Heap leaching of caliche minerals: Phenomenological and analytical models – Some comparisons

Edelmira D. Gálvez [a,b], Luis Moreno [c,d], Mario E. Mellado [b], Javier I. Ordóñez [d], Luis A. Cisternas [b,d,*]

[a] Dept. of Metallurgical Engineering, Universidad Católica del Norte, Antofagasta, Chile
[b] Centro de Investigación Científico Tecnológico para la Minería (CICITEM), Antofagasta, Chile
[c] Dept. of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm, Sweden
[d] Dept. of Chemical and Mineral Process Engineering, Universidad de Antofagasta, Antofagasta, Chile

ABSTRACT

Antofagasta, Chile, has one of the most important deposits of saltpetre in the world, which is called caliche. These deposits are mainly composed of nitrate, halite, sodium anorthite, and quartz. Minor species include anhydrite, glauberite, loeweite, calcite, polyhalite, probertite, and gypsum. Recently, several operations began to use heap leaching for the extraction of saltpetre. Modelling the heap leaching of caliche is not straightforward because of the many minerals and their different dissolution rates. Moreover, caliche may have a large fraction of soluble minerals, approximately 40%, which causes the heap to slump. In this work, we present two models. The first, which is a phenomenological model, is an extension of the model published by Valencia et al. (2008). The system is modelled as a column comprised of N small columns, and in each of these small columns, the height of the solids varies with time when the soluble minerals are dissolved. The liquid in each small column has the same composition (well-stirred reactor). The second model, which is an analytical model, is an extension of that published by Mellado et al. (2009) for low-grade minerals, such as copper and gold, which considers that the leaching phenomenon occurs on different scales of size and time. However, in this work, the time scale at the particle level is based on the Bruner and Tolloczko dissolution model. The objective of this work is to test the suitability of the analytical model as a tool for use in optimisation, for which the model needs to be solved many times. The phenomenological model was used to generate simulated experimental data. The results show that the analytical model may be a useful tool in optimisation.

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1. Introduction

Caliche minerals, which are found in Northern Chile, are primarily composed of nitrate ($NaNO_3$), halite (NaCl), sodium anorthite ($(Ca,Na)(SiAl)_4O_8$), and quartz. Minor species include anhydrite, glauberite, loeweite, calcite, polyhalite, probertite, and gypsum (Valencia et al., 2008). Soluble minerals found in caliche are not well identified. These soluble minerals are mixed with inert minerals, such as quartz and other silicates. The proportion of inert minerals is 50–60%. Caliche is an important raw material for obtaining sodium nitrate, potassium nitrate, sodium sulphate, and iodine (Lauterbach and Ober, 1995).

Heap leaching is used widely for the leaching of metals such as copper (Dixon and Hendrix, 1993; Casas et al., 1998; Thiel and Smith, 2004). In Chile, since 1990, heap leaching with water has been used to leach caliche minerals. The leaching of piled minerals represents a valid alternative for low-grade caliche due to excellent economic and technological possibilities and good levels of recovery when compared with the vat-leaching technology typically utilised for high-grade caliche.

The leaching of caliche differs from the leaching of copper, zinc, gold, and other metals. Regarding caliche, there are several soluble species but few in metal minerals. Copper, zinc, and gold minerals are leached by chemical reactions, however, caliche is dissolved. The variation of heap height over time is significant for caliche but not for metal ores.

There are several works related to the modelling of heap leaching, including phenomenological models (Bouffard and Dixon, 2001; Cariaga et al., 2005; Cross et al., 2006; Mellado and Cisternas, 2008) and empirical and hybrid models (Mellado et al., 2009, 2011). However, these works are applicable to poorly soluble minerals. To date, there is only one published manuscript related to highly soluble minerals (Valencia et al., 2008).

The objective of this work is to test the suitability of the analytical model as a tool for use in optimisation, where the model needs to be solved a very large number of times (hundreds of thousands).

Nomenclature

A	cross-sectional area of the modelled column (m^2)	R_μ^∞	recovery at infinite generalised dimensionless time (–)
C_s	solubility of soluble species (kg/m^3)	r_i	particle radius in small column i (m)
C_i	concentration in small column i (kg/m^3)	t	time (h)
D	particle diameter (m)	u_s	superficial bulk flow velocity (m/h)
H_{heap}	heap height (m)	V_{wi}	water volume in small column i (m^3)
H	initial height of the small columns (m)	α	fraction of soluble species (–)
h_i	height of column i (m)	ε	porosity of the column and heap (–)
k	mass transfer coefficient (m/h)	ε_a	air volume fraction (–)
k_μ	dimensionless kinetics constant (–)	ε_w	water volume fraction (–)
k_θ, k_τ	dimensionless adjusted parameters in Eq. (13) (–)	φ	dimensionless parameter (–)
N	number of small columns (–)	μ	generalised dimensionless time (–)
N_p	number of particles in each small column (–)	ω	dimensionless time delay (–)
Pe	Peclet number (–)	ρ	particle density (kg/m^3)
q	water flux through the column (m^3/m^2 h)	θ	dimensionless column-scale time (–)
R	initial particle radius (m)	τ	dimensionless particle-scale time (–)
R_t	recovery at time t (–)	π, β, γ	adjustable constants in Eq. (14) (–)
R_μ	recovery at generalised dimensionless time μ (–)		

The phenomenological model is used to generate simulated experimental data. The analytical model is fitted using a subset of this data and is then used to predict the other data points.

2. Heap leaching models

In this section, we present two models. The first, which is a phenomenological model, is an extension of the model published by Valencia et al. (2008). The system is modelled as a column comprised of N small columns. In each of these small columns, the height of the solid varies with time when the soluble minerals are dissolved. The liquid in each small column has the same composition (well-stirred reactor). The second model, which is an empirical knowledge-based model, is an extension of that published by Mellado et al. (2009), which considers two time and size kinetics scales and considers particle radius and heap height to be time-dependent properties.

Modelling the heap leaching of caliche minerals is not trivial due to factors such as (a) the caliche composition, which is a mixture of many minerals that may have different dissolution rates and (b) the large fraction of soluble minerals, which reaches values of approximately 40%; therefore, the heap height will decrease appreciably when the soluble minerals are dissolved.

The main soluble anionic chemical species in the caliche minerals are nitrate, chloride, sulphate, iodate, perchlorate, and tetraborate. The cationic species are sodium, potassium, magnesium, and calcium. Due to the large fraction of soluble minerals, the heap collapses during the leaching process; therefore, its height decreases with time. A heap of caliche minerals is formed by rocks of different sizes, from a few millimetres to hundreds of millimetres. It is expected that, initially, the minerals at or near the particle surface were solubilised. When a significant fraction of minerals has been dissolved, it is expected that the inert materials that remain on the particle surface were removed (e.g., by the collapse of the particle surface). However, the removal of the inert material is not important; due to the high content of soluble minerals in the caliche minerals, it is expected that the inert material that remains on the particle surface will have a small resistance to mass transport.

Another issue is the dissolution rate of the different soluble minerals in the particle. Here, it is assumed that the minerals beneath the particle surface will be dissolved only when these minerals are directly exposed to the action of the leaching solution at the particle surface. Therefore, mineral dissolution will be controlled by those soluble minerals that are found in large concentrations. Minerals that are present in small amounts are dissolved following the dissolution of the major minerals. Minerals that have a low dissolution rate may be separated from the particle simultaneously with the inert materials and be dissolved later. At present, this is not considered in the models.

To model the leaching of caliche minerals in heaps and to keep the models sufficiently simple, several assumptions are needed. These assumptions are listed below:

- The particles are spherical and are initially of the same size. They are non-porous.
- The soluble minerals and the inert material are homogeneously distributed in the particle.
- Only the soluble minerals that are on the particle surface are dissolved.
- The inert materials that remain at the particle surface after the removal of the soluble minerals are separated from the particle surface when the surface collapses.
- A one-dimensional system is used for the heap, i.e., it is assumed that the horizontal dimensions of the heap are large. Therefore, a column of caliche minerals in the centre of the heap is modelled.

Other situations that may be modelled are straightforward; one example is the leaching of caliche formed by particles of different sizes that dissolve simultaneously.

2.1. Modelling the heap as well-stirred reactors in series

To take into account the variation of the heap height with time in a simple way, the system is modelled as a column comprised of N small columns (Fig. 1). In each of these small columns, the height of the solid varies with time when the soluble minerals are dissolved. The liquid in each small column has the same composition (well-stirred reactor). Therefore, in each small column (reactor), all the particles have the same size, $r_i(t)$. The initial height of the heap is divided into small columns of initial height $H = H_{heap}/N$, where H_{heap} is the initial height of the heap, H is the initial height of each small column, and N is the number of small columns or well-stirred reactors.

When a column is represented by a series of small well-stirred reactors, the dispersive term is omitted in the equations describing
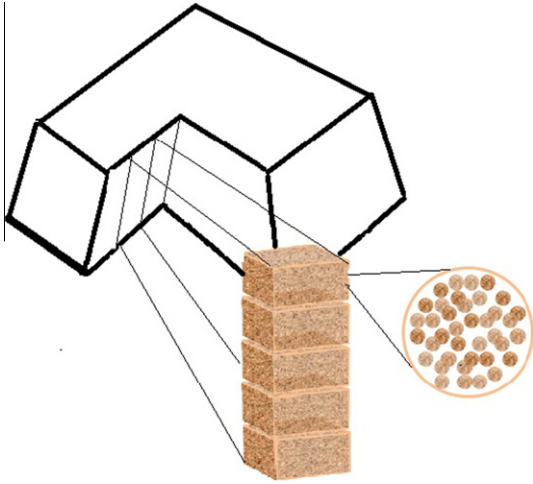
Fig. 1. An illustration showing the N small columns (or reactors).

the processes occurring in the column or bed. The dispersion is taken into account by the number of reactors used to model the heap. A system formed by a large number of small well-stirred reactors is equivalent to having a high Peclet number, i.e., a small dispersion. The opposite is true for a small number of well-stirred reactors (large dispersion). The relationship between the number of well-stirred reactors and the Peclet number is (Levenspiel, 1999)

$$Pe = 2N. \tag{1}$$

This relationship is valid only for high Peclet numbers. For low Peclet numbers, the relationship is approximated, e.g., for 5 reactors ($Pe = 10$), the error is 10%; however, for 10 reactors ($Pe = 20$), the error is only 5%.

Regarding the dissolution of the soluble minerals, it is assumed that the particles initially have the same radius, R. The variation of the particle radius with time is determined by the Bruner and Tolloczko dissolution model (Dokoumetzidis and Macheras, 2006), in which the rate of dissolution is proportional to the product between the exposed surface area and the difference between the solubility and the instantaneous concentration in reactor i at time t. Therefore, the variation of the particle radius with time in reactor i is

$$\frac{dr_i}{dt} = -\frac{k}{\alpha\rho}(C_s - C_i) \tag{2}$$

where r_i [m] is the radius of the particle in reactor i, t [h] is the time, k [m/h] is a mass transfer coefficient, ρ [kg/m³] is the particle density, and α is the fraction of the soluble species in the particle. C_s [kg/m³] is the solubility of the soluble species, and C_i [kg/m³] is the concentration of the species in the leaching solution in reactor i at time t. The term in parentheses represents the driving force for the mass transport.

Here, the equations are written assuming that only one mineral is dissolving from the caliche minerals or that all the soluble minerals are dissolving at the same rate. The material balance in the well-stirred reactor i, with cross-sectional area A, is

$$\frac{dV_{wi}C_i}{dt} = qA(C_{i-1} - C_i) - N_p(4\pi r_i^2)\rho\alpha\frac{dr_i}{dt} \tag{3}$$

where V_{wi} [m³] is the volume of water in reactor i, q [m³/m² h] is the water flux through the column, C_i [kg/m³] is the concentration in reactor i and C_{i-1} [kg/m³] is the concentration that flows into reactor i from reactor $i-1$. N_p is the number of particles in each reactor.

All the reactors have the same number of particles because the reactors have the same volume and the initial particle size is the same.

The small columns with height H are initially filled with caliche minerals; however, due to the dissolution of the soluble minerals, the column height decreases with time. It is assumed that the porosity of the bed is constant, i.e., the ratio between the void volume and total volume is kept constant. The small column is assumed to be water unsaturated with a water fraction of ε_w. Therefore, the total porosity, ε, comprises the air porosity, ε_a, and the water content, ε_w. The number of particles in each reactor may then be calculated as

$$N_p = \frac{AH(1-\varepsilon)}{\frac{4}{3}\pi R^3}. \tag{4}$$

Introducing the expression for the number of particles and the water content into Eq. (3),

$$A\varepsilon_w\frac{dh_iC_i}{dt} = qA(C_{i-1} - C_i) - \frac{3HA(1-\varepsilon)}{R^3}(r_i^2)\alpha\rho\frac{dr_i}{dt} \tag{5}$$

where h_i is the height of reactor i at any time t. Taking the derivative of the accumulation term and simplifying,

$$\frac{dC_i}{dt} = \frac{q}{\varepsilon_w}\frac{1}{h_i}(C_{i-1} - C_i) - \frac{3H\alpha\rho}{R^3}\frac{(1-\varepsilon)}{\varepsilon_w}\left(\frac{r_i^2}{h_i}\right)\frac{dr_i}{dt} - \frac{C_i}{h_i}\frac{dh_i}{dt}. \tag{6}$$

A relationship between the height of the small column and the radius of the particles in the column is required. This may be determined by performing a mass balance and assuming that the porosity is constant. In this case, the column height is directly proportional to the particle volume (r_i^3). Therefore, the following relationship may be written:

$$h_i = H\left[1 - \alpha\frac{(R^3 - r_i^3)}{R^3}\right] = H\left[1 - \alpha + \alpha\left(\frac{r_i}{R}\right)^3\right]. \tag{7}$$

Taking the derivative of Eq. (7) with respect to time, a relationship between dr_i/dt and dh_i/dt may be obtained

$$\frac{dh_i}{dt} = \frac{3H\alpha}{R^3}r_i^2\left(\frac{dr_i}{dt}\right) = -\frac{3H}{R^3}\frac{k}{\rho}r_i^2(C_s - C_i). \tag{8}$$

2.2. Analytical model

In this section, an analytical model based on the first-order kinetic equation is developed by following the approach used by Mellado et al. (2009). In that work, for first-order kinetics, the difference between the recovery at infinite time, R_μ^∞, and the recovery at dimensionless time μ, R_μ, was represented by

$$\frac{d(R_\mu^\infty - R_\mu)}{d\mu} = -k_\mu(R_\mu^\infty - R_\mu) \tag{9}$$

where μ is a generalised dimensionless time and k_μ is a dimensionless kinetics constant in the same time scale. The subscript μ is used in all the variables and parameters to indicate that they represent the kinetics at dimensionless time μ. The initial condition for solving Eq. (9) is that at dimensionless time ω, the variable R_μ begins to change (ω is the dimensionless delay of R_μ). The solution to this problem is known to be

$$R_\mu = R_\mu^\infty(1 - e^{-k_\mu(\mu-\omega)}) \qquad \text{for} \quad \mu \geq \omega. \tag{10}$$

Considering that the leaching phenomenon occurs on different scales of size and time and in relation to different phenomena that participate in the leaching process, expressions similar to Eq. (9) can be used to represent each of these phenomena. For the heap leaching model in Dixon and Hendrix (1993), it is observed that

the time scale at the heap level for the differential equations, after the non-dimensionalisation procedure, is given in terms of the dimensionless column scale time θ, which is expressed as

$$\theta = \frac{qt}{\varepsilon_w H_{heap}}. \tag{11}$$

This simple observation leads to one kinetic constant for our model in Eq. (10). Also, from the Bruner and Tolloczko dissolution model, Eq. (2), the dimensionless time scale at the particle level is given by

$$\tau = \frac{C_s kt}{r\alpha\rho}. \tag{12}$$

It is assumed that with the inclusion of both scales in the heap processing, i.e., both at the particle and the heap levels, the total recovery will be the sum of the recoveries on both scales, or $R_t = R_\tau + R_\theta$. Using Eq. (10) for each recovery, we obtain

$$R_t = R^\infty \left[1 - \varphi e^{-\left(\frac{k_\theta q}{\varepsilon_w H_{heap}}\left(t - \omega \cdot \frac{\varepsilon_w h_{heap}}{q}\right)\right)} - (1-\varphi) e^{-\left(\frac{k_\tau k C_s}{r\alpha\rho}\left(t - \omega \cdot \frac{\varepsilon_w h_{heap}}{q}\right)\right)} \right] \tag{13}$$

where $\varphi = R_\theta^\infty / R^\infty$. φ, k_θ, and k_τ are the adjustable parameters. h_{heap} is the heap height at any time. R^∞ is calculated using the following equation (Mellado et al., 2011):

$$R_\mu^\infty = \frac{\pi}{H_{heap}^\beta + \gamma}. \tag{14}$$

Because the height and particle radius vary with time in Eq. (13), an iterative process would be used for determining the recovery, R_t. It should be noted that the height and radius are directly related to the recovery as follows: $h_{heap} = H_{heap}(1 - \alpha R_t)$ and $r = R\sqrt[3]{1 - R_t}$.

3. Performed simulations

To show the characteristics and capabilities of the models, simulations were carried out for different parameter values. The values used in these simulations are shown in Table 1. The parameters chosen for these simulations are arbitrary.

### 3.1. Well-stirred reactors in series model

To show the properties of the model, simulations using the parameter values for the central case (Table 1) were carried out. Fig. 2 shows the concentration as a function of time at different locations in the column. For these parameters, it is observed that the soluble salts in the first and fourth reactors are depleted after approximately 130 and 180 days, respectively. For times longer than 210 days, soluble salts remain in the reactors in the lower part of the column. The same pattern is observed for the particle diameter, as shown in Fig. 3; particles disappear after approximately 130 days

Table 1
Values used in the simulations.

Entity	Central value	Interval
Heap height, m	10	8–12
Number of small columns	10	5–20
Particle diameter, m	0.15	0.10–0.20
Solid density, kg/m³	2000	
Mass transfer coefficient, m/h	0.0001	0.00003–0.0003
Solubility, kg/m³	200	100–400
Column porosity	0.45	
Water porosity in column	0.015	
Fraction of soluble material	0.40	
Water flux, m³/m² h	0.005	0.004–0.006
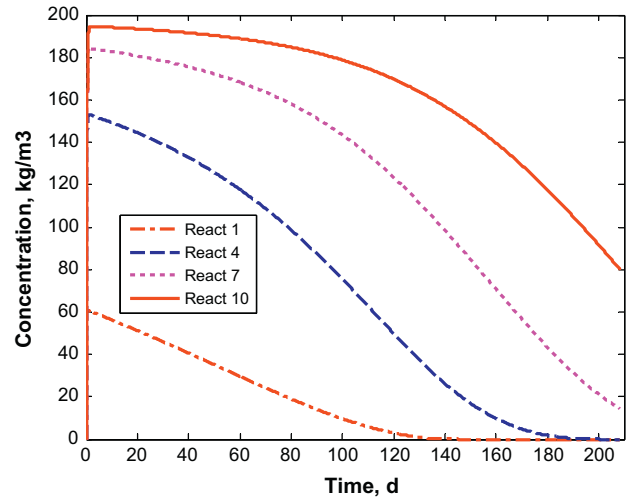
Fig. 2. Concentration as a function of time for the central case. Reactor 1 is located at the top of the column.
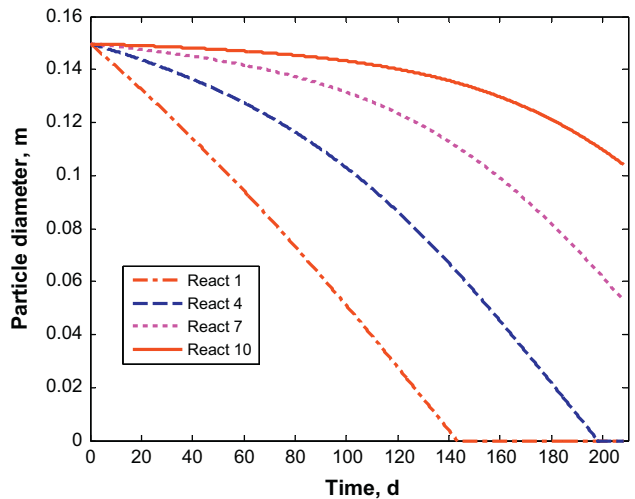
Fig. 3. Particle diameter as a function of time for the central case. Reactor 1 is located at the top of the column.

in the first reactor. The trend observed for the outlet concentration at different heights is similar to that reported in Valencia et al. (2008) for the case of nitrate. The observed differences may be due to the fact that in Valencia et al. (2008), the size of the particles in the columns was approximately 1–2 cm, whereas the particle diameter used in our simulations was 15 cm, which is closer to the sizes used in industrial heaps. This difference in particle sizes implies that the dissolution rate per bed volume is much lower in our case due to the smaller contact area between the particles and the leaching solution.

The relative recovery is shown in Fig. 4. For the entire column, the simulated recovery is slightly greater than 90% after 210 days. For the four reactors in the upper part of the column, the soluble salts had been depleted by that time. The trend shown by the simulations was similar to that of the nitrate recovery in the leaching experiments by Valencia et al. (2008), which used three small columns in series. Good agreement is observed in the recovery and outlet concentration obtained in those experiments and the simulations performed using the phenomenological model. Several experiments at the pilot scale under controlled conditions are
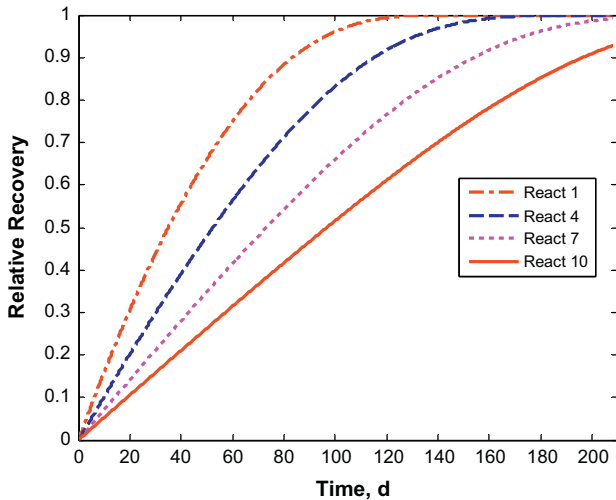
Fig. 4. Relative recovery of the soluble species as a function of time for the central case. Reactor 1 is located at the top of the column.

planned to validate the phenomenological model. The use of results from industrial heap leaching is also being considered.

The impact of the main parameters on the recovery of saltpetre from caliche minerals was evaluated in a sensitivity study. The parameters, its central values and the intervals used are shown in Table 1. The impact of the mass transfer coefficient, solubility, and number of reactors is shown in this section. The heap height, particle size, and irrigation rate, which may be modified to optimise the process, are shown and discussed in Section 3.2, where the predictions of the two models are compared.

3.1.1. Impact of the mass transfer coefficient

The mass transfer coefficient was varied from 0.00003 to 0.0003 m/h. As expected, the simulations showed that the recovery increased as the mass transfer coefficient increased (Fig. 5). However, mass transfer coefficients greater than 0.0003 m/h seemed to have a lower effect on increasing the recovery. This is because the recovery is controlled by salt solubility for high mass transfer coefficients. For the highest mass transfer coefficient, 0.0003 m/h, the salts were depleted after approximately 210 days; therefore, the height of the heap was 6 m. For the lowest coefficient, more
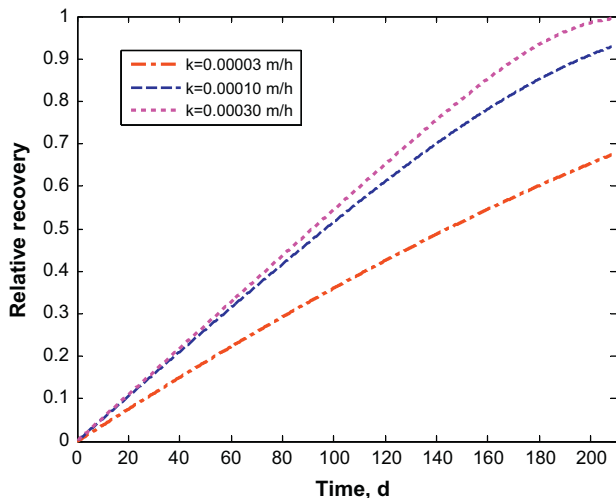
than 30% of the soluble salt remained in the column after 210 days, and the height of the column was approximately 7.3 m.

3.1.2. Solubility

These simulations showed that solubility has a large impact on the leaching process (Fig. 6). For example, when solubility was increased by a factor of 2, the time for salt depletion was reduced almost 50%. In addition, for the lowest solubility (100 kg/m^3), after 210 days, only approximately half of the soluble salts have been depleted. In simulations where these two parameters were varied at the same time (data not shown), it was found that the behaviour of the process was mainly determined by the combined effect of these two parameters; solubility and mass transfer coefficient.

3.1.3. Dispersion – number of small reactors

As indicated in Section 2.1, the number of reactors used for modelling the column determines the dispersion in the system. According to Eq. (1), the use of 5, 10, and 20 reactors is approximately equivalent to Peclet numbers of 10, 20, and 40, respectively. A Peclet number of 10 corresponds to a high dispersion, whereas a Peclet number of 40 corresponds to a moderate dispersion. Peclet numbers in this interval may be expected for systems formed by large, non-uniform particles. The results showed that the recovery is almost independent of the number of small reactors used for modelling the column of caliche minerals (Fig. 7). It is known that in systems where the reaction is important, the dispersion effect is masked by the reaction. Therefore, the simulations may be carried out by any numbers of small reactors between 5 and 20, and similar results would be obtained.

3.2. Analytical model

The results of the analytical model were compared with the results obtained with the phenomenological model by means of the recovery of the soluble species. Table 1 shows the data used in the simulations. The comparison was conducted using operational parameters, i.e., parameters that can be modified in an industrial process. These parameters are, for example, heap height, particle diameter, and irrigation rate. The other parameters (such as mass transfer coefficient and solubility) are important; however, they cannot be varied in an industrial process.

The analytical model's main application is in process optimisation because the calculations may be performed quickly. Therefore,
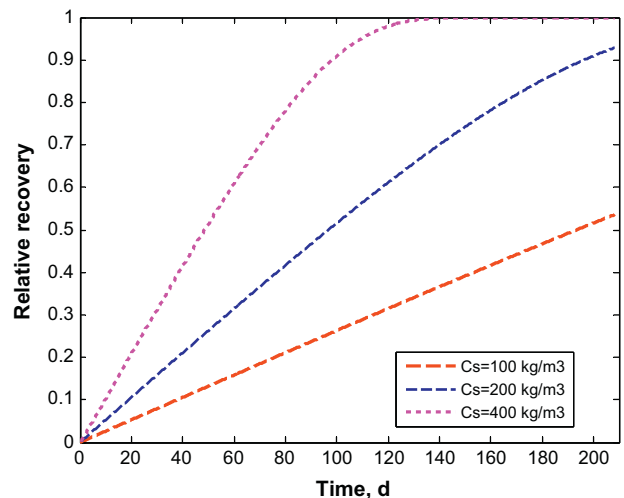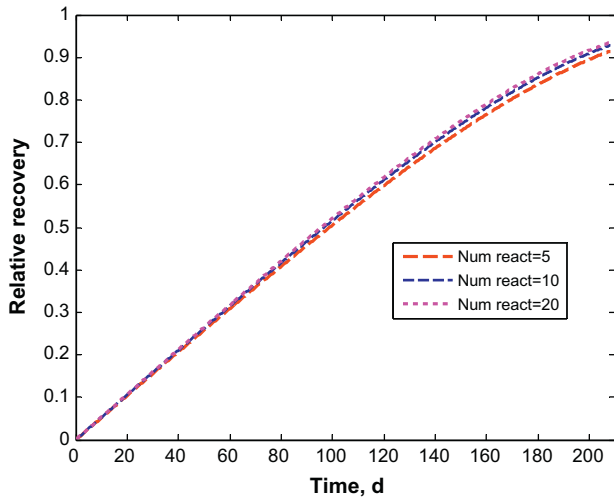

Fig. 5. Relative recovery of the soluble species as a function of time for different mass transfer coefficients, k.

Fig. 6. Relative recovery of the soluble species as a function of time for different solubilities, C_s.

Fig. 7. Relative recovery of the soluble species as a function of time for different numbers of small reactors used for modelling the column.

Fig. 8. Relative recovery of the soluble species as a function of time for different heap heights. The lines are the analytical model, and the markers are the simulated experimental data.

Fig. 9. Relative recovery of the soluble species as a function of time for different particle diameters. The lines are the analytical model, and the markers are the simulated experimental data.

the computational effort is small, even for problems requiring a large number of alternatives to be tested.

The properties of the analytical model were tested for different situations. In particular, the predictive capability of the model was tested when a small amount of information is used for fitting the model. The testing procedure for the analytical model was as follows: the phenomenological model is used to generate a set of data, which is considered to be simulated experimental data from an industrial leaching process. From these data (for example, the recovery of the soluble species), six times were chosen: 42, 83, 125, 146, 167, and 188 days. The analytical model is fitted using a subset of these data, and once the parameters of the analytical model have been determined, the model is then used for predicting the recovery for other cases. In these calculations, the recovery at infinite time was assumed to be 1.0 because 100% of the soluble species are recovered after a sufficiently long time in the phenomenological model.

For the analytical model, the parameters to be adjusted are as follows: the constants k_θ and k_τ in the exponentials (which characterise the reaction at the column and particle scales, respectively), the dimensionless time delay, ω, and the relative importance of the column scale in the leaching process, φ. Because the dimensionless recovery is used for the comparisons, the error of the fitting process is calculated as follows: the differences between the simulated experimental data and the recovery calculated by the analytical model are summed, which is then divided by the number of data points.

First, the fitting capability of the analytical model was tested. The simulated data was obtained using the phenomenological model for various values for the heap height, particle diameter, and irrigation rate, as shown in Table 2. The simulations were carried out for the six times indicated above (42 data points in total). The results, shown in Figs. 8–10, indicate that the fit of the analytical model to the simulated experimental data is good for the three cases. The average error of the fitting process is 1.8%. The results show that recovery decreases with height, and longer times are required to obtain a high recovery. Recovery also decreases with the initial particle diameter due to the smaller surface area available for mass transfer when the particle diameter increases. Finally, recovery increased with irrigation rate.

The capability of interpolation (or extrapolation) using the analytical model is tested by fitting the model to a subset of data points and then predicting the other data points. For interpolation,
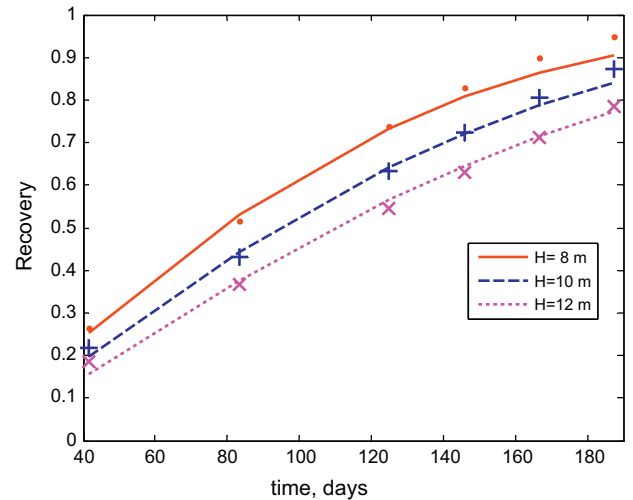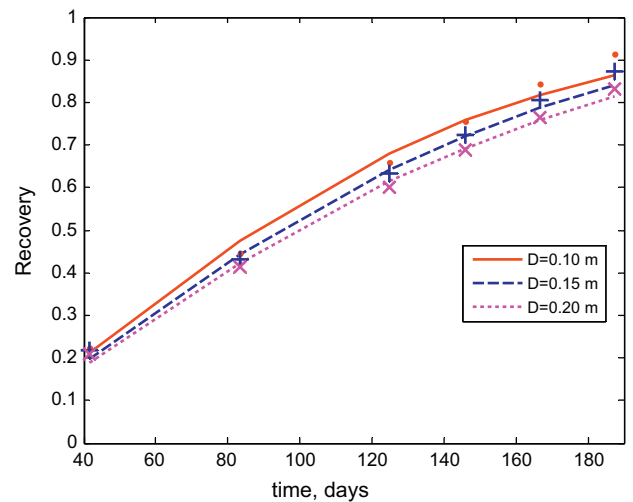
the model is fitted using the data points obtained with the endpoints of the interval for each parameter, and the central value of the parameter is predicted. For extrapolation, the data for the central value and one endpoint value are used for fitting, and the other endpoint value (Table 2) is predicted.

Several cases are considered in which the error is determined only for the fitted data points (Error 1), for all 42 points including the fitted points (Error 2), and for the interpolated or extrapolated points (Error 3). These errors are shown in Table 2 for the different calculated cases. In Case 1, the fitting is performed using the 12 points corresponding to the times of 42 and 167 days for the interval endpoints (shown in Table 2) for height, particle diameter, and irrigation rate. Then, in Case 2, the effect of height is considered, the model is fitted using 12 points for the heights of 8 and 10 m, and an extrapolation is carried out for 12 m. Similarity in Case 3, the effect of particle diameter was studied, the model is fitted using 12 points for the diameters of 0.10 and 0.20 m, and the recoveries for a particle diameter of 0.15 m are interpolated.
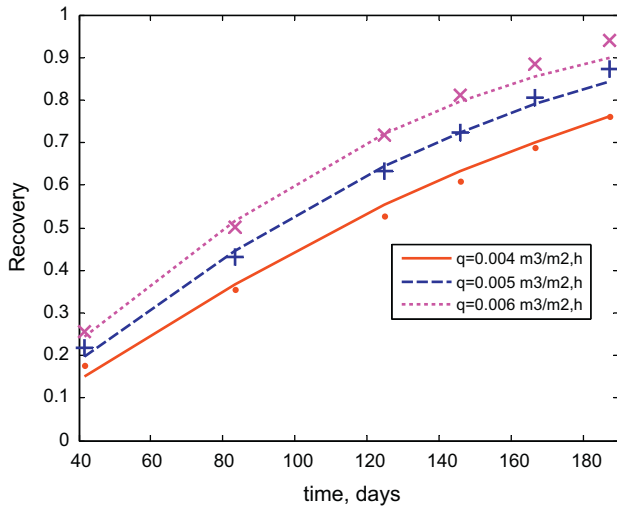
Fig. 10. Relative recovery of the soluble species as a function of time for different irrigation rates. The lines are the analytical model, and the markers are the simulated experimental data.
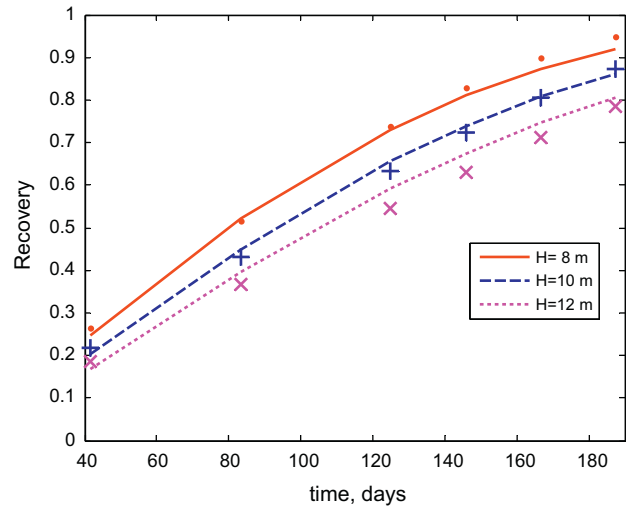
Fig. 11. Relative recovery of the soluble species as a function of time for different heap heights. The lines are the analytical model. The simulated data for the heap heights of 8 m (dots) and 10 m (+-markers) are fitted and extrapolated to 12 m (x-markers).

Finally, the effect of irrigation rate is considered in Case 4, the model is fitted using 12 points corresponding to the irrigation rates of 0.004 and 0.005 m^3/m^2 h and an extrapolation is carried out for the irrigation rate of 0.006 m^3/m^2 h.

Table 2 shows that the variations of the parameters evaluated in each case are generally not significant. This indicates that Eq. (13) is a good description of the heap leaching process. Almost the same parameters are obtained in spite of the number of data points used in the fitting process, which ranged from 12 to 42 points.

Using the values for the central case, the two time constants are calculated:

For the column scale, $\quad K_\theta = \dfrac{k_\theta q}{\varepsilon_w h} = 2.8 \times 10^{-4}$ [1/h]

For the particle scale, $\quad K_\tau = \dfrac{k_\tau k C_s}{r \alpha \rho} = 4.6 \times 10^{-4}$ [1/h]

K_θ and K_τ are the dimensional time constants, [1/h], for the column and particle scale respectively. These values indicate that the time to reach a recovery of 0.632 $(1-1/e)$ is approximately 160 days and that the time for depleting 0.632 $(1-1/e)$ of the particle is

approximately 92 days. In Table 2, the dimensionless time delay is presented, which may be converted to time in days using the expression

$$t_{delay} = \omega \cdot \frac{\varepsilon_w h}{q} = 11 \text{ days}.$$

From the values of φ, the term corresponding to the column scale is found to be more dominant than the term corresponding to the particle scale. Therefore, for the set of parameters used, the variation in the particle diameter is not affecting the results. However, for other sets of parameters, the particle scale in Eq. (13) may be important.

The errors obtained in the fitting process are small. This indicates that Eq. (13) describes the system well and that the model suitably captures the recovery trends in spite of the variation of the parameters. However, the most important characteristic of the model is that using a limited number of data points, reasonable predictions for the recovery of other parameter values may be obtained. For example, in case 4, the recovery data for two cases with irrigation rates of 0.004 and 0.005 m^3/m^2 h were used in the fitting process and the error was 1.5%. The largest error was obtained for the

Table 2
Errors for the different cases. Error 1: using the fitting data; Error 2: using all data points; Error 3: using the extrapolated/interpolated data in the category. The number of points is shown in parentheses.

	Reference	Case 1	Case 2	Case 3	Case 4
Case description					
Variable studied	All	Time	Heap height	Particle diameter	Irrigation rate
Action	Fitting	Inter/extra	Extrapolation	Interpolation	Extrapolation
Data points used in the fitting					
Number of data point	42	12	12	12	12
Time (days)	42, 83, 125, 146, 167, 188	42, 167	42, 83, 125, 146, 167, 188	42, 83, 125, 146, 167, 188	42, 83, 125, 146, 167, 188
Heap Heights (m)	8, 10, 12	8, 12	8, 10	10	10
Particle diameter (m)	0.10, 0.15, 0.20	0.10, 0.20	0.15	0.10, 0.20	0.15
Irrigation rate (m^3/m^2 h)	0.004, 0.005, 0.006	0.004, 0.006	0.005	0.005	0.004, 0.005
Results					
$k_\theta\,10^3$	8.53	8.53	8.66	9.00	8.33
k_τ	1.39	1.44	1.55	1.14	1.38
ω	9.09	7.34	5.85	8.78	7.77
φ	0.80	0.82	0.62	0.78	0.84
Error 1	1.8 (42)	1.3 (12)	1.5 (12)	1.8 (12)	1.5 (12)
Error 2	1.8 (42)	2.0 (42)	2.4 (42)	1.9 (42)	1.8 (42)
Error 3		2.5 (24)	3.4 (6)	1.6 (6)	2.0 (6)
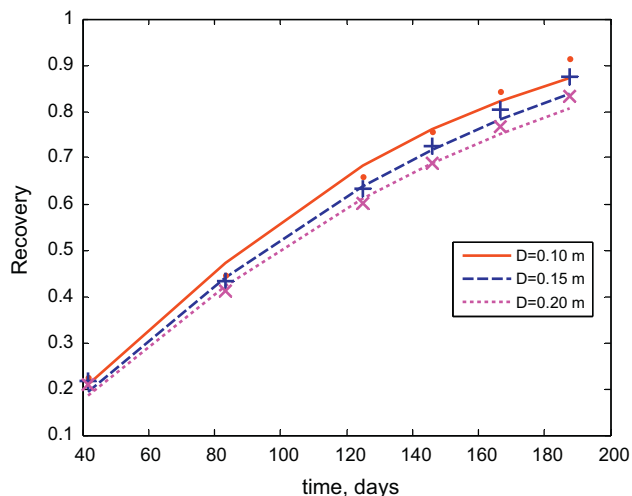
Fig. 12. Relative recovery of the soluble species as a function of time for different particle diameters. The lines are the analytical model. The simulated data for the particle diameters of 0.10 m (dots) and 0.20 m (x-markers) are fitted and interpolated to 0.15 m (+-markers).
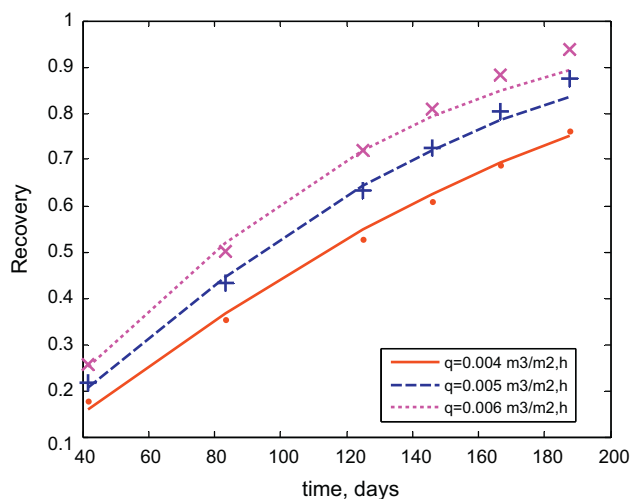
Fig. 13. Relative recovery of the soluble species as a function of time for different irrigation rates. The lines are the analytical model. The simulated data for the irrigation rates of 0.004 m^3/m^2 h (dots) and 0.005 m^3/m^2 h (+-markers) are fitted and extrapolated to 0.006 m^3/m^2 h (x-markers).

prediction of the recovery for irrigation rates of 0.006 and 0.005 m^3/ m^2 h. The results for these simulations are shown in Figs. 11–13. They show that, in spite of the small number of data points used in the fitting process, the predictions at other irrigation rates and even at other heap heights and particle diameters are satisfactory.

4. Discussion and conclusions

Two models are presented. One is a phenomenological model, which considers the decrease of the heap height when the soluble salts are dissolved. Another is an analytical model, which uses an exponential expression for calculating the recovery. This model is useful in an optimisation and sensitivity analysis in which an explicit equation is needed and/or the model is solved a large number of times. As indicated above, the main characteristic of the model is that a small number of data points may be used to predict other parameter values. Some differences are found between the phenomenological and analytical models, but they are not significant. However, the trends are clearly represented. The values used in the simulations are arbitrary; however, this is not a significant matter because the objective of the paper is to show the characteristics and capabilities of both models.

An acceptable agreement is found between both models; however, as expected, some differences are also found between them, mainly due to the particular characteristics of the models. The main characteristics and advantages of the analytical model are its simplicity and the small computational effort required. However, some difficulties are encountered in the simulations with this model when the leaching process is controlled by one or two parameters, e.g., when the dissolution reactions are determined by the salt solubility. In contrast, the phenomenological model can more accurately capture the interactions between the different parameters; however, the computational time is longer.

Therefore, the applicability of these models is different. The analytical model is useful in the optimisation of complex systems, e.g., when several heaps are simultaneously leached and in other post-modelling activities. This type of calculation requires a large number of simulations; therefore, long computing times would be required for using phenomenological models. In contrast, the phenomenological models are useful in determining the influence of different parameters on the leaching process. They are also useful in the study of new processes because parameter fitting is generally not required.

References

Bouffard, S.C., Dixon, D.G., 2001. Investigative study into the hydrodynamics of heap leaching processes. Metallurgical and Material Transactions B 32B, 763–776.
Cariaga, E., Concha, F., Sepúlveda, M., 2005. Flow through porous media with applications to heap leaching of copper ores. Chemical Engineering Journal 111, 151–165.
Casas, J.M., Martínez, J., Moreno, L., Vargas, T., 1998. Bioleaching model of a copper-sulfide ore bed in heap and dump configurations. Metallurgical and Material Transactions B 29, 899–909.
Cross, M., Bennett, C.R., Croft, T.N., McBride, D., Gebhardt, J.E., 2006. Computational modeling of reactive multi-phase flows in porous media: applications to metals extraction and environmental recovery processes. Minerals Engineering 19, 1098–1108.
Dixon, D.G., Hendrix, J.L., 1993. A mathematical model for heap leaching of one or more solid reactants from porous ore pellets. Metallurgical Transactions 24B, 1087–1102.
Dokoumetzidis, A., Macheras, P., 2006. A century of dissolution research: From Noyes and Whitney to the Biopharmaceutics Classification Systems. International Journal of Pharmaceutics 321, 1–11.
Lauterbach, A., Ober, G., 1995. In: Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed. vol. 14. Wiley-Interscience, New York, pp. 709–737.
Levenspiel, O., 1999. Chemical Reaction Engineering, third ed. John Wiley and Sons, New York.
Mellado, M.E., Cisternas, L.A., 2008. An analytical–numerical method for solving a heap leaching problem of one or more solid reactants from porous pellets. Computers and Chemical Engineering 32, 2395–2402.
Mellado, M.E., Cisternas, L.A., Gálvez, E.D., 2009. An analytical approach to heap leaching. Hydrometallurgy 95, 33–38.
Mellado, M.E., Casanova, M.P., Cisternas, L.A., Gálvez, E.D., 2011. On scalable analytical models for heap leaching. Computers and Chemical Engineering 35, 220–225.
Thiel, R., Smith, M.E., 2004. State of the practice review of heap leach pad design issues. Geotextiles and Geomembranes 22, 555–568.
Valencia, J.A., Méndez, D.A., Cueto, J.Y., Cisternas, L.A., 2008. Saltpeter extraction and modelling of caliche mineral heap leaching. Hydrometallurgy 90, 103–114.