Thermodynamic Model for the Design of a Process of Production of Copper Sulfate Pentahydrate from Copper Ores

Francisca J. Justel, María E. Taboada, Elsa K. Flores, Héctor R. Galleguillos, and Teófilo A. Graber*

ABSTRACT: In Chile, one of the ways in which small-scale mining industries sustain themselves is through the sale of copper ores to the state company ENAMI, which monetizes this product depending on the copper’s mineral grade. To sell this mineral, small mining companies must transport the product to ENAMI, which means a high monetary cost, added to the fact that there are large amounts of waste minerals that cannot be sold because of their low grade. The present work aims that small miners can process these copper ores in situ to commercialize a more valuable product, such as copper salts. Considering the high solar radiation and the scarce superficial water resources found in the north side of the country, a possible process alternative is the leaching of the ores using acid seawater solutions followed by crystallization by solar evaporation. As a necessary tool for this process design, the present work has developed a model able to predict the copper sulfate pentahydrate crystallization from multicomponent solutions, preventing the co-precipitation of undesired compounds (such as iron salts, sodium chloride, and sodium sulphate among others) that contaminate the final product. The Pitzer thermodynamic model was successfully applied to predict the crystallization process of copper sulfate pentahydrate from synthetic leaching solutions. These results were validated through experimental tests.

1. INTRODUCTION

Chile is one of the main copper producers worldwide, where a large percentage of copper production is carried out by large international mining companies (such as Codelco, BHP Billiton; Antofagasta Minerals, and Anglo American, among others). However, there is a sector that also contributes with the production of copper in the country, which is represented by the small and medium-sized mining companies (Pymes), where a large percentage of them sell their minerals to the National Mining Company (ENAMI) which processes them and subsequently inserts them into the world market.

In 2015, the annual copper production in Chile was around 5.832.551 tons, where of this total, the contribution of small mining companies was around 1%.

On the other hand, it is important to mention that in Chile approximately 180 tons of waste ore are produced monthly, which has a copper grade that varies between 0.5 and 2%, which is also susceptible to being processed.

However, small-scale mining industries do not have suitable technology and economic resources to carry out a technical-economic study to process, in situ, its copper ores to commercialize a more valuable product, such as copper sulfate pentahydrate (CuSO₄·5H₂O), which is one of the most common commercial products of copper because of the wide range of commercial uses and applications.

On the other hand, in Chile, mining activities are concentrated in the north of the country, which is one of the driest areas on the planet, with the highest solar radiation worldwide, scarce superficial water resources, and where there is an increasing demand for water by the different production activities as well as for human consumption; therefore, the mining sector requires the identification of alternative sources of water. One alternative is seawater, which can be a substitute for the limited freshwater resources in the region.

Considering the aforementioned background, and due to small mining companies having scarce monetary resources, it is necessary to perform a scientific and technological study to process impure solutions obtained from leaching, avoiding a purification stage such as solvent extraction (SX).

For this reason, this paper is a scientific complement that offers an alternative to this problem giving added value to these minerals and changing the business model by producing copper salts directly from the leaching solutions [pregnant
leaching solution (PLS) of waste minerals. These salts will be obtained from heap leaching, at a small scale, using resources such as seawater to prepare the leaching solution, and solar evaporation to crystallize copper sulfate pentahydrate, which would reduce investment costs. This alternative would allow the commercialization of waste minerals that actually cannot be sold to ENAMI, due to the restrictions of copper grade, combined with the high transport costs to the sales centers (all the ore must be transported, however, ENAMI pays only the copper ore, which represents approximately 2% of the total transported ore). The copper sulfate pentahydrate obtained as a new product has between 22 and 25% of copper, adding a higher value to the commercialized product by small miners.

Figure 1 shows the process scheme to obtain copper sulfate pentahydrate crystals from PLS, avoiding the SX stage normally used in this process.

In order to design this process, a crystallization equilibrium model is necessary. The thermodynamic Pitzer model is a recognized tool for the determination of activity coefficients, vapor pressures, water activities, solubilities, and saturation index. To carry this out, it is necessary to know the different binary and ternary ion interaction parameters of the Pitzer model through a rigorous bibliographic compilation.

Several authors have studied the applicability of the ion interaction model of Pitzer to correlate the solubility data at different temperatures. Harvie and Weare used this model to predict mineral solubilities at 298.15 K in the Na−K−Ca−Mg−Cl−SO4−H2O system at high ionic strengths concluding that the model can be used to predict solubilities in complex systems. Pabalan and Pitzer determined the mineral solubilities in binary and ternary electrolyte mixtures of the Na−K−Mg−Cl−SO4−OH−H2O system at high temperatures. Møller presented a temperature dependence model for the Na−Ca−Cl−SO4−H2O system that calculates the solubilities from dilute to high concentrations from 298.15 to 523.15 K. Later, Greenberg and Møller extended the model by including potassium interactions and increasing the temperature range from 273.15 to 523.15 K.

Christov studied the system Na−Cu−Cl−SO4−H2O at 298.15 K using the Pitzer model, where the crystallization of the simple salts CuCl2·2H2O and CuSO4·SH2O was evaluated.

Additionally, the simulation of the NaCl−CuCl2 (aq), Na2SO4−CuSO4 (aq), and CuCl2−CuSO4 (aq) systems was performed, demonstrating a good agreement between the experimental and calculated solubility isotherms. Later, Christov and Møller studied the H−Na−K−OH−Cl−HSO4−SO4−H2O system at high solution concentrations from 273.15 to 523 K, where a comparison with the experimental data validated the model.

Wang et al. predicted the solubility of gypsum at 298.15 K in the systems CaSO4−HMSO4−H2SO4−H2O (HM = Cu, Zn, Ni, Mn) up to saturated concentrations of heavy metal sulfates and to a H2SO4 concentration of 2 m by the Pitzer thermodynamic model, concluding that Pitzer model can be used to predict the solubility of gypsum in the quaternary system.

Justel et al. represented the solid−liquid equilibrium of the copper sulfate−sulfuric acid−seawater system using the Pitzer and the Born model to quantify the copper sulfate and sulfuric acid effect, respectively. Besides, the precipitated amounts of copper sulfate as a function of the sulfuric acid concentration were predicted. Then, Justel et al. determined the solid−liquid equilibrium of the CuSO4−H2SO4−seawater system from 293.15 to 333.15 K by means the thermodynamic study of the Cu−Na−H−SO4−Cl−HSO4−H2O system using the Pitzer model.

Garces used the ionic interaction model of Pitzer to determine activity coefficients of the evaporitic Andean deposits known as Salar de Loyoques in northern Chile. Through this model, the activity coefficients were evaluated, and it was determined that the first mineral precipitated was calcite, while gypsum and magnesite are close to equilibrium. These results are based on the calculations of the saturation index (I.S.), where a value of zero means that the solution is in equilibrium with respect to that phase. Positive or negative values of the I.S. indicate a situation of supersaturation or subsaturation, respectively, whose magnitude is a direct function of the absolute value of this quantity.

As shown above, several authors have used these thermodynamic models to work with electrolyte solutions, demonstrating that the Pitzer model is valid over a wide range of temperatures and concentrations.
Accordingly, this work develops a model useful to design crystallization processes using the Pitzer ion interaction model for the simulation and validating this information with experimental tests. The present methodology consists of calculating the supersaturation index using the activity coefficients of the Pitzer model, and according to its values to discriminate (or determine) the salts that would potentially precipitate during a natural evaporation process, which occurs with the natural salt brines. The model was validated using synthetic solutions with a similar composition to those obtained from leaching of mineral using mixtures of water, seawater, and sulfuric acid.

2. THERMODYNAMIC FRAMEWORK

2.1. Pitzer Ion Interaction Model. The Pitzer ion interaction model has been reported by several authors,\textsuperscript{5,7,15–17} which have stated that this approach can be used to calculate solubilities in complex systems and to predict the behavior of natural fluids.

This model begins with a virial expansion of the excess free energy: \( G^{ex}/RT \),\textsuperscript{5} as shown in eq 1.

\[
G^{ex}/RT = n_u f(I) + \sum_i \sum_j \lambda_{ij}(I)m_im_j + \sum_i \sum_j \sum_k \mu_{ijk}m_im_jm_k
\]

(1)

where \( n_u \) is the number of kilograms of solvent and \( m_{ijk} \) is the molality of species \( i, j, \) and \( k \). \( f(I) \) is the Debye–Hückel term which is a function of the ionic strength. \( \lambda_{ij} \) and \( \mu_{ijk} \) are the second and third virial coefficients, respectively, and represent the effects of short-range forces between ions.\textsuperscript{16}

Equation 2 is used to calculate the osmotic coefficient (\( \phi \)), and eqs 3 and 4 are used to model the activity coefficients of the cation (\( M \)) and anion (\( X \)), respectively, as follows:

\[
(\phi - 1) = \frac{2}{(\sum m_i)} A_{ij}^{1/2} + \sum c \sum a m_am_i(B_{ai}^{0} + ZC_{ca}) + \sum c \sum m_im_i(\Phi_{i}^{c} + \sum a m_am_iy_{ac}) + \sum a \sum m_am_i(\Phi_{ai}^{c} + \sum c m_am_iy_{ac})
\]

(2)

\[
\ln \gamma_{M} = z_m^{2}F + \sum a m_a(2B_{ma} + ZC_{ma}) + \sum c m_c(2\Phi_{mc} + \sum a m_am_iy_{Mai}) + \sum a \sum m_am_iy_{Mai}
\]

(3)

\[
\ln \gamma_{X} = z_x^{2}F + \sum c m_c(2\Phi_{xc} + \sum a m_am_iy_{Xai}) + \sum a \sum m_am_iy_{Xai}
\]

(4)

where the subscripts \( M, c, \) and \( c' \) represent the cations and \( X, a, \) and \( a' \) are the anions; \( z_M \) and \( z_x \) correspond to the ion charges, and \( m_c \) and \( m_a \) to the molalities (mol/kg solvent) of the cations and anions, respectively; \( I \) is the ionic strength; and \( b = 1.2 \) and remains constant for all solutes.

The indices \( c < c' \) and \( a < a' \) are the sum over all of the distinguishable pairs of dissimilar cations and anions, respectively. \( \psi_{ijk} \) are the ion-mixing interaction parameters, which are assumed to be independent of the concentration.

The function \( F \) is shown in eq 5.

\[
F = -A_{\phi} \left[ \frac{1}{b^{1/2}} + \frac{2}{b}(\ln(1 + b^{1/2})) \right] + \sum c \sum a m_am_iB_{ai}
\]

(5)

\[
B_{MX}^{0} = B_{MX}^{(0)} + B_{MX}^{(1)}(\alpha^{1/2}) + 2B_{MX}^{(2)}(\alpha^{1/2})
\]

(6)

The coefficients \( B_{MX}^{0} \) are functions of the ionic strength and in the case of electrolytes 1–1 and 1–2, these are represented by the eqs 7–9.

\[
B_{MX}^{(0)} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}(\alpha^{1/2})
\]

(7)

\[
B_{MX}^{(1)} = \beta_{MX}^{(1)}(\alpha^{1/2})
\]

(8)

\[
B_{MX}^{(2)} = \beta_{MX}^{(2)}(\alpha^{1/2})
\]

(9)

For electrolytes 2–2 (as copper sulfate), an additional term is added as shown in eqs 10–12:

\[
B_{MX}^{(0)} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}(\alpha^{1/2}) + \beta_{MX}^{(2)}(\alpha^{1/2})
\]

(10)

\[
B_{MX}^{(1)} = \beta_{MX}^{(1)}(\alpha^{1/2}) + \beta_{MX}^{(2)}(\alpha^{1/2})
\]

(11)

\[
B_{MX}^{(2)} = \beta_{MX}^{(2)}(\alpha^{1/2})
\]

(12)

where the symbols \( \beta_{MX}^{(0)}, \beta_{MX}^{(1)} \) and \( \beta_{MX}^{(2)} \) and \( \gamma_{MX}^{(c)} \) are solute specific parameters and the parameters \( \alpha_1, \alpha_2, \) and \( \beta \) are constants. For copper sulfate, \( \alpha_1 = 1.4 \) and \( \alpha_2 = 12; \) for copper chloride, \( \alpha_1 = 2.0 \) and \( \alpha_2 = 1.0; \) for an electrolyte with one or two univalent ions, \( \alpha_2 = 2 \) and \( \beta \) is not required.\textsuperscript{19}

The functions \( g \) and \( g' \) are given by eqs 13 and 14, as follows:

\[
g(x) = \frac{2[1 - (1 + x)e^{-x}]}{x^2}
\]

(13)
where \( x = a t^{1/2} \).

\( C_{MX} \) is related to the parameter \( C_{MX}^p \) as shown in eq 15.

\[
C_{MX} = \frac{C_{MX}^p}{2(\alpha^2 + x^2)^{1/2}}
\]  

(15)

Some terms containing \( C_{MX} \) parameters have a concentration dependence given by the function \( Z \) from eq 16.

\[
Z = \sum_i m_i |z_i|
\]  

(16)

Also, the equations for the second virial coefficients, \( \Phi \) are the following

\[
\Phi_{MX} = \theta_{MX} + E_{\theta_{MX}}(I)
\]  

(17)

\[
\Phi'_{MX} = E'_{\theta_{MX}}(I)
\]  

(18)

\[
\Phi_{MX}^\prime = \theta_{MX} + E_{\theta_{MX}}(I) + IE_{\theta_{MX}}(I)
\]  

(19)

where \( \theta_{MX} \) represents a single parameter for each pair of cations or anions and \( E_{\theta_{MX}} \) accounts for the electrostatic unsymmetrical mixing effects, which are dependent on the charge of the ions and ionic strength. \( E_{\theta_{MX}} \) and \( E_{\theta_{MX}}^\prime \) are zero when the ions \( i \) and \( j \) have the same charge.\(^5\)

The higher-order electrostatic terms \( E_{\theta_{MX}} \) and \( E_{\theta_{MX}}^\prime \) are calculated by the eqs 20 and 21 reported by Pitzer.\(^{20}\)

\[
E_{\theta_{MX}}(I) = \frac{z_i^2 z_j}{4I} \left( j(x_{MN}) - \frac{1}{2}j(x_{MM}) - \frac{1}{2}j(x_{NN}) \right)
\]  

(20)

\[
E_{\theta_{MX}}^\prime(I) = \left( \frac{E_{\theta_{MX}}}{I} \right) + \left( \frac{z_i^2 z_j}{8I^2} \right) \left( x_{MN}^J - j(x_{MM}) \right) - \frac{1}{2}x_{MM}^J - \frac{1}{2}x_{NN}^J - \frac{1}{2}x_{MM}^J\right)
\]  

(21)

where \( x_{MM} = 6z_{i}z_{j}a_{ij}t^{1/2} \).

The expression for \( J \) was given by Pitzer,\(^{20}\) as follows

\[
J = x(4 + C_{x}C_{i}C_{j}^{2}x^{2}c_{i}^{2}c_{j}^{2}t^{2})^{-1}
\]  

(22)

where the corresponding values of the parameters for the eq 22 are presented in Table 1.

### Table 1. Parameters for Eq 22\(^{20}\)

| parameters | \( C_1 \) | \( C_2 \) | \( C_3 \) | \( C_4 \) |
|------------|--------|--------|--------|--------|
| eq 22     | 4.5810 | 0.7237 | 0.0120 | 0.5280 |

\(^{a}\)On the other hand, \( J \) values are the derivative of \( J \) functions and were calculated from Pitzer.\(^{20}\)

2.2. Determination of Supersaturation Indices. In order to predict the salts that crystallize in the multicomponent system analyzed in the present work, the supersaturation index proposed by Krumgalz et al.\(^{15}\) and Garces\(^{25}\) has been used, where the degree of saturation of a brine with respect to a mineral of the formula \( M_{n}X_{v}nH_{2}O \) is defined by the following equation\(^{25}\)

\[
\Omega_{M_{n}X_{v}nH_{2}O} = \frac{m_{M_{i}X_{v}}^{n} - m_{X_{v}}^{n}H_{2}O}{K_{sp,M_{i}X_{v}}^{n}H_{2}O} \left( \frac{m_{M_{i}X_{v}}^{n} - m_{X_{v}}^{n}H_{2}O}{K_{sp,M_{i}X_{v}}^{n}H_{2}O} \right)
\]  

(23)

where the numerator of the equation is the product of the real ionic concentrations in a particular system and the denominator contains parameters, which are functions of temperature and pressure \( (K_{sp}, a_{H_{2}O}) \). Activity coefficients are estimated by applying the Pitzer model \( (eqs 3 \text{ and } 4) \).

Regarding the supersaturation indices’ results, a value of zero means that the solution is in equilibrium with respect to that phase. Positive or negative values indicate a situation of supersaturation or nonsaturation, respectively, whose magnitude is a direct function of the absolute value of this quantity.\(^{14}\)

### 2.3. Evaporation Crystallization Experiments.

In order to validate the thermodynamic model, batch evaporation crystallization experiments were carried out at room temperature \( (20 \pm 3)°C \). All reagents employed in this work were of analytical grade, and the solutions were prepared using an analytical balance (Mettler Toledo Co. model AX204, with 0.07 mg precision).

Based on the composition of leaching solutions (PLSs) obtained in previous experiments by this research group (data not shown), synthetic leaching solutions were prepared and used in the subsequent crystallization experiments. The following reagents (Merck) were used to prepare these synthetic PLSs: CuSO\(_4\)·5H\(_2\)O, Na\(_2\)SO\(_4\), FeCl\(_2\)·4H\(_2\)O, FeSO\(_4\)·7H\(_2\)O, H\(_2\)SO\(_4\), NaCl, NaHSO\(_4\), As\(_2\)O\(_3\), and H\(_2\)O (Merck pa).

Table 2 shows the composition of the synthetic PLS at two different conditions (PLS\(_1\) and PLS\(_2\)) used for the crystallization experiments, where PLS\(_1\) has a higher concentration of iron and a lower concentration of copper compared with the PLS\(_2\); they are among the ranges of interest for copper mining. It will allow us to validate the model at two different experimental conditions.

The crystallization using solar evaporation experiments were carried out in pyrex glass containers with a capacity of 4 L. The duration of the tests was approximately 15 days for PLS\(_1\) and 22 days for PLS\(_2\), reaching evaporation percentages of 46.02 and 62.55%, respectively (see Table 8). The obtained crystals were washed with distilled water at a ratio of 1 L H\(_2\)O/kg crystals. The composition of the crystallized solids was determined using atomic absorption spectroscopy (AAS). The AAS measurements were performed using a Varian atomic absorption spectrophotometer, model 220. For the photography of the crystals, a Zeiss microscope, model Axio Lab1, was used.

### Table 2. Composition (wt %) of Crystallization Solutions PLS\(_1\) and PLS\(_2\)

| samples | Cu (%) | Fe (%) | Na (%) | Cl (%) | H\(_2\)SO\(_4\) (%) |
|---------|--------|--------|--------|--------|------------------|
| PLS\(_1\) | 2.98   | 3.23   | 0.77   | 0.89   | 5.24             |
| PLS\(_2\) | 4.75   | 1.39   | 0.67   | 0.92   | 3.57             |

3. RESULTS AND DISCUSSION

3.1. Ion-Interaction Parameters of the Pitzer Model.

Interaction parameters were obtained by the bibliographic revision from previously published works. Several authors have determined the ion interaction parameters of the binary subsystems of this work (CuSO\(_4\)·5H\(_2\)O, CuCl\(_2\)·H\(_2\)O, Cu(HSO\(_4\))\(_2\)·H\(_2\)O, Na\(_2\)SO\(_4\)·H\(_2\)O, NaCl·H\(_2\)O, NaHSO\(_4\)·H\(_2\)O,
For the Cu–Na–H–Fe–SO₄–Cl–H₂SO₄–H₂O system, ternary systems have also been studied, where the parameters \( \psi_{ijk} \) and \( \theta_{ijk} \) which are necessary to determine the thermodynamic properties of electrolyte solutions, have been reported at different temperatures by several authors.

Some authors reported \( \theta_{ijk} \) parameters at 298.15 K. Values for \( \theta_{\text{CuSO}_4} \), \( \theta_{\text{CuCl}_2} \), and \( \theta_{\text{CuH}} \) were reported by Pabalan and Pitzer,

\[
\begin{align*}
\theta_{\text{CuSO}_4} & = 2.5270 \\
\theta_{\text{CuCl}_2} & = 1.6704 \\
\theta_{\text{CuH}} & = 3.5560
\end{align*}
\]

respectively. Additionally, a temperature dependence model of the \( \theta_{\text{CuSO}_4} \), \( \theta_{\text{NaHSO}_4} \), \( \theta_{\text{FeSO}_4} \), \( \theta_{\text{ClH}} \), and \( \theta_{\text{HClSO}_4} \) parameters was reported by Christov and Møller. All this information is summarized in Table 4.

For Na₂SO₄, NaCl, NaHSO₄, HSO₄⁻, HCl, H₂SO₄, FeSO₄, FeCl₂, and Fe(HSO₄)₂ at 298.15 K.

Table 3. Pitzer Binary Parameters (ψ⁰, ψ¹, ψ², and Ĉ₂₅) for Na₂SO₄, NaCl, NaHSO₄, HSO₄⁻, HCl, H₂SO₄, FeSO₄, FeCl₂, and Fe(HSO₄)₂ at 298.15 K.

| Substance          | ψ⁰     | ψ¹     | ψ²     | Ĉ₂₅   |
|--------------------|--------|--------|--------|-------|
| Na₂SO₄ (aq)         | 0.2340 | 2.5270 | -48.3300 | 0.0044 |
| NaCl (aq)           | 0.2176 | 0.5740 | 0.6340 | -0.0109 |
| NaHSO₄ (aq)         | 0.0321 | 0.3627 | 0.0988 |
| NaCl (aq)           | 0.0187 | 1.0993 | 0.0063 |
| NaHSO₄ (aq)         | 0.0754 | 0.2770 | 0.0114 |
| HSO₄⁻ (aq)          | 0.0105 | 0.0208 | 0.0280 |
| HCl (aq)            | 0.0910 | 0.0000 | 0.0552 |
| H₂SO₄ (aq)          | 0.0104 | 0.0411 | 0.0000 |
| FeSO₄ (aq)          | 0.2569 | 3.0879 | -42.0000 | 0.0209 |
| FeCl₂ (aq)          | 0.3359 | 1.5323 | -0.0086 |
| Fe(HSO₄)₂ (aq)      | 0.4337898 | 3.48 | 0.0000 |

Superscripts: a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z.

Table 4. \( \theta_{ijk} \) Parameter Values at 298.15 K Used in the Present Work.

| Substance          | \( \theta_{ijk} \) | \( \theta_{ijk} \) | \( \theta_{ijk} \) | \( \theta_{ijk} \) |
|--------------------|-------------------|-------------------|-------------------|-------------------|
| \( \text{CuSO}_4 \) | 0.0700            | 0.0770            | 0.0230            | -0.1190           |
| \( \text{CuCl}_2 \) | 0.0345            | 0.0000            | 0.0000            | 0.0000            |
| \( \text{FeSO}_4 \) | 0.0800            | 0.0000            | 0.0000            | 0.0000            |

*Values at 298.15 K were taken from: a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z.

In addition, some authors reported equations for the \( \psi_{ijk} \) determination as a function of the temperature. Here, the temperature dependence of \( \psi_{NaClSO₄} \) was determined using the model of Møller, which is valid from 273.15 to 423.15 K. In the case of \( \psi_{NaHSO₄} \), \( \psi_{NaCl} \), \( \psi_{NaSO₄} \), \( \psi_{HClSO₄} \), \( \psi_{H₂SO₄} \), and \( \psi_{FeCl₂} \), the model of Christov and Møller was used. The \( \psi_{ij} \) parameters at 298.15 K used in the present work are summarized in the Table 5.

Parameters values of \( \psi_{CuCl₂}, \psi_{CuNaSO₄} \), and \( \psi_{CuCl₂SO₄} \) at 298.15 K were obtained from the work of Justel et al. Values of \( \psi_{CuFe₃SO₄} \), \( \psi_{CuFe₃Cl₂} \), \( \psi_{CuFe₃HSO₄} \), \( \psi_{Na₃SO₄} \), \( \psi_{Na₃Cl₂} \), and \( \psi_{Na₃HSO₄} \) were considered as zero because they were not found in the literature.

3.2. Determination of Solubility Products, Activity Coefficients, and Supersaturation Indices at 298.15 K.

The solubility product \( (K_{sp}) \) is a value that can be obtained from the solubility, activity coefficient, and water activity of crystallized salts in H₂O. The solubility products of the solid phases \( K_{sp} \) at 298.15 K were determined by the following expression:

\[
K_{sp} = (m_M^{s\gamma})(m_X^{s\gamma})(x_{M\overline{M}_{\infty}}^{s\gamma}) \tag{24}
\]

From eq 24, saturation molality in a ternary system is obtained by

\[
(m_M^{s\gamma})(m_X^{s\gamma}) = \left( \frac{K_{sp}}{(x_{M\overline{M}_{\infty}}^{s\gamma})} \right) \tag{25}
\]

Table 6 shows the solubility product, activity coefficient, and water activity values of crystallized salts at 298.15 K.

At 298.15 K, there is a mean deviation of 0.0001 between the solubility product of copper sulfate obtained in the present work and the one reported by Christov for aqueous copper sulfate solutions. In the case of FeSO₄ there is a mean deviation of 0.0003 between the solubility product obtained in this work and the one obtained by Christov.

Table 7 shows the values of activity coefficients and supersaturation indices obtained in both cases (PLS₁ and PLS₂):

From supersaturation indices results, it is possible to conclude that in PLS₁, where the concentration of iron is higher than the concentration of copper, the crystallization of both copper sulfate and ferrous sulfate occurs. However, when the copper concentration is increased, and iron concentration decreased (PLS₂), the precipitation of copper sulfate pentahydrate occurs and the precipitation of ferrous sulfate is not observed.
From the thermodynamic model, it was predicted that if the solution had a Cu/Fe molar ratio greater than 2.05, only copper sulfate would precipitate. These results allow us to know the Cu/Fe ratio necessary to obtain only the precipitation of copper sulfate pentahydrate and, hence, facilitate the process design.

### 3.3. Validation of the Model through Evaporation Crystallization Experiments

The validation of the thermodynamic model through evaporation crystallization experiments at two different conditions was performed. Table 8 shows the evaporation percentages of the solutions, composition of crystals obtained, and yield (%) of crystallization experiments of the two initial solutions (PLS1 and PLS2).

These variations in the evaporation percentages are due to the fact that in the case of PLS1, the crystals that first appeared were, with the naked eye, contaminated (blue-yellowish color); due to this, the evaporation stopped before than in PLS2 because these did not correspond to high purity copper sulfate crystals that is the objective of this work. The opposite occurred in PLS2, where the crystals, at a glance, corresponded to copper sulphate pentahydrate; therefore, the evaporation percentage was higher to obtain a greater amount of crystals.

As can be seen in Table 8, there is a significant difference in the compositions of the crystals obtained from the two initial PLS solutions, where the percentage of CuT of the crystals obtained from PLS1 (9.42%) is lower than those obtained in PLS2 (24.00%); on the other hand, the Fe percentage of the crystals obtained from PLS1 (10.88%) is higher in PLS2 (0.28%). Concluding that crystals from PLS2 corresponds, mostly, to copper sulfate pentahydrate; on the other hand, a high concentration of Fe of crystals obtained from PLS1 can be attributed to the presence of ferrous sulfate in the crystals.

Figure 2 shows the supersaturation indices of copper sulfate pentahydrate and ferrous sulfate heptahydrate at 298.15 K, as a function of the Cu/Fe molar ratio, which varies from 0 to 2.6 approximately.

From Figure 2, it is observed that from a Cu/Fe molar ratio higher than around 2.05, according to the thermodynamic model, only the precipitation of copper sulfate occurs, which is the product of commercial interest; however, under this ratio, the precipitation of both copper sulfate and ferrous sulfate occurs. These results allow us to know the Cu/Fe ratio necessary to obtain only the precipitation of copper sulfate pentahydrate, and hence, facilitate the process design.
Table 8. Percentage of Evaporation, Composition, and Yield of Crystallization Experiments Performeda

| Sample                  | evaporation (%) | CuT   | FeT   | Cl    | SO₄   | Na    | copper yield (%) |
|-------------------------|-----------------|-------|-------|-------|-------|-------|------------------|
| crystals from PLS1      | 46.02           | 9.42  | 10.88 | <0.001| 35.91 | 0.0015| 44.27            |
| crystals from PLS2      | 62.55           | 24.00 | 0.28  | <1    | 36.30 | 0.377 | 71.91            |

CaT and FeT, correspond to the total copper and iron percentage of the crystallized solids.

4. CONCLUSIONS

The ion interaction model of Pitzer can be successfully used as an applied tool to predict the potential crystallization of salts from a multicomponent system as the PLS from the mining industry, where only the composition of the initial solution is required.

The copper sulfate pentahydrate obtained as a new product has around 22−25% of copper, adding a higher value to the commercialized product by small miners. As a conclusion, if the process proposed in the present work is used, the product to be sold by the small miners would increase its law tenfold, and the mass to transport would decrease by more than 20 times.

Figure 3. (a) Image of crystals obtained from PLS1 and (b) image of crystals obtained from PLS2.

The copper sulfate pentahydrate obtained as a new product is a product of commercial interest; on the other hand, under this ratio, the precipitation of both copper sulfate and ferrous sulfate is observed.

Because of this, from the experimental results, it is possible to conclude that the Pitzer thermodynamic model can be successfully used as an applied tool to predict the potential crystallization of salts from a multicomponent system as the PLS from the mining industry, where only the composition of the initial solution is required.

The copper sulfate pentahydrate obtained as a new product has around 22−25% of copper, adding a higher value to the commercialized product by small miners. As a conclusion, if the process proposed in the present work is used, the product to be sold by the small miners would increase its law tenfold, and the mass to transport would decrease by more than 20 times.

4. CONCLUSIONS

The ion interaction model of Pitzer can be successfully used as an applied tool to predict the potential crystallization of salts from a multicomponent system as the PLS from the mining industry, where only the composition of the initial solution is required.

For a Cu/Fe ratio higher than approximately 2.05, it was observed that only copper sulfate pentahydrate crystallizes, which is a product of commercial interest; on the other hand, under this ratio, the precipitation of both copper sulfate and ferrous sulfate is observed.

Crystals obtained from PLS1 have a more elongated shape in comparison with crystals obtained from PLS2, which have a rhomboid structure similar to that of copper sulfate pentahydrate crystals found in the literature. The change in the shape of the crystals obtained in PLS1 could be attributed to the higher presence of Fe in the crystal structure.

The present work corresponds to a contribution because it facilitates the design of the copper sulfate crystallization process to be carried out by small miners and realizes that the Pitzer’s thermodynamic model can be applied to optimize processes at the pilot and industrial scales.

AUTHOR INFORMATION

Corresponding Author

Teófilo A. Graber — Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta, Chile; Centro de Investigación Científico Tecnológico para la Minería (CICITEM), Antofagasta, Chile; orcid.org/0000-0002-5830-1194; Phone: +56 55 2637458; Email: teofil.graber@uantof.cl

Authors

Francisca J. Justel — Departamento de Ingeniería Metalúrgica y Materiales, Universidad Técnica Federico Santa María, Chile

María E. Taboada — Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta, Chile; Centro de Investigación Científico Tecnológico para la Minería (CICITEM), Antofagasta, Chile

Elsa K. Flores — Centro de Investigación Científico Tecnológico para la Minería (CICITEM), Antofagasta, Chile

Héctor R. Galleguillos — Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta, Chile

ACKNOWLEDGMENTS

The authors acknowledge CONICYT-Chile for financing this research through the FONDEF Project Code IT17M1001. The authors are also grateful of the Project ING2030 CORFO Code 16ENI2/71940.

REFERENCES

(1) SERNAGEOMIN Anuario de la Minería de Chile 2015; Servicio Nacional de Geología y Minería, 2015.

(2) Justel, F. J.; Claros, M.; Taboada, M. E. Solubilities and physical properties of saturated solutions in the copper sulfate + sulfuric acid + seawater system at different temperatures. Braz. J. Chem. Eng. 2015, 32, 629−635.

(3) Brantes, R.; Olivares, G. Best Practices and Efficient Use of Water in the Mining Industry; Cochilco (Chilean Copper Commission), 2008.

(4) Cochilco. Water Consumption Forecast in Copper Mining 2018−2029. DEPP 22/2017,2018.

(5) Harvie, C. E.; Weare, J. H. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO₄-H₂O system from zero to high concentration at 25°C. Geochim. Cosmochim. Acta 1980, 44, 981−997.

(6) Pabalan, R. T.; Pitzer, K. S. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO₄-2OH-H₂O. Geochim. Cosmochim. Acta 1987, 51, 2429−2443.

(7) Møller, N. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O...
system, to high temperature and concentration. Geochim. Cosmochim. Acta 1988, 52, 821–837.
(8) Greenberg, J. P.; Møller, N. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system to high concentration from 0 to 250 °C. Geochim. Cosmochim. Acta 1989, 53, 2503–2518.
(9) Christov, C. Thermodynamic study of the Na-Cu-Cl-SO₄-H₂O system at the temperature 298.15 K. J. Chem. Thermodyn. 2000, 32, 285–295.
(10) Christov, C.; Møller, N. Chemical equilibrium model of solution behavior and solubility in the H-Na-K-OH-Cl-HSO₄-SO₄-H₂O system to high concentration and temperature. Geochim. Cosmochim. Acta 2004, 68, 1309–1331.
(11) Wang, W.; Zeng, D.; Yin, X.; Chen, Q. Prediction and measurement of gypsum solubility in the systems CaSO₄+ HMSO₄+ H₂SO₄+ H₂O (HM= Cu, Zn, Ni, Mn) at 298.15 K. Ind. Eng. Chem. Res. 2012, 51, 5124–5134.
(12) Justel, F. J.; Taboada, M. E.; Jiménez, Y. P. Solid–liquid equilibrium and copper sulfate crystallization process design from a sulfuric-acid–seawater system in the temperature range from 293.15 to 333.15 K. Ind. Eng. Chem. Res. 2017, 56, 4477–4487.
(13) Justel, F. J.; Taboada, M. E.; Jimenez, Y. P. Thermodynamic study of the Cu-Na-H-SO₄-Cl-HSO₄-H₂O system for the solubility of copper sulfate in acid seawater at different temperatures. J. Mol. Liq. 2018, 249, 702–709.
(14) Garces, I. Aplicación del Modelo de Interacción Íónica de Pitzer para determinar Coeficientes de Actividad en Salmueras Naturales con Presencia de Boro. Inf. Tecnol. 2019, 30, 283–292.
(15) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 1973, 77, 268–277.
(16) Pitzer, K. S.; Kim, J. J. Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. J. Am. Chem. Soc. 1974, 96, 5701–5707.
(17) Pabalan, R. T.; Pitzer, K. S. Heat capacity and other thermodynamic properties of Na₂SO₄(aq) in hydrothermal solutions and the solubilities of sodium sulfate minerals in the system Na₂Cl-SO₄-OH-H₂O to 300°C. Geochim. Cosmochim. Acta 1988, 52, 2393–2404.
(18) Clegg, S.; Whitfield, M. Activity coefficients in natural waters. Activity Coefficients in Electrolyte Solutions; CRC Press, 1991; Vol. 2.
(19) Downes, C. J.; Pitzer, K. S. Thermodynamics of electrolytes. Binary mixtures formed from aqueous NaCl, NaSO₄, CuCl₂, and CuSO₄ at 25° C. J. Solution Chem. 1976, 5, 389–398.
(20) Pitzer, K. S. Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms. J. Solution Chem. 1975, 4, 249–265.
(21) Holmes, H. F.; Busey, R. H.; Simonson, J. M.; Mesmer, R. E.; Archer, D. G.; Wood, R. H. The enthalpy of dilution of HCl (aq) to 648 K and 40 MPa thermodynamic properties. J. Chem. Thermodyn. 1987, 19, 863–890.
(22) Tanaka, M. Modelling of solvent extraction equilibria of Cu(II) from nitric and hydrochloric acid solutions with (β-hydroxyoxime). Hydrometallurgy 1990, 24, 317–331.
(23) Marion, G. M.; Catling, D. C.; Kargel, J. S. Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars. Geochim. Cosmochim. Acta 2003, 67, 4251–4266.
(24) Baes, C. F., Jr.; Reardon, E. J.; Moyer, B. A. Ion interaction model applied to the cupric sulfate-sulfuric acid-water system at 25.5 degree.C. J. Phys. Chem. 1993, 97, 12343–12348.
(25) Krumsalgal, B. S.; Starinsky, A.; Pitzer, K. S. Ion-Interaction Approach: Pressure Effect on the Solubility of Some Minerals in Submarine Brines and Seawater. J. Solution Chem. 1999, 28, 667–692.
(26) Lovaer, J. A.; Padilla, A. P.; Galleguillos, H. R. Correlation of the solubilities of alkali chlorides in mixed solvents: Polyethylene glycol + H₂O and Ethanol + H₂O. Calphad 2012, 38, 35–42.
(27) Christov, C. Pitzer ion-interaction parameters for Fe(II) and Fe(III) in the quinary [Na+K+Mg+Cl+SO₄+H₂O] system at 298.15 K. J. Chem. Thermodyn. 2004, 36, 223–235.
(28) Giulietti, M.; Seckler, M. M.; Derenzo, S.; Schiavon, L. H.; Valarelli, J. V.; Nyvlt, J. Effect of selected parameters on crystallization of copper sulphate pentahydrate. Cryst. Res. Technol. 1999, 34, 959–967.