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When Life Cycle Thinking is Necessary for Decision Making: Emerging Cleaner Technologies in the Chlor-Alkali Industry

María Margallo, Raquel Onandía, Rubén Aldaco, Angel Irabien

Department of Chemical and Biomolecular Engineering, University of Cantabria, Av. de los Castros s/n, 39005 Santander, Spain
margallom@unican.es

The chlor-alkali industry sector produces chlorine, sodium/potassium hydroxide and hydrogen by the electrolysis of brine. Nowadays, three different electrolysis techniques are applied: mercury, diaphragm, and membrane cell technology. From all these technologies, the European Commission labels the membrane process as the Best Available Technique (BAT) for the chlor-alkali industry. The membrane cell technology has fewer exhausts to the environment and it is relatively more efficient in the use of electric power that mercury and diaphragm. Nevertheless, despite the fact that the overall energy intensity has been reduced, the issue of energy consumption is still a major matter. A promising approach for reducing the electricity demand of chlor-alkali electrolysis is using oxygen-depolarised cathodes (ODC). ODCs are long known and have been successfully used in chlorine production through electrolysis of hydrogen chloride (HCl). The achieved environmental benefit of this technique is a reduction of energy consumption. However, the overall reduction of energy consumption is lower, as some energy is required to produce pure oxygen and because hydrogen is not co-produced, which could otherwise be used in chemical reactions or to produce steam and electricity via combustion or fuel cells. In this sense, the reduced electricity demand does not necessarily imply cleaner chlorine production. For that reason, this work proposes the use of the life cycle assessment (LCA) methodology to determine the environmental performance of the existing electrolysis technologies and to compare it with the ODC technique.

1. Introduction

The chlor-alkali industry is the basis for approximately 55 % of the chemical industry in the countries of the EU-27 and the European free trade association (EFTA). This industry generated a turnover of almost 770 × 10^9 € in 2,008 and directly employed 39,000 people (Brinkmann et al., 2014). Chlor-alkali industry sector produces chlorine, sodium/potassium hydroxide and hydrogen by the electrolysis of brine. Nowadays, three different electrolysis techniques are applied: mercury, diaphragm, and membrane cell. The techniques differ from each other in terms of electrode reaction and electrode materials, and in the way, the produced chlorine is kept separate from sodium hydroxide and hydrogen (Eurochlor, 2013a). Nevertheless, the global reaction Eq(1) is common for all of the technologies and a fix ratio of the products is obtained. Particularly, 1,070–1,128 kg of NaOH (100 wt- %) and approximately 28 kg of H_2 are generated per t of Cl_2 produced.

$$2NaCl + 2H_2O \rightarrow 2\ NaOH + H_2 + Cl_2 \qquad (1)$$

Up to the end of the 20th century, the mercury cell technique dominated in Europe, while the diaphragm cell technique dominated in the United States and the membrane cell technique in Japan. However, this pattern has changed and during the period from 1997 to 2012, the share of the mercury and diaphragm cell techniques decreased significantly in the European countries, from 63 % to 26 % and from 24 % to 14 %, respectively, whereas the use of the membrane cell technique increased from 11 % to 59 %. Reasons for the change include the need to replace installations that have reached the end of their service life and environmental concerns over mercury emissions from mercury cell plants (Brinkmann et al., 2014). Moreover,

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the European Commission labels the membrane process as the Best Available Technique (BAT) for the chlor-alkali industry (Jung et al., 2013). In this sense, membrane has fewer exhausts to the environment and it is relatively more efficient in the use of electric power (Kiros and Bursell, 2008). Nevertheless, the disadvantages of this technology are the high-purity brine required, the low Cl_2 quality, the high steam consumption and great cost of membranes (Eurochlor, 2013a).

Despite the fact that the overall energy intensity has been reduced, the issue of energy consumption is still a major matter. A promising approach for reducing the electricity demand of chlor-alkali electrolysis is using oxygen-depolarised cathodes (ODC). ODC are long known and have been successfully used in chlorine production through electrolysis of hydrogen chloride (HCl). For chlor-alkali electrolysis, a pilot plant using ODC began operation only recently (Jung et al., 2014). The utilisation of ODC in chlor-alkali electrolysis is an integration of an alkaline fuel cell cathode into the membrane electrolysis cell. This lowers the cell voltage by about 1 V at current densities of industrial relevance (e.g. 4 kA/m^2), and thus the electrical energy consumption by about 30 %. The achieved environmental benefit of this technique is a reduction of energy consumption. However, the overall reduction of energy consumption is lower, as some energy is required to produce pure oxygen and because hydrogen is not co-produced, which could otherwise be used in chemical reactions or to produce steam and electricity via combustion or fuel cells (Brinkmann et al., 2014). In this sense, the reduced electricity demand does not necessarily imply cleaner chlorine production. For that reason, this work carried out a life cycle assessment (LCA) study to determine the environmental performance of the existing electrolysis technologies and to compare it with the ODC technique.

2. Life cycle assessment

LCA is a tool to assess the potential environmental impacts and resources used throughout a product´s life-cycle (Margallo et al., 2013). In this regard, LCA has become one of the most relevant methodologies to help organizations to perform their activities in the most environmental friendly way along the whole value chain (Mata et al., 2012).

2.1 Goal and scope

The goal and scope have to include the intended application of the study, the system boundaries, the functional unit and the level of detail to be considered (Margallo et al., 2014a). Moreover, goal definition is a very important step in an LCA study, because the choices made at this stage influence the entire study (De Marco et al., 2015). In this work, LCA was conducted from cradle to gate taking one ton of chlorine as functional unit. The study included salt mining and transportation, brine preparation and purification, electrolysis process, treatment of products and waste management (Figure 1). Out of the system boundaries were the internal transport in the plant, the construction of major capital equipment and the maintenance and operation of support equipment.

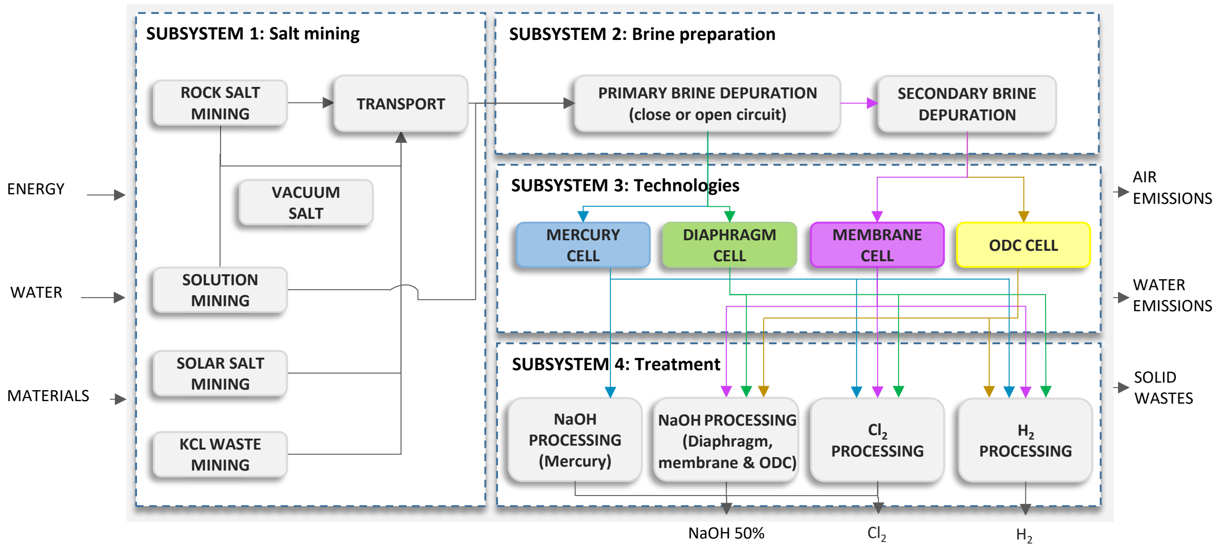

Figure 1: Diagram of the chlor-alkali process: salt mining, brine preparation and purification, electrolysis cell and processing of NaOH, H_2 and Cl_2

This paper evaluated and compared the three conventional electrolysis cells, which are mercury, diaphragm and membrane, with the new promising ODC technique. Therefore, the following four scenarios were studied in this work:

- *Scenario 1*. In this case mercury technology feed with KCl waste was considered. This salt source is widely applied in Spain, where 70 % of the sodium chloride used in chlor-alkali plants is obtained by purification of NaCl-containing wastes from the mining of potash (KCl) (Brinkmann et al., 2014). Moreover, a potash waste recycling supposes economic and environmental profits since the extraction of new salt is avoided. This salt was transported 50 km by train from the mine to the plant. Brine was prepared and purified in a close circuit system. Brine, water and electricity are the main inputs of the electrolysis, which operates ata current density of 10 kA/m^2. These are the normal working conditions of the mercury cells. This scenario sets out the most common situation found in the chlor-alkaki sector in the last 25 y.
- *Scenario 2.* This approach considered the same conditions for salt mining and transport and brine preparation. However, an additional purification stage (secondary purification) was included due to the high purity of the brine employed in the membrane technology. The electrolysis was conducted in a bipolar membrane cell with a current density of 5 kA/m^2. The NaOH treatment was integrated by means of a 3 effects evaporation that is the most sustainable alternative.
- *Scenario 3*. Diaphragm usually employs solution mining from rock salt as raw material. Solution mining is pumped 50 km to the open circuit system of the plant. This is one of the main differences in the brine purification system in the studied technologies. In addition, the extraction and pumping of solution mining is high energy-demand process. Finally, the same NaOH treatment conditions that in Scenario 2 were supposed for diaphragm cell.
- *Scenario 4.* The last case study evaluated the ODC technique using vacuum salt as raw material. The same salt transportation conditions and identical brine purification system (close circuit with primary and secondary purification) that in the membrane cell were considered. The operating conditions of the electrolysis were 6 kA/m^2, whereas as in the previous scenarios a 3 effects evaporation was employed for NaOH treatment. Hydrogen is not co-produced and oxygen is required in the electrolysis.

2.2 Allocations

In chlor-alkali process co-production of chlorine, sodium hydroxide and hydrogen, occur. In LCA the existence of several outputs, such as co-products, is known as a multi-output or multifunctional system *(*Margallo et al., 2014b). In these systems allocating material and energy inputs as well as environmental impacts between main product and co-product is a necessary issue (Malakul et al., 2012). According to the LCA methodology, allocation should be avoided by expanding the system to include the additional functions related to the co-products, wherever possible.

Table 1: Data source of the life cycle inventory

Data source	Temporal framework	Geographical representativeness
Brinkman et al., 2014	2008-2012	Europe
O`Brien et al., 2005	2005	Europe
Jung et al., 2014	2014	Europe
UHDE, 2015	2015	Europe
Schmittinger, 2000	2000	Europe
Eurochlor, 2013a	2013	Europe
Eurochlor, 2013b	2013	Europe
Mustafa and Abdullah, 2013	2013	Europe
ANE, 2012	2010	Europe
Westphal et al., 2012	2012	Europe
Goetfried et al., 2012	2012	Europe
NYSDEC, 2015	2015	Europe

System expansion should only be used where there is a dominant, identifiable displaced product, and if there is a dominant, identifiable production path for the displaced. However, in the chlor-alkali electrolysis this rule is not feasible because of the co-production of chlorine, sodium hydroxide, and hydrogen (Eurochlor, 2013a). Therefore, in this case mass allocation was applied to assign the inputs, outputs and environmental impacts to each co-product. Moreover, the comparison of the current technologies and ODC required a system expansion since ODC does not produce hydrogen. The production of hydrogen by means of catalytic reforming was included in the ODC scenario.

2.3 Data collection

The life cycle inventory (LCI) is one of the most effort-consuming steps and consists on the collection and interpretation of the data necessary for the environmental assessment of the observed system (Iannone et al., 2014).

In this study, most of the data were acquired from the BAT Document (or BREF document) for the production of chlor-alkali (Brinkmann et al., 2014). This document included data from 66 facilities in 2010 and 42 plants in 2012. Additionally, several data were obtained from literature or were based on own calculations, whereas secondary data came from PE International database (PE International, 2014). Table 1 gathers the main data sources and the temporal framework and geographical representativeness of the data. All the data were from Europe in order to assure its geographical representativeness, whereas the temporal framework varies from 2000 to 2015. However, most of the data are in the range of 2012-2015.

3. Life cycle impact assessment results

The life cycle impact assessment (LCIA) was conducted with the LCA software GaBi 6.0 (PE International, 2014) and using two main indicators primary energy demand and Global Warming (GW). The latter was based on the potential factors proposed by the Institution of Chemical Engineers (ICheme, 2002). An internal normalization was conducted for both impact categories. This type of normalization also known as case-specific normalization is division by-maximum (Norris, 2001). In particular, the normalized values are obtained by dividing the characterized environmental impacts by a maximum characterized environmental impact of alternatives (Ji and Hong, 2016). Figure 2 shows the dimensionless normalised results of primary energy demand and global warming impact for the scenarios under study.

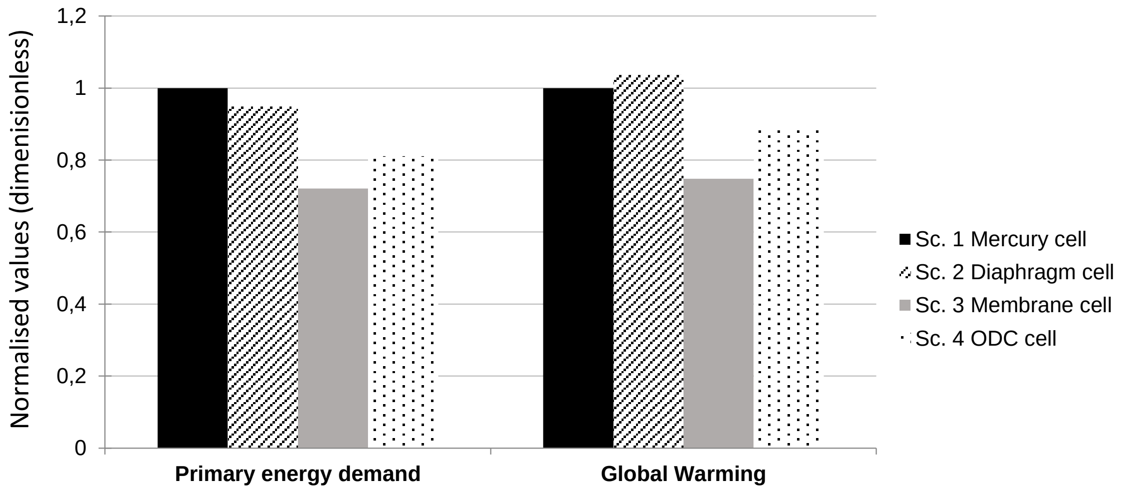

Figure 2: Life cycle impact assessment of Sc. 1 mercury cell; Sc. 2 diaphragm; Sc. 3 membrane cell and Sc.4 ODC technology

Mercury cell (Sc. 1) and diaphragm (Sc.2) presented the highest primary energy demand due to the electrolysis process. The energy demand in the electrolysis system had a contribution of 90 % to the total process. Despite the use of a KCl waste as raw material, the energy demand in the cell is very high in these technologies. On the other hand, membrane (Sc. 3) displayed the lowest consumption of energy. Particularly, a reduction of 28 % and 13 % regarding Sc. 1 and Sc. 2 was obtained with this technology. However, this energy improvement could be reduced with the use of other type of salt, such as vacuum salt and solution mining. The use of the ODC technology (Sc. 4) instead of the mercury cell (Sc. 1) reduced the energy consumption a 19 %. Moreover, as expected, in the electrolysis system bipolar membrane cell had a consumption of energy 1.25 times higher than the ODC technique. Nevertheless, despite the promising improvements of this novel electrolysis technique, the whole energy demand of the ODC process -including salt mining, brine preparation, electrolysis and product treatment- exceeded the energy requirements of the membrane technique. Particularly, the global consumption of energy of the Sc. 4 was 12 % higher than in Sc. 3. This is the result of the additional energy requirements for the production of oxygen and hydrogen.

Therefore, membrane cell with KCl waste as raw material seems the less energy demanding scenario whereas mercury presented the greatest energy demand. Nonetheless, a sensitivity analysis of the salt source should be conducted in a future work to determine its influence in the energy requirements.
Similar results were obtained for GW, with the membrane as the less impactful technology. However, in this case, diaphragm cell (Sc. 2) showed the greatest contribution to GW. Sc. 2 has a lower energy demand in the electrolysis system than Sc. 1, and as consequence a lower GW impact was observed in the cell. Nevertheless, diaphragm has a greater impact in brine preparation and NaOH treatment. The treatment of NaOH in Sc. 2 needs 2,646 kg of steam/FU, whereas in Sc. 1 there are not steam requirements. Regarding brine preparation and purification, Sc. 2 demands a higher amount of chemicals and a greater amount of waste is generated, increasing the impact of the waste transport and landfilling. Particularly, brine preparation in Sc. 2 had a consumption of NaOH 2.15 times greater and the amount of waste was 2.3 times higher.

4. Conclusions

This paper conducted an LCA study from cradle to gate of the chlor-alkali sector in Europe. The novelty of the work was the inclusion of the salt source that was omitted in most of the published works. The electrolysis system is the stage with the highest energy demand and the greatest contribution to GW. Nevertheless, the impacts of salt mining and NaOH treatment were also remarkable. According to the results, mercury and diaphragm are the less environmental sustainable techniques due to the high energy demand. However, a further study will require to include an ecotoxicity metric in order to evaluate the emissions of mercury in the mercury cell.
On the other hand, membrane is the most environmental friendly scenario with a global energy demand lower than the promising ODC. The oxygen requirements and the fact that hydrogen is not co-produced reduce the energy advantages of this novel technology. A sensitivity analysis of the salt source, type of NaOH treatment is required to conduct a more complete study of the four electrolysis techniques.

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