Hydrometallurgy 155 (2015) 61–68

Contents lists available at ScienceDirect

Hydrometallurgy

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

Use of discharged brine from reverse osmosis plant in heap leaching: Opportunity for caliche mining industry

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ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 5 March 2015
Accepted 3 April 2015
Available online 10 April 2015

Keywords:
Caliche
Reverse osmosis
Brine
Leaching
Seawater

ABSTRACT

Caliche is a highly water-soluble mineral that is exploited in northern Chile for its valuable content of iodine and nitrate, which are used in technological, medical, agriculture, dietary, and industrial applications. The processing of this mineral is through vat or heap leaching, where the species are dissolved using mainly fresh water and intermediate solutions. Since the deposits are located in zones with scarce water availability, one of the challenges for this industry is the search for new sustainable sources of water to face the process requirements. The use of groundwater sources by the mining industry has affected the domestic water supply for the nearest populations, increasing the need for new water alternatives as desalination of seawater by reverse osmosis (RO). A disadvantage of this method is the generation and discharge of highly concentrated brines to sea. In this work, the feasibility to use RO brine for caliche leaching was empirically proved through column-leaching experiments, which showed high recoveries of iodine and nitrate. Therefore, the use of RO brines may be an interesting option, on one side, for covering the increasing demand of processing water and, on the other side, to diminish the negative impact of brine disposal to the sea.

1. Introduction

In desalination there are two basic technologies for salt removal of seawater, which are by thermal evaporation or by using membranes. The thermal evaporation has been used hundreds of years ago in Middle East (UAE, Jordan, Kuwait and Saudi Arabia), but only in the 1950s began the industrial processing of seawater by this method. Later, in the 60s less expensive techniques based on membrane separation emerged, such as reverse osmosis (RO) (Fritzmann et al., 2007; Greenlee et al., 2009). Due to the fact that RO consumes 60% less energy than evaporation; it is the technology most used in the new desalination plants. Its widespread implementation has also been driven by the improvement of membranes and energy recovery processes (Morillo et al., 2014).

In Chile, the desalination of seawater is a growing activity that is concentrated in the northern region, being mainly driven by the mining sector (Table 1). Since 2003, when the first desalination facility was installed up to now, many projects have appeared with different capacities. It is expected that in the next years, uptake of seawater for desalination will increase.

While the development of the RO technology has allowed the use of seawater for human and industrial consumption as a feasible alternative, one of the negative consequences of its process is related to the effluents that are generated and how these are disposed. In the process of RO, brines are generated with high concentrations of dissolved solids that are commonly discarded to the sea due to its low cost. Current operations have yields close to 50% i.e. from 100 L of taken seawater; 50 L of desalinated water and 50 L of brine are produced. This type of discharges may have a negative environmental impact on the ecology of the outfall vicinity. There is evidence that, depending on habitat conditions and the hydrological characteristics where discharge occurs, exposure to these brines can cause osmotic stress to salinity-sensitive organisms, leading to increased turbidity, limiting photosynthesis and breaking existing trophic chains (Fritzmann et al., 2007; Roberts et al., 2010). One alternative to eliminate this problem is to find uses for the RO brines, like the leaching of copper oxides and caliche minerals.

Caliche is a mineral composed by a high proportion of water-soluble species at room temperature, such as nitrates (Nitratine, Humberstonite and Darapskite), sulphates (Glauberite, Polyhalite, Bloedite, Gypsum and Anhydrite) and chlorides (Halite) as shown in Table 3. Relatively high proportions of iodate (mainly Lautarite and Hectorfloresite) are contained in caliche ores compared with other minerals (Ericksen, 1983; Jackson and Ericksen, 1994). The importance of the exploitation of this resource is that it is the largest mineral natural source of iodine and nitrate (saltpetre) known (Ericksen, 1983). Iodine is primarily used in medical applications (contrast medium in X-rays) and as a

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http://dx.doi.org/10.1016/j.hydromet.2015.04.008
0304-386X/

Table 1
Main projects of seawater desalination in Chile (Cochilco, 2013; Moreno et al., 2014; CSEA, 2014).

Project	Company	Capacity, L/s	Status
Human consumption			
La Chimba plant	Aguas Antofagasta	600	In operation
Desaladora Sur plant	Aguas Antofagasta	400	In study
Industrial consumption			
Doña Inés de Collahuasi SCM, III expansion	Anglo American plc Glencore Mitsui & Co, Ltd.	1000	In study
Coloso plant	BHP Billiton	525	In operation
Coloso expansion	BHP Billiton	N/A	Approved
Radomiro Tomic expansion	Codelco	1100	In study
Candelaria	Freeport McMoran Copper & Gold	300	Under construction
El Abra	Freeport McMoran Copper & Gold	1300	In study
Cerro Negro Norte	CAP	200	Under construction
El Morro	GoldCorp	740	Under construction
Mantoverde	Anglo American	120	Under construction

N/A: Not available.

nutritional supplement for animals and humans, as well as in the production of LCD screens, among other products (Polyak, 2014). On the other side, nitrates are employed in the manufacture of fertilizers for crops with special nutritional requirements and as industrial salts for thermal storage in solar plants (SQM, 2012).

Chile is the world leader producer of iodine and natural nitrates, since 63% of the iodine produced worldwide in 2012 came from the exploitation of caliche, followed by Japan and United States that exploit seaweeds and subterranean brines, respectively (Polyak, 2014). Moreover, 50% of natural nitrate based fertilizers that is marketed, has a Chilean origin, then follow Jordan and Israel (Moreno et al., 2014).

The deposits of caliche are distributed in northern Chile, for about 2100 km^2 under a sterile layer called Chuca (Ericksen, 1983). After extraction of the ore by blasting or mechanical rupture, the caliche is leached in vats or heaps. For both cases, the dissolution of the species of interest from the solid matrix is carried out using water or intermediate solutions, because unlike most ores, the leaching of this mineral is governed by the solubility of the species (Valencia et al., 2008; Wheeler, 2010; Gálvez et al., 2012; Ross et al., 2013; Ordóñez et al., 2014a). For heap leaching, the ore is watered, usually by spraying, from the crown of the heap at low irrigation rates, between 1.5 and 6 L/h/m^2 (Wheeler, 2010). The leaching cycles last between 3 and 7 months, reaching a ratio leachant/caliche of about 1 m^3/t (CSEA, 2014), afterwards the leachate is treated to obtain the products of interest.

The sustained growth of population and mining industry results in an increasing demand for water. In areas where this situation coexists with natural scarcity of water resources, such as northern Chile, the looking for new sources of water supply is becoming increasingly necessary (Cisternas and Gálvez, 2014). Since water is essential for mineral processing, several initiatives about the best use of water within the processes have been implemented (Donoso et al., 2013; Gálvez et al., 2014); however it is known that in the near-future, sustainability of the mining projects will depend in more significant changes of water usage (Cochilco, 2013). In this regard, several researchers and companies have studied and used seawater as process water, both directly and after salt removal treatments as desalination (Moreno et al., 2011; Philippe et al., 2011; Ordóñez et al., 2013; Torres et al., 2013; Cisternas and Moreno, 2014).

This work is based mainly in two aspects; on the one hand, the growing demand for alternative water sources for mining industry and on the other hand, the increasingly existence of brines that will be discarded to sea. The work aims to validate experimentally by pilot tests that brines coming from reverse osmosis plants may be used in leaching of caliche mineral with similar performance than traditional leachants. In this context, the effluents produced in the desalination of seawater, instead to be disposed in the sea, should be pumped-up to the desert through distances of a few hundred kilometres and elevations of between 1000 and 2000 m.a.s.l. to be used in mining operations; e.g., leaching. The solution could be based on a configuration where seawater is transported to the desert and a fraction (or all) is desalinated and used in mining operations or as potable water and the brines (or no-desalinated water) used for leaching.

2. Experimental procedure

2.1. Column leaching experiments

Caliche used in the leaching experiments was obtained from natural deposits located in northern Chile. The material was size-screened between 1.3 and 3.8 cm, with an average particle diameter of 2.5 cm. The caliche was then loaded by batches in 5 Polyvinyl chloride columns of 0.2 m of diameter and 1.0 m of height. Table 2 details the chemical composition of soluble species of caliche ore.

Mineralogy of caliche was also examined by the semi-quantitative technique X-ray diffraction (XRD), being its main constituents: Quartz, Anhydrite, Glauberite, Halite and Nitratine, which represent about 75% of mass. The ore has a high fraction of soluble minerals, reaching 45% in mass (Table 3). Nitrate and chloride are present uniquely as Nitratine and Halite, respectively, both very soluble species. In opposition, sulphate is the anion mostly shared among mineral species with different solubilities, such as Anhydrite, Glauberite, and Loeweite. Through XRD iodine is not perceptible, due to its small relative abundance in the solid ores. However, it is known that usually iodine minerals are Lautarite ($Ca_2(IO_3)_2$), Bruggenite ($Ca_2(IO_3)_2 \cdot H_2O$) and Hectorfloresite ($Na_9(IO_3)(SO_4)_4$) (Jackson and Ericksen, 1994).

The RO brines were obtained from a desalination plant located in Antofagasta (Chile) and untreated seawater, used for comparison purposes, was collected by a submarine outfall in Antofagasta. The leaching was carried out during 22 days using 3 different irrigation rates and 2 solution temperatures. The conditions used in these experiments are detailed in Table 4.

Insulating foam (Ethylene Vinyl Acetate) was used to isolate the walls of the column and the solution container in the test with high temperature. The water was maintained at the required temperature by heaters controlled by thermostat.

The irrigation of leachants to columns was done continuously through peristaltic pumps and the containers with the leaching solution were covered from light to avoid the growth of algae. The leachant compositions are listed in Table 5. The wetting of caliche was done at the nominal rate and once the leachate begun to drip from the column bottom, the leaching was considered started. No recirculation of the leachate was conducted.

2.2. Sampling and chemical analysis

Liquid samples of leachates were taken every 12 h for the first 5 days of leaching, and then a daily sample was collected until the final of the experiments. Solid sampling was also done at the beginning for homogenized caliche and at the end for the residues of each column, when they were dismantled.

Table 2
Water-soluble composition of caliche (g/100 g) used in leaching experiments.

Anions						Cations			
NO_3^-	SO_4^{2-}	IO_3^-	Cl^-	ClO_4^-	BO_3^{3-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
7.8	15.6	0.04	7.0	0.02	0.09	8.7	2.0	1.5	0.6