



Reuse and management of brine in sustainable SWRO desalination plants

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ABSTRACT

Reverse osmosis is a widely used and rapidly growing desalination technology. Despite the many benefits the technology has to offer, still challenging to all desalination plants is the environmentally sensitive effects attributed to the discharge into the sea of the rejected brine, which can very often severely damage the receiving environment, and air pollutant emissions attributed to the energy demand of the process. The list of potential impacts can be extended; however, the available information on the marine discharges alone indicates the need for environmental mitigation measures. In order to safeguard a sustainable use of the desalination technology, there is a need to develop, in the short term, new management proposals to achieve a minimization of the impact and valorization of brine. These alternatives should be both economically viable and effective, not only for new setting up plants, but also for those already installed. An adequate treatment sequence has been proposed and developed for reusing and valorizing this saline waste from seawater reverse osmosis desalination plants (SWRO), in the well-known chlor-alkali industry by NaCl electrolysis in membrane cells. This alternative has been described from a technological, economical, and environmental point of view towards sustainability of SWRO desalination plants of Gran Canaria (Canary Islands, Spain). The conclusions drawn out of this work refer to knowledge and control improvements concerning to the sustainability of desalination processes, to reduce the impact generated by brine disposal, and to reassess this saline residue as raw material in the chlor-alkali manufacturing industry.

Keywords: Brine; Desalination; Reverse osmosis; Environmental impact; Chlor-alkali; Membrane cells

1. Introduction

Seawater desalination has become an important and ever-increasing industry which faces up the environmental concerns of water scarcity present in some countries. That is the case of Canary Islands (Spain) where the number of projected facilities and those

under construction has increased significantly in recent years and is leading in this sense, both in knowledge and technology. Nowadays there are 327 desalination plants in operation, located mainly in Gran Canaria, Lanzarote, Fuerteventura, and Tenerife [1].

Among the variety of existing desalination techniques, seawater reverse osmosis (SWRO) desalination is the most used system in freshwater production.

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Even though seawater desalination by RO contributes positively to the environment (e.g. reducing exploitation of nonrenewable drinking water sources) and at the same time to human health, it carries with certain drawbacks, among which two dealing with environmental consequences could be emphasized: (a) the high energy consumption, with the consequent emission of CO₂ and (b) the negative effect on the marine environment originated mainly by the discharge into the sea of great amounts of the hypersaline rejection water (brine) generated, which represents the main residue of the system. The list of potential impacts can be extended [2–4], however, the available information about the marine discharges of brine alone indicates the requirement for an exhaustive environmental evaluation of all mayor desalination plant projects.

The first problem has been significantly reduced through the use of renewable energy and implementation of improvements on the efficiency of the process. Regarding the second problem, brine resulting from SWRO desalination is essentially seawater concentrated by a factor that depends on the efficiency of the RO membranes (55–60%, with maximum concentrations reaching close to 90% [5]). In addition to the high concentration of salts we must add the discharge of waste products related to chemicals used for biofouling control (biocides), scale control (antiscalants), coagulants, corrosion inhibitors [6,7], and punctual discharges resulting from cleaning membranes (chemical cleaning), which generates highly concentrated flows of suspended solids and detergents.

Traditionally, the negative impact of the reverse osmosis process has been considered negligible due to chemical disposals with very low concentrations [8]. However, this saline residue has a proven impact on the marine environment, generating anoxic condition on the seabed, changing light conditions and impact on marine species and seagrass [9,10].

An overview on the composition and effects of these saline residues can be found in a WHO recent document [11], where they are discussed in detail by Lattemann and Höpner [6] and MEDRC [12].

Up to now, the brine discharge in marine medium is the most economical way and this may be regarded for small desalination plants while using a previous dilution together with an optimum discharge location. However, due to the recent development of this activity in our country, it is important that both the construction and operation of new setting up desalination facilities, and also those already installed, develop a sustainable management plan for the brine.

Bódalo et al. [13] in a recent article discuss about possible alternatives for the management of brine from desalination plants, including the injection of the

brine in the subsoil, using evaporation ponds and solar basins, the use of salt residues as products for the regeneration of wetlands, or the design of a desalination system for separating the salt without generating the concentrated effluent, therefore obtaining salt ready for sale. There are other ways of management for brine, as might be the use of brine in the cultivation of halophilic species, used in hydrotherapy, capacitive deionization, distillation membranes, nanofiltration, and selective precipitation. However, for the desalination plants already installed, the corrective measures to minimize brine disposal can be considered infeasible in many cases.

This emphasizes the need of introducing, in the short term, new management proposals for this particular case which should be both economically viable and effective, not only for new setting up plants, but also for those already installed. That is why reusing and/or valorizing the by-products of economic interest present in the obtained brine are necessary to create a sustainable desalination cycle.

This article has proposed and developed a suitable system for the reusing and valorizing of brine as an alternative to direct disposal. With a previous treatment, the brine from SWRO desalination plants, due to their high sodium chloride content, (doubling approximately seawater rates) could be used in the chlor-alkali manufacturing industry by electrolysis of NaCl in membrane cells for the production of chlorine, caustic soda, and hydrogen. In addition, this residue has an added value as a by-product and, what is more, it avoids the environmental impact that its disposal should imply. This study is particularly focused in Gran Canaria Island.

2. Reuse of brine: raw material for chlor-alkali manufacturing

The Canary Islands and specially Gran Canaria Island represent an almost perfect model of reference in the field of the water desalination accumulating more than 50 years of experience.

Desalination in the Canary Islands has contributed to the progress and development of the islands, considering that its main economic activity is the tourism. In addition, water desalination has improved the population life quality, allowing a safe and continuous supply of water for domestic, agricultural, and industrial consumption.

Gran Canaria has a total of 135 desalination plants, in which 34 of them were using SWRO systems [14]. In Table 1, the capacity of the SWRO desalination plants installed in Gran Canaria can be observed.

Table 1
Capacity of the SWRO desalination plants in Gran Canaria [14] (modified)

SWRO desalination plant	Location	Application	Capacity of production (m ³ /day)	Rejected brine (m ³ /day)
Granja experimental	Arucas	Agriculture	500	611
Comunidad Fuentes de Quintanilla		Domestic	800	978
Arucas-Moya		Domestic	10,000	12,222
Gáldar-Agaete I	Gáldar	Domestic	3,000	3,667
Gáldar II		Agriculture	7,000	8,556
Aragua		Agriculture	15,000	18,333
Guía I	Guía	Domestic	5,000	6,111
Guía II		Agriculture	5,000	6,111
Ayto. San Nicolás	San Nicolás	Others	5,000	6,111
Asociación de agricultores de la Aldea		Agriculture	5,400	6,600
Las Palmas IV	Las Palmas	Domestic	15,000	18,333
Las Palmas III		Domestic	65,000	79,444
El Corte Inglés, S.A.		Domestic	300	367
BAXTER S.A.		Industrial	100	122
Telde 2 ^a Fase	Telde	Domestic	16,000	19,556
Salinetas–Telde		Domestic	15,000	18,333
Mando Aéreo de Canarias		Domestic	1,000	1,222
Aeropuerto II		Domestic	500	611
Aeropuerto I		Domestic	1,000	1,222
Sureste I	Santa Lucía de Tirajana	Domestic	10,000	12,222
Sureste II		Domestic	15,000	18,333
Sureste III		Others	8,000	9,778
Puerto Rico I	Mogán	Domestic	4,000	4,889
Puerto Rico		Domestic	4,000	4,889
AQUALING		Domestic	2,000	2,444
Anfi del Mar II		Domestic	250	306
Anfi del Mar I		Domestic	250	306
Anfi del Mar		Domestic	1,500	1,833
Maspalomas II	San Bartolomé de Tirajana	Domestic	25,200	30,800
Maspalomas I Mar		Domestic	3,000	3,667
Bonny		Agriculture	8,000	9,778
Bahía Feliz		Domestic	600	733
		Total	252,400	308,489

The two most relevant desalination centers are Las Palmas III and IV and Sureste I, II, and III with a desalination capacity of 80,000 and 33,000 m³/day, respectively. Despite the large installed capacities, these systems do not include any desalination management plan for the brine generated in the process.

From the total capacity installed in the Island of Gran Canaria, more than 308,000 m³/day of rejected brine can be estimated. An overview of the chemical characteristics of this discharge is summarized in Table 2. This residue, which is currently being discharged directly into the sea, causing negative impacts on the marine environment, is a potential source of

chemical products such as chlorine, hydrogen gas, and caustic soda.

In this paper, we analyze the possibility of introducing chlor-alkali industries in the vicinity of the desalination plants in order to reuse and revalorize the brine from these SWRO plants.

3. Chlor-alkali industry

Membrane cells technology is a clean, economically viable technique for the reuse of brine from SWRO desalination plants, but, at the same time, it is

dependent on many factors, such as brine purity, flow density, and pH factor [16].

The brine from SWRO desalination plants may contain impurities such as: Mg^{2+} , Ca^{2+} , Fe^{2+} , Sr^{2+} and SO_4^{2-} , or others. These impurities have harmful effects on the membranes, in which they accumulate and precipitate. This causes a reduction in process performance and the useful life of the membranes. Since impurities damage the membranes faces there are nar-

row limits of concentration allowed for the process [17]. To achieve this, several technologies and processes to separate the ions that harm the membranes have been developed.

Fig. 1 summarizes the purification techniques for the conditioning of the brine from RO desalination plants as raw material in chlor-alkali processes using membrane cells. These techniques are basically: (1) first purification: chemical precipitation, clarification, and filtration; (2) multi-effect saturation by evaporation; (3) second purification: ion exchange; (4) electrolysis; and (5) depleted brine dechlorination [16].

Table 2
Chemical composition of reject brine from Sureste I, II, and III [15]

Parameter	Value	Units
Calcium	960.00	mg/L Ca^{2+}
Magnesium	2,867.00	mg/L Mg^{2+}
Strontium	14.55	mg/L Sr^{2+}
Barium	0.018	mg/L Ba^{2+}
Silicon	20.50	mg/L SiO_2
Nickel	0.01	mg/L Ni
Sulfates	6,050.00	mg/L SO_4^{2-}
Carbonates	0.00	mg/L CO_3^{2-}
Bicarbonates	1,829.00	mg/L HCO_3^-
Chlorides	41,890.00	mg/L Cl^-
Sodium	25,237.28	mg/L Na^+
Fluorides	1.82	mg/L F^-
Potassium	781.82	mg/L K^+
Boron	8.00	mg/L B
pH	7.50	–
Conductivity	85,200.00	$\mu S/cm$
TDS	79,660.00	mg/L

4. Case of study: Gran Canaria

We shall analyze each of the necessary treatment phases for the reassessment and revalorization of brine from the SWRO desalination plants situated in Gran Canaria Island.

Due to the usual homogeneity of these facilities, we will analyze in detail the plants of Las Palmas III and IV and the South-East I, II, and III. Thus, since the concentration of seawater is similar for both regions, we take as a starting point the chemical composition of the rejection brine of Sureste I, II, and III.

To achieve reuse of the saline residue, it is necessary to remove certain impurities, mainly $Ca^{2+} + Mg^{2+}$ (<20 ppb), Sr^{2+} (<0.04 ppm), and SO_4^{2-} (<6 g/L) [17], and next to carry out a concentration of NaCl from of the initial 61.5 g/L up to 280–305 g/L.

4.1. First purification: chemical precipitation, clarification and filtration

In this process phase, the addition of precipitant reactivities, which carry out the impurities removal, takes place. Most of the calcium appearing as $CaCl_2$, sulfates which appear as Na_2SO_4 , and magnesium found as $MgCl_2$ are removed by chemical precipitation. The reactions that take place are the following:

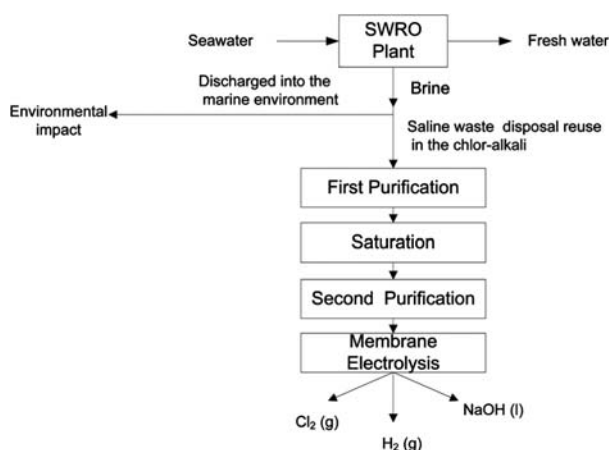
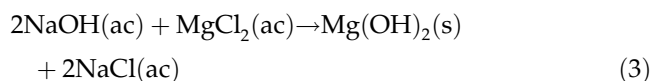
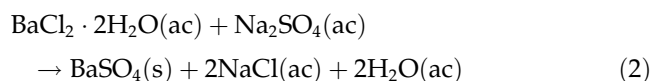
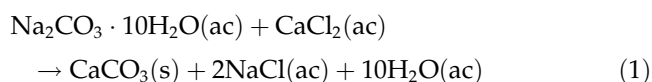


Fig. 1. General scheme for reassessment and valorization of the brine from SWRO plants in the chlor-alkali industry [16] (modified).

For this, three solutions were employed: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, and NaOH . The NaOH solution comes from the membrane cell at 32% in weight, once the NaCl electrolysis has taken place.

Throughout this phase, various different metals, such as strontium, iron, molybdenum, nickel, and chrome, may also precipitate as hydroxides during operation. All salts that precipitate together form a sludge that silts out and, consequently, are removed. For this, some potato starch will be used as flocculant. A precoat filtration of the decanted waters is used to eliminate small diameter suspended solids. This, generally, is a complementary operation to flocculation and sedimentation phases. Sand, anthracite, and diatomaceous earth may be used as filter medium contributory materials.

4.2. Multieffect evaporation saturation

With a concentration of about 61.5 g/L NaCl , brine requires a preconcentration to reach the suitable saturation level for carrying out the electrolysis in membrane cells.

The volume of water that evaporates during operation for obtaining a saturated NaCl at the desired concentration is determined by operation material balance, taking into account, at the same time, that the input NaCl amount equals the output NaCl quantity.

In order to determine the NaCl concentration reached in each one effect, it becomes necessary to know the volume of water evaporated in each one effect. For this, it is initially supposed that the evaporated water total volume in each particular effect is the same for both.

To carry out the energy balance, the heat transfer integral coefficient and the variation of the specific heat are calculated using the correlations established by Mandani et al. [18].

In order to optimize the exchanged energy in each evaporator and, therefore, diminishing the feed vapor expenditure coming from the boiler, a series of shell-and-tube preheaters, heated by each effect vapor, is used. The determination of the obtained temperatures in each exchanger has been calculated using the effectiveness-NTU method [19].

4.3. Second purification: ion exchange

The precipitation phase alone is not enough, by itself, to reduce calcium and magnesium. A brine depuration phase, as a second purification, must be planned in advance. The resin selection will depend upon both the input brine composition and on the loading cycle limit criterium.

4.4. Electrolysis

Once the brine is purified, both its heating (up to about 90 °C) and acidifying (at pH 4) become necessary in order to avoid 5 and 6 secondary reactions to form.



When the membrane cells electrochemical output amounts to about 60%, a 210–250 g/L [17] concentration reject brine is generated. This depleted brine is then recirculated as it comes out of the electrolyzers so that it can be mixed with that other brine coming from the multieffect evaporators without the need of dechlorination.

5. Results

The process diagram for the reassessment and valorization of the brine for chlor-alkali is shown in Fig. 2.

In the initial stage of brine purification, most of the calcium appears as CaCl_2 , sulfates are present as Na_2SO_4 , and magnesium is found as MgCl_2 , with a rate of 2.7, 9, and 11 kg/m³, respectively. These are removed by chemical precipitation. The ratios of these impurities are similar for both chemical compositions found in the rejected brine from Sureste I, II, and III and Las Palmas III and IV desalination plants. This process is largely controlled by the solubility product of the barium sulfate, magnesium hydroxide, and calcium carbonate. The concentrations of the precipitants are essentially fixed at levels which can be determined from their respective solubility. Barium chloride and sodium carbonate solubility at 20 °C are

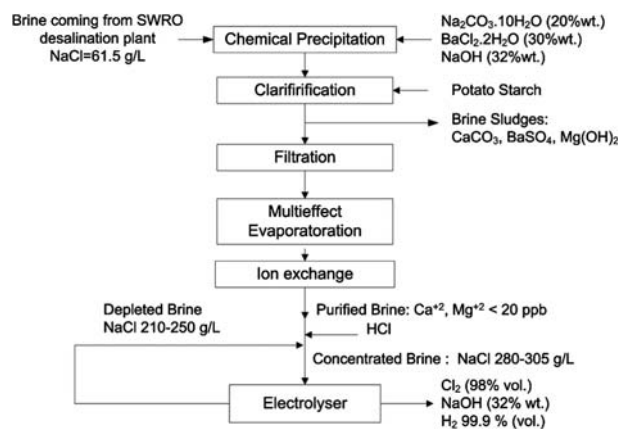


Fig. 2. Process diagram of reuse and revalorize of brine in chlor-alkali manufacturing.

Table 3
Concentration of the major undesirable impurities in the process of brine purification

Impurities	Initial	After first purification	After second purification
SO ₄ ²⁻	6.05 g/L	<5 g/L	<5 g/L
Ca ²⁺	0.96 g/L	<2 mg/L	<20 ppb
Mg ²⁺	2.87 g/L	<1 mg/L	

Table 4
Final composition of the products obtained after electrolysis of brine

Cl ₂	NaOH	H ₂
Cl ₂ > 98% (vol.)	NaOH 32% (wt)	>99.9% (vol.)
H ₂ < 2% (vol.)	NaCl < 20 ppm	

35.7 g and 21.5 g of anhydrous salt in 100 g of water, respectively [19]. Therefore a solution of 30 wt.% of BaCl₂·2H₂O and 20 wt.% of Na₂CO₃ can be used.

The variation in the concentration of undesirable impurities present in the process is summarized in Table 3.

All salts that precipitate together form a sludge that silts out and, consequently, is removed from the clarifier tank by means of flocculation using potato starch. The generated residues are mainly sludge coming from brine purification: barium or baryte sulfates (BaSO₄), calcium carbonate (CaCO₃), and magnesium hydroxide or bitter earth hydroxide (magnesia lacte) (Mg(OH)₂). From the environmental point of view, these industrial sludges do not pollute. Nevertheless, they should be adequately managed.

The clarified brine is filtered in a precoat filtration unit with diatomaceous earth before entering the multi effect evaporator unit where the residual calcium and magnesium and remaining metal ion impurities are removed. After filtration, brine contains the following impurities: Mg²⁺ < 1 mg/L, Ca²⁺ < 2 mg/L, SO₄²⁻ < 5 g/L.

Table 5
Results obtained after electrolysis of NaCl

SWRO plant	Rejected brine (m ³ /day)	Cl ₂ (98% vol.) (t/day)	NaOH (32% wt.) (t/day)	H ₂ (99.9% vol.) (t/day)
Las Palmas III and IV	97,777	3,536.2	12,469.1	99.8
Sureste I, II, and III	40,333	1,458.7	5,143.5	41.1
Others	170,379	6,162.0	21,727.7	173.8

Next, after a six-step multieffect evaporation in both cases with the respective preheating of the brine with six shell-and-tube preheaters, brine containing initially 61.05 g/L NaCl, reaches a concentration of 280–305 g/L NaCl.

Once brine is saturated, a second purification becomes necessary. This time using an ion-chelating exchange resin, type AMP (aminomethylphosphonic acid), and chosen by its greater effectiveness when eliminating Ca²⁺ and Mg²⁺ ions and remaining metal ion impurities.

Purified brine needs to be heated up to 90 °C in order to carry out the electrolysis with a current intensity of 5 kA. The chemical products obtained after electrolysis is carried out are: chlor gas (Cl₂), caustic soda (NaOH), and hydrogen (H₂). Final product composition can be viewed in Table 4, although a further processing is to be accomplished.

From the energy point of view, a consumption of about 2150 kWh/t NaOH is estimated. The obtained hydrogen will be used *in situ* for gaining electric energy through protonic exchange by means of fuel cells (PEMFC), so that some of this consumption will be self-supplied.

Specifically and in relation to the cases studies, the results obtained are summarized in Table 5.

6. Conclusions

In view of previous evaluations, the implementation of a chlor-alkali industry, annexed to reverse osmosis desalination plants, is a technically viable option to face direct saline waste discharges.

Concerning the possibilities of implementation, it does not require any sophisticated technology as the plant maintenance is simple. Thus, the membrane cell technology to produce chlor-alkali is technically and financially feasible. In addition, this technology is environment friendly and its installation does not require large spaces.

Although the island of Gran Canaria has been the study area to collect the data, the benefits put forward below can be extrapolated to any other area.

Among the benefits, the most significant and of a greater impact is, without any doubt, the environmental benefit. With the commissioning of such plants or reassessment system the direct discharges to the sea will be prevented, eliminating the environmental impact caused by direct discharges; with the result of the improvement of the marine environment ecological quality and, ultimately with the improvement of marine conservation, and a sustainable desalination cycle. Nevertheless, we must keep in mind that there are series of sludge resulting from purification of the brine which must be managed on the ground and solid waste due to the use of the membranes.

From a socioeconomic point of view, the benefit is wide and covers almost every field. Firstly, the ecological improvement, such as preventing seagrass loss, is due to brine discharges; thus, avoiding unnecessary expenses to restore the ecological level and consequently, improves considerably the economy of the areas where the implementing of this management to control brine discharges is carried out. Secondly, it is due to the development of a new source of chemical resources like chlorine, hydrogen gas, and caustic soda. These products have different final uses with very different dynamics of market. In the case of the obtained hydrogen, it will be used *in situ* to obtain electrical energy using proton exchange membrane fuel cells (PEMFC). On the one hand, chlorine can be used for the chlorination of public water supply, meeting the maximum concentration dictated by the WHO (0.5 ppm) covering the total demand for Gran Canaria. It could also be used by different industries which have required this product on the islands and in the management of waste (glass and paper) and food processing (containers, tanks disinfection, or processing lines in general). On the other hand, the sodium hydroxide can also be employed in detergent producing Canary industries, food industry (bottle cleaning and pH control), future biodiesel plants and, to a lesser extent, for common uses in industrial activity, in general (paint stripping, extracting agent in drying, glazing and even degreasing, and metal cleaning).

Moreover, the implementation of projects of this nature will create direct jobs, hiring highly qualified personnel. Socially, there is also a major benefit as the marine conservation and the protection of its ecosystems will enable the privilege to enjoy this natural treasure, preventing the extinction of species of high interest such as *Cymodocea nodosa*.

The industrial benefit is directly related to the financial benefit. Due to the implementation of the

discharge management system, many desalination plants will improve the quality of their discharges, thus improving publically the image of such production plants, because of their contribution to the protection and conservation of the marine environment, achieving a sustainable cycle of desalination.

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