Chlorine plant

Membrane cell rock salt electrolysis

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Process Technology Support

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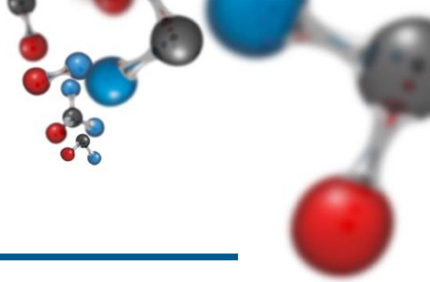

Overview of BorsodChem Zrt.

A. **One of the most integrated chemical plants in Hungary**
B. **More than 3,000 employees**
C. **The number of researchers and developers is about 50**
D. **One of Europe's leading manufacturers of MDI, TDI, PVC and chlor-alkali.**
E. **Use of products: construction, furniture industry, shoe manufacturing, machine building, automotive industry, adhesives, elastomers, seals, cleaning agents**
F. **Markets: Western Europe, Central and Eastern Europe, North and South America, Africa, Middle and Far East**
G. **Sustainability: Ecovadis - platinum grade**
H. **Continuous expansion**
I. **New plants starting soon:**

- Anilin
- MNB
- HPM
- WNA

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Source: website of Borsodchem Zrt. – www.borsodchem.com – view: 11. 15. 2021.

Overview of BorsodChem Zrt.

A. **The beginning: 1949 - Borsod Chemical Plant**

B. **1954 - Fertilizer production begins**

C. **1963 - First mercury cathode chlorine plant, PVC production begins**

D. **1991 - BorsodChem is established, isocyanate production begins (MDI plant)**

E. **2001 - Start of TDI plant**

F. **2006 - Start of membrane cell chlorine production**

G. **2011 - The Company becomes the property of Wanhua Industrial Group in China**

H. **2016 - Hydrochloric acid conversion (HOX) plant starts → chlorine production**

I. **2018 - Complete phasing out of mercury chlorine production**

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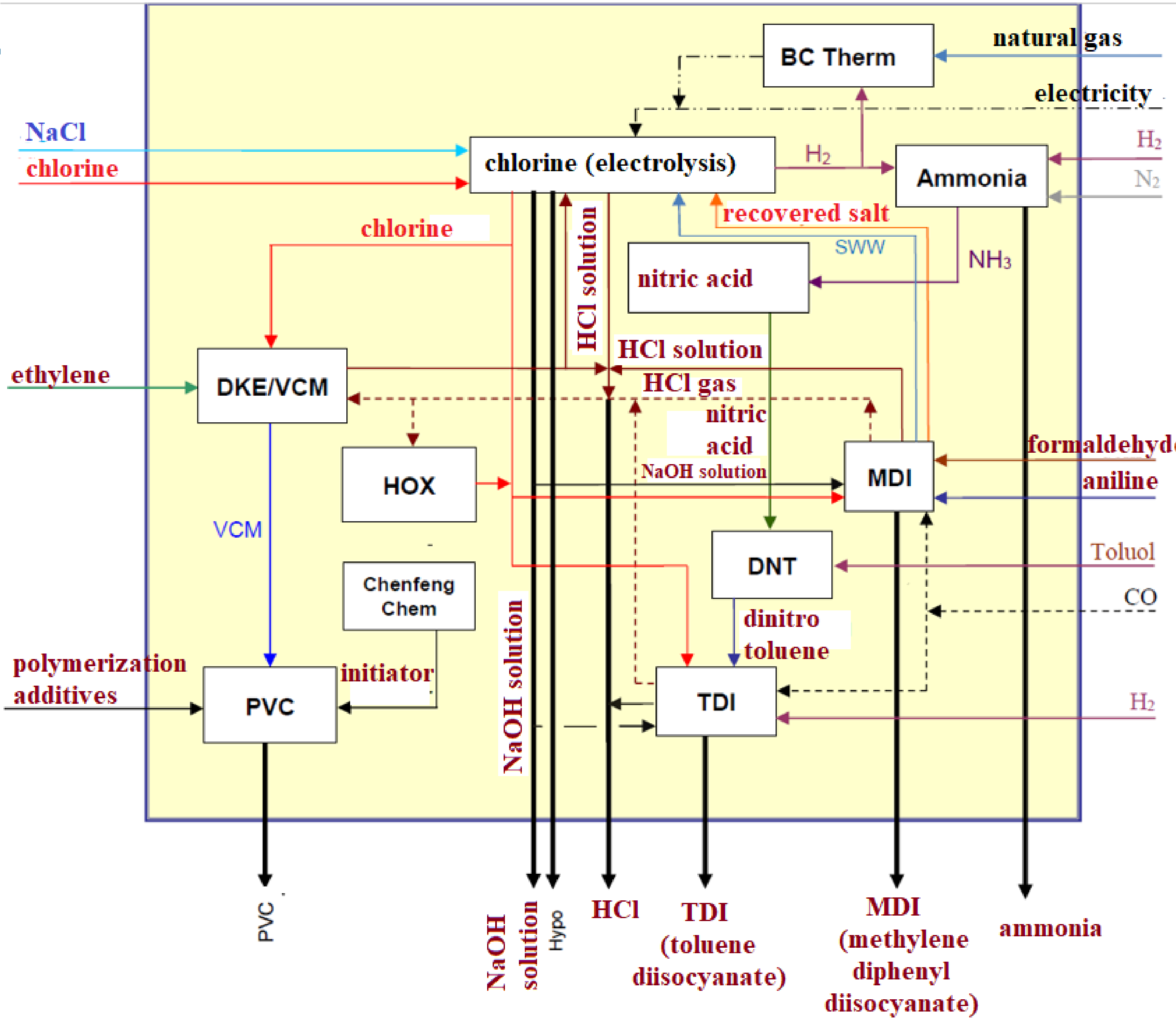
Source: website of Borsodchem Zrt. – www.borsodchem.com – view: 11. 15. 2021.

Overview of BorsodChem Zrt.



Source: Operational description of chlorine plant, MC-2 site, BorsodChem Zrt.

The past and present of chlorine production

A. **Minamata Convention (signed in 2013, ratified in 2017):** requiring the phasing out of mercury in mercury-based processes

B. Membrane cell technology is currently the BAT for chlorine production

Plant	Start-up	Capacity (kt/year produced chlorine)	Technology	Shutdown
NaOH plant	1963	16	Hg cathode, graphite anode	1987
HCl plant	1969	20	Hg cathode, graphite anode	1997
HgC plant	1978/79	110/130	Hg cathode, metal anode	2018
MC1 plant	2006, 2013	2006: 144 2013: 192	Membrane cell	
MC2 plant	2018	192	Membrane cell	

Source: Minamata Convention on Mercury - https://www.mercuryconvention.org/en, view: 11. 15. 2021.

Brine circle – production of super pure brine (SPB)

A. **Challenge: production of super pure brine - metal contaminants damage the membrane of the electrolysis cell**
   Recycling of salty industrial wastewater - salty wastewater cannot be discharged into fresh water

B. **Mass flow: ~700 t/h solution, continuous operation.**

C. **80% from mines (Transylvania) - ~ 500,000 t per year, the rest from the evaporated salt and salty process water recycled from the MDI, TDI and VCM plant**

Brine circle – production of super pure brine (SPB)

A. Requirements – super pure brine (SPB):

Al: <10 ppb

Mg: <20 ppb

Ca: <20 ppb

Ba: <100 ppb

Sr: <100 ppb

Fe: <50 ppb

SiO_2: <5 ppm

$NaClO_3$: <15 g/l (MC1), <5 g/l (MC2)

Na_2SO_4: <12 g/l (MC1), <10 g/l (MC2)

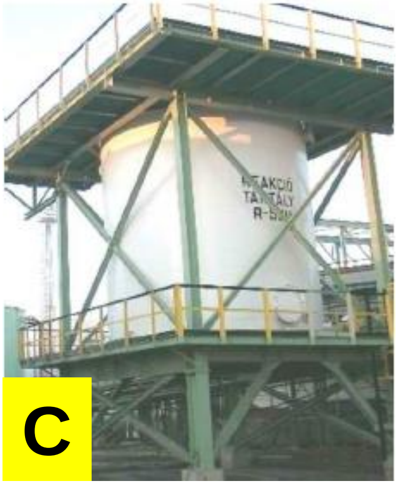
TOC: <10 ppm

Brine circle – production of super pure brine (SPB)

A. **Transport of salt to quick release**

B. **Dissolution in countercurrent in diluted brine returning from the electrolysis cell → Saturated solution at 70-80 °C - avoid crystallization!**

C. **Formation of carbonate and hydroxide precipitates from undesired metals**



Brine circle – production of super pure brine (SPB)

A. **Primary removal of precipitation: sedimentation**

B. **Filtration, stage 1: with anthracite-filled filters → 2-3 ppm purity**

C. **Filtration, stage 2: special candle filters with α-cellulose charge → ~ 1 ppm or less purity**

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Brine circle – production of super pure brine (SPB)

A. **Ion exchange using a special chelating resin mixture to remove residual dissolved metal ions → super pure brine**
Concentration, pH, resin regeneration mode are extremely important
Regeneration: with high purity NaOH and hydrochloric acid (self-produced)

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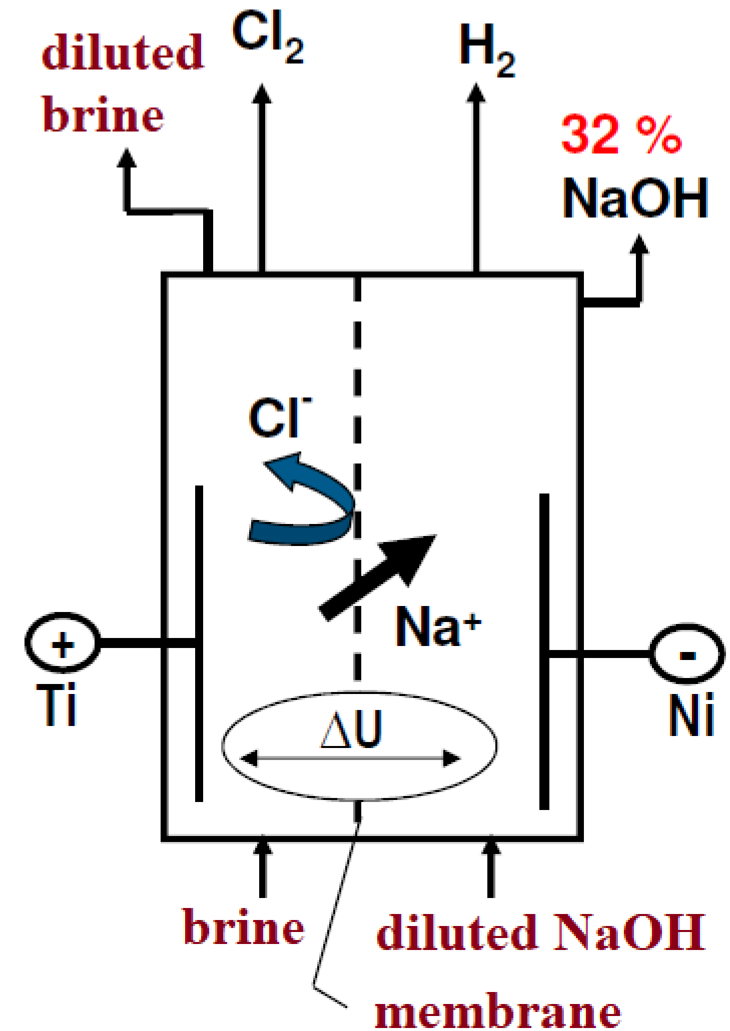
Membrane cell electrolysis - operation of an electrolysis cell

A. Advantages of the new procedure:

- Efficient gas-gas and gas-liquid separation
- High selectivity membrane →pure products
- Low ohmic resistance → energy saving
- Large area electrodes can be used → good efficiency
- Less space required

B. Disadvantages and difficulties compared to the mercury cathode process:

- Extremely pure raw material demand (brine)
- More sensitive technology



Source: Euro Chlor
www.eurochlor.org

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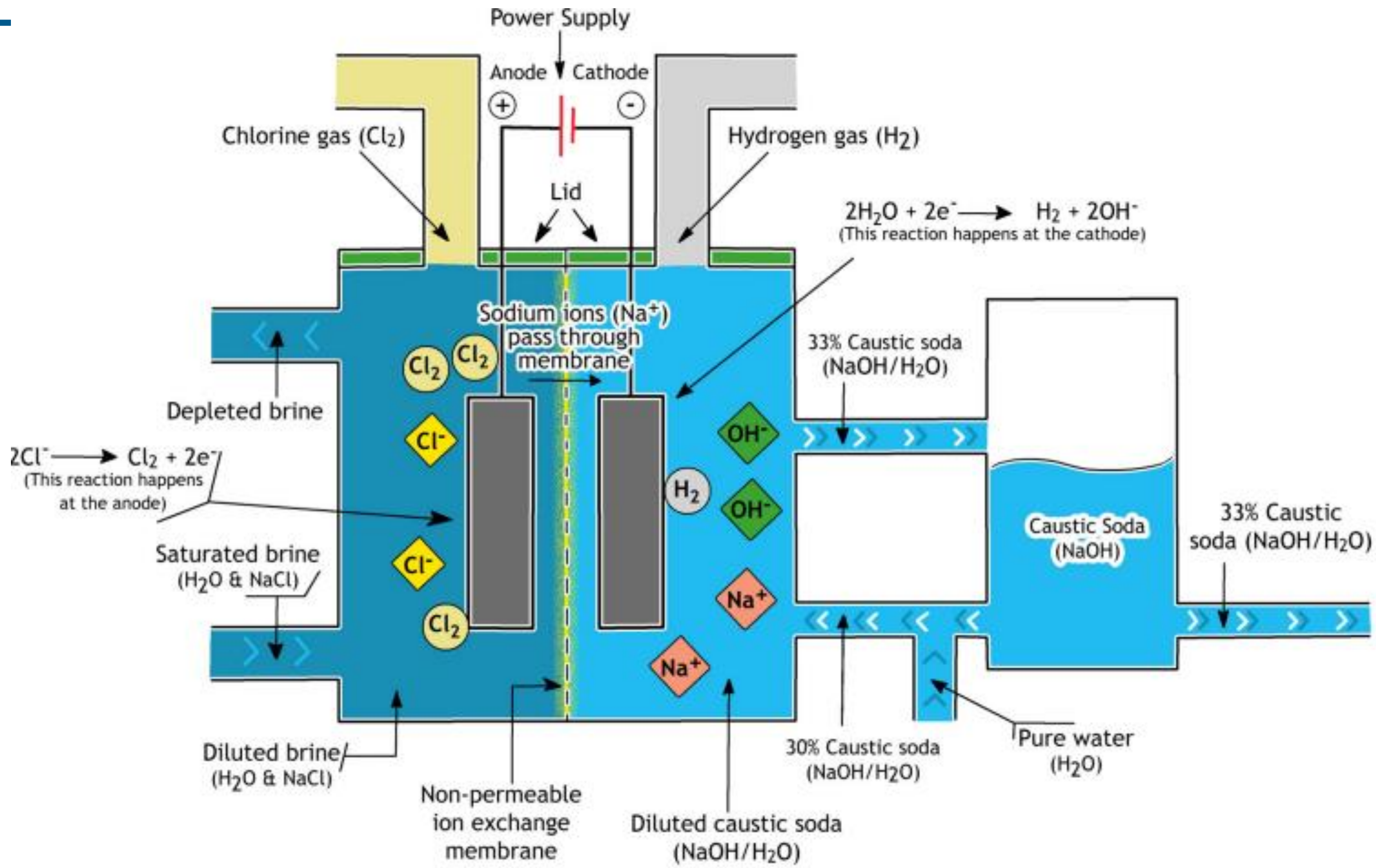
Membrane cell electrolysis - operation of an electrolysis cell



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Source: Euro Chlor
www.eurochlor.org

Membrane cell electrolysis - operation of an electrolysis cell – operational parameters (MC2 unit)

A. Downtransformation of 120 kV voltage from national power grid in 2 steps to ~ 600 V, creating direct current

B. 8 cell units connected in parallel, with 164 cells connected in series per unit

C. Rated voltage: 630 V (3.8 V per cell)

D. Rated current: 18 kA, normal operation: 14.4 kA

E. 4-5% of the annual Hungarian electricity consumption is used by BorsodChem, about 2/3 of which is used by the chlorine plant (!)

F. The operating parameters of the MC1 unit are similar, however, there are minor differences

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Membrane cell electrolysis - operation of an electrolysis cell

MC1 plant

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Membrane cell electrolysis - operation of an electrolysis cell

MC2 plant

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Treatment, separation and purification of crude products – hydrogen gas

A. With cooling, most of the water content can be condensed

B. Using drip separators

C. The total amount of hydrogen is utilized at BorsodChem: ammonia plant, synthetic hydrochloric acid production, BC power plant

D. Before the hydrogen is added to the common operating backbone, it is heated so that no water is condensated later.

Treatment, separation and purification of crude products – chlorine gas

A. Removal of dissolved chlorine in the remaining dilute brine:

- Vacuum chlorine remover: 0.35 bar vacuum, acidification with hydrochloric acid below pH 2
- Removal of residual chlorine by the addition of sodium sulphite (as chlorine would damage the SRS membrane in the brine circuit – the function of SRS membrane: sodium sulphate removal)

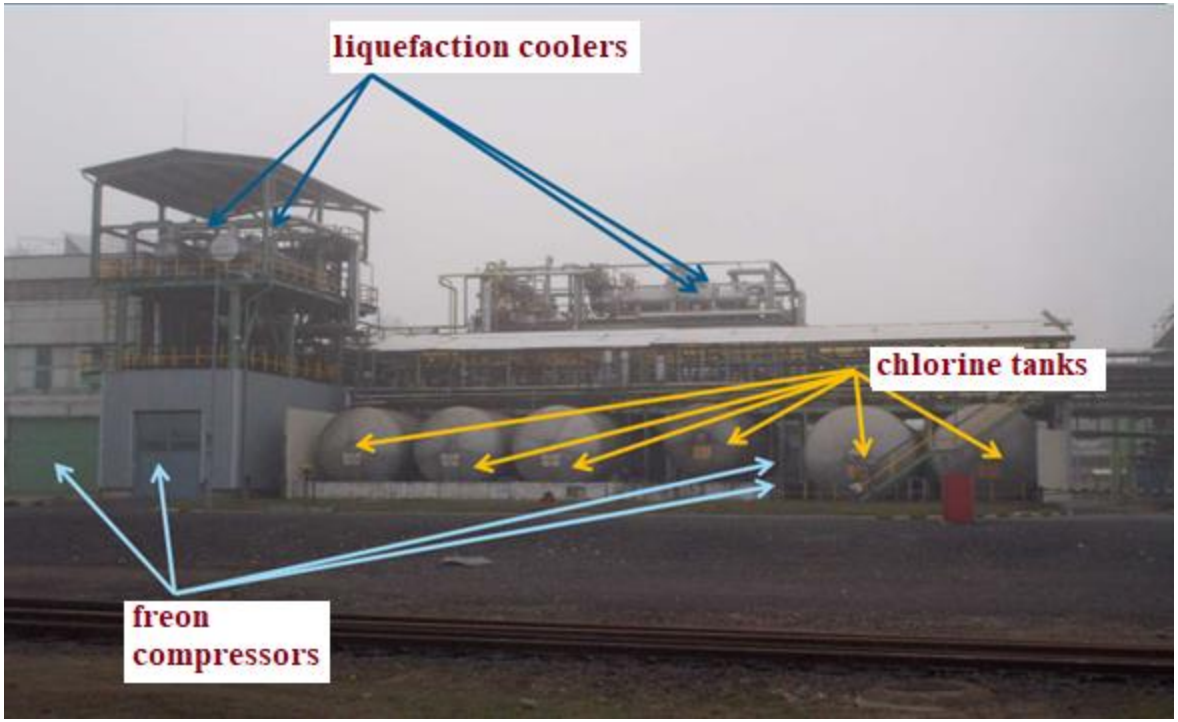
B. Dehydration of chlorine gas:

- Cooling to 10-14 ° C (avoid lower temperatures due to solid chloral hydrate formation)
- Removal of residual water by drying with concentrated sulfuric acid.
- Desulfurization on glass filter candles.

Treatment, separation and purification of crude products – chlorine gas

A. **Deoxygenation and liquefaction of chlorine gas**

- Oxygen is formed at the anode due to a side reaction.
- Removal by liquefaction. With multi-stage turbocompressors, pressure increase to 4-5 bar. Chlorine is liquefied and oxygen and other polluting gases are removed.

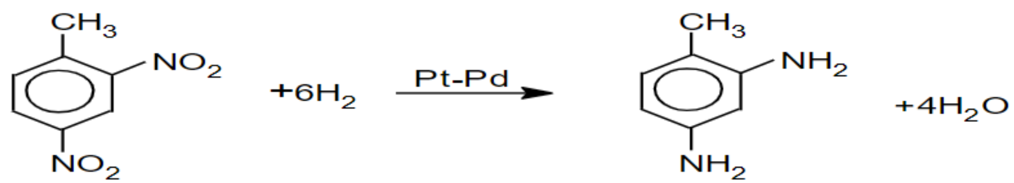


Treatment, separation and purification of crude products – chlorine gas

A. **Chlorine evaporation: steam-heated pipe in the pipe heat exchangers. Cause: Plants use chlorine in its gaseous state.**

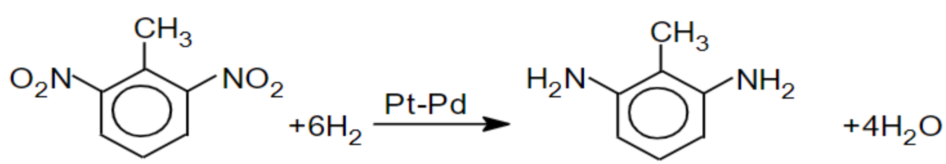
B. **Uses: TDI, MDI plant, indirectly PVC production, hypo production, high purity hydrochloric acid production. (The total amount will be used at the Kazincbarcika site.)**

Use of chlorine: TDI production



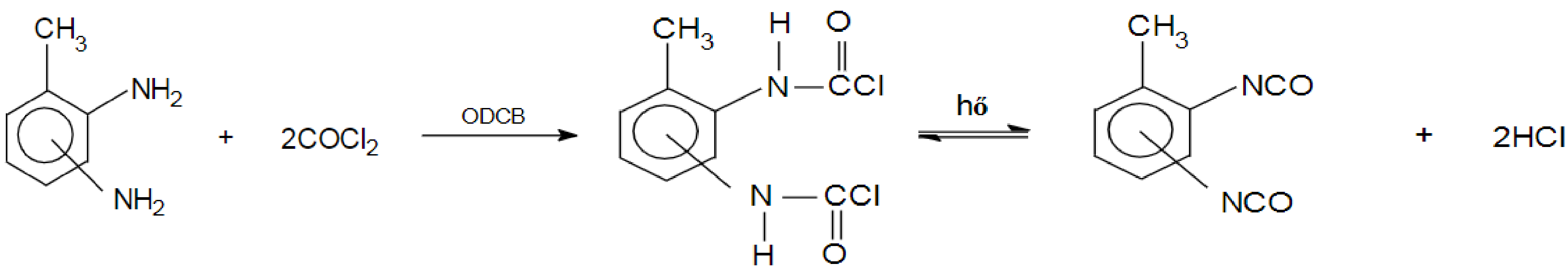
2,4 dinitro toluene
DNT

2,4 toluene diamine
TDA



2,6 dinitro toluene
DNT

2,4 toluene diamine
TDA



TDA

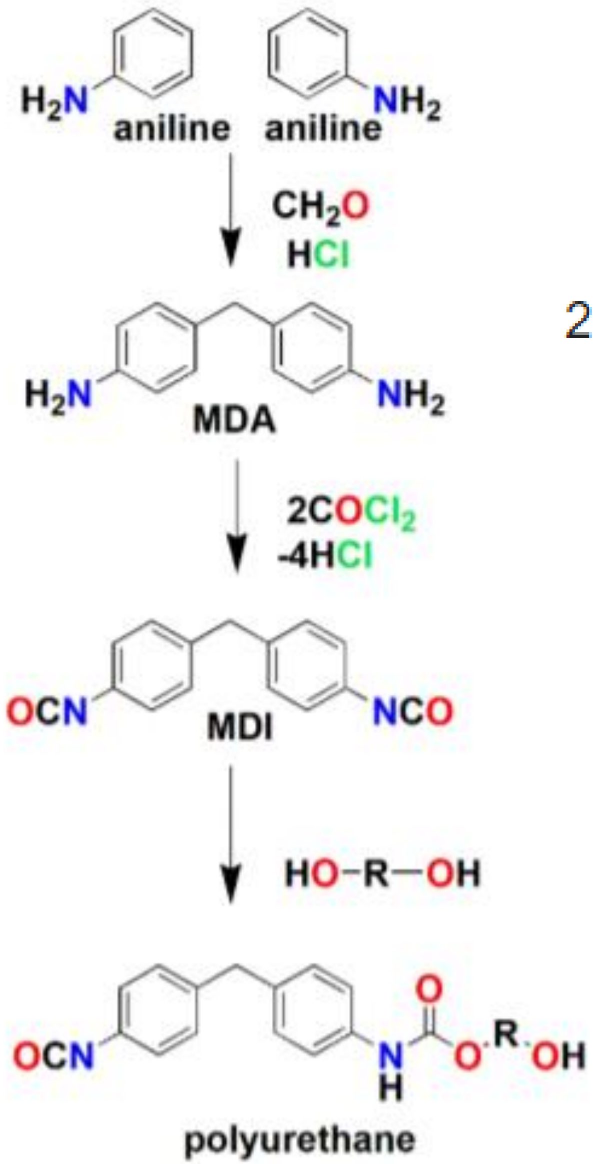
phosgene

carbamoyl chloride

TDI

Source: Operational description of TDI plant, BorsodChem Zrt.

Use of chlorine: MDI and VCM production



$$2\ H_2C{=}CH_2 + 4\ HCl + O_2 \rightarrow 2\ ClCH_2{-}CH_2Cl + 2\ H_2O$$

$$Cl{-}CH_2{-}CH_2{-}Cl \rightarrow H_2C{=}CH{-}Cl + HCl$$

VCM

Vinyl chloride

Source: Renáta Zsanett Boros: Izocianát Gyártás Elemi Reakcióinak Tanulmányozása – PhD dissertation, University of Miskolc, Antal Kerpely Doctoral School of Materials Science and Technologies, 2019

Treatment, separation and purification of crude products - sodium hydroxide

A. **32-33 w% NaOH can be obtained on the electrolysis cell, which is suitable for internal use.**

B. **Customers usually require 50% alkali → Concentrated NaOH required.**
3 stages with high pressure steam

C. **Internal use: MDI, TDI, VCM plant, chlorine plant (resin regeneration), HOX, Framochem.**

Related technologies - Sulfuric acid reconcentration

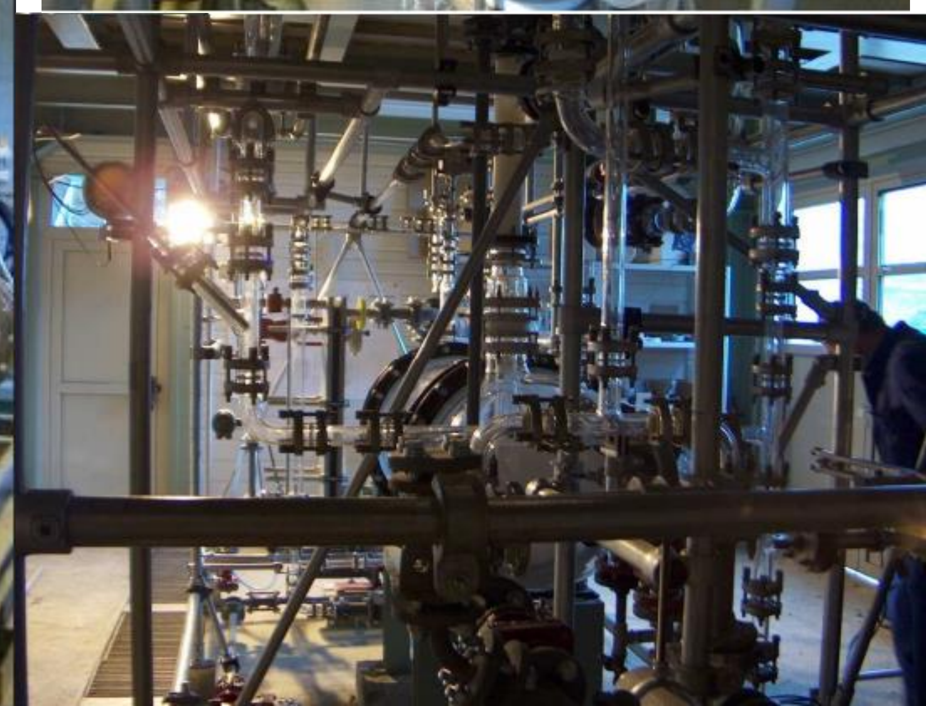
A. **The dilute sulfuric acid produced during the dehydration of the chlorine must be concentrated back.**

B. **Special conditions: 180 °C, 10 mbar vacuum - with multiple water ring vacuum pumps, steam jet pumps, vacuum ejectors**

C. **Dilute sulfuric acid contaminated with chlorine → Danger of corrosion → Ta, SiC heat exchangers, 2 cm thick borosilicate glass body**

D. **There are currently 3 units in operation, 2 of which are in the chlorine plant**

Related technologies - Sulfuric acid reconcentration



Related technologies – Alkaline evaporation

A. Applied temperature: 200 °C, with steam heating, rain film and superheat evaporator units.

B. Special construction materials required: SS/Ni201/C276 evaporators and heat exchangers

C. Evaporation takes place in 3 stages, with energy integration between the stages.

D. MC1 plant: two independent systems

E. MC2 plant: a high-capacity unit

Related technologies – Sulphate nanofiltration (SRS membrane)

A. **Sodium sulphate content of incoming brine: ~10-20 g/l**

B. **Sources of sodium sulphate:**
   - Rock salt from a mine
   - Recycled salt from MDI plant
   - Removal of residual chlorine after vacuum removal with sodium sulfite

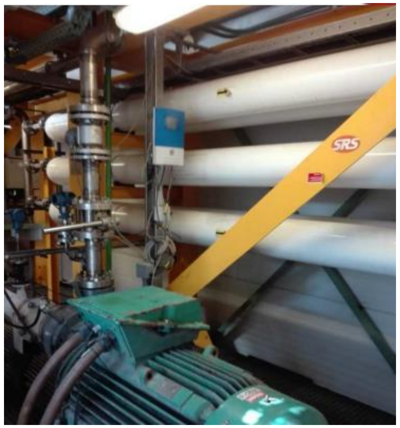
C. **Problem: The presence of other sodium salts reduces the solubility of NaCl**

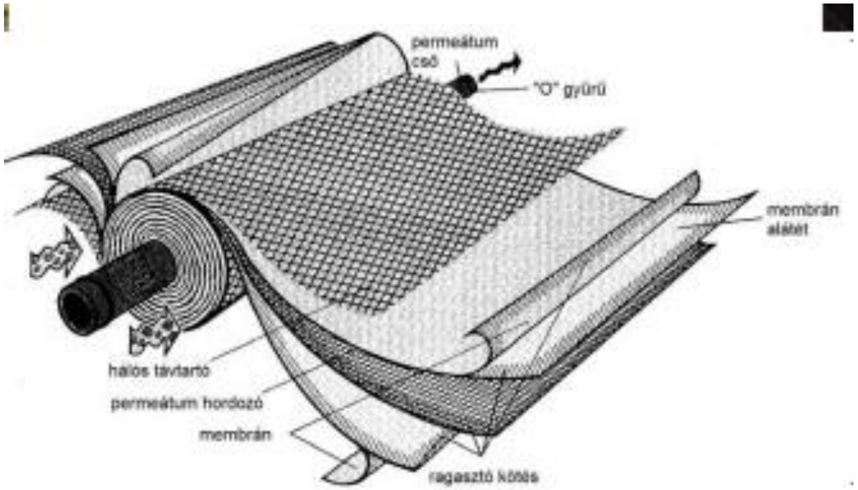
D. **Old process: precipitation with barium carbonate - problem: toxic property, continuous waste generation**

Related technologies – Sulphate nanofiltration (SRS membrane)

A. **Current process: nanofiltration with SRS membrane**
   - Sodium sulphate in the concentrate, NaCl in the permeate
   - Multi-member filter membrane system
   - About 40 barg overpressure
   - Density control
   - The permeate is returned to the brine circuit

B. **This process prepares the dechlorinated brine for sulfate crystallization**





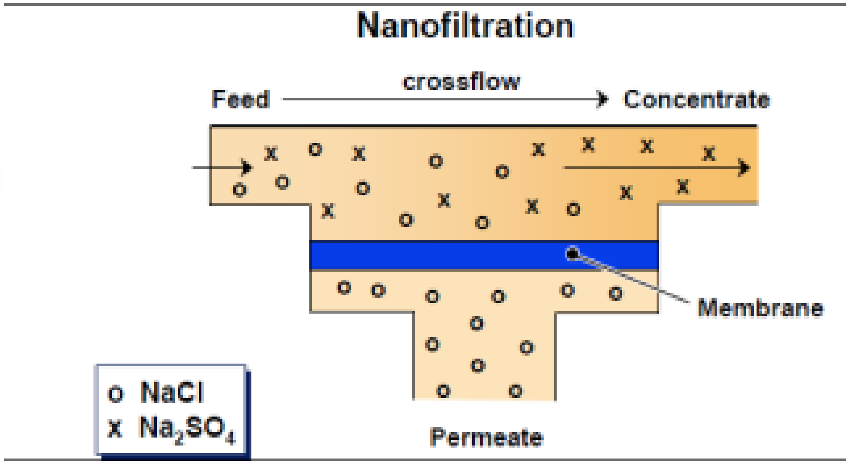


Figure 1. Principles of Nanofiltration

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Related technologies – Sulphate crystallization

A. **Incoming concentrate composition::**
   - ~130 g/l Na_2SO_4
   - ~ 180 g/l NaCl

B. **Two degrees of crystallization**
   - Na_2SO_4 removal: 91 °C (anhydrate)
   - NaCl removal: 51 °C

C. **Energy integration**

D. **Product: pure, dried Na_2SO_4 (anhydrate, NaCl content: <1%) – will be sold**

E. **The precipitated NaCl is not dried but returned to the brine circuit**

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Synthesis of super pure hydrochloric acid

A. **Production of super pure hydrochloric acid**
   - Also from chlorine liquefaction head gases (low pressure) and directly from high pressure chlorine
   - 3 independent units
   - Directed combustion of mixed head gases in hydrogen (!) - special silicon glass burner, combustion temperature up to 2400 ° C
   - Water is formed from polluting oxygen
   - Absorption in deionized water
   - Product: 33-35% hydrochloric acid at 14-20 ° C
   - Mainly internal use (regeneration of ion exchange resin, pH settings, dechlorination), smaller sales

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Hypo synthesis

A. NaOCl production

- From chlorine liquefaction head gases (low pressure)
- In case of emergency, it is suitable for the destruction of the entire amount of chlorine for 15 minutes
- 3 tower system
- Mainly external sales, less internal use

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Construction of MC2 plant

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Construction of MC2 plant

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Thanks for the attention!

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Source of pictures, informations:

Gábor Kovács (technológiai főmérnök, BorsodChem Zrt., chlorine plant)