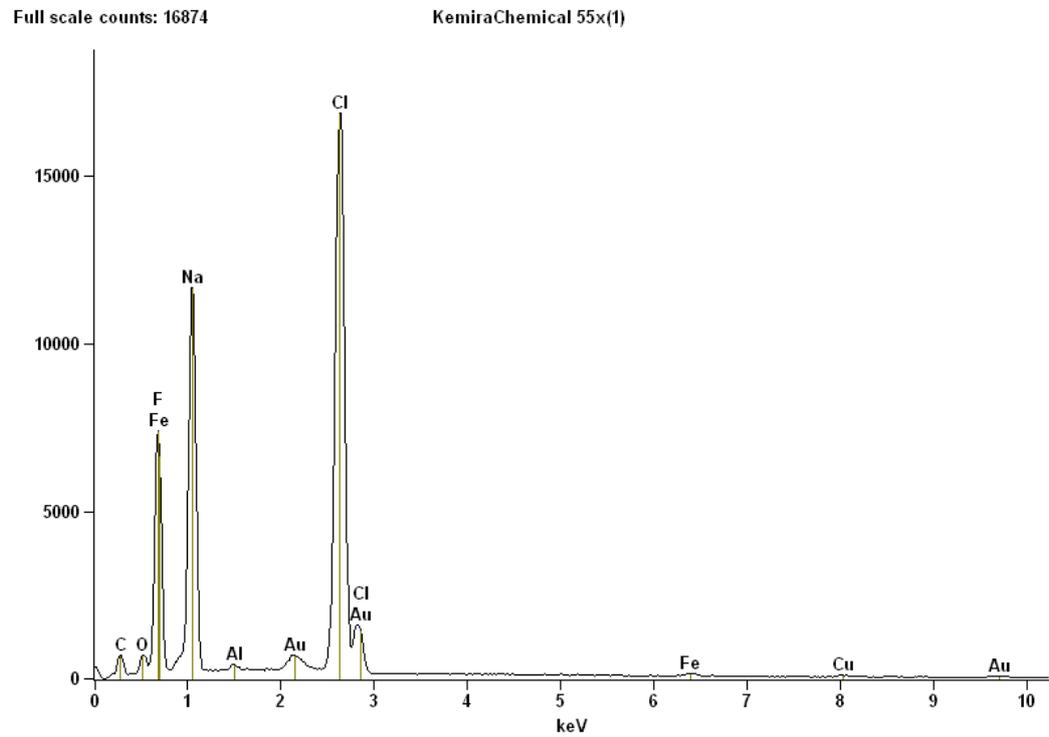


Fig. 1 Elemental composition of SEM-analysis.

Table I Quantitative results for 55x magnification.

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>
<i>C K</i>	7.33	+/- 0.14
<i>O K</i>	2.79	+/- 0.22
<i>F K</i>	27.92	+/- 0.19
<i>Na K</i>	24.82	+/- 0.14
<i>Al K</i>	0.33	+/- 0.03
<i>Cl K</i>	36.10	+/- 0.15
<i>Cu K</i>	0.72	+/- 0.09
<i>Total</i>	100.00	

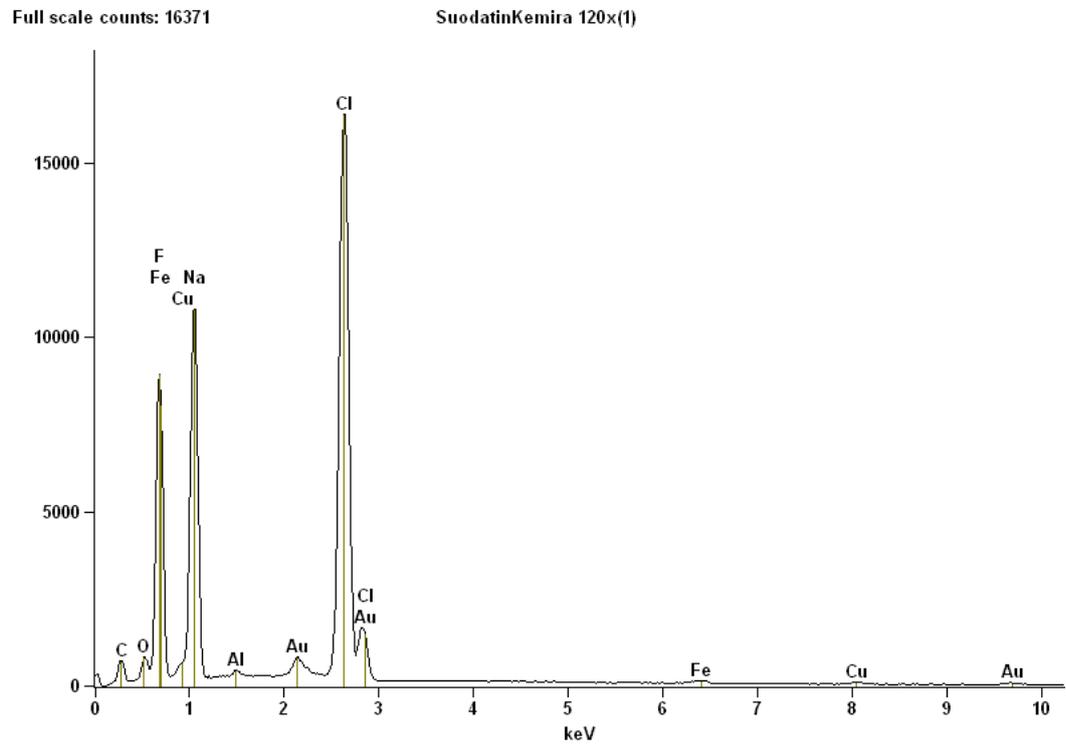


Fig. 2 Elemental composition of SEM-analysis.

Table II Quantitative results for 120x magnification.

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>
<i>C K</i>	7.15	+/- 0.13
<i>O K</i>	2.65	+/- 0.18
<i>F K</i>	31.70	+/- 0.16
<i>Na K</i>	23.72	+/- 0.13
<i>Al K</i>	0.26	+/- 0.03
<i>Cl K</i>	33.69	+/- 0.14
<i>Cu K</i>	0.83	+/- 0.08
<i>Total</i>	100.00	

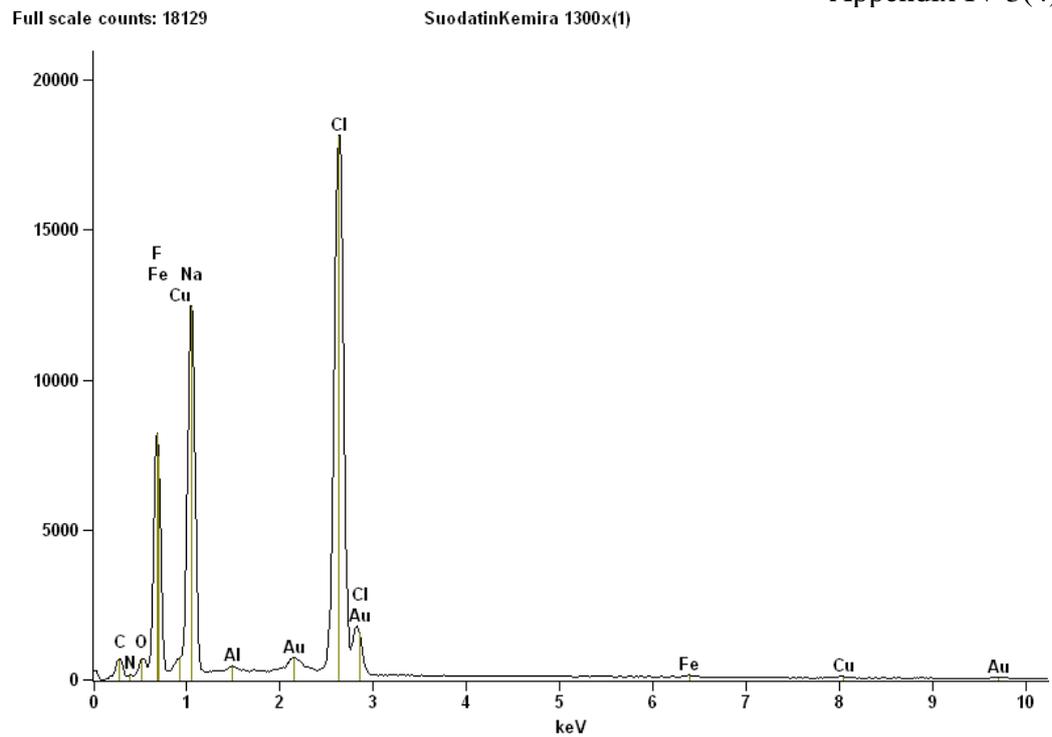


Fig. 3 Elemental composition of SEM-analysis.

Table III Quantitative results for 1300x magnification.

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>
<i>C K</i>	7.27	+/- 0.14
<i>N K</i>	1.72	+/- 0.25
<i>O K</i>	3.78	+/- 0.15
<i>F K</i>	28.82	+/- 0.15
<i>Na K</i>	24.15	+/- 0.13
<i>Al K</i>	0.23	+/- 0.02
<i>Cl K</i>	33.34	+/- 0.14
<i>Cu K</i>	0.70	+/- 0.08
<i>Total</i>	100.00	

Full scale counts: 9639

Suodatinkemira b1300x(3)

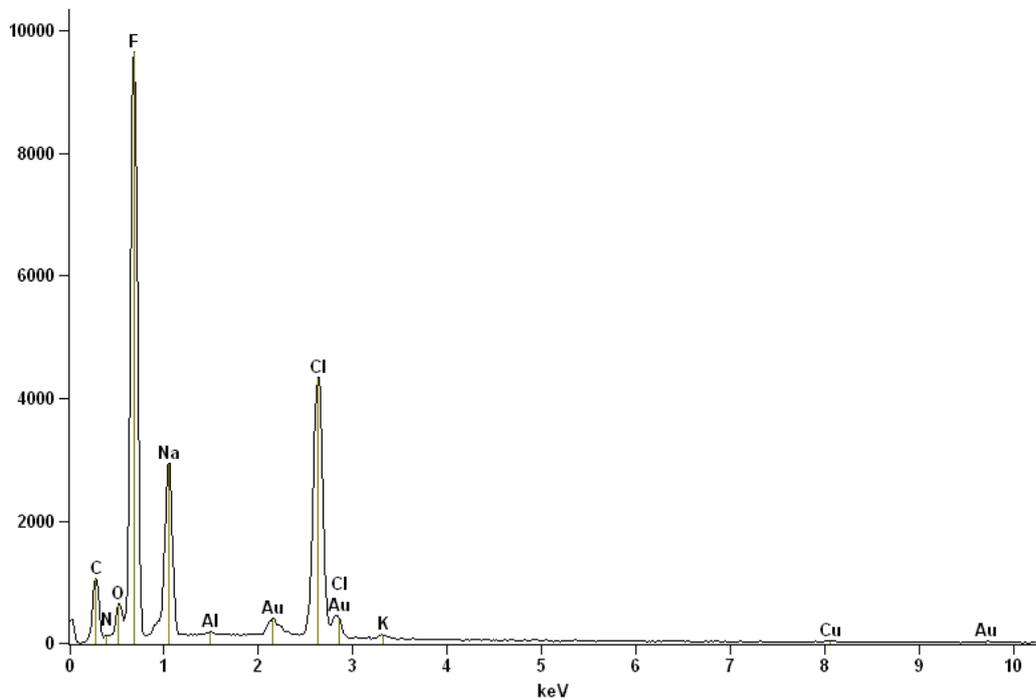


Fig. 4 Elemental composition of SEM-analysis.

Table IV Quantitative results for 1300(b)x magnification.

<i>Element Line</i>	<i>Weight %</i>	<i>Weight % Error</i>
<i>C K</i>	11.01	+/- 0.19
<i>N K</i>	1.40	+/- 0.38
<i>O K</i>	3.88	+/- 0.42
<i>F K</i>	50.70	+/- 0.33
<i>Na K</i>	12.69	+/- 0.15
<i>Al K</i>	0.28	+/- 0.03
<i>Cl K</i>	18.76	+/- 0.13
<i>K K</i>	0.33	+/- 0.03
<i>Cu K</i>	0.95	+/- 0.15
<i>Total</i>	100.00	