Desalination 281 (2011) 35–41

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Saline waste disposal reuse for desalination plants for the chlor-alkali industry The particular case of pozo izquierdo SWRO desalination plant

N. Melián-Martel *, J.J. Sadhwani, S. Ovidio Pérez Báez

Department of Process Engineering, University of Las Palmas de Gran Canaria, Campus de Tafira Baja, 35017, Las Palmas de Gran Canaria, Spain

ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form 15 July 2011
Accepted 16 July 2011
Available online 15 August 2011

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

ABSTRACT

Seawater desalination has become an important and ever-increasing industry which faces up the environmental situation of water scarcity present in some Mediterranean countries and in the Canary Islands (Spain). This activity presents several environmental drawbacks and negative impacts on marine ecosystems, originated mainly by the discharge into the sea of the generated brine. 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. As an alternative to brine disposal, an adequate system has been proposed and developed for the reuse of this saline waste coming from reverse osmosis desalination plants in the chlor-alkali industry by NaCl electrolysis in membrane cells. In this paper, the various treatment phases, necessary for the adaptation of this residue as an alternative raw material resource in the chlor-alkali manufacturing industry, are described. This study has been adapted to Pozo Izquierdo Reverse Osmosis Desalination Plant, in Gran Canaria.

This new and different residue reuse as raw material supposes the production and exploitation of new chemical resources, as for example: chlorine, hydrogen gas, and caustic soda.

1. Introduction

At present, seawater desalination seems to be the main and most feasible technological bet in order to satisfy the ever-increasing fresh water demand at the Spanish Mediterranean basin. At the same time, it has become the most important non-natural water resource in the Canary Islands.

Among the various several existing desalination techniques, reverse osmosis seawater desalination is the most common method used in fresh water production. This is due to both new advances in the technology and to its minor energy consumption and space requirement [1]. While a reverse osmosis desalination plant works, an important volume of reject water is generated, this being a concentrated seawater by-product, its concentration factor depending upon membrane efficiency (55–60%, the highest concentrations amounting to about 90%) [2], and several other additives used during the desalination process (anti-scaling, anti- fouling, biocides and cleaning chemicals) and heavy metals from corrosion [3–5]. In nearby coastal desalination plants, this reject water is mainly discharged into the marine environment which can very often severely damage the receiving environment. Anoxic condition on the seabed, changing light conditions and impact on marine species and seagrass could be generated.

An overview on the composition and effects of these saline residues can be found in a WHO recent document [6], where they are discussed in detail by Lattemann and Höpner [5] and MEDRC [7]. Moreover, in latest publications, special attention is drawn to some regional cases which present a desalination activity increase, such as the Red Sea [8], the Mediterranean Sea [9–11], the Arabian Gulf [12], and Gran Canaria Island coastline [13,14].

The environmental impact of this residue has been minimized both through adequate recommendations [15,5] and good strategy planning prior to desalination plants building. There are many emerging alternative technologies that can be combined to achieve a minimization and valorisation of brine and thus an appropriate management such as hydrotherapy uses, heat carrier fluid (in solar ponds or as a cooling fluid), wetlands regeneration, aquaculture, growth of halophilic species, capacitive deionization, membrane distillation, nanofiltration, osmotic power, evaporation ponds (by natural o induced means), selective precipitation, freezing–melting process and rapid-spray evaporation. However in desalination plants already installed, minimization corrective measures, being considered at present, are inviable in most cases. This fact emphasizes the need of developing new effective and economically viable proposals for this residue management, not only for new setting-up plants, but also for those already installed.

In this framework, the sodium chloride high content (doubling approximately that of seawater) in saline waste products coming from desalination plants, could be used through previous treatment, in the chlor-alkali manufacturing industry for chlorine production,

* Corresponding author. Tel.: +34 6601631 30; fax: +34 928 458975.
E-mail address: nmelian@proyinves.ulpgc.es (N. Melián-Martel).

0011-9164/$ – see front matter
doi:10.1016/j.desal.2011.07.040

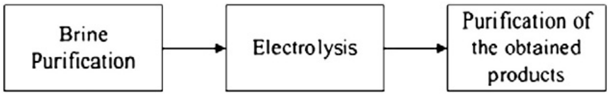

Fig. 1. Chlor-alkali process simplified scheme.

caustic soda, and hydrogen, by means of electrolytic processes. In addition, this residue has an added value as a byproduct and, what is more, it avoids the marine environmental impact its disposal should imply.

The importance of this study has, lies not only in the scientific field, but also in current practical application, both in the Canary Islands and in the rest of Spain.

1.1. Chlor-alkali manufacturing technologies

Chlor-alkali manufacturing industry produces chlorine and sodium hydroxide or potassium hydroxide through saline solution electrolysis. The main technology applied in the chlor-alkali industry is electrolysis, either in membrane, diaphragm or mercury cells, using mainly sodium chloride as raw material or potassium chloride, in a lesser degree, when it is used to produce potassium hydroxide.

The process global electrochemical reaction is as follows:

$$2\,NaCl + 2\,H_2O \xrightarrow{energy} Cl_2 + H_2 + 2\,NaOH \quad (1)$$

Energy, as direct current electricity, is supplied to drive the reaction. The amount of electric energy required will depend upon the electrolytic cell design, the voltage used and the brine concentration used. For each tonne of chlorine produced, 1.1 sodium hydroxide tonnes and 28 hydrogen kilograms are manufactured.

Broadly speaking, the process carried out in order to obtain chlorine, sodium, and hydrogen is the same one for the three different technologies. This process can be divided into three large phases, as it can be observed in Fig. 1.

However, there are important technical differences among these three technologies, both in terms of product quality and in relation to each technology operation [16]. One of the main differences among these technologies lies in those phases necessary for brine purification treatment. Diaphragm and mercury cell technology do not require high purity brine. Yet, membrane processes do require high purity brine. On the other hand, for diaphragm and mercury technologies, precipitation and filtration are the adequate measures for brine purification. However, for membrane cell processes, an additional brine treatment containing ion exchange resins is necessary.

In relation to operation systems, each process represents a different method of keeping aside the chlorine produced in the anode from both the caustic soda and the hydrogen produced in the cathode, either directly or indirectly. As a consequence, each process produces a different chlorine gas purity and a different caustic soda concentration [17]. In Table 1, some industrial characteristics of these processes are briefly shown.

The advantage mercury cell technology has, is that of producing a high purity caustic soda by a merely simple brine purification. However, this is the highest energy-consuming process (up to 3400 kWh of electric energy per chlorine tonne produced). Diaphragm processes produce low-quality caustic soda and moreover, they require a higher energy consumption than that required by membrane cells. Consequently, the installed capacity of these processes is being diminished [18]. All new chlor-alkali plants use membrane cell technology. This is due to the fact that the expenditure concerning capital investment, operating costs and energy consumption, are lower than that of diaphragm and membrane technology [16–18]. What is more, this is the most environmental friendly technology, yet this technology requires a high purity brine (see Table 2).

Among the electrochemical technologies studied in this work, membrane cell technology is a clean, economically viable technique for the reuse of these residue, but, at the same time, it is dependent on many factors, such as brine purity, flow density, and pH factor.

The treatment stages definition for chlorine production using membrane technologies is most clear, since its specifications and characteristics are well-known. The adaptation to a particular alternative resource for chlorine production, as it is that of saline residues coming from waters desalination, however, is a great challenge. Due to its composition and origin-dependence, the use of brine often implies several various treatments which have been, up to now, very little studied.

The total volume of impurities, present in these alternative resources, form a most diverse elements group, taken as a whole, and having different behaviors. The treatment of this saline residue must be carried out through both identification and quantization of all influential parameters, i.e., by a precise and exact brine analysis.

A practical case of about 8400 m^3/day brine reuse coming from Pozo Izquierdo desalination plant has been developed in the present study. It also shows one adequate method for brine purification and concentration for further use in chlor-alkali manufacturing production electrolytic cells. This study is focused on a particular case located in Gran Canaria Island.

2. Materials and methods

We shall analyze each treatment phase necessary for the reuse of saline residue coming from one reverse osmosis desalination plant sited in Gran Canaria Island, i.e., the particular case of Pozo Izquierdo SWRO Plant, which has been thoroughly studied.

2.1. Pozo Izquierdo desalination plant

This desalination plant is located in the south-eastern part of the Island, i.e., in Pozo Izquierdo (Tenefé Point) within Santa Lucía de Tirajana municipal area. Both the technical specifications and the residue chemical composition generated after desalination are shown in Tables 3 and 4 respectively.

Table 1
Comparative study among chlor-alkali electrolysis processes [17,18].

	Mercury cell process	Diaphragm cell process	Membrane cell process
Electric energy demand (kWh/t Cl_2)	3100–3400	2300–2900	2100–2600
Total energy demand (kWh/t Cl_2) for 50% of NaOH	3100–3400	3200–3800	2400–2900
NaCl purification	Simple	Simple	Expensive ($Ca^{2+} + Mg^{2+} < 20$ ppb)
NaOH quality	50 wt.% from cells, low chloride content	12 wt.% from cells, up to 1% chlorides in 50 wt.% NaOH	32 wt.% from cells, low chloride content
Cl_2 quality	<1% O_2 in Cl_2, no further cleaning	2–3% O_2, further cleaning required	1–3% O_2,further cleaning required [a]
Environmental issues	Hg used as cathode material	Asbestos used for diaphragms	None

[a] 0.5% O_2 with HCl addition to anolyte.