LUT University

School of Energy Systems

Energy technology

Master’s Thesis

Energy management software for sodium chlorate and chlor-alkali processes

Energianhallintatyökalu natriumkloraatti- ja kloori-alkaliprosesseihin

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ABSTRACT

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In this thesis research is done to determine if it is possible to increase efficiency of a sodium chlorate manufacturing process with software optimization. This thesis aims to make an initial design of optimization and energy efficiency monitoring software for Kemira Chemicals Joutseno site. The optimization is done in the sodium chlorate manufacturing process on the site and the monitoring part includes the entire site.

The major objective for optimization and monitoring software would be to increase site energy efficiency and reduce operating costs. The optimization part requires a dynamic model for the steam and hydrogen balances and this thesis provides all information for creating such models.

For the monitoring part, a survey was taken to research the energy awareness of the operators of the Joutseno site. Also, personnel had an opportunity to affect the designs created in this thesis.

As the outcome, this thesis presents a solid starting point for the development process of optimization software. The monitoring software could be implemented with little effort to the current automation system. It can be used to refine skills of personnel to further improve site efficiency.

TIIVISTELMÄ

LUT University
School of Energy Systems
Energiatekniikan koulutusohjelma

Kalle Malinen

Energianhallintatyökalu natriumkloraatti- ja kloori-alkaliprosesseihin

Diplomityö
2019
85 sivua, 27 kuvaa, 6 taulukkoa ja 7 liitettä
Tarkastajat: Professori Esa Vakkilainen
DI Janne Tynninen
Hakusanat: Natriumkloraatti, energiaoptimointi, energiatehokkuus

Tämän opinnäytetyön tarkoituksena on suunnitella lähtökohta optimointi- ja energiatehokkuuden seurantasovellukselle Kemira Chemicals Oy:n Joutsenon tehdasalueelle ja selvittää voidaanko sen avulla parantaa tehdasalueen tehokkuutta. Optimoinnin kohteena on tehdasalueen natriumkloraattituotantolinjat ja seurantasovellus kattaa koko tehdasalueen.

Optimointi- ja seurantasovelluksen tärkein tavoite on parantaa tehdasalueen tehokkuutta ja pienentää käyttökustannuksia. Sovelluksen optimointiosa tarvitsee dynaamiset simulaatiomallit tehdasalueen vety- ja höyrytaseesta. Tämä työ sisältää tarvittavat tiedot sopivien mallien kehittämiseksi.

Sovelluksen energiatehokkuuden seurantaosaa varten kartoitettiin prosessihenkilökunnan energiaymmärrys. Tämän lisäksi henkilökunnalle annettiin mahdollisuus vaikuttaa ohjelmistojen kehitykseen.

Lopputulemana tämä työ antaa hyvän lähtökohdan kloraattiprosessin optimointisovellukselle. Energiatehokkuuden seuranta voitaisiin toteuttaa osaksi nykyistä prosessinohjausjärjestelmää. Sen avulla voidaan parantaa prosessihenkilökunnan taitoja ja prosessin tehokkuutta.

ACKNOWLEDGEMENTS

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I want to express my gratitude towards Kari Luostarinen and Professor Esa Vakkilainen for guidance and academic support.

During the fall and winter of 2018, I spent countless evening and nights with this thesis. The huge workload in short time was not overwhelming because all the support I got from my family and friends. Therefore, I want to thank my family and Jenna for encouragement throughout my years of study. Lastly but not least, I would like to thank my fellow students, especially for time off and numerous cups of coffee.

29.12.2018 Lappeenranta

Kalle Malinen

CONTENTS

SYMBOLS AND ABBREVIATIONS

Latin alphabet

A	Area, m^2
c	concentration g/l
c_p	Specific heat capacity at constant pressure, kJ/kgK
E	Energy, J
	Thermoneutral voltage, V
F	Faraday’s constant, C/mol
M	Molar mass, g/mol
m	Mass, kg
p	Pressure, Pa
R	Ideal gas constant, J/molK
s	Heat of vaporization, kJ/kg
T	Temperature, °C
t	Time, s
V	Electrochemical potential, V
Q	Heat flow, W
	Electrical charge, C
x	gas content, v-%
z	number of electrons transferred in the reaction, -

Greek alphabet

ε	current efficiency, -
λ	equivalence ratio, -
η	efficiency, -
ρ	Density, kg/m^3

Abbreviations

AKD	alkyl ketene dimer
avg	average
Ca	calcium

Cl_2	chlorine
evap	evaporation
H_2	hydrogen
H_2O_2	hydrogen peroxide
H_2O	water
HClO	Hypochlorous acid
HCl	hydrochloric acid
Na	sodium
NaCl	sodium chloride
NaClO	sodium hypochlorite
$NaClO_3$	sodium chlorate
$Na_2Cr_2O_7$	sodium dichromate
NaOH	sodium hydroxide
NTP	normal pressure and temperature
O_2	oxygen
sat	saturation
VO2	oxygen consumption rate

1 INTRODUCTION

1.1 Background

In the near future, more electricity is produced in environmentally friendly ways to decrease greenhouse gas emissions. There are predictions, that capacities of solar and wind power are going to increase most rapidly, which can be seen for example from figure 1 (Demirel 2016, p. 50).

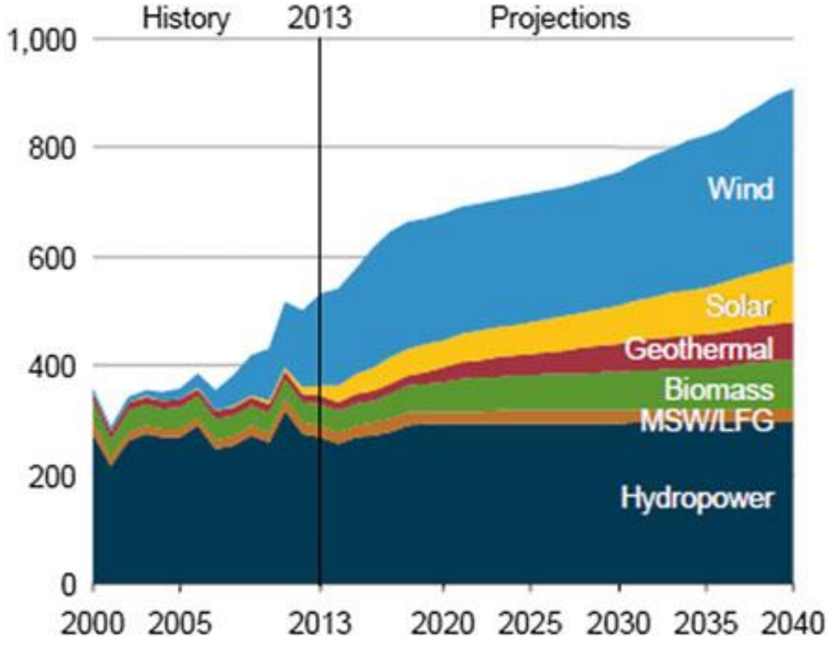


Figure 1. History and projection of distributions of renewable energy sources for electricity generations in the U.S. in billion kWh (Demirel 2016, p. 50).

In figure 1, the distribution among renewable energy sources for electricity generation in the United States is shown. Both wind and solar are non-controllable and weather-dependent. This requires more load or generation that can be easily regulated, which certainly will have an effect in the pricing of electricity in balancing power market.

Power grid must be constantly in balance. Balance of the grid means that electricity generation and consumption must be almost equal at all times. The imbalance in system can be monitored in frequency changes of systems voltage. In the Nordpool area frequency changes between 49,9 and 50,1 Hz are acceptable, where 50 Hz is desired value. The balance is achieved with regulating bids from the balancing power markets and by reserving capacity. (Fingrid 2017.)

Based on the EU Commission regulation (2017/2195) all transmission system operators shall apply the imbalance settlement period of 15 minutes in all scheduling area by end of 2020. Electricity market in Nordpool market area is going to implement 15-minute settlement period after second quarter of 2020 (Energinet et al. 2017). Currently power balancing market is done in 60-minute period. 15-minute period will allow balancing power market to adjust the power balance faster. Finnish transmission system operator has also started discussions of raising the maximum day-ahead market price of electricity to 9999 €/MWh from 3000 €/MWh (Fingrid 2016). The proposed maximum price is currently used widely in Europe.

For any energy-intensive process, these updates to the power balancing system can cause expenses if the local power management system and information flow around it are not fast enough. Although, these updates can also be an advantage for energy-intensive manufacturing processes with good abilities for power regulation via an increase in price variation in power balancing market. If all these changes take place, there can be situations where minimizing power consumption and selling reserved power to grid can bring a significant profit.

Sodium chlorate is manufactured from three main ingredients, which are salt, water and electricity. It is manufactured in the electrolysis process and the manufacturing process is very energy intensive. Sea or mountain salt used in sodium chlorate electrolysis is relatively cheap, which means that most of the production costs come from the price of the electricity alone**.**

Manufacturing process of sodium chlorate can be also easily power regulated. Therefore, it is suitable for balancing power market. Nowadays economic benefits can be achieved with careful planning of production, but for future more advantageous systems are necessary in large-scale production. These systems would allow maintaining ability to participate efficiently to the power balancing market, even with 15-minute settlement period**.** In this thesis, research is done to find base requirements for an optimization software that helps forecast process state and determine local power balance in multiple sodium chlorate production lines. In addition, this kind of optimization software can be used as powerful tool to make profit in power balancing market.

1.2 Objectives

The purpose of master this thesis is to determine which parameters are mandatory to make an automated system that gives instructions to operators how to balance sodium chlorate production lines with given total power. To achieve this, fundamental knowledge of sodium chlorate process energy consumption is required. Also, in this thesis, software for data collection and monitoring efficiencies is introduced. The purpose of monitoring interface is to give operators real-time information of site efficiencies and therefore help to spot causes for lowered efficiency.

The thesis was conducted at Kemira Chemicals Joutseno site. On Joutseno site, chlorate plant supplies hydrogen to site's chlor-alkali plant and has a common steam network with site's other plants. Therefore, to plan a functional energy management system for sodium chlorate production lines, hydrogen and steam balances must be taken into consideration.

For Kemira Chemicals, this thesis presents software improvements and optimization and monitoring software that could improve driving habits of operators and therefore increase site efficiency. Also, this thesis presents a solid starting point for the development of advanced production forecast and optimization software. The aim of the software is to reduce operational costs of plants and improve economic efficiency in sodium chlorate production while maintaining stable operation on the site.

1.3 Structure of the thesis

The thesis can be divided into three major parts. Chapters 3 to 4 present the process and theory used in sodium chlorate manufacturing. In those chapters, sodium chlorate manufacturing process is introduced, and the energy balance is generated mainly based on literary references.

In chapters 5 to 8, Joutseno site along with site-specific steam, hydrogen and energy balances are introduced. In those chapters, every major energy application is covered and balances for hydrogen, steam and energy are generated. These balances are researched for the initial design of simulation software.

The last major part of the thesis contains the information about the simulation tool and interviews of operators. The interviews were done to determine energy awareness of shift personnel and to involve operators in the design process of monitoring interface, which is later presented in this thesis. In this thesis, no complete software is created but most relevant requirements and potential approaches to calculations are proposed.

2 SODIUM CHLORATE

Sodium chlorate is colorless and odourless crystalline powder in standard atmospheric conditions (1 atm and 25 °C). The main use of this chemical is manufacturing of chlorine dioxide, which is used in paper bleaching process. Near 95 percent of sodium chlorate produced worldwide is consumed to manufacture chlorine dioxide. (CEFIC-Sodium Chlorate 2004.)

Chlorine dioxide cannot be compressed because concentrated chlorine dioxide is explosive. In addition, chlorine dioxide is an unstable gas that dissociates into chlorine and oxygen gases, therefore it cannot be effectively or safely transported and must be manufactured at the point of use. (World Health Organization 2000.)

First records of sodium chlorate electrolysis experiments dates to early 19th century. First commercial electrolysis cells were patented in 1851 by Watt and in 1886 first commercial chlorate production plant was built to Villers-St. Sepulchre in Switzerland. This plant used about 15 MWh of energy to produce one ton of potassium chlorate, whereas modern plants use about 5-6 MWh/ton. (Burney 1999, p. 8.) Potassium chlorate is a chemical with comparable properties to sodium chlorate and it is manufactured with exact technologies, only ingredients differ.

2.1.1 **Properties**

Like mentioned before, pure sodium chlorate is fully odorless and colorless crystalline powder, but in industrial applications, sodium chlorate is slightly yellowish. The yellow color comes from chromium, which is added to process to prevent oxygen generation during electrolysis. More on electrolysis reactions and auxiliary chemicals later in chapter 3. The melting point of sodium chlorate in normal atmospheric pressure is 248 °C. The boiling point of sodium chlorate is irrelevant because it starts to decompose at about 300 °C when there is no sign of boiling (Eka Chemicals 1998, p. 1). More properties of sodium chlorate are presented in table 1.

Sodium chlorate is strong oxidizer, but non-flammable on its own. It is also listed as dangerous to the environment due it being phytotoxic to all green plants. For a human, sodium chlorate is toxic only if ingested. Toxicity comes from sodium chlorate being oxidizer which leads to methaemoglobin formation. This can lead in most severe cases to haemolysis, which ultimately can even result in death if left untreated. (Ranghino et al. 2006.)

Table 1. Most common properties of pure sodium chlorate. All values are in NTP conditions. (Eka Chemicals 1998.)

Property	**Value**
Molar mass	106,45 g/mol
Melting point	248 °C
Density	2460 kg/m^3
Specific heat capacity in solid state	104,6 J/mol K 0,98 kJ/kgK
Specific heat capacity in liquid state	134,10 J/molK 1,28 kJ/kgK
Chemical formula	$NaClO_3$
Heat of solution	-23,45 kJ/mol -220,27 kJ/kg
Standard enthalpy of formation	-365,4 kJ/mol

The maximum amount of sodium chlorate soluble in water is presented in table 2. The solubility of sodium chlorate to water is a function of fluid temperature. Sodium chlorate is also soluble to glycerol and ethanol. Sodium chlorate can be handled either as an aqueous solution or as dry powder. Aqueous solutions are used in cases where transportation distance to the end user is short.

Table 2. Sodium chlorate solubility in water as a function of temperature (Seidell and Linke 1952).

The temperature of water [°C]	Mass of sodium chlorate in 100 ml fully saturated solution [g]	Mass of sodium chlorate in a kilogram of fully saturated aqueous solution [g]
0	79	441,3
10	89	470,9
25	105,7	513,9
40	125,0	555,6
100	220,4	687,9

From the values of table 2, an equation of saturation curve for sodium chlorate in aqueous solution can be formed. This is presented in the equation (1) below. This equation can be also presented in a form where saturation temperature is a variable. This equation is represented in the equation (2).

$$m = 2{,}4408T + 448{,}48 \tag{1}$$

$$T = 0{,}4097m - 183{,}74 \tag{2}$$

where m is soluble amount of $NaClO_3$ to one kilogram of the solution [g]
T is temperature of the solution [°C]

The density of sodium chlorate and chloride solution can be calculated at a given temperature with equation (3) (Eka Chemicals 1998). Sodium chloride is included in this equation because it is often present in solutions of sodium chlorate manufacturing process.

$$\rho = 0{,}9965 + 62{,}5x + 0{,}52x^2 + 69{,}3y^2 + 0{,}81xy + (25 - T)(4{,}5 + 0{,}05)(0{,}9x + y) \tag{3}$$

where ρ is density of sodium chlorate and chloride solution [kg/m^3]
x is amount of sodium chlorate in solution [wt-%]
y is amount of sodium chloride in solution [wt-%]
T is temperature of the solution [°C]

A correlation of specific heat capacity in constant pressure for sodium chlorate in solid form is presented in equation (4). In liquid form, the specific heat capacity can be assumed to be constant and was presented in table 2. (Campbell and Kouwe 1968.) Equation (4) gives the density in imperial units and equation (5) in metric units.

$$c_p(s) = (44{,}0\ \cdot 10^{-3}T + 10{,}92\,)\,\frac{\mathrm{cal}}{\mathrm{molK}} \tag{4}$$

$$c_p(s) = (184{,}096 \cdot 10^{-3}T + 456{,}89)\,\frac{\mathrm{J}}{\mathrm{molK}} \tag{5}$$

where c_{p}(s) is specific heat capacity for solid state [cal/molK] or [J/molK]

2.1.2 **Uses**

As earlier mentioned, the main use of sodium chlorate is manufacturing chlorine dioxide. To manufacture chlorine dioxide, sodium chlorate is mixed with an acid solution, such as hydrochloric acid. The generation of chlorine dioxide with sodium chlorate and hydrochloric acid is represented in reaction equation (6).

$$\mathrm{NaClO_3}\ +\ 2\,\mathrm{HCl} \rightarrow \mathrm{ClO_2} + \frac{1}{2}\,\mathrm{Cl_2} + \mathrm{NaCl} + \mathrm{H_2O} \tag{6}$$

Due to sodium chlorates phytotoxicity, it can be used as herbicides. However, it was banned from the public in EU in 2008 because it can be used to create homemade explosives. The ban is still in force and only products with 40 % or lower concentration of sodium chlorate can be sold to the public by EU regulation No 98/2013. But in other areas, for example in the United States, pure sodium chlorate crystals are publicly available (Foxall 2010).

Sodium chlorate and other chlorates can be used to store and regenerate oxygen. When heated, sodium chlorate starts to decompose and form sodium chloride and oxygen gas. This process is exothermic, which means that it releases heat, so decomposing continues without an external heat source. The oxygen generation reaction can be seen in reaction equation (7) below.

$$\mathrm{NaClO_3} \rightarrow 2\ \mathrm{NaCl} + 3\ \mathrm{O_2} \tag{7}$$

This method is used for example in airplanes and space stations, because of high oxygen to weight ratio and simple storage. In one kilogram of sodium chlorate, there are approximately 450 grams of pure oxygen gas. Therefore, one cubic meter of sodium chlorate contains approximately 1110 kilograms of oxygen gas. With normal oxygen consumption rate estimated by Nickson, this amount of oxygen gas allows a 75 kg adult to breathe for over two days (Nickson 2014). This is calculated in equations (8) and (9) below.

$$m_{02} = \frac{M_{O3}}{M_{NaClO3}} * \rho_{NaClO3} * 1\ m^3 = 1109{,}4\ kg \tag{8}$$

$$t = \frac{m_{O2}}{\frac{VO2_{avg}}{\rho_{O2}}} = 3105\ \mathrm{min} \approx 2d\ 4h \tag{9}$$

where	m_{O2} is mass of oxygen in one cubic metre of sodium chlorate	[kg]
	M_{O3} is molar mass of oxygen in sodium chlorate (=46 g/mol)	
	$VO2_{avg}$ is average oxygen consumption of 75 kg adult	[l/min]
	t is time	[min]
	ρ_{O2} is density of oxygen	[kg/m^3]

3 THEORY OF SODIUM CHLORATE PRODUCTION

In this chapter, a manufacturing process of sodium chlorate is explained, and all major process equipment and phases are introduced. In theoretical calculations, the main focus is on the energy consumption of different parts of the manufacturing process.

Sodium chlorate process can be divided to two parts, which are electrolysis process and crystallization combined with postprocessing. In addition to these processes, there are many more subprocesses, like hydrogen scrubbing and cooling. These are not included in this thesis. A general process chart of manufacturing process is presented in figure 2 below.

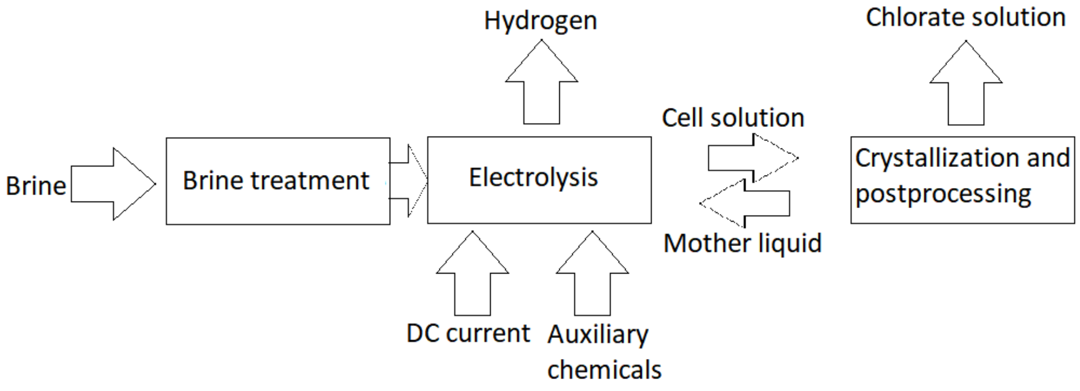


Figure 2. Sodium chlorate manufacturing process (European Commission 2007, p. 515).

In industrial scale manufacturing processes, there are always amount of impurities, for example calcium, magnesium and sulphate. Major part of the impurities come along with salt. (European Commission 2007, p. 516.) The concentration of these impurities will rise along time as manufacturing process is semi-closed loop. These impurities affect process in many ways, for example they can lead to unwanted reactions that reduce efficiency or mess up crystallization process. In this thesis, effect of impurities is neglected unless otherwise is stated. This is justified because most of the calculations are performed to find out optimal values.

To avoid impurities, the sodium chloride solution is filtered before entering the electrolysis process and cell solution is cleaned regularly with different methods. Any impurities in sodium chloride solution that is fed to the electrolysis can cause lowered efficiency and other problems in the manufacturing process.

3.1 Sodium chloride electrolysis

3.1.1 Electrolysis reactions

Sodium chlorate is manufactured with sodium chloride electrolysis process. Electrolysis is a technique that drives normally non-spontaneous chemical reactions with direct electric current. Electrolysis takes place in electrolytic cells and final reactions happen in reaction and retention tanks. There are many side reactions that occur in certain circumstances and lower the overall efficiency of electrolysis process. These reactions are prevented with auxiliary chemicals or maintaining desired properties in electrolyte. (Burney 1999.)

In sodium chlorate manufacturing process, electrolyte, also called cell solution, is aqueous solution of sodium chloride and sodium chlorate. As electrolysis reactions take place in the electrolysis cells, the concentration of sodium chlorate increases and concentration of sodium chloride decreases. The concentration of sodium chloride in input cell solution to the electrolysis cells is kept at decent level to ensure that electrolysis reaction can happen. In addition to sodium chlorate and chloride, cell solution also includes impurities and auxiliary chemicals.

In electrolysis cells, positively charged components of electrolyte travel to a negatively charged electrode or cathode and negatively charged components travel to a positively charged electrode or anode. This breaks the ionic bonds in ionic substances of cell solution. This reaction for sodium chloride is represented in reaction equation (10) and for water in reaction equation (11).

$$\mathrm{NaCl} \rightarrow \mathrm{Na}^+ + \mathrm{Cl}^- \tag{10}$$

$$\mathrm{H_2O} \rightarrow \mathrm{H}^+ + \mathrm{OH}^- \tag{11}$$

On the surface of anode, chlorate is produced. The following reaction equations, (12) to (16), present the electrochemical reactions that produce chlorate ion. Also, at the anodic side, reactions which form oxygen gas occur. The most significant of these is the reaction where water discharges to hydrogen and oxygen gas. This reaction was presented earlier as reaction equation (11). (Burney 1999.)

Reaction equations (14), (15) and (16) are balanced by cell solutions pH value. The optimal range for pH value is 5,8–6,4. Within these pH values side reactions are kept minimal, which ultimately means higher electrolysis efficiency. (Kivistö 2011, p. 2.)

$$2\ \mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 + 2\ \mathrm{e}^- \tag{12}$$

$$\mathrm{Cl}_2 + \mathrm{OH}^- + \mathrm{H}^+ \leftrightarrow \mathrm{HOCl} + \mathrm{H}^+ +\ \mathrm{Cl}^- \tag{13}$$

$$\mathrm{HOCl} \leftrightarrow \mathrm{H}^+ + \mathrm{ClO}^- \tag{14}$$

$$2\ \mathrm{HOCl} + \mathrm{ClO}^- \leftrightarrow \mathrm{ClO}_3^- + 2\ \mathrm{Cl}^- + 2\ \mathrm{H}^- \tag{15}$$

$$2\ \mathrm{H}_2\mathrm{O} \rightarrow +\mathrm{O}_2 +\ 4\ \mathrm{e}^- + 2\ \mathrm{H}_2 \tag{16}$$

In sodium chlorate electrolysis both hydrogen and oxygen can be generated. A mixture of hydrogen and oxygen become self-explosive when a concentration of oxygen rises above 5 vol-% (Schroeder and Holtappels 2005, p. 6). This is one of the reasons why oxygen generation should be kept minimal. Oxygen generation also lowers the chlorate ion generation efficiency. (Hedenstedt 2017, p. 9).

On the surface of the cathode, there is one major reaction, this reaction is presented below in reaction equation (17). In this reaction, water molecules reduce to hydrogen molecule and hydroxide ion. (Burney 1999).

$$2\ \mathrm{H}_2\mathrm{O} + 2\ \mathrm{e}^- \rightarrow \mathrm{H}_2 + 2\ \mathrm{OH}^- \tag{17}$$

In addition to reaction equation (17), there are also two important side reactions that occur on the surface of the cathode. These are presented in reaction equations (18) and (19). Reaction equation (18) represents a reduction of hypochlorite and reaction equation (19) reduction of chlorate. Both lower the chlorate ion generation efficiency and are suppressed by auxiliary chemicals in industrial scale electrolysis. (Burney 1999).

$$\mathrm{ClO^- + H_2O + 2\ e^- \rightarrow Cl^- + 2\ OH^-} \tag{18}$$

$$\mathrm{ClO_3^- + 3\ H_2O + 6e^- \rightarrow Cl^- + 6\ OH^-} \tag{19}$$

Perchlorate formation by oxidation of chlorate occurs at low rate. However, the concentration of the perchlorate in cell solutions may grow high enough to violate the production process. Perchlorate formation reaction is presented in reaction equation (20) below. (Hedenstedt, 2017 p. 9.)

$$\mathrm{Cl_2 + 2\ OH^- \rightarrow ClO^- + Cl^- + H_2O} \tag{20}$$

Negatively charged chlorate ion and positively charged sodium ion will combine to sodium chlorate when there is no external force preventing it. In practice, this reaction can occur when ions leave electrolysis cell. This reaction is presented below, reaction equation (21).

$$\mathrm{Na^+ + ClO_3^- \rightarrow NaClO_3} \tag{21}$$

Current efficiency can be used to measure the amount of unwanted reactions and therefore to determine the amount of energy losses caused by these reactions. In literature, there are several different methods presented to calculate current efficiency.

Jasic et al. (1969) proposed equation (22) below to calculate current efficiency. This equation requires measurement of hydrogen, oxygen and chlorine content in the gas that is produced in the electrolysis cells. An equation (23) is a revised and simplified version of equation (22) by Tilak and Chen (1999) but has proven to give decent results. In this equation, no chlorine measurement is required.

$$\varepsilon = \frac{100 - 3x_{02} - 2x_{Cl2}}{100 - x_{02} - x_{Cl2}} \tag{22}$$

$$\varepsilon = \frac{x_{H2} - 2x_{O2}}{x_{H2}} \tag{23}$$

where	ε is current efficiency	[-]
	x_{O2} is oxygen content in the gas	[%]
	x_{Cl2} is chlorine content in the gas	[%]
	x_{H2} is hydrogen content in the gas	[%]

3.1.2 Electrolysis cells

Electrolysis cell current efficiency has a major impact in manufacturing process efficiency. Therefore, many cell designs are corporative secrets. Many of the biggest sodium chlorate manufacturers have their own design. Designs can be separated to monopolar and bipolar designs. In monopolar designs, electrodes in the cell have only one polarity, negative or positive. In bipolar designs, all but two electrodes, that bring current in and out of cell, have positive charge in the one end and negative in the other end. (O'Brien et al. 2007, p. 388.) Differences of monopolar and bipolar cell designs are presented in figures 3 and 4.

Figure 3. Monopolar (left) and bipolar (right) electrolysis cell examples (Suzhou Fenggang Titanium Products and Equipment Manufacturing Co., Ltd 2014)

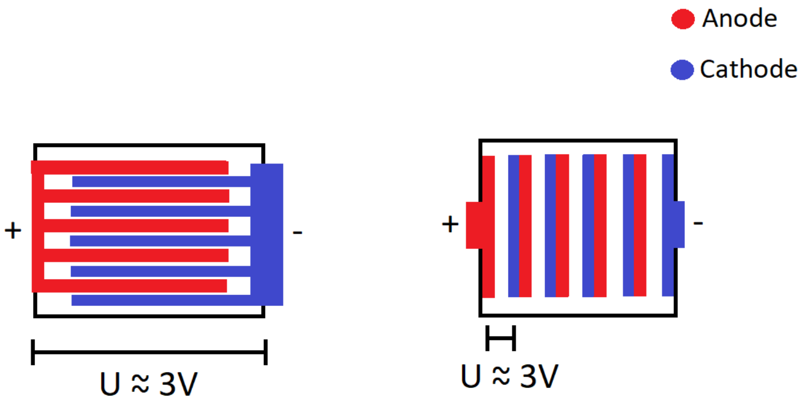


Figure 4. Anode and cathode arrangement in different electrolysis cell designs: monopolar on left and bipolar on right.

In industrial scale manufacturing processes, many monopolar cells are electrically in series to achieve high overall voltage of electrolysis unit. High voltage is wanted to lower electrical current of system. Electrical losses are more dependent on system's current than voltage and therefore lower current leads to smaller electrical losses. (O'Brien et al. 2007, p. 388.)

In bipolar cell unit, there are specific number of individual cells inside one unit. Therefore, a voltage over cell unit is higher and losses smaller than in monopolar design. Depending on design, units can be arranged electrically in series or parallel. (O'Brien et al. 2007, p. 388.) Both cell designs have their advantages and disadvantages which are presented below in the table 3.

Table 3. Cell design differences (O’Brien et al., 2007, p. 390).

Monopolar	Bipolar
+ Each cell can be monitored separately	- Only units can be monitored separately
+Each cell can be repaired separately, in some designs without shutdown	- Cell repair requires a shutdown
- More instruments required (= higher capital cost)	+ Fewer instruments required
- Higher unit voltage (more expensive rectifiers)	+ Lower overall voltage (less expensive rectifiers)
+/- Rectifier pricing more suitable for large-scale plants	+/- Rectifier pricing more suitable for small/medium scale plants

3.2 Crystallization

Crystallization is another main part of sodium chlorate manufacturing process. The most common way to crystallize sodium chlorate from cell solution is vacuum crystallization in strong tank called crystallizer. In crystallizer, water is evaporated in a near vacuum at moderate temperatures. This raises the concentration of sodium chlorate in the solution and allows crystallization of sodium chlorate. (European Commission 2007, p. 516.)

Any crystallization process has three major phases, which occur simultaneously in industrial scale applications. These three phases are attainment of metastability, the formation of nuclei and crystal growth. (Duke 1981.) These phases must be kept in balance to maintain stable operational conditions in the crystallizer. In vacuum crystallization, a rate of crystallization can be adjusted by alternating the pressure and furthermore the temperature of crystallizer and by adjusting residence time of sodium chlorate in crystallizator.

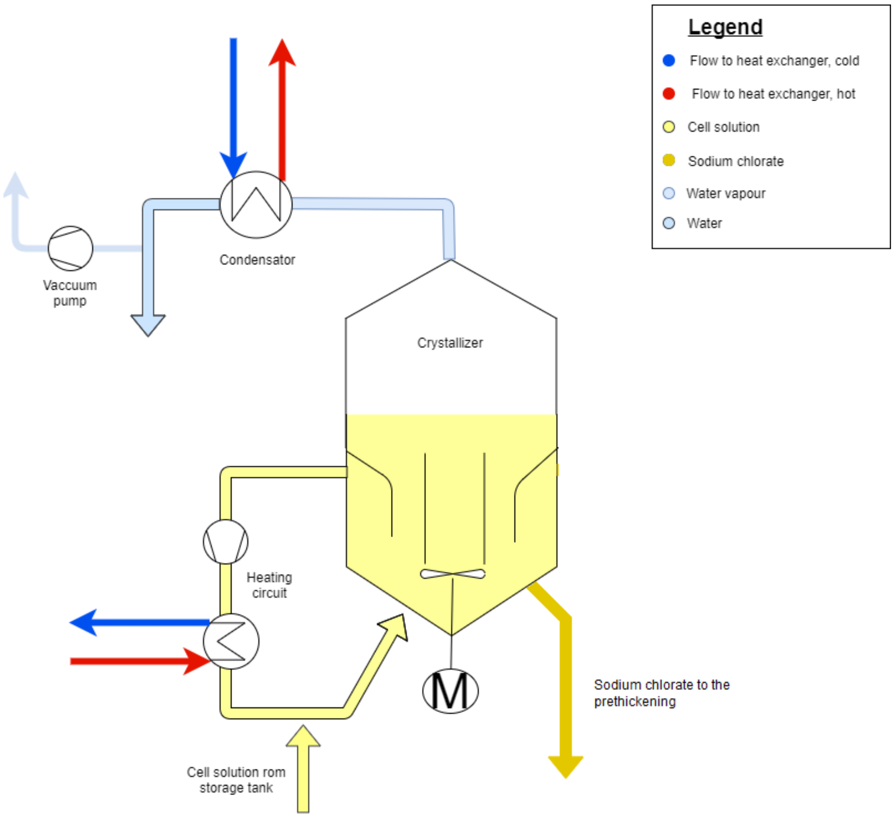


Figure 5. Crystallizer unit without evaporator

In the simplest design of crystallizer, like one presented in the figure 5, the cell solution is fed to the crystallizer from the bottom. A strong vacuum starts the water evaporation in the solution and water vapor exits with suction of vacuum creating units through the top. When water is evaporated from the solution, a concentration of sodium chlorate and chloride rises. As the concentration of sodium chlorate starts to rise, crystals start to form.

These crystals have a higher density than cell solution and therefore start falling to the bottom. To keep the bottom of the unit as fluidized and to bring small crystals to the surface of the solution, an agitator is implemented at the bottom. A solution with high sodium chlorate concentration exits from the bottom of the crystallizer.

During the crystallization process, a crystallization of sodium chloride should be kept minimum, because the amount of sodium chloride in a product is one of the quality factors. To prevent crystallization of sodium chloride, must mutual saturation curve for sodium chloride and chlorate be known for a specific temperature.

Sodium chlorate solubility to water is heavily temperature related whereas solubility of sodium chlorate stays almost constant in variable temperatures. Sodium chloride and sodium chlorate share a sodium ion, which have effect in mutual solubility. In this thesis, phase diagram for sodium chlorate – sodium chloride – water ternary system is recreated with data from literary source (Burney 1999). Recreated phase diagram is presented in the figure 6.

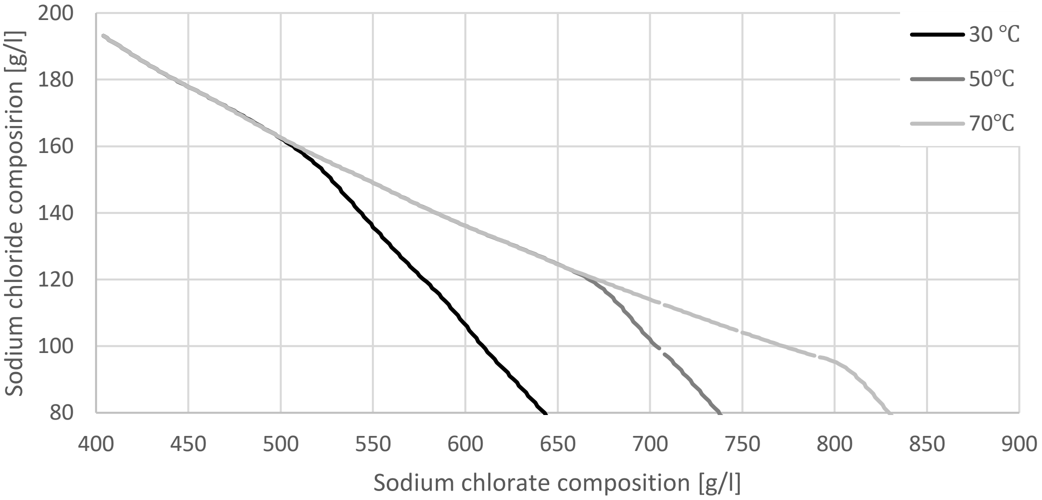


Figure 6. Phase diagram for sodium chlorate – sodium chloride – water ternary system

Crystallized sodium chlorate is washed in pre-thickening centrifuges. After washing, sodium chlorate is either dissolved in water or dried and then delivered to end user. The reason for washing is to prevent any sodium dichromate to leave the process.

3.3 Other process equipment

3.3.1 **Reaction tank and storage tank**

In the reaction tank, pH adjustments occur, and sodium chloride solution is added to the cell solution. In many designs, the cells are fed from the bottom of reaction tank and cell solution that exits from electrolysis cells is fed to the top of the tank and hydrogen is separated from cell solution before reaction tank. Also, all auxiliary chemicals, mother liquid (returning solution from crystallization) and sodium chloride solution are added from the top of the tank. The concentration of sodium chlorate in cell solution increases in a reaction tank and cell solution exits from the tank continuously from the upper part.

The tank is kept at an almost constant level, which means that the flow rate of cell solution from the tank is a sum of flow rates that are fed to the tank. Therefore, flow rates of reaction tank inlets and outlets have a significant impact on the process. Sodium chlorate manufacturing process can be illustrated as one semi-closed circuit, where mother liquid circulates inside process. A typical arrangement of the process is presented in figure 7.

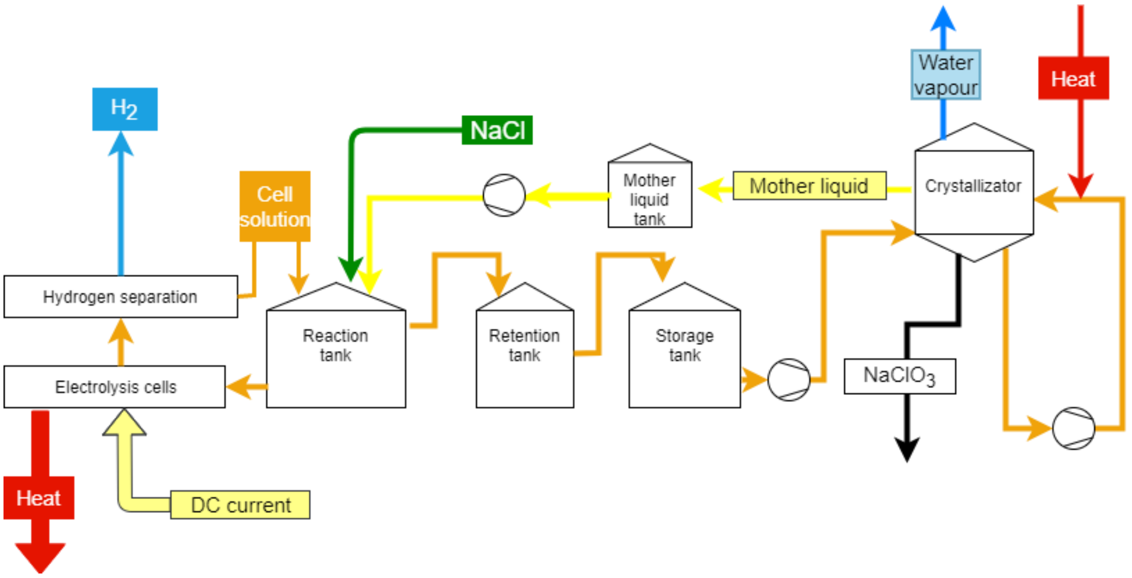


Figure 7. Simplified sodium chlorate manufacturing process.

The flow rates of circulation are adjusted so, that the sodium chloride concentration of cell solution is high enough to ensure a proper function in the electrolysis cells and low enough to prevent sodium chloride crystallization in a crystallizer.

3.3.2 Pre-thickening centrifuges

Sodium chlorate solution from the crystallizer is fed to the pre-thickening centrifuges. A typical pre-thickening centrifuge can be seen in figure 8. The main purpose of a centrifuge is to separate any sodium dichromate and cell solution residue from crystals. Before centrifuging it is ideal to separate any liquids from sodium chlorate crystals to allow better washing of sodium dichromate in a centrifuge.

Figure 8. D-ACT® Type PD-80 pre-thickening centrifuge by Ferrum (Ferrum 2018).

A centrifuge is mechanical equipment that has a basket made of a small holed web, which rotates at moderate speeds. The cell solution is fed to the basket and due to the rotation the remaining liquids escape through the web and only crystals are kept inside the basket. The basket mechanism pushes the crystals onward on the basket and high-pressure nozzles wash oncoming crystals to remove any leftover sodium dichromate. The solution, which is removed in the pre-thickening process is returned to the process due to it's high concentration of chemicals such as sodium dichromate and sodium chloride.

3.3.3 Crystal dissolving and drying

After pre-thickening centrifuges, sodium chlorate crystals are either dried or dissolved to the pure water. Drying process consumes energy to generate enough heat to allow all water to be evaporated. Also in dissolving, heat is required to raise solution temperature to allow better solubility. After drying, the concentration of a sodium chlorate crystal is nearly 99,5 % where a small amount of impurities is included (McKetta and Weismantel 1995). Typical analysis report of dry sodium chlorate crystals is shown in table 4.

Table 4. Typical analysis report of dry sodium chlorate crystals (McKetta and Weismantel 1995, p. 180).

Substance	**w-%**
$NaClO_3$	99,5
$NaCl$	0,2
H_2O	0,1
$Na_2Cr_2O_7$	0,0025

3.4 Typical auxiliary chemicals

Typical auxiliary chemicals and consumption of each per tonne of sodium chlorate produced are presented below in table 5.

Table 5. Typical auxiliary chemicals (CEFIC-Sodium Chlorate 2004).

Substance	**Chemical formula**	**Consumption (kg/t_{NaClO3})**
Sodium carbonate	Na_2CO_3	0,04 – 2
Calcium chloride	$CaCl_2$	0 – 0,46
Barium chloride	$BaCl_2$	Sometimes used instead of calcium chloride
Sodium dichromate	Na_2Cr_2O7	0,01 – 0,15
Sodium hydroxide	NaOH	15 – 30
Hydrochloric acid	HCl	15 – 30
Hydrogen peroxide	H_2O_2	1 – 3
Nitrogen gas	N_2	0,4 – 6

Sodium carbonate, calcium chloride and barium salts are used for precipitation of impurities in cell solution. Consumption of these chemicals varies on the filtering method used in the plant.

Sodium dichromate is used to protect electrolysis cell cathodes and to reduce oxygen formation in electrolysis. Sodium chromate helps to maintain the pH value of cell solution in a desired range, which prevents undesired reactions. (European Commission 2007, p. 519.) Use of sodium dichromate is well regulated due to its toxicity to environment and living organisms (Hedenstedt 2017, pp. 10–11). Sodium dichromate is recirculated in the manufacturing process, but tiny amounts of it exit from the process with the product.

Process pH adjusting is usually done with hydrochloric acid and sodium hydroxide. These two chemicals are suitable for sodium chlorate manufacturing process because end products from reactions that adjust pH value are the same chemicals that are already present in cell solution, such as sodium. These two chemicals are used also in the cell acid wash process. This is one of the ways to remove impurities from electrolysis cell surfaces.

Hydrogen peroxide is used to deform sodium hypochlorite**.** Sodium hypochlorite is deformed before to protect various steel parts in later parts of the process. (Kivistö 2018.)

4 ENERGY BALANCE OF SODIUM CHLORATE PROCESS

The major part of the energy consumption in sodium chlorate process is consumed in electrolysis. Electrolysis uses only electricity and produces heat which can be utilized in other parts in the process. Typically, electricity consumption of the manufacturing process is divided into two parts, which are consumption of electrolysis and auxiliary equipment. Most of heat energy used in the process is used to evaporate water in crystallization. In addition, lesser amounts of heat is also used to keep sodium chlorate solution hot enough to prevent unwanted crystallization in the circulation and storage vessels.

4.1 Energy consumption of electrolysis

Majority of electric energy is consumed to the break ionic bind in sodium chloride. This requires a lot of electrical energy as previously mentioned. Electricity consumption of any electrolysis process can be calculated with equation (24) below.

$$P = \frac{QV}{t} \tag{24}$$

where	P is electric energy used per time unit	[W]
	Q is amount of electric charge	[C]
	V is electric potential	[V]
	t is time of reaction	[s]

Electrical charge required to create unit mass of desired chemical with electrolysis can be obtained from Faraday’s Law, equation (25).

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right) \tag{25}$$

$$Q = \frac{mzF}{M} \tag{26}$$

where	m is mass of product	[kg]
	z is the number of electrons used per chlorate ion	[-]
	F is Faradays constant (=96500 C/mol)	[C/mol]
	M is molar mass of sodium chlorate	[mol/kg]

Now one can calculate the amount of energy needed to produce an unit mass of sodium chlorate by combining equations (24) and (26) to form equation (27).

$$P = \frac{mzFV}{Mt} \tag{27}$$

Equation (27) gives the theoretical amount of electrical energy needed to produce a unit mass of sodium chlorate. In the real-world applications, this energy is vastly different due to various side reactions that occur in electrolysis. To compensate that a current efficiency can be added to equation (27) to make it more usable in real-world calculations. Current efficiency can be obtained from experimental tests and normally ranges between 92 to 95 percent depending on cell design. (Hedenstedt 2017, p. 8.) Equation with current efficiency is represented in equation (28).

$$P = \frac{mzFV}{Mt\varepsilon} \tag{28}$$

where ε is current efficiency [-]

Current efficiency can also be calculated from a substance balance. However, this method requires accurate substance balance to acquire reliable results, which is challenging in industrial scale applications.

Now, the theoretical minimum specific energy consumption can be calculated. This can be done by assuming that no side reactions occur (ε = 1) and calculating the lowest cell voltage required to produce sodium chlorate. This voltage is also known as thermoneutral voltage E_c^0. Thermoneutral voltage of sodium chlorate or any other substance can be calculated with equation (29), which is presented below. (Hedenstedt 2017, p. 8.).

$$E_c^0 = \frac{\Delta_r G^0}{nF} \approx 1{,}68\ \mathrm{V} \tag{29}$$

where	E_c^0 is thermoneutral voltage	[V]
	$\Delta_r G^0$ is the difference of Gibb’s free energy	[kJ/mol]

Therefore, minimum energy consumption for generating one tonne of sodium chlorate can be obtained by using thermoneutral voltage as electrical potential in equation (27) to form equation (30). Furthermore, from this equation the specific energy consumption of sodium chlorate electrolysis calculated, which is shown in equation (31). Equation (30) can be used to calculate amount of generated sodium as function of electrolysis current like shown in equation (32).

$$\mathrm{P} = \frac{mzFE_c^0}{Mt} \tag{30}$$

$$\frac{\mathrm{Pt}}{\mathrm{m}} = \frac{6 \cdot 96485\, C/mol \cdot 1{,}68\, V}{106{,}45\, mol/g} \cdot \frac{10^6}{3600} = 2{,}538 \frac{MWh}{t} \tag{31}$$

$$\mathrm{P} = \frac{mzFE_c^0}{Mt} \Leftrightarrow E_c^0 I = \frac{mzFE_c^0}{Mt} \Leftrightarrow \frac{It}{m} = \frac{ZF}{Mt} \tag{32}$$

$$\Rightarrow \frac{It}{m} = \frac{6 \cdot 96485 \frac{C}{mol}}{106{,}45 \frac{mol}{g}} \cdot \frac{10^3}{3600} = 1510{,}64 \frac{kAh}{t}$$

where	m is mass of sodium chlorate (= 10^6 g $\Rightarrow$ 1 t)	[g]
	z is the number of electrons used per chlorate ion (= 6)	[-]
	F is Faradays constant (=96500 C/mol)	[C/mol]
	M is molar mass of sodium chlorate (= 106,44 g/mol)	[g/mol]
	t is time (=3600 s $\Rightarrow$ 1 h)	[s]
	I is electrolysis current	[A]

Furthermore equation (32) can be used to calculate production rate in industrial applications as a function of electrolysis current, current efficiency and number of sodium chlorate cells. This is presented in equation (33) below.

$$\mathrm{m}_{\mathrm{NaClO3}} = \frac{I n_{cell} \varepsilon}{1511 \left[\frac{kAh}{t}\right]} \tag{33}$$

where	m_{NaClO3} is production rate of sodium chlorate	[t/h]
	I is electrolysis current	[kA]

n_{cell} is number of electrolysis cells [-]
ε is current efficiency [-]

Modern sodium chlorate electrolysis has an operational voltage within the range of 2,85 to 3,30 V and current efficiency in the range of 92 to 95 %. Therefore, specific consumption of modern chlorate electrolysis cell is within the range of 4,5 MWh/t to 5,4 MWh/t. (Hedenstedt 2017, p. 8).

4.2 Crystallization

Crystallization can be assumed to require only heat energy. A small amount of electricity is used for circulating the solution inside crystallizer. In crystallization, the concentration of sodium chlorate in cell solution is increased until it starts to form crystals that can be separated from cell solution. In most cases, concentration is increased by evaporating water in a near vacuum, which allows the use of low temperatures in crystallizator. And furthermore, low temperatures allow the use of secondary heat sources for heating the crystallizator.

The energy required to crystallize sodium chlorate depends heavily on the amount of water need to be evaporated. Evaporation heat of water is 2257 kJ/kg or 40,66 J/mol. The energy needed to vaporize fluid to gas can be calculated with equation (34), which is presented below.

$$E_{vap} = s_w m = s_{mol} n \tag{34}$$

where s_{w} is specific heat of evaporation for specific fluid [kJ/kg]
s_{mol} is molar heat of evaporation for specific fluid [J/mol]
n is molar quantity [mol]

In this case, the ideal amount of water to be evaporated can be obtained from sodium chlorate – sodium chloride – water ternary system chart presented earlier in this thesis in figure 6.

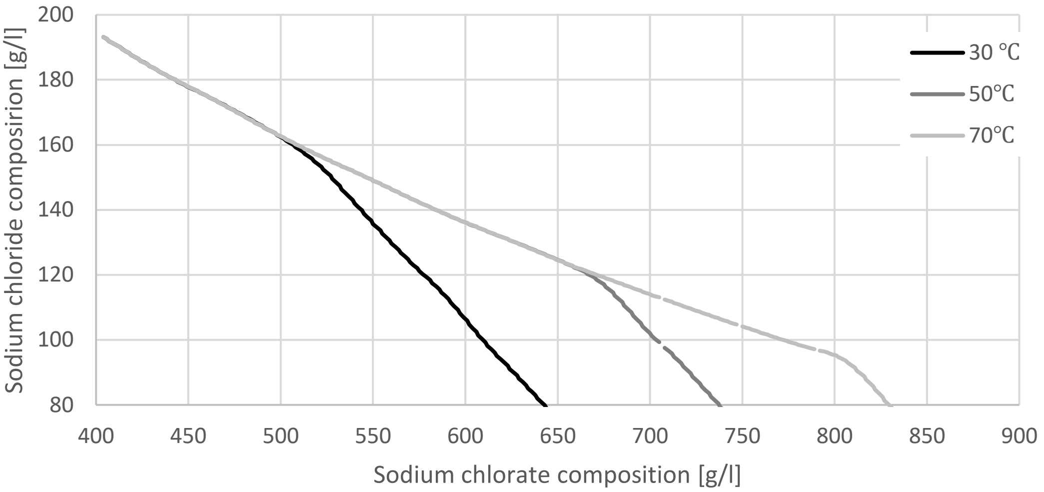


Figure 6. Phase diagram for sodium chlorate – sodium chloride – water ternary system

The temperature of cell solution before crystallization is between 70 to 80 °C and contains approximately 575 g/l of sodium chlorate and 100 g/l of sodium chlorite in industrial applications (Burney 1999, p. 25). If solubility follows the curve in figure 6, specific heat consumption of crystallization can be calculated as a function of incoming cell solution composition and crystallizer temperature.

From data in figure 6, equations (35) and (36) can be formed. These equations present the concentration of sodium chlorate and chloride at a eutonic point as a function of temperature. The eutonic point represents the composition of a solution saturated with respect to both salts (DeVoe 1998).

$$c_{NaClO3,sat} = -0{,}0325T^2 + 10{,}5T + 236{,}33 \tag{35}$$

$$c_{NaCl,sat} = -0{,}0186T^2 - 3{,}42T + 239{,}26 \tag{36}$$

where $m_{\mathrm{NaClO3,sat}}$ is concentration of sodium chlorate in eutonic point [kg/$\mathrm{l_{H2O}}$]
$m_{\mathrm{NaCl,sat}}$ is concentration of sodium chloride in eutonic point [kg/$\mathrm{l_{H2O}}$]
T is temperature [°C]

Furthermore, an equation (37) can be formed from the data of figure 6. This equation represents the saturation line of sodium chlorate in a given temperature in this ternary system.

$$c_{NaClO3} = -1{,}66\left(c_{NaCl} - c_{NaCl,sat}\right) + c_{NaClO3,sat} \tag{37}$$

where c_{NaCl} is concentration of sodium chloride [kg/l_{H2O}]

c_{NaClO3} is concentration of sodium chlorate [kg/l_{H2O}]

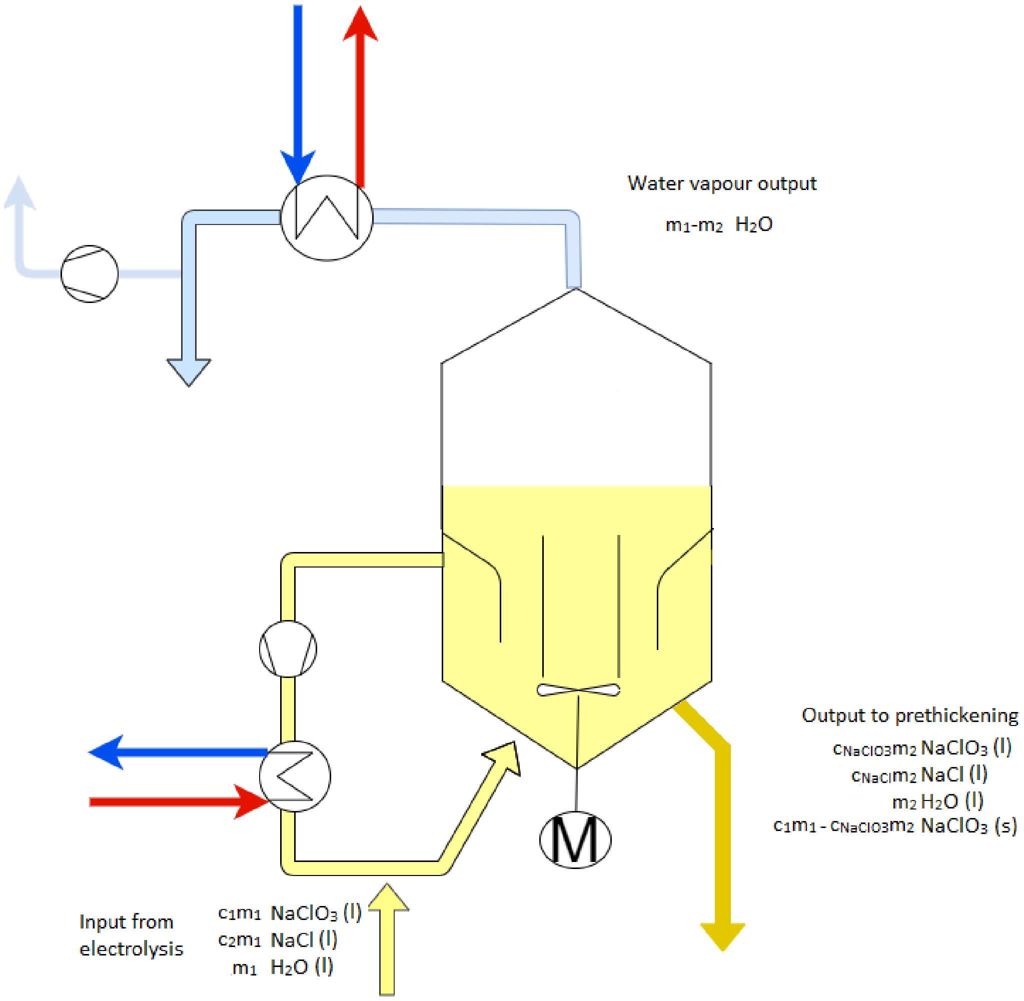


Figure 9. Crystallization unit mass balance.

Equations (35) and (36) and crystallization mass balance can now be used to determine the amount of water that is required to evaporate during crystallization. Crystallization unit mass balance is illustrated in figure 9.

Concentrations of the outlet flow can be obtained with equations (38) and (39) for idealized case. In industrial scale applications, a safety margin is present in sodium chloride concentration. Equation (37) can be used to determine values for outlet concentrations.

To maintain the mass balance, the ratio between incoming and outgoing sodium chloride flows must be equal, which allows forming equation (38) and furthermore equation (39), which presents the amount of generated water vapor in the crystallization process.

$$c_2\, m_1 = c_{NaCl} m_2 \Rightarrow m_2 = \frac{c_2 m_1}{c_{NaCl}} \tag{38}$$

$$m_{H2O,vapor} = m_1 - \frac{c_2 m_1}{c_{NaCl}} \tag{39}$$

where	c_2 is concentration sodium chloride at inlet	[kg/l_{H2O}]
	m_1 is inlet mass flow	[kg/s]
	m_2 is outlet mass flow	[kg/s]
	$m_{H2O,vapor}$ is mass flow of water vapor form system	[kg/s]

For inlet flow, previously introduced average concentration values can be used to calculate theoretical energy consumption in a average crystallization process as function of crystallizator outlet temperature. This is presented in figure 10. Part of the heat requirement is obtained from enthalpy flow of cell solution into crystallization. In industrial scale processes, composition of incoming fluid is also determined partly by electrolysis temperature, but more by sodium chloride concentration. This is kept at certain level to prevent issues in electrolysis cells caused by too low sodium chloride concentration.

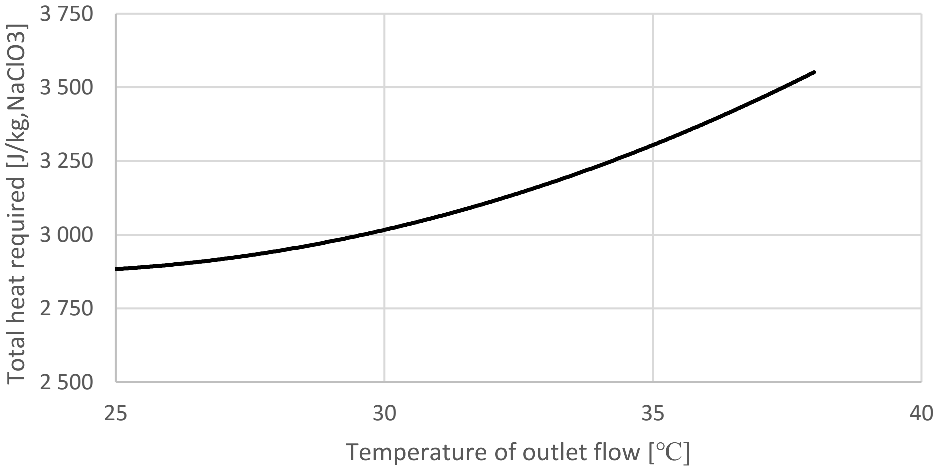


Figure 10. Specific heat consumption of crystallization

The water vapor, which is evaporated from cell solution, is condensed and then returned to process. The condensation requires cooling to function. Amount of cooling is reverse to amount of heating energy required to evaporate water.

In industrial plants, the crystallization process can be done in two phases separated by different pressure levels, for example, at 100 mbar(abs) and 30 mbar(abs). The crystallization reaction itself is intended to happen in the final phase of the crystallization process and the first phase only evaporates excess water with none to very little crystallization. Therefore, the first phase with higher pressure level is called vaporization.

When using two different crystallizers (vaporizer and crystallizer) at different pressure levels, the maximum temperature of cooling water can be higher, with same evaporation capacity. This can be verified, by returning to two example values mentioned earlier. Assuming that vaporizer works in pressure of 100 mbar(abs) and crystallizator at 30 mbar(abs), the temperature of cell solution follows curve presented in figure 11.

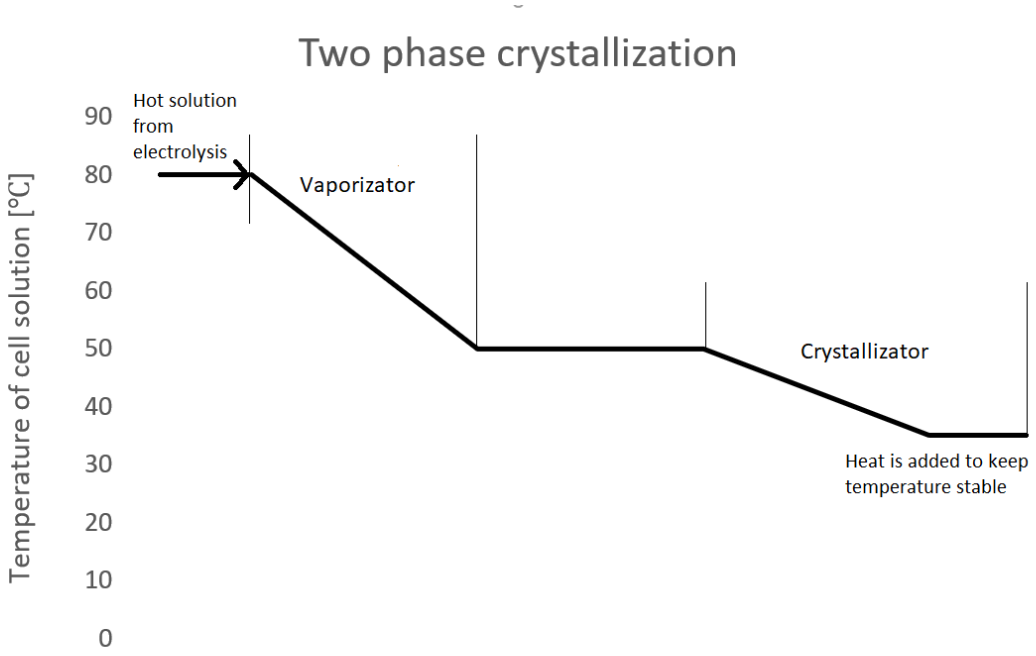


Figure 11. Two-phase crystallization process

Water vaporization pressure as a function of temperature is presented in figure 12. Values for curve are obtained from August-Roche-Magnus approximation, which is presented in equation (40). From this figure can be seen, the water evaporation temperature as a function of pressure and vice versa. From this figure temperature levels for figure 11 or any other crystallization process can be obtained.

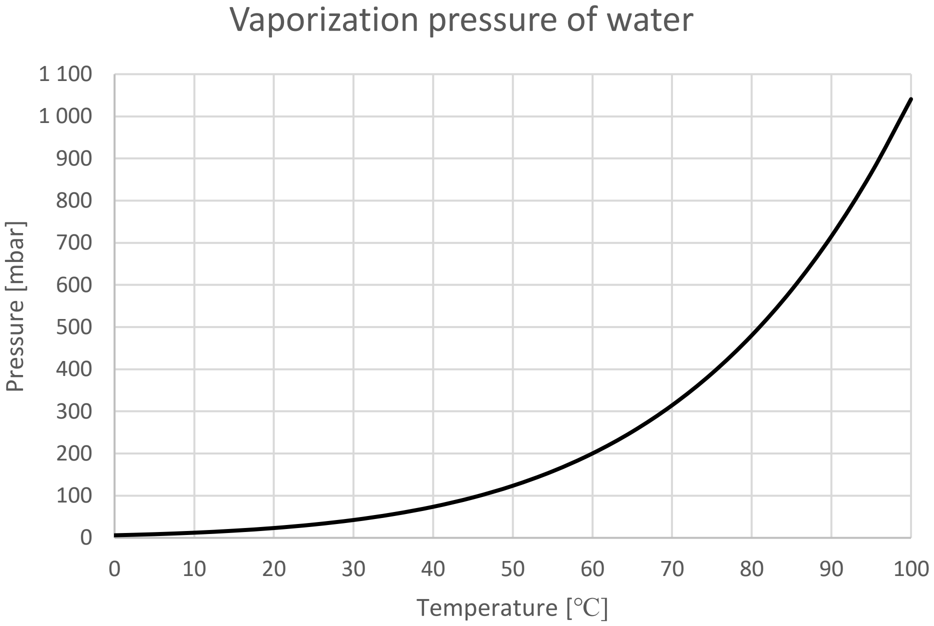


Figure 12. Vaporization pressure of water

$$p_{vap} = 6{,}1094 \cdot \mathrm{e}^{\frac{17{,}625\mathrm{T}}{\mathrm{T}+243{,}04}} \tag{40}$$

where	p_{vap} is vaporization pressure of water	[mbar]
	T is temperature	[℃]

4.3 Energy balance

Electrolysis and crystallization consume major part of process energy consumption. The rest of energy consumption is divided among different auxiliary processes and equipment. No research is done within this thesis to precisely determine consumption of these. Consumption of these equipment is only a few percents of total electricity consumption (European Commission 2007, p. 518). Now simplified energy balance of sodium chlorate process can be made. This is represented in figure 13.

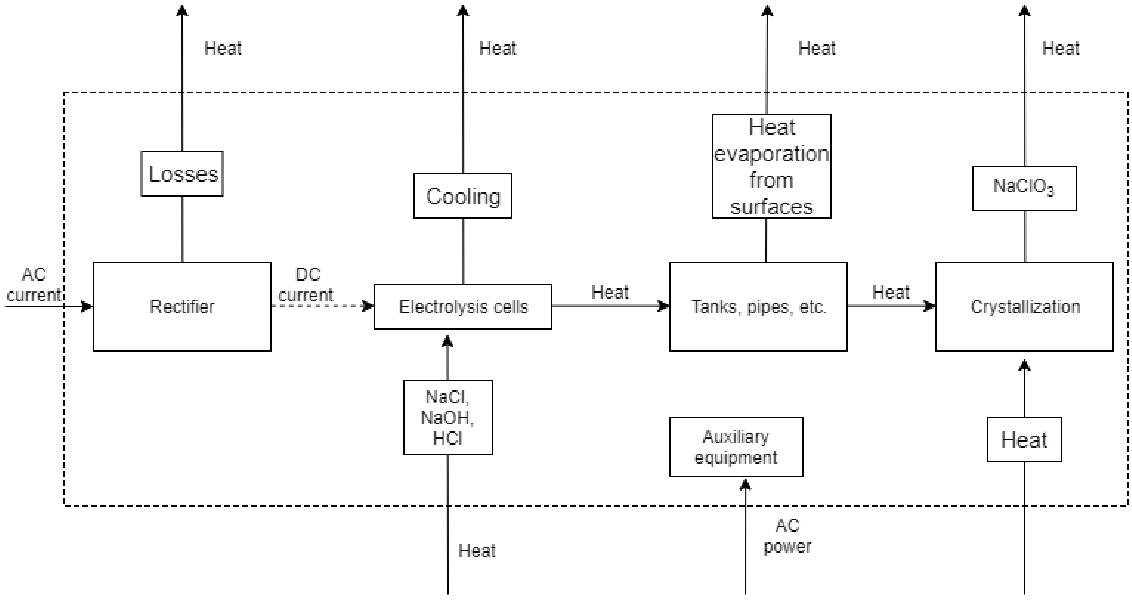


Figure 13. Simplified energy balance of sodium chlorate manufacturing process

In simplified energy balance, energy flows into the systems are enthalpy flow of sodium chloride solution and other chemicals, electric energy to rectifier(s), heat to crystallization and electricity to auxiliary equipment. Energy flows from system are enthalpy of sodium chlorate solution, excess heat from electrolysis and heat generated from losses of AC/DC conversion and evaporated heat from different surfaces of process equipment.

The temperature of cooling water from electrolysis can be up to 80 °C, which is more than enough to evaporate water at near vacuum pressure. This allows the use of electrolysis cooling water as a heat source in crystallization. If heat transfer units have enough capacity, cooling water from electrolysis can even cover all the heating in crystallization. This decreases the specific external energy consumption of manufacturing process. The excess energy of electrolysis cooling water can also be utilized in different applications, for example in district heating.

5 JOUTSENO SITE

Figure 14. Joutseno site. (Kemira 2017)

Joutseno site consists one chlor-alkali, one alkyl ketene dimer and one chlorate plant. The site also includes a power plant with two different hydrogen boilers and one back pressure turbine. In figure 14, sodium chlorate production lines are visible in front, two big white buildings, a hydrogen powerplant in the middle, smaller blue building, and in the back the chlor-alkali plant. The first buildings were built in around 1975 to the site and since then new production lines and capacity increments have been made to site.

5.1 Chlorate plant

The chlorate plant in Joutseno consists of three separate production lines: N1, N2 and N3. Newest of these lines, N3, is in a separated building, therefore it is separated totally from production lines N1 and N2. Older production lines N1 and N2, are constructed in the same building and they share many process equipment.

The main products of chlorate plant are sodium chlorate as solid and as an aqueous solution. Also, a significant amount of hydrogen is generated during the manufacturing process as side-product, which is consumed in chlor-alkali plant and in boilers on site.

5.2 Chlor-alkali plant

The chlor-alkali plant was the second production line of Joutseno site. There has been several modernizations and process modifications. The main products of the chlor-alkali plant are sodium hydroxide, hydrochloric acid and sodium hypochlorite.

Sodium hydroxide is a product of electrolysis in the chlor-alkali plant. However, the electrolysis process is different compared to the chlorate electrolysis. In chlor-alkali plant cells have a special membrane, which keeps hydroxide ion and chlorine separated. Electrolysis reaction is presented in the equation (41) below. Chlorine from electrolysis is used to create hydrochloric acid and sodium hypochlorite. The main use of sodium hydroxide produced in Joutseno is in pulp process in cellulose separation.

$$\mathrm{NaCl\ (aq) + H_2O(aq) \rightarrow\ NaOH\ (aq) + \frac{1}{2}Cl_2(g) + \frac{1}{2}H_2(g)} \tag{41}$$

Sodium hypochlorite is manufactured by chlorinating sodium hydroxide. This reaction is presented in reaction equation (42) below. Manufacturing of sodium hypochlorite is well suited to the Joutseno site, because all the chemicals, which are used to produce it, are made locally on site. Sodium hypochlorite can be used as a disinfectant or as a household bleaching agent.

$$\mathrm{Cl_2(g) + 2\ NaOH\ (aq) \rightarrow NaCl\ (aq) + NaClO(aq) + H_2O(aq)} \tag{42}$$

Hydrochloric acid is created in hydrochloric acid burners. These burners burn hydrogen in chlorine gas, with no oxygen present. The product of this reaction is hydrogen chloride gas. This reaction is presented below in reaction (43). Hydrogen chloride is dissolved in water to create hydrochloric acid. Hydrochloric acid is used in various applications, for example, to make steel, as an auxiliary chemical in other processes and in many other applications (American Chemistry Council, 2003).

$$\mathrm{H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g)} \tag{43}$$

5.3 Hydrogen power plants

There is one hydrogen power plant in Joutseno site, which contains two boiler units. The bigger, HK21, is top fired furnace which can produce up to 18,5 MW heat energy. It also features a 4 MW back pressure turbine, which can be bypassed in case of a steam shortage. The smaller boiler, HK20, is a fire-tube boiler and can also be fired with oil in case of a hydrogen shortage. Maximum heat from the smaller boiler is 10 MW. Hydrogen used in boilers is produced exclusively in sodium chlorate plants.

These boilers can utilize roughly 60 percent of hydrogen of sodium chlorate lines at full production speed. An increase of power generation capacity could be one way to increase hydrogen usage and therefore increase the overall efficiency of the entire site.

5.4 Alkyl ketene dimer plant

Alkyl ketene dimer or AKD plant was moved to Joutseno in 2013. In Joutseno site, AKD plant is located within the chlor-alkali plant. The most generic form of these organic compounds is a waxy solid particle as part of the solution that contains a stabilizer. It is most commonly used in the sizing of paper and hydrophobization of cellulose fibers. In Joutseno, AKD is made in the non-continuous process.

Solid raw materials are heated in the reactor. After heating, additives are added to the reactor to stabilize and to adjust pH value of the solution. When the solution leaves reactor it is emulsified and cooled. Cooling of the solution at this point is considered as a crucial point, which determines the product quality. The most relevant part of the AKD process for this thesis is heating, which is done with steam and therefore has an effect on the site steam balance.

6 STEAM AND HYDROGEN BALANCES

Steam is produced on the Joutseno site in two different boilers, HK20 & HK21. Steam is used in all plants on the Joutseno site. The steam production and major steam applications are shown in figure 15 below.

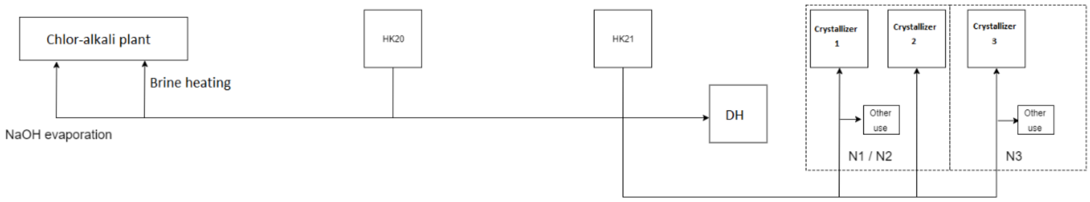


Figure 15. Joutseno site steam consumption map.

Steam network on Joutseno site contains two different pressure levels, 8 bar(g) (high-pressure) and 3 bar(g) (low-pressure). Most applications use low-pressure steam. High-pressure steam is used mostly in vacuum creating units.

Steam consumption can be divided between chlor-alkali plant applications and sodium chlorate applications. Steam usage of AKD plant is irregular. Steam is used in reactor heating and in cases where pipelines or other process equipment must be heated for cleaning.

6.1 Steam production

All site’s heat energy is produced from hydrogen during normal operational conditions. Theoretical heat energy from burning hydrogen is 141,80MJ/kg (HHV). Hydrogen consumption of heat generation can be obtained from equation (44) below and it is presented in the equation (44).

$$P_{heat} = q_{m,H^2} H_{H^2} \eta_{th} \tag{44}$$

$$q_{m,H^2} = \frac{P_{heat}}{H_{H^2}} \tag{45}$$

where		
	P_{heat} is generated heat from combustion	[MW]
	$q_{\mathrm{m,H}^2}$ is mass flow of hydrogen to boiler	[kg/s]
	H_{H^2} is higher heat value of hydrogen	[MJ/kg]
	η_{th} is thermal efficiency of boiler	[-]

Both hydrogen boilers share the same principle to calculate heat generation, but boiler efficiencies vary between two units. In Joutseno site steam is produced according to the consumption and in normal operating conditions, there is hydrogen excess.

6.2 Chlor-alkali plant steam usage

The chlor-alkali plant uses steam to heat up sodium chloride solution and to evaporate water from sodium hydroxide solution to raise its concentration. Steam consumption of sodium chloride solution heating is a function of outdoor temperature and electrolysis current. Steam consumption of evaporation unit in sodium hydroxide evaporation is determined by the mass flow of sodium hydroxide to evaporation.

The energy consumption per time unit of sodium chloride solution heating can be calculated with equation (46) below. The mass flow of sodium chloride solution is adjusted by electrolysis current and temperature target after heat exchanger is determined by outlet temperature of sodium hydroxide solution after electrolysis cells. A temperature rise of sodium chloride solution in electrolysis cells is determined by electrolysis current.

$$P_{brine} = q_{m,brine} \Delta T c_{p,brine} \tag{46}$$

where		
	P_{brine} is heat consumption of sodium chloride heating	[kW]
	$q_{\mathrm{m,brine}}$ is mass flow through the heat exchanger	[kg/s]
	ΔT is temperature difference over heat exchanger	[°C]
	$c_{\mathrm{p,brine}}$ is specific heat capacity of sodium chloride solution (=3,25 kJ/kgK)	

In chlor-alkali plant, sodium chloride solution is in the closed circuit and therefore any energy losses during the circulation must be compensated with heating. Major losses happen in the facility where more sodium chloride is added to the circulation and when chlorine gas is separated from sodium chloride solution after electrolysis cells.

The other significant application of chlor-alkali plant that uses steam is evaporation of excess water in 50 % sodium hydroxide manufacturing. In this process concentration of sodium hydroxide solution is increased from 33 % to 50 %. Energy consumption of evaporation can be calculated with equation (47).

$$E_{NaOH} = m_{H2O} s_w \tag{47}$$

where E_{NaOH} is energy that is required in 50 % sodium hydroxide process [kW]

m_{H2O} is mass of water to be evaporated [kg/s]

s_{w} is enthalpy of vaporization of water [kJ/kg]

In the chlor-alkali plant, evaporation is done in a near vacuum, this allows the use of heat of sodium hydroxide to evaporate water. In addition of heat flow of sodium hydroxide, steam is required. Steam consumption can be determined with the energy balance of evaporation system, which is presented in figure 16.

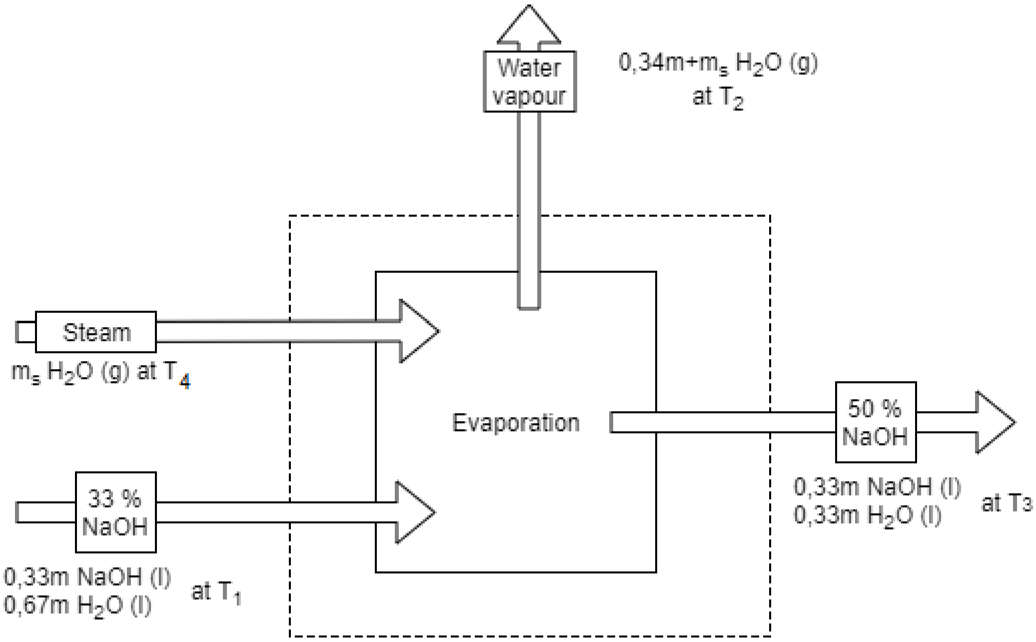


Figure 16. The energy balance of evaporation in 50 % sodium hydroxide manufacturing process.

Steam consumption can be calculated with equation (48) presented below if temperatures before and after the evaporation process are known. This equation can be simplified if reference state is set to be outlet state of outflow of sodium hydroxide solution. Outflow water vapor can be also considered to be fully saturated. Superheating of the water vapor is very unlike due to a strong vacuum in the water-steam separators.

$$m_S \Delta h_s + m \Delta h_{33\%} = \frac{2}{3} m \Delta h_{50\%} + (\frac{1}{3} m + m_s) \Delta h_{H2O} \tag{48}$$

where	m_s is mass flow of steam into system	[kg/s]
	Δh_s is enthalpy difference of incoming steam to the system	[kJ/kg]
	m is mass flow of incoming solution to the system	[kg/s]
	$\Delta h_{33\%}$ is enthalpy difference of incoming solution to reference state	[kJ/kg]
	$\Delta h_{50\%}$ is enthalpy difference of outgoing solution to reference state	[kJ/kg]
	Δh_{H2O} is enthalpy difference of water vapor to reference state	[kJ/kg]

Enthalpy difference of 33 % sodium hydroxide can be obtained with the assumption that pressure of incoming 33 % solution is the same as the pressure of outgoing 50 % solution. The error caused by this simplification is rather small. For example, for water, the specific enthalpy at 25 °C and 1 bar(a) is 104,9 kJ/kg and at the same temperature, but at 20 bar(a), the specific enthalpy is 106,7 kJ/kg. In evaporation process of sodium hydroxide, the pressure difference of incoming and outgoing sodium hydroxide should not be more than a few bars, so enthalpy difference caused by pressure difference is even smaller than in example with water.

Amount of steam that is used in preheating can be obtained from the energy balance of preheater. In preheater 33 % sodium hydroxide solution is heated and temperature difference can be obtained from measurements. Steam from heater one can be assumed to be fully saturated before preheater and to condensate inside preheater.

6.3 Sodium chlorate production line steam consumption

The main use in sodium chlorate plant for steam is crystallization. The theoretical heat consumption for crystallization was presented in chapter 4. Based on calculations of chapter 4, steam consumption rate can be calculated with equation (49). This equation is formed in a similar manner like equation (48) was for chlor-alkali plant's steam consumption of sodium hydroxide evaporation process. However, there are heat recovery systems, which reduce the consumption and therefore are included in this equation.

$$m_S = \frac{Q - m_{cs}\Delta h_{cs} - Q_{HR}}{s_w} \tag{49}$$

where	m_s is steam consumption of crystallization	[kg/s]
	Q is heat consumption of crystallization	[kW]
	m_{cs} is mass flow of cell solution to crystallization	[kg/s]
	Δh_{cs} is specific enthalpy difference of cell solution	[kJ/kg]
	Q_{HR} is quantity of heat recovery	[kW]
	s_w is enthalpy of vaporization of water	[kJ/kg]

In Joutseno, production lines N1 and N2 share a crystallization unit that contains one vaporizer and two crystallizators. In the newest production line N3, there is vaporizer and one crystallizator.

Steam consumption in chlorate process is depended on the workload of the crystallization. A load of crystallization can be handled as a separate unit from electrolysis. Therefore, a steam consumption is not directly a function of electrolysis current, but there is a correlation between steam consumption and sodium chlorate production rate in electrolysis cells.

In short term, some variation is acceptable between crystallization rate and sodium chlorate production rate, mainly because Joutseno site's chlorate lines have decent cell solution storage capabilities. However, in long-term, sodium chlorate production in electrolysis cells should be equal to sodium chlorate output from the crystallizer.

7 HYDROGEN BALANCE

Hydrogen is side-product on both chlor-alkali and sodium chlorate manufacturing processes. It is used to create hydrochloric acid in chlor-alkali plant and to generate energy in boilers on the site. Therefore, a balance between hydrogen production and consumption is critical to maintain stable production on all production lines on the site. Hydrogen network of Joutseno site is presented in figure 17 below.

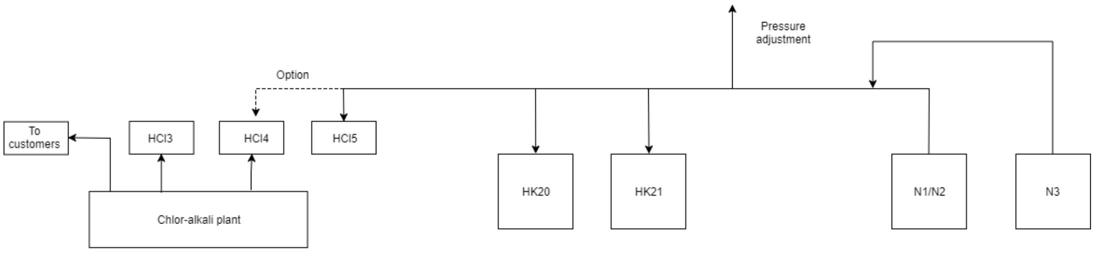


Figure 17. Map of hydrogen consumption application in the Joutseno site

From figure 17 can be seen that there are two separate hydrogen networks on Joutseno site. One is specific to chlor-alkali plant only and another one supplies one hydrochloric acid burner and both steam boilers. In general, there is hydrogen excess in network, but in situations in which sodium chlorate production lines are running with low electrolysis current, sufficiency of hydrogen can become a challenge.

7.1 Hydrogen production

Electrolysis process of sodium chlorate was presented in chapter 3 and the electrolysis reaction of the chlor-alkali plant was also presented in chapter 5. From those reaction, equations can be seen that hydrogen generation rate is a function of electrolysis current. In this thesis, study is taken only in sodium chlorate hydrogen production because the chlor-alkali plant has a separate hydrogen network. Hydrogen production speed can be obtained from sodium chlorate electrolysis reaction, which is shown in reaction equation (50) below.

$$\mathrm{NaCl\ (aq)} + 3\ \mathrm{H_2O(aq)} \rightarrow\ \mathrm{NaClO_3} + 3\ \mathrm{H_2(g)} \tag{50}$$

From this reaction equation, it can be seen that for one molecule of sodium chlorate, three molecules of hydrogen gas are produced. From molar masses of these substances, a relation between the production speed of sodium chlorate and hydrogen can be found. For each kilogram of sodium chlorate, 0,0568 kilograms of hydrogen gas is produced. This rate can be combined with the rate of chlorate production as a function of the current of electrolysis (equation 33) to determine a relation between current and hydrogen production rate.

In equation (51) is presented hydrogen production rate as a function of electrolysis current of chlorate production lines N1, N2 and N3. It is noteworthy that this equation does not present theoretically accurate amount of hydrogen production rate, but it is a sufficient estimation. This equation does not include any losses as it assumes that only reaction in electrolysis is the one presented in equation (50).

$$m_{H2} = 0{,}0568\left(\frac{I_{N1}}{1{,}51}\varepsilon_{N1}n_{N1} + \frac{I_{N2}}{1{,}51}\varepsilon_{N2}n_{N2} + \frac{I_{N3}}{1{,}51}\varepsilon_{N3}n_{N3}\right) \tag{51}$$

where		
	m_{H2} is hydrogen production rate	[kg/h]
	ε_{Nx} is current efficiency of chlorate line x	[-]
	I_{Nx} is electrical current of chlorate line x	[kA]
	n_{Nx} is number of cells in chlorate line x	[-]

7.2 Hydrogen applications

Main uses for hydrogen on the site are hydrochloric acid production and energy production. In addition to these, some of the hydrogen produced in the chlor-alkali plant is sold directly to the customers. Hydrogen consumption in the steam generation was presented earlier in equation (45).

Hydrogen consumption of hydrochloric acid burner can be obtained from the reaction equation (52). This represents the formation of hydrochloric acid in a burner. From this reaction equation, the molar ratio between inlet hydrogen gas and outlet hydrochloric acid can be obtained. It is noteworthy, that inside hydrochloric burner is typically hydrogen excess. Therefore, hydrogen consumption is little higher than what is obtainable from reaction equation (52). This can be compensated with multiplier λ. A corrected version of hydrogen consumption of hydrochloric burner is presented in the equation (54).

$$\mathrm{H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g)} \tag{52}$$

$$\lambda\mathrm{H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g) + (1 - \lambda)\ H_2\ (g)} \tag{53}$$

$$m_{H2} = m_{HCl}\frac{2}{\lambda}\frac{M_{H2}}{M_{HCl}} \tag{54}$$

where	m_{H2} is hydrogen consumption rate in HCl burner	[kg/h]
	m_{H2} is HCl production rate in HCl burner	[kg/h]
	λ is chlorine-hydrogen equivalence ratio	[-]
	M_{H2} is molar mass of hydrogen	[kg/mol]
	M_{H2} is molar mass of hydrochloric acid	[kg/mol]

In the chlor-alkali plant, there are two hydrogen compressors, which are used to compress hydrogen to transportation vessels. Hydrogen consumption of these is not relevant to this thesis, because they are not located on the same hydrogen network with sodium chlorate plants.

8 SITE ENERGY BALANCE

According to the Euro Chlor (2017), installed chlorine production capacity in Joutseno chlor-alkali plant is 75 kilotonnes of chlorine annually. With average energy consumption of membrane cell technique, which is used in Joutseno, a maximum annual consumption can be roughly estimated to be 200 GWh (Brinkmann et al. 2014, p. 67).

A similar calculation can be done for sodium chlorate plant, although there is no accurate public data for annual production rate. Production rate is assumed to be the maximum rate, which was estimated during the expansion process of sodium chlorate production capacity (Kaakkois-Suomen ELY-keskus 2016). For energy consumption, an average value for modern chlorate electrolysis process, presented earlier in this thesis, can be used. Therefore, the maximum energy consumption of sodium chlorate lines is roughly 850 GWh annually.

These electrolysis processes combined form a majority of total electricity consumption. Although it is noteworthy that calculated values above are estimations of theoretical maximum consumption rates, which contain many estimations and are presented for illustrative purposes only. Even though, the value clearly represents the energy intensity of the site.

8.1 Energy production

Like earlier mentioned, there are two steam boilers on the Joutseno site and turbine attached to the steam network. The current maximum power outlet from the turbine is 4 MW. In an optimal scenario, the turbine produces power at maximum rate constantly. According to the steam and hydrogen balance calculations, this should be possible if at least two sodium chlorate lines are producing hydrogen at a moderate rate.

In addition to the boiler units, there are several heat regeneration cycles on the site. Most significant of these are heat regeneration from cell solution of chlorate production lines N1 and N3 and heat regeneration from cell circulation in the chlor-alkali plant.

8.2 Energy consumption

8.2.1 Electrical energy

Like mentioned earlier, the electrolysis process consumes the majority of total electricity consumption. There are also many pumps and fans that consume electricity. Consumption of this equipment is often referred as auxiliary equipment power, which is specific for each production line.

For sodium chlorate process, a typical range for auxiliary equipment electricity consumption is from 100 to 500 kWh per tonne of sodium chlorate produced (European Commission 2007, p. 518) and for a chlor-alkali process from 60 to 600 kWh per tonne of chlorine produced (Brinkmann et al. 2014, p. 71). Auxiliary equipment electrical consumption can be expected to be relatively constant and can be estimated if annual production rate of the plant is known.

The only major loss in electrical energy is AC/DC conversion loss in transformer rectifiers. The efficiency of large current transformer rectifier varies within the range of 94 to 98 depending on type, voltage and load. (Rodriguez et al. 2005). As sodium chlorate and chlor-alkali electrolysis have similar operational voltages, efficiencies of transformer rectifiers of both production plants are within the range presented.

8.2.2 Heat energy

Heat is used in many applications on the site. On the chlor-alkali plant, consumption is focused on two major applications, which are sodium chloride heating and evaporation in the manufacturing process of 50 % sodium hydroxide. Heat is recovered from the electrolyte and is used to heat loading bays and sodium chloride, where it directly decreases steam consumption. In addition, some areas require heating during winter months, but this energy consumption is neglected in this thesis because of little and irregular consumption. It is also noteworthy that most of heating required for many parts of the plant is generated by process equipment. Insulating hot surfaces to improve the efficiency of the manufacturing process and replace heating with more modern equipment could be topic for future research. The AKD plant uses steam to heat process solutions.

On the sodium chlorate production lines, the heat consumption focuses on crystallization unit and on dissolving and drying of sodium chlorate. In the sodium chlorate plant, there are several heat recovery systems. In the N1, there is one district heating heat exchanger attached to cooling water circulation. The cooling water of cell solution of N2 can be used to heat N1/N2 crystallizator and heat from N3 cooling circuit is used in multiple applications, for example in crystallization. These reduce steam consumption significantly.

There is one district heating heat exchanger attached directly to high-pressure steam network (KL1) and another one in one of the sodium chlorate lines (KL2). District heating is the only outgoing energy flow from the site (enthalpy flows of products can be neglected). There are no direct inputs for heat to the site and therefore all heat required by the process is produced within the site.

There are good measurements about of district heating power because it is a trade item. Heat flow to district heating is depended on the usage of the district heating. The stable operation of processes is prioritized over steam input to the district heating. The heat exchanger of the sodium chlorate plant works as a primary source for district heating, and one on the steam network works only if necessary.

8.3 Energy and heat balance

When all applications that produce or consume energy are separated, energy balance for the whole site can be formed. The energy balance is presented in the equation (55).

$$E_{in} + E_{gen} = E_{cons} + E_{out} \tag{55}$$

where	E_{in} is input energy into the site	[MJ]
	E_{gen} is amount of energy production on site	[MJ]
	E_{cons} is energy consumption on site	[MJ]
	E_{out} is outlet energy from the site	[MJ]

Energy flows can be separated into electrical and heat energy. This is essential to form a more specific energy balance.

$$E_{el,in} + E_{el,turb} + Q_{gen} = E_{el,cons} + Q_{cons} + Q_{DH} \tag{56}$$

where $E_{\mathrm{el,in}}$ is electricity input to the site [MJ]
$E_{\mathrm{el,turb}}$ is electricity production of the turbine [MJ]
Q_{gen} is generated heat in the steam boilers [MJ]
$E_{\mathrm{el,cons}}$ is electricity consumption on the site [MJ]
Q_{cons} is heat consumption on the site [MJ]
Q_{DH} is heat outlet from the site to district heating [MJ]

The heat and electrical energy balances can be furthermore separated from the energy balance presented in equation (56). Heat balance is represented in equation (57). The remaining part of equation (57) forms the energy balance of electrical energy, equation (58).

$$Q_{gen} = Q_{cons} + Q_{DH} \tag{57}$$

$$E_{el,in} + E_{el,turb} = E_{el,cons} \tag{58}$$

8.3.1 **Heat balance**

The heat is transported in site either with steam or hot water. Only relevant applications that use a significant amount of hot water are the crystallizator of N3, the district heat exchanger in N1 and the sodium chloride heat exchanger in the chlor-alkali plant. In case of hot water shortage, all these can be heated with steam. The heat balance is presented in equation (59).

$$\begin{aligned} Q_{gen} + Q_{rec,N1} + Q_{rec,N3} + {} & = Q_{cons,N1/N2} + Q_{cons,N3} + Q_{DH} + \\ \mathrm{Q_{rec,NaOH}} \quad & \quad\; Q_{brine} + \; Q_{NaOH} \end{aligned} \tag{59}$$

Heat production (Q_{gen}) is a sum of heat output of two boilers. Smaller boiler unit runs at constant heat outlet, which is manually regulated, and the larger boiler unit is automatically adjusted so that pressure of the steam network stays constant. In normal operational conditions, both steam boilers run on hydrogen.

Currently, there is no balancing automation between the two boilers. The way the load is shared between units depends on the operator. More research should be done to find the most efficient way to generate energy with current equipment. The newer boiler, HK21 has a turbine, which in optimal scenarios would run constantly at maximum load to reduce hydrogen excess.

The recovery heat from N1 and N3 production lines and the chlor-alkali plant can be calculated if temperature difference and mass flow (or volume flow) of heat exchanger water side are known at certain points of the process. For heat recovery of the N1 production line, quantity can be calculated from district heating circuit heat exchanger. For N3, the calculations can be done with data from cell solution heat exchanger. For the chlor-alkali plant, there is also enough measurements available.

9 ENERGY EFFICIENCY ON JOUTSENO SITE

In this thesis, research is done to find out if the site efficiency can be increased with software changes and better monitoring. The major increase in the efficiency could be found from optimization software but first proper data must be collected. Currently, this data is collected manually to different spreadsheets. To automatize this process, software changes are proposed that will make important parameters and the site balances visible to the operators in real-time.

In this chapter, requirements for the monitoring and simulation software are presented. This chapter also includes parameters that can be used to monitor the site efficiency and the plant-specific efficiencies. As a part of this thesis, interviews and survey were made to figure how operators and shift supervisors understand energy efficiency.

9.1 Survey and interview results

The questionnaire used in the survey is presented in appendix I. Response rate of the survey was 35 %. Consequently, results are statistically non-significant and cannot be used to represent the whole group. Therefore, no accurate conclusion cannot be made from these results, the survey is neglected from this thesis.

Interviews were much more successful, with the participation rate of over 90 %. The clear majority of the shift supervisors and shift workers gave interviews. Therefore, results can be considered statistically significant. Along with the interviews many innovative ideas came out and they are presented later in this chapter. The personnel were interested in energy efficiency and a majority had noticed the increase in the relevancy in energy efficiency in the past few years.

The Chlor-alkali electrolysis is not able to withstand fluctuation of electrolysis current easily as sodium chlorate electrolysis. Therefore, the electrolysis current is held constant for extended periods and operators has fewer clear ways to affect overall efficiency. This is reflected in how much personnel of the chlor-alkali plant thinks energy efficiency affects their daily work routines. Personnel of the sodium chlorate plant think that efficiency has a significant role in their work routines. However, this does not reflect in knowledge and interest in efficiency between personnel of the chlor-alkali and sodium chlorate plants.

There was some difference among shift workers understood energy efficiency. In shifts were energy efficiency was best understood, at least one person mentioned that personal interest and personality drive towards thinking of plant efficiency. In addition, they regularly have unofficial conversations where they share their ideas and thoughts with supervisor and co-workers. Conversations like this should be encouraged as there seems to be a correlation between energy awareness and these conversions.

Shift supervisors have at least indirect correlation in their shifts' ideology in energy efficiency. This could be noticed by comparing the interviews of shift supervisor with his or her subordinates. They all had similar thoughts about what has the most effect in efficiency and how it could be improved.

When asked how shift supervisors and operators monitor the plant efficiency, answers were quite different. There was no common answer to the question. Many of the personnel mentioned that real-time measurement for steam usage could be a good meter for efficiency monitoring, but currently, only few real-time measurements exist.

After the interviews operators and shift supervisors were asked to comment on the initial designs of the software interface that is presented in chapter 10. The designs received good reception and some enchantments were suggested. Along with the suggestions to improve the designed interface, several suggestions were introduced to improve the current automation system, for example, the standardization of units used in the automation system and adding a few measurements. These measurements are introduced more precisely in chapter 10 as they are also included in the monitoring interface.

One of the most interesting suggestion to improve the site efficiency was implementing of a heat pump system to recover heat from cooling water at certain parts of the processes. Usually, the temperature of cooling water after heat exchanger is not high enough to be utilized with a conventional heat exchanger in other parts of the processes. The outlet temperature could be increased by increasing heat transfer surface area and decreasing mass flow in the water side. Another way to utilize this heat is to use a heat pump process.

A heat pump is a system, where heat energy is transferred from a lower temperature source to a higher temperature with special refrigerant made for the purpose. This process requires electricity to compress refrigerant. The Ratio of heating capacity and electricity consumption is referred as the coefficient of performance or COP. New large capacity designs could provide COP value within the range of 3–6 when using moderate temperature (0–40 °C) heat source (Calefa, 2018)**.**

9.2 Parameters to monitor the efficiency

For both electrolysis processes, the most valuable performance indicator is specific energy consumption per mass unit of product. This can be divided into specific electrical and heat energy consumption. Specific electrical energy consumption is a function of cell room total efficiency and transformer rectifier efficiency.

As impurities build up in electrolysis cells, the electrical resistance of the cell increases. Furthermore, overall efficiency decreases as more of the electricity is used to overcome increased resistance. On Joutseno site, the amount of impurities in electrolysis cells is measured with k-constant. K-constant represents current corrected voltage difference over an electrolysis cell. Current correction decreases the error caused by an increase in optimum voltage when current is increased. Therefore, k-constant can be used to compare different production lines with different electrical currents more accurately.

For heat energy, a steam consumption is the most relevant parameter to monitor. Theoretical steam consumption for each component could be calculated, but as heat recovery systems decrease the steam consumption, it should be taken into consideration. As the goal is to increase economic efficiency and therefore decrease the steam consumption, an optimal specific steam consumption rate can be calculated by reducing the maximum heat of recovery systems from theoretical heat consumption.

As mentioned in chapter 4, in the crystallization process of sodium chlorate manufacturing process water is evaporated from the solution. As evaporation is an endothermic reaction, heat is required. The quantity of heat is directly a function of water amount that needs to be evaporated. Therefore, mass of evaporated water can be compared to the rate of crystallized sodium chlorate to monitor efficiency of the crystallization process.

This approach gives more information about water balance of sodium chlorate manufacturing process than presenting the efficiency as a unit of used heat per mass of crystallized sodium chlorate.

9.3 Limitations

To determine the limiting factors that affect the production rate of sodium chlorate manufacturing process, the process should be split to electrolysis and crystallization. As sodium chlorate is formed in the electrolysis, short timed limitations in the crystallization capacity can be overcome with no limitation in the electrolysis power if there is enough free volume in the cell solution storage tanks before crystallization unit.

There are two different factors which may limit production capacity in the electrolysis process. They are misfunctioning of auxiliary equipment or other electrical or mechanical problems and insufficient cooling capacity.

Production limitations from misfunction of process auxiliary equipment are not covered within this thesis. This will have some impact in validly of the simulation software design. These effects are represented later in this thesis.

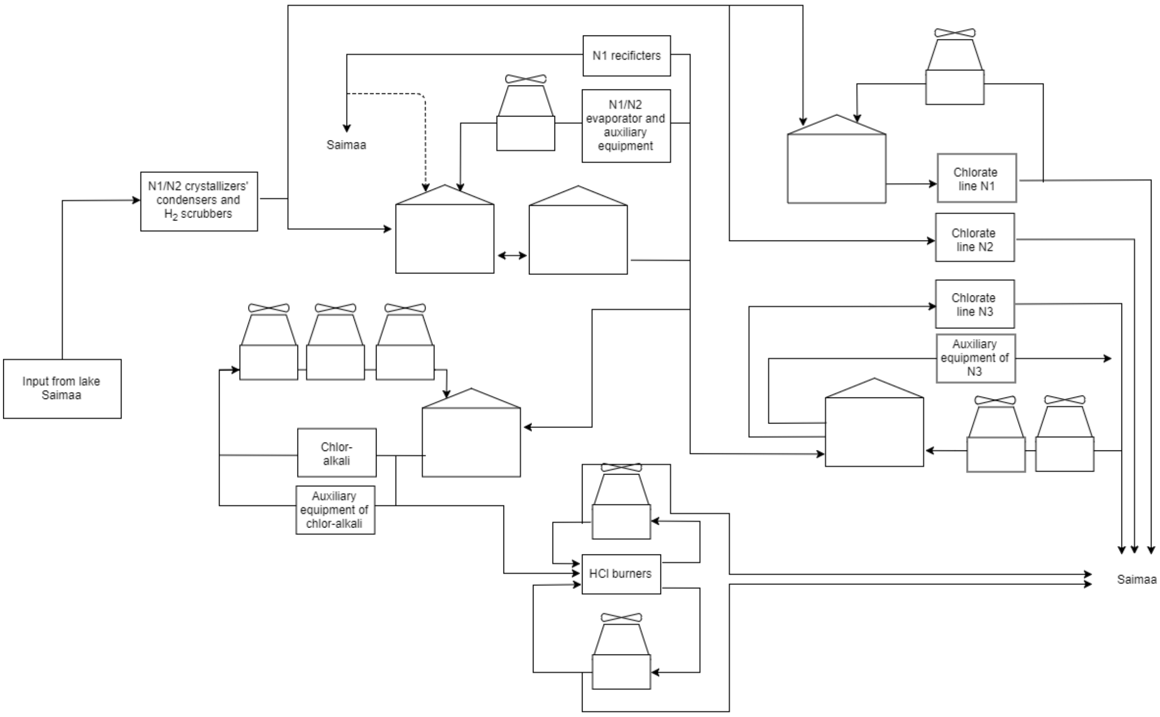


Figure 18. Simplified cooling circuit of Joutseno site.

Cooling water for Joutseno site is taken from nearby lake Saimaa. The water is pumped to the cooling water storage tanks through condensers of the N1 and N2 crystallization unit. From these tanks, the water is pumped to different applications. Crystallization capacity is a function of the cooling capacity of evaporators. Consequently, it is a function of a temperature of incoming cooling water from lake Saimaa. Therefore, the temperature of Saimaa a significant factor that affects the crystallization process of N1 and N2.

There are also many cooling towers on Joutseno site: four in the sodium chlorate plant and five in the chlor-alkali plant. The cooling capacity of a cooling tower is a function of the wet bulb temperature of the outside air (Environmental Defense Fund 2013). Consequently, relative humidity and temperature of the air have also impact in the total cooling capacity of Joutseno site.

From figure 18, it can be seen that the cooling circuits of N1 and N3 sodium chlorate production lines are equipped with cooling towers. The cooling capacity of the crystallization unit of N1 and N2 is depended only on the temperature of incoming cooling water from Saimaa. Crystallization of N3 is included in the cooling circuit of N3 electrolysis and therefore is equipped with cooling towers and is not depended on the temperature of lake Saimaa.

During a hot summer season, a temperature of lake Saimaa can rise to the level where condensation capacity of the crystallization unit of N1 and N2 decreases significantly. This may limit the maximum production rate. In addition, a prolonged hot season can make it difficult to cool N1 and N2 electrolysis because there are no powerful cooling towers in their cooling circuits. However, in Finland hot summer periods tend to be relatively short, so it should carefully calculate if it is cost-efficient to increase the cooling capacity of the N1 and N2 crystallization unit and electrolysis of the processes.

10 ENERGY MANAGEMENT SOFTWARE FOR CHLORATE PRODUCTION ON JOUTSENO SITE

Process efficiency of Joutseno plant is at the appropriate level and within this thesis, no process improvements are researched to improve it. Research is done to improve efficiency via software improvements. As energy consumption is the most dominant part of the manufacturing costs of sodium chlorate manufacturing process, even researching small improvements in efficiency is beneficial.

Currently, Joutseno site power consumption limits are generated manually for each day, based on electricity pricing forecast. However, the power consumption limits and the production rate are determined by production planning. Joutseno site also participates to power balancing markets. As electricity consumption is high on Joutseno site, power balancing markets can bring serious economic benefit.

As sodium chlorate does not significantly decompose in normal storage conditions, it is almost always profitable to produce more sodium chlorate, if relatively cheap electricity is available and crystallization units can handle the extra load and/or storage tanks have enough free volume.

In this thesis, an initial design of optimization software is introduced along with its requirements. The monitoring part of this software is more closely introduced in this chapter and process optimization part of this software is introduced in the next chapter. No finished software is produced among this thesis and only idealized software is introduced.

10.1 Optimization software

The purpose of this idealized optimization software is to monitor and forecast the state of the process and give information to operators about the most efficient power balance between sodium chlorate production lines. History of measurement data should be stored for research purposes. This software is assumed to run along with existing process automation software, although for some more complex calculations an external extension with more advantaged calculation software environment may be required.

The idealized software can be split into two parts, which are the optimization calculation and the monitoring process state. The optimization part will contain all calculations that are necessary for finding the most optimized power balance between sodium chlorate lines and to forecast daily production rates. The purpose of the monitoring part is to monitor and gather data for optimization and allow operators to monitor the current state of the process from the efficiency point of view.

On the Joutseno site, the sodium chlorate manufacturing process is running along with other plants, which use hydrogen from the chlorate production lines. Therefore, the hydrogen balance, and furthermore steam balance, must be included in the monitoring part. This is mandatory to avoid any potential problems that may occur in case of hydrogen shortage as the stable operation of the site must be prioritized over optimization.

10.2 Example windows for the monitoring interface

These example windows are created for illustration purposes and future development. The initial versions of these windows were introduced to the operators and based on their feedback some adjustments were done. The information is divided into five different main groups and the front page is generated to gather the most relevant information. These groups are listed below with little descriptions in table 6. The information about one group is gathered to one window of monitoring interface. In addition, a front page or summary page of site efficiencies is also created. The visual appearance of windows is matched to the existing automation software on the site.

Table 6. Pages included in the monitoring interface.

Name of page	**Description**
Front page	Contains only the most informant parameters of efficiency and forms a link between optimization and monitoring part.
Steam and hydrogen balances	Contains stem and hydrogen balance and allows monitoring usage or production of each major application.
Chlorate production	Contains information useful information about parameters that affect the steam consumption of all three sodium chlorate production lines.
Chlor-alkali	Contains information useful information about parameters that affect the steam consumption of all chlor-alkali plant.
Hydrogen power plant	Contains information from both boiler units and turbine for monitoring steam production.
Water balance	Contains information on site's water usage and allows monitoring water usage of each major application.

All these pages are presented more closely in the following pages of this thesis. Larger figures of example windows are presented as appendices II to VII without English translations.

10.2.1 Front page

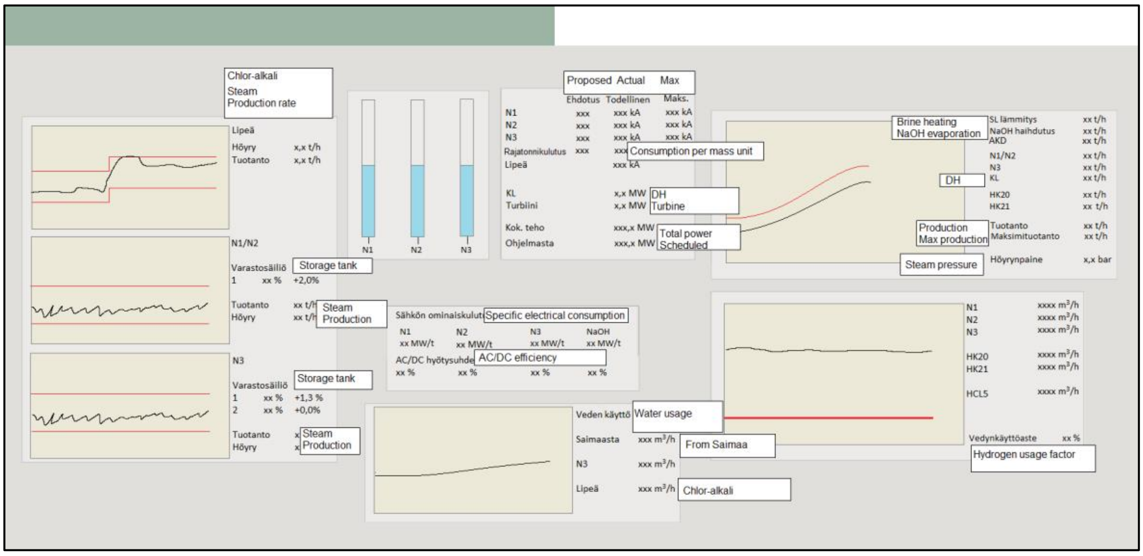


Figure 19. An example window for the front page.

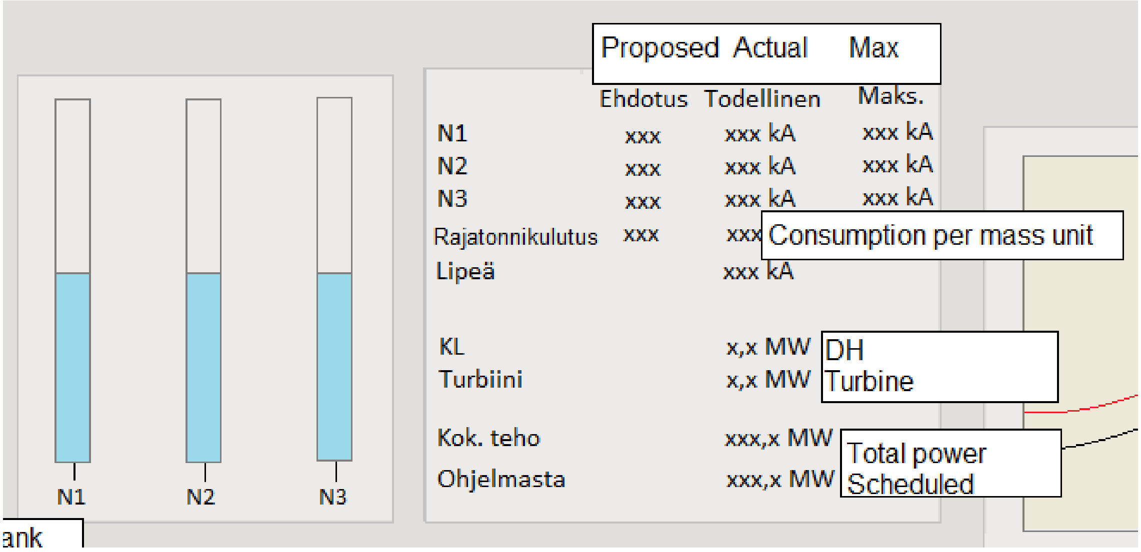
The main purpose of these windows is to guide an operator to operate the process the most efficient way and the purpose of the front page is to be the best tool for an operator to gain information of the current state of site efficiency.

On the left side of figure 19, measurement data is presented for steam consumption of chlor-alkali and of both crystallization units of sodium chlorate plant separately. These curves are explained more thoroughly later in this chapter.

In the lower middle part is presented measurement data for water consumption of the Joutseno site. The inlet water pumps use a significant amount of electricity and therefore unnecessary use of pumps should be avoided.

The right side of figure 19 contains the measurement data for steam and hydrogen networks. The upper right part of the figure contains a steam consumption rate and maximum possible production rate. Next to these curves, there is a table which contains steam usage for all major steam consumption and production applications separately. The lower right part of figure 19 presents a curve for current hydrogen production and minimum possible rate of hydrogen production to maintain hydrogen balance. Next to these curves, hydrogen generation and consumption rates are presented for each relevant application separately.

For chlorate production line operators, this page also contains information that is generated from the optimization part of this software. The most relevant result is energy consumption of production per mass unit separately for each production line. The highest cost efficiency is achieved in the scenarios where the average of lines' production cost per unit mass is as low as possible. A line specific relative cost is presented visually, and more precise numerical values are visible in the table. These are presented more accurately in figure 20, which represents the upper-middle part of figure 19.



Proposed Actual Max

	Ehdotus	Todellinen	Maks.
N1	xxx	xxx kA	xxx kA
N2	xxx	xxx kA	xxx kA
N3	xxx	xxx kA	xxx kA
Rajatonnikulutus	xxx	xxx	
Lipeä		xxx kA	
KL		x,x MW	
Turbiini		x,x MW	
Kok. teho		xxx,x MW	
Ohjelmasta		xxx,x MW	

Consumption per mass unit

DH
Turbine

Total power
Scheduled

Figure 20. Information for sodium chlorate production lines balancing.

10.2.2 Steam and hydrogen balances page

Site's hydrogen and steam balances are presented in this window. In figure 21, an example window is presented. With information from this page, an operator should be able to get information about the current state of steam and hydrogen networks. This can be useful when considering increasing steam usage at certain application or when reducing hydrogen consumption in cases where it is already low.

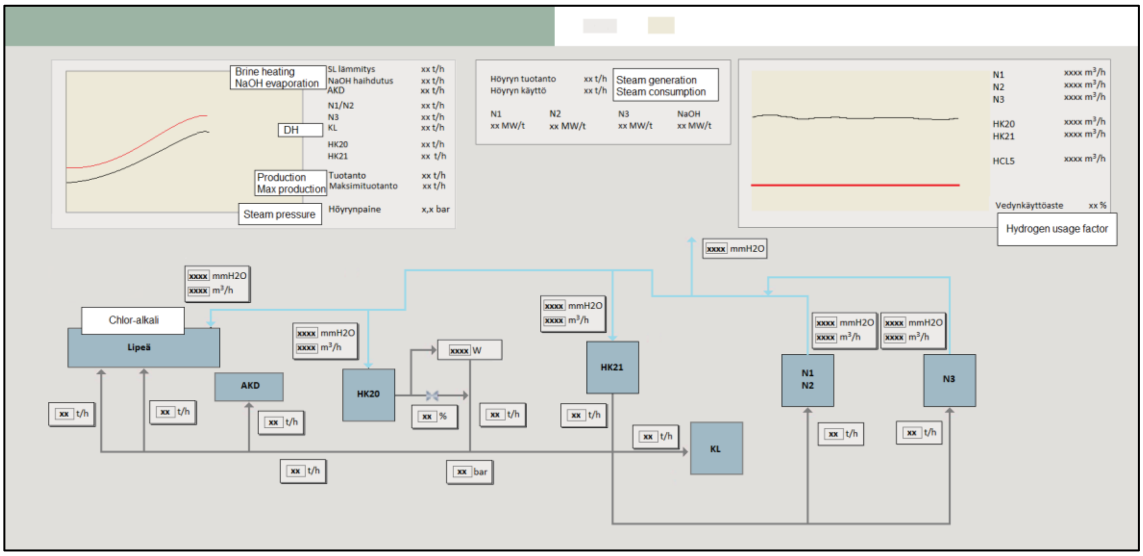


Figure 21. Example window for monitoring hydrogen and steam balances.

In this window, there is a chart where all mass flows and pressures of steam are presented in each relevant application. Steam balance chart is in the lower part of figure 21. To form this chart, all applications should have at least a mass flow measurement. In addition, pressure measurement could be informative in certain parts of the map.

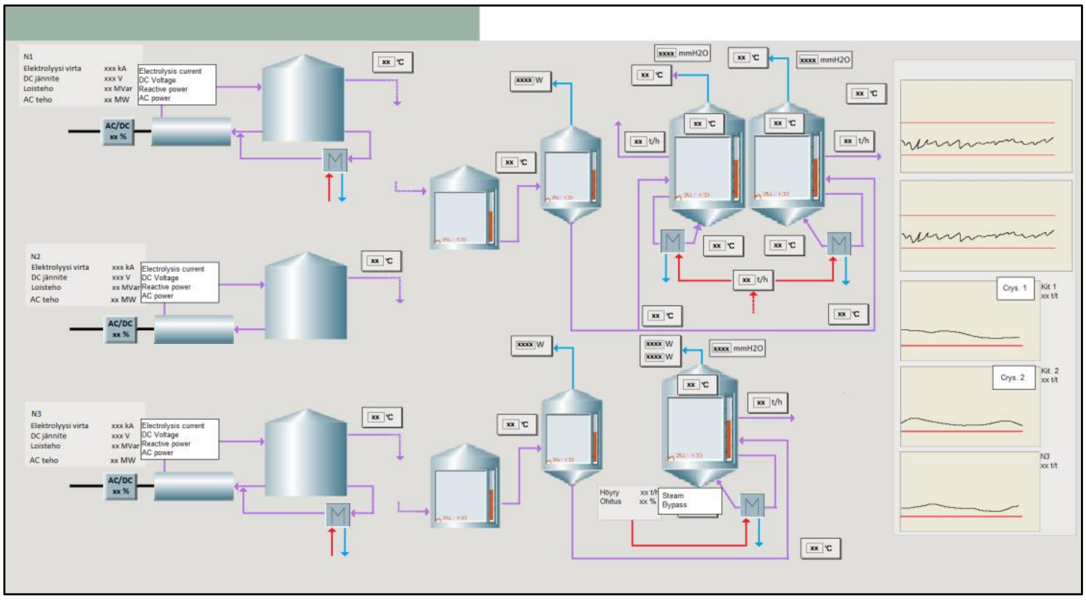
The hydrogen balance is presented as similar map as steam balance. This balance is shown in figure 21 middle part. For all hydrogen generation or consumption applications, there are pressure and flow measurements. Flow measurements can be presented as volume or mass flow. Currently, on the Joutseno site there are volume flow meters, but for calculations, a preferred unit is mass based.

In the upper part of figure 21, there are the curves and tables, which were briefly introduced along with the front page. The curves on the left represent steam balance. The black curve represents measured combined generation from both boiler units and is presented as an absolute value and shows a history of the given time window. The red curve represents a calculated maximum steam generation rate and it is presented similarly with combined steam generation. Time interval of the curve should be determined in the future development phase. The calculated maximum value of the steam generation rate is from optimization tool. The table next to curves has data only from measurements and it presents steam consumption of each major application.

The upper right part of figure 21, presents similar curves for hydrogen balance that is presented in the left for steam. In the curve, the black line represents the current hydrogen production rate and red curve represents minimum production rate to maintain stable operation of hydrogen applications.

10.2.3 Plant-specific pages

In the plant-specific pages, all major components which affect the energy efficiency of process are shown. From these pages, an operator can easily see if adjustments are necessary to improve efficiency. As the purpose of these pages is only to point potential causes for low efficiency, no adjustments are available in any of these pages. This also reduces the amount of data that must be visible and simplifies the big picture, which helps an operator to focus on the most relevant data.



N1
Elektrolyysi virta xxx kA
DC jännite xxx V
Loisteho xx MVar
AC teho xx MW

N2
Elektrolyysi virta xxx kA
DC jännite xxx V
Loisteho xx MVar
AC teho xx MW

N3
Elektrolyysi virta xxx kA
DC jännite xxx V
Loisteho xx MVar
AC teho xx MW

Höyry xx t/h
Ohitus xx %

Figure 22. Example window of the sodium chlorate production lines N1 and N2.

For the sodium chlorate production lines, example window is presented in figure 22. In this figure, various measurements are presented for each sodium chlorate production line separately. In addition, there are text boxes for each line, which present the most relevant information from the electrolysis. Curves containing information from crystallization which were presented along with front page are also visible in this window. In addition to these curves, there are presented a separate set of curves. These present the amount of water evaporated per tonne of sodium chlorate crystallized for each crystallizer unit separately. The red line represents an optimal ratio, which can be obtained with empiric tests and black represents the current value.

Efficiency losses of the electrolysis processes are not included in this window. This simplification is made to decrease the amount of information in the window. Efficiency is caused by a range of factors and it is challenging to monitor precisely. The optimization of current efficiency is possible and creating automation to keep cell solution properties as optimal should be considered as a topic for future researches.

The text boxes in figure 22 contain measurement data for each line separately from electrolysis current, voltage, reactive power and AC power.

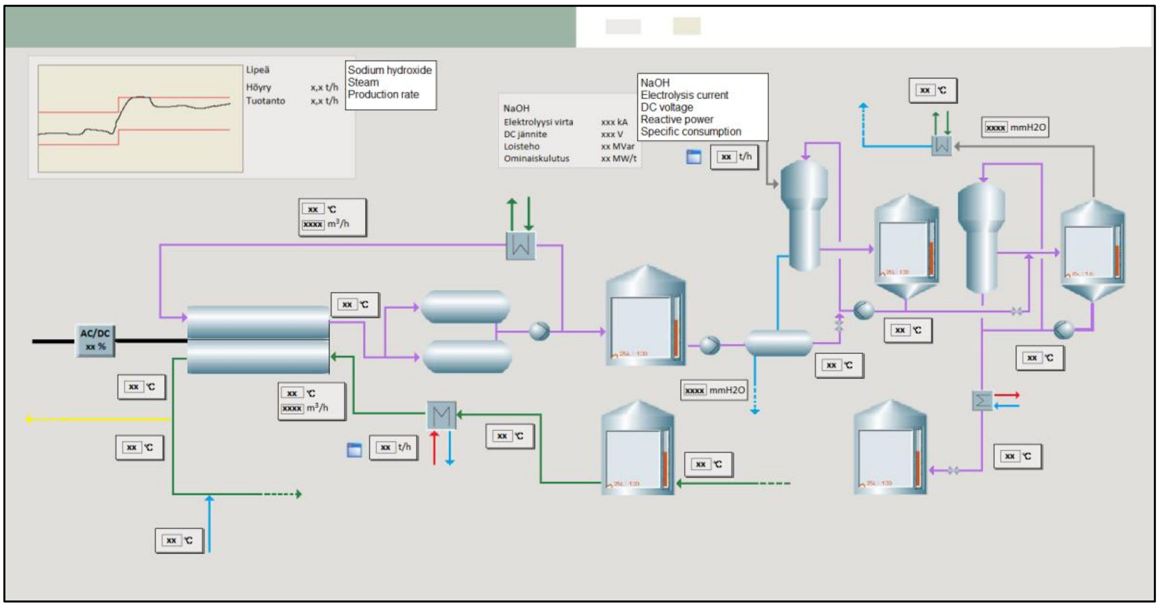


Figure 23. Example window of the chlor-alkali electrolysis.

For chlor-alkali electrolysis, an example window is presented in figure 23. The window contains information about 50 % sodium hydroxide production and no information about manufacturing processes of sodium hypochlorite and hydrogen acid. The efficiency of these two is less relevant to the topic of this thesis. They can be further investigated as separate topics if necessary and can be added as separate pages for this monitor interface.

In the upper left corner of figure 23, there is a specific heat consumption curve of the chlor-alkali plant, which was introduced along with the front page. In this curve, the upper red line presents maximum value for steam consumption of chlor-alkali, which is considered normal. Lower red line presents the optimal target of steam consumption. The data for these lines comes from the optimization software. It is noteworthy that these are a function of different variables and the optimal and maximum value varies. The black curve is the combined heat consumption of sodium hydroxide evaporation and sodium chloride heating processes.

The other text box in the figure contains measurement data from electrolysis current, voltage, AC side reactive power and specific electrical consumption per produced chlorine tonne.

The most relevant part of figure 23 is the process chart of 50 % sodium hydroxide process and electrolysis. All temperature, flow rate and pressure measurements that influence the steam consumption of the chlor-alkali plant, are presented in this figure.

10.2.4 **Boiler and turbine page**

This page will cover the turbine and boilers more accurately. The main purpose of this page is to demonstrate the current state of energy generation equipment. Energy generation is done entirely on different software, so in-depth parameters are not shown on this page. The purpose of this page is only to give information for operating steam applications. An example window is presented below in figure 24.

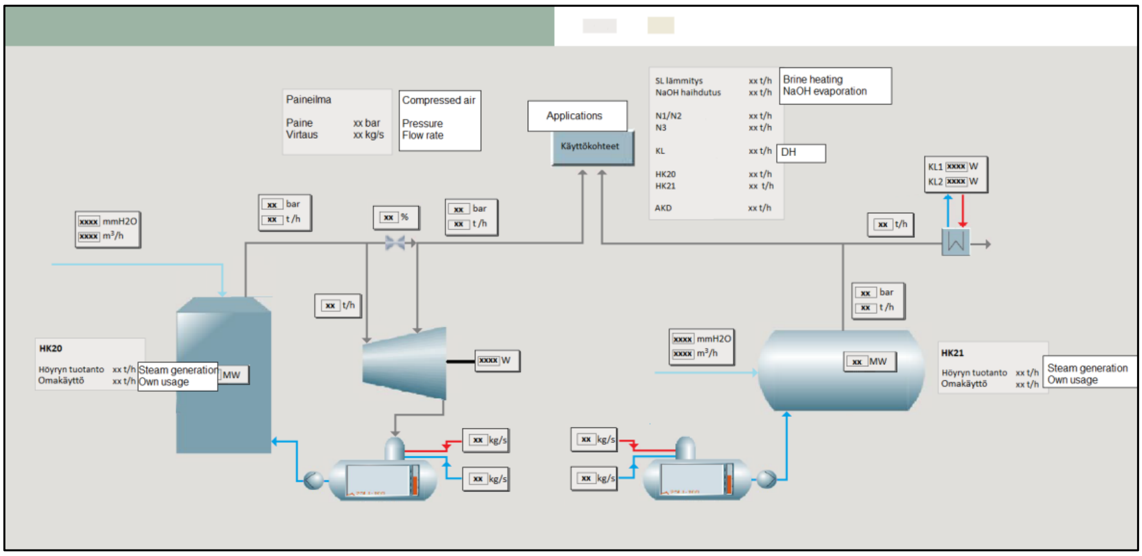
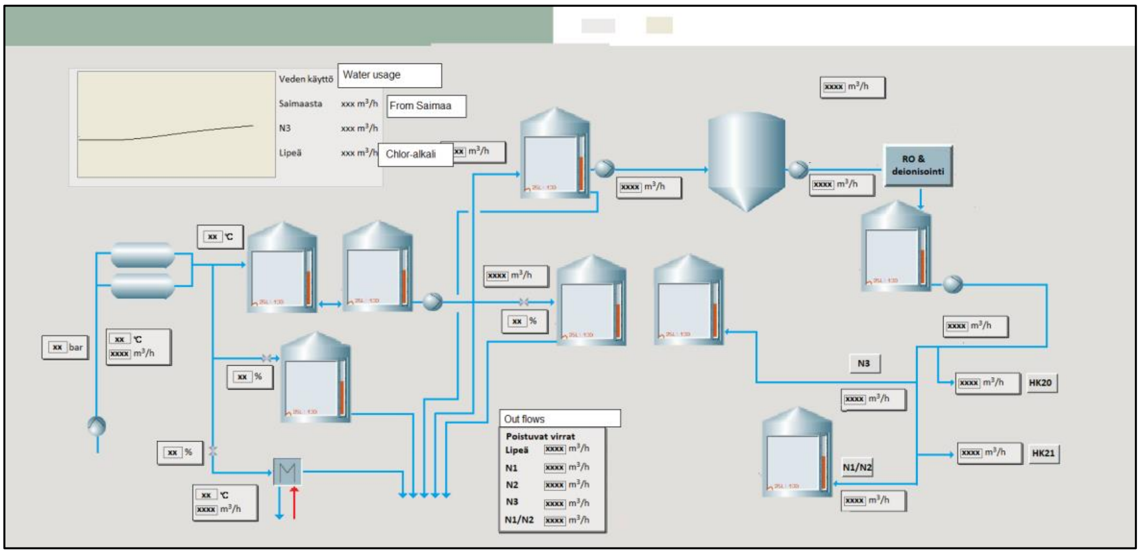


Figure 24. Example window of steam generation and turbine page.

In this window, data from air compressors and district heating heat exchangers are also included. From air compressors, pressure and volume flow of compressed air is shown in this window in the upper left corner. And from district heating heat exchangers, heat powers are shown in the upper right corner. In the upper middle part, there is a table which was introduced along with the front page. This table contains data of steam usage of all major applications.

10.2.5 Water balance

The purpose of this window is to give information on water usage for the entire site. This window combines data from many current pages and therefore it helps an operator to get knowledge for site-wide usage. From the page, an operator cannot make any adjustments. Some simplifications are done for the water circuit to give more attention to major applications. The window contains only a water usage map, which is represented in figure 25 and curve from the front page.



Veden käyttö
Saimaasta xxx m³/h
N3 xxx m³/h
Lipeä xxx m³/h

Poistuvat virrat
Lipeä xxxx m³/h
N1 xxxx m³/h
N2 xxxx m³/h
N3 xxxx m³/h
N1/N2 xxxx m³/h

Figure 25. Example window of water balance.

There are several semi-closed loops within the cooling circuit and these are excluded from this window. Also, as this figure only presents the water mass balance on the site, no extensive temperature measurements are included. In addition to the cooling circuit, some measurement points of demineralized water are present in this figure. There is also one completely new point for mass flow measurement for demineralized water. This was one of the improvements which was proposed during interviews by multiple shifts.

This picture could be improved with temperature measurements and more precise flowchart. This would allow more research on the cooling capacities and give a tool for hottest summer months when cooling capacity can limit production rates. Improving this window requires much groundwork to be done but does not provide much more information for the topic of this thesis. Therefore, improvements are left for future researches.

11 OPTIMIZATION CALCULATION TOOL

In this chapter, an idealized optimization calculation tool is presented. As this thesis does not include a finished tool, but gives initial point for more precise software development, difficulties that may occur during software development phase cannot be determined. Although, the proposed software is designed as realistically as possible.

The input parameters for this software are assumed to contain weather forecast, with different parameters, like the temperature of outdoor air and lake Saimaa and estimated price of electricity. In addition to these, amount of sodium chlorate to be produced in a time unit must be given as input. There could be different more precise short-term data and long-term data to maintain manufacturing rate reliability for longer periods as major priority must be to maintain the reliable supply rate of chemicals to customers.

The requirements for data are determined based on simple calculation tool of own creation. The tool is created with Microsoft Excel and can be used to illustrate the calculation of finished software. The tool is not covered more in this thesis as it was created just for personal knowledge.

11.1 Required data from measurements

As the software is created for optimization of the sodium chlorate manufacturing processes, significantly less data is required from the chlor-alkali process. From the chlor-alkali plant, data is required to calculate the steam consumption on the chlor-alkali plant, the hydrogen usage of the hydrochloric acid burner HCl5 and the power consumption of the chlor-alkali plant.

From the power plant, data is required only to calculate the hydrogen and steam balances. The hydrogen consumption of both boilers and the steam production rate is required. The steam production rate could also be estimated, but as there are ready measurement instruments installed, they can be used. In addition to these, the turbine outlet power should be forwarded for the calculation tool.

From the sodium chlorate plant, more data is required. This data can be split into three groups, which are crystallization capacity, production capacities and storage capacities. The crystallization capacity is required to estimate the amount of chlorate that can be crystallized. There are a few ways to estimate it. Crystallization is limited generally by cooling capacity of condensation unit. From current measurements, a regression analysis can be made to find out the relation between various outdoor conditions and condenser temperature. Also, the relation between condenser temperature and crystallization rate of sodium chlorate should be determined. These two combined gives a relation between maximum crystallization capacity and various outdoor conditions. In these analyses, the composition of cell solution should be included as it influences crystallization rate.

The production rate of sodium chlorate in the electrolysis process can be accurately calculated with equations presented in chapter 4. However, these calculations have some variables, which are challenging to determine with proper accuracy. A typical value can be used with a consistent coefficient, which is determined by empiric tests. And for losses caused by impurities, k-constant is required.

Level of cell solution storage tanks of cell solution is the key factor for the optimization software. The software aims to keep the cell solution storage tank levels within user-defined range. In addition, the level of product storage tanks is needed.

To determine the steam and hydrogen balances, data from the measurements of hydrogen generation and steam consumption of each production line is necessary. In addition to these requirements, some constants regarding cell design and AC/DC efficiencies are also mandatory. AC/DC efficiencies need to be monitored in real time because it is one of the factors affecting power balancing between sodium chlorate lines. AC/DC efficiencies could be also calculated within the optimization tool if enough data is available for the optimization tool.

In case of any limitations in the process that have an effect on maximum capacity, the optimization calculations need to be recalculated. As optimization calculation parameters would be inaccessible to the operators, a possibility to set minimum and maximum electrical current limits of each production line are required. Also, as Joutseno participates in the balancing power market, an hourly maximum or minimum electrical power must be user-definable.

11.2 Data filtering and calculation process

As simulation receives the data real-time and some calculations happen with short time intervals, a measured data should be carefully filtered. This helps to prevent error in calculations caused by measurement errors and short-time fluctuations in measurement results.

As some measurements do not require any data filtering, a precise analysis of the need for data filtering is not done, but ways to filter data are presented. One way, which is also the simplest, is to store measurement data from the last five measurings and take an average or median. This adds latency, which can be an issue in some processes where real-time calculations are mandatory. Although in this case latency of even several seconds does not make any difference to the outcome, because calculations are done in relatively long intervals.

The calculations of the proposed software could be split into various parts based on the time between the need of recalculation. The most frequent calculations are performed to keep data in monitoring part of the software refreshed. The optimal time interval for these could be from 30 to 60 seconds. This could be done also inside the monitoring interface if the existing automation system allows it.

The power balancing calculations between sodium chlorate lines could be done once the maximum power of the site changes. Currently, this means once an hour, but in near future, with 15-minute settlement period in the power market, this value should be reduced to 15 minutes. Also, the optimization calculations should be recalculated every time when the maximum power or maximum or minimum current of any production line is changed. The optimization calculations include many various parts and various time periods. The calculation process is presented in figure 26 below.

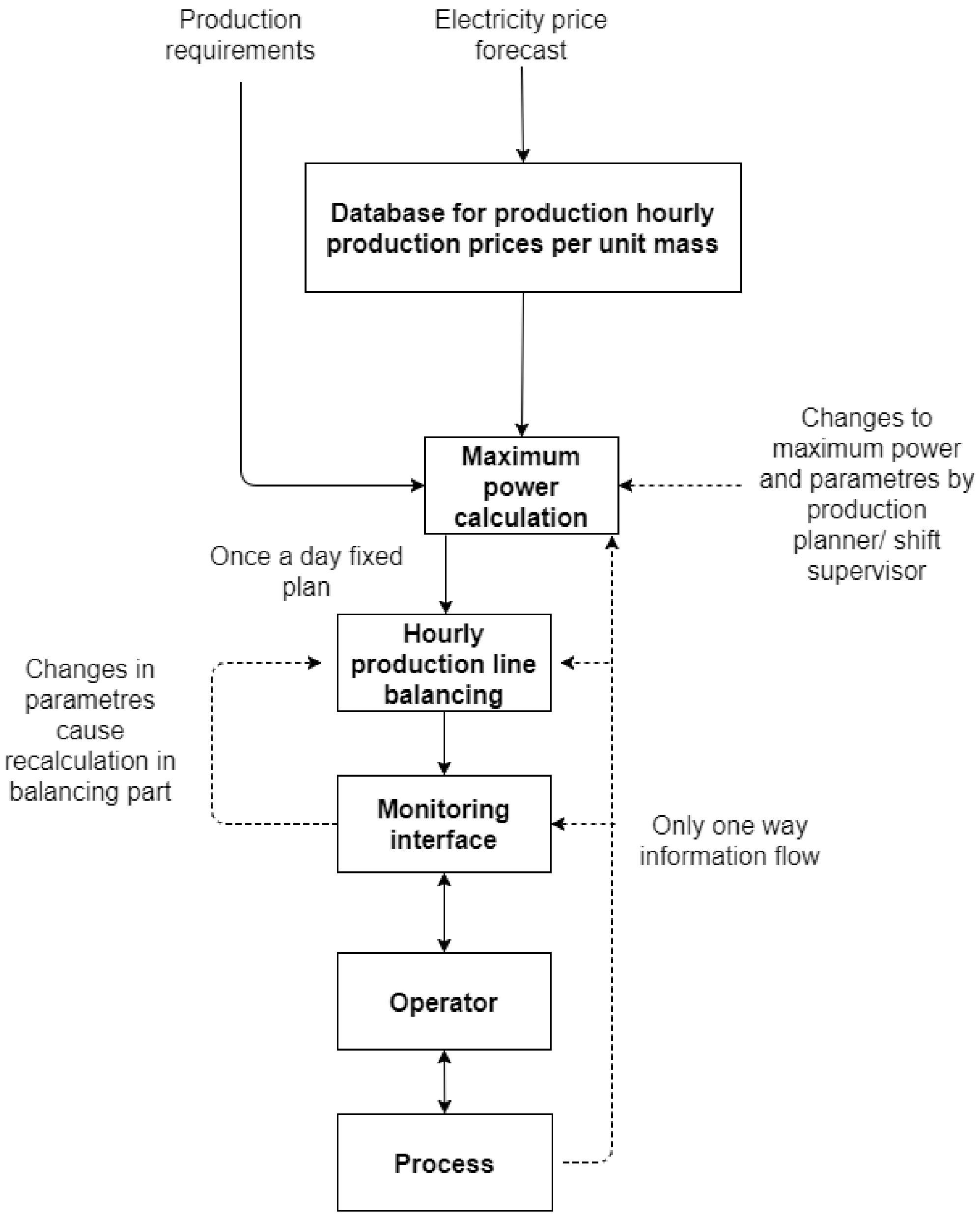


Figure 26. Schematics of the optimization software.

Firstly, with the electricity pricing forecast, the software creates a database for expected manufacturing cost of chlorate tonne for every hour (or 15 minutes). With this database and production requirements, the software determines the need of production for the predetermined time period. This predetermined time period should be the same what is used in the production planning. As the period increases, potential for optimization also increases, but the reliability of electricity forecast decreases.

The line balancing tool receives information of maximum power and then starts to test different combinations for electrical currencies. With three production lines, there are more than 200 000 different current combinations, 60 per one line. Therefore, some logic which eliminates unnecessary combinations is mandatory to keep the calculation process efficient.

For each combination that completes the power requirement and line-specific limitations, line specific and average price per unit mass produced is calculated. Line-specific limitations contain various approaches to determine if production line can store or crystallize all the planned production. The combination with the lowest average price per unit mass produced is considered as the most optimal.

The hydrogen balance is calculated for each combination. If a combination causes hydrogen shortage, it will create a notification to the operator to determine where to reduce hydrogen consumption. The most efficient location to reduce hydrogen consumption is to reduce steam usage and therefore steam production rate.

11.3 Challenges and improvements

There are several challenges and topics which require more research before this kind of software could be implemented as part of the process. These are presented below.

- Measurements and their accuracy
- Maintaining production rate reliability with optimization software
- Cost efficiency and payback time
- Cooling capacity and precise water balance
- Hydrogen network pressure balance
- A dynamic model for the manufacturing process

The monitoring part requires a few new measurements mostly for the water usage chart. However, they are not mandatory. Along with these for more advantaged water balance and cooling capacity measurement more research is necessary. The future research should be able to determine current cooling capacity more precisely and make a dynamic model of current water usage. This model could be further used for finding the most cost-efficient way to increase the cooling capacity. Along with that study, heat regeneration potential from the cooling water circuit should be further researched.

Hydrogen produced in the sodium chlorate can contain some oxygen or other gas components and therefore precise measuring is challenging. The density of hydrogen gas is low compared to other gases that may be present in the mixture. Therefore, a measurement with no density correction is even at best only informative and does not provide accurate measurements. Density correction could be achieved with online gas mixture composition measurements or with meter types that can be equipped with online density measurements, like Coriolis flow meter (Emerson 2018).

One challenge for this kind of optimization software is unpredictability in power markets. The cost savings that could be achieved with the optimization are not high enough to sacrifice the stability of the product delivery rate. Therefore, before implementing any kind of optimization software there should be a long enough test period.

This thesis does not contain any financial calculations regarding viability or payback time of this kind of tool. The implementation of optimization software could cost a significant amount, but the monitoring interface can be produced with less effort and costs. Monitoring interface can be implemented as a separate part from the optimization part with no loss in functionality.

Currently, all the hydrogen produced for the hydrogen network is not usable because of pressure losses in the piping. This must be resolved or taken into consideration in designing of optimization software. Future research could be done to determine causes for pressure losses.

The last proposed future research topic is creating a dynamic model for the sodium chlorate manufacturing process. This model would allow much more precise estimation of process state. It could be used for testing the possible variations and simplifications in calculations of simulation software. The model also allows making calculations for potential future process improvements more easily and precisely.

12 SUMMARY

The aim of this thesis was to determine the base requirements and an approach method to create an optimization tool for a sodium chlorate production line. The thesis was conducted at Kemira Chemicals Joutseno site. Development of this kind of optimization tool is a relevant topic for any energy intensive process as in near future, electricity pricing will be converted to a 15-minute settlement period. The objective of this thesis would have been inaccessible if the theory behind sodium chlorate production, thus energy consumption of the process, would not have been fully understood.

To obtain the required information to the determine the requirements, a literary review was done with energy consumption point of view. As energy consumption of sodium chlorate manufacturing is formed by consumption of electrolysis and crystallization, these two processes were taken under more precise research. Theoretical consumption and models could have been created by literary references. These models essential for simulation tool calculations as they present production rate as a function of maximum electrical and heat consumption.

The thesis included also interviews and survey for shift personnel of Joutseno site. The aim of these was to determine the energy awareness of operators and their supervisors. Results of the survey could not be used because low participation rate, but interviews were used to determine the energy awareness of shift personnel.

Overall energy awareness and knowledge among shift personnel is at commendable level. However, variations can be found between shifts. These variations could be levelled, with aid of shift supervisor. Knowledge and awareness level of supervisor is reflected directly to his or her subordinates. Therefore, focus should be put on keeping each shift supervisor’s knowledge up to date.

In the last parts of this thesis, the set objectives were completed. These parts contain all necessary requirements for optimization software and present an idealized way to develop optimization software for a sodium chlorate process. Also, in the last part of the thesis, major challenges and future research topics, which are necessary to make idealized software, were determined.

As a propose to Kemira Chemicals, a monitoring interface, like the one idealized in this thesis, should be further development and standardized along with all sodium chlorate manufacturing processes. This kind of standard way to measure efficiencies in multiple locations can provide crucial information to increase overall efficiency.

As sodium chlorate manufacturing process in Joutseno is controlled by the operator in charge, there should be information available that the operator can use to determine the most efficient manner. During the interviews, the clear absence of a common measurements for efficiencies was found. Therefore, with standardized monitoring interface, local benefits are also achievable.

The monitoring interface can also be used to educate shift personnel and it allows self-learning for the most motivated ones. Shift personnel and engineering team can find correlations between certain factors to fine-tune the process to increase efficiency.

All the objectives set for this thesis were accomplished. In addition, many future research aspects were found. The most relevant of these are the creating of a dynamic model for cooling circuit and refreshing and standardizing measurements in the site.

In addition, site efficiency could be increased with an optimization software, but it will not be cost efficient before settlement period is converted to the 15-minute period due to complex calculations required for the process state forecast. However, efficiency could be increased with more precise monitoring. Efficiency monitoring can be used to spot causes for the lowered efficiency and ultimately to find methods to prevent decreases in the efficiency.

13 REFERENCES

American Chemistry Council, 2003. Hydrochloric acid – HCl - An acid with many uses [WWW Document]. Available: https://chlorine.americanchemistry.com/Science-Center/Chlorine-Compound-of-the-Month-Library/Hydrochloric-Acid-HCl-An-Acid-With-Many-Uses/ (accessed 19.11.18).

Brinkmann, T., Santonja, G.G., Schorcht, F., Roudier, S., Sancho, L.D., 2014. Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali.

Burney, H.S., 1999. Chlor-alkali and Chlorate Technology. The Electrochemical Society.

Calefa. 2018. Heat pumps [WWW Document] Available: http://www.calefa.fi/en/technologies/heat-pumps/ (accessed 13.12.2018)

Campbell, A.N., Kouwe, E.T., 1968. Studies on the thermodynamics and conductances of molten salts and their mixtures. Part VI. Calorimetric studies of sodium chlorate and its mixtures with sodium nitrate. Can. J. Chem. 46, 1287–1291.

CEFIC-Sodium Chlorate, 2004. Mini-process BREF for Sodium Chlorate.

Chris Nickson, 2014. Oxygen Extraction Ratio [WWW Document]. Life Fast Lane. Available: https://lifeinthefastlane.com/ccc/oxygen-extraction-ratio/ (accessed 18.11.18).

Demirel, Y., 2016. Energy: Production, Conversion, Storage, Conservation, and Coupling, 2nd ed, Green Energy and Technology. Springer International Publishing.

DeVoe, H., 1998. Thermodynamics and Chemistry [WWW Document]. Chemistry LibreTexts. Available: https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/DeVoe’s_%22Thermodynamics_and_Chemistry%22/13%3A_The_Phase_Rule_and_Phase_Diagrams/13.3_Phase_Diagrams%3A_Ternary_Systems (accessed 15.12.18).

Duke, D.A., 1981. Theory of crystallization. In: Mineralogy. Encyclopedia of Earth Science. Springer US, Boston, MA

Eka Chemicals, 1998. Some data and solubility information for Sodium Chlorate [WWW Document]. Available: http://www.pyrobin.com/files/Natriumchlorat.pdf (accessed 8.10.18).

Emerson, 2018. Micro Motion ELITE Coriolis Flow Meters [WWW Document]. Available: https://www.emerson.com/fi-fi/automation/brands/micro-motion/micro-motion-elite-coriolis-flow-meters (accessed 14.12.18).

Energinet, Statnett, Svenska kraftnät, Fingrid, 2017. Higher time resolution: Information to stakeholders [WWW Document]. Available: https://www.fingrid.fi/globalassets/dokumentit/fi/tiedotteet/sahkomarkkinat/2017/information-to-stakeholders-nov-2017.pdf (accessed 16.11.18).

Enviromental Defense Fund, 2013. Cooling tower efficiency guide property managers [WWW-Document]. Available: http://business.edf.org/files/2014/03/Cooling-Tower-Handbook_FINAL.pdf (accessed 30.12.18).

Euro Chlor, 2017. Euro Chlor - Chlorine Production Capacities per country [WWW Document]. Available: http://www.eurochlor.org/facts-figures-glossary/chlorine-production-capacities-per-country.aspx (accessed 11.12.18).

European Commission, 2007. The BAT (Best Available Techniques) Reference Document (BREF) - Large Volume Inorganic Chemicals – Solids and Others (LVIC-S).

Ferrum, 2018. Continuous performance D-ACT® pusher centrifuges [WWW Document]. Available: https://www.ferrum.net/wAssets/pdf/gbz/downloads/prospekte/english/Ferrum-D-ACT_en.pdf (accessed 2.11.18).

Fingrid, 2016. Our shared journey - a roadmap towards achieving a green power system [WWW Document]. Available: https://www.fingrid.fi/globalassets/dokumentit/en/electricity-market/development-projects/our_shared_journey_a_roadmap_towards_achieving_a_green_power_system.pdf (accessed 15.12.18).

Fingrid, 2017. Maintenance of power balance [WWW Document]. Fingrid. Available: https://www.fingrid.fi/en/grid/electricity-system-of-finland/maintenance-of-power-balance/ (accessed 8.10.18).

Foxall, K., 2010. Sodium chlorate – General information [WWW Document]. Health Protection Agency. Available: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/318215/hpa_Sodium_chlorate__General_Information_v1.pdf (accessed 27.12.18).

Hedenstedt, K., 2017. Energy efficiency in the sodium chlorate process: From electrocatalysis to pilot plant investigations.

Jaksic, M.M., et al., Journal of the Electrochemical Society, 1969. 116.

Kaakkois-Suomen ELY-keskus, 2016. Kemira Oy Joutsenon kloraattitehtaan laajennus, SOIHTU, Lappeenranta [WWW Document]. Available: http://www.ymparisto.fi/fi-FI/Asiointi_luvat_ja_ymparistovaikutusten_arviointi/Ymparistovaikutusten_arviointi/YVA-hankkeet/Kemira_Oy_Joutsenon_kloraattitehtaan_laajennus_SOIHTU_Lappeenranta (accessed 11.12.18).

Kemira. 2017. Tervetuloa Joutsenon tehtaalle!. [Video]. Available: https://www.youtube.com/watch?v=rvf1VsbrJGs&t=1s (accessed 10.12.18)

Kivistö, J., 2018 [Email conversation]. Kemira. Unpublished confidential document

Kivistö, J., 2011. Käyttöohje: natriumkloraattielektrolyysi. Kemira. Unpublished confidential document

McKetta, J., Weismantel, G., 1995. Encyclopedia of Chemical Processing and Design: Volume 51 - Slurry Systems: Instrumentation to Solid-Liquid Separation. CRC Press.

O’Brien, T.F., Bommaraju, T.V., Hine, F., 2007. Handbook of Chlor-Alkali Technology. Springer Science & Business Media.

Ranghino, A., Costantini, L., Deprado, A., Filiberti, O., Fontaneto, C., Ottone, S., Peron, M., Ternavasio Cameroni, G., Zamponi, E., Guida, G., 2006. A case of acute sodium chlorate self-poisoning successfully treated without conventional therapy. Nephrol. Dial. Transplant. 21, 2971–2974.

Rodriguez, J.R., Pontt, J., Silva, C., Wiechmann, E.P., Hammond, P.W., Santucci, F.W., Alvarez, R., Musalem, R., Kouro, S., Lezana, P., 2005. Large Current Rectifiers: State of the Art and Future Trends. IEEE Trans. Ind. Electron. 52, 738–746.

Schroeder, V., Holtappels, K., 2005. Explosion characteristics of hydrogen-air and hydrogen-oxygen mixtures at elevated pressures. 5th Conference on risk assessment and Management in the civil and industrial settlements.

Seidell, A., Linke, W. 1952. Solubilities of Inorganic and Organic Compounds. Van Nostrand

Suzhou Fenggang Titanium Products and Equipment Manufacturing Co.,Ltd, 2014. Chlorate Electrolyzer [WWW Document]. Available: http://www.sztitanium.com/product1.asp?id=59&classID= (accessed 2.11.18).

Tilak, B.V. and C.-P. Chen, Calculation of the current efficiency of the electrolytic sodium chlorate cell. Journal of Applied Electrochemistry, 1999. 29: p. 1237-1240.

World Health Organization, 2000. Disinfectants and disinfectant by-products [WWW Document]. Available: http://www.inchem.org/documents/ehc/ehc/ehc216.htm#SubSectionNumber:2.2.2 (accessed 18.11.18).

APPENDIX I: QUESTIONNAIRE TRANSLATED IN ENGLISH

Kyselyn vastauksia käytetään täysin anonyymisti. Jokaiseen kohtaan vastaaminen on vapaaehtoista.

Alkutiedot

Vuoromestari ☐
Operaattori, lipeä ja AKD ☐
Operaattori, kloraatti ☐
Muu, lipeä ☐
Muu, kloraatti ☐

1. Yleisesti ottaen, koko tehdasalue toimii energiatehokkaasti

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

2. Koen ymmärtäväni mitä energiatehokkuudella tarkoitetaan liittyen omaan työhöni

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

3. Energiatehokkuus on parantunut uusien investointien myötä viime vuosina

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

4. Tiedän miten voin tarkkailla tehtaan energiatehokkuutta

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

5. Koen että voin vaikuttaa tehtaan energiatehokkuuteen

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

6. Esimieheni odottaa minun ymmärtävän energiatehokkuuden tärkeyden

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

7. Helpottamalla energiatehokkuuden seurantaa uskoisin pystyväni toimimaan tehokkaammin

Eri mieltä ☐ ☐ ☐ ☐ ☐ Samaa mieltä

8. Selitä lyhyesti mitä on energiatehokkuus työssäsi

9. Kuinka usein keskustelet työkavereiden kanssa laitoksen energiankäytöstä tai muusta aiheeseen liittyvästä? (Myös "kahvipöytäkeskustelut" yms. vapaamuotoisemmat).

10. Kolme tärkeintä keinoa, joilla koet voivasi vaikuttaa energiatehokkuuteen

1.
2.
3.

11. Kolme tärkeintä energiatehokkuutta kuvaavaa mittaria/suuretta

1.
2.
3.

12. Arvioi tehtaan (lipeä/kloraatti) energiatehokkuutta asteikolla 1-5

Paljon parannettavaa ☐ ☐ ☐ ☐ ☐ Ei juurikaan parannettavaa

Kiitos kyselyyn osallistumisesta! Alla olevaan kenttään voit kirjoittaa anonyymisti kehitysideoita/ ajatuksia aiheesta.

APPENDIX II: EFFICIENCY MONITORING, FRONT PAGE

Lipeä	
Höyry	x,x t/h
Tuotanto	x,x t/h

N1/N2		
Varastosäiliö		
1	xx %	+2,0%
Tuotanto		xx t/h
Höyry		xx t/h

N3		
Varastosäiliö		
1	xx %	+1,3 %
2	xx %	+0,0%
Tuotanto		xx t/h
Höyry		xx t/h

	Ehdotus	Todellinen	Maks.
N1	xxx	xxx kA	xxx kA
N2	xxx	xxx kA	xxx kA
N3	xxx	xxx kA	xxx kA
Rajatonnihinta	xxx	xxx	
Lipeä		xxx kA	
KL		x,x MW	
Turbiini		x,x MW	
Kok. teho		xxx,x MW	
Ohjelmasta		xxx,x MW	

Sähkön ominaiskulutus

N1	N2	N3	NaOH
xx MW/t	xx MW/t	xx MW/t	xx MW/t

AC/DC hyötysuhde

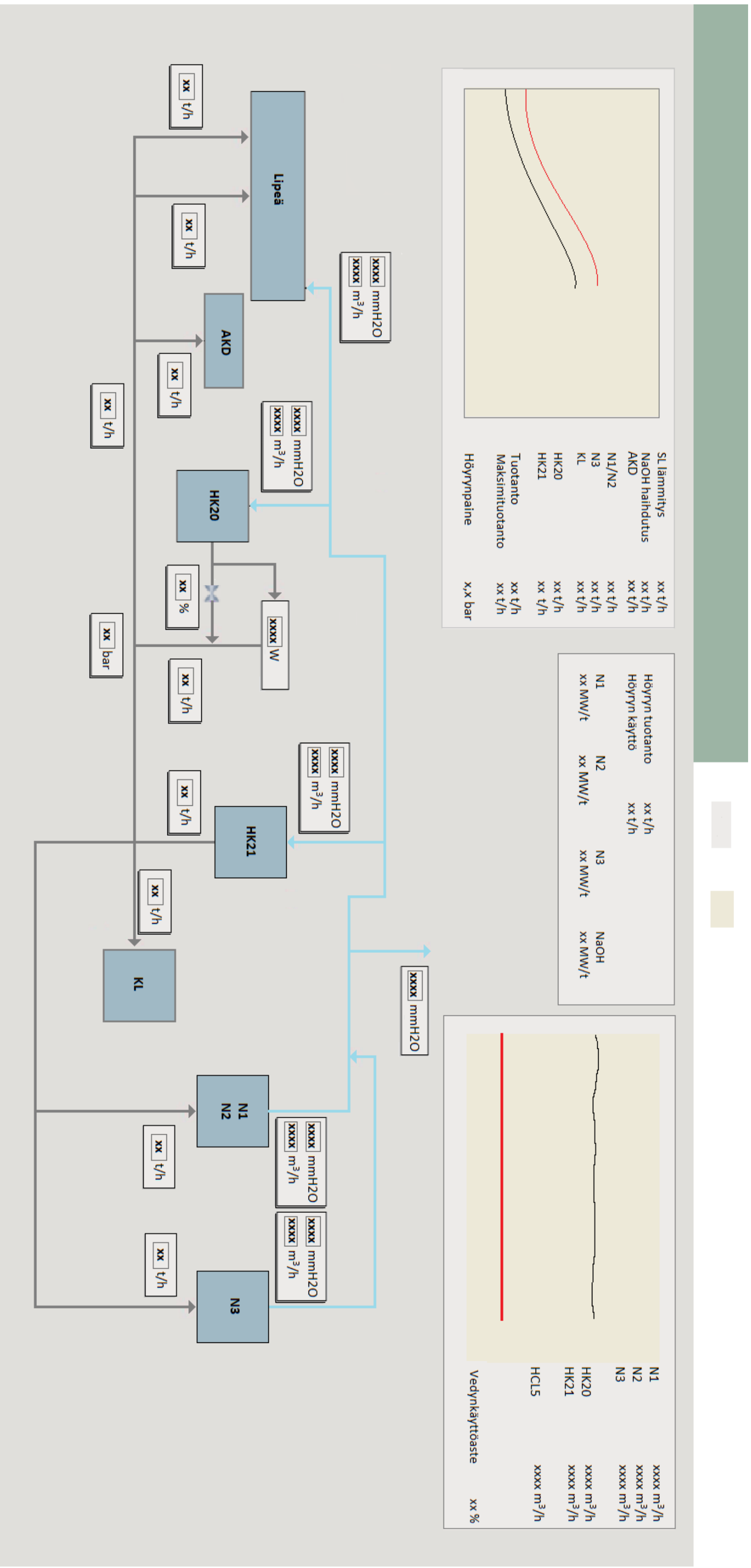
xx %	xx %	xx %	xx %

Veden käyttö	
Saimaasta	xxx m^3/h
N3	xxx m^3/h
Lipeä	xxx m^3/h

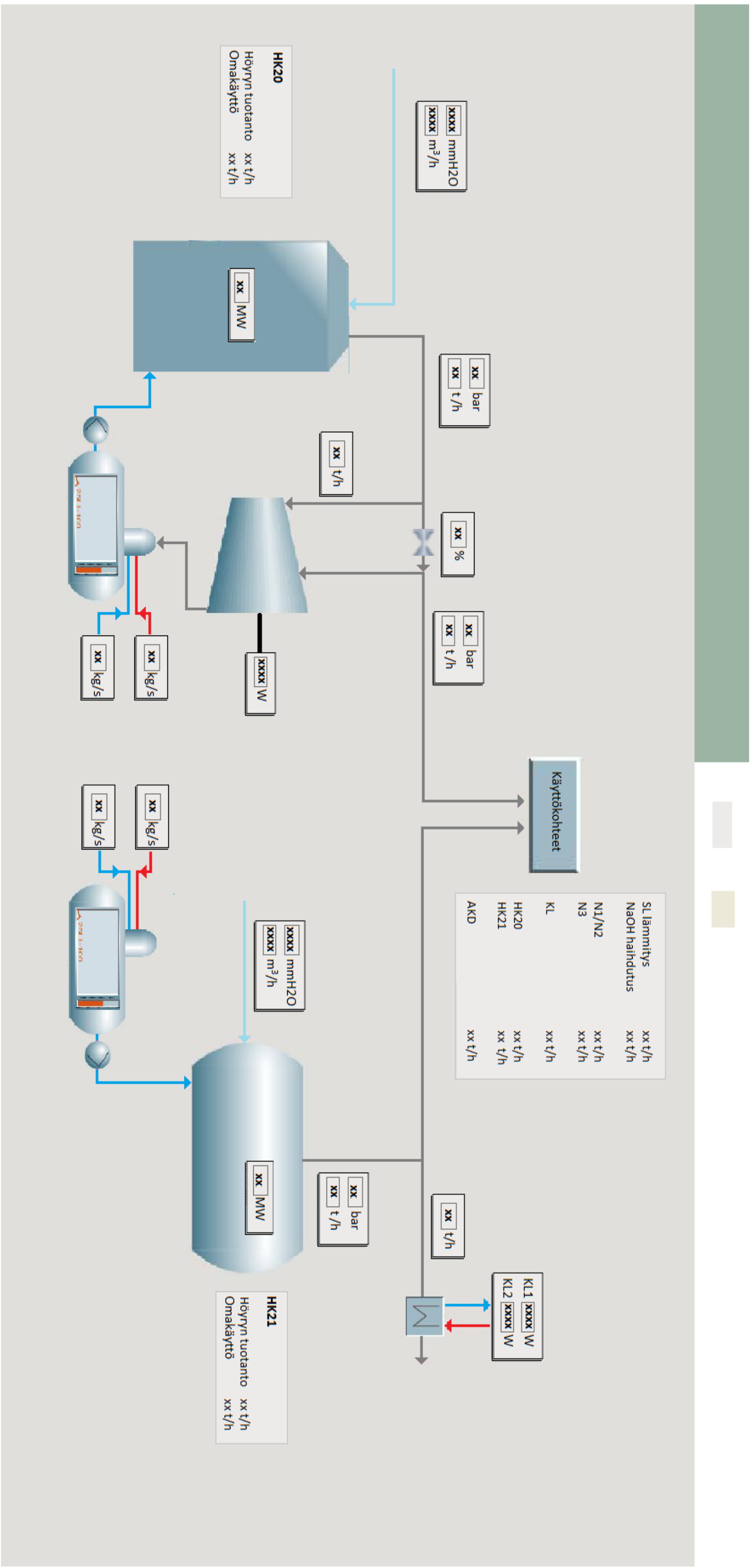
SL lämmitys	xx t/h
NaOH haihdutus	xx t/h
AKD	xx t/h
N1/N2	xx t/h
N3	xx t/h
KL	xx t/h
HK20	xx t/h
HK21	xx t/h
Tuotanto	xx t/h
Maksimituotanto	xx t/h
Höyrynpaine	x,x bar

N1	xxxx m^3/h
N2	xxxx m^3/h
N3	xxxx m^3/h
HK20	xxxx m^3/h
HK21	xxxx m^3/h
HCL5	xxxx m^3/h
Vedynkäyttöaste	xx %

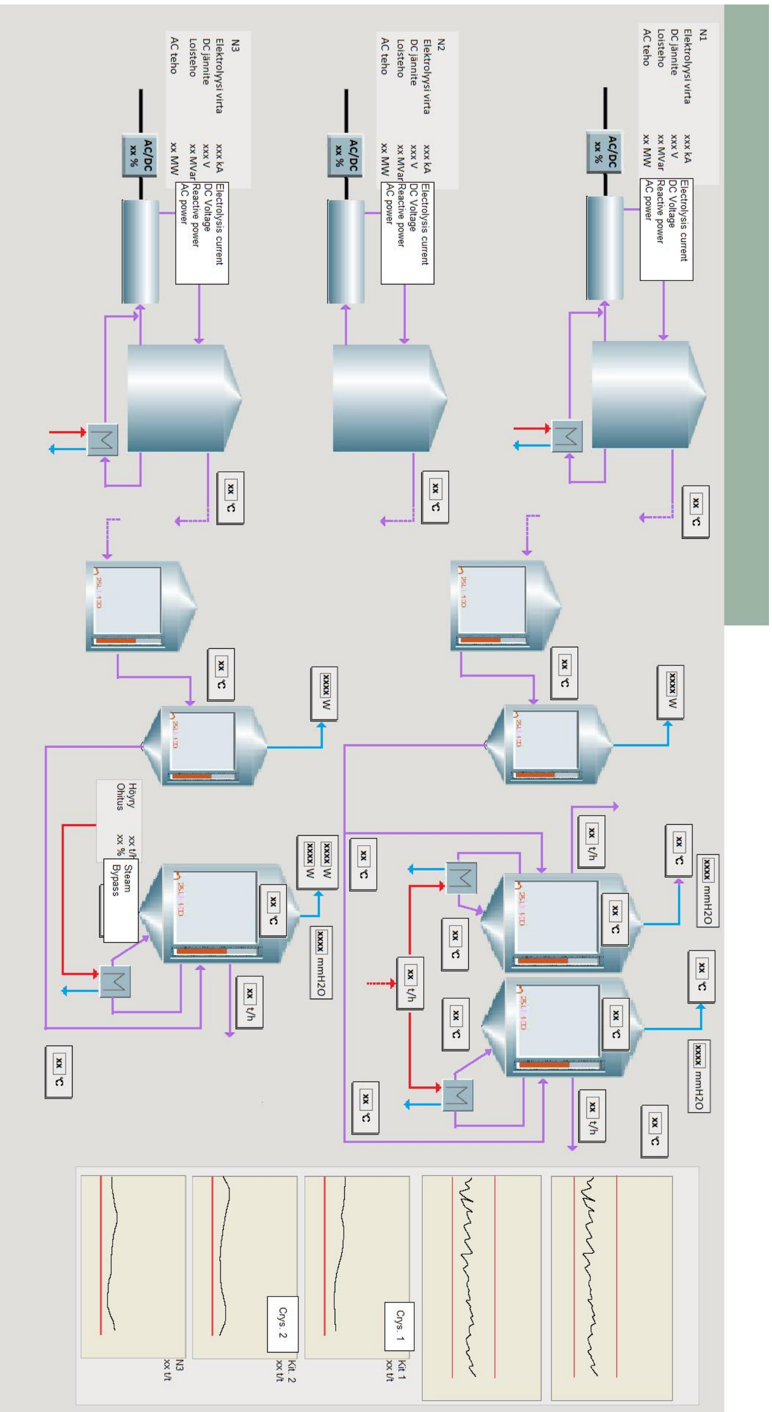
APPENDIX III: EFFICIENCY MONITORING, STEAM AND HYDROGEN BALANCES



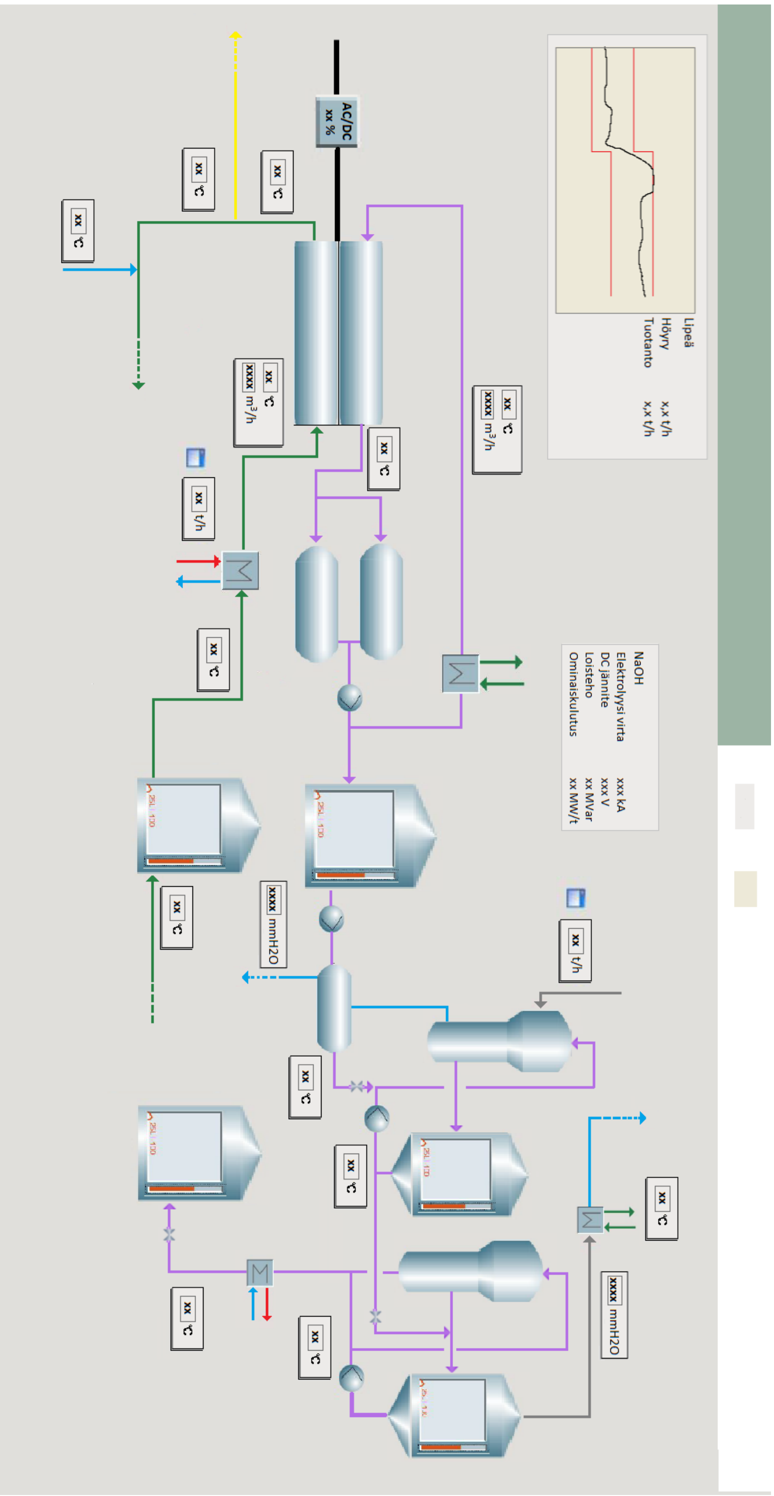
APPENDIX IV: EFFICIENCY MONITORING, POWER PLANT



APPENDIX V: EFFICIENCY MONITORING, SODIUM CHLORATE PLANT



APPENDIX VI: EFFICIENCY MONITORING, CHLOR-ALKALI PLANT



APPENDIX VII: EFFICIENCY MONITORING, WATER BALANCE