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Original Article

Thermodynamic modeling of phases equilibrium in aqueous systems to recover potassium chloride from natural brines

Ruberlan Gomes da Silva[a,*], *Marcelo Seckler*[b], *Sonia Denise Ferreira Rocha*[c], *Daniel Saturnino*[d], *Éder Domingos de Oliveira*[d]

[a] *Mineral Development Centre of Vale, Santa Luzia, MG, Brazil*
[b] *Department of Chemical Engineering, Universidade de São Paulo (USP), São Paulo, SP, Brazil*
[c] *Department of Mining Engineering, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG, Brazil*
[d] *Department of Chemical Engineering, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG, Brazil*

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ABSTRACT

Chemical fertilizers, such as potassium chloride, ammonium nitrate and other chemical products like sodium hydroxide and soda ash are produced from electrolyte solutions or brines with a high content of soluble salts. Some of these products are manufactured by fractional crystallization, when several salts are separated as solid phases with high purity (>90%). Due to the large global demand for potassium fertilizers, a good knowledge about the compositions of salts and brines is helpful to design an effective process. A thermodynamic model based on Pitzer and Harvie's model was used to predict the composition of crystallized salts after water removal by forced evaporation and cooling from multicomponent solutions or brines. Initially, the salts' solubilities in binary systems (NaCl–H_2O, KCl–H_2O and $MgCl_2$–H_2O) and ternary system (KCl–$MgCl_2$–H_2O) were calculated at 20 °C and compared with literature data. Next, the model was compared to our experimental data on the quinary system NaCl–KCl–$MgCl_2$–$CaCl_2$–H_2O system at 20 °C. The Pitzer and Harvie's model represented well both the binary and ternary systems. Besides, for the quinary system the fit was good for brine densities up to 1350 kg/m^3. The models were used to estimate the chemical composition of the solutions and salts produced by fractional crystallization and in association with material balance to respond to issues related to the production rates in a solar pond containing several salts dissolved, for instance, NaCl, KCl, $MgCl_2$ and $CaCl_2$.

* *Corresponding author.*
E-mail: ruberlan.silva@vale.com (R.G.d. Silva).

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1. Introduction

The solubility prediction of electrolytes in aqueous solutions is essential for a variety of processes such as brines and seawater desalination, drowning-out crystallization as well as liquid–liquid extraction in chemical, mineral and hydrometallurgical industries [1]. For example, solar evaporation is applied to brine ponds in northern regions of Argentina and Chile to produce saleable salts like potassium chloride, potassium sulphate and lithium salts [2]. The process is based on fractional crystallization [3], which provides separation of inorganic salts with purities compatible with market requirements. Thermodynamic models are useful tools to estimate the solution composition during crystallization, which is needed for reliable industrial process design. In this context, Pitzer's ion-interaction model and its extended Harvie and Weare's model [4–6] are suitable tools because they are reliable for predicting salt's solubility in multicomponent aqueous systems with high ionic strength over a wide range of temperatures (0–300 °C) [7–9]. Considering this, it is the objective of this study to analyze the technical feasibility of recovering potassium chloride from a natural complex brine, here represented as the quinary system NaCl–KCl–$MgCl_2$–$CaCl_2$–H_2O. Given the lack of information for such quinary system, experimental data on solubilities have been determined and compared to Pitzer's ion-interaction model predictions. The validated model has been used to develop a technically feasible fractional crystallization process.

2. Material and methods

Batch crystallization experiments with a natural brine from a dry salt lake located at the north of Argentina were performed in a 2 l jacketed glass crystallizer. Temperature was controlled by an electric heating system at 85 ± 3 °C. A mechanic stirrer at 250 RPM provided mixing, using a 45° pitched blade impeller. Table 1 shows the chemical composition of the natural brine under investigation.

The natural brine sample was distributed in four recipients and concentrated by forced evaporation at 85 °C at ambient pressure (~1 atmosphere). Thereafter, the pulps were cooled to 20 °C to increase yield and kept under stirring for 24 h at 250 RPM in order to achieve equilibrium. The initial brine (1.198 g/cm^3 at 20 °C) was concentrated up to 1.250 g/cm^3 at 20 °C, which is now called the Step 1 in this methodology. The solid and liquid phases in equilibrium were then separated by vacuum filtration. The liquid phase with 1.250 g/cm^3 was subjected to another cycle of evaporation at 85 °C followed by a cooling process to 20 °C in order to increase its density to 1.304 g/cm^3 at 20 °C and this is the Step 2. The crystallization and solids separation procedures were repeated two more times to produce brines with densities of 1.354 g/cm^3 at 20 °C in Step 3 and 1.427 g/cm^3 at 20 °C in Step 4. The evaporation at 85 °C is required to concentrate the brine samples to desired densities in a timely manner and then cooling to 20 °C. The temperature of 20 °C was chosen because it is the average brine temperature processed in dry salt lakes, like Salar de Atacama in Chile [2]. The less soluble and more abundant salts, for example NaCl, crystallized at the beginning of the process, whereas the more soluble and less abundant ones ($CaCl_2$·$MgCl_2$·12H_2O) crystallized at the end of the experiment. Sodium, potassium, magnesium, calcium and chloride contents in solution were analyzed as well as in the wet salts obtained in each step.

The solutions were diluted and the respective wet salts dissolved in doubly deionized water to determine the sodium, potassium, magnesium and calcium contents by PerkinElmer NexION 200D ICP-MS. The chloride concentrations in the liquid and solid phases were determined by titration with a standard solution of $AgNO_3$ in the presence of drops of 0.1% (w/v) K_2CrO_4 as an indicator.

Samples for X-ray diffraction were ground below 200 # TYLER MESH (0.074 mm) and analyzed on PANalytical Model X'PERT PRO MPD (PW 3419) with PW3050/60 (θ/θ) goniometer, X-ray ceramics tubes, anode of Cu (Kα1 = 1.540598 Å) and PW3373/00 model (2000 W-60 kV). Diffraction patterns were acquired from 5° to 75°2θ at 0.02 steps. The identification of all minerals was done with X'Pert HighScore version 2.1b software from PANalytical.

3. Results and discussion

The solubility equilibrium constant, K_{SP}, at a fixed temperature and pressure for the dissolution reaction of hydrated salt ($M_{\nu M}X_{\nu X}\cdot\nu_0H_2O$), having ν_M positive ions (M), of charge $_{zM}$, and ν_X negative ions (X) of charge $_{zX}$, as well ν_0 molecules of water (Eq. (1)) [8] is expressed by Eq. (2) [8]:

Example:

$$\begin{aligned} M_{\nu M}X_{\nu X}\cdot\upsilon_0H_2O &= \upsilon_M\cdot M^{+zM}+\upsilon_X\cdot X^{-zX}+\upsilon_0\cdot H_2O \\ CaCl_2\cdot 12H_2O &= 1\cdot Ca^{+2}+2\cdot Cl^{-1}+12\cdot H_2O \end{aligned} \quad (1)$$

$$\ln K_{sp} = -\left[\frac{(\nu_M\cdot\mu^\circ_M+\nu_X\cdot\mu^\circ_X+\nu_0\cdot\mu^\circ_{H_2O})}{R\cdot T}\right]+\left[\frac{(\mu^\circ_S)}{R\cdot T}\right] \quad (2)$$

where μ° is the standard chemical potential of solids (μ°_S), water ($\mu^\circ_{H_2O}$) and for the ions solution (μ°_M and μ°_X) at a given temperature (T) and R is the gas universal constant. The standard state for the aqueous ions and electrolytes was taken to be a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The solid

Table 1 – Density and chemical composition of the natural brine.

Density at 20 °C (g/cm^3)	NaCl (g/L)	KCl (g/L)	$MgCl_2$ (g/L)	$CaCl_2$ (g/L)	$CaSO_4$ (g/L)	Total salts (g/L)
1.198	244.17	17.20	28.20	58.50	0.19	348.26

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