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DECARBONISATION OPTIONS FOR THE DUTCH CHLOR-ALKALI INDUSTRY

E.L.J. Scherpbier, H.C. Eerens

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Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dutch chlor-alkali industry

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Authors

E.L.J. Scherpbier, H.C. Eerens

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Prof.dr.ir. C.A. Ramirez (Delft University of Technology)

Dr.ir. J.H. Kwakkel (Delft University of Technology)

J.R. Ybema (AkzoNobel Specialty Chemicals/Nouryon)

Prof.dr.ir. S.A Klein (AkzoNobel Specialty Chemicals/Nouryon)

MIDDEN project coordination and responsibility

The MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network) was initiated and is also coordinated and funded by PBL and TNO. The project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. Correspondence regarding the project may be addressed to:

D. van Dam (PBL), Dick.vanDam@pbl.nl, or S. Gamboa Palacios (TNO),

Silvana.GamboaPalacios@tno.nl.

Erratum

An earlier version of this report was published in 2020, but contained errors in Figure 3 and Tables 1 and 3. Furthermore, a number of corrections were made in the tables in Section 4. This version also includes a number of minor updates.

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TNO Energy Transition has a twofold mission: to accelerate the energy transition and to strengthen the competitive position of the Netherlands. TNO conducts independent and internationally leading research and we stand for an agenda-setting, initiating and supporting role for government, industry and NGOs.

An earlier version of this report was reviewed by Nouryon. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the companies.

Contents

Summary	4
INTRODUCTION	5
Scope	5
Reading guide	6
1 CHLOR-ALKALI PRODUCTION IN THE NETHERLANDS	7
1.1 Background	7
1.2 Production	8
1.3 Overview of the economics in the chlor-alkali industry	9
2 CHLOR-ALKALI PRODUCTION PROCESSES	11
2.1 Overview	11
2.2 Steam generation	11
2.3 Caustic soda preparation	12
2.4 Brine preparation	12
2.5 Electrolysis	12
2.6 Caustic soda processing	14
2.7 Hydrogen processing	15
2.8 Chlorine processing	15
2.9 Summary	15
3 CHLOR-ALKALI PRODUCTS AND USE	18
3.1 Products	19
3.2 Environmental issues	20
3.3 Transport issues	21
4 OPTIONS FOR DECARBONISATION	21
4.1 Overview	21
4.2 Technology specifications	23
5 DISCUSSION	28
REFERENCES	30
Bibliography	30
Consulted experts	32
APPENDIX A: EXPLANATION OF BRINE PREPARATION PROCESS	33
APPENDIX B: EXPLANATION OF MEMBRANE ELECTROLYSIS	35
APPENDIX C: EXPLANATION OF CHLORINE PROCESSING	37

FINDINGS

Summary

The Dutch chlor-alkali industry exists of three production plants located in Delfzijl and Botlek (Nouryon) and Bergen op Zoom (Sabic), and together produce roughly 850 kilotons of chlorine, 950 kilotons of caustic soda, as well as 24 kilotons of hydrogen per year.

The chlor-alkali industry is mostly intensive on its electricity usage. The Dutch chlor-alkali industry in 2016 consumes 3.2 PJ of natural gas resulting in approximately 180 kilotons of CO₂ emissions, and imports 6.6 PJ of electricity resulting in roughly 890 kilotons of indirect CO₂ emissions. From this conceptualisation, it becomes apparent that the real challenge in decarbonising the chlor-alkali industry does not lay in its reduction of direct emissions, but more in lowering its indirect emissions.

The chlor-alkali manufacturing process can be conceptualised in a series of steps; steam generation, caustic soda preparation, brine preparation, electrolysis, caustic soda processing, hydrogen processing and chlorine processing. Across the industry, the electrolysis process is the single largest consumer of electricity causing indirect emissions, whereas the steam generated in combined heat and power plants causes the direct emissions.

A key opportunity for decarbonisation in the chlor-alkali industry lies in the reduction of indirect emissions. This study shows that this can be achieved through the large-scale implementation of zero-gap membrane electrolyzers to reduce electricity consumption. Using current CO₂ intensity of power generation in the Netherlands these reductions are estimated between 90 and 120 kilotons of CO₂ annually. Currently 10 zero-gap membrane electrolyzers are installed in Nouryon's plant in Botlek. Based on estimates from this research, the implementation of approximately 30 more zero-gap membrane electrolyzers across Nouryon's plants in Botlek and Delfzijl, as well as Sabic's plant in Bergen op Zoom, can reduce the chlor-alkali's electricity consumption by 0.4 to 0.6 PJ per year. Investment costs for these emission reduction steps are estimated between 75 to 125 million euros.

For the industry's direct emissions the placement of electric and biomass boilers or geothermal energy are the key decarbonisation options.

FULL RESULTS

Introduction

This report describes the situation in the base year 2016 of the Dutch chlor-alkali manufacturing industry and the options and conditions for its decarbonisation. It is part of the MIDDEN project: the Manufacturing Industry Decarbonisation Data Exchange Network. MIDDEN aims to support industry, policy makers, analysts and the energy sector in their common efforts to achieve deep decarbonisation. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

In the Netherlands, chlorine producers include Nouryon (previously named AkzoNobel Specialty Chemicals – names are used interchangeable in this report) and Sabic. These companies operate on three different chlorine production facilities in the Netherlands.

Production locations include:

- Botlek (Nouryon/AkzoNobel Specialty Chemicals)
- Delfzijl (Nouryon/AkzoNobel Specialty Chemicals)
- Bergen op Zoom (Sabic).

Processes include:

1. Steam generation
2. Caustic soda preparation
3. Brine preparation
4. Electrolysis
5. Caustic soda processing
6. Hydrogen processing
7. Chlorine processing.

Products include:

- a) Chlorine
- b) Caustic soda
- c) Hydrogen

The main decarbonisation options implementable by 2030 are:

- Electrolysis by zero-gap membrane electrolyzers,
- Capacity increase to utilise peak-shaving production,
- Steam generation by electric or biomass boilers.

The main decarbonisation options implementable by 2050 are:

- Steam generation by geothermal heat generation,
- Steam generation by hydrogen boilers,
- Steam generation by electric boilers.

Reading guide

Section 1 introduces the chlor-alkali industry in the Netherlands. Section 2 describes the situation in base year 2016 for chlor-alkali production processes in the Netherlands. Subsequently, the relevant products to these processes are described in Section 3. Options for decarbonisation are systematically quantified and evaluated in Section 4. The feasibility and requirements of those decarbonisation options are discussed in Section 5.

1 Chlor-alkali production in the Netherlands

1.1 Background

The chlor-alkali production industry has played an important role in Dutch society since the end of the Second World War and the growth of the Dutch chemical industry. AkzoNobel had mercury electrolysis plants for chlor-alkali production in Hengelo and Delfzijl since the 1930s and opened its third mercury electrolysis plant in Botlek in 1961 (AkzoNobel, 2018). In the late 1980s, General Electrics (present-day Sabic) opened a membrane electrolysis plant in Bergen op Zoom. The Dutch chemical industry's heart lays by the port of Rotterdam, whereas the raw material needed to produce chlorine, salt, can predominantly be found in underground salt layers in the east (Hengelo) and northeast (Delfzijl) of the Netherlands. As such, chlorine was transported by train throughout the Netherlands.

Dutch Emission Guidelines, introduced in the late 1990s, stipulated all chlorine production must be switched to mercury free processes by 2010, while new mercury electrolysis processes could no longer be started. As regulation of chlorine production and chlorine transport tightened, multiple chlorine production facilities were closed down; Solvay Chemie (in Herten) closed in 1999, and AkzoNobel's mercury electrolysis facilities were closed in Hengelo and Delfzijl by 2002. By 2006, AkzoNobel halted its chlorine production in Hengelo completely, leaving three chlorine production facilities in the Netherlands (Botlek, Delfzijl and Bergen op Zoom). At the end of March 2018, AkzoNobel Specialty Chemicals (new name Nouryon) was sold to the American private equity company Carlyle (Verbraeken, 2018)¹.

The demand for chlorine was so large that the Dutch chlorine industry also exported their products to Germany and Sweden by train. By the 1970s, AkzoNobel, the Netherlands' largest chlorine producer, transported over 300,000 tonnes of chlorine per year (Beukers & Van den Tweel, 2006). In the 1990s, following increasing concerns from environmental organisations and regulation measures on chlorine transport in neighbouring countries, Dutch public opinion on chlorine transport changed (Beukers & Van den Tweel, 2006, see also section 213.3). By 2018, chlorine transport occurs incidentally between Botlek and AkzoNobel's chlorine plant in Germany. In 2018, a new agreement was formulated between the government and AkzoNobel to completely get rid of chlorine transportation by 2021. Instead of building extra chlorine storage facilities, the government supported AkzoNobel's investment in a second chlor-alkali plant in Botlek (Verbraeken, 2018b). As of 2021, a second, fully independent chlor-alkali plant will be operational in Botlek. This plant is projected to have an annual production capacity of 150 kilotons of chlorine.

¹ In 2021, Nouryon announced that its industrial chemicals section would proceed under the name Nobian.

Nationwide, the chlor-alkali manufacturing industry employs approximately 1,000 people in 2018 (Klein & Ybema, interview, 2018; Sabic, 2018). Indirect employment is estimated at around 3,000 people (Klein & Ybema, interview, 2018; Sabic, 2018).

1.2 Production

Chlorine is produced by the electrolysis of salt. The laws of chemistry define that for every tonne of chlorine that is produced, 1,129 kg of caustic soda is also produced, together with 28.4 kg of hydrogen (EuroChlor, 2017). This product combination is often referred to as one electrochemical unit (ECU). Although caustic soda and hydrogen can easily be produced in other ways, chlorine cannot. As such, the chlorine production industry is inseparable from the production industries of caustic soda and hydrogen, and thus, production plants that produce these products are together referred to as the chlor-alkali manufacturing industry. Total chlorine production in the Netherlands is roughly 850 kilotons, alongside 930 kilotons of caustic soda and 24 kilotons of hydrogen per year.

For these production levels, the chlor-alkali industry uses roughly 6.5 TJ (1.8 GWh) of electricity and 1.6 TJ thermal energy, given an energy consumption per kiloton chlorine production of 7.7 TJ (2.1 GWh) of electricity, and 1.9 TJ of thermal energy. Direct emissions associated with the chlor-alkali industry are around 184 kt/year (NEa, 2017). The indirect CO₂ emissions are much higher (890 kt)² due to the electrical energy intensity of the process and proportion of Dutch electricity that is generated with the help of fossil fuels.

Chlorine is obtained in the Netherlands at three locations, by means of membrane electrolysis of undried vacuum evaporated salt dissolved in water. Table 1 shows the location of the chlorine production facilities across the Netherlands, as well as their production numbers, and CO₂ emissions. With 850 kilotons of chlorine produced in 2016, the Netherlands is the fourth largest chlorine producer of Europe. The chlorine production plant in Botlek is the largest membrane electrolysis facility of Europe.

Table 1 Chlor-alkali production and CO₂ emissions (2016) in the Netherlands

Site	Production (kt/yr; EuroChlor, 2017)			Electricity use	CO ₂ emissions kt/y	
	Chlorine	Caustic soda	Hydrogen	PJ/yr	Direct (NEa, 2018)	Indirect ² (electricity)
Nouryon Botlek	640	700	18	5.0	133	671
Nouryon Delfzijl	120	130	4	0.9	27	126
Sabic Bergen op Zoom	90	100	2	0.7	24	94
Total	850	930	24	6.6	184	890

As can be seen from Table 1, the Dutch chlorine production industry is dominated by Nouryon; they produce almost 90% of chlorine in the Netherlands, three quarters of which is produced in the chemical industry park in Botlek. Sabic (formerly known as General Electrics) is responsible for the remaining 10% of Dutch chlorine production, which it uses in the production of plastics – predominantly polycarbonates.

In Table 1 also the direct and indirect (calculated from amount of electricity used) CO₂ emissions are given. The table shows the estimated electricity usage and calculated indirect CO₂ emissions of the chlor-alkali plants in the Netherlands, which are around five times the direct emissions, when we assume an emission intensity factor of 0.136 tonnes of CO₂ per GJ

² Calculated with CBS, 2017, integral park method for electricity plants for 2016 (0.49 kg CO₂/kWh)

(or 0.49 kg CO₂/kWh) of electricity produced (Schoots et al., 2017), representative to the electricity obtained from the Dutch power grid, and not through specific power suppliers. Although such an assumption is a simplification of reality, it is commonly deployed in studies to gain insight in the indirect emissions caused by an industry (Koelemeijer et al., 2017a; Werkhoven, 2018; VNCI, 2018). Thus, in considering strategies to lower the emissions of the chlor-alkali industry, considerations must also be made about technologies that help to reduce indirect emissions.

1.3 Overview of the economics in the chlor-alkali industry

The Dutch chlor-alkali industry makes an annual revenue of approximately 590 million euros per year, roughly 450 of which are obtained at Nouryon’s chlor-alkali plant in Botlek. Although much of the public, political and media attention is centred around the production of chlorine, it is interesting to note that the national revenue for caustic soda in 2018 is about 40% more than that of chlorine. Market prices of the separate products may fluctuate partly due to the fixed ratios between chlorine, caustic soda and hydrogen production in the chlor-alkali industry.

On the costs side, it is noted that the chlor-alkali industry is energy- and resource dependent. Roughly 40% of total production costs (see Table 2) are spent on electricity and gas. When depreciation is not taken into consideration, the chlor-alkali manufacturing industry spends almost half of its total operational costs on electricity (Brinkmann et al., 2014). This shows the extent of dependence of Sabic and Nouryon on the electricity prices which are determined predominantly on the European market.

Table 2 Financial overview of the Dutch chlor-alkali manufacturing industry. Prices from Eurostat (2020).

Chlor-alkali manufacturing financial overview			
Revenue	% of total	Assumption unit market price	Source
Revenue: Chlorine	38%	chlorine: 200 EUR/tonne	Brinkmann et al., 2014
Revenue: Caustic soda	53%	caustic soda 370 EUR/tonne	Brinkmann et al., 2014
Revenue: hydrogen	9%	hydrogen 1600 EUR/tonne	Brinkmann et al., 2014
Costs: Electricity	37%	0.066 EUR/kWh	Schoots et al., 2017
Costs: Salt	16%	Industrial vacuum salt: 57 EUR/tonne	Brinkmann et al., 2014
Costs: Gas	4%	6.8 MEUR/PJ	Schoots et al., 2017
Costs: Membranes	4%	20 EUR/ECU ³	Schmittinger et al., 2012

Another important cost aspect in the chlor-alkali industry is the trade-off between expenditures on high quality industrial salt and the refurbishment of membranes. The membranes used in electrolysis are expensive and there is a high business incentive to keep them in the best possible quality (Klein & Ybema, interview 1, 2018). The higher the purity of the salt, the longer the membranes can be used, and the lower the expenditures on the membranes. Higher purity salt, however comes at a cost (Schmittinger, 2012). In the European salt market, Nouryon’s industrial salt is of high quality, which gives it a competitive advantage over other chlor-alkali manufacturers (Stikkelman, interview, 2018). In terms of cost-efficiency, Nouryon believes its salt manufacturing plants are in the top 5%, whereas its chlor-alkali manufacturing plants are in the top 15% (Klein & Ybema, interview 2, 2018).

³ ECU = Electrochemical Unit; a unit of measure reflecting the chlor-alkali process outputs of 1 ton of chlorine, 1.13 tons of 100% caustic soda and 0.03 tons of hydrogen

Due to the high overall costs in the chlor-alkali manufacturing industry, the profitability of the industry is relatively low. Therefore, capital investments are difficult to make and innovation within the industry is hampered by uncertainty around gas and electricity prices (Klein & Ybema, interview 2, 2018).

2 Chlor-alkali production processes

2.1 Overview

The central aspect in the chlor-alkali manufacturing process is the electrolysis of sodium chloride (NaCl). This may be performed using several different techniques. Worldwide, roughly three distinct production methods are in use in the chlor-alkali production industry; membrane electrolysis, mercury-based cell electrolysis and diaphragm electrolysis. In the Netherlands, all chlor-alkali production is conducted via membrane electrolysis.

This central aspect in the chlor-alkali production chain is surrounded by a series of sub-processes that allow for the right proportions of sodium chloride and caustic soda to flow into the electrolyser at one time. As such, the chlor-alkali manufacturing process can be conceptualised as a series of sub-processes:

1. Steam generation
2. Caustic soda preparation
3. Brine preparation
4. Electrolysis
5. Caustic soda processing
6. Hydrogen processing
7. Chlorine processing.

These sub-processes are outlined below. More quantitative background information, calculations and derivations are presented in the Appendices.

2.2 Steam generation

Heat energy is generated in the form of low pressure steam for the processing of caustic soda (vaporisation) it is produced at a temperature of about 150 to 180°C and a pressure of 3 to 4 bar (Schmittinger et al., 2012). This steam is generated through on-site and off-site combined heat and power (CHP) plants. CHP technology, also known as cogeneration, refers to the use of a heat engine to produce useful heat (in the form of steam) and electricity simultaneously. The heat engines of Nouryon in Botlek, as well as that at the Sabic plant in Bergen op Zoom are both fueled with natural gas, leading to CO₂ emissions. Almost all CO₂ emissions in the chlor-alkali industry originate from the steam generation that occurs at the different CHP installations. Nonetheless, the cogeneration plants used in the industry are quite efficient; Nouryon's CHP plant in Botlek has an efficiency above 85% and is about 25% more efficient than the Dutch national average (De Buck & Afman, 2011).

In Delfzijl, on the other hand, the steam originates from three different sources; Eneco's converted biomass power station Bio Golden Raand (BGR); the gas-fired CHP plant Delesto, which is fully owned by Nouryon; and the waste incineration plant EEW Energy from Waste Delfzijl, in roughly equal shares. The large CHP plant Delesto is also used by multiple other industrial plants of the Delfzijl chemical cluster (Klein & Ybema, interview, 2018), and due to its size, it has a higher efficiency compared to smaller on-site CHPs – almost 90% (Klein & Ybema, interview 2, 2018). As such, the direct CO₂ emissions attributed to chlor-alkali

production in Delfzijl are small and therefore not directly reported to NEa, for this study an estimate of the direct CO₂ has been made.

2.3 Caustic soda preparation

Sodium hydroxide (NaOH), also known as lye or caustic soda is formed in the electrolysis process. After the electrolysis a solution of 32% caustic soda (of 90 °C) is formed and (partly) sent back to a dilution chamber. Here, it is combined with dilution water (of 20 °C) and depleted to 30% caustic soda (of 85°C) . This 30% caustic soda is used again for the electrolysis process, during which the more concentrated 32% caustic soda is produced. Waste heat originating from the electrolyzers is used to heat the depleted caustic soda to the required 90°C for the electrolysis process (Schmittinger et al., 2012). As such, there is a constant circular flow of caustic soda between these dilution chambers and the electrolyzers. This process is visualised in the right-hand side of Figure 1 (see Section 2.5). Every pass the excess caustic soda is tapped off for further processing.

2.4 Brine preparation

Brine is a high-concentration solution of salt in water. In different contexts, brine may refer to salt solutions ranging from about 3.5% (a typical concentration of seawater, on the lower end of solutions used for brining foods) up to about 26% (a typical saturated solution, depending on temperature). Lower levels of concentration are called by different names: fresh water, brackish water, and saline water. Brine naturally occurs on the Earth's surface (salt lakes), crust, and within brine pools on ocean bottom. High-concentration brine lakes typically emerge due to evaporation of ground saline water on high ambient temperatures.

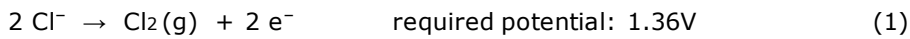
After the electrolysis process, 17% depleted brine is sent back to be processed and replenished to 23% concentrated brine. In this process, the depleted brine must be treated and dechlorinated using large pumps, hydrochloric acid and a small portion of 32% caustic soda (Brinkmann et al., 2014).

The dechlorinated depleted brine is subsequently combined with dilution water and industrial salt. This new mixture is heated again to 90°C using waste heat energy originating from the electrolyzers. This process requires a substantial amount of heat (approximately half of all waste heat produced at the electrolyzers goes to heating the newly formed concentrated brine). In Delfzijl, this step in the brine preparation process is slightly different: the dechlorinated depleted brine is combined with directly concentrated brine from the salt production industry in Delfzijl and vaporised again with a Multiple Effect Vaporisation (MEV) facility to form 23% concentrated brine. Lastly, the newly concentrated brine is passed through resins to remove traces of calcium, magnesium and other metals which are harmful to the membranes in the electrolyzers.

2.5 Electrolysis

Inside an electrolytic cell, two separate chambers are separated by a membrane; the first contains a positive anode and the second contains a negative cathode, as can be seen in Figure 1.

For the production process, heated 23% (by weight) concentrated brine (containing sodium chloride ions) is injected into the second chamber. Chloride ions Cl^- are oxidised at the anode – they lose electrons, to form chlorine gas $\text{Cl}_2(\text{g})$. Thus, the reaction that occurs at the anode is:



Meanwhile, at the cathode, caustic soda solution $\text{NaOH}(\text{aq})$ is fed into the second chamber. This solution is a mixture of caustic soda (NaOH) and water H_2O . The hydrogen ions H^+ in the water are reduced at the cathode – they gain electrons, to form hydrogen gas $\text{H}_2(\text{g})$, while releasing hydroxide ions OH^- into the solution. Thus, the reaction that occurs at the cathode is:

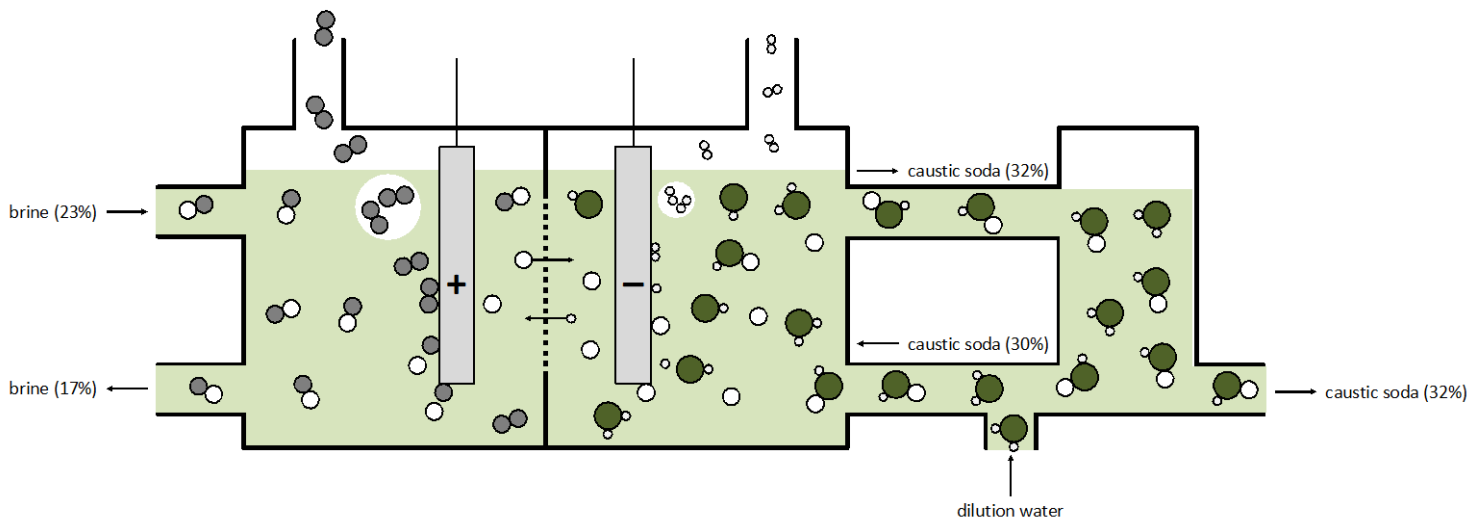
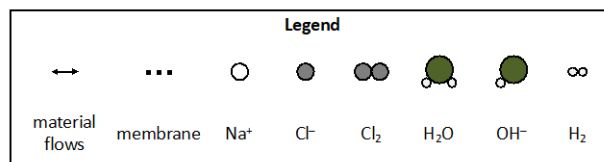
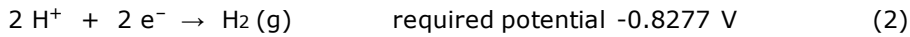
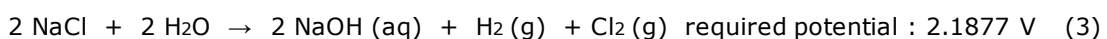


Figure 1 Overview of chemical reactions in electrolytic membrane cell

The membrane is permeable to positive ions such as H^+ and Na^+ , but not to negative ions such as Cl^- and OH^- . Thus, while these redox reactions occur, Na^+ ions move from the anode to the cathode chamber where they combine with OH^- to form extra caustic soda solution. This causes the brine concentration to decrease in the first chamber and the caustic soda concentration to increase in the second. To keep the nonspontaneous redox reaction in balance, the depleted 17% brine and concentrated 32% caustic soda are drained from their respective chambers and are replaced with equal amounts of 23% brine and 30% caustic soda.

The overall reaction of the membrane electrolysis process, depicted in Figure 1, can thus be described with the following equation:



Using electrical laws⁴ the required amount of energy (expressed in GJ or kWh per ton Cl₂), for 1 tonne of Cl₂ plus 1.1282 tonne of NaOH plus 28.4 kg H₂, can be calculated (EuroChlor, 2011) as 1654 kWh (5.95 PJ/Mt Cl₂). Due to resistance across the induced current between the anode and the cathode an additional voltage is needed. Usually for the production of chlorine a voltage of 2.5 to 3.5 V (an over-potential of 0.3-1.3 V). is required, this resistance leads to the production of heat (236-990 kWh/t Cl₂ or 0.85-3.56 PJ/Mt Cl₂).

The smaller the distance between the anode and the cathode, the smaller the resistance. Since 2012, new cell designs have incorporated so called 'zero-gap technology', which minimise the distance between the anode and the cathode (see Figure 2 below), allowing for lower voltage of approximately 0.17 V or 130 kWh/t Cl₂ (0.47 PJ/Mt Cl₂) (Garcia-Herrero et al., 2018, Brinkmann et al., 2014). Although the energy costs drop, the capital costs increase. In the Netherlands, only the Botlek chlor-alkali makes use of the zero-gap technology. About 10 out of the 30 electrolyzers in Botlek have the zero-gap technology implemented (Klein & Ybema, interview 2, 2018). All other electrolytic cells still use finite gap technology.

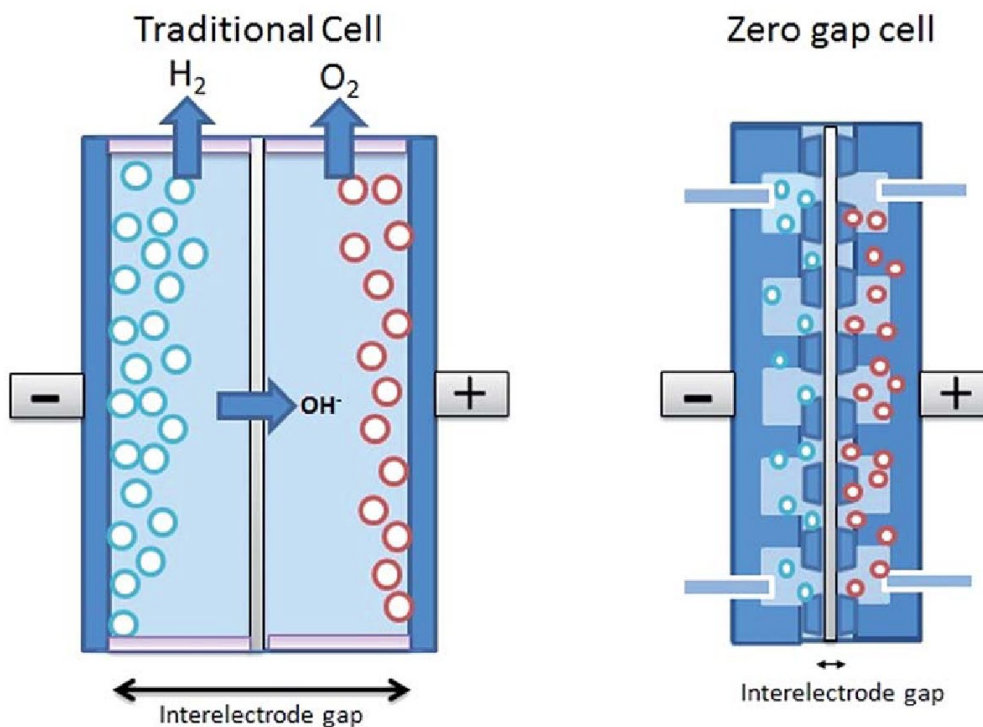


Figure 2 Zero gap technology compared with a conventional electrolysis cell (Phillips and Dunnill, 2016).

2.6 Caustic soda processing

About nine tenths of the 32% caustic soda that is drained from the electrolytic cells is sent back to the caustic soda preparation step. The remaining caustic soda is processed to produce high concentration 50% caustic soda to meet market demands (Brinkmann et al., 2014).

⁴ $W=I.V$, 1 mol Cl₂ requires $2 \cdot 96.5$ kC or $193 \cdot 2.1877 = 422$ kJ/mol or 5.95 PJ/Mt or 1654 kWh/tonne Cl₂

The 32% caustic soda is upgraded to 50% caustic soda through multiple effect evaporation. In terms of process steps, this technology is identical to the MEV of brine explained in section 2.4. The exact conditions for caustic soda vaporisation are explained in another MIDDEN report (Scherpbier and Eerens, Decarbonisation options for the Dutch salt industry, 2021). This process requires a considerable amount of energy by heat (1.5 PJ/Mt chlorine); approximately 80% of the total steam demand for the chlor-alkali manufacturing industry is used for this vaporisation (Schmittinger et al., 2012).

In Botlek and in Bergen op Zoom, water from the caustic soda solution is vaporised using two vacuum pans connected in series, whereas in Delfzijl, four vacuum pans are connected in series (Klein & Ybema, interview 2, 2018). As such, the MEV process in Delfzijl is about 20% more efficient than on the other two locations.

2.7 Hydrogen processing

Due to the high temperature in the electrolyzers (90 °C), the hydrogen gas captured from the electrolysis process is mixed with large amounts of vaporized water (Brinkmann et al., 2014). The water vapour and hydrogen gas mixture (approximately 75% water vapour, 25% hydrogen gas) is cooled, to allow the water to condense (1.4 kt/Mt chlorine), and pure hydrogen gas is left (Schmittinger et al., 2012). The condensed water (20 °C) is then used for creating a new brine solution. During the cooling circa 0.03 PJ/Mt is released to the atmosphere. Subsequently the hydrogen gas is compressed using large electric pumps and transported along pipelines to end-users within the chemical clusters where the various plants operate.

2.8 Chlorine processing

The chlorine gas captured upon electrolysis, just like the hydrogen gas, is also mixed with water vapour due to the high temperatures in the electrolyzers (approximately 20% steam, 80% chlorine gas) (Brinkmann et al., 2014). The chlorine is cooled (0.06 PJ/Mt chlorine) to remove the largest proportion of water vapour (200 kt/Mt chlorine). Subsequently the chlorine is dried using highly concentrated sulphuric acid; whereupon it is compressed and liquified with large electric pumps (Schmittinger et al., 2012). The water captured is fed back to the dechlorination unit.

2.9 Summary

An overview of the chlor-alkali end-to-end manufacturing process is shown in Figure 3 and Table 3. A more detailed explanation of the chlor-alkali manufacturing process, including calculations, derivation and assumptions made, can be found in the Appendices.

Table 3 Chloride, Soda and Hydrogen production, normalized to 1000 kt chlorine per year.

	kt/yr	PJ/yr	Remarks
Inputs			
Salt (98%)	1600		Industrial salt quality
Water	2400		Purified
HCl (32%)	0.18		
<i>Energy</i>			
Steam		1.9	From natural gas fired CHP
Electricity		8.6	1 PJ from natural gas fired CHP, 7.6 from grid (accounting for indirect CO ₂ emissions)
Outputs			
Chlorine (100%)	1000		Liquified
Soda (50%)	1130		And 1130 kt/yr water
Hydrogen	28		
CO ₂	209		From natural gas fired CHP

Chlor-alkali manufacturing process

Normalized for 1 kt chlorine production

All data rounded to 1 or 2 decimals

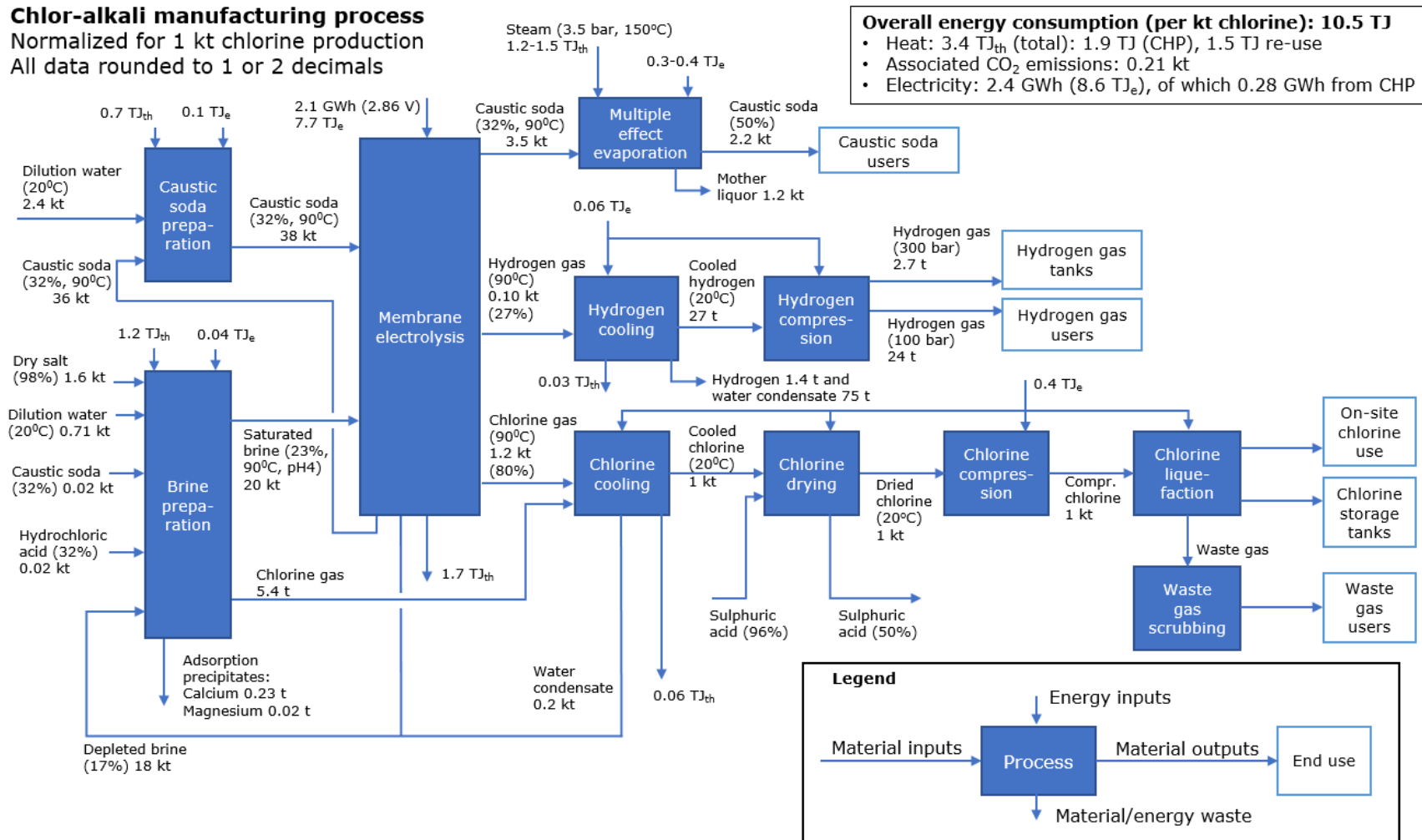


Figure 3 Chlor-alkali production process, normalised for 1 kt of chlorine. Subscript 'e' refers to electricity, 'th' to thermal energy (heat). The percentage in the mass flows refer to percentage pure material. Remaining fraction is water.

3 Chlor-alkali products and use

The chlor-alkali industry has three distinct products, which each have separate applications and industries in which they are used. An estimated 55% of European chemical production depends on chlor-alkali products (EuroChlor, 2017). Figure 4 shows the applications for the chlorine and caustic soda produced in Europe.

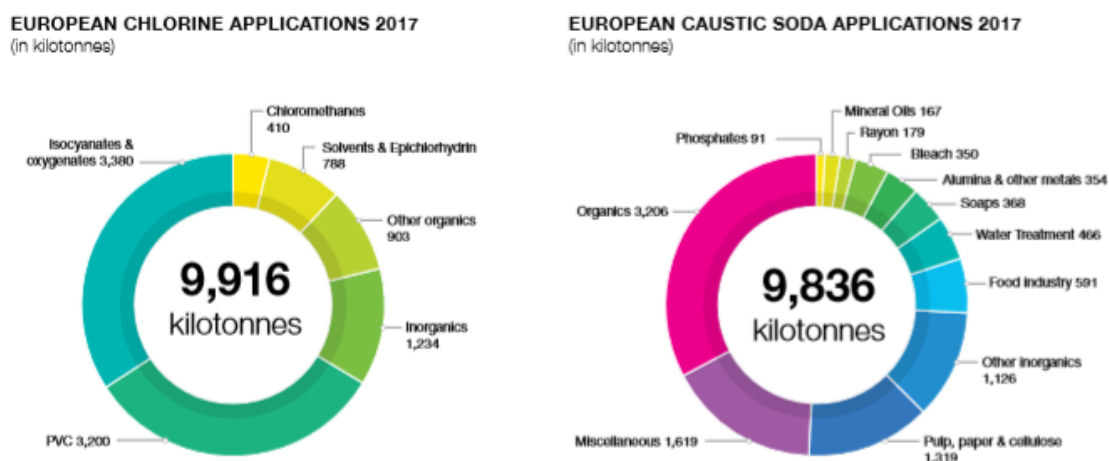


Figure 4 Applications of chlorine and caustic soda in Europe (EuroChlor, 2019)

Table 4 lists the different main usages of the different products resulting from the chlor-alkali manufacturing industry. Below, a further explanation is given as to the application of the products across different industries.

Table 4 Chlor-alkali products in the Netherlands. Prices from Eurostat (2020).

Product	Market value [EUR/tonne]		Mass share in market	Main usages
	Lower est.	Upper est.		
Chlorine	180	220	31%	Production of plastics (PVC, Teflon, etc.), Monochloroacetic Acid production
Caustic soda	310	400	68%	Organic chemical production, paper and pulp industry, food industry, metal industry, water treatment, bleach
Hydrogen	1500	1700	1%	Petrochemical industry, fertilizer production, electronics industry, fuel source

Chlorine

Chlorine, commonly known as a disinfectant for drinking water and swimming pools, has a large amount of applications in the chemical industry. About two thirds of all chlorine in Europe is used in the production of plastics such as polyvinylchloride (PVC), polyurethanes, epoxy-resins and neoprene (EuroChlor, 2017). In the Netherlands, this proportion lays even higher; about 80% of all chlorine produced in the Netherlands is used the plastics manufacturing industry by companies including Shin-Etsu, Hexion, Huntsman, Lyondell, Dow Chemical, Covestro, Teijin and Lubrizol (Stikkelman, interview, 2018). Sabic's chlor-alkali production facility is fully vested in the production of plastics. These plastics are derived from different chlorine products – chloromethanes (CM) and ethylene dichloride (EDC) – which are manufactured on-site within the chlor-alkali manufacturing plants of Nouryon and Sabic. Nonetheless, the production costs of CM and EDC are minor and are therefore not included within the scope of this investigation.

The remaining chlorine is used in the production of monochloroacetic acid (MCA), which in turn is used for pesticide production, the production of medical drugs and dyes. As such, approximately 85% of all produced medicines make use of the chlor-alkali production industry, as well as 25% of all medical equipment (EuroChlor, 2017). Furthermore, half of the chemicals used to protect crops and to sustain food production and quality are based on the chlor-alkali industry.

A negligible proportion of chlorine produced in the Netherlands is used for other disinfecting purposes such as water treatment (Klein & Ybema, interview, 2018). Nonetheless, even within this application, chlorine has a high impact; 90% of all European drinking water is made safe with the help of chlorine (EuroChlor, 2017).

Caustic soda

Just as chlorine, caustic soda is widely used across a wide range of different industrial processes. Almost a third of caustic soda produced is used as reactant in the production of organic chemicals. Approximately 15% (140 kt) of produced caustic soda is used by the paper and pulp industry. Principal uses in pulp and paper production include the cooking/processing of Kraft pulps, the extraction of lignin during the pulp bleaching sequences, and the on-site manufacture of sodium hypochlorite. The general pulp bleaching procedure involves a bleaching sequence during which impurities and colored matter in the pulp are oxidized and/or converted to alkali-soluble forms, and an extraction sequence during which the impurities are removed. Extraction stages almost invariably use caustic soda.

Caustic soda is essential in the food industry (approximately 6% of total production), in water treatment (5%), in the process of refining aluminium from bauxite (4%), in detergent and soap manufacturing (4%), as a bleach mainly in the textile sector (3%), in the production of mineral oils (2%) and in the synthesis of rayon, a synthetic fibre (2%). The remaining production of caustic is attributed to many more applications, such as rubber recycling, acid neutralisation and the pharmaceutical industry.

Hydrogen

Hydrogen is also a co-product of the electrolysis of brine (28.4 kg per tonne of chlorine). This high-quality hydrogen (purity > 99.9 %) is usually used on an adjacent site or sold.

3.1 Environmental issues

Apart from the CO₂ emissions attributed to the chlor-alkali manufacturing industry, the industry has some other effects on the living environment that require careful consideration. These are briefly elucidated below.

Chlorine spills

Chlorine is a hazardous chemical, and human exposure to high concentrations of chlorine can cause permanent damage or even be fatal. Furthermore, if chlorine spills into the environment, this can have detrimental effects on living organisms. Since the implementation of strict regulations on chlorine production the limiting of chlorine transportation in 2001, the number of incidents involving chlorine leaks has fallen rapidly (Du Pré, 2018). Between 2010 and 2018, only five chlorine spills were reported, only one of which affected humans; in 2011 two workers became unwell after a lightning strike caused a small chlorine gas leak in (then) AkzoNobel's plant in Botlek.

Following a series of earthquakes in 2014 in the northern provinces of the Netherlands, a government investigation confirmed that there is no higher risk for external safety based on expectations for the Delfzijl Chemicals Park. (Then) AkzoNobel's plant in Delfzijl was deemed to be earthquake resistant by independent experts (Verbraeken, 2018a). As such, there is no higher risk of chlorine spills in Delfzijl than in other Dutch chlor-alkali plants.

Other emissions

Other pollutant outputs which may occur in the chlor-alkali industry include chlorates, bromates, sulphate, heavy metals, sulphite, organic compounds and halogenated organic compounds and spent acids from the chlorine drying (Brinkmann et al., 2012). Nonetheless, all these emissions are minor and closely monitored by regulators. The mercury and diaphragm electrolysis techniques are far more polluting, and so the Dutch chlor-alkali industry is seen as having a relatively low impact on its environment (Paar, 2010). Other environmental effects are connected to the waste treatment (incineration and recycling) of chlorine containing products at the end of the life cycle.

3.2 Transport issues

Even though chlorine trains were largely banned in the Netherlands as of 2006, (then) AkzoNobel and the Dutch government signed an agreement in which it was determined that incidental transport for the maintenance of factories would still be possible (Verbraeken, 2018a). Nouryon now has one production line for chlorine in Rotterdam-Botlek. If it does not run – for example due to major maintenance – occasional transports from Germany are needed to meet the demand for chlorine. This is seen by industry stakeholders because of strict regulations on chlorine storage (Klein & Ybema, 2018). If Nouryon could store chlorine on its chlor-alkali plant site, it could build up reserves to reduce the dependence of transports from Germany.

In 2018, a new agreement was formulated between the government and (then) AkzoNobel to completely get rid of chlorine transportation by 2021. Instead of building extra chlorine storage facilities, the government supported AkzoNobel's investment in a second chlor-alkali plant in Botlek (Verbraeken, 2018b). As of 2021, a second, fully independent chlor-alkali plant will be operational in Botlek. This plant is projected to have an annual production capacity of 150 kilotons of chlorine and will be fitted with the best available technologies in the chlor-alkali industry. Although in absolute sense, chlorine production will increase because of these developments, political and public opposition to chlorine production is likely to decline (Stikkelman, interview, 2018). The 'chlorine trains' had become such a politicised issue that this compromise between (then) AkzoNobel and the government is seen as a positive development for all involved stakeholders (Boot, interview, 2018).

4 Options for decarbonisation

4.1 Overview

As of 2018, a series of innovative technologies is under development that may provide opportunities in terms of efficiency, cost reduction or sustainability of the chlor-alkali manufacturing industry. These different emerging technologies are categorised across a series of categories deployed in other technological studies of the chemical industry (VNCI, 2018; Den Ouden, Lintmeijer & Van Aken, 2017; Deloitte, 2012); sustainable heat generation, efficiency and electrification, circularity and recycling, and sustainability across the product chain. These different developments are discussed below.

Sustainable heat generation

Since the beginning of the 21st century, a great number of different technologies have been rising that allow for more sustainable generation of heat (Dombi, Kuti & Balogh, 2014). According to a study of the Dutch Association of the Chemical Industry, these include biomass boilers, electric boilers and geothermal heat supply (VNCI, 2018).

Biomass boilers generate steam by burning wood chips, logs, pellets, or other similar organic material. The capital cost of installing a biomass boiler is a multiple of that of a fossil fuel-fired boiler (Dombi et al. 2014). Although the combustion of biomass also generates CO₂ emissions, biomass is considered a carbon-neutral form of energy because the amount of CO₂ released from the combustion process is later re-absorbed by new plants and trees that are planted in the biomass industry. Although this philosophy is increasingly questioned in the literature (Ros, 2015; Van Vuuren et al., 2017), biomass boilers are nonetheless seen as a technology through which steam generation in the chemical industry can be made more sustainable (VNCI, 2018).

An electric boiler is a device that uses electrical energy to boil water, rather than through the combustion of a fuel source. State-of-the-art industrial electrical boilers convert electrical energy to thermal energy with efficiencies up to 99% (Den Ouden, et al., 2017). Capital expenditures for electric boilers are relatively low, and upon installation, the electric boilers can easily and rapidly be deployed. Thus, this technology offers industries flexibility, and allows them to operate at times of low electricity prices, thus reducing the factory's dependence on gas-fired boilers or a CHP (Deloitte, 2012).

Geothermal heat generation refers to the production of steam using thermal energy stored inside the Earth's crust. Although geothermal energy is not yet ready in 2018 to be implemented as a new source for steam generation, experts predict it will be available before 2040 (Deloitte, 2012). A study by the Netherlands Organisation for Applied Scientific Research (TNO) showed that the in the north-east of Groningen and the north-west of Friesland geothermal energy may be used to generate low-temperature steam (temperatures up to 150°C). The chlor-alkali manufacturing plant in Delfzijl is located precisely in these respective areas, and so this may prove to have a high potential for sustainable heat generation after 2030 (Boxem, Veldkamp, & Van Wees, 2016). Furthermore, the TNO study showed that there is a potential for geothermal steam generation in the east of the province

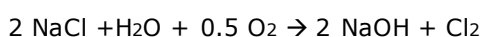
of Zeeland, precisely where Sabic's chlor-alkali production plant is located (Boxem, Veldkamp, & Van Wees, 2016). This may prove to be an interesting technology to invest in after 2030, when the experts deem that the technology will be ready for implementation (VNCI, 2018).

Efficiency and electrification

Just as with the Multiple Effect Vaporisation (MEV) technology for brine, the efficiency of MEV vaporisation of caustic soda increases by about 10% for each extra effect that the vaporisation process passes through. Investment costs for MEV facilities for caustic soda are considerably higher; because of its irritant and corrosive nature extra safety regulations are in place for the multiple effect vaporisers. Furthermore, caustic soda has a higher boiling point, so energy costs for both steam generation as well as for the vacuum pumps are considerably higher than those of brine vaporisation (Brinkmann et al., 2014). It is not cost-effective to have more than five vacuum pans for the vaporisation of caustic soda (Schmittinger et al., 2012). The vaporisation process may, in the long run, also be made more efficient by deploying Mechanical Vapour Recompression. Due to the higher steam temperature requirements, the MVR technology is estimated to be ready for implementation in caustic soda vaporisation after 2030 (Klein & Ybema, interview 2, 2018).

Membrane cell designs are refined and optimised continually in the competitive chlor-alkali industry (O'Brien, Bommaraju & Hine, 2007). In 2005, the so called 'zero-gap technology' was developed. With this technology, the distance between the anode and cathode is minimised as they are placed very closely to the membrane wall. This technology has become widely adopted since 2010 (Klein & Ybema, interview 2, 2018), but due to the high investment costs, chlor-alkali plants that had switched to membrane electrolysis before 2005 are struggling to catch up. The zero-gap technology is said to be deployed partially Nouryon's chlor-alkali plant in Botlek since 2017, thus realizing significant energy savings (AkzoNobel, 2017); the energy usage of their chemical processes was said to have been reduced by 10%.

Instead of producing hydrogen at the cathode the electrolyse process can also be altered to use an oxygen depolarized cathode (ODC), replacing the production of hydrogen by the use of oxygen (Chavan & Turek, 2015, Moussallem et al, 2008):



The required electrical potential is reduced by 1.23 V or 30-40%. In economic terms the benefit is less, the reduction in electricity (~650-850 kWh/tonne or 35-50 euro) is outweighed by the reduced income in hydrogen (~28 kg H₂ or 35-50 euro).

Sustainability across the product chain

Chlorine is used as a building block to produce plastics (PVC) worldwide. PVC is a robust material and has a longevity of centuries – thus having a potentially detrimental impact on the environment. Re-use of PVC as granulate is possible, but the used process cut the average length of the polymer limiting the re-use to 4-5 cycles. New technologies are increasingly investigating alternatives to plastics across its wide range of uses. There is a rapidly growing 'green building' movement that has developed many successful alternatives to PVC production. As these technologies develop further and their production costs decline, this may influence the chlor-alkali industry. Nonetheless, experts involved in the chemical industry believe that the demand for chlorine is likely to keep steadily increasing until the year 2050 (Kleijne, email, 2018).

4.2 Technology specifications

Each existing and alternate technology is mapped into the Technology characteristics dataset of the MIDDEN database, and all data on material flows, energy flows and investment costs are normalised per unit of main output of the specific process.

In the MIDDEN project the capital costs are primarily calculated as Total Overnight Costs, with no assumption about interest rate. In addition the capital expenditure (CAPEX) costs can be presented. In this report we use for CAPEX calculations the following assumptions: a capital to loan investment ratio of roughly 1:4, an expected return rate on capital investments of 15%; an expected return rate on loaned investments of 3%; and a depreciation period of 10 years.

Figure 5 gives a modular overview of the technology characteristics for the chlor-alkali manufacturing industry. The figure shows how for a specific process within the industry under consideration, different technologies are used to produce the outputs generated by the process step. For example, the vaporisation process (Step 4) contains three deployed technologies deployed across the salt industry as of 2016, and one alternate technology, each of which are quantified in the technology characteristics dataset.

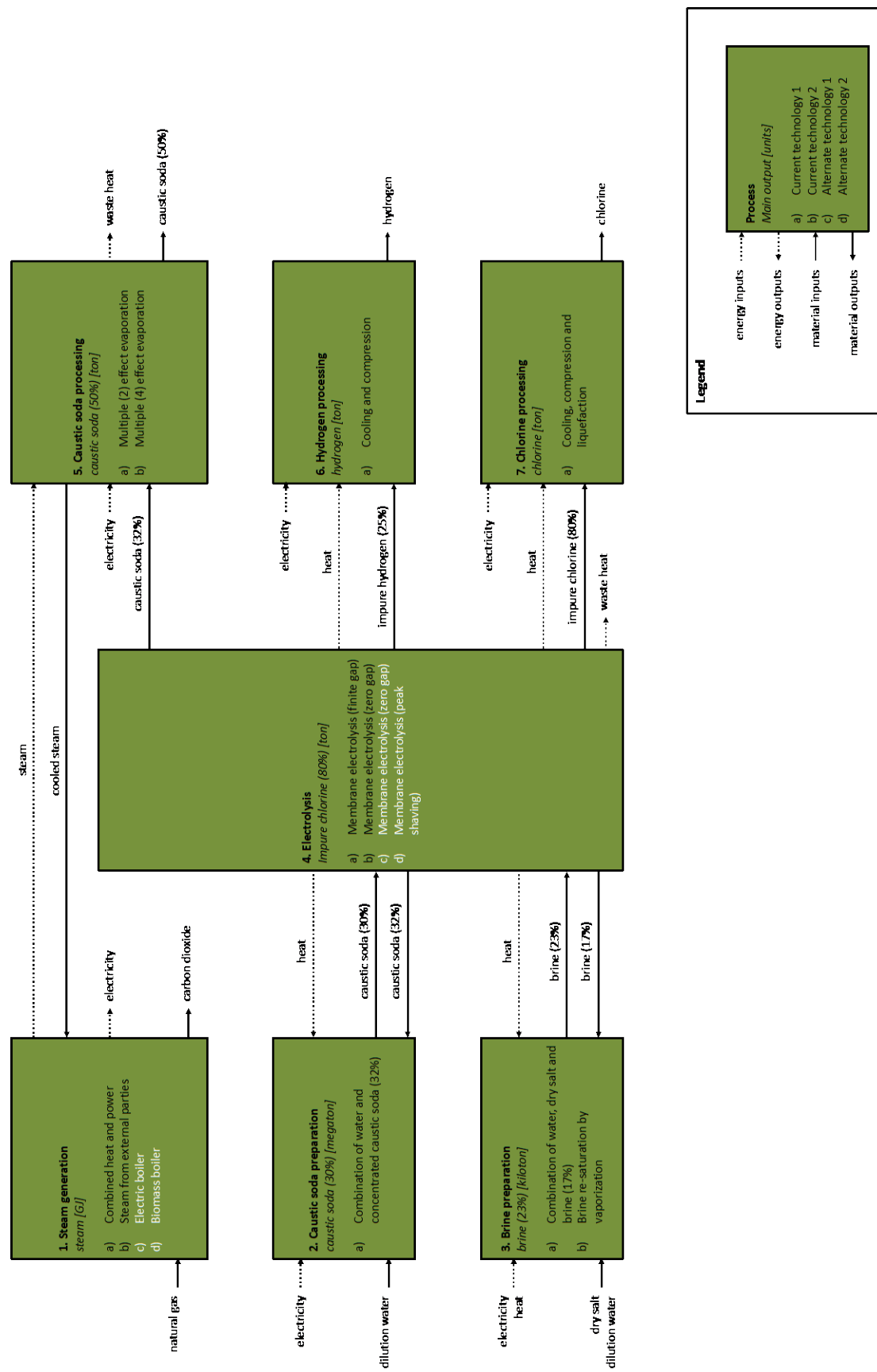


Figure 5 Modular overview of MIDDEN dataset for chlor-alkali manufacturing industry

Electric boilers

Electric boiler technology for small-scale industrial processes has existed for numerous years, but their deployment in the chemical industry has only recently become attractive due to lower investment costs, the increased temperatures at which they can generate steam, and the low electricity prices in the Netherlands (VNCI, 2018). Using green (renewable) electricity this technology produces carbon-free steam.

In an electric boiler, electricity runs through a heating element, which heats water via a heat exchanger. The water is heated hot enough until it boils, upon which saturated steam can be transported to the necessary plant facility. Electric boilers require little equipment to be installed, and as such their investment costs are substantially lower than other sustainable steam generation technologies (Ros & Schure, 2016). Furthermore, once placed, the maintenance costs of electric boilers are relatively low, as compared to (bio)fuel-heated boilers need periodic refurbishment of their tubing systems.

Table 5 Technological specification of electric boilers (Lensink & Schoots, 2021)

Parameter	Value	Unit
Reference output capacity	19.8	MWe
Efficiency	99	%
Investment costs	0.115	MEUR/MWth
Fixed O&M costs	0.0567	MEUR/MWth/yr
Economic lifetime	15	years

In 2018 the average electricity price (0.052 EUR/kWh or 14.4 euro/GJ) is still high compared to the gas prices, 0.19 EUR/m³ or 6 EUR/GJ. Towards 2030 it is expected that the electricity price will go up to 0.057 EUR/kWh or 15.8 euro/GJ and the gas price to 0.25 EUR/m³ or 7.9 EUR/GJ (PBL, 2019). To reach a break-even point the EU-ETS price for the CO₂ emission of natural gas needs to increase to 130 euro/tonne CO₂, making this a competing technology beyond 2030. Table 5 gives an overview of the main relevant parameters for the conceptualisation of this technology in the MIDDEN dataset.

Biomass boilers

Biomass boilers, just like electric boilers, form a more sustainable source of steam generation. Biomass boilers can generate high pressure steam at temperatures up to 200°C, which is largely enough for the chlor-alkali manufacturing industry (VNCI, 2018). Biomass is the collective name for a wide range of wood types; it can include pellets, chips and logs. Biomass is considered a carbon-neutral form of energy, as the amount of CO₂ released by burning biomass is later re-absorbed by the plants. Furthermore, biomass prices are generally more stable than those of other energy carriers such as gas and electricity (Ros & Schure, 2016).

The technology of industrial biomass boilers is very similar to that of regular gas-fired boilers. By burning biomass, water is heated via a heat exchanger which eventually boils to form steam. After passing through the brine vaporisation process, cooled or condensed steam can be passed back into the biomass boilers where it can be heated again. Loss of water throughout this circular process is compensated by adding treated fresh water. The treated water in the piping system is periodically refreshed to avoid corrosion.

Biomass boilers are more expensive than electric boilers but have lower operating and maintenance cost (VNCI, 2018). State-of-the-art biomass boilers have efficiency rates ranging between 85% and 90% (Schoots et al., 2017). Since the biomass is combusted in large chambers, biomass boilers require a substantial amount of space to be installed.

Industry stakeholders (Kleijne, e-mail, 2018; Lintmeijer, interview, 2018) believe that the placement of biomass boilers in chlor-alkali manufacturing plants can help it reduce its CO₂ emissions. Although they foresee that the placement of electric boilers will be financially more attractive in the long term, the diversification of steam generation processes is attractive as it decreases a plant's dependence on the prices of a single energy carrier. Since biomass pellets have a relatively stable price (industrial pellets cost around 163 \$/ton or 8.50 EUR/GJ, see Canadian Biomass Magazine, 2017 and World Bioenergy, 2014), biomass boilers remain an interesting alternative technology for 2030 (gas prices are 6-8 EUR/GJ, with EU-ETS prices between 10-40 EUR/tCO₂ this technology becomes competitive) to consider when evaluating technologies to decarbonise the chlor-alkali manufacturing industry. Since it is more capital intensive than electric boilers and there can be a shortage of biomass on the long term, which will increase its prices, the industry stakeholders do not see it as a viable technology alternative for the salt manufacturing industry. Table 6 gives an overview of the main relevant parameters for the conceptualisation of this technology in the MIDDEN dataset.

Table 6 Technological specification of biomass boilers⁵ (Lensink & Schoots, 2021)

Parameter	Value	Unit
Reference output capacity	10-20	MWth
Efficiency	90	%
Investment costs	0.76-0.88	MEUR/MWth
Fixed O&M costs	0.051-0.052	MEUR/MWth/yr
Economic lifetime	12	years

Zero-gap membrane electrolyzers

Zero-gap membrane electrolyzers consist of an electrolytic cell where the anode and the cathode are placed extremely close to the membrane wall that separates them; the distance between the electrodes is less than or equal to 1 mm (Brinkmann et al., 2014). Minimisation of the distance between the electrodes leads to a minimisation of the voltage drop across the electrolyte, and thus saves electric energy (typical around 0.19-0.24 V or 6-8%). However, with the minimisation of electrode distance, bubbles are more likely to be entrapped between the membrane wall and the electrodes, which causes the voltage drop to increase again. This is avoided by special coating of the membrane with a porous inorganic material (O'Brien et al., 2007). The development of this coating layer has caused zero-gap technology to become widely adopted across the European chlor-alkali industry as of 2005 (Brinkmann et al., 2014).

Although the chlor-alkali's direct emissions are not lowered by the zero-gap technology, it has a serious influence on its electricity usage, and thus helps to reduce indirect emissions. Since the indirect emissions of the chlor-alkali industry are considerably higher than the direct emissions, this alternate technology seems promising in reducing the net emissions of the Netherlands as a whole (Klein & Ybema, interview, 2018).

Since the electricity savings from zero-gap electrolyzers are considerable, the technology is financially attractive as a long-term investment for companies in the Dutch chlor-alkali industry. However, since Nouryon and Sabic had changed from diaphragm and mercury electrolyzers to the more expensive membrane electrolyzers prior to 2005, they had been slowly to invest in the zero-gap technology once it became available (the first zero-gap electrolyser was installed in their Frankfurt plant in 2014, see Geipel-Kern, 2014). A change from finite gap electrolyzers to zero-gap electrolyzers requires considerable new investments

⁵ Ranges indicate values for boilers with solid biomass or B-quality wood as fuel, assuming 7500 hours/yr

and requires the writing off previous considerable investments in the finite gap electrolyzers (Klein & Ybema, interview, 2018). Furthermore, the maintenance costs of the membranes themselves, as well as those of the coating layer are considerable (Schmittinger et al., 2012). For the 2017 process description it is assumed that approximately 1/3 of the electrolyzers at Nouryon are zero-gap electrolyzers.

Dutch chlor-alkali industry specialists see the implementation of zero-gap electrolyzers as the most serious investment in their industry until 2030 (Kleijne, email, 2018). As such, not only the chlor-alkali's direct emissions, but also its considerable indirect emissions can be reduced.

Capacity increase to utilise peak-shaving production

When a chlor-alkali plant deploys peak-shaving production, it adapts its production levels to the electricity prices. This is potentially not only financially interesting but can also help making the production of chlorine more sustainable by making direct use of the electricity generated from renewable sources (Krebbekx et al., 2015).

Increasing production when electricity prices are low and reducing production when electricity prices are high requires larger storage capacities to ensure product delivery with clients. Chlorine storage capacity is strictly regulated in the Netherlands, so flexible operation of a chlor-alkali plant is only possible for short periods of time without influencing the constant supply to chlorine customers. Thus, the number of hours that peak-shaving can be applied depends on the amount of storage capacity and on the extra production capacity.

Nouryon has already closely investigated peak shaving and formulated a business case for the implementation of the technology (Klein & Ybema, interview 2, 2018). Upon the construction of their second independent chlor-alkali plant in Botlek as of 2021, Nouryon can supply dozens of megawatts of interruptible flex power with for their new chlorine plant (Verbraeken, 2018b). The costs for flexible operations are mainly determined by possible investments in extra capacity and ICT, which are necessary to make flexibility possible. Once the extra capacity is available and the operating system of the plant has been set up in such a way that flexible operation is possible, the further costs for flexible operation are mainly for ICT and adjustment of procedures.

5 Discussion

In order to identify robust strategies through which the chlor-alkali manufacturing industry can be decarbonised, the industry was studied and analysed in collaboration with stakeholders. By means of an analysis of the different processes at play and the various technologies implemented across the three chlor-alkali production plants in the Netherlands, four alternative technologies were identified that can support decarbonisation efforts of the chlor-alkali manufacturing industry by 2050; the placement of electric and biomass boilers to reduce the industry's direct emissions, and zero-gap membrane electrolyzers to tackle the industry's electricity consumption, and thus its indirect emissions. The major step in decarbonising the electricity used for electrolysis lies with the generation of carbon free electricity in the power sector. This is beyond the focus of this report.

The Dutch chlor-alkali industry in 2016 consumes 2.8 PJ of natural gas resulting in approximately 180 kt of CO₂ emissions, while using almost 6.1 PJ of electricity resulting in roughly 760 kt of indirect CO₂ emissions. From this conceptualisation, it becomes apparent that the main challenge in decarbonising the chlor-alkali industry does not lay in its reduction of direct emissions, but more in lowering its indirect emissions.

This study shows that the large-scale implementation of zero-gap membrane electrolyzers is a technology that can aid to reduce the indirect net emissions of the chlor-alkali industry. Across the current chlor-alkali industry, currently 10 zero-gap membrane electrolyzers are installed in Nouryon's plant in Botlek. Based on estimates from this research, the implementation of approximately 30 more zero-gap membrane electrolyzers across Nouryon's plants in Botlek and Delfzijl, as well as Sabc's plant in Bergen op Zoom, can aid to reduce the chlor-alkali's electricity consumption by 0.4 to 0.6 PJ per year. This measure will require a considerable investment of approximately 85 to 100 million euros, which is only financially feasible when electricity prices are considerably higher. Moreover, it will require the replacement of finite-gap membrane electrolyzers, which have been installed across the Dutch chlor-alkali industry in the early 2000s, which may require the premature depreciation of capital for the chlor-alkali producers. Depending on how the CO₂ intensity of power generation in the Netherlands develops, the total indirect emission reductions (using the CO₂ intensity for electricity production for 2016) are estimated between 90 kt of CO₂ per year to 120 kt annually.

Based on this research, the small-scale implementation of biomass boilers as well as electric boilers can support Sabc and Nouryon meet the thresholds for direct emission reductions stipulated by the ETS. The necessary investments in electrifying steam generation are relatively minor; an investment of EUR 150,000 in electric boilers can already reduce the direct emissions by more than 20 kt of CO₂ per year by 2030.

The direct emissions of the chlor-alkali industry are almost all attributed to the steam generation process needed for vaporisation of caustic soda. Based on findings in the empirical research, this study has focused on the implementation of sustainable alternatives for heat generation. Nonetheless, based on the expert elicitation conducted in this research, these sustainable alternatives may be less desirable in a transition to zero net emissions beyond 2030. Beyond 2030, the salt-chlor-alkali production chain is likely to become more dependent on hydrogen-based steam generation and geothermal steam generation.

Another aspect that could considerably reduce the direct emissions of caustic soda production is if the demand for high concentration caustic soda were to change to lower concentration caustic soda. However, this can only be achieved by developments downstream, and is not studied within the scope of this research. Nonetheless, in the light of MIDDEN and the study of chain effects of material flows across the entire Dutch industrial sector, this is an important aspect to monitor in future research.

By studying the chlor-alkali industry on a process level, and through the discussions of technological developments with a large range of industry stakeholders, the key technologies that can aid to enable an energy transition in the chlor-alkali industry were identified. Despite the future of Dutch chlor-alkali industry facing a complex palette of opportunities and risks for decarbonisation, this investigation has shown that the most robust way forward is to focus on the large-scale implementation of zero-gap electrolysers. The small-scale implementation of sustainable heat generation facilities can allow the chlor-alkali plants to fulfil emission demands stipulated by the EU-ETS till 2030. The extent to which the indirect emissions of the chlor-alkali can be reduced by 2030 is predominantly dependent on the carbon intensity of power generation in the Netherlands, and not in the hands of the chlor-alkali industry stakeholders.

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Appendix A:

Explanation of brine preparation process

The brine preparation process contains two separate salt sources, each of which are prepared in a different way. The membrane electrolysis process allows for the recirculation of depleted brine from the electrolysis cells, and thus a central aspect of the brine preparation is the treatment of depleted brine. Secondly, newly supplied salt must also be dissolved to re-saturate the brine that is fed back into the electrolytic cell. This second aspect includes the supply and dissolution of salt, and treatment of the brine.

Brine saturation

The salt that is supplied to the chlorine production plants in the Netherlands originates from solution-mined, vacuum evaporated dry salt, which contains small traces of water (2 wt%).

For the different chlorine production facilities, the salt is delivered in different ways. For the chlor-alkali production facility at Botlek, and the vacuum salt is transported by ship from Hengelo. Similarly, for the Sabic chlorine plant in Bergen op Zoom, the salt is produced off-site and is transported to the production facility. Lastly, the chlor-alkali production plant in Delfzijl uses salt that was solution mined by AkzoNobel in an on-site production plant. The dry salt is subsequently diluted with dilution water and with depleted brine that is returned after electrolysis and dechlorination.

Brine treatment

The salt that is supplied to the chlorine production plants in the Netherlands originates from solution-mined, vacuum evaporated salt and has extremely high purity; the dry basis of the vacuum salt contains 99.95% NaCl. An overview of the vacuum salt quality is given in Table 9.

Table 7 Vacuum salt quality

Contents	Mass fraction (ppm)	Weight percentage (wt.%)
<i>Dry basis</i>		98%
NaCl		97.951%
Sulphates	400.00	0.0392%
Calcium	12.00	0.00118%
	1.00	0.000098%
Magnesium		
Iron	1.00	0.000098%
Copper	0.04	0.00000392%
	50.00	0.00490%
Insolubles		
<i>Wet basis</i>		2%
Water		2%

For the membrane cells that are used in the electrolysis, water hardness (the amount of magnesium and calcium dissolved in the brine) must be below 20 parts per billion (ppb). Specially designed resins enable ion exchange to reduce the water hardness. These resins require periodic regeneration with caustic soda (NaOH) and hydrochloric acid (HCl), which, in turn produces wastes.

This resin technology enables the membranes in the electrolytic cells to have a useful life of 4 years (Brinkmann et al., 2014). Over that period, the calcium and magnesium will be precipitating on the membranes, but this occurs very gradually and results in a gradual decline in the efficiency of the cell as well as an increase in the power consumed by the cell. The required purity level will depend on the operating current density of the electrolytic cell. The ion exchange resin is periodically regenerated with HCl and NaOH. The pH going into the ion exchange is typically measured to avoid damaging the resins.

Brine heating

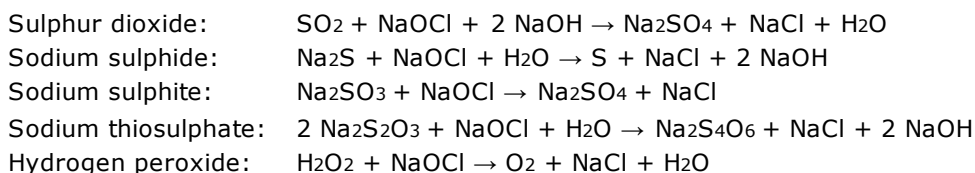
After the ion exchangers, the brine is transferred to storage tanks to be pumped into the cell room. The pure brine is heated to the necessary temperature of approximately 90°C (temperatures vary per production plant between 80°C and 90°C).

Brine dechlorination

Brine exiting the cell room must be treated to remove residual chlorine and control pH levels before being returned to the saturation stage. This can be accomplished via dechlorination towers with acid and sodium bisulphite addition. Failure to remove chlorine can result in damage to the ion exchange units. Brine should be monitored for accumulation of both chlorate anions and sulphate anions, and either have a treatment system in place, or purging of the brine loop to maintain safe levels, since chlorate anions can diffuse through the membranes and contaminate the caustic, while sulphate anions can damage the anode surface coating.

For the membrane cell technique, complete dechlorination is achieved by passing the brine by using chemical reducing agents such as sulphite. Residual levels were reported to be < 0.5 mg/l or below the detection limit (Euro Chlor, 2011) and < 0.1 mg/l (Dibble and White, 1988).

Chemical reducing agents such as sulphur dioxide (SO₂), sodium sulphide (Na₂S), sodium sulphite (Na₂SO₃), sodium thiosulphate (Na₂S₂O₃) or hydrogen peroxide (H₂O₂) are used to destroy the free chlorine in the brine. The chlorine or hypochlorite is reduced to chloride (Cl⁻). The choice of the chemical reducing agent is influenced by cost, availability, and ease of handling. Depending on the reducing agent, the following reactions take place (Brinkmann et al., 2014).



Chemical reducing agents have the advantage of also reacting with chloramines and bromamines. Enough residence time and an excess of reducing agents are required to ensure the complete destruction of free chlorine. In order to control the heat of the exothermic reaction, diluted solutions are used to limit the temperature to about 50 °C. For example, to reduce 1 kg of chlorine absorbed, 4.45 kg of reactive agent Na₂S₂O₃ or 89 kg of diluted 5 wt.-% solution are required (Brinkmann et al., 2014).

Appendix B:

Explanation of membrane electrolysis

General description

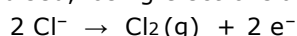
Chlorine, hydrogen and caustic soda are obtained by the electrolysis of brine. All three products are highly reactive, and the membrane electrolysis technology has been developed to separate these different products and keep them apart.

This technology has several key advantages as opposed to mercury and diaphragm electrolysis methods deployed in other European countries: the process costs less energy per unit of product than mercury and diaphragm electrolysis; the caustic soda produced is very pure; no environmentally harmful substances such as mercury and asbestos are used (Struker, 1994).

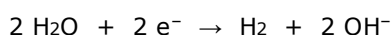
The electrolytic cell consists of two chambers – a cathode chamber and an anode chamber – separated by a cation-exchange membrane. This membrane is permeable to positive ions such as H^+ and Na^+ , but not to the negative ions such as Cl^- and OH^- . The membrane is impermeable to water, which is why saturated brine (23 wt%) is continuously fed into the membrane anode cell while the depleted brine after electrolysis (17 wt%) is drained. Conversely, at the cathode cell, lower concentration aqueous sodium hydroxide (30 wt%) is fed into the system than is drained back out (33 wt%).

In the two electrolytic cells, different reactions occur, which each have an influence on the production process.

At the anode, chloride ions are oxidised, losing electrons and becoming chlorine gas:



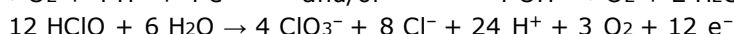
At the cathode, positive hydrogen ions pulled from water molecules are reduced by the electrons provided by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution:



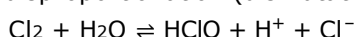
The ion-permeable ion exchange membrane at the centre of the cell allows the sodium ions (Na^+) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda ($NaOH$). The overall reaction of the membrane electrolysis process, depicted in Figure 2, can thus be described with the following equation:



Aside from the above reactions, some side reactions occur during electrolysis, which lead to efficiency losses. At the anode, water is oxidised to oxygen and hypochlorous acid is oxidised to chlorate.



Hypochlorous acid is formed by disproportionation (dismutation) of chlorine in water:



Chlorate is also produced by chemical reactions in the anolyte:



These four major side reactions are repressed by lowering the pH value. The pH value is usually lowered by acidifying the brine with hydrochloric acid to pH < 6. This does not only reduce the formation of oxygen, hypochlorite and chlorate, but also increases the lifetime of the anode coating.

Because of the corrosive nature of chlorine production, the anode must be made from a non-reactive metal such as titanium (commonly RuO₂, IrO₂ and TiO₂ coating on a Ti substrate), whereas the cathode can be made from a more easily oxidised metal such as nickel (commonly nickel coated with noble metal-based coatings).

The membrane electrolysis generally operates at high temperature to keep its electrical conductivity high and with the right electrolyte concentrations to achieve a desirable rate of osmotic water transport and maintain the right equilibrium water content in the polymer. Table 10 gives typical operating conditions according to O'Brien et al. (2007) and Brinkmann et al. (2014).

The temperatures of the feed caustic and brine are monitored and controlled throughout the electrolysis process. Pressure control valves control the pressures in the chlorine and hydrogen headers. The production rate is controlled by changing the voltage of each cell throughout the process.

Table 8 Membrane electrolysis operating conditions

Parameter	Allowable range	Typical value
Feed brine concentration	270–305 gpl	300gpl
Exit brine concentration	190–230 gpl	200gpl
Feed brine pH	< 11.6 at 23°C	
Exit brine pH	>2	2–4
Feed NaOH concentration	28–32% (w/w)	30%
Exit NaOH concentration	30–33% (w/w)	32%
Exit caustic temperature	80–90°C	87°C
Exit brine temperature	80–90°C	87°C
Differential pressure	5–30mbar	20mbar
Current density	1.5–6.0 kA m ⁻²	
Cell voltage	2.35–4.00 V	

Appendix C:

Explanation of chlorine processing

Full processing of chlorine gas takes a hot, wet vapor at approximately atmospheric pressure and converts it to a cold, dry liquid under significant positive pressure. The common processing steps therefore are cooling, drying, compression, and liquefaction. The severity of the two latter processes depends on the desired degree of recovery of chlorine as the liquid and on the composition of the gas produced in the cells.

From chlorine processing, 200 kg of condensed water per tonne of chlorine cooled from 90 °C to 25 °C are typically recycled (EuroChlor, 2011). The output chlorine has approximately the following impurities: oxygen (0.5–2.0 vol-%), hydrogen (0.03–0.3 vol-%).

Cooling is accomplished in either one stage with chilled water or in two stages with chilled water only in the second stage. The chlorine can be cooled indirectly, directly or through a combination of both. The indirect method causes less chlorine to be condensed or absorbed and generates less chlorine-saturated water for disposal. For the direct cooling method, water is sprayed into the top and flows counter current to the chlorine. This treatment thoroughly washes the chlorine; however, dechlorination of the wastewater consumes a large amount of energy. This direct method has the advantage of better mass transfer characteristics and higher thermal efficiencies (Brinkmann et al., 2014). In closed-circuit cooling, the advantages of both methods are combined. To avoid solid chlorine hydrate formation, the gas is not cooled below 10°C. Maintaining temperatures above 15 °C prevents blockages in the process equipment (Schmittinger et al., 2006).

Chlorine after cooling is still too wet for processing in ferrous-metal equipment. Chlorine from the cooling system is saturated with water vapour. There still is 1–3 vol-% of water in the chlorine, which must be reduced to avoid corrosion and to minimize the formation of hydrates. The chlorine drying is conducted with concentrated sulfuric acid (96 – 98 wt. %), and the moisture level is reduced to less than 20 mg/m³.

The dried chlorine gas is usually compressed before use. The level of compression depends on the application. A large fraction of the world's output of chlorine is consumed on site. The production of ethylene dichloride (EDC) is the single largest-volume use. The dry gas supply pressure then is determined by the needs of the EDC process.

Some of the compressed gas is also liquefied with an electric compressor. An increase in liquefaction pressure equates with an increase in energy costs of chlorine compression. Nonetheless, this results in an overall reduction in energy requirement. To achieve a liquefaction pressure of 0.8 MPa, at room temperature conditions, the electrical energy requirement for the liquefaction of 1 tonne of chlorine gas is 42 kWh/t (Schmittinger et al., 2015).