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# Environmental challenges of the chlor-alkali production: Seeking answers from a life cycle approach

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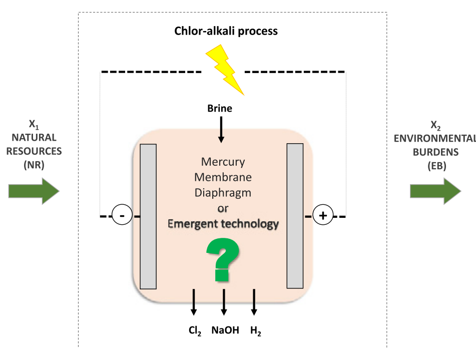
## HIGHLIGHTS

- Environmental profile of emerging vs current chlor-akali technologies
- LCA approach based on natural resources and environmental burdens methodology
- Majority of impacts due to energy consumption in electrolysis stage
- Hydrogen valorisation through electricity generation to tackle energy dependency
- Expected results for emergent technology worsen due to lack of hydrogen production.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Life Cycle Assessment (LCA) has been used to assess the environmental sustainability of the chlor-alkali production in Europe. The three current technologies applied nowadays are mercury, diaphragm, and membrane cell technology. Despite, having achieved higher energy efficiencies since the introduction of membrane technology, energy consumption is still one of the most important issues in this sector. An emerging technology namely oxygen-depolarised cathodes (ODC) is suggested as a promising approach for reducing the electrolysis energy demand. However, its requirement of pure oxygen and the lack of production of hydrogen, which could otherwise be valorised, are controversial features for greener chlorine production.

The aim of this work is to evaluate and compare the environmental profiles of the current and emerging technologies for chlorine production and to identify the main hot spots of the process. Salt mining, brine preparation, electrolysis technology and products treatment are included inside the system boundaries. Twelve environmental impact categories grouped into natural resources usage and environmental burdens are assessed from cradle to gate and further normalised and weighted. Furthermore, hydrogen valorisation, current density and allocation procedure are subjected to sensitivity analysis. Results show that the electrolysis stage is the main contributor to the environmental impacts due to energy consumption, causing 99.5–72% of these impacts. Mercury is the less environmentally sustainable technology, closely followed by diaphragm. This difference becomes bigger after normalisation, owing to hazardous waste generated by mercury technique. Conversely, best results are obtained for ODC instead of membrane scenario, although the reduction in energy requirements is lesser than expected (7%).



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## 1. Introduction

The development of novel chemical processes and products in the twenty first century is based on the application of Supply Chain Management (SCM) and Life Cycle Assessment (LCA) methodologies (Garcia-Herrero et al., 2016). These innovations are related to the development of communication technologies and economic and social globalization (Irabien et al., 2009). Furthermore, the design of environmental sustainable products and processes should be addressed following the twelve principles of green chemistry: pollution prevention, atom economy, less hazardous chemical routes, safer processes, use of renewable raw materials and reutilisation of secondary materials according to circular economy (Anastas and Warner, 2000; Anastas and Zimmerman, 2003; Grossmann and Westerberg, 2000).

The chlor-alkali industry produces chlorine, sodium/potassium hydroxide and hydrogen by the electrolysis of brine. Chlorine and sodium hydroxide are important commodities used in a wide range of applications. Indeed, these two key building blocks underpin more than 55% of the European chemical industry turnover (2010: almost 721 billion euro). The Chlor-alkali directly employed 39,000 people at 70 manufacturing locations in 22 countries. However, almost 2,000,000 jobs are directly or indirectly related to chlorine and its co-product caustic soda when the numerous downstream activities are taken into consideration (Brinkmann et al., 2014). The growth and future development of this sector is being mainly based on market demand, environmental concern and limitations and energy prices. Furthermore, technological development of processes and the adjustment of the sector to the new context of continuous improvement are additionally factors that will determine the future of the chlor-alkali industry.

Currently, the chlor-alkali process is mainly represented by 3 technologies: mercury cell, diaphragm cell and membrane cell. Their major features are outlined in Table 1. The main difference among these technologies lies in the separation configuration of the simultaneous chlorine and sodium hydroxide co-produced. Catholyte and anolyte are separated in diaphragm and membrane cell processes by a diaphragm and a membrane, respectively. Conversely, the sodium amalgam is the separation barrier in the mercury technology.

Up to the end of the 20th century, the mercury cell technique was the prevailing technology in Europe (55%), while the diaphragm cell technique dominated in the United States (75%) and the membrane cell in Japan (90%) (EC, 2000). This pattern has changed during the first decade of the 21st century. Since 1984, no new plants based on the mercury cell technique have been built, and only a few diaphragm cell plants have been installed. All new plants, including those erected in India and China, are based on the membrane cell technique (Brinkmann et al., 2014). Currently, the world share of chlor-alkali technologies is 74% membrane, 17% diaphragm and 4% mercury and other technologies (IHS, 2016), which indeed is similar to the European distribution (62% membrane, 15% diaphragm, 23% mercury).

Although a slight difference can be observed according to mercury plants, they are currently being converted or decommissioned, since the European Commission stated that this process must be phase out by December 2017 (EC, 2013).

On the other hand, despite the use of asbestos fibers is prohibited by the REACH regulation (EC, 2006), EU Member States can grant an exemption for the use of chrysotile asbestos-containing diaphragms in existing electrolysis installations. Around 13% of the global diaphragm cell plants' capacity was based on non-asbestos diaphragms in 2010 while this share was approximately 30% in the EU-27 (Brinkmann et al., 2014). Currently, asbestos free diaphragms are being developed (Lakshmanan and Murugesan, 2014).

Membrane technology is the most recent breakthrough in chlorine production. Since its introduction in 1970, lower environmental impacts and higher energy consumption efficiency than the conventional technologies are its main benefits. Despite the total energy requirements of the process are reduced by using this technology, energy consumption is still one of the most important issues in chlor-alkali sector.

The chlor-alkali process requires around 2500–3500 kWh per ton of chlorine, which involves an important environmental impact (Di et al., 2007; IPPC, 2007; Weisser, 2007). Process intensification is addressed nowadays to the replacement of the hydrogen evolution cathode by an oxygen-depolarised cathode (ODC) (Moussallem et al., 2012). This technology has been well known for a long time and is successfully used in chlorine production from hydrogen chloride. However, only a few examples are currently available: a 20 kt/y chlorine plant in Leverkusen (Germany) that began operating in 2011 by Bayer/UHDE, and a 80 kt/y installation in Shandong (China) sold by Bayer/UHDE to Befar group that started operation in 2015 (Brinkmann et al., 2014). Consequently, practical experience with a new industrial scale plant and with the retrofitting of existing installations needs to be gained. It is based on the integration of an alkaline fuel cell cathode into the membrane electrolysis cell, which lowers electricity consumption by about 30%. However, pure oxygen is required as raw material and hydrogen is not co-produced.

According to this overall context, the intensification of the process should take into account the contributions of every life cycle stage from the extraction of raw materials to the treatment of products and waste generation. In this sense, Life Cycle Assessment (LCA) is a powerful tool to assess the environmental performance of processes and products on a life cycle basis. LCA methodology enables the identification of the best environmental measures that conduct to a more sustainable production.

The chlor-alkali process has been studied from a LCA perspective and several studies are available in the literature. Boustead (2005a, 2005c) reported the mass-allocated eco-profiles of chlorine and sodium hydroxide based on company data, which were requested by the Association of European Plastics Manufacturers (APME). Although salt production is not included in the study, the products treatment is considered. These works lack from the interpretation stage and inventories are not reported. Furthermore, disaggregated results for each technology, as well as the contribution of the different stages involved, are not shown. Hence, scenarios under study are difficult to assess. Martins et al. (2007) sourced all the Life Cycle Inventory (LCI) data from the outdated Buwal database (Buwal, 1996). The assessment is not a proper LCA study, but is focussed in the description of the tridimensional sustainability methodology proposed and its application.

The most complete and recent LCA study of the chlor-alkali industry is the European eco-profile requested by this sector (Eurochlor, 2013).

**Table 1**
Advantages and drawbacks of electrolytic chlor-alkali technologies. Adapted from Lakshmanan and Murugesan (2014).

| Technology | Advantages | Drawbacks |
|---|---|---|
| Diaphragm | Low quality requirements for brine raw material<br>Low electric energy consumption | Some cells still use asbestos<br>High thermal energy consumption for NaOH treatment<br>Low NaOH and chlorine quality |
| Mercury | Low quality requirements for brine raw material<br>High products quality | Mercury utilisation<br>High electricity consumption<br>High costs of environmental protection |
| Membrane | Low electricity consumption<br>Safe raw materials<br>High NaOH quality | High quality requirements for brine raw material<br>Low chlorine quality<br>High thermal energy consumption<br>High cost of membranes |
| ODC | Low electrolytic requirements and high energy efficiency<br>Safe raw materials<br>High NaOH quality | Strict cathodes requirements for optimum operation<br>Lack of production of hydrogen<br>Pure oxygen requirements<br>High quality requirements for brine raw material |