



## Seawater leaching of caliche mineral in column experiments



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### ABSTRACT

Caliche is a mineral that contains a high fraction of soluble minerals and that is exploited in Northern Chile through vat or heap leaching for the production of iodine and nitrate. In this zone, the water availability is scarce, being a critical issue for the mining industries and whereby the use of other leaching agents as seawater may be a viable alternative. For this reason in the present study, column-leaching experiments using seawater were performed, including different irrigation rates and column heights. It is found that the highly soluble minerals such as nitrate and iodate are rapidly leached, while for other minerals like sulphate and chloride, the outlet concentration increased once that part of the sodium has been removed. Crystals of sodium sulphate were found at the column bottom, when this was dismantled. An existing phenomenological model (Gálvez et al., 2012) was used to analyse the changes of concentration of nitrate and iodine (as iodate) with a good agreement between the experiments and the simulations. On the other hand, for sulphate and chloride a new model was developed, which takes into account the dissolution and precipitation phenomena of these ions. The model was able to capture the trends observed in the experiments for the outlet concentrations of the modelled ions.

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### 1. Introduction

The caliche mineral is composed of sodium nitrate, sodium chloride, sodium sulphate, potassium chloride, and minor salts. At present, iodate is the most important component from economical point of view. Insoluble species such as quartz and other silicates are also present (Ericksen, 1983; Pokorny and Maturana, 1997; Valencia et al., 2008). In some cases, the soluble fraction of the caliche can reach values up to 40% (Gálvez et al., 2012). Typical water-soluble species that can be found in caliche are listed in Table 1.

At early years, the processing of caliche was done in mobile installations, with stirred and heated tanks, which was applicable to high-grade caliche ores with up to 50% of nitrate minerals (Lauterbach, 2004). When the amount of soluble minerals decreased in the caliche, new techniques were developed. The Shanks technology, introduced in 1878 used double wall tanks heated with vapour. In 1920, the Guggenheim process was introduced, which is characterized by the grinding of the caliche and lower temperatures (Valencia et al., 2008; Wisniak and Garcés, 2001). Nowadays, the gradual diminishing of caliche's grades and an increase of the costs have resulted in the implementation of heap leaching, which was productively applied to this mineral at the beginning of 1990's, almost 20 years later than to the metallic minerals (Fleming, 1992; Valencia et al., 2008).

Although the heaps are watered mainly with fresh water, in actual operations, mixed solutions between intermediate solutions from leaching downstream steps and fresh water are also used (Wheeler, 2010). Due to the exploitation of this mineral done in places where the fresh water resources are scarce; the feasibility to use seawater as main leaching agent in the process has been studied (Taboada et al., 2012). In a similar approach, Torres et al. (2013) studied the use of seawater in the leaching of residual salts from evaporation ponds to recover remaining nitrate.

In industrial operations, the caliche heaps reach heights of up to 10 m and are irrigated by aspersion with a nominal irrigation rate of 2 L/h/m<sup>2</sup>. The process is divided into 3 steps: impregnation, where the material is wetted; leaching, where the soluble species are dissolved and collected as enriched solution; and washing, where the remainder soluble species are removed using a leaching agent with low ion concentration. Each heap is formed by the accumulation of 600,000 to 900,000 t of caliche mineral. In the leaching step, fresh water or half-enriched solutions are used as leaching agents. The percolated solutions are transported to the iodate extraction plant, which by a reduction step retrieves iodine. The resulting solution is further conducted to evaporation ponds, in which the nitrate is crystallized mainly as sodium nitrate. In a next step, sodium nitrate reacts with potassium chloride, obtained from salt deposits, to produce potassium nitrate as final product, which is used as a fertilizer (Fig. 1). More details about the process can be reviewed in Pokorny and Maturana (1997).

The needs of water resources for the mining operations are very high for the arid region of Antofagasta, consuming about 60% of the fresh

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## Nomenclature

### Roman letters

$A$	Cross-sectional area, $m^2$
$C$	Concentration, $kg/m^3$
$C_s$	Solubility concentration, $kg/m^3$
$H$	Initial column height, $m$
$k$	Mass transfer coefficient, $m/h$
$k_r$	Dissolution coefficient, $1/h$
$kp$	Product of solubility <sup>1</sup>
$M$	Molar quantity, $mol$
$N$	Number of data
$N_p$	Number of particles
$q$	Irrigation rate, $m^3/m^2/h$
$r$	Particle radius, $m$
$t$	Time, $h$
$V$	Volume, $m^3$
$X$	Molar concentration, $mol/L$

<sup>1</sup> The product of solubility has units of molar concentration raised to the power of the sum of the stoichiometric coefficients of the products in the equilibrium.

### Greek letters

$\alpha$	Mass soluble fraction
$\epsilon_w$	Water porosity
$\rho$	Particle density, $kg/m^3$

### Subscripts

$i$	Output, current tank
$i - 1$	Input, previous tank
$m$	Mineral

water in their processes. Considering that the availability of water is scarce in Northern Chile, several mining industries are gradually consuming seawater in their operations. In most of the cases, after desalination process the seawater is pumped to the mining plants, located at more than thousand metres above sea level. The desalination treatment leads to an increase of energy costs and may cause some pollution problems when water with higher salinity is returned to the sea. Given this scenario, the direct use of seawater is being a focus of research in the field of sustainability, especially for caliche heap leaching, where leaching agents have, in many cases, concentration higher than that in the seawater. Depending on the size of operation, the exploitations of caliche are between 4 and 19 million of tonnes per year, for which the ratio leachant/caliche is around  $0.8\text{--}1.2\text{ m}^3/t$  of heaped caliche and with global water consumption for the whole process from 800,000 to

$7,000,000\text{ m}^3$  per year, which does not consider the recirculation of water.

In contrast to the leaching of metallic ores, where the process is mediated by chemical reactions, the caliche treatment is governed by simple dissolution (Valencia et al., 2008). Another important difference is that the fraction of soluble species may reach up to 40% or more. When the soluble minerals are removed by the leaching solution, the pieces of caliche mineral may collapse, reducing their size and thus decreasing the heap height along the leaching. Reductions about 20% can be reached in actual operations.

Regarding the leaching modelling, heap leaching process is a complex system that includes physical and chemical phenomena and interactions between them, such as: dissolution, precipitation, chemical reactions, stagnant liquid, diffusion, and convective and dispersive transport among other phenomena. There is a great interest to develop mathematical models, in order to simulate, design, optimize and understand the process (McBride et al., 2012). Modelling of caliche leaching is more complicated because caliche mineral is formed by a mixture of minerals with different equilibrium constants and dissolution rates and a high fraction of soluble minerals that produce significant changes in the heap height (Gálvez et al., 2012).

Leaching is the starting point in the hydrometallurgical mining chain thus improvements in its performance may reflect global benefits. There are different strategies of modelling that permit the representation of real phenomena using mathematical relations, like empirical, phenomenological and hybrid models.

Mathematical models have been widely used in chemical processes and insofar that the computational capabilities are developing, the use of more complex models, such as phenomenological ones, including several processes simultaneously, is becoming more common. Other types of models are the hybrid ones, which combine experimental observations with theoretical knowledge giving analytical expressions for the main processes. They are useful in process optimization, where the model is typically solved hundreds or thousands of times (Mellado et al., 2009).

In spite of the importance of heap leaching of caliche, no data is found in the open literature about the leaching of this mineral. There are possibly some studies about this topic, but they are not available for the scientific community.

The aim of this study is to evaluate the feasibility to use seawater in column leaching of caliche. Therefore, leaching experiments in columns were carried out varying the irrigation rate, the height of the column, and the leaching agent. The highly soluble minerals, such as nitrate and iodate, are rapidly leached. The results were analysed using a phenomenological model previously developed by Gálvez et al. (2012) with the objective to validate the model. For the other ions such as sulphate and chloride, where the dissolution is controlled probably by the effect of the ion common, a new model was developed in order to understand the processes occurring in the column. This model includes dissolution and precipitation of the ions when they are transported along the column. Sodium sulphate crystallizes at the column bottom and in the bottles used for leachate recollection.

## 2. Experimental procedure

### 2.1. Leaching column experiments

The experiments were performed in columns of 0.2 m in diameter. The caliche was loaded in batches, distributing homogeneously the mineral to avoid stratification and channelling. The caliche was irrigated during 20 days, testing different leaching agents, bed heights and irrigation rates (Table 2).

The process of leaching begun with a wetting stage, where the caliche was irrigated with the leaching agent until leachate started to flow out from the bottom. This point was considered as the leaching start. Upon completion of leaching, the material was downloaded and

**Table 1**

Common water soluble species in caliche minerals.  
Extracted from Jackson and Ericksen (1994).

Ion	Mineral	Formula
Nitrate	Nitratine	$NaNO_3$
	Niter	$KNO_3$
Sulphate	Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
	Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$
	Glauberite	$CaNa_2(SO_4)_2$
	Gypsum	$CaSO_4 \cdot 2H_2O$
Chloride	Anhydrite	$CaSO_4$
	Halite	$NaCl$
	Sylvite	$KCl$
Iodate	Lautarite	$Ca(IO_3)_2$
	Hectorfloresite	$Na_3(IO_3)(SO_4)_4$

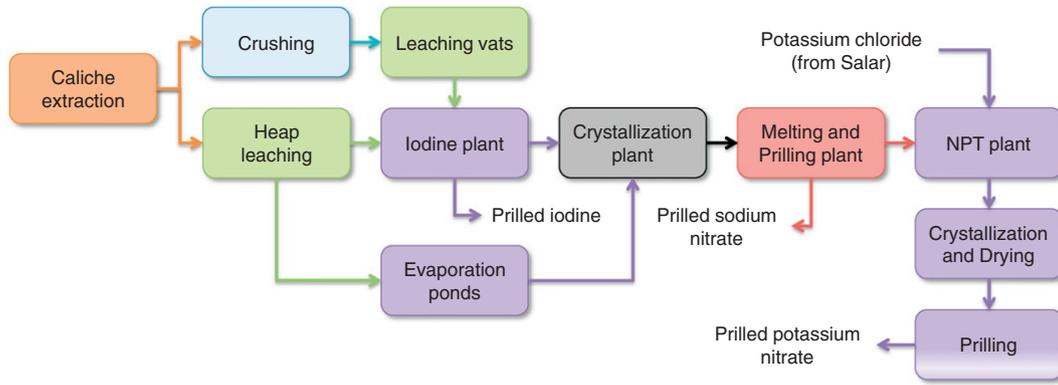


Fig. 1. Flowsheet of caliche processing. Adapted from Sirocco Mining (2012) and SQM (2012).

solid samples were taken to determine moisture and composition. The irrigation rates employed in wetting and leaching stages were equal to values listed in Table 2.

2.2. Sampling and chemical analysis

Leachate was collected at the column bottom in a plastic bottle, from which a 300-mL sample was taken 12 h after leaching start, and afterwards, samples every 24 h were collected. Solid samples also were taken, from both initial caliche and residue, quartering dried material to choose 300 g of representative sample. The solid samples were mixed with distilled water and stirred in a relationship solid:liquid (kg:L) 1:10 for 6 h; the mixture was then filtered and the liquid chemically analysed.

Nitrate was analysed by UV molecular absorption spectroscopy (UV2, Unicam UV/Vis). The sulphate content in the samples was determined by gravimetry. Sodium, potassium, magnesium and calcium were measured by atomic absorption spectroscopy (220FS, Varian) and chloride and iodine through volumetry. Perchlorate was determined with an electrode-specific method and density by pycnometry.

2.3. Caliche

The mineral employed in the leaching experiments was obtained from Northern Chile. In order to avoid a possible obstruction of the columns, the material was firstly screened, choosing particles with a size above 2.36 mm in diameter. The soluble chemical composition of screened caliche is listed in Table 3.

A granulometric analysis of the caliche mineral used in the column experiments was carried out using the Tyler sieves: 0.525", 0.371", 4, 6, and 8. From the granulometric curve, which is shown in Fig. 2, a value of 6.8 mm was determined for the median.

2.4. Leaching agents

The seawater (SW) used as leachant was extracted from the Antofagasta's coast (Chile), using a submarine outfall. The water was filtered with a 0.2 µm pore diameter membrane filter and stored in plastic

Table 2 Column leaching experiments run for 20 days.

Leaching agent	Irrigation rate (m³/m²/h)	Bed height (m)
Seawater	0.003	0.6
Seawater	0.006	0.6
Seawater	0.003	1.0
Tap water	0.006	1.0
Rich solution	0.006	0.6
Seawater + Rich solution	0.006	1.0
Seawater + Rich solution	0.004	0.8

containers. Seawater was protected from the light to avoid the proliferation of algae. In order to approach actual heap leaching processes, where the leaching solutions are recirculated, loaded solutions also were employed, which were prepared by stirring caliche with seawater at a solid:liquid ratio (kg:L) of 1:1 for 1 h. After a decantation for one day, the supernatant solution was separated and used as a leaching solution (LX). From this rich solution another leaching solution (diluted solution, DS) was obtained by diluting the rich solution with seawater in a 1:1 ratio. Tap water (TW) was also used without further treatment. The chemical analysis of these leaching solutions is shown in Table 4.

3. Mathematical models used in the evaluation of the experiments

3.1. Model for the highly soluble species

It is expected that the dissolution of the highly soluble species such as nitrate and iodate controls the decreasing of particle size. For both ions, a previously developed model (Gálvez et al., 2012) was applied to evaluate their outlet concentration. In this 1-D model, the column is represented as well-stirred reactors (mini-column) in series. An important characteristic in the leaching of caliche ores is the reduction of particle size provoked by collapsing. In the model, the diminution of particle size insofar leaching progresses is based on a mass balance of the particle with the help of the Brunner and Tolloczko model (Dokoumetzidis and Macheras, 2006). Eq. (1) shows the mass balance on the particle.

$$\frac{dr_i}{dt} = -\frac{k}{\alpha\rho}(C_s - C_i) \tag{1}$$

The dissolution of the ions in terms of the concentration along the heap height, is determined by a mass balance in the column (Eq. (2)):

$$\frac{dV_m C_i}{dt} = qA(C_{i-1} - C_i) - 4\pi r_i^2 N_p \alpha \rho \frac{dr_i}{dt} \tag{2}$$

where the left hand side term represents the accumulation, the first term on the right hand side considers the advection from a reactor to the next one, and the last term refers to the dissolution of ion. This model was formulated to describe the dissolution of very soluble species contained in the caliche minerals, such as nitrate and iodine.

Table 3 Chemical composition (%w/w) of caliche.

Anions						Cations			
NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	IO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	BO <sub>3</sub> <sup>3-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
3.674	9.410	0.046	4.194	0.036	0.060	5.575	0.579	0.971	0.597

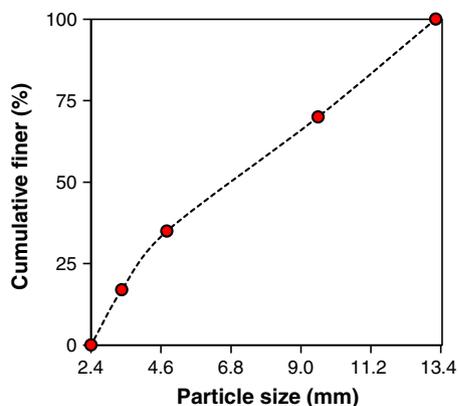


Fig. 2. Experimental particle size distribution of caliche. The dashed line was drawn to facilitate the view.

The particle radius and heap height diminution are also addressed by the model. Other components, as chloride or sulphate, cannot be described for this model because the dissolution of these components is probably dependent of sodium concentration. For this reason, a new model was developed to handle these species, which is described below.

### 3.2. Chemical reaction modelling

The composition of the caliche is very complex, with several soluble minerals, which are in some cases a compound formed by several cations. The most frequent soluble anions are nitrate, chloride, and sulphate; while the main soluble cations are sodium, calcium, magnesium, and potassium. At the beginning of the leaching process, the highly soluble sodium nitrate is leached increasing strongly the concentration of sodium. Therefore, some minerals containing sodium, such as sodium sulphate and sodium chloride may reach the saturation and precipitate (Cisternas, 2009).

A model for taking into account the effect of the common ion and its implication on the less soluble species was developed, which comprises the anions sulphate, chloride, and nitrate and the cation sodium. This is an important simplification, since other cations and anions are also present in the soluble minerals. The modelled system is a one-dimensional column, located at the heap centre, which is formed by well-stirred reactors (mini-column) in series. The model considers the chemical reactions in each reactor (dissolution and precipitation) and the transport of solute from a reactor to the next one. This simplified system comprises five well-stirred reactors in series, three sodium minerals and four ions (sulphate, nitrate, chloride, and sodium). Equations are detailed in Appendix A.

## 4. Results and discussion

### 4.1. Results of the experiences

The performance of the leaching experiments was evaluated by using the concentration of the leachate collected at the column bottom. Although sampling was done every 12 h at the beginning and 24 h afterward, in the figures the variation of the concentration is shown in

terms of the volume ratio (volume of leaching solution passed through the column divided by initial bed volume,  $V_1/V_B$ ). This is done for comparing directly the performance of the different experiences, which were performed for different irrigation rates and have different heights (volume). No significant changes were noticed after the volume ratio of 2 for all ions and experiments; hence the concentrations collected are showed up to that point.

The ions considered in the study were: nitrate, sulphate, iodine, sodium, potassium, magnesium, chloride, perchlorate and calcium. Fig. 3 shows the outlet concentration for a leaching column irrigated with seawater in general may be observed that the highly soluble ions are removed rapidly; their concentrations reached low values for rather low volume ratios; 0.5 for nitrate and about 0.7 for iodine and perchlorate.

Final levels of most of the ions resulted similar to the concentrations of the feeding, as can be compared with the data of Table 4. At the end of the experiments, calcium and sulphate show concentrations higher than that at the feed.

An interesting situation is observed for the ion sulphate, its concentration increases at the beginning, reaching a peak at volume ratio of about 0.3 and decreasing continuously afterwards. This phenomenon occurs as a consequence of the high dissolution rate of sodium nitrate. The fast dissolution of nitrate provokes an increase of free sodium levels in the column, which interacts with sulphate and resulting in a precipitation of sodium sulphate. This situation was corroborated through the observation of crystals at the bottom of the column that appeared after 4–5 days of leaching. Subsequent chemical analysis of these crystals ratified the composition of sodium sulphate. An important part of sodium comes from sodium nitrate dissolution; hence, the levels of sodium decrease rapidly at initial stages due to the high solubility of sodium nitrate. For this reason, when part of the highly soluble sodium nitrate has been removed and the sodium concentration declines, the concentrations of sulphate and chloride (in some extent) increase.

The different behaviours of calcium leaching in comparison with the other ions are notorious. In all the columns, the calcium concentration is constantly increasing, this could be due to the calcium sulphate minerals present in caliche (as gypsum and anhydrite) have very low solubilities and the outlet concentration of calcium is controlled by the sulphate levels, therefore the calcium concentration increases when sulphate concentration decreases. For magnesium and potassium, the concentration patterns are similar and their dissolution rates appear to be controlled by their own kinetics, which showed to be slow.

Comparing the results of the columns irrigated with seawater and tap water, no big differences are observed. As expected, the outlet concentrations for chloride and sodium at long time are higher for the columns irrigated with seawater, because the content of these ions in the leaching solution (seawater) is higher (Table 4). For sulphate, the levels in SW and TW were similar and low; however the dissolution rate using SW as a leachant is slower than TW. This behaviour is explained by the sodium concentrations in leaching agents, which in SW is higher and this ion is controlling the releasing of sulphate, therefore, retarding its removal from the columns.

Considering all experiments, the lowest concentration levels for all ions were reached by the column watered with TW, while the highest ones by the LX column. The key to explain this difference of behaviour that was observed clearly at long times is the composition of these

Table 4  
Chemical composition ( $\text{kg/m}^3$ ) of leaching solutions.

Leaching solution	Anions						Cations			
	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{IO}_3^-$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{BO}_3^{3-}$	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
SW	0.211	2.661	0.000	19.709	0.120	0.161	11.124	0.361	1.576	0.171
TW	0.000	0.130	0.010	0.350	0.010	0.000	0.190	0.020	0.030	0.090
DS	15.017	28.060	0.099	39.131	0.011	0.197	33.760	2.707	4.505	0.417
LX	29.300	53.716	0.198	59.879	0.012	0.384	56.274	5.023	7.697	0.465

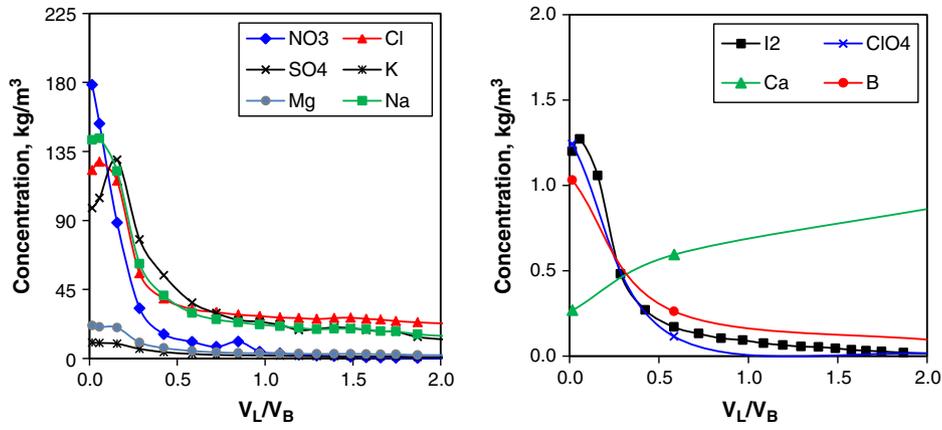


Fig. 3. Outlet concentration of major and minor ions from column leached with SW,  $q = 0.003 \text{ m}^3/\text{m}^2/\text{h}$  and  $H = 0.6 \text{ m}$ . Lines were added to facilitate the view.

leaching agents. It is possible to remove almost all ions (including sulphate) with relatively low water volume passed through the column only with TW. However, small differences were observed between columns irrigated with SW and TW. Other minor ions such as perchlorate and boron do not show big differences between different leaching agents. In general, the concentration levels were higher for seawater and lower for tap water.

The release of ions in the column with a higher irrigation rate is faster, reaching the steady state after a short time. However, if the irrigation rate is duplicated, this does not mean that the removal rate is increased in the same proportion, because other factors are involved such

as solubilities of controlling species, intrinsic dissolution kinetics, and mass transfer resistance. Using a solution with a higher concentration of ions than seawater and tap water, the concentration levels are higher because the extractive capability is less. As could be expected, LX solution had the lowest extracting capability, because the concentration of all ions was the highest, whereas for experiences leached with DS, an intermediate behaviour between SW and LX was obtained (Fig. 4).

In the basis of the dissolution trend, it is possible to divide the ions in 3 groups depending on their behaviours: i) the most soluble ions, like nitrate, iodine and perchlorate, exhibit a rapid concentration reduction, with the highest values at the beginning of experience, ii) intermediate

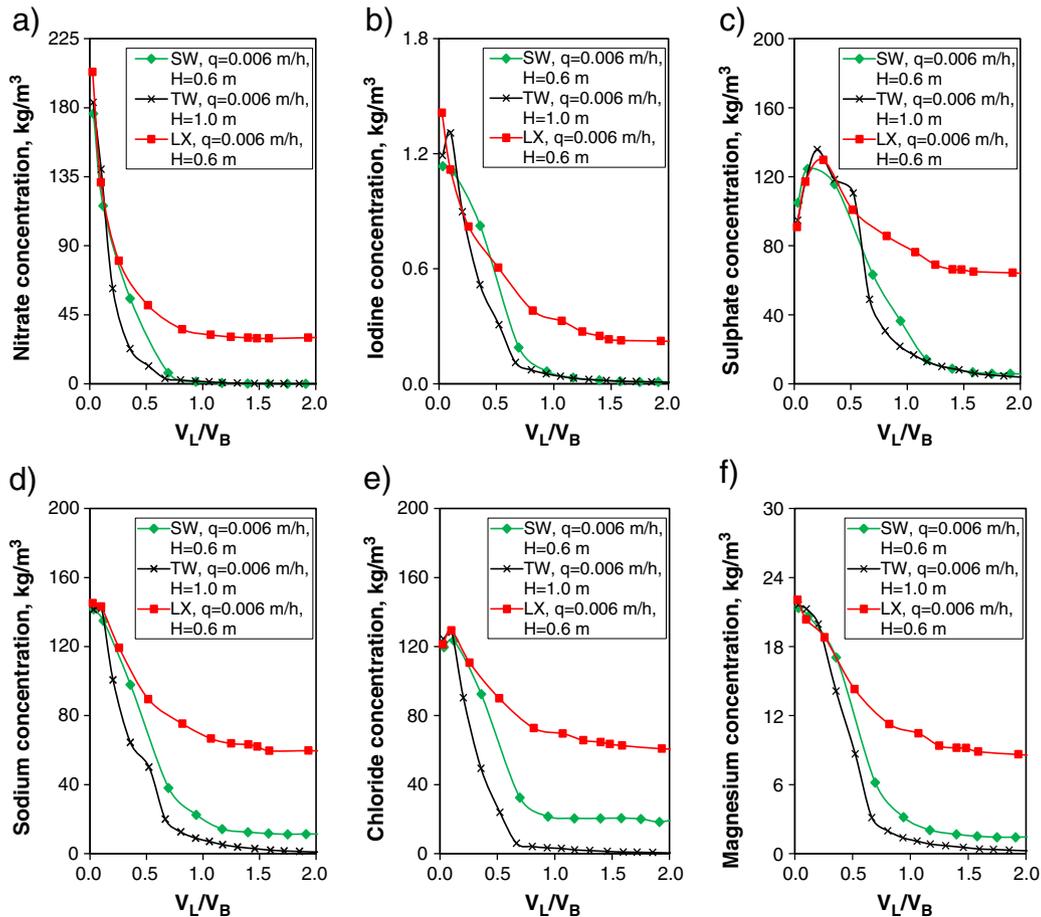


Fig. 4. Experimental dissolution of selected ions in columns irrigated with seawater, tap water and charged solution. Lines were added to facilitate the visualization.

ions, such as sodium, potassium and magnesium, where the diminution of concentration started with certain delay depending on the concentration of other ions, and iii) the less soluble species as sulphate and chloride, which reach the saturation and start to precipitate within the column due possibly to the high sodium concentration existent in the column in the initial period; when the sodium concentration decreases these ions start to dissolve.

In these column experiments a small particle size was used (particle diameter of 6.3 mm). Therefore, it is expected that the influence of the particle was small and the dissolution of the different ions in a large extent is controlled by the solubility limitations and dissolution rate.

#### 4.2. Evaluation using the phenomenological model

##### 4.2.1. Fitting of mathematical model

A previously developed model (Gálvez et al., 2012) was evaluated using the experimental data collected in the present work. Nitrate and iodine species were chosen, since both are highly soluble ions and therefore its dissolution rate is less dependent of the concentration of other species forming caliche. Table 5 presents the parameter values used as input data for the modelling. Within the data listed, water porosity and porosity are estimated from experimental observations. The nitrate and iodine fractions were determined as the average of the respective fractions for the caliches is loaded in the seven columns.

In the phenomenological model, the mass transfer coefficient ( $k$ ) was fitted independently for each experiment and each ion (nitrate and iodine) by using the least square method. The function to minimise is, in this case, the square sum of the difference between the experimental and model calculated concentration values. The  $k$  values obtained in the fitting process are listed in Table 6.

The importance of  $k$  is that it describes the rate at which the soluble ions are dissolved. Higher values of  $k$  indicate that the ion solubilisation is faster. The results show that the mass transfer coefficient for nitrate is around three times greater than for iodine in all experiences. The concentration at column bottom for both ions is initially very high, falling drastically when  $V_L/V_B$  is about 0.25 for nitrate and about 0.50 for iodine. It is clearly observed that among the seven experiences for each ion those columns with a high irrigation rate show higher mass transfer coefficients (Fig. 5).

The quality of the fitting process is determined by using the relative standard deviation (RSD), which is calculated in terms of difference between experimental and modelled concentrations. In order to compare these values between ions (nitrate and iodine) the standard deviation was divided by the solubility concentration for each of these ions,  $C_s$ . This is shown in Eq. (3).

$$RSD = \frac{100}{C_s} \sqrt{\frac{\sum (C^{exp} - C^{mod})^2}{N}} \quad (3)$$

As can be seen in Table 6, the level of fitting obtained between the modelled and experimental concentrations for both nitrate and iodine was, in general, good with most of the relative standard deviations about 3.5% for nitrate and about 3% for iodine. The highest deviations could be attributed to experimental issues such as channelling in the

**Table 5**

Values employed in the simulation.

Parameter	Value
Particle diameter, m	0.006
Mineral density, kg/m <sup>3</sup>	1900
Water porosity in column	0.08
Porosity	0.45
Nitrate fraction in caliche	0.037
Iodine fraction in caliche	0.00046
Number of well-stirred reactors in the model.	4

**Table 6**

Mass transfer coefficient,  $k$ , of nitrate and iodine using phenomenological model for each experience.

Leaching agent	Irrigation rate (q), m <sup>3</sup> /m <sup>2</sup> /h	Column height (H), m	Nitrate		Iodine	
			$k$ , m/h	RSD, %	$k$ , m/h	RSD, %
SW	0.003	0.6	1.61E–5	4.5	0.60E–5	2.5
SW	0.006	0.6	2.95E–5	2.4	1.13E–5	1.0
SW	0.003	1.0	1.34E–5	8.0	0.47E–5	6.7
TW	0.006	1.0	1.99E–5	3.9	0.90E–5	2.3
LX	0.006	0.6	3.36E–5	3.0	0.94E–5	2.9
DS	0.006	1.0	3.14E–5	3.1	0.97E–5	3.7
DS	0.004	0.8	1.19E–5	3.9	0.52E–5	4.9

bed or retention of leaching solution. However these small variations are acceptable, considering the normal fluctuations observed in column leaching experiments.

##### 4.2.2. Effect of operational variables on mass transfer coefficient

Operational variables such as irrigation rate, column height, and type of leaching solution were studied in the column experiments. Particle diameter was not studied, since all the columns were loaded with the same material size. The coefficient of mass transfer is predominantly determined by the irrigation rate, since a larger rate implies that the resistance to mass transfer is reduced. Therefore, it is expected that the mass transfer coefficient for experiments performed with of highest irrigation rate was the largest, which is physically consistent due to the higher rates provoking a thinning of liquid layer overlying particles. On the other hand, the effect of the other variables would be small, since the leaching solution is taken into account in the particle balance (Eq. (1)) and the column height by the mass balance of the bed (Eq. (2)).

The obtained mass transfer coefficients proved to be highly dependent of irrigation rate; the lowest values for the coefficient were found for the experiments with an irrigation rate of 0.003 m<sup>3</sup>/m<sup>2</sup>/h and the highest values for irrigation rate of 0.006 m<sup>3</sup>/m<sup>2</sup>/h. The mass transfer coefficient as a function of the irrigation rate is shown in Fig. 6 for nitrate and iodine. In both cases the trend lines are very similar. An increase of the irrigation rate by a factor 2 increases the mass transfer coefficient by the same factor.

When similar plots were done for studying the effect of leaching agents, it was found that no correlation exists between the mass transfer coefficient and the type of leaching solution. The same conclusion was obtained when the impact of the initial height of the column on the mass transfer coefficient was studied; no correlation was observed.

According to the above studies, the model was validated in terms of that the values of the mass transfer coefficient obtained for the seven experiences correspond with the trends that could be expected from the theory.

#### 4.3. Modelling of ionic interaction through chemical reaction model

Outlet concentration for sulphate and chloride presents different behaviours to that shown by nitrate and iodine. In the initial period the concentration of sulphate and chloride is increased when the concentration of the sodium and nitrate decreases. This type of behaviour cannot be described by the phenomenological model used for the nitrate and iodine. Due to the different trends of dissolution between the ions nitrate and iodine for a side and sulphate and chloride for the other side, a new model was developed for the last group, considering the chemical reactions that are occurring in the column. These interactions include the dissolution of minerals and precipitation of a part of them when the solubility product is exceeded.

The objective of this simplified modelling is to reproduce the trends observed in the column experiments, overcoming phenomena related with chemical interaction between ions that share common ion, which in this case is sodium. Sodium is associated to nitrate, sulphate

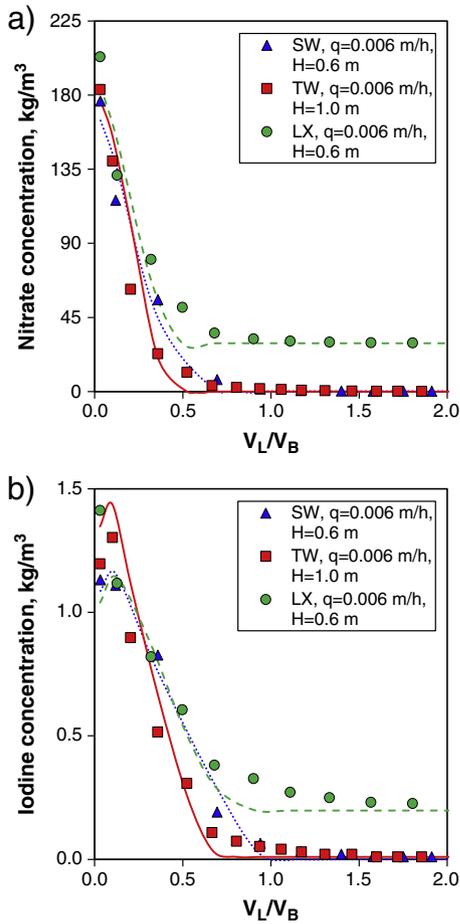


Fig. 5. Concentration of a) nitrate and b) iodine in experiments irrigated with poorer solutions. Markers are experimental data and lines are phenomenological model fitted (dotted: SW, solid: TW and dashed: LX).

and chloride; since the solubility of sodium nitrate is high (around 478 kg/m<sup>3</sup> as a compound pure) compared with sodium sulphate (205 kg/m<sup>3</sup>) and sodium chloride (320 kg/m<sup>3</sup>), it is expected that the solubility product for this mineral was reached at the initial period, when the concentration of sodium is very high in the leachate. In order to keep the model very simple, it is assumed that the caliche is formed by three soluble minerals (sodium nitrate, sodium sulphate, and sodium chloride) and only four ions (sodium, nitrate, sulphate, and chloride). It is assumed that the column is formed by five well-stirred reactors in series, for each reactor, four mass balance equations are required, one for each ion. In addition three dissolution/precipitation equations, one for each mineral, are needed.

The amount of soluble minerals was determined by analysis of the solid samples. It was assumed that nitrates and chlorides form minerals only with sodium, for the soluble sulphate only a fraction is considered; sodium sulphate. Calcium sulphate is also found in the caliche in large amounts, but this mineral starts to be dissolved in the last part of the leaching process. The solubility constants were determined using the concentrations existent in the leachate at the beginning of the leaching process, when it is expected that the leaching solution is saturated with respect to sodium sulphate and sodium chloride. In the simulations, it is assumed that the solubility constant keeps the same value along all the leaching process, in spite, it is probable that the value of the solubility constant changes along the process, when the activities change due to the decreasing ionic strength of the solution. It is also assumed that the dissolution of the sodium nitrate is not limited by its solubility, due to its high value.

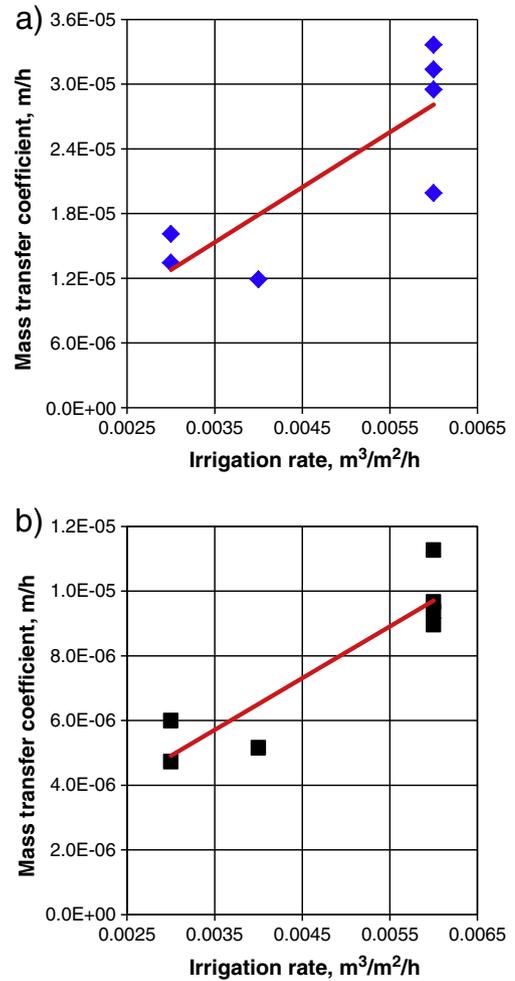


Fig. 6. Effect of irrigation rate on the mass transfer coefficient. a) Nitrate and b) iodine.

The dissolution constants for the sulphate, nitrate, and chloride sodium minerals ( $k_{r1}$ ,  $k_{r2}$  and  $k_{r3}$ ) in the model (see Appendix A) were fitted with the experimental data using the least square method. In the seven cases, the model was able to reproduce the trends observed in the outlet concentration with time. Some fitting results are shown in Fig. 7 for column experiments leached with SW, TW and LX (operational details are set forth in the caption of Fig. 7). The model reproduces the more important characteristics of the experimental data; the increase of the sulphate and chloride concentration at the beginning, once that part important of the sodium nitrate has been dissolved and removed from the column.

These results are encouraging, in order to develop a model that may describe the outlet concentration from heap leaching with time. However, the modelling requires a lot of information, which are not available, at least, in the public technical literature. Mineralogy of the caliche, solubility products of these minerals, and dissolution rates are some of the information that is fundamental for this kind of chemical simulation. Due to that the solutions having a large ionic strength, which varies with time, the determination of the activity coefficients is also very important.

In these simulations, due to the rather small particle size used, it was assumed that the soluble minerals were directly accessible to the leaching agents from the beginning. In the practical operations of heap leaching the size of the particles may be of the order of 1 m or more. Therefore, in a rigorous modelling these factors have to be considered. But these results show that this type of modelling is necessary in order to understand the leaching of caliche and its complexity.

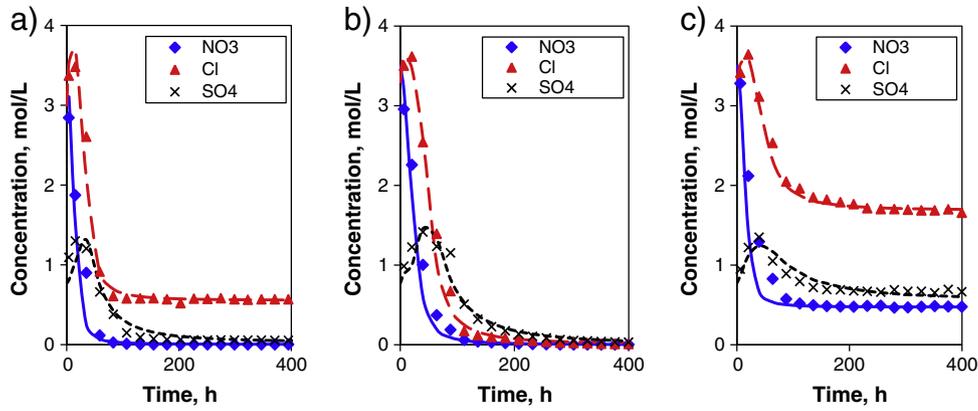


Fig. 7. Experimental (markers) and simulated outlet concentration (lines) using a chemical reaction model for columns: a) SW,  $q = 0.006 \text{ m}^3/\text{m}^2/\text{h}$ ,  $H = 0.6 \text{ m}$ , b) TW,  $q = 0.006 \text{ m}^3/\text{m}^2/\text{h}$ ,  $H = 1.0 \text{ m}$  and c) LX,  $0.006 \text{ m}^3/\text{m}^2/\text{h}$ ,  $H = 0.6 \text{ m}$ .

## 5. Conclusions

Column leaching experiments were done, which showed the differences of dissolution behaviours of the distinct species forming caliche. Nitrate and iodine leave the column quickly, regardless the operational conditions employed. The dissolution of potassium and magnesium is apparently controlled by their solubilities. Perchlorate compounds have the highest solubilities and for this its concentration decreases abruptly.

Variation of outlet concentration of nitrate and iodine was analysed using a previously developed phenomenological model. The results show that the model may describe adequately the behaviour for these ions in the leaching process, fitting only the mass transfer coefficient ( $k$ ) for each column, and demonstrating that this parameter is independent of the leaching agent and column height, nevertheless a correlation of irrigation rate and the mass transfer coefficient was observed, which follows the theoretical behaviour that  $k$  increases as the irrigation is higher.

On other hand, the experiments show that precipitation of sodium sulphate occurred in the initial stages of leaching. This reaffirms the concept that within a heap, there is a dynamical dissolution/precipitation process during leaching, controlled by the different solubilities of minerals that are forming caliche. In order to contribute to the understanding of this phenomenon, a new model was developed and tested, with good levels of agreement. The model was applied to the minerals containing sodium in the caliche, simplified to 3 species: sodium nitrate, sulphate, and chloride. It includes dissolution and precipitation of these minerals.

The results of experiments show that it is possible to use seawater, without desalination, directly in the leaching of caliche minerals. No important differences are found in the recovery of most of the ions in the caliche; in particular for nitrate and iodine that are the most important products. However the effect of seawater on the materials (pumps and piping) would be studied in detail. In future work, it is planned to improve the chemical model for including the mineralogy of the soluble species in the caliche, the activity coefficients and applied the model for large particles, which are used in the industrial heap leaching (Run of Mine, ROM).

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## Appendix A

The system is then formed by 3 sodium minerals,  $M$  (amount in moles in each reactor) and 4 ions,  $X$  (concentration in moles per litre),

in the equations  $i$  is the reactor. The mass balance for the ions in each reactor is:

Ion sulphate

$$\frac{dX_{1,i}}{dt} = \frac{1}{V\varepsilon_w} \left[ qA(X_{1,i-1} - X_{1,i}) - \frac{dM_{1,i}}{dt} \right]. \quad (\text{A1})$$

Ion nitrate

$$\frac{dX_{2,i}}{dt} = \frac{1}{V\varepsilon_w} \left[ qA(X_{2,i-1} - X_{2,i}) - \frac{dM_{2,i}}{dt} \right]. \quad (\text{A2})$$

Ion chloride

$$\frac{dX_{3,i}}{dt} = \frac{1}{V\varepsilon_w} \left[ qA(X_{3,i-1} - X_{3,i}) - \frac{dM_{3,i}}{dt} \right]. \quad (\text{A3})$$

Ion sodium

$$\frac{dX_{4,i}}{dt} = \frac{1}{V\varepsilon_w} \left[ qA(X_{4,i-1} - X_{4,i}) - 2\frac{dM_{1,i}}{dt} - \frac{dM_{2,i}}{dt} - \frac{dM_{3,i}}{dt} \right]. \quad (\text{A4})$$

For the sodium minerals the dissolution equations are:

Sodium sulphate

$$\frac{dM_{1,i}}{dt} = -k_{r1}M_{1,i} \left( 1 - \frac{X_{4,i}^2 X_{1,i}}{Kp_1} \right). \quad (\text{A5})$$

Sodium nitrate

$$\frac{dM_{2,i}}{dt} = -k_{r2}M_{2,i} \left( 1 - \frac{X_{4,i} X_{2,i}}{Kp_2} \right). \quad (\text{A6})$$

Sodium chloride

$$\frac{dM_{3,i}}{dt} = -k_{r3}M_{3,i} \left( 1 - \frac{X_{4,i} X_{3,i}}{Kp_3} \right). \quad (\text{A7})$$

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