Environmental challenges of the Chlor-Alkali production: seeking answers from a life cycle approach

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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%).

**Keywords:** Life Cycle Assessment, Chlor-Alkali industry, membrane technology, oxygen depolarised cathode technology.
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).
### Table 1 Advantages and drawbacks of electrolytic chlor-alkali technologies. Adapted from Lakshmanan et al. (2014).

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

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 et al., 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 2,500-3,500 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 20kt/y chlorine plant in Leverkusen (Germany) that began operating in 2011 by Bayer/UHDE, and a 70 kt/y installation in Shandong (China) sold by Bayer/UHDE to Befar group that started operation in 2015 (Thyssenkrupp, 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). The methodology employed is the same as described in the APME work (Boustead, 2005b). Salt production and products treatment are included in the study. Life Cycle Impact Assessment (LCIA) results are estimated according to updated characterisation factors of CML (CML, 2012). Economic allocation is also applied in this work. However, results are again shown as average European values, without revealing technologies sharing or stages contribution.

Recent works compared membrane and ODC technologies from a LCA perspective. While Jung et al., (2014) applied the impact assessment method ReCiPe, Käthelhön et al., (2015) assessed the environmental costs and benefits of introducing the emergent technology by studying the relationship between global warming impact and sales volume. Other stages such as brine and products treatments are excluded. The influence of hydrogen co-production is more deeply studied, as it is not produced by ODC technology. Conversely, a more detailed case study of the electrolytic
production of sodium hydroxide in China is presented by Hong et al. (2014). Despite its completeness in the consideration of raw materials extraction such as brine, its representativeness is limited.

As described, the environmental chlor-alkali studies have been focused on the electrolytic stage, neglecting the impact of the up and downstream processes. However, as the energy demand of the electrochemical process is reduced the impact of raw materials extraction and products treatment becomes more significant. Consequently, it is necessary to assess the environmental sustainability of the different current chlor-alkali technologies across the whole life cycle and compare them to the emergent technology. As far as the authors are aware, there are no LCA studies in the literature that develop a comprehensive and integrated assessment where all the life cycle stages are included. On the other hand, results from the different studies are difficult to compare, since different methodologies are applied. In this sense, this work aims to compare the current and emergent chlor-alkali technologies in Europe and the identification of the main stages contributing to the total environmental impacts caused by the whole life cycle of the chlor-alkali process. Results from this study are extrapolated to the global situation provided the regional differences are considered.
2. Methodology

The reported LCA study is carried in accordance with the requirements of the ISO 14040 and ISO 14044 international standards (ISO, 2006a; ISO, 2006b). According to them, LCA should be applied in 4 stages: (a) definition of the goal and scope of the study, (b) LCI; (c) LCIA and (d) interpretation.

2.1 Goal and scope

The main goal of this study is to assess the environmental sustainability of the different alternatives for chlorine production in the chlor-alkali industry and to compare the environmental profiles of the current and emerging technologies in the sector. A further goal is to identify the main stages contributing to the environmental performance of the different technologies (i.e. ‘hot spots’). This will provide the proper framework to evaluate the opportunities of success for emerging technologies integration in the sector.

The scope of the study is from ‘cradle to gate’, which comprises extraction, manufacture and transportation of raw materials to the plant, the chlor-alkali process and the management of the waste generated. Hence, 4 subsystems are considered within the system boundaries: salt mining and transportation, brine preparation and purification, electrolysis process and treatment of products and waste management (Fig. 1). The generation of sodium hypochlorite is not considered in the study as its co-production is often minimised in the process and its environmental impacts are negligible. Construction of major capital equipment and the maintenance and operation of support equipment are excluded from the study as the contribution of infrastructure to the impacts of processes is typically negligible owing to the long lifetimes of industrial installations (Falano et al., 2014).
Fig. 1. System boundaries for the chlor-alkali process
2.2 Functional unit

The functional unit is the quantitative reference for which the inputs and outputs of the process under study are related (ISO, 2006b).

The function of the chlor-alkali process is the combined production of chlorine, caustic soda and hydrogen. The process manufactures in a fixed ratio 1 ton of chlorine, 1.13 ton of caustic soda (sodium hydroxide) and 0.03 ton of hydrogen. This product combination called electrochemical unit (ECU) is considered as functional unit. The reason for this assumption lies in the impossibility of independently control the production of the three products.

This functional unit was previously proposed by Jung et al. (2013), where two different approaches are described for the selection of the functional unit and handling with the multi-functionality issue. These options, further illustrated in Jung et al. (2014), are: (i) expanding the functional unit to include hydrogen production by system expansion in the technologies that do not manufacture hydrogen or (ii) subtracting the additional function of hydrogen production from the systems that deliver this product (i.e. avoided burdens). The former is the approach selected for this work, based on the fact that mercury, diaphragm and membrane cell techniques deliver the so-called ECU and only ODC technology lacks from hydrogen production. The second approach implies the selection of just chlorine and caustic soda production as functional unit and was followed by Kätelhön et al., (2015).

Conversely, 1 kg of chlorine was selected as functional by other studies (Boustead, 2005b; Eurochlor, 2013). In particular, the study of Eurochlor (2013) also reported LCI and LCIA results for the production of 1 kg of sodium hydroxide (in 50 % solution), 1 kg of hydrogen, 1 kg of sodium hypochlorite and the use of 1kg of sodium chloride as average salt mix input to the
participating European chlorine production sites. Further information about how is tackle multi-functionality problem in this work is gathered in section 2.4.

2.3 Description of the systems under study

The chlor-alkali industry produces chlorine, sodium hydroxide and hydrogen simultaneously from the electrolysis of sodium chloride in solution.

The currently commercial technologies that are mercury, diaphragm and membrane cell processes are outlined in scenarios S1-S3, while the ODC emerging technology is illustrated by scenario S4.

Further details are summarised in Table 2 and described as follows:

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Salt Type</th>
<th>Salt Transport</th>
<th>Type of Transport</th>
<th>Brine Circuit</th>
<th>Secondary Purification</th>
<th>Electrolytic Technology</th>
<th>Current Density (KA/m²)</th>
<th>NaOH Concentration</th>
<th>H₂ Valorisation Rate (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Brine</td>
<td>50 km</td>
<td>Pumping</td>
<td>Open</td>
<td>No</td>
<td>Mercury</td>
<td>10</td>
<td>Not required</td>
<td>80 %</td>
</tr>
<tr>
<td>S2</td>
<td>Brine</td>
<td>50 km</td>
<td>Pumping</td>
<td>Open</td>
<td>Yes</td>
<td>Bipolar membrane</td>
<td>5</td>
<td>3 effects</td>
<td>80 %</td>
</tr>
<tr>
<td>S3</td>
<td>Brine</td>
<td>50 km</td>
<td>Pumping</td>
<td>Open</td>
<td>No</td>
<td>Diaphragm</td>
<td>4</td>
<td>3 effects</td>
<td>80 %</td>
</tr>
<tr>
<td>S4</td>
<td>Brine</td>
<td>50 km</td>
<td>Pumping</td>
<td>Open</td>
<td>Yes</td>
<td>ODC</td>
<td>6</td>
<td>3 effects</td>
<td>No H₂ produced</td>
</tr>
</tbody>
</table>

Table 2. Scenarios under study for the chlor-alkali process

(1) NaOH delivered by mercury cell is obtained at 50% concentration, which is enough to be traded as a commodity. Further detail about products quality is provided in Table S5 in the supporting material (SM).

- **Scenario 1 (S1).** This scenario sets out the most common technology found in the chlor-alkali sector up to the end of the 20th century, which is mercury technology. This technique differs from the rest under study in the fact that there is no physical barrier dividing catholyte and anolyte compartments. In this sense, the separation is achieved by means of
the sodium amalgam generated from the reaction of sodium and mercury. Mercury technology employs solution mining from rock salt as raw material. Solution mining is pumped 50 km to the open circuit system of the plant for brine purification. Brine, water and electricity are the main inputs of the electrolysis, which operates at a current density of 10 kA/m\(^2\). These are the normal working conditions of mercury cells. Demercuration of products is considered as well as the treatment of the waste generated.

• **Scenario 2 (S2).** In this case, membrane technology in bipolar configuration is considered. Same conditions for salt mining, transport and brine preparation as in scenario 1 are assumed. However, an additional purification stage (secondary purification) is included due to the high purity requirements of the brine used in the membrane technology. The cell operates under a current density of 5 kA/m\(^2\), which is the normal operation condition (Brinkmann et al., 2014). The NaOH treatment is integrated by means of a 3 effects evaporation that is the most environmentally sustainable alternative.

• **Scenario 3 (S3).** Asbestos-free diaphragm technology is illustrated by this scenario, which is the best available technology for diaphragm cells (Brinkmann et al., 2014). Same conditions for salt mining, transport and brine preparation as in scenario 1 are assumed. This technology operates under a normal current density of 4 kA/m\(^2\). The same NaOH treatment conditions that in Scenario 2 are supposed. However, the composition of the cell liquor is different in membrane and diaphragm scenarios, as the latter is less concentrated in NaOH and more concentrated in NaCl (see Table S4 in the SM). During evaporation, most of the salt precipitates. This salt is very pure and is generally employed for brine
preparation. This fact was considered in the modelling of diaphragm scenario, through the recovery of solid salt and condensates from the concentration step (see Fig. S1c of the SM).

- Scenario 4 (S4). The last case study evaluated is ODC technique. It is an emerging technology whose difference regarding membrane technology lies in the utilisation of oxygen-depolarised cathodes instead of hydrogen evolution materials. As a consequence, pure oxygen is required as raw material in the electrolysis and hydrogen is not co-produced. Same conditions for salt mining, transport and brine preparation than in the membrane cell are considered (S2). The operating conditions of the electrolysis are 6 kA/m², whereas in the previous scenarios a 3 effects evaporation is employed for NaOH treatment.

More details on the description of the systems under study are available in section S1 of the supporting material (SM), where the flow diagrams of the scenarios under study are outlined.

2.4 Allocation procedures

Production processes in chemical industry are often multioutput or multifunctional systems, which means that several valuable products and co-products are generated. According to LCA methodology, allocation procedure should be avoided by expanding the system to include the additional functions related to co-products, wherever it is possible. That is the subtraction from the system under study of the environmental impacts of the alternative system to produce the same amount of co-product. However, 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 product. When system expansion is not feasible, allocation can be applied, which is the partitioning and distribution of the inputs and outputs of the multiproduct process over its co-
products (Weidema, 2001). That is the case of the chlor-alkali process, where chlorine, sodium hydroxide and hydrogen are co-produced (Eurochlor, 2013).

Since the functional unit was defined as the combined production of chlorine, sodium hydroxide and hydrogen allocations rules are not applied. However, the sensitivity analysis includes mass and economic allocation procedures in order to assign the environmental impacts to each co-product. In this sense, differences between applying or not applying allocation can be assessed.

On the other hand, the current technologies and ODC technique cannot be directly compared, since ODC does not produce hydrogen which could otherwise be used in chemical reactions or to produce steam and electricity via combustion or fuel cells. Then, a system expansion is considered to compare the current technologies to the emergent technique. Steam reforming of natural gas has been chosen because more than 80% of the hydrogen produced as primary product (not as by product) is produced using this process (Jung et al., 2013; Käthlön et al., 2015).
2.5 Life Cycle Inventory

The relevant input and output data for the assessed systems are collected in a LCI (Iribarren et al., 2010). The inventory data were divided into the 4 subsystems shown in Fig. 1. Detailed inventories per subsystem, as well as the data sources are available in the SM (Tables S1-S5).

Most of the primary data for this study are sourced from the Best Available Techniques Document for the production of chlor-alkali (Brinkmann et al., 2014) and Eurochlor (2013), while secondary data came from PE International database (2014). Regarding ODC, since there are no LCI data available yet, data for this work have been sourced from the supplier UHDE (2015), previous work in the field (Jung et al., 2014) and combined with membrane data when no ODC specific information was available.

2.6 Life Cycle Impact Assessment

The Life Cycle Impact Assessment (LCIA) translates the inventory data to a reduced number of environmental indicators, which lead to the identification of hot-spots and aids in the definition of environmental improvement actions (Lozano et al., 2009). LCIA involves two mandatory (i.e. classification and characterisation) and two optional steps (i.e. normalisation and weighting). LCIA results are obtained by modelling the chlor-alkali process by means of the software GaBi 6.0. The methodology proposed in this work was developed by Margallo et al. (2014) and includes the 4 LCIA steps.

First, in the classification step, the inventory data are grouped by impact categories according to the substances’ potential to contribute to the different environmental impacts (Lo et al., 2005). Then, the impact of each emission or resource consumption is modelled quantitatively using a
characterisation factor (CF), which expresses the substance potential impact (Bare, 2010). Two main variables are proposed to conduct the environmental sustainability assessment: natural resources consumption (NR) and environmental burdens (EB), providing a broad overview of the environmental performance of the process.

NR includes the consumption of energy ($X_{1,1}$), materials ($X_{1,2}$) and water ($X_{1,3}$) for the considered process, while the EBs include the primary burdens to the environmental compartments: air ($X_{2,1}$), water ($X_{2,2}$) and land ($X_{2,3}$). These indicators are based on the environmental sustainability metrics developed by the Institution of Chemical Engineers (IChemE, 2002). In particular, the EBs are classified in 12 impact categories and distributed into each environmental compartment as outlined in Table 5. Environmental burdens to air are described by atmospheric acidification (AA), global warming (GW), human health (carcinogenic) effects (HHE), stratospheric ozone depletion (SOD), photochemical ozone (smog) formation (POF). The impact categories studied for the water compartment are aquatic acidification (AqA), aquatic oxygen demand (AOD), ecotoxicity to aquatic life (metals to seawater) (MEco), ecotoxicity to aquatic life (other substances) (NMEco) and eutrophication (EU). Finally, EB to land are given by the amount of generated hazardous and non-hazardous waste and its management. These environmental impact categories are a subset of the international set employed in environmental management to focus in the areas where the activities of industrial processes are more significant (Margallo et al., 2014).

LCA results attached to environmental impact categories are usually expressed in different and complex units. Normalisation offers a reference situation of the pressure on the environment for each impact category and enables the results adjustment to have common dimensions (Sleeswijk et al., 2008). Internal and external normalisation procedures can be distinguished. The former is
considered as a prerequisite to weighting and is conducted by dividing the results in each category by the maximum value obtained in that category (Norris, 2001). Conversely, external normalisation aims at assessing the relative significance of results across categories. For this purpose, scores in each category are divided by an estimation of the total impacts in that category for a chosen system or region over a chosen period of time.

The consumption of NR \((X_i)\) varies from plant to plant. Hence, to understand if the consumption of a plant is acceptable and to compare each plant, a valid reference should be used (Margallo et al., 2014). In this sense, the average weighted consumption of European plants according to its level of implementation in 2014 (23% mercury, 62% membrane, 15% diaphragm) is selected as reference value for internal normalisation \((X_{\text{ref},i})\) (Eurochlor, 2015). On the other hand, the EBs indicators present different units depending on the impact category considered. To compare them within the same basis, the threshold values stated in the European Pollutant Release and Transfer Register (E-PRTR, 2006) regulation are considered for external normalisation (see Table S6 in the SM), leading to normalised values \((X_{2,j,k}^*)\) (Irabien et al., 2009). The threshold values of these pollutants can be used as an important support in the normalisation process because they provide an overview of the environmental performance of the installation at a European level (Margallo et al., 2014). Therefore, NR and EB dimensionless variables are estimated according to Eq. (1) and (2):

\[
X_{1,i}^* = \frac{X_{1,i}}{X_{\text{ref},1}} \quad \text{Eq. (1)}
\]

\[
X_{2,j,k}^* = \frac{X_{2,j,k}}{X_{\text{ref},2,j,k}} \quad \text{Eq. (2)}
\]
Where \( i \) represents the different NR indicators (energy, materials and water), \( j \) designates each environmental compartment (air, water and land) and \( k \) describes the environmental impacts to the corresponding compartment.

In the subsequent step, the normalised variables pass through a weighting procedure. Weighting ranks impact categories according to their relative importance (EC JCR, 2010) and provides a composite indicator by subjecting the impact categories to mathematical combination (Molinos-Senante et al., 2014). The 3 normalised NR (\( X_{1,i}^* \)) and the 12 normalised EB variables (\( X_{2,j,k}^* \)) are aggregated according to Eq. (3) and Eq. (4) to obtain the NR dimensionless index (\( X_1 \)) and the EB dimensionless indexes to air (\( X_{2,1} \)), water (\( X_{2,2} \)) and land (\( X_{2,3} \)):

\[
X_1 = \sum_{i=1}^{\text{n}} \alpha_{1,i} X_{1,i}^* \quad n \in [2,3] \quad \text{Eq. (3)}
\]

\[
X_{2,j} = \sum_{j=1}^{\text{m}} \beta_{2,j,k} X_{2,j,k}^* \quad m \in [1,2] \quad \text{Eq. (4)}
\]

Where \( \alpha_{1,i} \) is the weighting factor for energy materials and water variables; \( \beta_{2,j,k} \) is the weighting factor for EB. Specifically, it is considered that the three NRs are equally relevant, thus \( \alpha_{1,i} = \frac{1}{3} \) for each \( i \). This is assumed because it is the clearest way to obtain a single index that allows a comparison across several systems (Margallo et al., 2014).
3. Results and discussion

3.1 Natural resources

NR enables the relative comparison in terms of final resources utilisation, including energy, materials and water. The consumption of energy ($X_{1,1}$), materials ($X_{1,2}$) and water ($X_{1,3}$) in the four subsystems under study (i.e. salt mining, brine preparation, technologies and products treatment) is studied. Table 3 shows the normalised results regarding the European weighted average. It can be appreciated that the consumption of natural resources for mercury (S1) and diaphragm (S3) technologies is over the European average, which also represent the worst scenarios. Conversely, membrane (S2) and ODC (S4) technologies, are below this reference values.

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>European average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>1.10</td>
<td>0.79</td>
<td>1.03</td>
<td>0.73</td>
<td>1.00</td>
</tr>
<tr>
<td>Materials</td>
<td>1.17</td>
<td>0.91</td>
<td>1.04</td>
<td>0.92</td>
<td>1.00</td>
</tr>
<tr>
<td>Water</td>
<td>1.15</td>
<td>0.80</td>
<td>0.97</td>
<td>0.69</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.14</strong></td>
<td><strong>0.83</strong></td>
<td><strong>1.015</strong></td>
<td><strong>0.78</strong></td>
<td><strong>1.00</strong></td>
</tr>
</tbody>
</table>

**Fig. 2.** NR dimensionless values for the main stages of the process: solution mining, brine preparation, electrolysis and treatment. Oxygen and hydrogen processes are included for ODC technology S1: mercury technology, S2: membrane technology, S3: diaphragm technology, S4: ODC technology.
As displayed in Fig. 2, this is mainly due to the electrochemical reaction, which is the main hot spot of the process. It is the most energy intensive stage and this is further reflected in the consumption of materials and water for primary energy production. A more detailed description for each resource usage is provided below.

- **energy ($X_{1,1}$).** It includes the consumption of electricity, steam, diesel and natural gas. The four scenarios agree that the electrolytic process is the main contributor to this metric, ranging from 99 to 80%. S1 is the most energy intensive scenario, followed by S3. However, it must be highlighted that despite using the best available technology, S4 represents only a 7% reduction with regard to S2. The main reason of this unexpected slight reduction lies in the fact that S4 considers the additional consumption of energy sources for oxygen and hydrogen production. The former is required as raw material and the latter is given by the system expansion procedure for comparison purposes to the rest of scenarios. For scenario S3, NaOH treatment is the second main hot-spot of the process. The reason of this lies in the lower quality of NaOH product delivered by diaphragm technology, which results in higher purification requirements.

- **materials ($X_{1,2}$).** The consumption of salt as main raw material and reactants required for solution mining, brine preparation and treatment of hydrogen, NaOH and oxygen for ODC are considered in this variable. Reactants included sodium carbonate, NaOH 25%, HCl 25% and activated carbon. The consumption of materials related to the transformation of primary energy is the main hot spot in these metrics, although its contribution is lower than in $X_{1,1}$ and $X_{1,3}$. Conversely to $X_{1,1}$ results, the consumption of materials for S4 is higher than for S2, owing to the requirements of pure oxygen for ODC technology. The solution mining step contributes around 20% to the total consumption of materials, reflecting the salt requirements for the
This contribution is lower for diaphragm technology (5%), since some of the salt is recovered in the NaOH treatment process and reused for brine preparation.

- **water (X\textsubscript{i,8}).** This variable includes the consumption of water for the electrolytic process, sodium hydroxide solution and other stages. Primary energy transformation is essentially the main contributor to this variable, ranging from 98% for S1 to 95% for S4. The contribution of other stages are negligible, except the production of oxygen in S4, which accounts for nearly 7%.

Although NR metrics address resources depletion through quantifying their consumption, they do not explicitly deal with the impact of natural resources scarcity. In this sense, the Abiotic Depletion Potential (ADP) impact category is added to this study. This metric is extracted from the baseline characterisation method recommended in the Dutch LCA handbook (Guinée et al., 2002), which is the current best available practice for this impact category. ADP reflects the depletion of natural resources, including energy resources and is subdivided into two different indicators: ADP\textsubscript{elements} and ADP\textsubscript{fossil}. The former describes the loss of natural elements availability and considers factors such as the ultimate reserve available, the resources that are potentially available given technique and economic constraints and the current available reserves. It is measured in kg of equivalent depleted antimony. ADP\textsubscript{fossil} represents the loss of energy availability and its characterization factors are based on net calorific values at the point of extraction of the fossil fuels.

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADP\textsubscript{elements} Kg Sb-eq.</td>
<td>1.38·10\textsuperscript{-3}</td>
<td>1.10·10\textsuperscript{-3}</td>
<td>1.25·10\textsuperscript{-3}</td>
<td>1.01·10\textsuperscript{-3}</td>
</tr>
<tr>
<td>ADP\textsubscript{fossil} MJ</td>
<td>3.81·10\textsuperscript{4}</td>
<td>2.88·10\textsuperscript{4}</td>
<td>4.08·10\textsuperscript{4}</td>
<td>3.05·10\textsuperscript{4}</td>
</tr>
</tbody>
</table>
As can be seen in Table 4, both ADP\textsubscript{elements} and ADP\textsubscript{fossil} are related to the depletion of natural resources for energy production. According to ADP\textsubscript{elements}, S1 is the scenario most unsustainable for resources availability due to the depletion of copper, gold and lead for electricity production. The use of natural gas for steam production is the main contributor to ADP\textsubscript{fossil}, where S3 shows the highest score due to the NaOH concentration step.
3.2 Environmental burdens

Environmental burdens to air, water and land are summarised in Table 5. The three main stages contributing to the environmental impacts are outlined: salt production, electrolysis reaction and NaOH concentration.

EB to air are directly related to energy consumption. In this sense, the electricity grid mix selected, which depends on the geographical location of the technology, may have a significant influence on the quantity of greenhouse gas emissions and consequent results. In this sense, the Spanish grid mix is employed for all the scenarios.

As previously assessed, S4 obtained the lowest scores for this set of metrics, followed by S2. Conversely, S1 resulted the worst scenario for the majority of categories considered. This is due to the fact that the most energy intensive stage is the electrolytic process, which accounts for more than 95% in every EB to air. This contribution is lower for scenario S4 in POF category, due to the assumed production of hydrogen. Followed far behind the electrolytic stage, the NaOH treatment process is the second main hot spot for scenario S3. This is due to energy requirements of diaphragm technology to meet NaOH standard quality.
Table 5. Environmental burdens for scenarios S1, S2, S3, and S4. Electrolysis, salt production, and NaOH treatment stages are shown.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Electrolysis</td>
<td>Salt</td>
</tr>
<tr>
<td>AA (X_{2,1})</td>
<td>10^7 kg SO_2 eq · t^-1 ECU</td>
<td>754.3</td>
<td>12.4</td>
<td>2.1·10^-7</td>
</tr>
<tr>
<td>GW (X_{2,2})</td>
<td>10^7 kg CO_2 eq · t^-1 ECU</td>
<td>297.8</td>
<td>9.5</td>
<td>2.5·10^-3</td>
</tr>
<tr>
<td>HHE (X_{2,3})</td>
<td>10^7 kg Benzene eq · t^-1 ECU</td>
<td>248.5</td>
<td>2.1</td>
<td>1.7·10^-4</td>
</tr>
<tr>
<td>POF (X_{2,4})</td>
<td>10^7 kg C_2H_4 eq · t^-1 ECU</td>
<td>107.2</td>
<td>7.0</td>
<td>6.3·10^-4</td>
</tr>
<tr>
<td>SOD (X_{2,5})</td>
<td>10^8 kg CFC_11 eq · t^-1 ECU</td>
<td>133.7</td>
<td>0.7</td>
<td>9.5·10^-6</td>
</tr>
<tr>
<td>AOD (X_{2,6})</td>
<td>10^7 kg O_2 eq · t^-1 ECU</td>
<td>515.9</td>
<td>54.8</td>
<td>0.012</td>
</tr>
<tr>
<td>AqA (X_{2,7})</td>
<td>10^6 kg H^+ eq · t^-1 ECU</td>
<td>83.0</td>
<td>176.4</td>
<td>1.6·10^-4</td>
</tr>
<tr>
<td>MeCO (X_{2,8})</td>
<td>10^7 kg Cu eq · t^-1 ECU</td>
<td>234.1</td>
<td>5.0</td>
<td>1.9·10^-7</td>
</tr>
<tr>
<td>NMMeCO (X_{2,9})</td>
<td>10^7 kg CH_2O. eq · t^-1 ECU</td>
<td>774.8</td>
<td>16.3</td>
<td>6.2·10^-3</td>
</tr>
<tr>
<td>EU (X_{2,10})</td>
<td>10^7 kg PO_4 eq · t^-1 ECU</td>
<td>558.4</td>
<td>17.4</td>
<td>8.3·10^-3</td>
</tr>
<tr>
<td>HW (X_{2,11})</td>
<td>kg HW · t^-1 ECU</td>
<td>0.037</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>HNW (X_{2,12})</td>
<td>kg HNW · t^-1 ECU</td>
<td>0.0</td>
<td>49.70</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Atmospheric acidification (AA), global warming (GW) and human health effects (HHE) are the most important categories owing to the emissions of sulphur dioxide, greenhouse gases (CO$_2$, CO, NO$_x$, CH$_4$) and organic emissions to air (dioxins and formaldehyde) and heavy metals (As) in the generation of energy, respectively.

Regarding EB to water, the electrolytic step represents again the major contributor to the environmental impacts. The depleted brine leaving the electrochemical cell, which contained mainly chloride and chlorate, became an effluent. Those emissions are included in non-metallic ecotoxicity to aquatic life. However, a negligible impact is attributed to them in comparison to energy consumption. Aquatic oxygen demand (AOD) and eutrophication (EU) are the most relevant categories for water compartment.

The effluent that would be produced if the sulfuric acid is not valorised, would have an important impact in AA category. In this work, a system expansion is conducted to include 60% sulfuric acid as raw material, avoiding the consumption of fresh concentrated sulfuric acid (98%). In practice, this acid is valorised in every industrial plant for pH treatment or it is sold to acid consumers, such as aluminium sulphate producers.

It must be remarked that the impact of mercury emissions from S1 is not reflected in either EB to air or water compartments. First, this is due to the fact that IChemE metrics do not include mercury emissions in air impact categories. Regarding water indicators, it is just considered its impact in MeCO category as an emissions to seawater. However, the system modelled in this study considered the emission of mercury to freshwater.

Given the relevance of mercury in this work, a review of the available metrics in GaBi 6.0 is conducted. Only USEtox indicators consider this metal (USEtox, 2010). The USEtox model is an
environmental model for characterisation of human and ecotoxicological impacts in LCIA, developed under a UNEP-SETAC initiative (Hauschild et al., 2008; Rosenbaum et al., 2008). USEtox is designed to describe the fate, exposure and effects of chemicals. In contrast to other impact categories such as GW, the impact categories in USEtox do not use a reference substance. Instead, the characterisation factors are expressed in terms of comparative toxic units (CTU) per kg of emission. Human effect factors relate the quantity taken into the potential risk of cancerous and non-cancerous effects expressing cases per kg of chemical emitted (CTUh). Effect factors for freshwater ecosystems are based on species-specific data of concentration at which 50% of a population displays an effect, expressed as an estimate of the potentially affected fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted (PAF m$^3$-day·kg$^{-1}$). The final unit is comparative toxic units (CTUe).

| Table 6. USEtox metrics for scenarios under study. Characterisation factors update to February 2010. |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| USEtox, Ecotoxicity (recommended)               | CTUe            | 91.5            | 58.0            | 72.0            |
| USEtox, Human toxicity, cancer (recommended)   | 10$^{-6}$ CTUh  | 4.43            | 0.38            | 0.49            |
| USEtox, Human toxicity, non-canc. (recommended)| 10$^{-4}$ CTUh  | 5.20            | 0.40            | 0.49            |

As can be shown in Table 6, results from the ecotoxicity indicator are strongly related to the consumption of energy, not being so obvious the impact of the technology under study. Conversely, the impact of mercury emissions is clearly reflected in human effects metrics. In this sense, scenario S1 shows values 10 times higher for human effects toxicity in comparison to the rest of electrolytic technologies.

In addition to the consideration of mercury metal, some other differences have been found between USEtox and IChemE characterisation models. HHE includes the carcinogenic effects on human
health of emissions to air, while USEtox Human toxicity also considers emissions to water and land. Regarding halogenated organic emissions to air, HHE includes a characterization factor for unspecified dioxins (in addition to PCBs), which are the main contributor to this impact category, whereas USEtox does not consider the emission of unspecified dioxins. Among inorganic emissions to air, USEtox Human toxicity (cancer) do not account for antimony or cobalt, although its observed contribution in HHE is negligible with regard to arsenic. These metals are considered in Human toxicity (non-cancer) instead. Finally, it must be highlighted that IChemE metrics do not consider air and land ecotoxicity, which represents on average a 30% of the USEtox ecotoxicity impacts in the systems under study. Characterisation factors for MEco and NMEco are described for emissions to sea water, while the majority of ecotoxicity impacts in the water compartment are due to emissions to fresh water according to USEtox. For these reasons, using IChemE metrics in combination to USEtox characterisation model is a good choice to describe the toxicity impacts of a system.

Regarding EB to land, hazardous and non-hazardous wastes are reported. The majority of solid wastes are generated in the primary brine treatment stage. This waste stream is non-hazardous in every scenario under study. Hazardous wastes are produced in S1, as a result of hydrogen and NaOH treatment for mercury removal. To a lesser extent, they are also obtained from the mercury electrochemical cell due to the mercury content in the muds.
Table 7 displays the normalised results using the threshold values of the E-PRTR regulation. EBs to air, water and land for the scenarios under study are compared to the European average. After normalisation, POF and HHE became the most relevant categories among air metrics. Regarding EB to water, the most important category became EU, followed by MeCO and NMeCO. It must be highlighted that EB to air (X\textsubscript{2,1}) in S1 emerges as the most significant EB category after normalisation procedure due to POF impact category. As a result, S1 is the less environmentally sustainable scenario, which represents mercury technology. The second less sustainable scenario is S3, represented by diaphragm technology, which presents a 7% lower X\textsubscript{2} than S1. Finally, the best scenarios are S2 and S4, being ODC technology a 9% more environmentally friendly than
membrane technology. NR and EB values for the scenarios under study are summarised and compared in Fig. 3.

**Fig. 3. NR and EB dimensionless variables for scenarios S1, S2, S3 and S4.**
3.3 Sensitivity analysis

3.3.1 Hydrogen valorisation alternatives

The aim of this analysis is to study the environmental impact of the different hydrogen management alternatives in membrane technology. Four scenarios are considered for this assessment. Base case is represented by S2, where 80% valorisation of hydrogen is assumed. Three alternative scenarios are considered:

- **S2-elect.** This scenario comprises the valorisation of hydrogen through electricity production in fuel cells. A 50% efficiency is considered for the fuel cell. Moreover, the system is modelled assuming an electricity production of 20 kWh per kg of hydrogen. The avoided burdens associated to electricity production are assumed to partially compensate the energy consumption of the electrolytic cell.

- **S2-fuel.** The replacement of natural gas by hydrogen as fuel source is considered in this scenario. Hydrogen is a clean fuel that does not generate either carbon dioxide or other greenhouse gas emissions. The high heating values of both fuels are taken into consideration for assessing the replacement rate of natural gas by hydrogen. This value is estimated at 3.2 kg of natural gas per kg of hydrogen. Furthermore, 58 kg CO₂/GJ is taken as reference value for combustion emissions.

- **S2-non_value.** This scenario describes the total emission of hydrogen to the atmosphere. None valorisation technique is assumed for this scenario.

The results for the scenarios described are shown in Fig. 4. As can be observed, the most efficient and environmentally sustainable scenario is S2-elect, which describes the use of H₂ for electricity production. As this valorisation option is directly related to energy consumption, all NR and EB
are expected to decrease in such scenario. In this sense, environmental impacts are reduced around 19%.

After S2-elect, S2-fuel became the best performing scenario. Improvements are observed for EB to air and energy consumption. However, the environmental impacts are diminished to a lesser extent than in S2-elect case (2%). This reduction is larger for GW category owing to the avoided CO$_2$ emissions generated in the combustion of natural gas. EB to land is not affected by the sensitivity analysis and thus it has been removed from Fig. 4.

**Fig. 4.** NR and EB dimensionless variables for scenarios S2, S2-elect, S2-fuel and S2-non_value.
3.3.2 The influence of the current density

The objective of this sensitivity analysis is to assess the influence of the current density (KA/m\(^2\)) in the chlor-alkali process. This variable is strongly related to the electricity requirements of the process and then it is expected to present a significant influence in the LCA study.

Three different scenarios are compared for this purpose. Scenario S2 is taken as base case. In such scenario, a current density of 5 KA/m\(^2\) is considered. The current density of the base case is modified to conduct the sensitivity analysis. Current densities in bipolar membrane cell range from 1.4 to 6.5 kA/m\(^2\), while the average minimum and maximum values are 2.9 and 5.4 kA/m\(^2\), respectively (Brinkmann et al., 2014). Then, the values of 4 and 6 KA/m\(^2\) are considered suitable for describing the two additional scenarios.

The environmental results are shown in Fig. 5, comprising the dimensionless NR and EB values. The current density is one of the most important factors that influences the specific energy consumption of the electrolytic process. It plays a key role in the development of new plants at the design stage. The lower the current density it is, the lesser is the electricity consumption at the expense of higher investment costs.

The results obtained evidence once again the significant contribution of the electricity consumption in the chlor-alkali process. A directly proportional relationship is observed between the current applied and the NR and EB variables. Only EB to land is not affected by this parameter, as waste generation is related to salt and brine treatment. EB to land is again not modified by this alternative and has been eliminated from the comparison.
3.3.3 *The influence of the allocation method*

The Society of Environmental Toxicology and Chemistry (SETAC) strongly recommend LCA practitioners to base the allocation procedure on physic-chemical considerations (Lundie et al., 2007). ISO guidelines (ISO, 2006a) propose a preferred sequence of different approaches according to its feasibility. This order of preference is based on, avoiding allocation by dividing the system in sub-processes or expanding the system to include the additional functions wherever it is possible. Where allocation cannot be avoided, environmental impacts should be distributed according to physical criteria, such as mass or energetic content. Finally, other criteria such as economic value can be applied (Chen et al., 2010).

As previously described, the functional unit of this work is comprised of 1 ton of chlorine, 1.128 tons of sodium hydroxide (100%) and 28.5 kg of hydrogen. The production of 50% NaOH solution is considered for the 4 scenarios under study and then the generation of 2.256 tons of 50% NaOH. Hydrogen is excluded from the mass allocation analysis applying a cut rule, as its production is
below 1% of the total production. Table 8 outlines the results obtained for the different scenarios according to mass allocation. As can be observed, the contribution of sodium hydroxide is estimated at 70% and the rest is allocated to chlorine (30%).

Table 8. Dimensionless EB results for the chlor-alkali scenarios according to mass allocation procedure.

<table>
<thead>
<tr>
<th></th>
<th>Scale</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine allocation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EB to air (X_{2,1})</td>
<td>10^{-4}</td>
<td>4.45</td>
<td>3.19</td>
<td>4.24</td>
<td>2.68</td>
</tr>
<tr>
<td>EB to water (X_{2,2})</td>
<td>10^{-6}</td>
<td>5.53</td>
<td>3.81</td>
<td>4.68</td>
<td>3.14</td>
</tr>
<tr>
<td>EB to land (X_{2,3})</td>
<td>10^{-5}</td>
<td>22.02</td>
<td>5.28</td>
<td>8.23</td>
<td>5.28</td>
</tr>
<tr>
<td>X_2</td>
<td>10^{-4}</td>
<td><strong>6.71</strong></td>
<td><strong>3.76</strong></td>
<td><strong>5.11</strong></td>
<td><strong>3.24</strong></td>
</tr>
</tbody>
</table>

| Sodium hydroxide allocation |       |       |       |       |       |
| EB to air (X_{2,1}) | 10^{-4}| 10.03 | 7.21  | 9.57  | 6.05  |
| EB to water (X_{2,2}) | 10^{-6}| 12.48 | 8.60  | 10.56 | 7.09  |
| EB to land (X_{2,3}) | 10^{-5}| 49.69 | 11.92 | 18.57 | 11.92 |
| X_2                 | 10^{-4}| **15.13** | **8.49** | **11.54** | **7.31** |

Conversely, economic allocation is based on market prices of the manufactured products, which often are cyclic and volatile. This allocation procedure is a significant source of controversy that has been considered inadequate to manage the environmental dimensions of activities (Pelletier and Tyedmers, 2010). Despite its limitations, economic allocation can be useful to discuss the effect of market demand in hydrogen production and the impact of hydrogen economy evolution in ODC implementation.

Prices for the 2006-2011 period are considered in this work (Table 9). The production of hydrogen gains importance in this analysis owing to its higher market price than chlorine and sodium hydroxide. This allocation method presents a significant uncertainty for chlorine and sodium hydroxide. Economic allocation factors are displayed in Table 9. As was observed in the mass allocation procedure, around 70% of the environmental impacts are attributed to sodium hydroxide. The contribution of chlorine becomes lower (23%), as opposed to hydrogen allocation.
factor (7%) that increases significantly due to its higher market value. Results from economic allocation are displayed in Table 10.

Table 9. Economic allocation factors for the chlor-alkali sector.

<table>
<thead>
<tr>
<th>Production (kg)</th>
<th>Price (€/kg)</th>
<th>Profit (€)</th>
<th>Economic allocation factor(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>1</td>
<td>0.165</td>
<td>0.165</td>
</tr>
<tr>
<td>Sodium hydroxide (50%)</td>
<td>2.256</td>
<td>0.224</td>
<td>0.505</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0285</td>
<td>1.697</td>
<td>0.048</td>
</tr>
<tr>
<td>Total</td>
<td>3.2845</td>
<td>0.719</td>
<td>1.000</td>
</tr>
</tbody>
</table>

(1) The economic allocation factors are slightly different for S4 since hydrogen is not co-produced. In such case, 0.246 and 0.754 are used for chlorine and sodium hydroxide, respectively.

As can be inferred from the comparison to mass allocation, the production of chlorine is less penalised when price-based information is included in the analysis, due to its higher demand and lower market price.

All the scenarios under study did not produce the three described products. That is the case of S4, as it does not produce hydrogen. Thus, environmental impacts in S4 are assigned to chlorine and sodium hydroxide according to the factors described in Table 9 footnote. In this case, the contribution of sodium hydroxide according to its market value is higher (75%) than when mass allocation is applied. This methodology highlights the environmental impacts related to chlorine and sodium hydroxide, which results from the lack of hydrogen production in the emergent technology (ODC). Furthermore, the value of hydrogen can vary not just as a result of market prices, but also as a consequence of the valorisation alternative considered. For example, the prices of natural gas and electricity may have a significant influence if its use as fuel or its use for electricity production in fuel cells are considered, respectively.
Table 10. Dimensionless EB results for the chlor-alkali scenarios according to economic allocation procedure.

<table>
<thead>
<tr>
<th></th>
<th>Scale</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorine allocation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EB to air ($X_{2,1}^*$)</td>
<td>$10^{-4}$</td>
<td>3.32</td>
<td>2.39</td>
<td>3.17</td>
<td>2.15</td>
</tr>
<tr>
<td>EB to water ($X_{2,2}^*$)</td>
<td>$10^{-6}$</td>
<td>4.13</td>
<td>2.85</td>
<td>3.50</td>
<td>2.52</td>
</tr>
<tr>
<td>EB to land ($X_{2,3}^*$)</td>
<td>$10^{-5}$</td>
<td>16.44</td>
<td>3.94</td>
<td>6.15</td>
<td>4.23</td>
</tr>
<tr>
<td>$X_2$</td>
<td>$10^{-4}$</td>
<td>5.01</td>
<td>2.81</td>
<td>3.82</td>
<td>2.59</td>
</tr>
<tr>
<td><strong>Sodium hydroxide allocation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EB to air ($X_{2,1}^*$)</td>
<td>$10^{-4}$</td>
<td>10.19</td>
<td>7.32</td>
<td>9.72</td>
<td>6.58</td>
</tr>
<tr>
<td>EB to water ($X_{2,2}^*$)</td>
<td>$10^{-6}$</td>
<td>12.67</td>
<td>8.73</td>
<td>10.72</td>
<td>7.72</td>
</tr>
<tr>
<td>EB to land ($X_{2,3}^*$)</td>
<td>$10^{-5}$</td>
<td>50.45</td>
<td>12.10</td>
<td>18.85</td>
<td>12.97</td>
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<tr>
<td>$X_2$</td>
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<td>15.36</td>
<td>8.62</td>
<td>11.71</td>
<td>7.96</td>
</tr>
<tr>
<td><strong>Hydrogen allocation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EB to air ($X_{2,1}^*$)</td>
<td>$10^{-4}$</td>
<td>0.97</td>
<td>0.70</td>
<td>0.93</td>
<td>0.00</td>
</tr>
<tr>
<td>EB to water ($X_{2,2}^*$)</td>
<td>$10^{-6}$</td>
<td>1.21</td>
<td>0.83</td>
<td>1.02</td>
<td>0.00</td>
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<tr>
<td>EB to land ($X_{2,3}^*$)</td>
<td>$10^{-5}$</td>
<td>0.48</td>
<td>0.12</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>$X_2$</td>
<td>$10^{-4}$</td>
<td>1.47</td>
<td>0.82</td>
<td>1.12</td>
<td>0.00</td>
</tr>
</tbody>
</table>
4. Conclusions

The assessment of the life cycle environmental impacts of the chlor-alkali sector in Europe reveal that the main variable contributing to the usage of resources and environmental burdens generated by the process is the energy consumption. Regarding the different stages involved in the chlor-alkali process, the main responsible of the environmental impact is the electrolytic process, followed far behind by salt production and sodium hydroxide afterwards.

The results suggest that mercury scenario is the less environmentally sustainable, owing mainly to the mercury related environmental burdens and, to a lesser extent, to its electric energy consumption.

The outcomes of this study conclude that the most environmentally sustainable technology currently implemented in Europe is the membrane technology. The operation conditions and the technology used for sodium hydroxide concentration involve a reduction in energy consumption close to 30% with regard to mercury technology. Conversely, scenarios represented by diaphragm technology are strongly penalised by the significant amount of thermal energy required for NaOH treatment.

Hydrogen valorisation as fuel or through its use for electricity production involves a reduction of the environmental burdens in every system under study, being the latter the most beneficial option.

Current density is identified as one of the most significant variables affecting the LCA results. This is mainly due to its direct relationship with the electricity consumption and thus with the intensity in environmental resources usage and environmental burdens generated. Moreover, one of the technological objectives of this sector is achieving higher current densities to maximise the
installation capacity. Hence, current density is a crucial parameter to study as it could change the future environmental profile of the process.

Mass and economic allocation procedures remark that sodium hydroxide is responsible for around 54% of the environmental impacts, although the contribution for the latter can vary as a result of the fluctuations in the circumstantial chlorine/NaOH pairing price.

The emergent technology based on oxygen-depolarised cathodes (ODC) presents improvements regarding the energy consumption. However, the reduction in the energy demand is lower than described in the literature. When a system expansion is conducted to include the lacking hydrogen production and the oxygen requirements are also included as well, the reduction in energy consumption for ODC technology is lower than expected. This decrease with regard to membrane technology is just 7%, when the available references reported 25% reductions.

The upcoming trends in the sector in terms of environmental sustainability will be the conversion of monopolar technology in bipolar and the use of ODC technology. The latter is likely to represent the emergent technology under development, although its medium-term industrial set-up is not expected. After a strong industrial reconversion for mercury technology replacement, the sector will require a firm support to assume the energy intensification related investments. This effort will directly affect the competitiveness of the European chlor-alkali sector and should be encouraged by the development of politic and financial tools.

Taking into account that technological trends in the chlor-alkali sector, such as membranes operating at higher density currents and higher salt quality requirements, the raw material extraction and preparation should be studied in order to identify the most sustainable option.
Future prospects are addressed to the need of an optimised sustainability assessment that integrates environmental and economic-energetic variables into a single global index, which provides the suitable framework for decision-making process. Furthermore, it is necessary the introduction of the social dimension with the aim of completing the three pillars of sustainability. To ensure the life cycle sustainability of the chlor-alkali industry, it is necessary a strategic plan involving all the sector stake-holder. In the European context, both the European Commission and the Member States, should intensify the research and development support in collaboration with the installations and knowledge institutions, leading the future of this industry.

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