

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
School of Technology
Master's Degree Program in Chemical and Process Engineering

Tiina Hyytinen

CHROMIUM MASS BALANCE IN SODIUM CHLORATE PROCESS

Examiners: Professor Marjatta Louhi-Kultanen
Lic.Sc. (Tech.) Eija Säöksjärvi

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
Teknillinen tiedekunta
Kemiantekniikan koulutusohjelma

Tiina Hyytinen

Natriumkloraatiproessin kromitase

Diplomityö

2014

92 sivua, 6 kuvaa, 11 taulukkoa, 3 liitettä

Tarkastajat: Professori Marjatta Louhi-Kultanen
TKL Eija Sääksjärvi

Hakusanat: ainetase, kromi
Keywords: mass balance, chromium

Kuudenarvoista kromia käytetään natriumkloraatin valmistuksessa prosessin tuotantotehokkuuden ja turvallisuuden parantamiseksi. Kromia kuitenkin poistuu prosessista muutamaa reittiä pitkin. Koska kuudenarvoisella kromilla on syöpää aiheuttavia, mutageenisia sekä lisääntymiselle myrkyllisiä ominaisuuksia, olisi tärkeää ymmärtää, miten kromi kulkeutuu prosessin eri osiin, ja kuinka paljon sitä poistuu prosessista. Tämä on tärkeää, jotta osataan hallita kromin käytöstä aiheutuvat riskit, sekä toisaalta myös tehostaa kromin käyttöä prosessissa.

Työn tarkoituksena oli tuottaa tietoa kromin käytöstä natriumkloraatiprosessissa. Työssä tutkittiin kromitasetta prosessin keskeisimmissä yksikköoperaatioissa. Myös kromin saostumista katodien pinnalle arvioitiin määrällisesti. Eri prosessinäytteistä tutkittiin lisäksi kromin hapetusasteita. Edellä mainittuja tutkimuskohteita varten määritettiin prosessinäytteiden kromipitoisuus. Eri prosessioperaatioille suoritettiin lisäksi taselaskelmat.

Työn tuloksena esitettiin kromitase sekä yksikköoperaatioille että koko prosessille. Erinäisten epätarkkuustekijöiden vuoksi tasetta ei kuitenkaan pystytty määrittämään halutulla tarkkuudella, ja siksi työssä esitettyä tasetta voidaan pitää vain suuntaa antavana laskelmana. Katodien pinnalle saostunutta kromin määrää pidettiin kuitenkin oikean suuruusluokan tuloksena. Prosessinäytteiden hapetusasteita ei voitu arvioida, sillä saadut kokonaiskromitulokset eivät olleet täysin luotettavia.

Huolimatta tulosten epätarkkuudesta, työ tuotti tärkeää tietoa prosessin toiminnasta kromin suhteen. Työtä voidaan hyödyntää jatkossa monin tavoin prosessin kromitaseen seurannassa.

ABSTRACT

Lappeenranta University of Technology
School of Technology
Master's Degree Program in Chemical and Process Engineering

Tiina Hyytinen

Chromium mass balance in sodium chlorate process

Master's Thesis

2014

92 pages, 6 figures, 11 tables, 3 appendices

Examiners: Professor Marjatta Louhi-Kultanen
Lic.Sc. (Tech.) Eija Säöksjärvi

Keywords: chromium, mass balance

Hexavalent chromium is used in the manufacture of sodium chlorate in order to increase the efficiency and the safety of the process. Chromium is discharged from the process through couple of routes. Because of the carcinogenic, mutagenic and reproductive toxic effects of hexavalent chromium, it should be understood how chromium is transferred in the process, and how much of chromium is discharged from the process. This is important in order to take the proper risk management measures, and also to further intensify the use of chromium in the process.

The objective of the thesis was to increase the knowledge regarding the use of chromium in the sodium chlorate process. The work included examination of the chromium balance for the most essential unit operations of the process. Moreover, precipitation of chromium on the surface of the cathodes was estimated. Additionally, the oxidation degree of the chromium species was researched in different process conditions. All of the aspects were studied by determining the chromium content for different process samples. Balance calculations were executed for the unit operations of the process.

As a result for the study, a chromium mass balance was presented for the unit operations and the entire process. Due to the many uncertainties related to the results, the desired accuracy in the conducted balance calculations was not achieved, and thus the obtained balance can be considered only as a preliminary result on chromium balance. However, the amount of chromium that had been reduced on the cathodes was considered to be correct order of magnitude. The obtained total chromium results were not fully reliable, and therefore analysis regarding the oxidation degree of chromium in the varying process conditions could not be done.

Regardless of the limitations in the reliability of the results, important knowledge was produced regarding the functioning of the process in terms of chromium. The study can be utilized in many ways in the follow-up of the balance in the future.

ACKNOWLEDGEMENTS

The experimental study was conducted at Kemira Oyj's manufacturing site in Joutseno.

First of all, I am thankful for my employer, Kemira Oyj, for giving me the opportunity to execute this study.

I would like to thank Professor Marjatta Louhi-Kultanen and Lic.Sc. (Tech.) Eija Sääksjärvi, the examiners of this master's thesis.

I would also like to thank for the professional Joutseno personnel for assisting me in the practical work. Special thanks for Juha Hujanen for being my instructor, enlightening me the philosophy of the chlorate manufacture, and giving me the valuable advices regarding the experimental study.

I would like to express my deepest gratitude for my mother Eija and my mother-in-law Liisa, for taking care of my children, and thus enabling the compilation of this thesis and completing my studies during the last years. Additionally, I want to thank the other family members, too, for all your help and support.

Finally, I want to say to my husband, Eero, that without your help, encouragement and patience, I would not have been able to finalize this never-ending project. Thank you!

Tiina Hyytinen

Contents

GLOSSARY	8
1 INTRODUCTION	9
1.1 Background.....	9
1.2 Objectives and outlining of the research.....	11
1.3 Materials and methods	11
1.4 Structure of the thesis	13
2 MANUFACTURE OF SODIUM CHLORATE	14
2.1 Chemistry related to the manufacture of sodium chlorate.....	14
2.1.1 Reactions related to the chlorate generation.....	15
2.1.2 Main side-reactions during the chlorate electrolysis	16
2.2 Production of sodium chlorate	17
2.2.1 Brine preparation	19
2.2.2 Electrolysis	20
2.2.3 Dehyponing of the cell liquor.....	22
2.2.4 Crystallization	22
2.2.5 Washing, drying and storage	23
2.3 By-product generation	23
2.4 Raw material consumption	24
2.5 Waste generation	25
3 STATUS OF SODIUM DICHROMATE IN THE MANUFACTURE AND IN THE REACH REGULATION.....	27
3.1 Role of sodium dichromate in the sodium chlorate process.....	27
3.2 Hazard classification and inclusion in the Authorization list	29
3.3 Authorization procedure	31
4 ALTERNATIVE MANUFACTURING TECHNOLOGIES AND SUBSTITUTE SUBSTANCES TO SODIUM DICHROMATE.....	34
4.1 Substitute substances to sodium dichromate	34
4.1.1 Sodium molybdate	34
4.1.2 Rare Earth Metal (REM) salts	35
4.1.3 Trivalent chromium	35
4.2 Overview of the hazard properties for the identified alternative substances	36
4.3 Alternative production technologies.....	38

4.3.1 Novel electrode coatings.....	38
4.3.2 Novel electrode materials	39
5 REMOVAL OF CHROMIUM FROM CHLORATE LIQUORS.....	41
5.1 Selective reduction with precipitation.....	42
5.1.1 Water soluble sulfides.....	42
5.1.2 Inorganic sulfur containing compounds.....	43
5.1.3 Ammonia / hypochlorite	43
5.1.4 Barium chloride.....	44
5.2 Electrochemical method	44
5.3 Ion exchange technique	45
6 INTRODUCTION TO THE EXPERIMENTAL STUDY	46
7 DEFINITION OF THE CONTROL VOLUMES AND THE SAMPLING POINTS.....	48
7.1 Brine treatment.....	50
7.2 Electrolysis.....	50
7.3 Retention tank and the storage vessel	51
7.4 Crystallization, centrifugation and the mother liquor circulation	51
7.5 Process condensate and the salt solution circulation.....	52
7.6 Hydrogen and effluent gas treatment	52
7.7 Maintenance break and the cell liquor treatment	53
8 SAMPLING, ANALYSIS AND THE RESULTS CALCULATION	56
8.1 Collection of the samples	56
8.2 Chromium analysis of the samples.....	56
8.3 Collection of the flow and surface level data.....	58
8.4 Calculation of the results	59
9 RESULTS.....	64
9.1 Sodium dichromate concentrations of the process samples	64
9.2 Chromium mass balance within the control volumes	65
9.3 Consumption of fresh sodium dichromate	67
9.4 Discharge of chromium from the process	68
9.5 Accumulation in the process liquors	69
9.6 Chromium mass balance for the process	70
9.7 Accumulation of chromium on the cathode surface	70
9.8 Total chromium analysis.....	72
10 CONCLUSIONS	74

10.1 Sodium dichromate concentrations and chromium mass balance within the process operations.....	74
10.2 Discharge of chromium from the process	77
10.3 Chromium mass balance for the process	79
10.4 Reduction of chromium on the cathode surface.....	80
10.5 Total chromium analysis.....	81
11 SUMMARY	84
REFERENCES	87
APPENDICES	
APPENDIX 1: Analysis results and the dilution ratios	
APPENDIX 2: Source for flow values and chromium concentrations	
APPENDIX 3: Chromium mass flows for the unit operations	

GLOSSARY

AOX	Adsorbable Organic Halogens
CLP	Regulation on Classification, Labeling and Packaging of chemicals
CMR	Carcinogenic, Mutagenic, Reprotoxic
CSA	Chemical Safety Assessment
CSR	Chemical Safety Report
DSA	Dimensionally Stable Anode
EC	European Committee
ECF	Elemental Chlorine-Free
ECHA	European Chemical Agency
ES	Exposure Scenario
HER	Hydrogen Evolution Reaction
MSC	Member State Committee
RAC	Committee for Risk Assessment
REACH	Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals
SEAC	Committee for Socio-economic Analysis
SVHC	Substance of Very High Concern

1 INTRODUCTION

1.1 Background

Due to environmental issues, producers of chemical pulp are required to decrease the AOX emissions formed during the pulping process. Therefore, instead of using elementary chlorine in the bleaching, the use of chlorine dioxide has been globally acknowledged as more environmentally-preferred chemical, in so called elemental chlorine free (ECF) bleaching. Chlorine dioxide is produced at the pulp mill from sodium chlorate, and that is, indeed, the main application for sodium chlorate. The production of sodium chlorate is a very energy consuming process as the manufacture is based on the electrolysis of brine. Approximately 5000 – 6000 kWh (BREF, 2007) of energy is consumed per one ton of produced sodium chlorate, and the energy expenses may be amounted as much as 70 % of the total production costs (Cornell, 2002). Thus, as the use of sodium chlorate has increased due to ECF bleaching, the development of the manufacturing process has been of interest for sodium chlorate manufacturers, mainly in terms of energy efficiency, during the last decades. The development work has primarily been focused on the research of novel electrode materials in order to improve the efficiency of the process. Also, the functioning mechanism of a necessary additive, sodium dichromate, has been examined. Thereafter, finding an alternative for sodium dichromate has been the focal point. Today, within European Union, the use of sodium dichromate in the production of sodium chlorate is reviewed in very detailed level due to regulatory reasons. Namely, because of the carcinogenic, mutagenic and toxic reproductive (CMR) effects sodium dichromate has, the further use of it will be authorized as of September 2017.

The authorization is a procedure defined in European Union chemical legislation, the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals). One of the fundamental objectives of the REACH is the improvement of the protection of humans and the environment from the risks posed by the chemicals. This aim is accomplished for the most hazardous substances, so called substances of very high concern (SVHC), namely by the authorization process. It is to ensure the control of proper risk management measures with

respect to the handling of a SVHC substance. The procedure aims also at the complete replacement of such chemicals by less hazardous alternatives without compromising the functioning of the EU market. The authorization procedure is an extensive process consisting of steps including the identification and the inclusion of a SVHC to the so called Authorization list; application for authorization; decision making regarding the authorization and the term of the permit; and the review of the permit. (ECHA, 2011; European Commission, 2013)

Sodium dichromate was added to the Authorization list in April, 2013. Ever since, the European chlorate manufacturers have been preparing extensive analysis required for the application for authorization. Thus, the process is currently ongoing, and the latest application date for the authorization is 31st of March, 2016. The so called sunset date is 21st of September, 2017. After the sunset date, the use of sodium dichromate is prohibited without the authorization. (European Commission, 2013)

Since the authorization procedure is new, only one authorization being granted so far, it is not completely known what kind of additional requirements regarding the use could be included in the authorization, if one is granted. However, it is clearly stated in the guidance document that in granting the authorization and setting any conditions, all discharges, emissions and losses are considered (ECHA, 2011). Therefore, it could be assumed that the set conditions and monitoring obligations might be dependent on the functioning of the process. As the the authorization is aimed to completely substitute the substance, it is also assumable that within some timeline, especially in the review of the authorization, the obligations could be tightened. Thus, it was considered important to research the behaviour of chromium in the sodium chlorate process to understand the current situation.

1.2 Objectives and outlining of the research

The experimental study included in this thesis was conducted at Kemira Oyj's sodium chlorate plant, in Joutseno. The purpose of this study was to determine the chromium mass balance for the sodium chlorate process, since it has not been researched before. Mass balance analysis can be utilized in chemical engineering for instance in reviewing the functioning of the process, and in determining the possible development and specific research needs for the concerned process. The determination of the chromium mass balance included the identification of the consumed and the discharged amounts of chromium. Additionally, the chromium balance was investigated in the unit operations in order to analyze the chromium behavior in the different parts of the process. An additional purpose was to provide information about the oxidation degrees of chromium in the varying process conditions.

The study was executed primarily to answer the following questions:

- What is the overall consumption of chromium in the process?
- In what amounts chromium is discharged from the process? By which routes the discharge is taken place?
- Is any chromium gaps identified within the process?
- In which oxidation degree the chromium is present in different process conditions?

In practice, these questions were answered by accomplishing a quantitative analysis of all the operations incorporating chromium.

1.3 Materials and methods

The formation of the chromium mass balance required determination of the chromium mass flows within the process, and the calculation of the discharged

amounts. For this purpose, samples were collected from parts of the process, matching the defined boundaries of the control volumes.

The samples were collected approximately once a week during the late winter, when the process is typically operated in stable mode with full capacity. The samples were taken by a process worker from sampling points which were agreed before the start of the study. From each sampling point, two bottles were filled after sufficient flushing.

Once the samples were collected, the analysis was started immediately in order to prevent crystallization of samples with high chlorate content. In case samples were not analyzed right after the sampling, they were diluted 50:50 to prevent the crystallization. The samples were analyzed for hexavalent chromium, since due to the oxidizing matrix of the liquors, it was assumed that the chromium is present in oxidized form. To assure this, part of the samples were analyzed also for total chromium. With respect to the preparation of the samples, and the actual analysis, all steps were done in accordance to the analysis instructions.

The flow data required for the certain balance calculations was obtained either from the process control system or from the local flow meters. In case flow meter had not been assembled at all, the amount of flow was calculated with the balance equations. The study utilized also information from varying sources, such as PI-diagrams, daily production records, the task forms filled by the process workers, and the analysis result forms from the laboratory.

Overall, the experimental study was comprised of the planning phase with regard to the sampling and the definition of the control volumes; of the actual sampling, analyzing and the data collection phase; and of the balance calculation phase.

1.4 Structure of the thesis

The content of the thesis is not solely related to the production process and its chromium balance, but also topics regarding the possible changes are discussed. The thesis starts, however, with the description about the manufacturing of sodium chlorate. The production process is represented comprehensively, since the understanding of the operations was essential for the experimental study. Also, the chemistry behind the chlorate manufacture, as well as the required raw materials and formed waste are described. The role of sodium dichromate in the process is discussed in chapter 3. Also, the main features of the authorization process are described in the same chapter, likewise the hazardous properties of the substance. In chapters 4 and 5, it was concentrated to the possibilities to substitute sodium dichromate or to intensify its use. The chapters are summarized based on the available studies and patents, and the author was not capable to judge their practical suitability for the purpose.

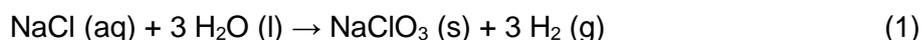
The report concerning the experimental study is covered by chapters 6 to 11. First, the initial condition is described, following with the aspects related to the planning phase. The more detailed description about the plant specific process flows is given here. Sampling, description of the conducted analysis, and the equations and the principles used in calculation of the results, are discussed in the following section. The results are reported in chapter 9 and the conclusions in chapter 10. The main findings of the study, their relation to the authorization, and the recommended actions are reported in the last chapter.

2 MANUFACTURE OF SODIUM CHLORATE

Sodium chlorate, NaClO₃, is an intermediate product that is manufactured from an aqueous solution of sodium chloride in electrochemical process. It is an efficient oxidizing chemical. The main application of sodium chlorate is the in-situ production of chlorine dioxide, ClO₂, at the pulp mill. Chlorine dioxide is further used for elemental chlorine free pulp bleaching (ECF bleaching). Based on records, even 95 per cent of bleaching of Kraft pulp within European Union utilizes chlorine dioxide, and thereof sodium chlorate. Other uses of sodium chlorate, although minor ones, are production of dyes, leather tanning and finishing, metal treatment, mining industry and use in explosives. (BREF 2007)

2.1 Chemistry related to the manufacture of sodium chlorate

In industrial scale sodium chlorate is produced from sodium chloride brine by electrolysis. Electrolysis means a process where chemical reaction takes place by passing an electric current through an ionic substance, the electrolyte, and results in chemical reactions at the electrodes, and the separation of the materials. The electrochemical generation of sodium chlorate is the second largest application of electrolysis. The process can be described by the overall chemical reaction:



In the process sodium chloride is oxidized to sodium chlorate whereas water is reduced to gaseous hydrogen. As the process is a multistage reaction, it is necessary to explore more in detail the electrochemical and chemical reactions occurring during the generation of sodium chlorate.

2.1.1 Reactions related to the chlorate generation

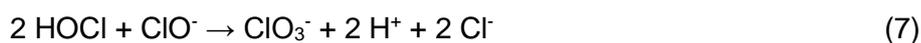
The main electrochemical reactions of the process, represented by reactions 2 and 3, occur in the electrolysis cell. While the electric current passes through the electrolyte in the chlorate cell, chloride ions, Cl^- , are oxidized to chlorine, Cl_2 , at the anode. Respectively, the hydrogen ions, H^+ , are reduced to hydrogen, H_2 , at the cathode.



As given in reactions 4 to 6, chlorine gas formed at the anode dissolves in the boundary layer and reacts with water forming hypochlorous acid, HOCl , and hypochlorite, ClO^- .



Finally, chlorate, ClO_3^- , is formed from hypochlorous acid and hypochlorite according to reaction 7:



The generation of chlorate proceeds slowly, and is at its optimal rate when the concentration ratio $[\text{HOCl}]:[\text{ClO}^-]$ is 2. This equilibrium state occurs at pH value equal to $(\text{pK}_a - \log 2)$, where pK_a refers to the equilibrium constant of reaction 6. Thus, the optimal pH range in the electrolysis cell is 5,9 – 6,7. Also temperature

affects strongly on the rate of the chlorate formation. (Cornell, 2002; Tilak & Chen, 1999)

2.1.2 Main side-reactions during the chlorate electrolysis

There are several possible side-reactions during the chlorate production by electrochemical means. Most important of those, are the reactions causing inefficient function of the chlorate cell, and those affecting the safety of the plant.

Oxygen gas is an undesired, but also unavoidable by-product during the electrolysis. Presence of oxygen in the cell liquor increases the energy consumption by decreasing the current efficiency of the cell. Moreover, it creates a safety risk at the plant. Excess oxygen in the cell gas, which is composed of H₂, Cl₂ and O₂, may create an explosive gas mixture with hydrogen. Cell gas may contain maximum 3 % of O₂ and/or 7 % of Cl₂. During the electrolysis process, oxygen may be formed by:

- the anodic oxidation of water;
- chemical decomposition of hypochlorous acid and hypochlorite in the bulk solution; and
- direct oxidation of hypochlorite at the anode. (Tilak & Chen, 1999)

While the chlorine is evolved at the anode, water is oxidized to oxygen. This reaction is thermodynamically possible at the potentials at which chlorine is generated. The generation of oxygen is increased in more alkaline conditions, and it is decreased with higher total current density. Electrode material affects also the selectivity towards the oxygen evolution. Moreover, the sodium chloride concentration has an important influence on the oxygen evolution. In case sodium chloride concentration is < 100 g/l, oxygen generation accelerates. Therefore, sodium chloride concentration should never decrease under 100 g/l.

Oxygen content in the cell gas may increase also due to the chemical decomposition of hypochlorous acid and hypochlorite in the bulk solution. Catalytic ions, such as Ir, Co, Ni, Fe, Cu and Mn, may act as catalysts and further increase the chemical decomposition of hypochlorite in the bulk solution. Therefore, the catalytic ion contents should be minimized in the brine and in the cell liquor. Direct oxidation of hypochlorite at the anode is possible as well. However, it is controlled by maintaining the pH slightly acidic, and by rapid circulation of the cell liquor in order to minimize the hypochlorite concentration at anode surface. (Cornell, 2002; Tilak & Chen, 1999).

At the cathode, reduction of chlorate and hypochlorite to chloride are the main side-reactions. By these reactions the current efficiency may be decreased significantly, since they are favored both thermodynamically and kinetically. Chlorate reduction is dependent especially on the electro-catalytic properties of the electrode material, whereas hypochlorite reduction is more mass transport dependent. Chlorate reduction is also accelerated on deteriorated surfaces of iron cathode, as iron oxides are involved on the reduction reaction. (Tilak & Chen, 1999; Wulff & Cornell, 2006)

Chlorate may be oxidized also to perchlorate. Although the formation of perchlorate is minor at 0.05 % efficiency rate, it may violate the whole product, especially in closed loop system, in case it accumulates in the cell liquor. (Tilak & Chen, 1999)

2.2 Production of sodium chlorate

Sodium chlorate is produced by a continuous process that is sensitive to operating conditions, chemical side reactions and impurities contained in the raw materials. The efficiency and even the safety of the process may be decreased by the factors interfering with the steady-state operation. Nevertheless, the process is highly optimized and consists of operations illustrated in Figure 1.

As each sodium chlorate plant is designed differently and may be complex by its recycle circuits, the flow chart is not complete, and it is supposed to give only an overview of the main operations and streams. Following sections will discuss the manufacturing process more in detail.

2.2.1 Brine preparation

The main chemical raw material, sodium chloride, is dissolved in warm water to form a saturated sodium chloride solution, the brine. The quality of the sodium chloride and water is an important factor in the process in order to maintain the performance of the electrolysis cells. Typically very pure or partially purified evaporated salts are used. Incoming process water is treated with chemical and physical means. Still, the brine needs to be purified. Calcium, magnesium and sulfates are the main impurities naturally occurring in sodium chloride. Calcium and magnesium may be deposited on the cathodes resulting increased energy consumption, whereas sulfates may accumulate on the surface of the heat exchanger, or contaminate the end product. Removal of the dissolved impurities can be achieved by means of salt metathesis reaction with the addition of Na_2CO_3 , NaOH and CaCl_2 in order to form insoluble compounds. Instead of calcium chloride, also barium chloride, BaCl_2 , may be applied. Additionally, fluoride and iron are purified from the brine too, if needed. Resulting precipitates are separated by pressure leaf filter with the assistance of diatomaceous earth as a filter precoat and filter aid. Sometimes, pressure leaf filtration is followed by secondary purifying operations. (BREF, 2007; Tilak & Chen, 1999)

Despite of the brine treatment, certain impurities may be present still in the cell liquor due to incomplete brine purification. As they tend to accumulate in chlorate cell with time, it is necessary to precipitate them from the chlorate liquor. Periodically, a small portion of the recycled mother liquor, or alternatively cell liquor, goes to the chemical treatment in order to reduce the concentrations of the impurities. (Tilak & Chen, 1999)

2.2.2 Electrolysis

In the electrolysis stage, brine is converted to chlorate by electrochemical and chemical means. Figure 2 describes the different elements related to the chlorate formation.

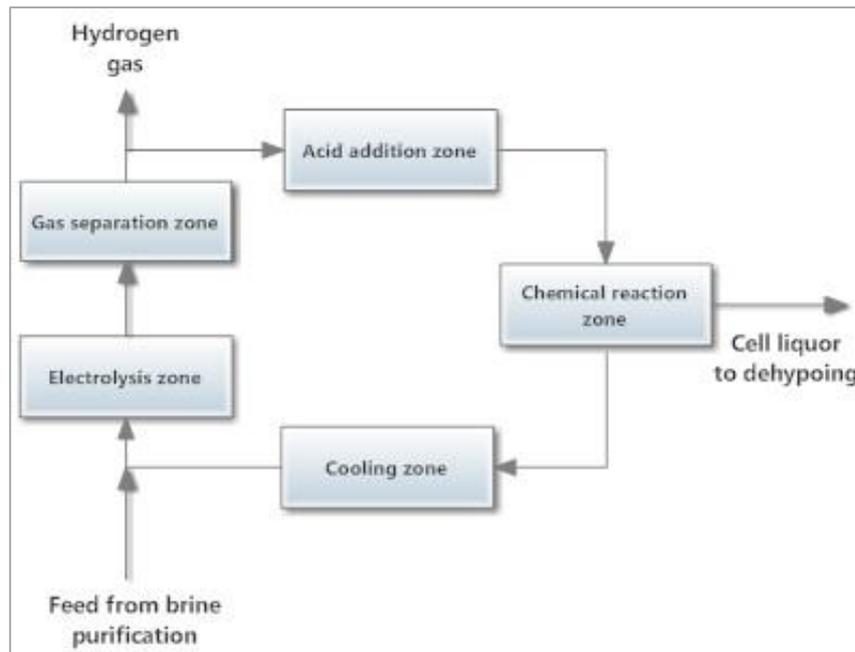


Figure 2. Elements of the chlorate formation. (Tilak & Chen, 1999)

Typical cell liquor contains 500 – 600 g/l sodium chlorate, 100 - 150 g/l sodium chloride and 3 - 5 g/l sodium dichromate. Additionally, there may be impurities present in the electrolyte, such as sodium sulfate and perchlorate. This liquor, also called the electrolyte, is circulated in the electrolysis system between the elements of the chlorate cell. More brine is added constantly to it and a portion of it is lead to the following process step.

The electrochemical reactions are taken place in the electrolysis zone which is generally called as the cell room. The cell room consists of cell boxes which have cathodes and anodes constructed in it. Anodes are made of titanium coated usually with mixed metal oxide solution, and correspondingly, cathodes are made of steel or titanium. The electrolyte is introduced to the lower part of the cell box.

Direct current (DC) is entered the cell box through busbars from rectifiers. As the current passes through the electrolyte, hydrogen is evolved at the cathode. The hydrogen separation occurs either in the electrolysis cell, in a separate vessel or in the chemical reactor, depending on the system configuration. The impurities contained in the hydrogen gas are removed. In addition to the cathodic hydrogen generation, chlorine is formed at the anode. It is dissolved in the solution forming hypochlorous acid and hypochlorite ions which are further reacted to form chlorate. The transformation into chlorate occurs in the chemical reaction zone. Relatively long period of retention time is required for chlorate formation due to slow reaction kinetics. The conversion rate is dependent also on the temperature and the pH of the electrolyte. Therefore, aqueous hydrochloric acid is added to the cell liquor in order to maintain proper conditions for chlorate formation. The acid addition is usually done right before the entrance of the cell liquor to the chemical reaction zone. Due to endothermic nature of the electrolysis reaction, the excess heat should be removed. This is done in the cooling zone that may be located within the chemical reactor or in a separate heat exchanger. The heat energy obtained in cooling is utilized in other process steps. The liquor circulation between the cells and the reaction tanks is achieved by either a hydrogen gas lift or by pumping. Typically, about 575 g/l sodium chlorate and 100 g/l sodium chloride are contained in the finished cell liquor. (BREF, 2007; Tilak & Chen, 1999)

There are different kinds of system configurations available for the chlorate cell. However, the main elements discussed earlier are contained in each configuration type. The electrochemical reactions are taken place in undivided cell, which are either monopolar or bipolar. The cells and the reactors may be operated in parallel or in series. To maximize the efficiency and the safety of the cell, the pH of the process is carefully controlled. The usual pH range is 6.0 – 7.0. Optimal temperature of the chlorate cell system is about 70 – 80 °C. Other factors affecting the economics of the process are electrolyte composition, current density and concentration, and the design of the chlorate cell system. Typical operating conditions for chlorate process using steel cathode and Pt/Ir coated anode are represented in table 1. (Tilak & Chen, 1999)

Table 1. Typical operating conditions for a chlorate cell. (BREF, 2007; Tilak & Chen, 1999)

Parameter	Value	Unit
pH	6.0 – 7.0	-
Temperature	70 – 80	°C
Current density	2 – 3	kA/m ²
Average cell voltage	2.75 – 3.6	V

2.2.3 Dehyponing of the cell liquor

The cell liquor from the electrolysis should be treated in order to remove the remaining hypochlorite ions. This is done mainly by chemical additives, possibly combined with temperature control. Unless the concentration of hypochlorite is reduced from the liquor, it can promote severe corrosion of the process equipment. Hypochlorite concentration is reduced by heating the liquor to 85 – 95 °C and applying sodium hydroxide for the pH control. This promotes transformation of hypochlorite to chlorate. The remaining traces can be removed totally by treating the liquor with reducing agents. Usually, hydrogen peroxide is favored due to clean and effective nature of the treatment. (Tilak & Chen, 1999)

2.2.4 Crystallization

After the dehyponing stage the treated chlorate liquor is usually 70 – 80 °C, and it contains sodium chlorate, sodium chloride, sodium dichromate and impurities. The liquor is fed to crystallization in order to separate the chlorate from the other components. This is typically conducted in a draft tube baffle (DTB) evaporative crystallizer. By a large propeller circulator, the suspended crystal magma is moved upwards in a central baffle tube to upper boiling evaporative zone, and downwards to the lower crystallizer zone. In the upper zone, supersaturated liquor is formed first, which then mixes with the crystal magma in the lower zone. Proper sized crystals are withdrawn from the bottom of the crystallizer section, whereas crystal fines are withdrawn from the upper part of the crystallizer zone and re-dissolved in the hot feed liquor. Typical operating conditions for a vacuum

crystallizer are approximately 30 - 35 °C and a pressure of approximately 0.025 bar absolute. The vacuum is obtained by a combination of a steam jet vacuum, a steam booster and a barometric condenser. Heat can be added to the crystallizer via a plate heat exchanger. Advantage of the method is that the heat energy contained in the cell liquor is utilized for the crystallization. Crystallization may be conducted also by cooling the liquor and adding sodium chloride to the solution to alter the solubility equilibrium, and thus promoting the crystallization. (Tilak & Chen, 1999)

2.2.5 Washing, drying and storage

The concentrated crystal slurry coming from the crystallizer contains about 15 w-% of crystals. Next, the crystals are separated from the mother liquor in hydrocyclone, and then washed with water in a pusher centrifuge. A thorough wash is needed in order to remove sodium dichromate residues from the crystals. After the centrifugation, the crystals contain about 1.0 – 1.5 w-% of moisture. In case dry crystals are manufactured, the moisture content is further reduced to 0.1 w-% in fluidized bed dryer with hot air. Fine chlorate particles contained in the used drying air are removed by scrubber systems. In order to produce liquid sodium chlorate, the crystals from centrifugation are dissolved in purified water to the desired concentration. The crystal and solution product are stored in a cool, dry and fireproof building before transportation to customer. (Tilak & Chen, 1999)

2.3 By-product generation

In addition to sodium chlorate, the process produces also hydrogen as a by-product. Hydrogen gas is evolved at the cathodes of the electrolysis cells. Approximately 60 kg of hydrogen is generated per ton of produced sodium chlorate. The amount of produced hydrogen is independent of the used production technology. The gas needs to be purified in order to remove the excess chlorine and oxygen contained in it. The purification is conducted by using caustic scrubbers, or alternatively leading the gas through carbon filter beds. The purified hydrogen gas may be compressed and delivered for utilization as an

energy source in heat and electricity production. Alternatively, it may be burned in boilers for steam generation at the chlorate plant. (BREF, 2007)

2.4 Raw material consumption

Sodium chlorate is manufactured from sodium chloride salt and water by electrochemical means. In theory, the process consumes 549 kg of sodium chloride per ton of produced sodium chlorate. In practice, the consumption is about 550 – 580 kg. The purity of the salt is of great importance, but likewise, the quality of the process water should be controlled as well. Therefore, the incoming process water is usually purified by varying means. In order to produce one ton of sodium chlorate, approximately 0.4 – 2.7 m³ of purified process water is needed. Remarkably larger amount of water is used in cooling operations, about 70 – 400 m³ per ton of produced sodium chlorate. (BREF, 2007)

Sodium chlorate process is extremely energy intensive, and therefore electrical and thermal energy are the major inputs of the process. The approximate total energy consumption is 5 000 – 6 000 kWh per ton of produced sodium chlorate. Most of the energy is consumed during the electrolysis. It uses direct current (DC) electric power, which is obtained by using rectifiers and transformers. The rest of the consumed energy is transferred into the cooling water systems and to the air of the facility. The heat can be partly recovered from electrolyte solution by heat exchangers, and it can be utilized during the crystallization. Yet, externally produced heat in a form of steam is required for crystallization and drying. (BREF, 2007)

Additionally, some auxiliary chemicals are used in the process. Table 2 lists the substances, their application and the approximate consumption.

Table 2. Typical auxiliary chemicals, their use and consumption in sodium chlorate process. (BREF, 2007)

Additive	Use	Consumption kg / 1000 kg of produced NaClO ₃
Na ₂ CO ₃	Precipitation of calcium in brine treatment	0.04 - 2
CaCl ₂	Precipitation of sulfate in brine treatment	0 – 0.46
Diatomaceous earth	Filter aid in the filtration of brine	N/A
Na ₂ Cr ₂ O ₇	-Acts as a buffer agent to maintain pH -Suppresses undesired reactions -Prevents corrosion of steel	0.01 – 0.15
NaOH	-Precipitation of magnesium in brine treatment -Hydrogen gas scrubbing -pH control in dehyponing - Neutralization after acid wash	15 – 30
HCl	-pH control of the cell liquor -Acid wash of the cells	15 – 30
H ₂ O ₂	Removal of hypochlorite in dehyponing	1 – 3
N ₂ (gas)	Purging of the installation	0.4 – 6

2.5 Waste generation

Waste that is produced in the sodium chlorate process can be divided into process sludge, spent filter materials and waste waters. It is important to separate chromium containing and chromium free waste. Sodium dichromate is a necessary additive in the process. It contains hexavalent chromium, Cr(VI), which

has carcinogenic effects. The chromium species are discharged from the process through the waste generated by the process.

The main solid waste of the process originates from the brine purification. Sludge from the treatment does not contain chromium unless chromium containing process water is used for the salt dissolution. In the brine treatment, impurities of the salt are precipitated chemically. The solid impurities are accumulated at the bottom of the dissolving tanks where they are removed by filtering. Composition and the amount of the formed sludge depend on the quality of the incoming salt. Typically, the sludge is consisted mainly of calcium carbonate, magnesium hydroxide and calcium sulfate. (BREF, 2007)

Chromium containing sludge may be created during few steps of the sodium chlorate process. At some plants, accumulated sulfate and calcium ions are removed by treating the cell liquor periodically with precipitating chemicals followed with filtration. In such case, also part of the chromium is precipitated, and ended up in the sludge. Additionally, some chromium is precipitated in the cell room and the reaction tank along other solids. The solids are formed as steel cathodes corrode due to oxidizing effect of the cell liquor. The precipitate is removed during scheduled maintenance when the electrolytic cells are washed with hydrochloric acid. The waste acid is filtered forming a chromium containing filter cake. (BREF, 2007)

The process streams may be filtered at couple of stages of the process. This is essential before leading them to the electrolysis in order to avoid entrance and accumulation of impurity particles in the cell room. Therefore, the filtering materials, such as filter cartridges, sock filters and paper bags used for disposing of them, are counted as solid waste generated by the process. These waste materials may be contaminated with chromium, depending on the filtered material. (BREF, 2007)

3 STATUS OF SODIUM DICHROMATE IN THE MANUFACTURE AND IN THE REACH REGULATION

Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, is an orange, crystalline solid that is manufactured from ores containing trivalent chromium oxides. It is produced both in anhydrous and dehydrate form. Sodium dichromate has several applications, including, for example, metal finishing, anticorrosion agent in coatings, wood preservative, cleaning agent and vitamin K production. It is used also as an intermediate in production of tanning salts and Cr(VI) pigments, and in the manufacture of Cr(III) oxides.

The consequence of sodium dichromate with regard to the efficiency of the sodium chlorate process is significant. With the current technology, sodium chlorate could not be produced cost-effectively, or even safely, without the addition of chromium species to the process. However, hexavalent chromium is identified as a CMR substance, and due to this, the use of it will be a subject to authorization as of 21st of September, 2017. The role of sodium dichromate in the production process is discussed hereinafter. Also the regulatory status and the authorization process are summarized shortly.

3.1 Role of sodium dichromate in the sodium chlorate process

Sodium dichromate is used as a necessary additive in the chlorate process. Typically, sodium dichromate concentration in the electrolyte is 3 – 5 g/l, and the total consumption is between 0.01 – 0.15 kg per ton of produced sodium chlorate. Sodium dichromate contains hexavalent chromium, and it is identified as a human carcinogen. Regardless of the extensive work for finding a substitute substance for sodium dichromate, all of the current industrial production technologies rely on its use. The benefits related to the use of sodium dichromate are discussed more in detail in the following sections. (BREF, 2007).

Buffering action

As mentioned earlier, the optimal pH range for chlorate cell is 5.9 – 6.7. Due to the HOCl/OCl⁻ equilibrium, the system has a natural buffer capacity. The use of sodium dichromate enhances the buffering action in the critical pH range according to the following equilibrium reaction:



Sodium dichromate is a weak base that maintains the acidity at a similar level. Therefore, it resists the pH changes from the addition of another acid or base. In chlorate liquors, the buffer capacity is directly proportional to the hypochlorite and dichromate concentrations, and equal to the sum of the individual contributions of hypochlorite and dichromate. Thus, due to buffering action, sodium dichromate addition enables chlorate formation at the optimal level by maintaining the pH at the optimal range. (BREF, 2007; Viswanathan & Tilak, 1984)

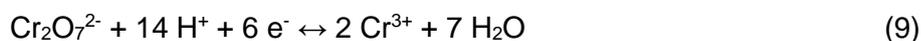
Inhibition of anodic oxidation reactions

Oxygen evolution paths include oxygen discharge from water molecules and the direct oxidation of hypochlorite. Because electrolysis is conducted in undivided cell, and thus, there is no membrane separating the products from anode and cathode, oxygen is mixed with hydrogen evolved at the cathode. This causes a risk for explosion. As discussed already, the use of sodium dichromate maintains the pH of the electrolyte slightly acidic. As both of the oxygen evolution reactions favor alkaline conditions, therefore the amount of oxygen generated via these routes can be minimized by sodium dichromate addition.

Suppression of cathodic inefficiency reactions

Cathodic reduction of chlorate and hypochlorite at the cathode are the main inefficiency reactions in the chlorate process. These reactions can be suppressed by sodium dichromate addition. Small amount of sodium dichromate in the

electrolyte creates about 10 nm thick film of chromium(III) hydroxide, $\text{Cr}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, on the layer of the cathode by reduction of Cr(VI) during the cathodic polarization according to reaction 9:



The film suppresses electrochemically the unwanted reduction of hypochlorite and chlorate by creating an adverse potential gradient. However, the hydrogen generation can still occur at the cathode regardless of the created film. Material of the cathode, electrode potential and concentration of the dichromate affect the thickness and the growth rate of the film. (Cornell, 2002; Wagner, 1954)

Protection of steel cathodes

Usually cathodes used in the electrolytic chlorate cells are made of titanium or steel. Steel has a tendency to corrode in the electrolyte solution that contains highly oxidizing agents hypochlorite and chlorate. The corrosion is undesirable as it shortens the lifetime of the cathodes and also contaminates the electrolyte liquor with metal particles. The impurities may cause short-circuits and lower the rate of electrolyte circulation obstruction in the narrow electrode gaps. Also the end-product may be contaminated. On the other hand, corrosion of the cathode material also renews the surface constantly by removing the deposits from the surface. The presence of sodium dichromate in the chlorate liquor may have a retarding effect on the corrosion due to formed chromium hydroxide film. However, there are contradictory aspects on this. (Cornell, 2002; Viswanathan & Tilak, 1984; Wulff & Cornell, 2006)

3.2 Hazard classification and inclusion in the Authorization list

Sodium dichromate is a hazardous substance that is acutely toxic after oral, dermal or inhalation exposure. It is also corrosive to skin, and it is expected to cause damage to the eyes. Available epidemiological data indicate that sodium dichromate may cause an allergic skin reaction, and also an occupational asthma after inhalation. The carcinogenic, mutagenic and reproductive toxic effects are

well-known. Due to before mentioned hazards, sodium dichromate is classified as carcinogenic, mutagenic and reproductive toxic (CMR) substance according to Regulation (EC) No. 1272/2008. Additionally, repeated exposure on sodium dichromate causes local inflammation in the respiratory track, and systemic toxic effect in kidneys. (ECB, 2005) Sodium dichromate has a harmonized classification listed in Annex VI to CLP Regulation. The hazard classes, categories and statements are represented in Table 3.

Table 3. Harmonized classification of sodium dichromate.(ECHA, 2011)

Hazard Class and Category	Hazard statement
Oxidizing Sol. 2	H272: May intensify fire; oxidizer.
Acute toxicity 3	H301: Toxic if swallowed.
Acute toxicity 4	H312: Harmful in contact with skin.
Skin corrosion 1B	H314: Causes severe skin burns and eye damage.
Skin sensitization 1	H317: May cause an allergic skin reaction.
Acute toxicity 2	H330: Fatal if inhaled.
Respiratory sensitization 1	H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled.
Muta 1B	H340: May cause genetic defects.
Carc. 1B	H350: May cause cancer.
Repr. 1B	H360FD: May damage fertility or the unborn child.
STOT RE 1	H372: Causes damage to organs through prolonged or repeated exposure.
Aquatic Acute 1	H400: Very toxic to aquatic life.
Aquatic Chronic 1	H410: Very toxic to aquatic life with long lasting effects.

Sodium dichromate was identified as a Substance of Very High Concern (SVHC) according to Article 57 (a), (b) and (c) of REACH Regulation, and was therefore included in the candidate list for authorization on 28 October 2008, according to ECHA's decision ED/67/2008. Considering the high volumes of supplied sodium dichromate in the end-uses, and the risk for significant worker exposure in some of the end-uses, ECHA indicated sodium dichromate as a high priority substance,

and recommended it to be included in the Authorization list in December, 2011. By Commission Regulation EU/348/2013, sodium dichromate was added to Annex XIV of REACH Regulation on 17 April 2013. (ECHA, 2011; European Commission, 2013)

3.3 Authorization procedure

Authorization procedure is a process of the European Union chemical legislation, the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulation, which entered into force on 1st of June, 2007. REACH is aimed at, inter alia, to improve the protection of humans and the environment from the risks posed by the chemicals. For the chemicals imposing severe and irreversible risk for human health and the environment, the aim is managed in authorization procedure. It is to ensure the control of proper risk management measures with respect to the handling of the substances of very high concern (SVHC substances). The procedure is aimed also at the complete replacement of such chemicals by less hazardous alternatives without compromising the functioning of the EU market.

Identification and inclusion of a SVHC substance to Authorization List

The first step of the process is to identify the SVHC substances. In article 57 of the REACH regulation it is outlined, that the substances having the following intrinsic properties may be included to the so called Authorization List, Annex XIV of the REACH Regulation:

- a) substances classified as carcinogenic in category 1A or 1B;
 - b) substances classified as germ cell mutagenic in category 1A or 1B;
 - c) substances classified as reproductive toxic in category 1A or 1B, and substances having adverse effects on sexual function and fertility or on development;
 - d) substances which are persistent, bioaccumulative and toxic (PBT);
 - e) substances which are very persistent and very bioaccumulative (vPvB);
- and

- f) substances which do not fulfill the criteria of points (d) or (e), but for which there is scientific evidence of serious effects on human health or the environment of an equivalent level of concern compared to points (a) to (c).

The Member State (MS) or ECHA can propose the substance to be identified as SVHC upon request of the European Committee (EC). In case the substance is identified as SVHC, it is added first to the so called Candidate List. The substances listed in the Candidate List are prioritized, and substances having the highest scores are recommended to be added in the Authorization List. After the recommendation, there is a public consultation period, after which the Member State Committee (MSC) makes an opinion, ECHA finalizes it, and EC makes the final decision about the inclusion to the Authorization List. The decision contains information on the last application date and the so-called sunset date, after which the substance must not be used if the user does not have a granted authorization for the use.

Application for Authorization

The Application for Authorization (AFA) is made by manufacturer, importer or downstream user of the substance. The authorization is applied for a certain use of the substance. The applicant can take either the so called adequate control route or the so called socio-economic route. In the adequate control route it should be demonstrated, that the risks arising from the continued use of the substance are properly controlled, by means of a chemical safety assessment (CSA), recorded in chemical safety report (CSR). In CSA it is determined, what is the level of the risk posed by the substance, and how the risk is controlled in terms of risk management measures. In addition, the possible alternative substances and technologies must be analyzed. In case such are available, a substitution plan must be included. The adequate control route can be applied only for SVHC substances for which an effect threshold limit can be determined. Otherwise, it is needed to take the socio-economic assessment (SEA) route. In the SEA route it is demonstrated that the risks arisen from the use of the substance are outweighed by the socio-economic benefits, and that no suitable alternatives are available. The analysis of alternatives is required, anyway. The

socio-economic benefits are demonstrated in the socio-economic analysis. (ECHA, 2011)

The decision and the term of the permit

After submitting the application for authorization, the opinion regarding the authorization is drafted within ten months by the Committee for Risk Assessment and the Committee for Socio-economic Analysis. In addition to the information given in the application, all relevant information available is considered. Once the draft opinion is available, the applicant has a possibility for commenting. The final opinions are sent to the Commission and the Member States. The final decision on granting or refusing the authorization is decided by the Commission.

The authorization is specified with information regarding the legal entity, identity of the substance, the use for the granted authorization, conditions for the granted authorization, the time-limited review period, and any monitoring arrangements.

Authorizations are reviewed within specified time-line, which is specified in the granted authorization. A review report must be submitted 18 months before the expiry date of the time-limited review period. In the review report only the parts of the original authorization application that have changed, need to be included. Authorization may also be reviewed at any time if circumstances change so that the risks are affected, or the socio-economic impact is affected. (ECHA, 2011)

4 ALTERNATIVE MANUFACTURING TECHNOLOGIES AND SUBSTITUTE SUBSTANCES TO SODIUM DICHROMATE

Most important benefit of sodium dichromate in the chlorate production is its nature to form the chromium hydroxide film on the cathode, and thereby to prevent the reduction of hypochlorite and chlorate species. Moreover, due to buffering characteristics of sodium dichromate, the chlorate formation may reach the optimum level. Sodium dichromate has an additional role as inhibiting the evolution of excess oxygen, which in turn enhances the safety and the economics of the chlorate cell. On the other hand, sodium dichromate has a negative effect on both the cathodic and the anodic potentials. However, it is important that the suitable alternative substance or manufacturing technology has similar beneficial properties than sodium dichromate to enable an economically competitive production process. The substitute substance should not have any toxic properties, either.

4.1 Substitute substances to sodium dichromate

4.1.1 Sodium molybdate

Li et al. have studied the function of sodium molybdate, Na_2MoO_4 , as a replacement for sodium dichromate in the chlorate production. Sodium molybdate was identified having similar kind of buffering properties than sodium dichromate. Sodium dichromate has a buffer capacity over the pH range of 5 – 7, whereas sodium molybdate acts as a buffer agent between pH 5 – 6 by forming $\text{HMoO}_4^-/\text{MoO}_4^{2-}$ equilibrium in solution. Although the range is not totally optimal for the chlorate formation, but, nevertheless, the buffer action of sodium molybdate was regarded effective in the laboratory scale pilot cell. It was also observed that hydrated MoO_2 forms an effective film similar to chromium hydroxide film, and thus the parasitic reactions at the cathode were suppressed. In addition, lower cathode surface potential was obtained than with sodium dichromate, which improved the electric efficiency of the process. Due to safety aspects, oxygen content in the off-gas is an important parameter of the process. With molybdate additive, the oxygen level varied between 3.7 – 4.8 %. This level of oxygen present in the off-gas is potentially dangerous. The current efficiency of the

system was reported to be 91 – 92 %, which is significantly lower than with sodium dichromate (96 %). (Li, Twardowski, Mok, & Tam, 2007)

4.1.2 Rare Earth Metal (REM) salts

In a study by Gustavsson et al. (2010) the applicability of rare earth metal salts as a replacement for sodium dichromate is described. It was concluded that by the use of yttrium chloride, samarium chloride and lanthanum chloride the cathodic hypochlorite reduction was suppressed. Also hydrogen evolution reaction was activated by the addition of rare earth metal ions to 0.5 M sodium chloride solution at 25 °C. But, when the operating temperature was increased to 70 °C, the effect was hindered. At more concentrated sodium chloride solutions, the activation caused by REM ions was disappeared totally. The conclusion was that high sodium chloride concentration is detrimental to the activating effect, especially at industrial conditions typically maintained in the chlorate cell. Thus, REM salts are not suitable to replace sodium dichromate in the chlorate process. (Gustavsson, Nylén, & Cornell, 2010)

4.1.3 Trivalent chromium

Hedenstedt et al. (2012) have used trivalent chromium compounds in the in-situ formation of hexavalent chromium compound to substitute the direct addition of sodium dichromate to the chlorate process. The trivalent chromium compound was introduced directly to the specific process stream, where it was oxidized to hexavalent chromium. Alternatively, the trivalent chromium compound was first oxidized in a separate vessel and then lead to the specific stream. No externally added hexavalent chromium compounds were utilized in the method. However, the use of trivalent chromium compound is based on the same chemistry than with hexavalent chromium compounds. Suggested chromium (III) compounds, for example chromium trichloride, CrCl_3 , may be added as salts, as solutions, or as melts in case the melting point is sufficiently low. Also other chromium compounds having a valence number less than six are suitable for the method. (Hedenstedt & Edvinsson Albers, 2012)

4.2 Overview of the hazard properties for the identified alternative substances

As one of the main reasons for the desire of substituting sodium dichromate in the chlorate process are its carcinogenic, mutagenic and toxic reproductive properties, it is essential to look for alternatives not having such toxic hazards. All of the notified health hazards for the alternative substances, obtained from ECHA's classification and notification inventory, are summarized in table 4.

Because none of the classification is harmonized, there is some variance in the assigned hazard statements indicating the severity of the specific hazard. Nevertheless, all of the substances are irritant or corrosive to eyes and skin, are sensitizing to skin and respiratory tract, and additionally some of them are acutely toxic. Only single notifications for sodium molybdate and chromium trichloride indicate CMR properties. Thus, the alternates seem to have similar hazard properties than sodium dichromate except for the CMR properties.

Table 4. Hazardous properties of the alternative substances. (ECHA)

Substance	Hazard statement
Sodium molybdate, Na_2MoO_4 CAS 7631-95-0	H302: Harmful if swallowed. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H319: Causes serious eye irritation. H332: Harmful if inhaled. H335: May cause respiratory irritation. H341: Suspected of causing genetic effects. H351: Suspected of causing cancer. H361: Suspected of damaging fertility.
Chromium trichloride, CrCl_3 CAS 10025-73-7	H301: Toxic if swallowed. H302: Harmful if swallowed. H312: Harmful in contact with skin. H314: Causes severe skin burns and eye damage. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H318: Causes serious eye damage. H319: Causes serious eye irritation. H330: Fatal if inhaled. H332: Harmful if inhaled. H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled. H373: May cause damage to organs.
Yttrium (III) chloride hexahydrate, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ CAS 10361-92-9	H302: Harmful if swallowed. H312: Harmful in contact with skin. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H318: Causes serious eye damage. H319: Causes serious eye irritation. H332: Harmful if inhaled. H335: May cause respiratory irritation.
Samarium (III) chloride hexahydrate, SmCl_3 CAS 10361-82-7	H315: Causes skin irritation. H316: Causes mild skin irritation. H317: May cause an allergic skin reaction. H319: Causes serious eye irritation. H320: Causes eye irritation. H335: May cause respiratory irritation
Lanthanum (III) chloride, LaCl_3 CAS 10099-58-8	H315: Causes skin irritation. H317: May cause an allergic skin reaction. H318: Causes serious eye damage H319: Causes serious eye irritation. H335: May cause respiratory irritation.

4.3 Alternative production technologies

In addition to efforts used for finding a substitute substance to sodium dichromate, there has also been research focused on developing novel production technologies that would enable sodium chlorate production without the use of sodium dichromate. The studies have concentrated on developing novel electrode coatings for cathodes and novel electrode materials. The functionality requirements for the chlorate cathode are electric efficiency during the chlorate synthesis in terms of low overpotential for hydrogen evolution, and the inactivity against hypochlorite and chlorate reduction reactions in the presence and in the absence of sodium dichromate. It is also important that the material has high stability against the mechanical stress during the hydrogen evolution, and that it is resistant to corrosive conditions of the process and to impurities present in the electrolyte solution. Moreover, the cathodes should be easily and cost-effectively manufactured in addition to the ease of use in the chlorate cell. (Cornell, 2002)

4.3.1 Novel electrode coatings

Iron-molybdenum

Krstajic, Jovic and Martelli (2007) have studied chlorate production by electrolytical means using cathodes that were coated with an iron-molybdenum alloy. The cathodes were made from carbon steel sheets. After preparations they were immersed in a bath for iron-molybdenum alloy electrodeposition. The bath solution consisted of ferric chloride, sodium molybdate, sodium bicarbonate and sodium phosphonate. The deposition was resulted in 20 micrometer thick alloy, which comprised of 47 % by weight of molybdenum and 53 % by weight iron. The cathodes were tested in a commercial chlorate cell. High energy efficiency of the system was achieved in comparison with similar cell assembly containing non-coated cathodes made of carbon steel. Also, the hypochlorite and chlorate reduction was inhibited by activated test cathodes, reaching the overall cell efficiency of 95 – 98 %. (Krstajic, Jovic, & Martelli, 2007)

Ruthenium dioxide

Cornell (2002) has researched the use of ruthenium dioxide coated titanium cathodes for hydrogen evolution. The cathodes were prepared by an industrial thermal decomposition method, and were microporous by structure. The tested cathodes were active in terms of hydrogen evolution reaction and resulted in lower overpotential for hydrogen evolution than with iron cathodes. In the absence of sodium dichromate, the chlorate reducing reaction was occurred fast on ruthenium dioxide layer, and it was the dominating reaction when tested in industrial conditions. After sodium dichromate addition, the reduction reactions were hindered. (Cornell, 2002)

Zirconium oxide

Brown & Carlson have described an invention of a zirconium plate coated with zirconium oxide, which can be used as a cathode member in an electrolytic cell for hypochlorite production. The invention, nevertheless, is not limited to hypochlorite generation, but is applicable also in chlorate production. The plates were planar elements made of zirconium or other suitable zirconium alloys. The plates were pretreated in order to obtain suitable surface roughness, and then covered with zirconium oxide layer. Zirconium oxide layer contained zirconium oxide as a main component and other optional species as minor components. The plates were tested in a test cell equipped with coated titanium anode as a counterelectrode. The zirconium oxide layer showed good performance in terms of hypochlorite reduction. (Brown & Carlson, 2010)

4.3.2 Novel electrode materials

Schulz et al. studied the use of cathodes made of nano-crystalline alloys consisting of titanium, ruthenium, iron and oxygen, and additionally either chromium, manganese, vanadium, tungsten, antimony, platinum, or lead, in the electrochemical synthesis of sodium chlorate. The alloy has a crystalline form with a particle or grain size less than 100 nanometers. The alloy is prepared by mechanically grinding the mixture of the given metals or their oxides under inert or oxygen-containing conditions. The formed powder is compacted to form the

cathodes to be used in the chlorate cell. The cathodes were reported to be stable in the electrolyte solution, and improved the electric efficiency of the synthesis. In addition, the cathodic hypochlorite decomposition did not occur. In case the alloy comprises up to 50 % of chromium, the use of sodium dichromate could be reduced substantially, or even eliminated completely. (Schulz; Van Neste; Boily; & Jin, 1997)

5 REMOVAL OF CHROMIUM FROM CHLORATE LIQUORS

Sodium dichromate concentration in the electrolyte solution is 3 to 5 g/l. Regardless of the closed process and recycling of solutions, part of chromium is emitted through water, sludge, the product and other solid waste. Overall discharge of the chromium containing waste is approximately 0.1 – 1 kg per ton of produced sodium chlorate. Majority of the chromium loss is due to the escape from the process along the sludge formed during the treatment of the brine and the cell liquor. The output of chromium through the product is approximately 0,005 kg per ton of produced sodium chlorate. Emissions to water are negligible. Since efficient function of the process requires sufficient concentration of sodium dichromate in the cell liquor, and due to the constant chromium losses, sodium dichromate is added to the electrolyte regularly. Total consumption of sodium dichromate is 0.01 – 0.15 kg per ton of produced sodium chlorate. (BREF, 2007)

Chlorate manufacturers have already applied a number of techniques to separate the chromium from the end-product and to intensify the use of sodium dichromate in their processes. Most important of those are:

- an efficient treatment of the brine in order to decrease the amount of impurities entering the cell room, which in turn reduces the need for precipitation treatment of the electrolyte solution;
- sodium chlorate recovery by crystallization, which results in high purity end product;
- washing and centrifugation of the formed crystal; and
- an efficient recycling of sodium dichromate along the process streams.

Regardless of the above mentioned procedures, part of the chromium is still discharged from the process because of the presence in the liquor undergoing the concerned operation. Due to tightening legal requirements, it would be beneficial if the use of chromium was further intensified in sodium chlorate

process. This could be done by removing the chromium from the chlorate liquor before it is undergone a production step where chromium is lost, e.g. cell liquor treatment. The concentrated chromium slurry could be regenerated before it is fed back to the process. There are some methods available, many of them discovered already in the 1970's, to separate chromium from concentrated chlorate solutions. (Colman & Tilak, 1995)

5.1 Selective reduction with precipitation

Chromium can be separated from chlorate liquors by reducing the hexavalent chromium to divalent and/or trivalent chromium compounds, and by adjusting the pH, if required, in order to facilitate chromium precipitation at low solubility pH range. Namely, chromium solubility is dependent on both the pH and the temperature of the treated solution. Chromium reduction can be achieved by several compounds. However, suitability of the reducing chemicals are limited by the purity requirements of the sodium chlorate product, the potential chlorate co-reduction, and also the conditions of sodium chlorate process.

5.1.1 Water soluble sulfides

The hexavalent chromium values can be removed by the use of water soluble sulfides, such as sodium sulfide, sodium bisulfide, potassium bisulfide or hydrogen sulfide. At least three-molar proportion of the water soluble sulfide compound is needed to convert one mole proportion of sodium dichromate to trivalent stage. After the precipitation chemical is employed to the chlorate liquor, the solution is acidified to pH of below about 5, which results in the precipitation of insoluble trivalent chromium compound. The pH of the slurry is adjusted to about 7, and thereafter the formed precipitate may be separated. (Partridge & Hildyard, 1974)

5.1.2 Inorganic sulfur containing compounds

Sodium dichromate can be removed from aqueous sodium chlorate liquors by chemical precipitation with inorganic sulfur containing compounds to form insoluble chromium hydroxide compound, and by suitable separation technique. First, the pH of the impure chlorate solution is adjusted to about 9 – 13 with sodium hydroxide to facilitate the formation of the reduced chromium compound. The inorganic sulfur compound is added in a specific molar ratio to sodium dichromate. The formed chromium compounds may be partly or completely reduced, and to enhance the complete reduction, the pH is adjusted to about 2 – 4. At this pH range, the completely reduced chromium compounds may be in soluble form, and therefore the pH is adjusted to about 6 – 8, when the reduced chromium hydroxide becomes less soluble. The resulting solid chromium hydroxide particles may be separated by a suitable technique, such as filtration or settling. Typical inorganic sulfur containing compounds which can be employed in the process, include, inter alia, thiosulfates, bisulfates, metabisulfites, bisulfites and thiosulfates of alkali metal and alkali earth metals, and also ferric sulfite, ammonium bisulfate, and mixtures thereof. In order to avoid the reaction between the employed precipitation chemical and sodium hypochlorite present in the chlorate liquor, the latter should be chemically decomposed before chromium removal. (Kaczur & Mendiretta, 1979)

5.1.3 Ammonia / hypochlorite

The reduction of chromium (VI) to chromium (II) or (III) can be achieved by using ammonia and sodium hypochlorite under alkaline conditions. The process uses ammonia in excess, but it can be recovered and recycled. The actual reaction kinetics is uncertain, but nevertheless, sodium dichromate is partially reduced during the chemical treatment. The excess ammonia is then removed by distillation, and concentrations of less than 50 mg/l of ammonia are achieved. The complete reduction and precipitation of chromium is conducted by adjusting the pH of the liquor with hydrochloric acid. Due to operation of the sodium chlorate process, the pH of the liquor should be maintained within 6 to 7.5. At this range, the solubility of the reduced chromium compound is less than 0.2 mg/l, required that the temperature of the liquor is 80 °C. Cross-flow filtration could be

used for the separation of the chromium precipitate. In case cross-flow filtration is operated in back pulse mode, the chromium oxide may be concentrated up to 50 grams of chromium per litre of liquor. (Alford, 1992)

5.1.4 Barium chloride

Chromium removal by chemical precipitation method is achieved by first adjusting the pH of the chlorate liquor to about 7 – 8, when hexavalent chromium is present as chromate ion. The chromate is then precipitated with barium chloride, carbonate or hydroxide, using stoichiometric amount of the salt. The precipitated chromate is slightly soluble, and can be separated from the solution by suitable means. The separated precipitate is treated with acid in order to dissolve the chromium species for re-use in chlorate cell. Before returning the chromium back to the process, the remaining barium ions should be removed. This is obtained by precipitating them with, for example, soluble sulfates. The solution is then recycled to the electrolysis. (Scholander & Brännland, 1969)

5.2 Electrochemical method

Hexavalent chromium values can be removed from aqueous chlorate solutions by electrochemically reducing the hexavalent chromium to trivalent chromium, depositing the reduced chromium as chromium hydroxide on the cathode layer. The electrolyte flows through the three-dimensional cathode structure having a high surface area, which permits a sufficient contact time required for the chromium reduction. The cathode may be constructed of graphite or various other electro-conductive metals, alloys, oxides or other compounds. The anode may be comprised of any material, for example, graphite or metal. The applied voltage between the electrodes is between 2 to 3 volts, and the superficial current density between 200 to 300 A/m², depending on the electrode materials and the design of the cell. As the chromium hydroxide deposits on the cathode surface, the exposed surface area of the cathode decreases causing loss of effectiveness with respect to chromium removal. The cathode may be regenerated by removal of trivalent chromium deposit by conversion to soluble hexavalent chromium. The

regeneration may be achieved by circulating chlorine or hypochlorite through the electrode. (Lipsztajn, 1987)

5.3 Ion exchange technique

In ion-exchange technique, dichromate ions are retained from chlorate solution by passing the dichromate containing stream through a strongly basic quaternary ammonium chloride ion-exchange resin. As the chlorate solution is acidic the hexavalent chromium is present as dichromate. When the pH is adjusted to basic, dichromate is converted to chromate. Therefore, as the ion exchange resin becomes exhausted with the captured dichromate ions, it is regenerated by passing basic sodium chloride brine through the bed, when the dichromate ions are transformed into chromate ions. Chromate ions are more easily removed from the fully loaded resin as they are less tightly held by the resin than the dichromate ions. The chromate can be released from the resin and returned back to the electrolysis cell after the pH adjustment. (O'Brien, 1974)

6 INTRODUCTION TO THE EXPERIMENTAL STUDY

The experimental study was conducted at Kemira Oyj's production site in Joutseno. The study examined the sodium chlorate manufacturing process, and more specifically, the behavior of chromium within the process. The study aimed at defining a chromium mass balance for the process, covering the main operations where chromium is incorporated. Motive for this is that today the use of chromium in a form of sodium dichromate is researched and analyzed very extensively, due to an on-going authorization process, regulated in the European chemical legislation, the REACH regulation. The experimental study was conducted in order to support the current and the future needs related to the balance analysis of sodium dichromate. The mass balance can be utilized in chemical industry for reviewing the functioning of the process, and in determining the possible development and specific research needs for the process.

Before this study, the chromium mass balance had been analyzed only at very general level at the Joutseno sodium chlorate plant. The rough calculations were based on the input of chromium and the output through the product. Typically, sodium dichromate is present in the cell liquor in concentrations of 3 to 5 g/l. As the amount of chromium present in the process is decreased constantly due to a minor discharge through the product, batches of sodium dichromate are introduced to the process when needed. The consumption of sodium dichromate has been followed by recording the added amounts. The other raw materials and additives introduced to the process do not contain any chromium species. The raw salt and the water are chromium-free already once entering the plant, but however, they are undergone a treatment process to remove other impurities from them. (Hujanen, 2014)

Previously, it has been assumed that the chromium is discharged via the product, and more extensively, through the sludge formed during so called cell liquor treatment. The treatment operation is Joutseno specific task, and it is described more in detail in chapter 7. The discharged amounts through the product have been determined based on the production volumes, whereas the removal through

the sludge has not been quantified by research at all. It has rather been assumed that the difference between the input of chromium and the output through the product equals the amount emitted through the sludge. Within the process, there has not been any follow-up of the chromium amounts in the process streams other than the regular analysis of the dichromate concentration in the cell room and in the product. The chromium has not really been an issue to be focused on. (Hujanen, 2014)

Based on the initial condition, it was decided that the study will be focused on the process operations where chromium is involved. These included the whole production process and also the monthly executed cell liquor treatment. The production process was reviewed in order to identify the possible chromium gaps. The cell liquor treatment was studied to obtain more specific figures about the chromium discharge through the formed sludge. Also, the amount chromium reduced on the cathodes was determined. Furthermore, it was desired to research the oxidation degrees of chromium in different process conditions. As a result, the study was to provide a chromium mass balance for the sodium chlorate process.

Overall, the experimental study was comprised of the planning phase with regard to the sampling and the definition of the control volumes; of the actual sampling, analyzing and the data collection phase; and of the balance calculation phase. The execution of these steps and the factors affecting them, are reported in the next chapters followed with the results and the final conclusions.

7 DEFINITION OF THE CONTROL VOLUMES AND THE SAMPLING POINTS

Research of the chromium mass balance on the unit operation level is important to identify the possible chromium gaps within the process. The definition of that required regular collection of process samples. As the process is consisted of several operations, it was divided into separate control volumes, and the process samples were collected from sampling points matching the boundaries of the formed control volumes. After detailed study of the Piping and Instrumentation diagrams (PI-diagrams), the control volumes were defined around the main unit operations, considering also the existence of the sampling possibility and a flow meter. However, there were some limitations in those, and therefore all essential process streams could not be analyzed for their chromium mass flow. The control volumes and the sampling points are illustrated in figure 3. It should be noted, that all of the streams and the vessels are not included in the figure in order to keep the flow chart as simple as possible. The sampling points are marked in the figure, too.

Operations and the streams that are incorporated within the control volumes are described in the following sections in order to give an overview about the essential streams regarding the determination of the chromium balance.

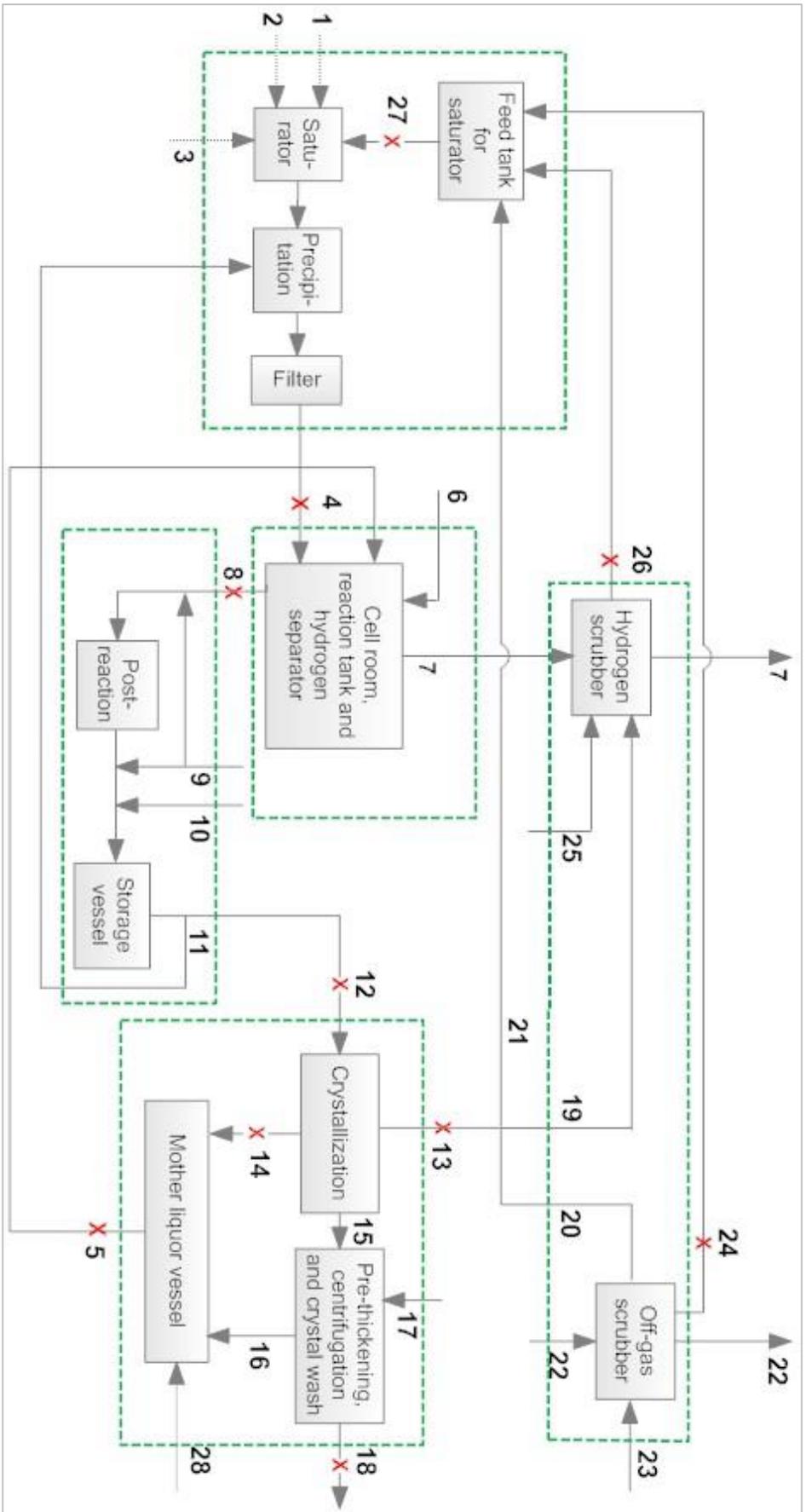


Figure 3. Defined control volumes are illustrated with dashed line and the sampling points with red mark, respectively.

7.1 Brine treatment

The purpose of the brine treatment is the preparation and the purification of the saturated sodium chloride solution, the brine, and the control of feeding it to the electrolysis. The brine is prepared from solid raw salt (1), water (2) and from the salt solution coming from the neighboring plant (3). The input of these streams is not constant, but however, it is regular as the ambient sodium chloride concentration in the cell room is controlled by the intake of these streams. The brine is prepared in the saturator, wherefrom it is pumped through couple of storage vessels to the continuous bag filter and thereafter, to the electrolysis. Before the filtration, part of the brine is fed to a precipitation unit together with treated chlorate liquor (11) coming from the storage vessel. The idea of the precipitation is to remove certain impurities, such as iron, calcium, fluoride, magnesium, phosphorus and silicon. In the preparation of the brine, also some circulated streams are utilized in terms of chemical and heat values. The chlorate containing process condensate (13) formed in the crystallization, and the hypochlorite streams (24, 26) formed in hydrogen and gas treatment units, are collected in the feed tank of the saturator, and used for the saturation of sodium chloride. (Hujanen, 2014; PI diagrams, 2009)

With respect to the balance calculations, the limitation in this control volume was the missing flow meters between the vessels. Also, due to some internal circulation of the feeds between the different vessels, no reliable balance calculations could be done in between, and thus the boundaries of the control volume were extended to cover all of the operations described previously.

7.2 Electrolysis

The control volume of electrolysis is composed of the reaction vessel, the cell room and the hydrogen separator. The electrolyte is circulated continuously at fast rate between these bodies. The electrolysis feeds, the treated salt solution

(4) and the mother liquor (5) elsewhere from the process, are introduced to the electrolysis via the reaction vessel, as well as hydrogen chloride (6) which is used for the pH control. The formed cell liquor (8) is departed from the control volume through the reaction vessel as an overflow. The formed hydrogen gas (7) is removed from the electrolysis through the hydrogen separator. (PI diagrams, 2009)

7.3 Retention tank and the storage vessel

The cell liquor (8) is treated with sodium hydroxide (9) and hydrogen peroxide (10) in order to remove the remaining hypochlorite ions from the cell liquor. Sodium hydroxide is added in two phases, before the retention tank and right after it, followed with an addition of hydrogen peroxide. The treated chlorate liquor is stored in the storage vessel before it is pumped to the crystallization. Additionally, constant amount of the liquor (11) is fed to the precipitation unit of the salt solution treatment. (PI diagrams, 2009)

7.4 Crystallization, centrifugation and the mother liquor circulation

In the crystallization, the chlorate liquor (12) is superheated inducing the evaporation of water, and further, the forming of the crystals. The evaporated water contains also some chlorate, and this process condensate (13) is collected in an own storage vessel. Inside the crystallizer, part of the mother liquor (14) is removed behind the upper part of the settling zone, and the stream is pumped to the mother liquor vessel. As a result of the crystallization, a crystal suspension (15) consisting of 15 w-% of crystals in mother liquor is produced. The stream is pumped to pre-thickening followed with the centrifugation, where the crystals are separated and washed with water (17). The mother liquors from the pre-thickener and the centrifuge (16) are collected also in the mother liquor vessel, wherefrom it is pumped back to the electrolysis. Due to limitations related to the sampling possibilities, the mother liquor from the centrifuge could not be analyzed. (Hujanen, 2014)

Mother liquor vessel works also as a passage point for fresh 60 w-% sodium dichromate solution (28) to the process. In case the concentration in the cell room has decreased to certain level, fresh sodium dichromate solution is pumped to the mother liquor vessel, wherefrom it is spread further in the process. (Hujanen, 2014)

7.5 Process condensate and the salt solution circulation

The chlorate containing process condensate (13) is collected in an own vessel wherefrom it is pumped to several operations. The condensate stream is utilized in hydrogen and effluent gas scrubbing operations to detach the remaining chlorine ions contained in the streams. Additionally, it is fed to the dust scrubbers as well as to the centrifuges for clean-up purposes of the equipment, and also to collect the valuable chemical species attached on them. However, most of the condensate stream is pumped straight to the feed tank of the saturator, and thus utilized in the saturation of the raw salt (21). The outlet feeds from all scrubbing operations are collected eventually in the feed tank of the saturator, too. The loop for the chlorate containing condensate is called as salt solution circulation. As the feeds for the scrubbing units are irregular, and also relatively negligible, they were not included in the study, except for the hydrogen and effluent gas washing operations. (PI diagrams, 2009)

7.6 Hydrogen and effluent gas treatment

The chlorine-containing hydrogen gas (7) formed during the electrolysis is separated from the cell liquor in hydrogen separators, and run to the hydrogen scrubber. In the scrubbing towers the hydrogen gas is washed with process condensate and sodium hydroxide (25). The purified hydrogen gas is led out from the process for further utilization, whereas hypochlorite solution (26) formed in the scrubbing tower is pumped either to the effluent gas scrubbing unit, or to the feed tank of the saturator. The hypochlorite from the effluent gas treatment (24) is

collected also in the same tank. Circulation of hypochlorite solution from hydrogen scrubbing to off-gas scrubbing is not included in figure 3 in order to simplify the flow chart. (PI diagrams, 2009)

7.7 Maintenance break and the cell liquor treatment

As it was initially known that chromium is discharged extensively during the cell liquor treatment, samples were collected in different phases of the treatments. The accumulation of chromium on the surfaces of the cathodes was determined by collecting so called shut-down samples. The progress of the maintenance break and the samples that were collected during the operation, are explained in following sections.

Shut-down

At Joutseno sodium chlorate plant, the used salt contains high amounts of sulfate ions which accumulate in the process causing major problems in the operation. Therefore, portion of the chlorate liquor is treated regularly in order to decrease the amount of the undesirable sulfate ions. The treatment is carried out monthly for the cell liquor, by turns from cell room N1 or N2. Once the cell room is emptied, it is possible to accomplish other maintenance tasks as well. The maintenance break is started by executing several shut-down tasks within the whole process, and last shutting down the electrolysis current. The cell liquor is kept in the cell room still for about 15 minutes, because the corrosive nature of the cell liquor contributes the removal of impurities from the surfaces of the electrodes and the cell room. Additionally, sodium dichromate, part of which has been precipitated on the surface of the cathodes, is dissolved again in the cell liquor as the current is off. To determine the amount of chromium accumulation on the cathodes, shutdown samples were taken from the cell room just before switching off the current, and after 15 minutes from the shut-down. (Hujanen, 2014)

Cell liquor treatment

The actual cell liquor treatment is done in separate treatment vessels. First, the cell liquor is pumped into a treatment vessel A. The pH of the liquor is adjusted to acidic, and calcium chloride slurry is mixed with cell liquor to precipitate the sulfate ions. The mixture containing solid calcium sulfate, is pumped through a filter press to a treatment vessel B. After the removal of the sulfate ions, high amounts of calcium ions are contained in the liquor. Calcium is detrimental for the functionality of the electrodes as well, and therefore the liquor is treated a second time. First, the liquor is pumped back to the treatment vessel A where the pH is adjusted to alkaline. Sodium carbonate slurry is added to the liquor generating calcium carbonate precipitate. The slurry is run through again the filter press until the desired calcium ion concentration is achieved. It may take up to a couple of days to complete the filtration. The treated liquor is pumped gradually back to the process via the precipitation unit of the salt solution. The operation is illustrated also in figure 4. (Hujanen, 2014; Operating instruction, 2010; PI diagrams, 2009)

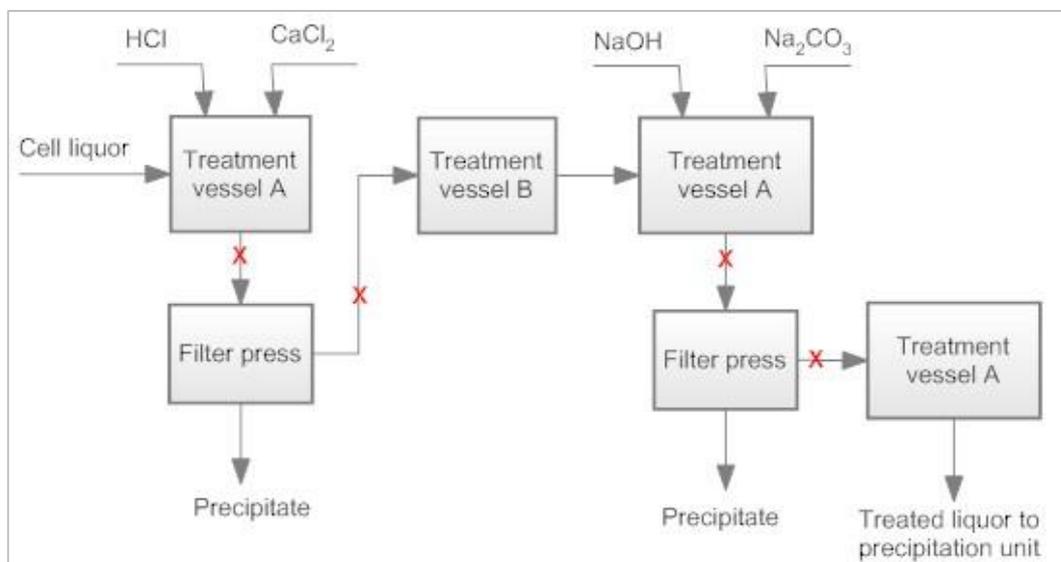


Figure 4. The flow chart for cell liquor treatment. The samples were collected from the marked streams. (PI diagrams, 2009)

Following samples were taken during the cell liquor treatment in order to research the amount of chromium discharge during the different phases of the operation:

- after the addition of calcium chloride just before the filtration
- sulfate-free filtrate
- after the addition of sodium carbonate just before the filtration
- calcium-free filtrate

8 SAMPLING, ANALYSIS AND RESULTS CALCULATION

8.1 Collection of the samples

The process samples were collected approximately once a week between March, 21st and May, 13th. The process samples were taken by the process workers from marked sampling taps which were agreed commonly before the start of the experimental study period. From each sampling point two sample bottles were filled after sufficient flushing of the piping. Shutdown samples as well as the samples from the liquor treatment were collected by the process worker who was in shift during the respective treatment operation. The operations were scheduled by the management.

8.2 Chromium analysis of the samples

The samples were analyzed for their chromium content in the plant's central laboratory. The analyses were done on the same day the samples were collected, but in case the immediate analyzing was not possible, the samples were diluted 1:1 to prevent their crystallization. As the process conditions are very oxidizing, it was considered that the chromium is present in the hexavalent state. Therefore, all samples were analyzed namely for hexavalent chromium with a spectrophotometer. The aim was also to analyze part of the samples for total chromium to confirm the oxidation degree of chromium from different process samples.

Determination of sodium dichromate concentration by spectrophotometer

Hexavalent chromium reacts with 1,5-diphenylcarbazide and forms a purple complex in slightly acidic conditions. By measuring the absorbance of the known solutions by the spectrophotometer, the hexavalent chromium concentration of the unknown sample can be analyzed from the calibration curve.

The samples were first diluted in order to adjust the dichromate concentration of the sample to the measurement range. The dilution was acidified with 5 weight percent of sulfuric acid, after which 0.5 ml of 1,5-diphenylcarbazide was added to the solution. The purple complex was formed within a minute, after which the solution was measured. Sodium dichromate concentration of the sample was calculated from equation 10:

$$Na_2Cr_2O_7 \left(\frac{mg}{l} \right) = a \cdot d \quad (10)$$

where

a = concentration from the calibration curve

d = total dilution ratio of the sample

The concentrations from the calibration curve, and the dilution ratios of the process samples, are available for all measurements in appendix 1. The obtained sodium dichromate concentration was transformed to hexavalent chromium concentration by multiplying it by 0.379, which is the ratio of the molecular weights of chromium and sodium dichromate.

Determination of total chromium concentration by AAS

The total chromium content was determined from acidified sample by atomic adsorption spectroscopy (AAS) in air-acetylene flame. The measurement was executed at the wavelength of 357.9 nm.

The analysis was done with the linear calibration method. For the calibration curve, six standard samples from 0.1 to 2.0 mg/l were prepared from so called work solution, containing 10 mg/l of chromium. The work solution was diluted from a commercial standard solution with chromium concentration of 1 g/l. Based on the results of the standard samples, a calibration curve was drawn.

The process samples were acidified with sulfuric acid and hydrochloric acid. The samples were measured, and the total chromium concentration of the measured sample was calculated from the calibration curve. The final chromium concentration was determined by taking into account the dilution ratio:

$$Cr \left(\frac{mg}{l} \right) = a \cdot d \quad (11)$$

where

a = concentration from the calibration curve

d = total dilution ratio

8.3 Collection of the flow and surface level data

The sodium chlorate process is controlled with Metso DNA automation system. The system enables the control of the process as well as the monitoring from individual PC's. The functionality of exporting continuous measurement data to Excel was utilized in gathering the data regarding the flows and the surface levels of the vessels. The data was collected from the time period when the actual collection of the samples took place. The flow data was taken as an average for the sampling period, and the surface level values were taken as a difference between the beginning and the end of the actual sampling period. Because all of the flow meters were not integrated to the process control system, for some process streams the flow data was obtained from the local flow meters. The source for the flow data that were used in the balance calculations, are given in appendix 2. In case the data is obtained from automation system, it is marked with "DNA", whereas "local" stands for a local flow meter.

8.4 Calculation of the results

Once the analyses were accomplished, and all the data regarding the flows and the surface levels were collected, the results were calculated in excel sheets. First, the chromium mass flow was determined for each individual process stream. Principally, the chromium mass flow was calculated always based on the chromium content of the analyzed sample and the respective flow data obtained from the local flow meter or from the automation system. If this was not possible, the chromium mass flow was calculated according to the balance equations, which are presented later. Besides the chromium mass balance calculations, total mass flow for the process streams were determined based on the stream specific density. The used figures for densities were average values of the regular measurements by the central laboratory. If such average value was not available, it was measured during the study.

Mass balance equations

A mass balance, also known as a material balance, is a technique which is used to analyze physical systems by applying the law of conservation of mass. In the sense of mass balance, the conservation of mass means that the material entering the system must also leave the system or accumulate within the system. This means that the material cannot be created or disappeared spontaneously. By applying this method in chemical engineering, it is possible to detect mass flows that could otherwise stay unidentified.

The general form of the mass balance equation is as follows:

$$In = Out + Accumulation \quad (12)$$

This form can be used for a system without a chemical reaction, or, in case of a chemical reaction, for a single chemical species not incorporated in the reaction. The form of the equation can be applied both for systems consisting of one

operation, and for systems consisting of several operations. In case of several operations, the system is typically divided into sub-systems, the control volumes. The mass balance analysis is applied for all of the control volumes. The total mass of the input stream is the sum of the masses before the actual entry to the system. Respectively, the total output mass is the sum of the masses that is departed from the system.

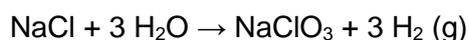
The mass can enter the system in two major ways, by diffusion or by convection. However, the diffusion can be dismissed in case the velocity entering the system is large and the concentration difference is small. Then, the mass entering or leaving the system is due to convection, which can be represented as follows:

$$m = \dot{m} = \sigma \cdot \dot{V} \quad (13)$$

The equation can be applied both for the total amount of the entering species as well as for single chemical species. In case the balance is analyzed for single chemical species, σ stands for the mass concentration, whereas in case of total mass σ stands for the density of the stream.

Amount of hydrogen removed from the process

For the mass balance in control volume of electrolysis, the departing amount of hydrogen gas had to be noticed. The amount of the formed gas was calculated from the total reaction:



It was assumed that the incoming streams - the brine, the mother liquor and hydrochloric acid solution - are mixed immediately with the cell liquor due to the extreme liquor circulation between the cell room and the reaction vessel. First,

the amount of sodium chloride in moles which is brought into the electrolysis among the total feed, was calculated based on the average sodium chloride mass concentration in the cell room, 105 kg/m³. The mass of hydrogen gas was then obtained from the stoichiometry of the total reaction.

$$\dot{m}_{H_2} = \frac{V_{incoming\ streams} \cdot c_{NaCl,av.}}{M_{NaCl}} \cdot 3 \cdot M_{H_2} \quad (14)$$

The mass of the forming hydrogen gas was then subtracted from the input mass flow in order to obtain the mass flow for the output flow. This amount of water that is removed among the gas as humidity was neglected from the calculations.

Amount of suspension created by the crystallizer

The amount of suspension was needed to specify the total and the chromium mass flows for mother liquors coming from the crystallizer and from the centrifuge. The amount of the suspension was calculated from the production rate of the crystal, and from the typical solid content of the suspension. The crystal production rate was obtained from daily production figures.

$$\dot{m}_{susp} = \frac{m_{crystal,prod}}{0.15} \quad (15)$$

Based on the amount of the suspension, the chromium mass flows could be determined for all of the concerned streams by using the basic equations.

Shutdown samples

It is known that when the electrolysis current is on, part of the sodium dichromate contained in the cell liquor is reduced on the surface of the cathodes forming approximately 10 nm thick solid layer. However, the amount of chromium

accumulated on the cathodes is not necessarily directly proportional to the thickness of the layer. The amount could be estimated based on the geographical surface area of the cathodes, but then the roughness of the cathodes is not considered. Because the precipitated chromium is oxidized and dissolved in the cell liquor once the electrolysis current is switched off, the amount was determined by measuring the dichromate concentration before C_{BS} and after $C_{15 \text{ min}}$ the shutdown. The volume of the cell liquor $V_{\text{cell liquor}}$ was obtained from the process control system.

$$m_{\text{reduced}} = V_{\text{cell liquor}} \cdot (C_{BS} - C_{15 \text{ min}}) \cdot 0.379 \quad (16)$$

In order to analyze the magnitude of the result, the thickness of the film d_{film} was determined by first calculating the amount of precipitated chromium per m^2 of the cathode area, and then dividing with the density of the reduced compound ρ :

$$d_{\text{film}} = \frac{m_{\text{reduced}}/A_{\text{cathodes}}}{\rho} \quad (17)$$

According to Cornell, the reduced chromium compound is chromium (III) hydroxide, $\text{Cr}(\text{OH})_3$ (Cornell, 2002). Therefore, density value of 3.11 g/cm^3 was used in the calculation of the film thickness.

Cell liquor treatment

Chromium is discharged during the cell liquor treatment due to the co-precipitation along other impurities present in the liquor. The cell liquor treatment is a two-step process where sulfate and residual calcium ions are removed by salt metathesis, by applying pH control agent and the actual precipitating chemicals. In the first step, the pH of the cell liquor is acidic. Thus, chromium co-precipitation is not likely to occur in significant amounts as hexavalent chromium is in the soluble dichromate form in acidic conditions. It is assumed that the

majority of the chromium discharge is taken place in the second step of the treatment, since in alkaline conditions the hexavalent chromium is present in less soluble chromate form, and is therefore more exposed to the capture by the filter press.

The total amount of chromium discharge was calculated based on the analyzed samples collected during the treatment operation, and of the corresponding volume of the liquor. The initial amount of chromium before the actual treatment was obtained from the second shutdown sample $C_{15 \text{ min}}$. The volumes of the cell liquor in each step of the treatment were obtained from the process control system.

9 RESULTS

9.1 Sodium dichromate concentrations of the process samples

The sodium dichromate concentrations were analyzed from the process samples in order to define the chromium mass balance within the process, but also to understand how the concentrations in each stream are changed in time, especially with respect to the cell liquor treatments and sodium dichromate additions. Additionally, as sodium dichromate is analyzed regularly only from few sample types by the central laboratory, it was important to provide information about chromium content for the other process streams as well. The results are represented in table 5.

Table 5. Sodium dichromate concentrations of the different process streams were analyzed with spectrophotometer, except for samples 24 and 26. The corresponding results were obtained by total chromium analysis.

Date	4, mg/l	5, mg/l	8, mg/l	12, mg/l	13, mg/l	14, mg/l	18, mg/kg	24, mg/l	26, mg/l	27, mg/l
21.3.	221	4135	3433	3573	253	4215	7	89	93	204
27.3.	CELL LIQUOR TREATMENT									
28.3.	159	3385	3088	2853	124	3630	12	74	73	152
2.4.	156	3640	3025	3105	156	3705	13	74	87	153
9.4.	143	3470	3090	3105	160	3510	11	66	80	155
17.4.	CHROMIUM ADDITION									
22.4.	148	3855	3443	3488	192	4090	13	66	81	216
24.4.	CELL LIQUOR TREATMENT									
2.5.	115	2815	2843	3033	94	3415	3	58	66	105
7.5.	CHROMIUM ADDITION									
13.5.	174	4405	3853	3898	100	4405	8	74	97	186

The timing for the liquor treatment operations and the sodium dichromate additions are informed, too. The numbering of the sample refers to the streams described in the previous chapter. The description is given also in appendix 2.

9.2 Chromium mass balance within the control volumes

The chromium mass balance within the process operations was determined in order to analyze the chromium behavior in the process and to identify possible chromium gaps. The chromium balance was calculated based on the analysis results presented in table 5, and thus the chromium mass flows stand for the chromium (VI). As a result, for all of the sampling occasions, a separate mass balance was obtained. One of those was chosen to be represented as a typical mass balance for the process operations. As a selection criterion, it was considered important that the balance describes the process being on full operation. Moreover, the accuracy of the mass balance of the liquors within the control volumes and in the whole process was reviewed. The mass balance for the process is represented in figure 5. It was determined based on the samples that were collected on 2nd of April, 2014. The balance calculations for the other sampling occasions, except for 28th of March, are given in appendix 3. The balance for March 28th was not included, since the process flows had been very unstable during the sampling, and the calculated balance was very irrational, containing also negative values.

The chromium feed into the process, nor the output of it through the process sludge, were not included in the represented balance, as those were done irregularly on a batch basis. The results for the total input and the output of chromium are summarized in the following sections.

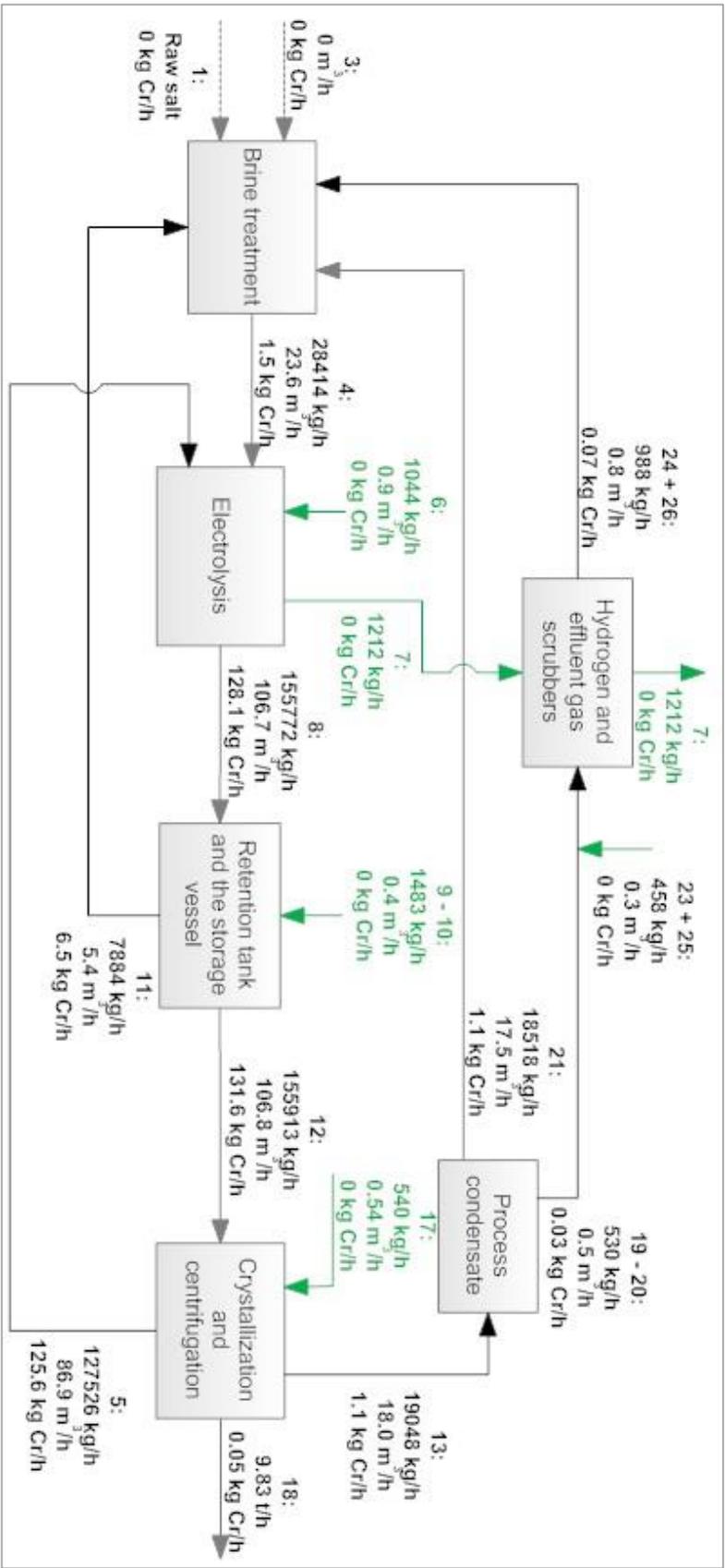


Figure 5. Mass balance was calculated for the chromium and the total flows. Total flows are given also in volumetric units.

9.3 Consumption of fresh sodium dichromate

For the determination of the chromium mass balance for the entire process, it was needed to identify the consumption of the fresh sodium dichromate during the observation period, 18th of March till 6th of May. Sodium dichromate was added to the process when the concentration in the cell room had decreased below a specified limit. The consumption was recorded by weighing the storage container. The addition was done three times during the spring. The observation period was started on 18th of March when the first addition was done. The second addition was in the middle of April, and the third addition was done in the end of the observation period, on 7th of May. The last addition was no longer included in the chromium mass balance.

The supplier of the commercial sodium dichromate solution had informed that the solution is consisted of 60 w-% of sodium dichromate. Thus, this value was used in the calculations of the chromium additions. Dates and the added amounts are given in table 6.

Table 6. Additions of sodium dichromate solution to the process.

Date	18.3.2014	17.4.2014	7.5.2014
Amount of the commercial Na ₂ Cr ₂ O ₇ solution added to the process, kg	330	300	480
Amount of chromium added to the process, kg	79	72	114

The total amount of chromium consumed in a form of fresh sodium dichromate during the observation period, was 151 kg.

9.4 Discharge of chromium from the process

Chromium discharge from the process was assumed to take place through the product and the sludge formed in the cell liquor treatment. The discharged amounts through these routes were calculated for the observation period, 18th of March till 6th of May.

Discharge through product

The discharge of chromium through the product was calculated based on the daily production figures. A value of 3.2 mg/kg was used for chromium content for the crystal. This figure was an average of all of the respective measurements executed by the central laboratory and the author during the observation period. The value was based on the hexavalent chromium analysis. The total chromium output through the product was 35.4 kg during the observation period.

Discharge during cell liquor treatment

Chromium was discharged also through the sludge which was formed during the cell liquor treatment. The discharged amounts from two cell liquor treatments, executed in March and in April, were included in the study. The chromium discharge $m_{\text{total discharge}}$ was calculated from the difference of the amount in the beginning of the treatment $m_{15 \text{ min}}$ and in the end of it $m_{\text{calcium filtrate}}$. The main results are summarized in Table 7.

Table 7. The chromium discharge among the sludge was determined from the initial and the final concentration of the cell liquor.

Maintenance break	$m_{15 \text{ min}}$ kg Cr (VI)	$m_{\text{calcium filtrate}}$, kg Cr(VI)	$m_{\text{total discharge}}$, kg Cr(VI)
March	128.7	115.0	13.7
April	121.2	103.3	17.9

The total discharge of hexavalent chromium through the sludge was 31.6 kg between 18th of March and 6th of May.

9.5 Accumulation in the process liquors

The total amount of chromium, which is present in the process, is a dynamic amount, in other words, the amount is changed constantly due to the continuous discharge and the batch-wise additions of sodium dichromate. Also the amount of the process liquors is varied from day to day. Thus, there may be great fluctuation in the measured chromium concentration although the actual amount had not really changed that much. To be able to form the chromium mass balance for the process, it was needed to consider also the amount of chromium present in the liquors in the beginning and in the end of the observation period. These amounts are represented in table 9. The difference reflects the chromium accumulation in the process liquors. This was calculated from the chromium concentration in the cell liquor, and from the respective volume of all process liquors. The latter was obtained from the surface level data of the process vessels. The chromium concentration on 18th of March was analyzed before the commercial sodium dichromate solution was added to the process.

Table 8. Total amount of chromium in the process.

Date	$V_{\text{process liquors,}}$ m^3	$C_{\text{cell room,}}$ $\text{kg/m}^3 \text{Cr(VI)}$	$m_{\text{total,}}$ kg Cr(VI)
18.3.2014	700	1.20	838
6.5.2014	704	1.14	800

It can be seen that the total amount of chromium present in the process had decreased during the observation period. It means that chromium was consumed also from the internal storage of the process.

9.6 Chromium mass balance for the process

The chromium mass balance for the process was done for the observation period, from 18th of March till 6th of May, 2014. The balance is consisted of the identified inputs and outputs specified in the previous sections. In the sense of the balance principles, the addition of fresh sodium dichromate and the consumption from the process liquors were considered as the input to the process, totally 189 kg of chromium (VI). Respectively, chromium discharge through the product and the sludge were considered as the output from the process, totally 67 kg of chromium (VI). The balance for the sodium chlorate process is illustrated in Figure 6.

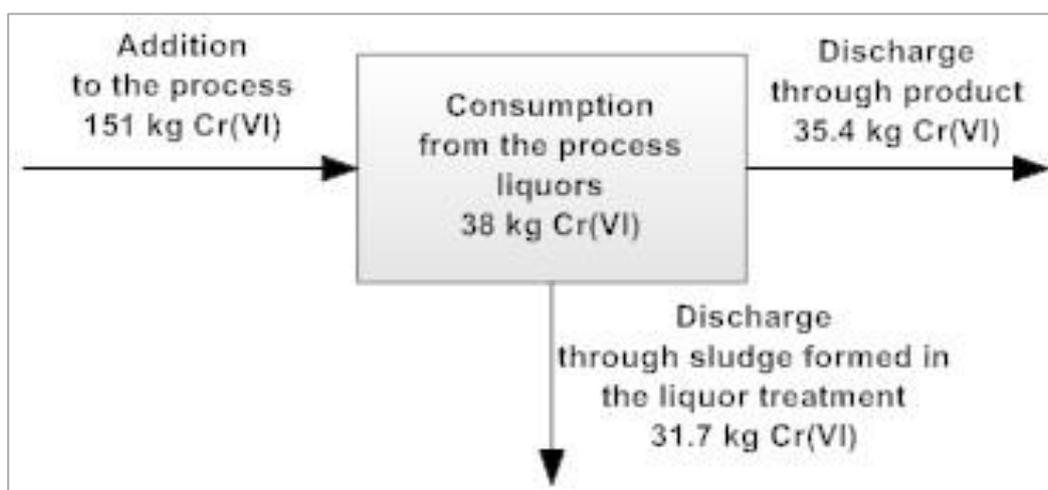


Figure 6. Chromium mass balance in the sodium chlorate process was consisted of different factors.

It can be seen that the identified consumption of chromium is significantly larger than the identified discharge of it.

9.7 Accumulation of chromium on the cathode surface

In addition to the chromium mass balance, the accumulation of chromium on the surfaces of the cathodes was studied during the shutdown of electrolysis. As the

chromium accumulation is occurred when the electrolysis is started, and as the chromium is dissolved in the cell liquor again after the shutdown, the net effect with respect to the balance was considered to be zero. Thus, the chromium mass balance was not affected by the precipitation on the cathodes. Nevertheless, the shutdown samples were taken during the maintenance breaks on March, April and May. In March and May the maintenance break was in the cell room N2, and in April in the cell room N1. The amount of the reduced chromium on the cathodes m_{reduced} was calculated from the difference of the chromium concentration in the cell liquor before the shutdown C_{BS} and 15 minutes later $C_{15 \text{ min}}$. It should be noted that the actual reduction has occurred when the electrolysis has been started up after the maintenance break. Because the maintenance break is accomplished for the two cell rooms in turns, the amount of reduction analyzed in March, has actually occurred already in January, and similarly, the amount of reduction analyzed in April, has actually occurred in February. Results are available in table 9.

Table 9. Accumulation of chromium on the surface of the cathodes was determined from the shutdown samples. The respective film thickness was calculated, too.

Maintenance break	C_{BS} , kg/m ³	$C_{15 \text{ min}}$, kg/m ³	$V_{\text{cell liq.}}$, m ³	m_{reduced} , kg Cr (VI)	d_{film} , nm
March	3.330	3.615	93.6	10.6	1058
April	3.380	3.560	91.0	6.5	604
May	3.653	3.783	97.5	5.0	502

The thickness of the reduced chromium layer, d_{film} , was determined suggesting, that the compound consisted of trivalent chromium hydroxide. Based on literature, the density of the compound is 3.11 g/cm³. The total geometrical surface area of the cathodes in cell room N1 was 3220 m², and in cell room N2 3460 m², respectively.

9.8 Total chromium analysis

Some samples were analyzed also for total chromium in order to research the oxidation degree of chromium in the different process streams. The concentrations were obtained by the linear calibration method. The analysis was done for the process samples that were collected on 13th of May, and the results are represented in table 10. The respective hexavalent chromium concentrations obtained by the spectrophotometer are included in the table, too. The hexavalent chromium results are not available for the hypochlorite solutions coming from the scrubbing units, due to inapplicability of the spectrophotometric method.

Table 10. Comparison of the total and the hexavalent chromium concentration for the process samples collected on 13th of May, 2014.

Process stream	Cr(VI), mg/l	Total Cr, mg/l
4	69	39
5	1749	1863
8	1529	1373
12	1547	1373
13	40	42
14	1749	1863
24	N/D	74
26	N/D	97
27	74	64

Two of the process samples, 8 and 12, were analyzed also on another day to check the repeatability of the method. Further, sample 8 was analyzed also by standard addition technique to further compare the obtained results. The results are summarized in Table 11.

*Table 11. Two samples, 8 and 12, were analyzed on different days with linear calibration method, indicated with *. Sample 8 was analyzed also by standard addition technique, which is indicated with **. The hexavalent chromium result is given for comparison.*

Process stream	C ₁ , mg/l total Cr *	C ₂ , mg/l total Cr *	C ₃ mg/l total Cr **	C, mg/l Cr (VI)
8	1373	1792	1092	1529
12	1373	2028	N/D	1547

10 CONCLUSIONS

10.1 Sodium dichromate concentrations and chromium mass balance within the process operations

The aim of the regular collection of the process samples during the experimental study period was not solely to determine the chromium mass balance within the process operations, but also to follow the chromium concentrations in the streams as the actual amount of chromium in the process is changed. All of the analysis results obtained from the spectrophotometer and the dilution ratios are listed in appendix 1. In the first collection day it was noticed that immediate analysis is required as the samples with high chlorate content tended to crystallize fast as they cooled down. Due to this, some results from the first collection day are not reliable as it was not succeeded to re-dissolve all of the formed crystals. Crystallized sample had higher chromium content than non-crystallized ones. Anyway, from the appendix 1 it can be seen that the parallel results were well aligned. This accounts the reliability of the obtained results, and also of the chromium balance calculations for the unit operations. In addition, the downward and upward trend in the chromium content can be noticed, reflecting the decrease or increase of chromium in the process. However, the amount of chromium present in the process should not be analyzed solely based on the concentration without the information about the total volume of the process liquors.

The mass balance represented in figure 5 was calculated based on the samples collected on 2nd of April. The balance calculations were executed for chromium species, but also for the total mass flows. The total mass flows are given additionally as volumetric flows, since the flow data was received in volumetric units from the process control system.

Considering the total mass flows throughout the process, the mass flows are in balance on a good level. Only the amount of process condensate created at the crystallizer was too high. The designed efficiency for evaporation is 1.2 ton of

process condensate per ton of produced crystal. This difference was most probably due to the calculation method, and also the used density values in the control volume of crystallization and centrifugation. Namely, as the volumes of the streams are great, even a small inaccuracy in the used densities may have escalated the inaccuracy in the final result. However, the faulty amount of the condensate stream did not specifically affect the chromium balance as the chromium content in the condensate stream was very low, and therefore the meaning of the amount of condensate with respect to the chromium contained in it, was minimal.

Regarding the chromium balance itself, there were few points that should be highlighted. First, when the input of chromium to the control volume of electrolysis and to the crystallization and centrifugation were compared, the chromium amount was risen by 4.5 kg between these process steps. Secondly, during the crystallization and centrifugation, 4.9 kilograms of chromium were vanished from the system. Moreover, even though approximately 7.6 kilograms of chromium were recycled back to the brine treatment, only 1.5 kilograms of chromium were present in the brine feed to the electrolysis. All of the individual chromium balance calculations for the different sampling occasions are presented in appendix 3. By reviewing these, it can be seen that the before described phenomena is repeated each time, although not relatively in similar amounts.

There are some possible reasons for the imbalance. First, the reliability of the measurement results is essential. With large volumes, the chromium amount in a stream with high chromium concentration can easily be varied few kilograms in case the measurement result is not exactly correct. This is anyway a little unlikely reason for all imbalance issues, because the obtained results for the parallel samples were always very well aligned, and as said, the imbalance was detected on each sampling occasion. Another possibility could be, that part of the chromium is reduced in the process condensate stream, and therefore not appealed in hexavalent chromium results obtained by the spectrophotometer. This would explain the chromium gap in control volumes of crystallization and centrifugation, and also in that of brine treatment. The chromium content is risen again after the electrolysis and the dehyponing treatment. This could be due to the

oxidizing effect of the electrolysis. The literature did not include specifically information about the oxidation degrees of chromium in chlorate streams. The matrix of the chlorate liquor is oxidizing, consisting of chlorate, hypochlorite and perchlorate ions. However, there are no study results available about the topic. At Kemira Oyj's sodium chlorate plants, there has not been any comparative analysis between the hexavalent and total chromium contents in the different streams of sodium chlorate process.

Also, the possibility of false values from the flow meters should be considered. It is likely that the imbalance in the crystallization and centrifugation is explained by the total effect of inaccuracy in the flow values and the analysis results. But, the imbalance in the brine treatment cannot be explained solely by that, since approximately 80 % of the incoming chromium was vanished during the respective treatment.

Based on the results, some focus should be put to the research of chromium behavior in the brine treatment. As there was limited information available regarding the flows, the brine treatment was examined very narrowly in this study. In the future, attention should be paid especially on the effect of the precipitation unit and the following continuous filtration to confirm if some discharge is occurred there. The pH of the brine that is run through the filter is between 10 and 11, which means that the hexavalent chromium is present as chromate ion, meaning, in the less soluble form. The precipitate that is retained by the bag filter could be sampled and sent for analysis while the filter is cleaned. In case chromium has been retained, more detailed study could be organized to estimate the amount of the discharge.

The lack of flow meters and their integration to the process control system caused some challenges in the determination of the balance within the process. Practically, making more exact calculations around the control volumes was impossible. On the other hand, the flows and the surface levels of the vessels were very constant when the plant was on full operation. Nevertheless, it would anyway be important to record the flows, e.g. in case the process is to be

developed. The research of the balance within the process cannot be done in very detailed level if the backbone for the analysis is based mainly on coarse figures, or even worse, on calculated figures.

10.2 Discharge of chromium from the process

It was assumed that the discharge routes for chromium are the product and the sludge, which is generated during the precipitation of sulfate and calcium ions from the cell liquor. One of the targets of this study was to specify more in detail the discharged amounts, especially the one emitted through the sludge.

Product

The amount of residual chromium present in the formed crystal is dependent on the functioning of the crystallizer and the washing operation. When the crystallization is succeeded well, the crystals are biggish and also uniform in their appearance. Then, the remaining chlorate liquor is washed off easier from the voids and the surface of the crystals, and thus, lower residual chromium content is achieved in the final product. Typically, crystallization is functioned constantly in Joutseno sodium chlorate process during the late winter. Therefore, the timing of the experimental study period was optimal. In this study, the discharge through the product was calculated based on the average chromium concentration of the crystal, which was determined from all of the crystal measurements conducted during the observation period. The used average value, 3.2 mg/kg, was anyway clearly higher compared to the typical chromium concentration of the crystal, approximately 1 - 1.5 mg/kg. The crystal sample was not analyzed for any other crystal properties, such as crystal size distribution. However, it was clearly visible in case crystallization or the crystal wash had not succeeded well. An indication of a bad quality of the crystal was the small size of a single crystal, and kind of a sticky appearance of the crystal sample. In such case, the residual chromium content was higher, because, apparently, the washing water did not flush the chlorate liquor from the smaller crystal voids.

Sludge formed during the cell liquor treatment

Before the experimental study, it was estimated that the sludge created during the cell liquor treatment was the main discharge channel for chromium out of the process. The results from treatments executed in March and in April show, that chromium was removed during the treatments 13.7 – 17.9 kg per treatment, totally 31.7 kg, which is the same order with the discharge through the product. However, it is probable, that the figure is only a minimum amount of the actual discharge, as there were certain issues that affect the reliability of the overall result.

The original purpose was to quantify the amounts of chromium that was removed during the different phases of the treatment. The target was not achieved as there was no reliable data available about the volume of the liquor after the first filtration. This is due to the incorrect signal given by the surface level transmitter of the treatment vessel B. Therefore, only the total discharge amounts for the operations were determined. Anyway, there was an issue related to the sampling, which further affected the reliability of the discharge rate of the treatment. From the liquor treatment executed in March, the second filtrate was not sampled at all due to unclear reason. Therefore, the result for the discharge was calculated based on the sample, which was taken just before the start of the second filtration after sodium carbonate was applied into the liquor. Thus, it is likely that the discharge would have been greater than the result indicated. Moreover, the graph illustrating the surface level of the vessel A, which was read to obtain the data regarding the volume of the treated liquor, was slightly unstable. Therefore, the probable inaccuracy of the used value has again affected the final result.

It is difficult to analyze the discharge rates of the treatments based on only two results. There was no significant difference in the chromium output along the sludge in March and April. The discharge was approximately 15 kg per treatment, corresponding about 10 to 15 percent of the chromium that was present in the non-treated cell liquor. One could, however, assume that the amount of chromium co-precipitation is related to the amount of sulfate and calcium ions present in the liquor. Namely, the dosage of the precipitation chemicals is

depended on the specific ion concentration of the impurities. Additionally, as the filtration is continued until the desired ion concentration has been achieved, the duration of the filtration may have affected the chromium discharge rate, too.

To better understand the chromium discharge during the cell liquor treatment, it would be required to collect the samples in the future as well. In case there was a relation between the initial dichromate concentration of the cell liquor to be treated and the discharged amounts, it would be possible to consider the timing of the cell liquor treatment, and thus reduce the chromium discharge. In other words, the treatment should be carried out when the initial chromium concentration is rather low than high. Naturally, this would be possible only if it had no effect on the functionality of the process, nor the product quality due to the higher sulfate and calcium concentrations. Surely, the effect to the chromium discharge would anyway be only a couple of kilograms.

10.3 Chromium mass balance for the process

The chromium mass balance was reviewed during March, 18th and May, 6th. According to the records, the direct input of the commercial sodium dichromate solution to the process was 151 kg. The sum of the discharges among the product and the sludge during the same time period was only 65 kg. When considering also the 38 kg of consumption of chromium from the process liquors, the difference between input and output is even greater. The overall consumption of chromium was 189 kg, and the identified discharge was only 65 kg. Thus, approximately 120 kg of chromium is consumed from the process with no identification.

The difference between the consumed chromium and the identified discharge seems major, but most probably it can be explained by the uncertainties related to the used values in the calculations. The amount of accumulation in the process liquors was calculated from single measurement results in the beginning and in the end of the observation period. Only 0.1 g/l of inaccuracy in the sodium

dichromate measurement result affects the total chromium amount present in the process liquors by 26 kg assuming the total liquor volume to be around 700 m³. Moreover, the liquor volumes were taken as an average for the day, and therefore it is possible, that the actual volume had been greater or smaller during the sampling. Already 10 m³ of inaccuracy in the liquor volume changes the amount of chromium present in the process by 11 kg, assuming the sodium dichromate concentration to be 3 kg/m³. Clearly, it can be concluded that with great volumes, the uncertainties have major effect on the overall results. Further, the total amount of chromium was determined now only on the first day and on the last day of the observation period. In case it had been followed more often, the information could have been used in monitoring the change in the total chromium amount in the process as chromium is added to the process, or discharged from it.

Additionally, it should be pointed out that sodium chlorate process is a closed process. Thus, there are no other discharge routes for chromium, except the previously discussed filtration unit in the brine treatment. In case the 122 kg of imbalance would be explained solely by the filtration, it would mean over 2 kg of retention to the filter per day. It sounds very unlikely, although the chromium imbalance in the brine treatment might indicate that some retention is actually occurred there.

Most probably the imbalance between the input and output of chromium is due to the uncertainty of all of the individual results included in the balance, and also some level of discharge in the brine treatment. The great volumes are the main reason for the uncertainty. Unfortunately, the brine treatment could not be studied more closely because of the limitations related to the flow data.

10.4 Reduction of chromium on the cathode surface

The amount of chromium reduced on the cathodes was researched during the maintenance break operations. According to the results, around 5 to 10 kg of

chromium had been precipitated on the cathodes during the start-up of the electrolysis. This amount was higher than expected, and it was clearly measurable from the concentration difference. To be able to estimate the order of magnitude of the results, the thickness of the chromium layer was calculated.

There are only few studies that have discussed the thickness of the layer on the cathode (Ahlberg Tidblad & Mårtensson, 1997). In those studies, the thickness was reported to be less than 10 nm. The reported results were obtained with surface analytical techniques. In this study, the thickness of the layer was calculated to be about 500 – 1000 nm, being about 50 to 100 times greater compared to the values given in the literature. However, there are few points that may have affected the results.

First, the condition of the cathode affects the surface area, and thereby also the amount of chromium reduced on it. As it is known, the electrodes are affected by extreme corrosion, which deteriorates the surface enlarging its area. Assuming that chromium is reduced similarly on the corroded surface than on the smooth one, the calculated thickness of the film would be directly proportional to the real surface area. However, the results were calculated based on the geometrical surface area.

Ahlberg Tidblad & Mårtensson (1997) had concluded also in their study that the thickness of the film is dependent on the initial concentration of the cell liquor during the film creation, too. This might explain the varying results in the film thickness, especially the result from March. However, the obtained results seem rational, being close to the correct order of magnitude.

10.5 Total chromium analysis

The comparison between the hexavalent and total chromium concentration was conducted in order to research the oxidation degree of chromium in the different

process conditions. Due to the slight chromium imbalance within the process, discussed in previous chapters, this part of the study became highly interesting.

From tables 10 and 11 it can be seen that there is variable difference in the results between the hexavalent and the total chromium concentrations. Main focus is on the point, that in many samples the total chromium result was lower than the respective hexavalent chromium result. This cannot be the case, as the total chromium result should be the same than the hexavalent one, or even higher in case there is also reduced chromium present in the sample. Only for samples 14 and 5 the total chromium results were higher, and for sample 13 the result was approximately the same. However, according to the results, the chromium content was smaller for process condensate from crystallizer, 13, than for the hypochlorite solutions, 24 and 26. These issues were concluded as possible indication of unreliable results for total chromium.

After it was noticed there is some inconsistency in the results, it was decided to analyze two samples again and either of those also by the standard addition method to assure the repeatability and the selectivity of the method for the specific sample types. The parallel results had variation, especially with sample 46. Also, the result obtained by the standard addition technique was significantly lower in comparison with the results from calibration curve method. These conclusions were made without actual statistical analysis. However, it was not considered rational to carry on with the total chromium analyses, and therefore part of the samples that were supposed to be analyzed in the first place, were not.

The final results were affected by the measurement inaccuracy and also by the great dilution ratios, which were for samples with high chromium content as high as 5000 due to the specified measurement range of 0.1 – 1 mg/l. Therefore, it would be recommended to validate the method also for higher concentrations. Also, it could have been more rational if the total chromium analyses were performed by the standard addition technique rather than by the used linear

calibration method. This could have minimized the effect of the possible interfering species in the sample matrix.

Additionally, the validation of the method should be performed with all types of process samples that are to be analyzed with it. The used method had originally been developed for water samples. However, in the past, it had been successfully used also for samples originating from sodium chlorate process. Now, the method was validated again in-house for the purpose of this study. The validation was done with two process samples, corresponding to samples 8 and 26. Before the start of the total chromium analyses, the results of the validation were not completely known.

In case the total chromium analyses are to be performed for the process samples, it would be required to continue the validation of the method. Otherwise, the method will not be reliable for all purposes. The requirements for the quality characteristics of the method are, however, dependent on the need.

11 SUMMARY

The aim of the work was to research the behavior of chromium and, especially, its mass balance in sodium chlorate process. The work included a study regarding the balance for the unit operations of the process, the identification of the chromium consumption and the discharge of it, and additionally an examination regarding the oxidation degrees of chromium in different process conditions. Based on other balance analysis made for the plant, it was initially expected, that some inaccuracy may be included in the results because of the uncertainties related to the research method. It was, however, considered important to research the chromium balance because it had never been studied before.

For the chromium balance, process samples from different streams and operations were collected and analyzed for hexavalent chromium. Based on the oxidizing matrix of the process streams, it was assumed that chromium is present in the oxidized form, and therefore the spectrophotometric, standardized method was seen as suitable for the purpose. Some of the samples were, however, analyzed also for total chromium with newly deployed AAS method, just to assure the oxidation degree of chromium. The balance calculations were made based on the obtained results, and the gathered flow data.

The main finding of the study was that remarkably larger amount of chromium was consumed in comparison with the identified discharge. During the observation period, the total input to the process was 189 kg, while the discharge through the sludge and the product was only 67 kg. More than half of the used chromium was vanished with no identification. The balance analysis that was made for the unit operations, detected some level of imbalance, too. This could, however, be explained mainly by the uncertainties related to the research method. Nevertheless, the identified imbalance in the brine treatment was significant, as approximately 80 % of chromium introduced to the control volume was not detectable in the output stream. This was considered as an indication for possible discharge route, especially as a filtration unit is incorporated in the

concerned part of the process. The process samples were analyzed also for total chromium content to study the oxidation degrees of chromium in the different process streams. The obtained results were mostly smaller than the corresponding hexavalent chromium results, and thus they were not considered fully reliable. Therefore, the imbalance in the brine treatment could not be verified being due to the reduction of chromium. However, it is possible that the imbalance of the entire process can partly be explained being due to the possible discharge of chromium during the brine treatment.

Although the difference between the consumption and the identified discharge seem major, it should be kept in mind that the result can be considered only directional due to the great uncertainties. Most of the results were determined from the analyzed concentration and the volumetric flow. In case either of the values was slightly inaccurate, the deviation between the obtained and the true result was multiplied. Moreover, there were certain issues regarding the sampling during the cell liquor treatment, and thus, the identified amount of the discharge through the sludge was probably only a minimum.

Regardless of the uncertainties related to the results, few issues should be pointed out. Most importantly, the reason for the identified chromium gap in the brine treatment should be clarified. Namely, it should be kept in mind that the authorization is aimed at ensuring the proper risk management measures. In terms of the identified imbalance, it would be important to clarify the possibility for the additional discharge route, in order to control the exposure in the concerned operations, for instance, in the filter clean-up. Therefore, the sludge formed in the filtration unit of the brine treatment should be analyzed. Additional samples from the surrounding streams could be collected, too, in order to support findings from the analysis of the sludge. Moreover, the discharge rate during the cell liquor treatment could be specified better by collecting more representative samples from the coming treatments. By these steps, the chromium losses could be identified more detailed. Moreover, it would be important to start the regular follow-up of the chromium mass balance already, since that can be one of the monitoring obligations set in the authorization. This could be done by calculating the total amount of chromium present in the process liquors, and by comparing

the figure and its change to the determined or estimated discharges and chromium additions.

The meaning of the study turned out to be a preliminary research about the chromium mass balance. Information regarding the discharges and their amounts was obtained, but unfortunately only in limited level of reliability. Due that, the inaccuracy was escalated also in the total chromium mass balance. Therefore, the chromium mass balance could not be determined with desired accuracy. However, the study gave new information regarding the diffusion of chromium in different parts of the process. Also, it revealed possibly a discharge route that had not been considered earlier. Finally, the study can also be utilized in the future follow-up of the chromium balance.

The use of sodium dichromate has significant effects on the functionality of the process, especially in terms of cost-effectiveness. Therefore, it would be critical that the use of sodium dichromate in the manufacture of sodium chlorate would be granted in authorization, especially as it seems that no proper substitutes are available. The decision is of great importance, considering also the competitiveness of the European pulping industry, and the requirements regarding the AOX emissions.

REFERENCES

Ahlberg Tidblad, A. & Mårtensson, J (1997). In situ ellipsometric characterization of films formed by cathodic reduction of chromate. *Electrochimica Acta*, 42 (3), 389 – 398.

Alford, R. E. (1992). Cyclochrome - The Recycle of Sodium Dichromate In Sodium Chlorate Manufacture. In T. Wellington (Ed.), *Modern Chlor-Alkali Technology*.

Balej, J., Bennett, J. E., Gallone, P., Sheikh, S. A., Vogt, H., Wintzer, P. (2000). Chlorine Oxides and Chlorine Oxygen Acids. In *Ullmann's Encyclopedia of Industrial Chemistry*.

BREF. 2007. IPPC Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Solids and Others industry. European Commission.

Brown, C. W., & Carlson, R. C. (2010). Patent No. WO 2010/037706 A1. International application.

Colman, J. E. & Tilak, B. V. (1995). Sodium Chlorate. In McKetta, J. J. (Ed), *Encyclopedia of Chemical Processing and Design* (pp 126-189).

Cornell, A. (2002). *Electrode Reactions In the Chlorate Process*. Doctoral Thesis. Stockholm: Royal Institute of Technology.

ECB. (2005). European Union Risk Assessment Report: Chromium Trioxide, Sodium Chromate, Sodium Dichromate, Ammonium Dichromate, Potassium Dichromate. 3rd Priority List, Vol. 53.

ECHA. (2011). Background document for sodium dichromate. Retrieved, 14 January 2014, from http://echa.europa.eu/documents/10162/13640/backgroundoc_sodium_dichromate_en.pdf.

ECHA (2011). *Guidance on the preparation of an application for authorisation*. Version 1. European Chemicals Agency.

European Commission. (2013). Commission Regulation (EU) No. 348/2013 of 17 April 2013 Amending Annex XIV to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Brussels.

Gustavsson, J., Nylén, L. & Cornell, A. (2010). Rare earth metal salts as potential alternatives to Cr(VI) in the chlorate process. *Journal of Applied Electrochemistry* (40), 1529-1536.

Hedenstedt, K. & Edvinsson Albers, R. (2012). Patent No. WO 2012/084765 A1. International application.

Hujanen, J. (2014). Manager, Technology and EHSQ. Several interviews in 2014.

Kaczur, J. J., Mendiretta, S. K. (1979). US Patent No. 4259297. United States.

Krstajic, N., Jovic, V., & Martelli, G. N. (2007). Patent No. WO 2007/06381 A2. International application.

Li, M., Twardowski, Z., Mok, F. & Tam, N. (2007). Sodium molybdate - a possible alternate additive for sodium dichromate in the electrolytic production of sodium chlorate. *Journal of Applied Electrochemistry* (37), 499-504.

Lipsztajn, M. (1987). US Patent No. 4699701 A. United States.

O'Brien, T. F. (1974). US Patent No. 3835001. United States.

Operating instruction (2010). Sulfaatin saostus ja jäännöskalsiumin poisto klooraattiliuoksesta. Kemira Oyj.

Partridge, H. & Hildyard, J. (1974). US Patent No. 3843769. United States.

PI diagrams (2009). PI diagrams for Kemira Oyj's Joutseno sodium chlorate process.

Schulz, R., Van Neste, A., Bouli, S., & Jin, S. (1997). Patent No. 1997/004146. International application.

Scholander, A. F. & Brännland, R. K. A (1969). US Patent No. 3427236. United States.

Tilak, B. & Chen, C. P. (1999). Electrolytic Sodium Chlorate Technology: Current Status. In H. S. Burney, N. Furuya, F. Hine & K.-I. Ota (Eds), *Chlor-Alkali and*

Chlorate Technology: R.B MacMullin Memorial Synopsium (pp. 8 – 40).
Pennington, New Jersey: The Electrochemical Society, Inc.

Viswanathan K. & Tilak B. V. (1984). Chemical, Electrochemical and Technological Aspects of Sodium Chlorate Manufacture. Journal of The Electrochemical Society, 131 (7), 1551 – 1559.

Wagner, C. (1954).The Cathodic Reduction of Anions and the Anodic Oxidation of Cations. Journal of The Electrochemical Society, 101 (4), 181 – 184.

Appendix 1: Analysis results and the dilution ratios

Table 1. The hexavalent chromium results obtained from the spectrophotometer. The overall sodium dichromate concentration was calculated by multiplying the obtained concentration with the dilution ratio.

Sampling date	Sample no.	4, mg/l	5, mg/l	8, mg/l	12, mg/l	14, mg/l	13, mg/l	18, mg/kg	27, mg/l
21.3.2014	1	0.173	0.420	0.674	0.712	0.419	0.514	0.142	0.322
	2	0.181	0.407	0.699	0.717	0.424	0.498	0.135	0.332
28.3.2014	1	0.129	0.337	0.625	0.568	0.362	0.249	0.223	0.235
	2	0.126	0.340	0.610	0.573	0.364	0.246	0.245	0.250
2.4.2014	1	0.125	0.369	0.607	0.623	0.370	0.319	0.304	0.236
	2	0.124	0.359	0.603	0.619	0.371	0.305	0.292	0.252
9.4.2014	1	0.116	0.342	0.621	0.623	0.355	0.332	0.225	0.2495
	2	0.113	0.352	0.615	0.619	0.347	0.306	0.202	0.2495
22.4.2014	1	0.120	0.384	0.689	0.709	0.397	0.374	0.257	0.366*
	2	0.116	0.387	0.688	0.686	0.421	0.394	0.272	0.326*
2.5.2014	1	0.187*	0.284	0.570	0.601	0.343	0.190	0.052	0.171
	2	0.180*	0.279	0.567	0.612	0.340	0.186	0.049	0.166
13.5.2014	1	0.276*	0.433	0.755	0.802	0.438	0.199	0.180	0.299
	2	0.280*	0.448	0.786	0.757	0.443	0.202	0.149	0.295
Dilution ratio		1250 *625	10000	5000	5000	10000	500	N/A	625 *312.5

Appendix 2: Source for flow values and chromium concentrations

Table 1. The sources for the flows and the chromium concentrations which were used in the balance calculations. Local source for volumetric flow refers to local flow transmitter, whereas Aspen refers to process control system.

Process stream	Description of the stream	Source for volumetric flow	Source for chromium concentration
1	Raw salt	N/A	Chromium free
2	Water	N/A	Chromium free
3	Salt solution from neighboring caustic soda plant	DNA	Chromium free
4	Treated brine to electrolysis	DNA	Analysis
5	Mother liquor to electrolysis	DNA	Analysis
6	HCl	Local	Chromium free
7	Hydrogen gas	Calculated	Chromium free
8	Cell liquor from electrolysis	Calculated	Calculated
9	NaOH to dehyponing	Local	Chromium free
10	H ₂ O ₂ to dehyponing	DNA / calculated	Chromium free
11	Chlorate liquor to brine precipitation	Local	Analysis
12	Chlorate liquor to crystallization	DNA	Analysis
13	Process condensate from crystallization	Calculated	Analysis
14	Mother liquor from crystallization	DNA / Calculated	Analysis
15	Suspension from crystallization	Calculated	Calculated
16	Mother liquor from centrifugation	DNA / Calculated	Calculated
17	Water to crystal washing	Local	Chromium free
18	Crystal from centrifugation	DNA / Calculated	Analysis
19	Process condensate to H ₂ scrubber	Local	Analysis
20	Process condensate to off-gas scrubber	Local	Analysis
21	Process condensate to feed tank for saturator	Calculated	Analysis
22	Off-gas	N/A	Chromium free
23	NaOH to off-gas scrubber	N/A	Chromium free
24	Hypochlorite from off-gas scrubber	Calculated	Analysis
25	NaOH to H ₂ scrubber	Local	Chromium free
26	Hypochlorite from H ₂ scrubber	Calculated	Analysis
27	Circulated salt solution	N/A	Analysis
28	60 w-% of sodium dichromate	Weighed	Supplier data

Table 1.1 Chromium mass flows (kg/h) for control volumes electrolysis EL, and for crystallization and centrifugation CC.

Date	IN _{EL}		Total	OUT _{EL} 8	IN _{CC} 12	13	14	OUT _{CC}		18	Total
	4	5						16	18		
21.3.	2.2	144.5	146.6	147.9	155.3	2.0	78.0	66.5	0.03	146.5	
2.4.	1.5	125.6	127.1	128.1	131.6	1.11	71.5	54.1	0.05	126.7	
9.4.	1.4	119.7	121.1	131.8	130.9	1.06	68.6	51.1	0.04	120.8	
22.4.	1.3	134.7	136.0	146.5	150.5	1.4	79.2	55.6	0.05	136.2	
2.5.	0.6	81.6	82.2	94.6	97.5	0.1	55.1	26.8	0.01	82.0	
13.5.	1.1	123.7	124.8	145.8	147.6	0.6	86.5	37.1	0.03	124.2	

Table 1.2 Chromium mass flows (kg/h) for control volume of hydrogen and effluent gas treatment HEGT, and salt solution treatment STT.

Date	IN _{HEGT}			OUT _{HEGT}			IN _{STT}			OUT _{STT} 4	
	19	20	Total	24	26	Total	11	21	24		26
21.3.	0.02	0.02	0.04	0.03	0.04	0.07	7.4	2.96	0.03	0.04	10.4
2.4.	0.01	0.01	0.02	0.03	0.03	0.06	6.5	1.09	0.03	0.03	7.7
9.4.	0.01	0.01	0.02	0.03	0.03	0.06	6.6	1.04	0.03	0.03	7.7
22.4.	0.01	0.01	0.02	0.02	0.03	0.05	7.4	1.38	0.02	0.03	8.8
2.5.	0.01	0.01	0.02	0.02	0.02	0.04	6.1	0.08	0.02	0.02	6.22
13.5.	0.01	0.01	0.02	0.03	0.04	0.07	8.3	0.58	0.03	0.04	8.9