Chlorine

HIGHLIGHTS

Processes and technology status – Most chlorine is manufactured by the electrolysis of sodium chloride solutions. The primary raw material for this process is rock salt (sodium chloride), available worldwide usually, as underground deposits of high purity [1].

Cost – Chlor-alkali production relies on energy-intensive electrochemical technology; hence, the price of electricity represents roughly 40% of the operating cash cost [2].

Potential and barriers – The barriers ahead of chlorine production are related to the high cost and energy requirements of the process. Therefore, coupling the Chlor-alkali process with other electrocatalytic processes holds great potential for future energy conservation and storage [3].

Chlorine – Chlorine (Cl_2), as a chemical precursor, is crucial for many important industrial processes, including polymer synthesis, disinfection goods production, pharmaceutical manufactures, and wastewater treatment [3]. Chlor-alkali produces the base chemicals chlorine (Cl_2) and sodium hydroxide (NaOH), as well as hydrogen (H_2) as a byproduct in the conventional process [4].

Process overview - Key feedstocks for chlorine production are salt and electricity. Chlorine is produced through the Chlor-alkali process in which electricity is applied to a solution of salt water or brine. The electricity separates metal (sodium potassium, magnesium, or calcium) from chloride in the diaphragm, membrane, or mercury cell process and converts chloride ions to elemental chlorine. Chlorine is, also, produced in several other ways, for example, by electrolysis of molten salts and by non-electrolytic processes [5].

The two oldest methods, diaphragm and mercury cells have been used for over 100 years throughout the world and have been proven to be the most environmentally unfriendly through their use of asbestos and mercury, respectively [6].

Membrane Cell Technology – Membrane cell technology uses sheets of perfluorinated polymer ion exchange membranes to separate the anodes and cathodes within the electrolyzer [5]. A

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membrane plant uses less electricity than a mercury plant but requires more steam to obtain the standard commercial concentration of caustic soda [7], [2]. Typically, a membrane plant may require about 15% fewer personnel than a mercury cell plant [2]. Figure 1 shows an industrial Chlor-alkali cell line with membrane cells [8].

Figure 1. Chlor-alkali cell line with membrane cells [8]

The power capacity of the 50 MW is the average capacity of industrial Chlor-alkali electrolysis processes employing membrane cells in Europe. This results in the chlorine production of 21.9 t/h for all the processes.

Cost and energy – The cost of the Chlor-alkali industry is energy- and resource-dependent. The required amount of electrical energy for an electrolyzer is around 6-9.5 PJ/Mt Cl_2. Roughly 40% of total production costs are spent on electricity and gas[9]. Natural gas fuels heat engines to produce the low-pressure steam for the processing of caustic soda. Besides, the industrial vacuum salt costs 57 $€_{2014}$/t, and the cost of required electricity is 237.6 [1] $€_{2017}$/kJ.

For the production of 850 kt/y chlorine, 1600 kt/y of industrial quality salt (98%) and 2400 kt/y purified water, besides 0.18 kt/y of HCl (32%) are required. This process utilizes 2.8 PJ/y steam and 6.1 PJ/y electricity and generates 950 kt/y soda (50%), 24 kt/y hydrogen as a byproduct, and emits 180 kt/y CO_2. In the current technologies, steam is generated from natural gas-fired CHP. Moreover, the emission-related to the electricity (6.1 PJ/y) is equal to 760 kt indirect CO_2 [9].

Production and consumption in Belgium – The production capacity of chlorine in Belgium in 2020 was 1074 kilotons [10]. Table 1 shows Chlor-alkali sites and their capacities in Belgium.

Table 1. Chlorine production plants in Belgium, 1st January 2020 capacities [11]:

Company	Site	Produced Cl_2 (kt) [11]
INOVYN	Lillo	500
INOVYN	Jemeppe	174
Vynova	Tessenderlo	400

[1] Converted from 0.066 $€_{2017}$/kWh

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Potential and barriers ahead of chlorine production – The barriers ahead of chlorine production are the high cost and energy requirements of the process. The dimensionally stable anode (DSA) technology can make the Chlor-alkali process more sustainable in the future, and cost reduction of DSA opens new opportunities for sustainable and more affordable chlorine production [3]. In addition, chlorine production from seawater electrolysis is a promising strategy that can be achieved through the manufacturing of multi-component metal oxides [3]. Relying intensively on electricity, the Chlor-alkali process can play an important role in the enhancement of grid resilience as well [12]. Furthermore, a gas diffusion electrode that allows for the use of oxygen as the feed, and the oxygen depolarized cathode (ODC), leads to energy savings of up to 30% due to the lower thermodynamic decomposition voltages [13].

Emission from Chlor-alkali processes - The Chlor-alkali industry emits indirect CO_2 during the production of the electricity that is utilized in the sector. The process itself does not emit direct CO_2. The average electricity consumption per ton of chlorine leads to 2.1 tons of $CO_{2\text{-eq}}$ [7]. Table 2 compares the energy requirements of each cell type and the carbon dioxide emissions associated with the production energy [14].

Yearly estimated total indirect CO_2 emissions related to Belgian chlorine–production volume – As reported for the year 2020, the total chlorine production in Belgium was equal to 1074kt [11]. Considering emission from the Chlor-alkali process equal to 2.1 tons of $CO_{2\text{-eq}}$, the yearly indirect emitted CO_2 in Belgium is about 2.255 * 10^6 $t_{CO_2\text{-eq}}/t_{Chlorine}$.

Table 2. Average energy consumption and emissions for brine cells [14]

Cell type		Mercury	Diaphragm	Membrane	Membrane with ODC
Energy consumption (MWh/t_{Cl2}) [2]	Electrolysis	3.4	2.7	2.6	1.8t
	Evaporation	0	0.6	0.2	0.2
CO_2 emissions/t		1.8	1.7	1.5	1.0

[2] Estimated

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Decarbonization options for the Dutch Chlor-alkali industry - A key opportunity for decarbonization in the Chlor-alkali industry lies in the reduction of indirect emissions by the utilization of green electricity at electrolyzers. For direct emission reduction, placement of electric and biomass boilers or utilization of geothermal energy is required. Moreover, the large-scale implementation of zero-gap membrane electrolyzers can reduce electricity consumption [9].

Table 3. Summary Table: Key Chlorine Data and Figures

Technical Performance	
Feedstocks	Salt [98% purity; 1882 kt/y] and purified water [2823 kt/y]*
Products	Chlorine (Cl_2) [1000 kt/y]; Sodium hydroxide (NaOH) [1117.6 kt/y] ; and, Hydrogen (H_2) [28.24 kt/y] *
Required energy	Electricity [7.18 PJ/y] and Steam [3.29 PJ/y]*
Emission	CO_2 [211.8 kt/y]*
Chlorine production in Belgium	**2020** [10]
Chlorine (INOVYN and Vynova)	1074 kt
Costs and energy	
Energy (Electricity)	0.85-3.56 PJ/Mt_{Cl2}.
Salt cost	57 $€_{2014}$/t
Electricity cost	237.6 $€_{2017}$/kJ

* For 1000 kt/y Chlorine (Cl_2) production

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