1 **Connecting wastes to resources for clean technologies in the chlor-alkali industry: a life cycle**
2 **approach**

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7

8 **Abstract**

9 Our current economic model is experiencing increasing demand and increasing pressure on resource
10 utilisation, as valuable materials are lost as waste. Moving towards a circular economy and supporting
11 efficient resource utilisation is essential for protecting the environment. The chlor-alkali industry is one of
12 the largest consumers of salt, and efforts have been made to reduce its electricity use. Furthermore, KCl
13 mining wastes have received increasing attention because they can be transformed into value-added
14 resources. This work studies the influence of using different salt sources on the environmental sustainability
15 of the chlor-alkali industry to identify further improvement opportunities. Rock salt, solar salt, KCl waste
16 salt, vacuum salt and solution-mined salt were studied. Membrane cells in both bipolar and monopolar
17 configurations were studied and compared to the emergent oxygen-depolarised cathode (ODC) technology.
18 Life cycle assessment (LCA) was applied to estimate the cradle-to-gate environmental impacts. The natural
19 resource (NR) requirements and the environmental burdens (EBs) to the air and water environments were
20 assessed. The total NR and EB requirements were reduced by 20% when vacuum salt was replaced with
21 KCl. Moreover, the environmental impacts estimated for the monopolar membrane using KCl were
22 comparable to those generated for the bipolar membrane using VS. The difference between the monopolar
23 and bipolar scenarios (17%) was slightly higher than that between the bipolar and ODC technologies (12%).
24 This work demonstrates the importance of studying every life cycle stage in a chemical process and the
25 environmental benefit of applying a circular economy, even in energy intensive industries such as the chlor-
26 alkali industry.

27

33 **1. Introduction**
34
35 The development of sustainable and competitive processes is currently transitioning the economy away
36 from the traditional "take, make and dispose" linear model to a circular model (EC, 2014). This circular

model is the cornerstone of the circular economy strategy adopted by the European Commission to help European businesses and consumers transition towards more sustainable resource use (EC, 2015). The circular economy concept involves a production and consumption system that minimises material and energy losses through extensive reuse, recycling and recovery, and this concept is gaining popularity in Europe and elsewhere (EEA, 2014; MacArthur et al., 2015). A circular economy contributes to "closing the loop" of product life cycles, providing both economic and environmental benefits (Huysman et al., 2015). In particular, in a circular economy, materials are recovered from products at the end of the product's life cycle, connecting wastes to resources (Fig. 1). To effectively make such changes, resource efficiency within processes must be improved by establishing new uses for existing technologies, implementing new advanced processes, enhancing end of life (EOL) waste management, increasing recycling towards achieving zero-waste processes and promoting cradle-to-cradle recycling. These changes will not only provide European industries with a competitive advantage but also reduce their dependency on foreign sources for raw materials (SPIRE, 2013). These principles originate from life cycle thinking, which states that to reduce the environmental impacts of an economic system, the whole life cycle of the activity—from the extraction of raw materials ('cradle') to the return of wastes to the ground ('grave')—must be considered. This framework is defined by the ISO 14040 series of life cycle assessment (LCA) standards (2006a; 2006b) and has been documented in the literature since the 1990s (Azapagic & Clift, 1999; Dennison et al., 1998).

The chlor-alkali industry, which accounts for approximately 55% of the European chemical industry, has a high resource demand (Brinkmann et al., 2014). This industry produces chlorine together with sodium hydroxide and hydrogen through the electrolysis of NaCl solution in water (i.e., brine) (Lakshmanan et al., 2014). Currently, the industrial electrolytic production of chlorine using salt as a raw material is conducted using mercury cells, diaphragms or membranes. These techniques have been modified over the years to satisfy environmental policies and market demand. Although the prevalent technology for many years, the mercury cell technique has been greatly affected by the mercury emission reduction policies. The European Commission stated that this technique must be phased out by December 2017; therefore, current mercury cell installations are being converted or decommissioned (EC, 2013). The diaphragm technology has also been subjected to regulation due to its use of asbestos fibres (EC, 2006).

As a result, the membrane cell technique has been labelled the best available technology (BAT) by the European Commission (Brinkmann et al., 2014). Currently, more than 60% of the total European capacity uses this technique. Despite its reduced electricity use, the membrane cell technique still has an issue with high energy consumption, which has important environmental impacts (Di et al., 2007; IPPC, 2007; Weisser, 2007).

A promising approach for reducing the electricity consumption of chlor-alkali electrolysis is to replace the hydrogen evolution cathode with an oxygen-depolarised cathode (ODC) (Moussallem et al., 2012). This technique lowers the cell voltage by approximately 1 V using industrial current densities (e.g., 4 kA/m^2), reducing the electricity consumption by 30% (Kiros & Bursell, 2008). Despite reducing the environmental impacts associated with electricity generation, this method does not necessarily result in cleaner chlorine production as some energy is required to produce pure oxygen. In addition, the ODC technique does not

1 coproduce hydrogen, which could otherwise be used in chemical reactions or to produce steam and

2 electricity via combustion or fuel cells.

3 The chlor-alkali industry is one of the largest consumers of salt, and efforts have been made to reduce its

4 electricity use. This industry consumes over 250 million tons of salt, which is nearly 60% of global salt

5 production (IGME, 2013). Chlorine mainly exists in the environment as sodium chloride (NaCl), or

6 ordinary table salt, which constitutes approximately 3.7% of seawater (Ayres, 1997). In addition to

7 seawater, sodium chloride can be sourced from different types of deposits, such as mineral halite, or in

8 solution (Westphal et al., 2010). Distinct salt types can be defined according to the source: (i) rock salt is

9 recovered through traditional mining from underground deposits, (ii) brine is produced by forcing water

10 into underground deposits of rock salt, (iii) vacuum salt is produced by purifying and evaporating either

11 brine or dissolved rock salt, and (iv) solar salt is obtained during the solar evaporation of seawater in large

12 ponds (Eurochlor, 2013). In addition to these sources, purified NaCl-containing wastes from KCl mining

13 are receiving increasing attention. This NaCl source is an example of a circular economy since it enables

14 the transformation of wastes into a value-added resource. In fact, 70% of the salt employed in Spain for

15 chlorine production is sourced from the purification of this potash mining waste (Brinkmann et al., 2014).

16 Although NaCl is the main component of common salt, other impurities are always present; $CaSO_4$ and

17 $MgSO_4$ are the most abundant. These impurities in salt are costly because they dissolve in water along with

18 NaCl and need to be removed. For example, an excess of magnesium causes hydrogen evolution on the

19 anode, leading to an explosive mixture of hydrogen and chlorine and the subsequent release of poisonous

20 chlorine gas to the environment (Sedivy, 2009). Therefore, as the compositions of salt from different

21 sources vary widely, the preparation method is determined by the quality requirements of each technology.

22 Concerning the use of water resources, the preparation of brine is a water-intensive stage in chlor-alkali

23 systems. Brine preparation can be conducted in closed circuits, where the depleted brine from the

24 electrolysis cell is resaturated with solid salt and fed back to the cell, or in once-through systems, where the

25 depleted brine becomes an effluent after electrolysis (Brinkmann et al., 2014). Recirculation circuits can

26 reduce wastewater generation from 11 to 2 tonnes of water per ton of chlorine produced. Once-through

27 systems are typically employed using solution-mined salt because the system balance can be controlled

28 only by direct discharging. This configuration is mostly used in plants located close to seawater, where

29 pollutant emissions are less restricted.

30 Since electrolytic technologies can reduce energy consumption, the impacts of other stages, such as raw

31 material extraction and production, become more significant (Garcia-Herrero et al., 2017). To assess the

32 opportunities for integrating this novel technique into the chlor-alkali industry, the processing requirements

33 of the cell itself must be considered in addition to the electricity requirements. The technical improvements

34 also constrain the raw material requirements and, in particular, the salt sources used.

35 LCA is a suitable tool for estimating and quantifying the environmental impacts of the whole life cycle of

36 a process, and this method has already been used to assess the environmental sustainability of chlor-alkali

37 processes (Boustead, 2005a; Boustead, 2005b; Eurochlor, 2013, Jung et al., 2013; Jung et al., 2014;

38 Kätelhön et al., 2015). However, these studies often excluded salt production and purification or neglected

its contribution. A more detailed literature review is available in a previous study (Garcia-Herrero et al., 2017). Hong et al. (2014) also conducted a more detailed analysis and assessed every life cycle stage, including salt extraction by well drilling. Despite its limited representation, the results from that study suggested the importance of considering the salt mining and preparation stages. The purpose of this paper is to assess the influence of using different salt sources on the environmental sustainability of the chlor-alkali industry and to identify opportunities for further improving the process development. This paper is divided into two parts: (i) the LCA of different salt sources used in the chlor-alkali industry (rock salt, solar salt, vacuum salt, solution-mined salt and KCl waste salt), including brine preparation (once-through or closed circuit) and waste management and (ii) the LCA of the chlor-alkali process when applying the circular economy concept to the salt source to compare membrane technology (bipolar and monopolar electrolysers) with the emergent ODC technology. As far as the authors are aware, this is the first LCA study of the chlor-alkali industry that models the different salt sources, analyses the best available and emergent technologies and includes circular economy principles along the supply chain.

2. Methodology

This study followed the ISO 14040/44 guidelines (2006a; 2006b). According to these guidelines, the LCA methodology consists of 4 stages: (i) definition of the goal and scope of the study, (ii) life cycle inventory (LCI) analysis, (iii) life cycle impact assessment (LCIA) and (iv) interpretation of the results.

2.1 Goal and scope

The first goal of this study is to assess the influence of using different salt sources on the environmental sustainability of the chlor-alkali industry. Rock salt, solar salt, vacuum salt, solution-mined salt and KCl waste salt are studied for this purpose. As mentioned previously, this study focuses on KCl waste salt as an example of the circular economy concept. The second goal of this study is to identify opportunities for further improving process development. Membrane cells, labelled the BAT, and ODC, depicted as the emerging technology, are therefore explored in this work.

The scope of this study is from cradle to gate, and the system boundaries are outlined in Fig. 2. The construction and maintenance of major equipment are excluded because the impacts from infrastructure are typically negligible when compared to the impacts of processes due to the long lifetimes of industrial plants (Garcia-Herrero et al., 2016).

Functional unit

Chlor-alkali technologies typically produce a fixed ratio of 1 ton of chlorine to 1.1 tons of caustic soda (sodium hydroxide) and 28.5 kg of hydrogen. This is the typical ratio achieved using mercury cells, diaphragms and membranes. Since this study aims to first compare the different salt sources for membrane technology, the mixed ton is selected as the functional unit. The second part of this study compares membrane and ODC technologies using the most environmentally friendly salt source. Since ODC lacks hydrogen coproduction, an allocation procedure (described in the allocation section) was applied to this system to compare the same functions in both technologies.

1   System description

2   This study considers 4 subsystems for describing the chlor-alkali process: salt extraction, brine preparation,

3   electrolysis and products treatment (Fig. 2). Regarding salt extraction, rock salt, solar salt, vacuum salt and

4   solution-mined salt are the most common salt sources. Rock salt is obtained by mechanically mining

5   underground deposits. Solar salt is produced by the solar evaporation of seawater. Vacuum salt is

6   manufactured by purifying and concentrating dissolved rock salt, for which mechanical vapour

7   recompression (MVR) or multiple effect (ME) evaporation can be employed. To be used as feedstock, the

8   solid salts are dissolved in water and purified. A primary purification system is required for impurities

9   precipitation. Once-through or closed configurations are possible. Further purification is conducted in an

10   ion exchange unit for brine softening.

11   The purified brine is subjected to electrolysis. Typically, the electrolysis of sodium chloride in solution

12   produces chlorine at the anode, while sodium hydroxide and hydrogen are delivered to the cathode.

13   However, using ODCs instead of hydrogen evolution materials modifies the global cell reactions (Garcia-

14   Herrero et al., 2017): pure oxygen is additionally required, and hydrogen is not coproduced. Membrane

15   cells can be operated in both monopolar and bipolar configurations. Regarding products treatment, chlorine

16   is dried using concentrated sulphuric acid (98%). After this process, an effluent containing sulphuric acid

17   diluted to 60% is obtained. NaOH is concentrated to the commercial 50% purity using 3-effect evaporators.

18   Hydrogen is obtained with a high quality (>99.9%). More details on the description of these subsystems

19   are available in sections S1-S4 of the supporting material.

20

21   Studied scenarios

22   According to the first goal of this study, the abovementioned salt sources are assessed. For comparison, the

23   same electrolytic technology is assumed for this first assessment. Bipolar membrane electrolysers are

24   selected as the base case for the following reasons: (i) membrane technology is labelled the BAT, (ii) bipolar

25   cells require lower energy consumption and operating costs than monopolar electrolysers, and (iii)

26   monopolar electrolysers have been commercialised since only 2011 to maintain existing plants and for new

27   small-capacity plants (Brinkmann et al., 2014). The most representative configurations are selected for the

28   brine system. Membrane cell plants usually operate with brine recirculation, although solution mining often

29   uses once-through systems. Therefore, 6 scenarios are defined (Table 1): BM-RS, BM-SS, BM-KW, BM-

30   VSR, BM-VSE and BM-SM, which describe the combination of bipolar membrane electrolyser and rock

31   salt, solar salt, KCl waste salt, vacuum salt using MVR evaporation, vacuum salt using ME evaporation

32   and solution mining, respectively. Finally, according to the second goal of this work, 2 additional scenarios

33   are studied: MM-KW and ODC-KW, which represent the monopolar membrane and ODC techniques,

34   respectively. The same salt source (KCl waste) is assumed for these final two scenarios to allow comparison

35   to BM-KW.

36

1   Table 1 Descriptions of the studied scenarios.

Scenario	BM-RS	BM-SS	BM-KW	BM-VSR	BM-VSE	BM-SM	MM-KW	ODC-KW
Salt type	Rock salt	Solar salt	KCl waste	Vacuum salt using MVR or ME		Solution mining	KCl waste	
Brine circuit	Closed	Closed	Closed	Closed		Once-through	Closed	
Electrolytic technology	Bipolar membrane						Monopolar membrane	ODC

2

3   *Allocations*

4   The chlor-alkali process is a multioutput or multifunctional system since several added-value products and

5   coproducts are obtained. As previously described, chlorine, sodium hydroxide and hydrogen are

6   simultaneously produced in the membrane cell, and this combined production is selected as the functional

7   unit.

8   However, the emerging ODC technology does not coproduce hydrogen, which could otherwise be

9   valorised. According to ISO 14044 (2006b), the allocation procedure must be avoided where possible, and

10   multifunctional problems should instead be handled using system expansion. Consequently, for comparison

11   with the membrane scenarios, the system boundaries in the ODC technology are expanded to include the

12   additional function of hydrogen production through catalytic reforming.

13   In contrast, a 60% sulphuric acid effluent is obtained when treating the chlorine systems. System expansion

14   is assumed again to consider the consumption of this acid as a raw material for another process. Then, the

15   environmental impacts related to this effluent are subtracted from the systems.

16

17   **2.2 Life cycle inventory and main assumptions**

18   A life cycle inventory (LCI) quantifies all the relevant energy, materials and water requirements as well as

19   air, water and land emissions for the entire life cycle of a product, process, or activity (Coventry et al.,

20   2016). The primary data were collected from some specific plants, bibliographic data and mass balances.

21   Most of the primary data for this study were obtained from the BAT reference document for the production

22   of chlor-alkali (Brinkmann et al., 2014). Background data, such as the energy production processes, tap

23   water production and waste management processes, were collected from the PE International database (PE

24   International, 2014).

25   The inventory data are given in Tables 3-6. Table 3 shows the data for the extraction of the different salt

26   types. Since rock salt mining involves no chemical reactions and minimal processing requirements, it is

27   assumed that only energy is required for its extraction (Goetfried et al., 2012). For solar salt, the electricity

28   consumption data for the different pumps, conveyors and machines were taken from a West Australia plant

29   and assumed to be comparable to those of plants in the Mediterranean area. Salt washing and thermal salt

30   drying are not considered (Goetfried et al., 2012). The quantity of sea bittern (i.e., dense residual liquor

31   obtained after the precipitation and harvesting of NaCl salt) and solid wastes were estimated using the

32   method from Mustafa and Abdullah (2013) and Baseggio (1974). The LCI data for KCl waste were sourced

from the Spanish National Association of Electrochemistry (ANE, 2010). The system was credited for using another process waste, so zero burdens were assumed for the raw material production. Only the electricity used for KCl waste purification is considered in this scenario. Due to the lack of data for vacuum salt production, the cumulative energy demand reported by Goetfried et al. (2012) is taken as an approximation of the energy requirements. Steam for ME evaporation is assumed to be produced from natural gas at an efficiency of 90%. The energy requirements for the production of solution-mined salt are estimated considering both the energy consumed during solution mining and the energy requirements for transportation to the chlor-alkali plant. An 85% pump efficiency is assumed. Solid wastes are estimated as a function of the impurities entering the system. The calcium and magnesium precipitation are assumed to form $CaCO_3$, $Mg(OH)_2$ and $CaSO_4$.

Table 2 LCI data for salt extraction

	Rock salt	Solar salt	KCl waste salt	Vacuum salt	Solution-mined salt	Units
Inputs						
Salt (% NaCl)	1.85 (96)	111.93[1] (2.68)	-	1.73 (96)	1.65 (100)	t·t ECU^{-1}
KCl waste	-	-	2.31 (86.71)	-	-	t·t ECU^{-1}
Electricity	360.75	123.76	244.44	4126.76[2] /3730.02[3]	56.69	MJ·t ECU^{-1}
Water	-	-	0.78	0.40	5.23	m^3·t ECU^{-1}
NaOH	-	-	-	2.49	-	kg·t ECU^{-1}
Na$_2$CO$_3$	-	-	-	2.16	-	kg·t ECU^{-1}
Outputs						
Salt (% NaCl)	1.85 (96)	1.82 (98)	1.94 (91.11)	1.66 (99.97)	6.6[4] (25)	t·t ECU^{-1}
Solid waste	-	149.42	232.80	26.71	-	kg·t ECU^{-1}
CaSO$_4$	-	100	61.7	55	-	%
CaCO$_3$	-	-	11.7	36.4	-	%
Mg(OH)$_2$	-	-	9.1	8.6	-	%
Insoluble	-	-	17.5	-	-	%
Effluent (% Chloride)	-	5.46 (19)	0.78 (24)	5.20 (25)	-	m^3·t ECU^{-1}

[1]Seawater consumption.
[2]Electricity requirements for MVR evaporation.
[3]Steam consumption for ME evaporation. Process steam production from natural gas with a 90% efficiency is assumed.
[4]Expressed as solution mined brine.

Table 3 LCI data for brine preparation

	Rock salt	Solar salt	KCl waste salt	Vacuum salt	Solution-mined salt	Units
Inputs						
Salt (% NaCl)	1.85 (96)	1.82 (98)	1.94 (91.11)	1.66 (99.97)	14.28 (25)	$t \cdot t\ ECU^{-1}$
Steam	292	292	292	292	292	$kg \cdot t\ ECU^{-1}$
Water	0.22	0.21	0.22	0.06	0.13	$m^3 \cdot t\ ECU^{-1}$
NaOH	2.78	2.72	2.9	-	5.35	$kg \cdot t\ ECU^{-1}$
Na_2CO_3	12	12	12	-	12	$kg \cdot t\ ECU^{-1}$
HCl	28	28	28	28	28	
Outputs						
Brine	6.6	6.6	6.6	6.6	14.3	$t \cdot t\ ECU^{-1}$
Solid waste	23.2	21.2	20.1	0.46	45.9	$kg \cdot t\ ECU^{-1}$
$CaSO_4$	33.9	36.4	34.3	63.63	-	%
$CaCO_3$	44.7	42.8	31.36	36	92	%
$Mg(OH)_2$	21.4	20.8	11.7	0.37	8	%
Insoluble	-	-	22.64	-	-	%
Effluent (% Chloride)	0.81 (17)	0.79 (17)	0.32 (17)	0.06 (17)	11.07 (17)	$m^3 \cdot t\ ECU^{-1}$

Table 4 LCI data for the electrolysis technologies

	Bipolar membrane (BM)					Monopolar membrane (MM)	ODC	
	Rock salt	Solar salt	KCl waste salt	Vacuum salt	Solution-mined salt	KCl waste salt	KCl waste salt	Units
Inputs								
Salt	1.85	1.82	1.94	1.66	1.65	1.94	1.94	$t \cdot t\ ECU^{-1}$
Electricity	20.41	20.41	20.41	20.41	20.41	25.02	16.13	$GJ \cdot t\ ECU^{-1}$
Water	2.02	2.04	1.95	1.57	1.51	1.95	1.95	$m^3 \cdot t\ ECU^{-1}$
Oxygen	-	-	-	-	-	-	0.25	$t \cdot t\ ECU^{-1}$
Outputs								
Chlorine (% w/w)	1 (91.36)	1 (91.36)	1 (91.36)	1 (91.36)	1 (91.36)	1 (91.36)	1 (91.36)	$t \cdot t\ ECU^{-1}$
NaOH (% w/w)	1.13 (33)	1.13 (33)	1.13 (33)	1.13 (33)	1.13 (33)	1.13 (33)	1.13 (33)	$t \cdot t\ ECU^{-1}$
Hydrogen (% w/w)	0.03 (99.99)	0.03 (99.99)	0.03 (99.99)	0.03 (99.99)	0.03 (99.99)	0.03 (99.99)	0	$t \cdot t\ ECU^{-1}$
Chlorine to water	1.9	1.9	1.9	1.9	1.9	1.9	1.9	$g \cdot t\ ECU^{-1}$
Chlorate to water	1750	1750	1750	1750	1750	1750	1750	$g \cdot t\ ECU^{-1}$
Bromate to water	0.18	0.18	0.18	0.18	0.18	0.18	0.18	$g \cdot t\ ECU^{-1}$
Chlorine to air	7.5	7.5	7.5	7.5	7.5	7.5	7.5	$g \cdot t\ ECU^{-1}$

1   Table 5 LCI data for the product treatment

	Membrane[1]	ODC	Units
Inputs			
Chlorine (% w/w)	1 (91.36)	1 (91.41)	t·t ECU^{-1}
NaOH (% w/w)	1.13 (33)	1.13 (33)	t·t ECU^{-1}
Hydrogen (% w/w)	0.03 (99.99)	0	MJ·t ECU^{-1}
Steam	518	518	kg·t ECU^{-1}
H$_2$SO$_4$ (98%)	23	23	kg·t ECU^{-1}
Outputs			
Chlorine (% w/w)	1 (98.6)	1 (98.7)	t·t ECU^{-1}
NaOH (% w/w)	1.13 (50)	1.13 (50)	t·t ECU^{-1}
Hydrogen (% w/w)	0.03 (99.99)	0	MJ·t ECU^{-1}
H$_2$SO$_4$ (60%) effluent	28	28	kg·t ECU^{-1}

2   [1]Valid for bipolar and monopolar electrolysers with every type of salt

3

4   The LCI data for the brine preparation are outlined in Table 4. The driving force for the brine circulation is

5   excluded using a steel rule since its contribution is less than 5% of the total energy consumption. Feed flows

6   of 12 and 20 m^3 per functional unit are assumed for the once-through and closed systems, respectively. The

7   same assumptions are made for the solid wastes as in the vacuum salt scenario.

8   The inventory of the electrochemical subsystem is described in Table 5. The electricity requirements for

9   the bipolar and monopolar membranes as well as for the ODC were estimated as a function of the current

10   density and were assumed to be 5 and 6 kA/m^2, respectively, based on the reported data (Brinkmann et al.,

11   2014) and the supplier's recommendations (UHDE, 2015). Concerning the product generation, 33% NaOH

12   production was assumed in both the membrane and ODC techniques (Table 6). Further details for the

13   electrolysis and product treatment can be found in a previous work (Garcia-Herrero et al., 2017).

14   The electricity for all processes was assumed to be sourced from the Spanish electricity grid, and all the

15   relevant transport processes are included. Since the European production of salt accounts for approximately

16   20% of worldwide production, an average distance of 50 km is assumed from the salt production site to the

17   chlor-alkali plant. Although large distances are not representative within European installations, this

18   situation is often observed in other regions. All types of salt (excluding solution-mined salt) are assumed

19   to be transported to the plant by train, while solution-mined brine is pumped.

20

21   **2.3 Life cycle impact assessment**

22   LCIA quantifies the potential for environmental impacts over all stages in the delivery of a product or

23   service (Bare, 2010). LCIA is performed using the LCA software GaBi 6 (PE International, 2014), and the

24   environmental sustainability assessment (ESA) methodology developed by Irabien et al. (2009) is used.

25   Two sustainability metrics are considered: natural resources (NRs) and environmental burden (EB). The

26   former considers the consumption of NRs, integrating energy ($X_{1,1}$), materials ($X_{1,2}$) and water ($X_{1,3}$). The

27   EB metric is composed of 10 impact categories that represent the EBs to the air ($X_{2,1}$) and water ($X_{2,2}$). The

28   EB to air considers the following impact categories: atmospheric acidification (AA), global warming (GW),

29   human health (carcinogenic) effects (HHE), photochemical ozone formation (POF) and stratospheric ozone

1 depletion (SOD). The EB to water is described by aquatic acidification (AqA), aquatic oxygen demand

2 (AOD), ecotoxicity to aquatic life (metals to seawater) (MEco), ecotoxicity to aquatic life (other substances)

3 (NMEco) and eutrophication (EU). These metrics are based on those proposed by the Institute of Chemical

4 Engineers and computed using the potency factors established by this institution (IChemE, 2002). These

5 metrics provide a balanced view of the environmental impacts of the inputs (resource usage) and outputs

6 (emissions, effluents and waste) (Garcia et al., 2013). The NRs are internally normalised (Eq. 1), while the

7 EBs are normalised using the threshold values of the European Pollutant Release and Transfer Register (E-

8 PRTR, 2006) (Eq. 2).

9 $$X_{1,i}^* = X_{1,i} \ / \ X_{1,i}^{ref} \tag{1}$$

10 $$X_{2,j,k}^* = X_{2,j,k} \ / \ X_{2,j,k}^{ref} \tag{2}$$

11

12 where i represents the consumption of energy, materials, and water; j represents air and water environments;

13 k represents the environmental impacts to air and water; $X_{1,i}$ is the consumption of the ith NR; $X_{1,i}^*$ is the

14 normalised value of $X_{1,i}$; $X_{1,i}^{ref}$ is the NR taken as a reference value; $X_{2,j,k}$ is the EB to air and water; $X_{2,j,k}^*$

15 is the normalised value of $X_{2,j,k}$; and $X_{2,j,k}^{ref}$ is the reference value for EB normalisation.

16 Next, the normalised indicators are subjected to a weighting procedure, as described in Eqs. 3 and 4.

17

18 $$X_1 = \sum_{i=1}^{i=n} \alpha_{1,i} X_{1,i}^* \qquad n \in [1,3] \tag{3}$$

19 $$X_{2,j} = \sum_{k=1}^{k=m} \beta_{2,j,k} X_{2,j,k}^* \qquad m \in [1,2] \tag{4}$$

20

21 where X_1 is the NR index that includes the energy, materials and water consumption; $\alpha_{1,i}$ is the weighting

22 factor for the materials and water variables; $X_{2,j}$ represents the EB indexes for air and water; $\alpha_{1,1}$ is the

23 weighting factor for the energy variable; and $\beta_{2,j,k}$ is the weighting factor for the EB (Margallo et al., 2014).

24

25 **3   Results and discussion**

26 As mentioned in the Goal and Scope section, the focus of this study is the salt source. Therefore, the

27 different salt alternatives are first assessed and compared assuming bipolar membrane technology. After

28 determining the most environmentally sustainable salt source, other technological options are explored

29 from cradle to gate. All the results presented in this section (Figs. 3-6 and Table 7) were obtained using

30 GaBi software.

31 **3.1 Comparison of the different salt sources for bipolar membrane technology**

32 **3.1.1   Natural resources**

33 Each of the different salt sources are considered for bipolar membrane technology. The environmental

34 results of the salt extraction and brine preparation subsystems are shown in Figs. 3 and 4. In Fig. 3, the

35 vacuum salt scenarios show the highest average NR demand due to the electricity (BM-MVR) and steam

(BM-ME) evaporation requirements for vacuum production, which account for nearly 90% of the total resource consumption. The second highest resource demand is for the secondary treatment, which is dominated by the steam consumption for ion-exchange regeneration. In particular, BM-VSR involves nearly twice as much energy (13084 MJ·t ECU^{-1}) and 5 times as much water (349 t·t ECU^{-1}) than BM-VSE, mainly due to the higher amount of resources required for electricity production than for steam production. The difference is less pronounced when comparing the material consumption (16%), since both scenarios use rock salt as the raw material.

Regarding the energy indicators, the solar salt (1916 MJ·t ECU^{-1}) and solution-mined salt (1949 MJ·t ECU^{-1}) are the least energy intensive scenarios. Notably, when vacuum salt is excluded from the analysis, secondary treatment is the main contributor to energy consumption, accounting for nearly half of the total energy use. The other half of the energy requirement is shared between salt mining (25%) and primary treatment (24%). The salt mining contribution is higher in the rock salt scenario due to the electricity and fuel requirements during its extraction.

The material consumption is significantly influenced by the energy consumption. Salt extraction is the main contributor to material consumption, followed by secondary treatment, due to the primary energy transformation during material consumption. BM-SM is the worst performing scenario in this category after vacuum salt. This result is due to the higher requirements for brine production in solution-mined brine since, unlike the other salt sources, it delivers only 25% salt content after salt mining. In contrast, BM-SS (795 kg) and BM-KW (872 kg) are the best scenarios. Kl waste salt benefits from the assumption of zero burdens, which reflects the use of a raw material from the waste of another process. Thus, the materials accounted for during salt extraction are related to the transformation of primary energy. The contribution of primary treatment ranges from 62 kg (BM-VS) to 315 kg (BM-SS). This step accounts for the reactants (Na_2CO_3, NaOH and HCl) required for impurity precipitation and pH adjustment and thus depends on the quality of the salt obtained after mining.

The water consumption is the largest for BM-SS, not BM-VSE (when BM-VSR is excluded). This result is mainly due to the high quantity of seawater consumed during solar salt production. BM-SM, closely followed by BM-KW, is the best scenario for this indicator, and the use of HCl and NaOH during primary treatment are the main contributors.

The contribution of transport and waste management to NR consumption is negligible.

3.1.2 Environmental burdens

As observed in the NR assessment, BM-VSR again exhibits the worst environmental performance for every EB category. This scenario releases an average of 5.6 times more pollutants than the other scenarios, mainly due to its electricity requirements for vacuum production. The exception is the high contribution of the AOD during primary treatment of the other salt sources, which is mainly due to the emission of methanol from Na_2CO_3 production to freshwater. The impact of this step is nearly negligible for vacuum salt since the main precipitation process is conducted before evaporation. The EBs of BM-VSR are approximately

1   3.5 times greater than that of BM-VSE. This difference is much smaller for GWP (1.25 times) due to the

2   CO_2 and NO_x emissions from steam and electricity production.

3   Although no scenario scores better than the others in every impact category, BM-SS and BM-KW are the

4   most environmentally sustainable options for most categories. The difference between both scenarios is on

5   average less than 1%. An exception is SOD, for which BM-SM is the best scenario due to the lower energy

6   requirements of salt mining.

7   The environmental impacts of the BM-SM scenario are lower than or similar to those of BM-SS and BM-

8   KW for the AA, HHE, AOD, MeCO and NMeCO categories. This result is mainly due to the low EBs of

9   salt extraction in BM-SM. However, more brine is treated in the once-through systems than in the closed

10   systems; thus, the reactant requirements and solid waste generation are the largest for BM-SM. Therefore,

11   BM-SM is the worst scenario for the AqA category, mostly due to the solid waste generated. This effect is

12   also observed in POF and, to a larger extent, in GW and EU.

13   The extraction of rock salt (361 MJ·t ECU^{-1}) is the most energy intensive salt mining process after vacuum

14   salt (4127 MJ·t ECU^{-1}). Consequently, BM-RS is the second worst scenario. A larger content of soluble

15   impurities (4%) was assumed in the rock salt than in the other salt sources. Hence, the impacts of waste

16   generation are higher in BM-RS than in the other closed-circuit alternatives.

17   Salt extraction is the main stage contributing to the EBs in this first assessment (Fig. 4). On average, salt

18   extraction is responsible for 35% of the process impacts when the first two subsystems are considered.

19   Hence, the environmental impacts of this stage should not be neglected when assessing the environmental

20   sustainability of a chlor-alkali process. This contribution is higher in the air-impact categories, such as AA,

21   HHE and SOD, due to the emission of SO_2 and halogenates during electricity generation. The second largest

22   contributor is the primary brine treatment (31%) due to the use of Na_2CO_3 and HCl. A lower contribution

23   (15%) is observed for secondary treatment and waste management (16%). Although the contribution from

24   transportation is on average 2% for the assumed distance (50 km), this contribution could reach 20% of the

25   total impact for distances of 500 km, according to Goetfried et al. (2012).

26   Following the normalisation and weighting procedure described in Eqs. 1-4, the X_1 and X_2 indexes were

27   estimated. Table 7 displays the dimensionless values for every scenario, showing the contributions of the

28   EB to air ($X_{2,1}$) and water ($X_{2,2}$) to the final X_2 index. Colour coding is used to facilitate comparison. Lower

29   impacts are marked in green, while higher impacts are highlighted in red. Although BM-VSR clearly

30   presents the worst environmental performance, a single scenario did not score the best for every index. For

31   example, BM-KW presents the lowest NR demand (X_1), followed by the 33% more intensive SS scenario.

32   However, BM-SS, closely followed by BM-KW, emerges as the best performing scenario for the EB (X_2).

33   Since the difference in X_2 between both scenarios is small (7%) and the decision is clear when only X_1 is

34   assessed, BM_KW is considered to be the best scenario.

35

Table 6 Dimensionless NRs (X_1) and EBs (X_2) of the salt extraction and brine preparation (subsystems 1 & 2) for the scenarios under study.

	BM-RS	BM-SS	BM-KW	BM-VSR	BM-VSE	BM-SM
X_1	0.31	0.25	0.17	1.00	0.57	0.38
$X_{2,1}$	$7.47 \cdot 10^{-5}$	$6.13 \cdot 10^{-5}$	$6.58 \cdot 10^{-5}$	$2.64 \cdot 10^{-5}$	$1.60 \cdot 10^{-4}$	$8.84 \cdot 10^{-5}$
$X_{2,2}$	$5.60 \cdot 10^{-7}$	$4.15 \cdot 10^{-7}$	$4.85 \cdot 10^{-7}$	$2.90 \cdot 10^{-6}$	$6.28 \cdot 10^{-7}$	$5.05 \cdot 10^{-7}$
X_2	$7.52 \cdot 10^{-5}$	$6.17 \cdot 10^{-5}$	$6.63 \cdot 10^{-5}$	$2.67 \cdot 10^{-4}$	$1.60 \cdot 10^{-4}$	$8.89 \cdot 10^{-5}$

3.2 Circular economy applied to the chlor-alkali process

KCl mining wastes were estimated to be the most sustainable source of salt for the chlor-alkali process, while vacuum salt produced using the MVR technique showed the worst environmental performance. Bipolar membrane technology, which has been labelled the BAT, was used for this assessment. This section focuses on electrolytic technology and explores other alternatives using KCl wastes as the salt source. Based on their design, monopolar and bipolar electrolysers can be distinguished within membrane technology. Monopolar configurations present higher ohmic losses, which involve increased electricity consumption. The results obtained for both configurations are compared to the emerging ODC technology in Fig. 5. These results include the electrolysis and product treatment subsystems that were excluded in the previous analysis. Once again, the bipolar membrane using vacuum salt (BM-VSR) was used as a reference for NR internal normalisation and is represented as a horizontal line (Fig. 5a). Moreover, the EBs of BM-VSR are indicated by the grey region in Fig. 5b.

The monopolar design (MM-KW) consumes the largest amount of NRs (Fig. 5a), exceeding the energy and water consumption for bipolar membranes using vacuum salt from MVR. This result is mainly due to the electricity consumption of monopolar electrolysis, which is 25024 MJ·t ECU^{-1}, being higher than that of the bipolar technique, which is 20409 MJ·t ECU^{-1}. The emerging technology succeeds in reducing these requirements by 20% (16128 MJ·t ECU^{-1}). However, this difference is not significant when assessing the amount of total NRs consumed since the influence of all the subsystems involved in the chlor-alkali process must be assessed.

For example, the energy indicator shows that compared to the monopolar technique (MM-KW), bipolar technology (BM-KW) reduces the total energy demand by 17%, while a difference of less than 9% is observed between BM-KW and ODC-KW. The contributions of the different subsystems account for these differences. The electrolysis stage is responsible for 94% of the environmental impacts for the membrane techniques, whereas this impact is estimated to be 81% for the ODC technique. The lack of hydrogen production contributes 10% of the total energy consumption, followed by salt preparation and NaOH treatment. The contribution of KCl mining waste and brine preparation to this metric is 4%. While this contribution may appear to be negligible, the total energy requirements decrease by nearly 20% when vacuum salt (MVR) is replaced with KCl wastes. Similar conclusions are drawn for the water demand index, for which the difference between the bipolar and monopolar technologies is the same as that for the energy indicator. The MM-KW scenario exhibits similar water requirements as BM-VSR, whereas the water consumption of ODC technology is approximately 30% smaller.

All the scenarios have a lower material demand than BM-VSR, including MM-KW. The overall material consumption is reduced by 23% when the vacuum salt (BM-VSR) is replaced with KCl waste (BM-KW), indicating the global benefit of applying a circular economy to this process. The difference between the bipolar membrane and ODC decreases to 2% since the reduction in the electrolytic requirements for ODC is penalised by the consumption of pure oxygen as a reactant. After electrolysis, the pure oxygen is largest contributor to material consumption, accounting for 12%.

The normalised EBs to air and water are displayed in Fig. 5b. Before normalisation, global warming (GW) and, to a much lesser extent, atmospheric acidification (AA) showed the highest air impacts of all the scenarios due to the emissions of SO_2, greenhouse gases (CO_2, CO, NO_x, CH_4) and organic emissions to the air (dioxins and formaldehyde) from steam and electricity production. This finding agrees with previous LCA studies based on energy intensive industries, such as the cement (Ali et al., 2016) and iron industries (Li et al., 2016). Eutrophication (EU) and aquatic oxygen demand (AOD) have the largest impact to the water environment in all of the scenarios due to the water emissions of inorganic (ammonia, phosphate) and organic compounds (methanol, phenol) during the production of electricity and the manufacturing processes of Na_2CO_3 and HCl. During these three processes, the GW contribution ranges from 2206 to 2736 kg CO_2 eq., and the AA contribution ranges from 4.44 to 6.48 kg SO_2 eq. Conversely, slight variations from $3.32 \cdot 10^{-2}$ to $4.80 \cdot 10^{-2}$ and from $3.52 \cdot 10^{-3}$ to $4.93 \cdot 10^{-3}$ kg O_2 eq. are observed in the EU and AOD categories, respectively. The electrolytic nature of the chlor-alkali process is responsible for the large differences in the GW values. Approximately 90% and 74% of the GW impacts are due to the electricity consumption of the membrane and ODC technologies, respectively, while the rest are due to steam consumption during the secondary brine treatment and NaOH concentration. This influence is less significant in other categories in which the energy consumption is lower. For example, a significant and similar contribution is observed for the brine preparation step in the AOD and AqA water categories (13% for BM-KW, 11% for MM-KW and 15% for ODC-KW).

After normalisation, POF presents the largest air impact, while EU remains the highest contributor to the water compartment because the normalisation values are higher for GWP (10^8) than for POF (10^3), and they are much lower for the water categories. As estimated with the NRs, MM-KW is the worst scenario and produces slightly higher environmental impacts than BM-VSR for every category. The exception is AqA, in which both scenarios have the same impact.

Therefore, using monopolar technology with the best performing salt source is comparable to using the bipolar cell in combination with the worst alternative salt source. When the composite X_1 and X_2 indexes are assessed (Fig. 6), the difference between MM-KW and BM-VSR is less than 2%. Conversely, an average impact reduction of 17% is obtained when vacuum salt is replaced with KCl. This difference is lower for AOD (8%) since the impact of primary treatment is more relevant in BM-KW than in BM-VSR.

The difference between the monopolar and bipolar scenarios (17%) is larger than that between the bipolar and ODC technologies (8% for X_1 and 11% for X_2). The ODC technology has larger HHE and SOD air impacts (20%) and AqA (17%) and NMeCO (19%) water impacts. This result mainly occurs because the low contributions of hydrogen and oxygen production to these categories show the potential benefits of the lower amount of electricity demanded by ODC technology.

1 **Conclusions**

2 This study explored the environmental sustainability of the chlor-alkali industry from a resource

3 perspective, which is a novel study for this field. Furthermore, the environmental influence of applying a

4 circular economy to this industry was assessed using novel waste-resource technologies. Potash mining

5 wastes, which are a typical salt source in the Spanish chlor-alkali industry, were used as a raw material.

6 Other common sources of salt, such as rock salt, solar salt, vacuum salt and solution-mined salt, were also

7 studied. Vacuum salt was assumed to be sourced from rock salt processing using mechanical vapour

8 recompression (MVR) and multiple-effect (ME) evaporation. For the electrolyser technology, membrane

9 cells in both bipolar and monopolar configurations were studied and compared to the emergent oxygen-

10 depolarised cathode (ODC) technology.

11 The results suggested that vacuum salt is the least environmentally sustainable source of salt. On average,

12 vacuum salt exhibited the highest natural resource (NR) consumption and the largest environmental impact

13 of all the salt sources. This result was mainly due to the high electricity (MVR) and steam (ME)

14 requirements for vacuum production. Specifically, MVR resulted in twice as much NR consumption than

15 ME and almost 4 times the NR consumption of the other salt sources when considering both salt extraction

16 and preparation. Moreover, the environmental impact of MVR was nearly 6 times larger than those of the

17 other salt sources. Conversely, the lowest NR and EB requirements were, on average, achieved by the KCl

18 waste salt, showing the positive influence of using the waste of another process as a raw material.

19 Consequently, different electrolytic technologies were explored using KCl mining waste as the salt source.

20 The total NR and EB requirements of the chlor-alkali process decreased by 17% when vacuum salt (MVR)

21 was replaced with KCl. Moreover, the environmental impacts estimated for the monopolar membrane using

22 KCl were comparable to those generated using the bipolar membrane with vacuum salt. The best results

23 were obtained for the emerging ODC technology, and further application studies are recommended for this

24 method.

25 This work indicates the importance of studying every life cycle stage in chemical processes, starting from

26 the raw material extraction. In particular, the significant influence of the salt source for the chlor-alkali

27 process was demonstrated. In addition, the results of using KCl mining wastes show the environmental

28 benefits of applying a circular economy, even in energy intensive industries such as the chlor-alkali process.

29 Therefore, the study and application of wastes from other processes as potential raw materials should be

30 encouraged in the chemical industry.

31

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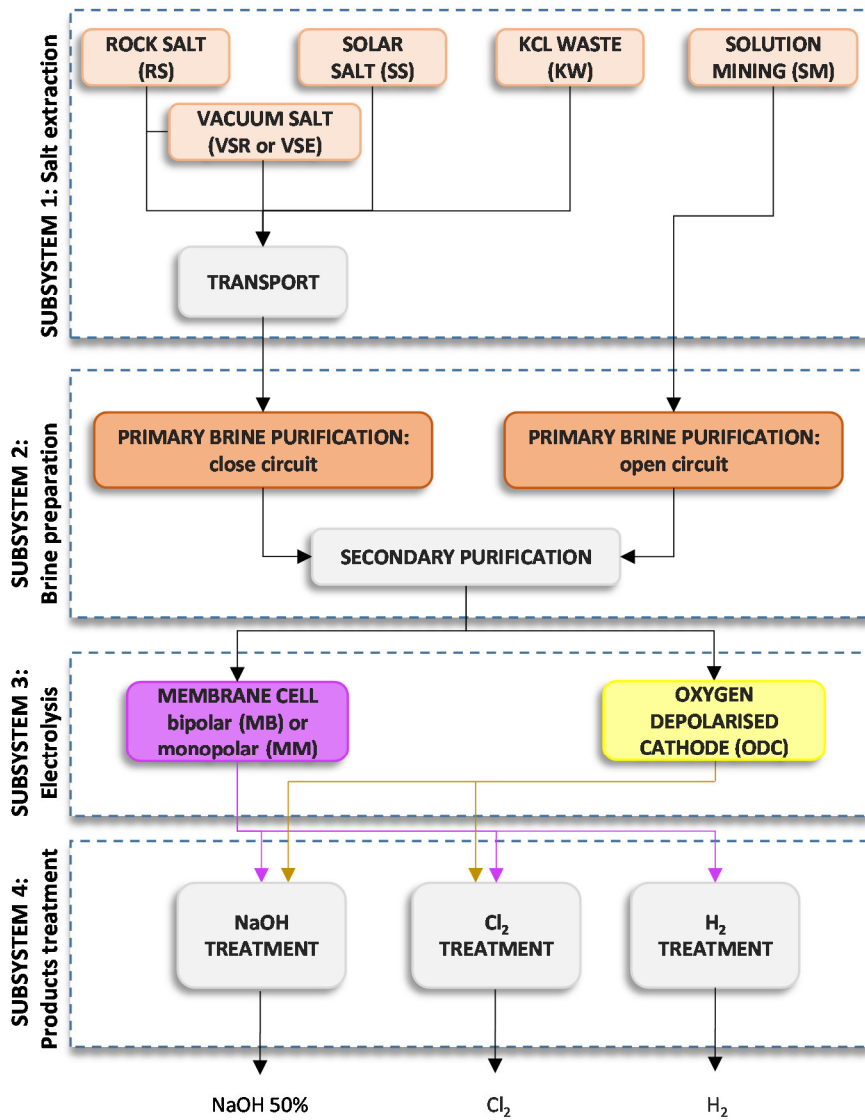
18   & Co. KGaA.

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1 **FIGURES**
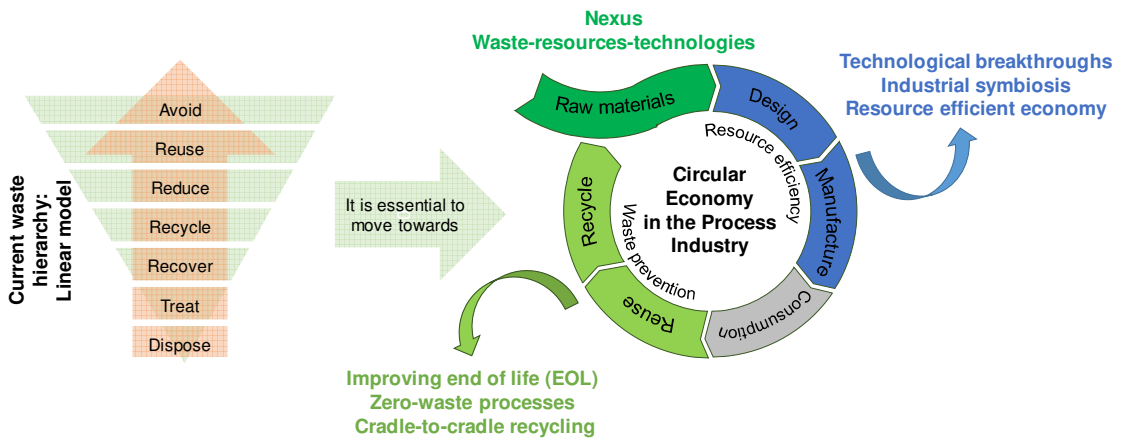
Fig. 1 Moving towards a circular model in waste prevention and resource reduction.
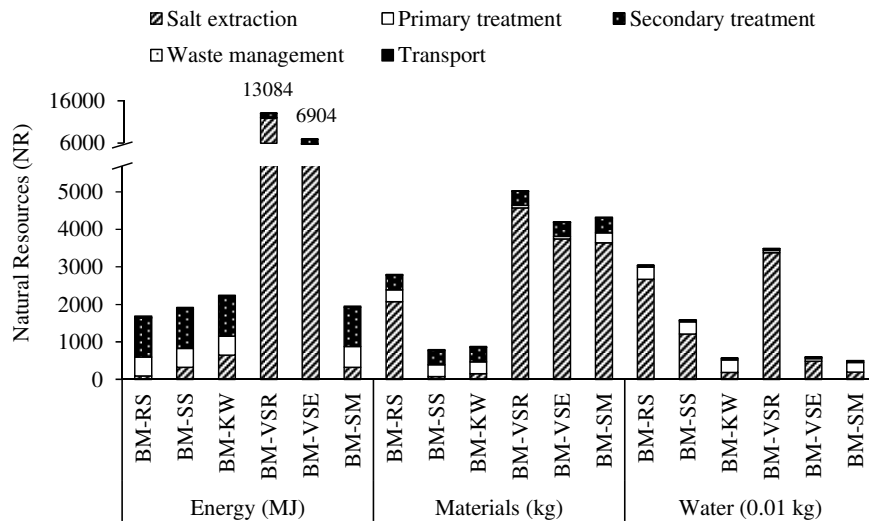
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**Fig. 2** System boundaries of the studied chlor-alkali systems.

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Fig. 3 Natural resource consumption for salt extraction and brine preparation in the studied scenarios. BM-RS: rock salt; BM-SS: solar salt, BM-KW: KCl waste salt; BM-VSR: vacuum salt produced using mechanical vapour recompression evaporation; BM-VSR: vacuum salt produced using multiple effect evaporation; and SM: solution-mined salt. The values for water consumption have been scaled to fit the graph. The original values can be obtained by dividing the values shown on the y-axis by the scaling factor given on the x-axis.

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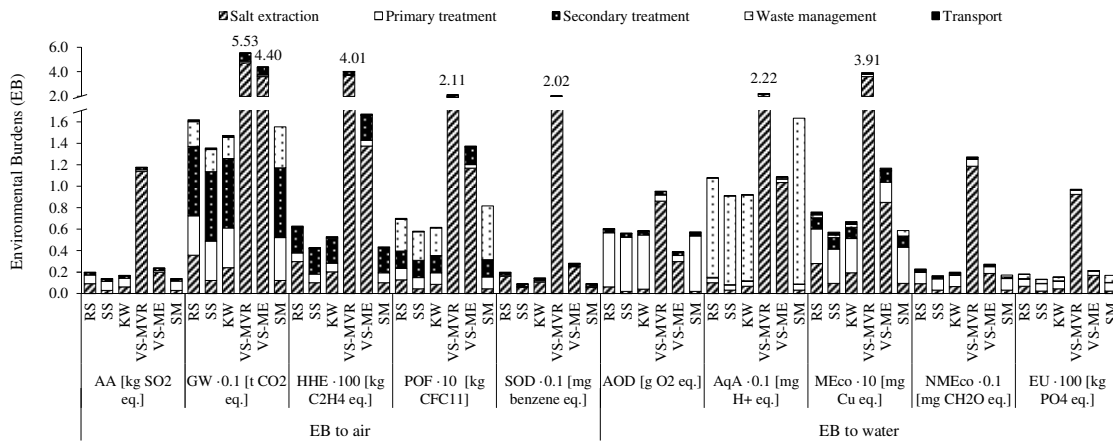
Fig. 4 Environmental burdens for salt extraction and brine preparation in the studied scenarios. AA: atmospheric acidification; GW: global warming; HHE: human health (carcinogenic) effects; POF: photochemical ozone formation; SOD: stratospheric ozone depletion; AqA: aquatic acidification; AOD: aquatic oxygen demand; MEco: ecotoxicity to aquatic life (metals to seawater); NMEco: ecotoxicity to aquatic life (other substances); and EU: eutrophication. The values for some impacts have been scaled to fit on the graph. The original values can be obtained by diving the value shown on the y-axis by the scaling factor given on the x-axis.
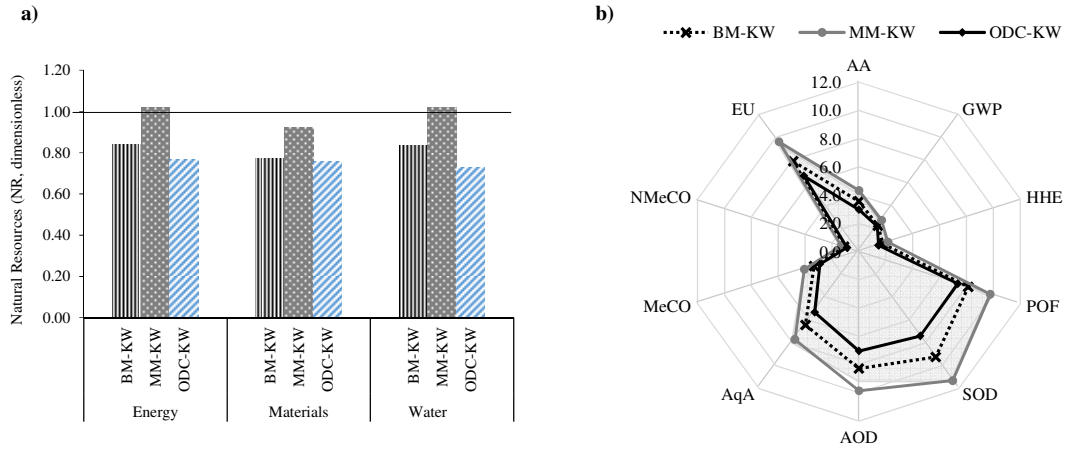
Fig. 5 Dimensionless NR (a) and EB (b) for the studied scenarios. BM-KW: bipolar membrane using KCl waste salt; MM-KW: monopolar membrane using KCl waste salt; and ODC-KW: oxygen-depolarised cathode (ODC) using KCl waste salt. The horizontal line (a) and the grey area (b) represent the NR and EB values for the bipolar membrane using vacuum salt (BM-VSR scenario), respectively.

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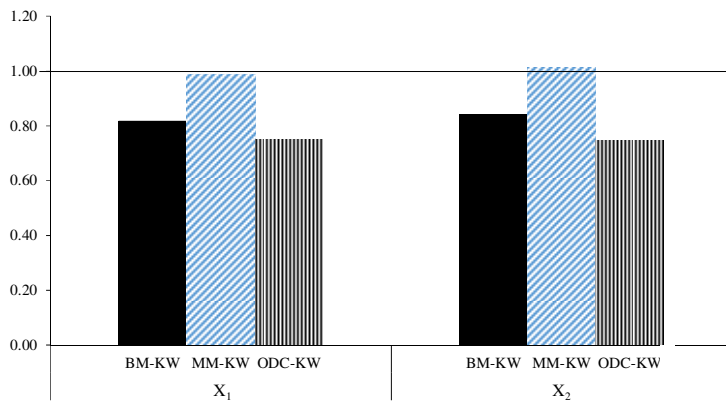
Fig. 6 X_1 and X_2 indexes for the studied technologies. The horizontal line represents the bipolar membrane using vacuum salt (BM-VSR scenario).