



PBL Netherlands Environmental  
Assessment Agency

# DECARBONISATION OPTIONS FOR THE DUTCH SALT INDUSTRY

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

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**Manufacturing Industry Decarbonisation Data Exchange Network**

## **Decarbonisation options for the Dutch salt industry**

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### **Authors**

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

### **Acknowledgements**

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

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

J.R. Ybema (Nouryon Specialty Chemicals)

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

Helen Roesink (Nedmag)

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

[Silvana.Gamboa@tno.nl](mailto:Silvana.Gamboa@tno.nl).

### **Erratum**

An earlier version of this report was published in 2019, but contained errors in relation to the description of the magnesium salt production. This version also includes a number of minor updates.

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A non-final 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.

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# FINDINGS

## Summary

The Dutch salt industry consists of four production plants in Delfzijl, Hengelo, Harlingen (sodium chloride salt) and Veendam (magnesium salt), which together produce roughly 6.6 million tonnes (Mt) of salt, annually. To produce 1 Mt of salt requires, averaged over all production types (vacuum, MVR, chemical) approximately 1.5 PJ of heat energy along with 75 GWh (0.26 PJ) of electricity. The annual turnover in the salt industry is approximately EUR 330 million and it spends approximately 35% of its total costs on electricity and natural gas.

Salt products can be divided in 4 sub-categories:

- a) Industrial salt (e.g.: Electrolysis salt, pharmaceutical salt, food salt, feed salt)
- b) Specialties salt (e.g.: Table salt, nitrite pickling salt, water-softening salt)
- c) Off-spec salt (e.g.: De-icing salt, road salt, dishwasher salt)
- d) Other salts (e.g.: Magnesium chloride brine and solid salt).

Most of the produced sodium chloride industrial salt is used in the chlor-alkali industry to produce chlorine, soda and hydrogen.

The salt manufacturing process consist of 6 steps; steam generation, salt extraction, brine purification, brine vaporisation, centrifugation and treatment. The steam generation process generates most of the direct CO<sub>2</sub> emissions in the salt by the deployment of CHP (combined heat and power) plants. Most of this steam is generated so that it can be used to vaporise the brine with multiple effect vaporisers.

In the salt manufacturing industry, the key opportunity for decarbonisation up to 2030 lies in the electrification of its heat processes by using mechanic vapour recompression technology for brine vaporisation and electric boilers to generate steam. These measures can reduce the direct CO<sub>2</sub> emissions by almost 40% by 2030, from 550 kilotonnes (kt) to approximately 350 kt of CO<sub>2</sub> per year. Investment costs for these emission reduction steps by 2030 are estimated between EUR 15 to 30 million (EUR 75–150 per tonne of CO<sub>2</sub>, 5%–10% of the annual turnover in the salt industry).

Further decarbonisation options for 2050 include:

- Continue and increase steam generation by using steam of the waste incineration Twence and the pyrolysis plant Empyro in Hengelo and the waste incineration REC by Frisia in Harlingen
- Steam generation by means of geothermal heat generation in Harlingen and Delfzijl
- Steam generation by means of hydrogen, including storage using empty salt caverns

In addition, there are some options (depending on the suitability of the empty salt caverns for high pressure options) that can facilitate the energy transition:

- Carbon Capture and Utilisation or Storage (CCUS) using empty salt caverns
- Compressed Air Energy/storage using empty salt caverns.
- Hydrogen storage using empty salt caverns.

# FULL RESULTS

## Introduction

This report describes the situation in 2016 for the Dutch salt production in the Netherlands and the options and preconditions for its decarbonisation. The study is part of the MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network). The MIDDEN project aims to support industry, policymakers, 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, **salt producers** include: Nouryon, Frisia Zout and Nedmag. These companies operate on four different salt production facilities in the North of the Netherlands and across 8 different salt extraction locations.

**Production processes** include mining salt (brine), brine purification, vaporisation; products include: sodium salt, magnesium salt.

The main **options for decarbonisation** are:

Electrification vaporisation using mechanic vapour recompression technology and electric/biogas/hydrogen boilers to generate steam. Further decarbonisation options for 2050 include:

- Continue and increase steam generation by using steam of the waste incineration Twence and the pyrolysis plant Empyro in Hengelo and the waste incineration REC by Frisia in Harlingen
- Steam generation by means of geothermal heat generation in Harlingen and Delfzijl
- Thermal oil heating by means of hydrogen by Nedmag.

In addition, there are some options (depending on the suitability and type of used sodium chloride salt caverns for high pressure options) that could facilitate the energy transition:

- Carbon Capture and Utilisation or Storage (CCUS) using empty salt caverns
- Compressed Air Energy/storage using empty salt caverns
- Hydrogen storage/use, using empty salt caverns.

### Reading guide

Section 1 introduces the Dutch salt industry. Section 2 describes the current situation (base year: 2016) for sodium salt production process in the Netherlands. The production of magnesium salts,  $MgCl_2$  and  $MgO$  (4% of the salt production) is not specifically described in this chapter. Section 3 describes the relevant products of the salt industry, while options for decarbonisation are systematically quantified and evaluated in Section 4. The feasibility of and requirements for those decarbonisation options are discussed in Section 5.

# 1 Salt production in the Netherlands

## 1.1 Background

The Netherlands has a long history with the salt manufacturing industry. The first underground caverns were discovered in 1886 in Delden, Overijssel. The *Koninklijke Nederlandse Zoutindustrie* (Royal Dutch Salt Industry) was the first company to exploit these caverns shortly after (Paar, 2010). This company later became a founding member of AkzoNobel salt branch (AkzoNobel, 2018). Throughout the 20th century, salt became an increasingly relevant product in the chemical industry, both for the Netherlands and neighbouring Germany. By 1994, three companies were involved in the Dutch salt manufacturing industry; Frima B.V. (currently Frisia Zout B.V.) near Harlingen; Billiton Delfstoffen (currently Nedmag B.V.) near Veendam and AkzoNobel (currently Nouryon) B.V. near Hengelo and Delfzijl. At the end of March 2018, AkzoNobel Specialty Chemicals was sold to the American private equity company Carlyle and renamed Nouryon<sup>1</sup>.

By 2018, over 750 people nationwide are directly employed in the salt manufacturing industry, and almost 3000 are indirectly involved with the industry (Nedmag, 2018; AkzoNobel, 2018). Due to the salt mining concessions and the salt manufacturing facilities lying in rural low populated areas, the salt manufacturing industry has proved to be an important source of economic activity in all four industry locations. Both companies operating in the plants' respective areas, as well as research institutes and universities have become closely involved with the activities in the salt manufacturing industry. In Hengelo, for example, Nouryon has formed strategic partnerships with Twence and Empyro, by which its steam generation process is made more sustainable (RVO, 2013).

## 1.2 Production

At present, in the Netherlands, salt production is conducted by three companies: Nouryon, Frisia Zout and Nedmag. These companies operate on four different salt production facilities and across eight different brinefields throughout the Netherlands. Together, they produce about 6600 kt of salt, annually. As per 1 January 2017, there were 16 extraction licences and no exploration licences in force for rock salt (NLOG, 2017). Furthermore, there was one licence application pending for production (NLOG, 2017).

Table 1 shows 8 of the 17 extraction locations. This is due to the fact that, at the remaining 9 extraction locations, no rock salt was mined in 2016. These locations are reserved for future use. For example, Nouryon has been granted a rock extraction licence at Isidorushoeve, but the salt extraction under the Ganzenbos (expansion of the Adolf van Nassau II) and the Adolf van Nassau II are currently producing enough salt to satisfy production needs.

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

**Table 1 Salt extracted and produced in 2016**

Rock salt extraction locations	Salt extracted [kt] (NLOG, 2017)	Associated plant	Salt produced [kt]
Twenthe-Rijn	1,300	Nouryon Delfzijl	2,500
Twenthe-Rijn (uitbreiding [expansion])	830		
Twenthe-Rijn (Helmerzijde)	320		
Adolf van Nassau II	1,400	Nouryon Hengelo	3,000
Adolf van Nassau II – uitbreiding [expansion]	1,600		
Barradeel	450	Frisia Zout Harlingen	880
Barradeel II	430		
Veendam	270	Nedmag Veendam	270
		<b>Total</b>	<b>6,650</b>

Salt manufacturing is an energy-intensive process. Every Mt of salt produced in the Netherlands requires 1.6 PJ of heat, together with 71 GWh (0.26 PJ) of electricity, producing a total of 120 kt of direct CO<sub>2</sub> emissions (see Figure 1). The associated CO<sub>2</sub> emissions per production plant are shown in Table 2.

Although the method of heat generation may differ across the different salt production plants in the Netherlands, the overall salt production process is relatively similar across different plants. These different processes are discussed in the next section.

**Table 2 CO<sub>2</sub> emissions of salt production plants**

Production plant	CO <sub>2</sub> emissions [kt/year] (NEa, 2017)	Share of CO <sub>2</sub> emissions	Share of production
Nouryon Hengelo	291	53%	37%
Nouryon Delfzijl	181	33%	46%
Frisia Zout Harlingen	2	0%	13%
Nedmag Veendam <sup>2</sup>	76	14%	4%
<b>Total</b>	<b>550</b>		

### 1.3 Overview of the economics in the salt industry

The total turnover in the salt manufacturing industry in the Netherlands is around EUR 460 million (CBS, 2018). The sodium-based salt manufacturing plants in Hengelo, Delfzijl and Harlingen together account for approximately EUR 340 million, whereas the magnesium-based salt plant in Veendam has a turnover of roughly EUR 120 million (Nedmag, 2016).

<sup>2</sup> This includes the CO<sub>2</sub> emissions related to the processing to Mg(OH)<sub>2</sub> by precipitation, and calcination to MgO followed by sintering of MgO which account over 95% of the emissions.

Table 3 emphasises the fact that the salt-manufacturing industry is extremely energy intensive; almost 40% of the total costs within the industry are attributed to gas and electricity expenses.

**Table 3 Financial overview of the Dutch sodium-based salt manufacturing industry**

Salt manufacturing financial overview			
Revenue	% of total	Assumption	Source
Industrial salt revenue	89%	Market price of industrial salt EUR 57 per tonne	Brinkmann et al., 2014
Specialties salt revenue	11%	Market price of specialties salt EUR 60 per tonne	Brinkmann et al., 2014
Off-spec salt revenue	6%	Market price of off-spec salt EUR 46 per tonne	Brinkmann et al., 2014
Costs	% of total	Assumption	Source
Natural gas	22%	price: EUR 6.8 per GJ	Schoots et al., 2017
Electricity	15%	price: EUR 0.066 per kWh	Schoots et al., 2017
Water	2%	price: EUR 0.36 per tonne	Schmittinger et al., 2012
Diesel	0%	price (reviewed every 3 years): EUR 868 per tonne (excl. energy tax and VAT)	Schoots et al., 2017

Salt production in Hengelo and Delfzijl is part of Nouryon's Specialty Chemicals branch. The production plant in Delfzijl produces industrial salt for Nouryon's chlor-alkali plant in the same chemical cluster; the production plant in Hengelo produces industrial salt for Nouryon's chlor-alkali plant in Botlek and for other clients, predominantly in Germany. From the latter salt production plant, industrial salt is transported to clients by cargo ship.



# 2 Salt production processes

## 2.1 Overview

As stated before in the introduction chapter, the production of magnesium salts is not specifically described in this chapter. The magnesium salt extraction produces  $MgCl_2$ , an insoluble salt which makes it a process with relatively low energy usage. The production of  $MgO$  from  $MgCl_2$  is an energy intensive process that requires high temperatures.

Sodium salt in the Netherlands is produced by means of extraction from rock salt from salt caverns. This rock salt, also known as halite, is the mineral natural form of sodium chloride ( $NaCl$ ). For every gram of salt, over 60% is chlorine ( $Cl^-$ ) and almost 40% is sodium ( $Na^+$ ). In its natural mineral form, it generally contains a range of impurities (e.g. magnesium, calcium and iron ions) and occasionally other evaporate deposit minerals (e.g. sulphates, halides and borates). The rock salt deposits have been formed hundreds of millions of years ago by the evaporation of epeiric seas, and thus lie deep underground (depths ranging between 350 and 1500 metres). For geological reasons, salt is produced in the northeast and east of the Netherlands; this is where the salt deposits of Zechstein and Trias lay. It is extracted as brine, which is the solution of rock salt in water. Upon extraction, the salt is processed so that it meets market demands.

The sodium salt manufacturing process can be conceptualised as follows:

1. Steam generation
2. Salt extraction
3. Brine purification
4. Brine vaporisation
5. Salt centrifugation
6. Salt treatment.

These sub-processes are subsequently discussed in the next paragraphs, based on the production of sodium salt. The production of magnesium salts differs from this description. A schematic overview of the end-to-end process is shown in Figure 1 at the end of this section.

## 2.2 Steam generation

Heat energy is generated in the form of steam, which for salt production is produced at a temperature of about 150 °C to 180 °C and a pressure of 3 to 4 bar (Holtkamp, 2011). The salt production plants in Hengelo, Delfzijl produce their steam in on-site combined heat and power (CHP) plants (AkzoNobel, 2018). Almost all direct  $CO_2$  emissions come from the steam generation that occurs at the different CHP installations. The cogeneration plants used in the salt production industry are quite efficient; Nouryon's CHP plants in Delfzijl and Hengelo have efficiencies above 85%.

Nouryon's salt production plant in Hengelo also imports some of the steam it uses from third parties (RVO, 2013). In addition to the use of its combined heat and power facility, Nouryon Hengelo is supplied with steam generated at Twence, a nearby waste incinerator. Via a 2.2 km long insulated overhead line between Twence and Nouryon, 4 bar superheated steam from Twence is delivered (AkzoNobel, 2018). Furthermore, Nouryon Hengelo also imports steam from the pyrolysis plant Empyro. This plant produces oils from wood chips. The waste heat the plant produces is used to produce steam, which is supplied to Nouryon's salt plant. Since 2015, Empyro has been supplying 3–8 tonnes of steam to Nouryon per hour. By using Empyro's steam, Nouryon was able to reduce its natural gas consumption by 3 million m<sup>3</sup> per year and thus achieve a CO<sub>2</sub> reduction of 5.9 kt (AkzoNobel, 2018). Nedmag has started a pilot project to use hydrogen from the electrolysis facility HyStock of Gasunie (Dagblad van het Noorden 17-09-19).

Although Frisia Zout is responsible for about 13% of salt production in the Netherlands, its CO<sub>2</sub> share is minimal. This is due to the fact that their heat energy to produce steam originates from a third party — a waste incineration plant: *Reststoffen Energie Centrale* (REC). This allows REC to have a high energy production efficiency at about 70%, whereas the average waste incineration plant in the Netherlands only has an efficiency of 30% (OMRIN, 2016).

## 2.3 Salt extraction

In the Netherlands, salt is extracted from the ground by means of solution mining. In this process, a borehole is drilled into an underground salt layer, whereupon fresh water is forced down that hole under high pressure, 17 bar (Warren, 2016). The salt dissolves, turning the fresh water into brine and creating a cavern in the salt layer. Upon saturation, which occurs when the sodium chloride brine contains about 25 weight per cent (wt%) of salt (Strucker, 1994; Sedivy, 2006), the brine is pumped out of the ground, and transported by pipeline to a purification installation.

The solution mining process is powered by large electric pumps that are used to generate the high pressure levels needed for the fresh water to be pumped down and the brine to be pumped up. Estimations of pumping energy needed are based on the depth of the solution-mined salt layer, as well as the length of the solution mining piping system. In Delfzijl, for example, the solution-mining facility is connected to the salt production plant with a complex network of pipelines, that are approximately 20 km in length (Klein and Ybema, interview 1, 2018). In this study, based on calculations and discussions with experts, about 79 TJ/Mt salt, a quarter of all electricity used in the end-to-end process, is attributed to the solution mining process.

## 2.4 Brine purification

The raw brine subsequently undergoes a purification process where the impurities are removed through a series of reactions. In the Netherlands, the most commonly occurring impurities in solution mined brine are sulphates, calcium salts and magnesium salts (Warren, 2016). These impurities are precipitated with chemicals and removed. Based on calculations in this study, the brine purification process produces approximately 150 kt of waste chemicals per year across the Netherlands. A more extensive explanation of the brine purification process is given in Appendix B. These waste chemicals – which consist mostly of barium sulphate, calcium carbonate and magnesium hydroxide – are commonly stored in the

empty salt caverns that are a result of the solution mining process (Klein and Ybema, interview 1, 2018).

One must note that the Nedmag salt production plant does not produce sodium-based salts, but rather magnesium-based salts. Hence the brine purification process is different but this is not explicitly considered within this study.

## 2.5 Water vaporisation

The water vaporisation process is very energy intensive; it uses 95% of the total heat energy consumption in the end-to-end salt production process. The purified brine, which consists of roughly a quarter of its weight as salt and three quarters fresh water is subsequently vaporised until it becomes a large salty slurry which contains approximately 10% water (AkzoNobel, 2018).

The principal technology used for the vaporisation process is multiple effect evaporation (MEE) or multiple effect vaporisation (MEV) with 3–5 connected vacuum pans (Klein and Ybema, interview 1, 2018) per production line. At one production line, Mechanical Vapor Recompression (MVR) is added. MVR technology is an energy recovery process in which low pressure water vapour that has evaporated from the brine is recompressed to higher temperatures and pressures and used as a heat source to vaporise more brine (Den Ouden et al., 2017).

The MEV technology makes use of the fact that a solution's boiling point lowers as the surrounding pressure is lowered with large vacuum pans. By connecting multiple vacuum pans in series and generating different pressures to each other, the evaporated water from one vacuum pan can be used to heat the next. The efficiency gain from this technology is considerable; MEV facilities are at least twice as efficient as single effect vaporisers; which means that the deployment of MEV technology halves the steam energy demand (Strucker, 1994).

A general rule of thumb observed is that for each extra effect added in a multiple effect vaporisation system, a 10% efficiency gain is made. A trade-off is that the investment costs are higher for each extra effect. In Europe, the maximum amount of effects deployed in the salt manufacturing industry is eight (Westphal et al., 2012). MEV facilities are relatively costly to invest in but require little maintenance and age slowly.

## 2.6 Salt centrifugation

The slurry, containing approximately 90% salt, is centrifuged in large drums to remove residual water and prevent salt crystallisation (Sedivy, 2006). The resulting salt contains roughly 2.5% moisture (Bakker, 2011). The large salt centrifuges used in the salt production facility in Hengelo can process 50 tonnes of salt per hour (AkzoNobel, 2018).

Across the Dutch salt manufacturing industry approximately 60%–80% of all centrifuged salt is used for industrial purposes (see Section 3.1.3). Of the remaining, 20%–30% is treated further (Klein and Ybema, interview 2, 2018) and 10% is rejected due to impurities in the salt. The rejected salts are usually stored and used to deice the roads (road salt).

## 2.7 Salt treatment

The 20%–30% of salt that is not used directly for industrial purpose, is stripped of the residual water and worked up to dry (specialties) salt with large rotary sifting machines. These machines use little electrical energy but require thermal energy to ensure the treated salt has a humidity level lower than 0.1% (Bakker, 2011). The sifted salt is supplemented with an anti-caking agent to prevent the formation of lumps, and to ensure easy transport and packaging. Commonly used anti-caking agents in the salt manufacturing industry include ferrocyanide E535 and meso-tartrate (AkzoNobel, 2018).



### Salt manufacturing process (sodium-based salt)

Normalized for 1 kt salt production

All data rounded to 2 significant figures

#### Overall energy consumption (per kt salt)

- Heat: 1.5 TJ (total): 1.2 TJ (CHP), 0.21 TJ (other sources), 4% re-use
- Associated CO<sub>2</sub> emissions: 120 t
- Electricity: 100 MWh (0.37 TJ) generated by CHP; 9 MWh (0.03 TJ) sold to electricity net
- Total electricity consumption: 71 MWh = 0.26 TJ

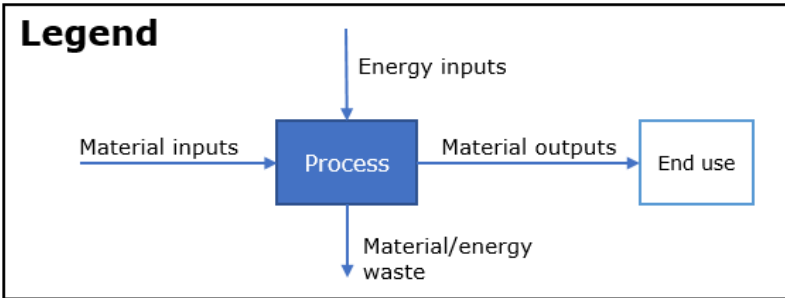
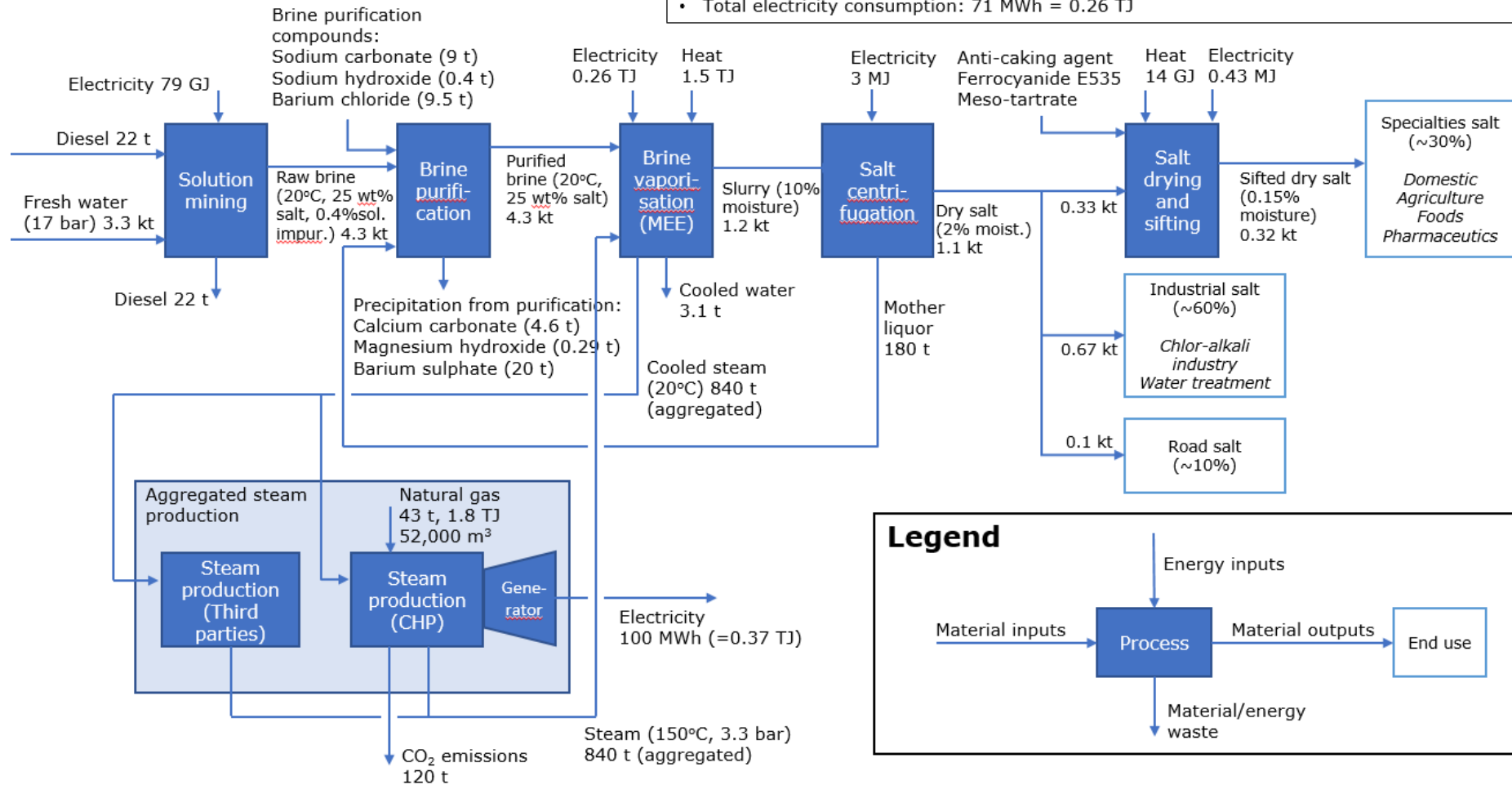


Figure 1 Mass and energy flows salt manufacturing process (for sodium-based salts)

# 3 Salt products and application

## 3.1 Products

Salt is used for the chlor-alkali industry, various metal industries, agriculture and animal husbandry, the food industry, road salt, the pharmaceutical industry and for consumption. The products generated by the salt manufacturing industry can loosely be categorised across four categories: industrial salt, specialties salt, off-spec salt and magnesium-based salt, as shown in Table 4.

The chemical industry is the largest industrial salt consumer using almost 80% of the total production in the Netherlands. This industry converts the salt mainly into chlorine and caustic soda which, in turn, are indispensable to the paper and pulp industry, the petrochemical industry, organic synthesis and glass production. 90% of the salt produced in Nouryon's plant in Hengelo is used in the chlor-alkali industry — at Nouryon's membrane electrolysis plant in Botlek (Klein and Ybema, interview 2, 2018).

Specialties salt is high quality, dry-sifted salt, used predominantly for human consumption. This is salt that is both directly sold to consumers, as well as salt that is used in the food industry and in water softening. The quality of this salt is closely monitored, as strict specific requirements for the different products within this product category. As a consequence, specialties salt is the most expensive type of sodium-based salt, as can be seen in Table 4.

Off-spec salt is salt that, just like specialties salt, has been dry sifted. Due to errors in the production chain this salt does not meet specified or standard requirements needed for human consumption; neither can it be re-processed to upgrade it to specialties salt (Bakker, 2011). This type of salt does however meet the environmental requirements for other applications such as road salt and is mostly used as such.

The magnesium-based salts form a separate category in the salt manufacturing industry.

**Table 4 Salt products in the Netherlands**

Product category	Market value [EUR/t]	Market share	Product examples
<b>Industrial salt</b>	50–60	79%	Electrolysis salt, pharmaceutical salt, food salt, feed salt
<b>Specialties salt</b>	50–75	10%	Table salt, nitrite pickling salt, water softening salt
<b>Off-spec salt</b>	40–50	7%	De-icing salt, road salt, dishwasher salt
<b>Other salts</b>	150	4%	Magnesium chloride

Source: Brinkmann et al. (2014)

## 3.2 Environmental effects

Apart from the greenhouse gas emissions attributed to the salt manufacturing industry, the industry has some other effects on the environment. These are briefly elucidated below.

### **Soil subsidence**

Upon the salt extraction from thick underground salt layers, large underground salt caverns are formed. These sodium salt caverns are often cylindrical in shape, over 100 metres in diameter, and have heights varying from 30 to 550 metres depending on the thickness of the salt layer (Paar, 2010).

The sodium salt caverns in Delfzijl and Harlingen, which are at depths ranging from 1,500 to 3,000 metres below ground have extremely large volumes (over 4 million cubic metres – the size of three football stadiums). These caverns have shown to be causing slight soil subsidence at the Earth's surface. In Delfzijl, soil subsidence levels have been recorded to range between 1 and 2 mm per year (Paar, 2010). In Harlingen, although amount of salt extracted is much lower than in Delfzijl, soil subsidence ranges between 4 and 5 cm per year. The affected area at the ground level is about 3 km in diameter.

Soil subsidence levels are closely monitored by the *Staatstoezicht op de Mijnen* (State Supervision of the Mines, SSM), beside the effect of normal operations the soil subsidence can be effected by the (future) collapse or breaching of unstable sodium salt caverns. So far dozens of unstable sodium salt caverns have been identified by the SSM (Paar, 2010). In 1991, a salt cavern collapsed in Hengelo, creating a hole at ground level of several metres deep and dozens of metres in diameter (Reijn, 2016). In April 2018 the ceiling of a mining cavern of Nedmag opened for a brief period and a limited amount of brine and diesel<sup>3</sup> spoiled into the deep underground. Further research after this incident found it unlikely the diesel/brine solution would reach the surface. The soil subsidence expected was increased to 76 cm under the 1977 level (SodM, 2019) and, higher than granted in the permit<sup>4</sup> (50 cm). As a consequence the locale water authority (Hunze en Aa's) has to take additional action (current measures assumed a maximum of 69 cm soil subsidence). Also the development of two new production sites (VE-5 and VE-6) have been put on halt, with new soil subsidence calculation showing 10 cm instead of 7 cm (SodM, 2018).

### **Brine leakages**

As the solution mined brine flows to the surface, it is pumped from the mining concessions to the salt processing factories across a complex network of pipelines of up to 50 kilometres in length. Due to the corrosive nature of brine, the transport pipelines have been seen to cause major leakages throughout the years (Verbraeken, 2018a).

Between 2014 and 2016, over 130 tonnes of salt have leaked into the environment at the salt mining concessions in Hengelo (Reijn, 2016). This caused trees to drop their leaves and profitable agricultural fields to be cleared for numerous years. Incidentally, Nouryon, who was responsible for the damages done have repaired and covered all damages. In May of 2018, following an underground brine leakage at Nedmag's concession in Veendam (see above), there were worries about the quality of the regional drinking water, but these worries proved to be unfounded (Nauta, 2018).

Nonetheless, monitoring remains extremely difficult and the leakages are a known risk factor in the salt manufacturing industry. The leaks are often discovered by local residents.

<sup>3</sup> The salt caverns of Nedmag contain 41 million liters of diesel, 2.75 million liters per cavern.

<sup>4</sup> After the breach it was expected that the 50 cm soil subsidence would already be reached by 2018 (Nedmag, 2018b)



Nouryon's two mining facilities in Hengelo and Delfzijl together have had a total of 19 brine leakage incidents on the transportation pipelines between 2015 and 2017 (Verbraeken, 2018a).

### **Blanket fluid spills**

Not only the brine is known to have spilled into neighbouring environments: diesel, that is used as a blanket fluid in the solution mining process, is also reported to spill into the environment. In 2016, 11,000 litres of diesel spilled into the environment following a major leak at one of the boreholes in Hengelo (Bakker, 2016). This fluid spill was reported almost 11 months after it occurred and led to severe damage of surrounding agricultural crops.

### **Other chemical spills**

The salt caverns are used for storage of waste chemicals from the salt manufacturing industry. Furthermore, some salt caverns are known to store natural gas and nitrogen. In Germany, crude oil is stored in salt cavities at Amtsvenn, just across the border at Enschede. That oil storage began to leak heavily in 2014 and led to major environmental damage (Reijn, 2016). Although no cases of chemical spills have been reported in the Netherlands, it remains an environmental risk of the salt manufacturing industry.

## 3.3 Environmental policies

The companies involved in the salt industry need to comply with the legal rules of the mining legislation, but also with laws and regulations in the field of working conditions and the environment. Of interest are the *Mijnbouwwet* (Mining Act), *Mijnbouwbesluit* (Mining Decree), *Mijnbouwregeling* (Mining Regulations), the *Besluit algemene regels milieu mijnbouw* (General Environmental Mining Decree), the *Wet algemene bepalingen omgevingsrecht* (Environmental Provisions Act) and the *Arbeidsomstandighedenwet* (Working Conditions Act) (AkzoNobel, 2018).

The Dutch Government has pledged to completely end Dutch natural gas production from the Groningen gas field by 2022. This has caused not only the Dutch public perception of gas to change, it has also made interest groups more critical of any type of mining activities in the Netherlands (Verbraeken, 2018a).

This rapid political shift is likely to have a direct effect on the salt manufacturing industry. Although the long-term hazards of salt solution mining are known to have a far smaller impact than that of natural gas fracking (Foulger et al., 2017), it may prove difficult for the companies involved in the salt industry to acquire new licences for salt extraction. This may impact their long-term salt production levels. Furthermore, Nouryon's salt manufacturing plants are fuelled on Groninger gas, and the foreseen closure has caused them to consider a more rapid transition to more sustainable sources of steam generation (Klein and Ybema, interview 1, 2018).

Apart from the political developments around gas production and a change in perception of the dangers of mining activities, the SSM has also tightened its supervision of the salt production industry following a series of brine, oil and chemical leakages between 2014 and 2018 (Verbraeken, 2018a, SodM, 2019). This may cause extra maintenance costs within the salt manufacturing industry due to an increase of safety and maintenance costs.

# 4 Options for decarbonisation

## 4.1 Overview

A wide range of new technologies is under development that may provide opportunities in terms of efficiency, cost reduction or sustainability of the salt 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 and Van Aken, 2017; Deloitte, 2012); sustainable heat generation, efficiency and electrification, and circularity and recycling.

Figure 2 gives a modular overview of the technology characteristics for the sodium salt 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 data set.

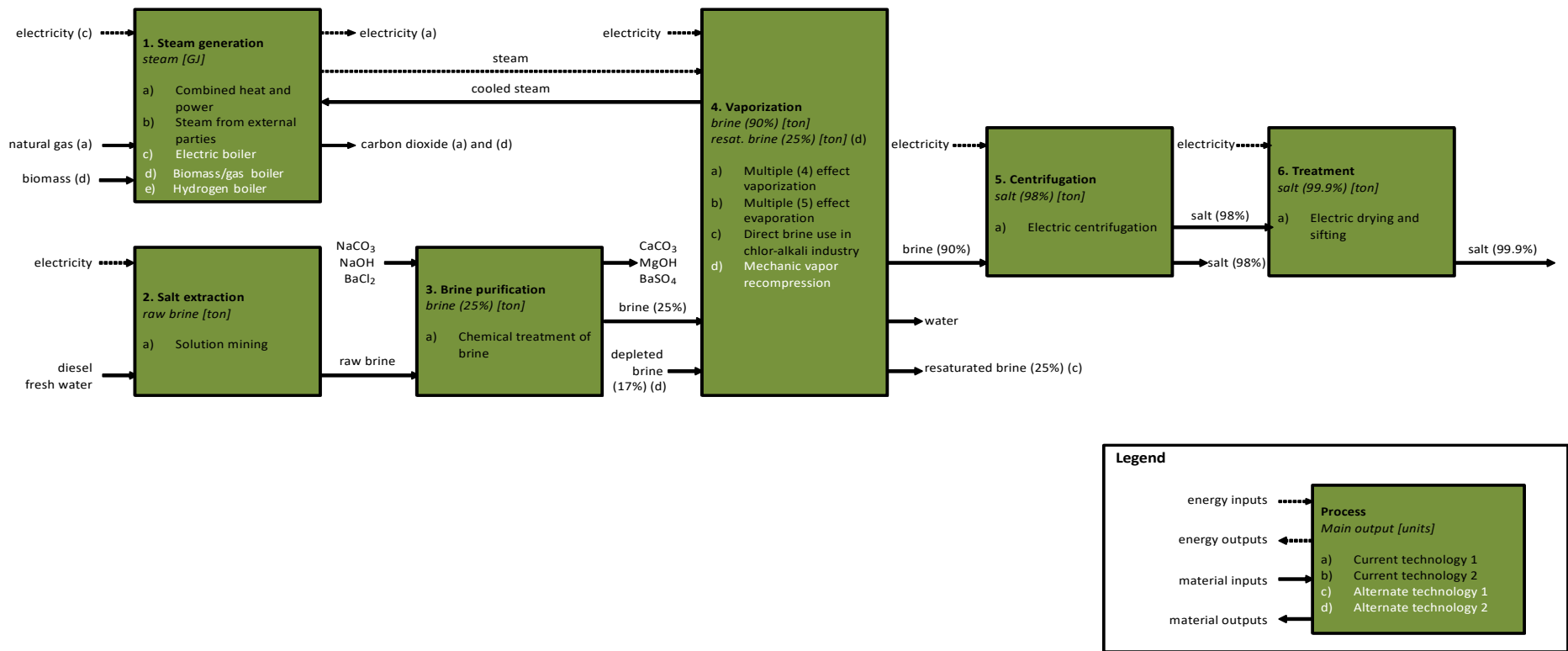


Figure 2 Modular overview of MIDDEN data set for the sodium salt manufacturing industry

## 4.2 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 and 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), but also biogas and hydrogen boilers are mentioned (Dagblad van het Noorden, 17-09-19).

### ***Biomass boilers***

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 CO<sub>2</sub> emissions, biomass is considered a carbon-neutral form of energy because the amount of CO<sub>2</sub> 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).

### ***Electric boilers***

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 natural-gas-fired boilers or a CHP (Deloitte, 2012).

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).

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 and Schure, 2016). Furthermore, once placed, the maintenance costs of electric boilers are relatively low, as, contrary to fuel-/biofuel-heated boilers, they do not need periodic refurbishment of their tubing systems (RVO, 2013).

**Table 5 Technological specification of a 20 MWe electric boiler**

Parameter	Value	Lower est.	Upper est.	Units
Unit of main output	1	x	x	GJ steam/hr
Capacity (20 MWe)	72			GJ steam/hr
Investment cost single unit	1.2	1.0	1.4	EUR million
Depreciation period	15	x	X	years
Refurbishment interval	10	x	X	years
Operating & maintenance cost single unit	0.040	0.036	0.044	EUR million /year
Electricity requirements per unit main output	72	71	73	GJ/hr
Water input per unit main output	1	0.95	1.15	t/hr
Capacity for 415 kt/yr brine (90% salt) of single unit at 90% utilisation (7900 hrs)	569	x	x	TJ steam/year

Source: Krebbekx et al. (2015), VNCI (2018)

According to industry stakeholders (Klein, e-mail, 2018, interview, 2018), the placement of electric boilers in salt manufacturing plants will reduce the plant's dependence on its combined heat and power plant. The low electricity prices in the Netherlands not only make investments in electric boilers interesting, they also make the deployment of on-site CHPs less attractive. Table 5 gives an overview of the main relevant parameters for the conceptualisation of this technology.

#### **Biogas and hydrogen boilers**

With some small modification natural gas boilers can be fed with biogas or green gas (biogas upgraded to natural gas specifications). Hydrogen can be used up to 25% of the feedstock. Biogas is made by anaerobic digestion of manure and agricultural waste and consists primarily out of methane and carbon dioxide. Carbon neutral hydrogen can be generated by electrolysis ("green" hydrogen), or by steam reforming, using biogas or natural gas ("blue hydrogen" in combination with capturing and storage or utilisation of CO<sub>2</sub>). There are no substantial additional capital costs involved. The price differences of the various feedstocks is the most important factor in the investment decision.

#### **Geothermal heat**

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 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 salt manufacturing plants in Delfzijl and Harlingen are located precisely in these respective areas, and so this may prove to have a high potential for sustainable heat generation after 2030 (Boxem, Veldkamp and Van Wees, 2016).

### **4.3 Efficiency and electrification**

In the salt manufacturing industry, different technologies exist that allow for further efficiency gains. Furthermore, electrification of certain industrial processes is considered to play an increasingly important role in transitioning towards a more CO<sub>2</sub> neutral industry (Ros and Schure, 2016).

### Multiple-Effect Vaporisers

The vaporisation of water can be made more efficient by the installation of more elaborate Multiple-Effect Vaporisers (MEVs) (Westphal et al., 2012). A general rule of thumb observed is that for each extra effect added in a multiple effect vaporisation system, a 10% efficiency gain is made. A trade-off is that the investment costs are higher for each extra effect. In Europe, the maximum amount of effects deployed in the salt manufacturing industry is eight (Westphal et al., 2012).

### Mechanical Vapour Recompression

A new technology used to vaporise the brine is called Mechanical Vapour Recompression (MVR). MVR technology is an energy recovery process in which low pressure water vapour that has evaporated from the brine is recompressed to higher temperatures and pressure and used as a heat source to vaporise more brine (Den Ouden et al., 2017). This technology thus allows the latent heat of low-pressure steam to be maintained within the system, and leads to considerable efficiency gains (Krebbekx, Lintmeijer, Den Ouden and Graafland, 2015). Since new steam is generated from vaporised brine, the necessary steam input of MVR is about 95% lower than that of MEVs. Although MVR requires substantial amounts of electrical energy for the recompression of vapour, the total electric and heat energy required for MVR technology is about half of that of a 5-effect MEV (Westphal et al., 2012).

As such, MVR is an energetically and economically attractive way to work up low pressure steam to high pressure steam so that it can be fed back into the industrial steam infrastructure. In combination with a combined heat and power (CHP), this offers possibilities for greater flexibility (Krebbekx et al., 2015).

**Table 6 Technological specification of a 13.3 MWe MVR unit for brine vaporisation**

Parameter	Value	Lower est.	Upper est.	Units
Unit of main output	1			tonne brine 90% wt NaCl
Unit of capacity	1			kt/yr
Capacity (for 540 kt salt) of single unit (8760 hrs)	600			kt/year
Investment cost single unit	15.1	13.5	16.5	EUR million
Operating & maintenance cost single unit	0.76	0.66	0.86	EUR million/yr
Refurbishment interval	10			yr
Steam requirement per unit main output	0.04	0.03	0.05	GJ/t
Electricity requirement per unit main output	0.7	0.65	0.7	GJ/t
Brine (25% wt NaCl) input per unit main output	3.6	3.5	3.7	t
Water output per unit main output	2.6	2.5	2.7	t

Source: Krebbekx et al. (2015), Westphal et al. (2012)

The installation of MVR facilities in salt manufacturing plants is seen by industry specialists as the most cost-effective investment to rapidly decarbonise the salt manufacturing industry (Klein and Ybema, interview 1, 2018). By lowering the demand for high pressure steam, the utilisation of on-site CHPs will directly be lowered, which directly reduces CO<sub>2</sub> emissions. An important aspect to investigate is the extent to which the increased electricity demand increases the indirect emissions of the salt manufacturing industry, and whether the net change in CO<sub>2</sub> emissions is still negative. This will also depend on the source and CO<sub>2</sub> footprint of the electricity. Table 6 gives an overview of the main relevant parameters for the conceptualisation of this technology.

## 4.4 Salt cavern applications

The large underground sodium salt caverns provide a lot of opportunities for the salt manufacturing industry. The thick permeable salt layer in which these caverns are nested are unreactive and thus offer many opportunities for temporary and permanent storage of a wide range of substances (Paar, 2010).

Up until today, Dutch salt caverns are mostly used for fossil fuel reserve storage. After the oil crisis in 1973, the Netherlands pledged to build up an oil supply large enough to sustain the country for three months, in the event of international tensions or war (Nijland, 2014). Furthermore, partly due to the liberalisation of gas markets in recent years, there is an increasing interest in the **storage of natural gas** in salt caverns in the Netherlands (Klein and Ybema, interview 1, 2018). In 2010, 10 caverns were prepared for the storage of natural gas in Hengelo (Paar, 2010).

Other resource storage opportunities are under development and gaining increasing interest. In 2017, Dutch natural gas infrastructure company Gasunie has invested in the development of a new **hydrogen** production (from solar power) and storage system in Nouryon's empty salt caverns, already used for the storage of natural gas (Tissink, 2017, Energystock, 2019). It hopes this can offer an answer to the volatile supply of sustainable electricity (Nedmag, 2018). The gas can be pumped back up and converted back into electricity with a fuel cell, used as a fuel or transported by pipeline to serve as a raw material for the chemical industry (Tissink, 2017).

The hydrogen storage technology being deployed is similar to that of carbon capture and storage (CCS). CCS is the process of capturing carbon dioxide as it is emitted from point sources, such as fossil-fuel-fired power plants, and **storing this CO<sub>2</sub>** in such a way that it does not enter the atmosphere. Various studies predict that CCS technology will become financially viable as a decarbonisation strategy in the European chemical industry (VNCI, 2018; Berkhout et al, 2015).

Salt caverns in neighbouring Germany have also been used for **Compressed Air Energy Storage** (CAES) (Klein and Ybema, interview 1, 2018). CAES is a relatively new technology in which ambient air is compressed and stored under pressure in an underground cavern during periods of electricity surplus. When extra electricity is required, the pressurised air is heated and expanded in an expansion turbine through which new electrical energy is produced. Although this technology is unlikely to be ready by 2030, it may prove to become an interesting technology to invest in in the longer term (VNCI, 2018).

# 5 Discussion

In order to identify robust strategies through which the salt manufacturing industry can be decarbonised, the industry was studied in depth and analysed in collaboration with stakeholders. Two alternative technologies were identified that can support decarbonisation efforts of the salt manufacturing industry; the implementation of electric boilers to generate steam, and the implementation of mechanical vapour recompressors (MVR) to vaporise the brine. Nouryon Hengelo and Nouryon Delfzijl already have a small pilot MVR facility.

This research indicates that the investment in MVR technology alone will not suffice to reach a 100% CO<sub>2</sub> reduction. The implementation of mechanical vapour recompressors will significantly reduce the steam demand on a plant level. The remaining steam demand can be imported from third parties (i.e. Twence) or by the deployment of industrial electric boilers (provided the electricity used is carbon-free generated). Preliminary research results indicate that the installation of approximately 50 to 100 industrial electric boilers across the plants where MVR technology is deployed are necessary to replace steam generation from closed down CHP facilities.

As a whole, the identified technological investments imply a gradual electrification of heat generation processes across the salt manufacturing industry. This electrification can replace the natural gas consumption (approximately 3.2 to 5.4 PJ per year), whereby the electricity consumption may rise by 1.9 to 4.0 PJ per year. For full decarbonization the electricity used should be generated with zero CO<sub>2</sub> emissions.



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# Appendix A:

## Explanation of solution mining process

Salt solution mining is defined as the mining of various salts by dissolving them in fresh water and pumping the resulting brine to the surface. The saturated raw sodium chloride brine that results from the salt solution mining process has a salinity of approximately 310 g/L, which corresponds to about 10 times the salinity of seawater. In the solution mining industry, a general rule is that between 7 and 8 m<sup>3</sup> of fresh water pumped into a cavity dissolves approximately 1 m<sup>3</sup> of halite.

In order to reach the underground salt layers, one or several boreholes are created at the surface. A single access hole is drilled, whereby water is pumped down at high pressure (approximately 1.7 MPa) (Strucker, 1994) to form a small cylindrical cavity underground filled with brine. The access to this cavity (also named cavern) may subsequently be increased by multiple drillings from the ground hole. Along these drillings, three concentric tubes allow for the fresh water to be pumped in, a liquid blanket to be pumped in and out, and for the brine to be pumped out.

Two types of solution mining techniques can be distinguished; 'direct circulation' (by bottom injection) and 'reverse circulation' (by top injection). In general, cavern development is initiated with direct circulation, whereupon after the cavern has the adequate shape, the circulation is switched to indirect circulation. With both methods, insoluble rocks gradually collect at the bottom of the cavern.

In both cases, the outermost casing of the tubing allows for a 'blanket fluid' to be pumped in and out of the cavern. This fluid blanket is less dense than the fresh water (1000 g/L) and brine (1200 g/L), and as such 'floats' on top of the other solutions. The halite cannot dissolve in this blanket fluid, and thus this layer protects the top of the cavern from dissolving. It is possible to control the shape of the cavity that is being formed by increasing and decreasing the volume of blanket fluid in the cavern. In the Netherlands, diesel (800 g/L) is often used as blanket fluid.

In the Netherlands, the depth at which solution mining processes occur ranges widely, depending on the salt production location. Table 7 gives an overview of depth ranges of the different concessions active in 2018.

**Table 7 Depth ranges of salt solution mining for active concessions in 2016**

Rock salt extraction licences:		Depth (m)	Salt layer name
<b>P1</b>	Adolf van Nassau II	700–1600	Strassfurt formation (Z2)
<b>P2</b>	Expansion Adolf van Nassau II	700–1600	Strassfurt formation (Z2)
<b>P5</b>	Barradeel	2250–3000	Strassfurt formation (Z2)
<b>P6</b>	Barradeel II	2250–3000	Strassfurt formation (Z2)
<b>P10</b>	Twenthe-Rijn	350–500	Röt formation
<b>P11</b>	Expansion Twenthe-Rijn	350–500	Röt formation
<b>P12</b>	Twenthe-Rijn Helmerzijde	350–500	Röt formation
<b>P14</b>	Veendam	1400–1800	Leine formation (Z3)

The processes at play at these different depths are outlined below.

#### **Shallow rock salt extraction (350–500m)**

At the Hengelo drilling site under the Twenthe-Rijn extraction licence, brine is extracted from two types of caverns. In the older type of the two, the cavern is developed through three boreholes, 40 metres apart. In the other cavern, the brine is extracted from one single central tubing system.

The Röt formation in which this process occurs is subdivided into four salt types; from top to bottom salt A, B, C and D. Between each layer lay thin dolomitic clay bricks. The raw brine production process takes place mainly in salt A and B, and occasionally in salt C. As can be seen from this, the development of all salt extraction was started at the bottom of the salt formation. As soon as the initial cavity has been developed, production of raw brine is conducted by means of solution mining, by leaching the cavity in both horizontal and vertical direction.

The caverns that are created under the Twenthe-Rijn extraction area form small cylinders of 100–120 metres in diameter and a height of approximately 25–30 metres. Above each cavern, a 'safety roof' of rock salt of sufficient thickness remains. This safety roof prevents the cavern from collapsing under its own weight, and thus prevents sinkhole formation at ground level. Future salt extraction will continue higher up above this safety roof.

Since the start of production in 1936 at the Hengelo concession more than 450 drillings have been made in the area and more than 75 million tonnes of salt have been produced, which amounts to about 130 successfully excavated caverns.

#### **Medium-depth rock salt extraction (600-1600m)**

The Winschoten and Zuidwending drilling sites, which fall under the extraction licences of Adolf van Nassau and Uitbreiding van Adolf van Nassau respectively, have salt caverns that fall under the medium depth salt extraction category. All twelve caverns at Winschoten and nine caverns in Zuidwending were created with a single borehole.

For the Winschoten concession the cavern roofs are at depths of 700–750 metres and have a height of approximately 550–630 metres. For the Zuidwending concession, these depths and heights are 450–500 and 800–850 metres, respectively. The caverns have a diameter of up to 125 metres and are 250 metres apart in a hexagonal grid. The total production since the start of production in 1954 (Winschoten) and 1967 (Zuidwending) was more than 90 million tonnes. This amounts to about 10 successfully excavated caverns.

The soil subsidence at the ground level due to volume convergence - the resulting decrease in the volume of a cavern due to the creep of the salt - amounts to 1 to 2 mm per year. The

total, cumulative subsidence since the start of the extraction, for example in Zuidwending, is approx. 4 cm in the centre of the soil subsidence basin.

The Nedmag solution mining facility near Veendam in the Netherlands produces magnesium from magnesium chloride brine by solution mining a Zechstein salt pillow, targeting beds that are rich in bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Target intervals at Veendam average 100 metres (combined) thickness at depths, dipping around  $20^\circ$ , at depths between 1,400 and 1,800 metres. About 100 metres of halite lies above the target magnesium salts and more than 1,400 metres occur below. Each year, the Nedmag plant produces 200,000 to 270,000 tonnes of high purity magnesium chloride. The wells producing  $\text{MgCl}_2$ -brine from 'squeeze caverns' at Veendam are saturated with respect to bischofite, rendering a high quality brine product with less than 1% by weight of non-magnesium chloride salts.

### **Deep rock salt extraction (2250–3000m)**

The deepest solution mines in the world are supervised under the extraction licences of Barradeel and Barradeel II. Concessions built under these licences deliver raw brine to the salt factory in Harlingen. Two caverns have been developed under Barradeel, and two more have been developed under Barradeel II. Salt extraction at Barradeel is slowly coming to an end.

The top 30 metres of the Strassfurt formation (Z2) contains carnallite deposits, which are soluble in water. To prevent the contamination of the brine, an oil blanket is used. The rock temperature in the vicinity of these caverns is approximately  $105^\circ\text{C}$ . As a result, 'salt creep' occurs at a high rate. This is a process where the raw brine crystallises on the edge of the tubing and top of the cavity, which may clog the system.

In the rock salt layers that are located closer to the Earth's surface, it usually takes one to two years before a sufficiently large cavity has developed to produce saturated brine. For deep extraction, the saturated brine can be extracted from the deep caverns within a few months. At these depths, the high pressure from the rock layers above, cause the rock caverns to stop increasing beyond a certain equilibrium (at a volume of approximately  $400,000\text{ m}^3$ ); the volume increase of the cavern from dissolving salt is compensated by the volume decrease due to volume convergence of the cavern. This can directly be observed at ground level; an extraction of  $230,000\text{ m}^3$  of halite per year leads to a subsidence bowl ( $\sim 5\text{ km}^2$ ) of approximately 4–5 cm deep at ground level. Since the total permissible soil subsidence is limited to 35 cm, there is a limit ( $1.6\text{--}2\text{ million m}^3$ ) to the amount of salt that can be extracted from a cavern. This is why the production of caverns is coming to a halt in Barradeel.

# Appendix B: Sodium chloride brine purification steps

At the sodium salt production facilities, large pumps extract the brine from the underground caverns, through pipelines over the ground to the brine purification facility.

Impurities from salt dissolved in brine are precipitated with chemicals and removed by various processes. The raw brine that was formed underground generally contains very few impurities. Table 8 shows the weight percentages of all solvents in raw brine that was produced from solution mining.

**Table 8 Weight percentages of solvents in raw brine**

Percentage of solvent	Solution-mined salt
NaCl %	25.0
Ca <sup>2+</sup> %	0.118
Mg <sup>2+</sup> %	0.011
SO <sub>4</sub> <sup>2-</sup> %	0.284
Insoluble %	-

Calcium is removed using soda (sodium carbonate), (the soda is obtained by the carbonation of CaO with carbon dioxide<sup>5</sup> from the combined heat and power (CHP) plant). Magnesium is removed using a diluted lye solution (sodium hydroxide *NaOH*) in kitchen salt. Sulphates can be removed with barium carbonate, barium chloride or calcium sulphate. The different precipitation processes are explained below:

The precipitation of calcium, magnesium and sulfate from brine is described by the following chemical reactions:



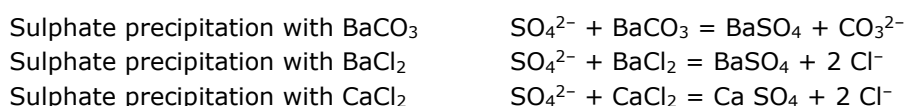
This chemical reaction shows that each 40 kg of calcium impurity entering the chlor-alkali process with salt requires 108 kg of soda ash for precipitation and formation of 100 kg of calcium carbonate.



This chemical reaction shows that each 24 kg of magnesium impurity entering the chlor-alkali process with salt requires 82 kg of sodium hydroxide for precipitation and formation of 58 kg of magnesium hydroxide.

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<sup>5</sup>  $\text{CaO} + 2\text{NaCl} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2 \text{ (s)}$



These chemical reactions show that each 96 kg of sulphate impurity entering the chlor-alkali process with salt requires either 197 kg of barium carbonate or 208 kg of barium chloride or 111 kg of calcium chloride for precipitation and formation of either 233 kg of barium sulphate or 136 kg of calcium sulphate. Upon purification, the brine is pumped through to the vacuum evaporation facility.

The cost associated with brine purification is the cost of chemical reagents and the investment and operating cost of the brine treatment plants. The cost of contaminated sludge disposal, purge decontamination and the loss of salt in purge also represent substantial costs.

**Table 9 Overview of impurity, reactant, precipitate and products involved in brine purification**

Impurity				Reactant			Precipitate			Product
Formula	Percentage in brine	Molar mass (g/mol)	Mass/1L brine (g)	Formula	Molar mass (g/mol)	Mass/1000L brine (g)	Formula	Molar mass (g/mol)	Mass/1000L brine (g)	Formula
CaCl <sub>2</sub>	0.00118	111	1.42	Na <sub>2</sub> CO <sub>3</sub>	108	1378	CaCO <sub>3</sub>	100	1276	2NaCl
MgCl <sub>2</sub>	0.00011	24	0.13	2NaOH	82	902	Mg(OH) <sub>2</sub>	58	319	2NaCl
Na <sub>2</sub> SO <sub>4</sub>	0.00284	96	3.41	BaCO <sub>3</sub>	197	6994	BaSO <sub>4</sub>	233	8272	Na <sub>2</sub> CO <sub>3</sub>
Na <sub>2</sub> SO <sub>4</sub>	0.00284	96	3.41	BaCl <sub>2</sub>	208	7384	BaSO <sub>4</sub>	233	8272	2NaCl
Na <sub>2</sub> SO <sub>4</sub>	0.00284	96	3.41	CaCl <sub>2</sub>	111	3941	CaSO <sub>4</sub>	136	4828	2NaCl

In Table 9, an overview is shown of the various precipitation processes deployed to purify the brine. Through a series of reactions, all existing impurities can be chemically removed from the brine, as the combination of reactions forms aqueous NaCl in all but one of the reactions. The sodium sulphate is therefore firstly precipitated with BaCO<sub>3</sub>, whereupon the resulting Na<sub>2</sub>CO<sub>3</sub> forms the reactant used to remove the CaCl<sub>2</sub> impurities. Although the companies involved in the salt manufacturing industry wish to keep their purification process confidential, it is likely that the purification process deploys the above described chemical reactions to achieve the high levels of purity needed for industrial salt.



# Appendix C:

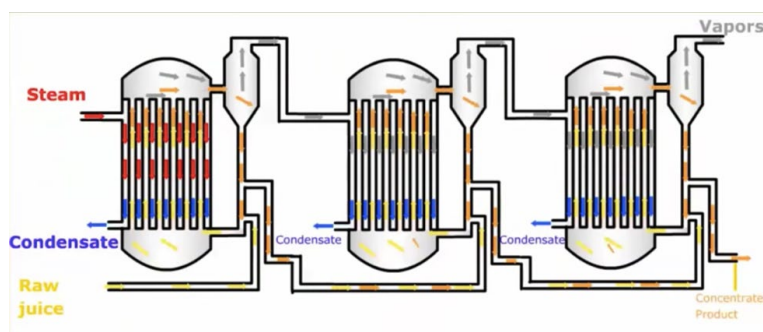
## Explanation of Multiple Effect Vaporisation

The brine is pumped into large vacuum pans. These pans are closed metal cylinders with conical bottoms. They are often arranged in a series of three, with each successive pan having a greater vacuum than the preceding pan. The vacuum pans operate on a simple principle: the boiling temperature of water decreases when the pressure is lowered. Furthermore, the resulting steam in the first pan is used to heat the second pan, and so on. Vacuum pans may operate at temperatures as low as 35 °C.

In the vacuum evaporation process, steam is fed to the first pan, causing the brine in the pan to boil. The steam from the boiling brine is used to heat the second pan. Since the pressure in the second pan is lower, the steam made by boiling the brine first pan allows the brine in the second to boil too. The pressure is lowered in each subsequent pan. This allows the steam made by boiling the brine in the previous pan to boil the brine in the next. More pans in a row allow for greater energy efficiency as less steam needs to be produced in the first place to cause the brine in the first pan to boil.

Steam from a power plant at a pressure of 3.3 bar and temperature of 150 °C heats the brine to its boiling point via a heat exchanger (2 bar, 120 °C), such that the dissolved salt crystallises. As the brine boils, salt crystals begin to form and sink to the bottom of the evaporator. This produces a thick mixture of salt crystals and salt solution, called a slurry, which is fed into another evaporator to repeat the process and concentrate the salt further. In subsequent steps, lower pressure and temperature are deployed; 0.9 bar and 95 °C, 0.3 bar and 70 °C, 0.1 bar and 50 °C.

Optionally, a concentrator is located between the last evaporator and the condenser. This extra evaporator will evaporate the brine that is not completely saturated to the point of saturation. The evaporator uses the vapour originating from the last evaporator of the vacuum evaporation facility (temperature approximately 50 °C). At the installation in Hengelo there are two evaporation installations consisting of four evaporators. An overview of the vacuum evaporation process is shown in Figure 3.



**Figure 3 Triple effect vacuum evaporator**