



Modeling validation of caliche ore leaching using seawater



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ABSTRACT

Leaching column experiments of caliche were performed using seawater as the leaching agent because the caliche deposits are located in Northern Chile where water resources are scarce. The use of seawater without desalination is an attractive alternative for mining operations. The experimental recoveries of different ions were modeled using a hybrid model, which uses empirical information and fundamental principles. The following ions were considered: nitrate, iodine, sulfate, chloride, sodium, potassium and magnesium. The model explicitly considers different column heights, irrigation rates, and leaching agents. A sensitivity analysis showed that parameters associated with the particle level predominantly determined the calculated recoveries. The predictive capability was also tested, and the results were generally good, except for the sulfate ion, the dissolution of which was controlled by the presence of other ions.

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1. Introduction

Caliche, also termed nitrate deposit, is a mineral composed of a high proportion of water soluble salts, of which nitrate, sulfate, and chloride are the main anions and sodium, magnesium, potassium, and calcium are the main cations. Nitrate and chloride are mainly found as sodium nitrate (nitratine) and sodium chloride (halite), respectively. Sulfate is frequently associated with a wide range of cations, the most relevant being the following: calcium, sodium, magnesium, and potassium. It is commonly found in complex salts, such as bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), and glauberite ($\text{CaNa}_2(\text{SO}_4)_2$). The largest sources of calcium are sulfates in the form of gypsum and anhydrite. Magnesium and potassium are associated with sulfate complex salts, such as bloedite and polyhalite. Sodium is present as chloride, nitrate, and sulfate. Another component, which occurs in lower proportions but has a high economic value, is iodine, which is found as lautarite ($\text{Ca}(\text{IO}_3)_2$) and hectorfloresite ($\text{Na}_9(\text{IO}_3)(\text{SO}_4)_4$) (Ericksen, 1983; Jackson and Ericksen, 1994; Pokorný and Maturana, 1997). Quartz and other silicates compose the insoluble fraction.

The caliche mineral is exploited by both vat and heap leaching; the latter has increased its importance due to the gradual diminution of grades (Wisniak and Garcés, 2001; Lauterbach, 2004). The heaps are irrigated with water or a mix of water and intermediate solutions drawn from downstream stages of the process (Wheeler, 2010). Currently, the feasibility of using seawater as the leaching agent has been discussed because caliche processing is performed in locations where fresh water resources are scarce. The use of seawater in metallic

mining in these areas is also under consideration (Taboada et al., 2012; Cochilco, 2012).

In contrast to the leaching of metallic ores, where the dissolution process is mediated by chemical reactions, caliche treatment is governed by simple dissolution (Gálvez et al., 2012; Valencia et al., 2008; Wadsworth, 1987). This difference leads to distinct operational conditions. Moreover, due to the high content of soluble species in the caliche, when the particles are dissolved, they decrease in size and thus, the heap height also decreases with time. Height reductions exceeding 20% can be achieved in actual operation.

Frequently, heap leaching is the first stage of mineral hydrometallurgical processing; therefore, a better understanding of the involved phenomena in this stage may help to improve the process in its totality, and optimal conditions of operation could be reached. Heap leaching is a complex system due to the simultaneous interaction of physical and chemical phenomena, such as simple dissolution of the mineral species, chemical interactions of the ions present in the leaching solution, presence of zones with stagnant solution in the heap, convective, diffusive, and dispersive transport for liquids and gases, heat generation and transport (Havlik, 2008; McBride et al., 2012).

For a better understanding of a process and its management or optimization, modeling is a useful tool by which a phenomenon or process can be studied. Models may be phenomenological or empirical and its selection depends on the objective to reach. Phenomenological models are appropriate when the interest is centered on the understanding of processes. Conversely, empirical models may be suitable when the focus is on optimization or for operations where the model must be solved hundreds or thousands of times. However, the small amount of information that can typically be obtained from this type of model is a limitation that has motivated the development of another family of

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Table 1
Treatments performed in caliche column leaching.

Experiment	Leaching agent	Irrigation rate (m ³ /m ² /h)	Bed height (m)
SW3S	Seawater	0.003	0.6
SW6S	Seawater	0.006	0.6
SW3L	Seawater	0.003	1.0
TW6L	Tap water	0.006	1.0
RS6S	Rich solution	0.006	0.6
DS6L	Seawater + rich solution	0.006	1.0
DS4M	Seawater + rich solution	0.004	0.8

expressions named hybrid models. The hybrid models, also named empirical knowledge-based models, combine relations obtained from experimental data with expressions based on fundamental principles. For this reason, a hybrid system gives more information than empirical models but may be solved a large number of times in a reasonable time because such systems are sufficiently simple. Therefore, in industrial operations, it is advantageous to employ hybrid models for tasks such as design and optimization (Trujillo et al., in press).

Although heap leaching is widely employed in both metallic and non-metallic mining, for the latter, modeling studies are currently emerging and are focused on understanding the dissolution phenomena and concentration variations of the major ions. Mellado et al. (2009) presented a hybrid model for the heap leaching of copper ores that captures the exponential trend of the recovery using a Bernoulli-type equation. The model was compared with other more complex models and achieved good levels of representation with less computational effort. Recently, Mellado et al. (2011b) proposed three analytical hybrid models that are sufficiently accurate for use in applications such as stochastic analysis and the planning of leaching operations.

The modeling of heap leaching has been widely developed for the processing of metallic ores; however, for the exploitation of water soluble minerals, such as caliche, the availability of information is limited. The first antecedent regarding the modeling of caliche leaching is the research of Valencia et al. (2008), which formulated empirical kinetic expressions to determine the recovery of mineral species of nitrate and magnesium and compared it with column experiment results. This article was the first approximation of the modeling of caliche in columns. An important approach to caliche heap leaching modeling was achieved by Gálvez et al. (2012), who developed two models, one of which is a hybrid model that was modified from Mellado et al. (2009), which was adapted for the dissolution of soluble particles. The other model is a phenomenological expression based on the model developed previously by Valencia et al. (2008), which considers particle size reduction using the model of dissolution proposed by Brunner and Tolloczko (Dokoumetzidis and Macheras, 2006). In more recent efforts, Ordóñez et al. (2013) collected empirical data from pilot column leaching experiments and used them to validate the phenomenological model proposed by Gálvez et al. (2012). Moreover, important observations about the dynamics of dissolution were noted, such as sodium sulfate crystallization during the caliche leaching.

This article aims to validate the hybrid model obtained in Gálvez et al. (2012) using the experimental data collected by Ordóñez et al. (2013). This validation is performed by adjusting some parameters

Table 2
Chemical composition of the caliche.

Ion	Concentration (%)	Analytical method
SO ₄ ²⁻	9.41	Gravimetry
Na ⁺	5.58	Atomic absorption spectroscopy
Cl ⁻	4.19	Volumetry
NO ₃ ⁻	3.67	UV molecular absorption spectroscopy
Mg ²⁺	0.97	Atomic absorption spectroscopy
K ⁺	0.58	Atomic absorption spectroscopy
IO ₃ ⁻	0.05	Volumetry

Table 3
Mineral composition of the caliche ore.

Specie	Formula	%
Albite	NaAlSi ₃ O ₈	26.3
Quartz	SiO ₂	19.9
Halite	NaCl	19.7
Nitratine	NaNO ₃	9.5
Glauberite	Na ₂ Ca(SO ₄) ₂	9.1
Anhydrite	CaSO ₄	7.3
Bloedite	Na ₂ Mg(SO ₄) ₂ · 4H ₂ O	3.3
Loewite	Na ₁₂ Mg ₇ (SO ₄) ₁₃ · 15H ₂ O	1.9
Polyhalite	K ₂ Ca ₂ Mg(SO ₄) ₄ · 2H ₂ O	1.6
Hydrochlorborite	Ca ₂ B ₄ O ₄ (OH) ₇ Cl · 7H ₂ O	1.4

and includes a sensitivity and predictability analysis. The parameters are adjusted using couples of experiments, and the obtained parameters are used to predict other experiments to demonstrate the applicability of this model in design and optimization tasks.

2. Experimental procedure

2.1. Leaching column experiments

Columns with a diameter of 0.2 m were used in the leaching experiments. To avoid stratification and channeling, the loading of caliche mineral was performed in small batches for every column. The leaching agents, initial bed heights and nominal irrigation rates used in each experiment are given in Table 1. Initially, each column was irrigated with the leaching agent at a rate of 6 L/h/m² until the leachate started to flow out from the bottom. Subsequently, the wetted caliche was irrigated at the nominal rate for 20 days.

The nomenclature of the experiments involves 4 characters; the first two are related to the leaching agent used: seawater (SW), tap water (TW), rich solution (RS) and diluted solution (DS). The third component of the abbreviation is the irrigation rate: 0.003 (3), 0.006 (6) and 0.004 (4) m³/m²/h. Finally, the last letter of the nomenclature is linked to the initial bed height: 0.6 (S—small), 0.8 (M—medium) and 1.0 m (L—large).

The leachate samples were collected from the column bottom 12 h after leaching began, and afterwards, samples were collected every 24 h, which were posteriorly analyzed. Solid samples were taken from the initial caliche and the residue. These samples were mixed with distilled water at a solid:liquid (kg:L) ratio of 1:10 and stirred for 6 h. The mixture was then filtered, and the liquid was chemically analyzed. Using a material balance, the experimental recoveries were calculated for each experiment for the most abundant ions of the caliche: nitrate, sulfate, chloride, iodate, sodium, potassium, and magnesium. The total recoveries for each ion consider the sum of the extracted fraction and the fraction remaining in the residue.

2.2. Caliche and leaching agents

The material was screened, and particles exceeding 2.4 mm in diameter were used to avoid possible obstructions in the columns. From a

Table 4
Chemical composition (kg/m³) of the leaching solutions (C_i).

Ion	TW	SW	DS	RS
NO ₃ ⁻	0.00	0.21	15.02	29.30
SO ₄ ²⁻	0.13	2.66	28.06	53.72
IO ₃ ⁻	0.01	0.00	0.10	0.20
Cl ⁻	0.35	19.71	39.13	59.88
Na ⁺	0.19	11.12	33.76	56.27
K ⁺	0.02	0.36	2.71	5.02
Mg ²⁺	0.03	1.58	4.51	7.70

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