Abstract

Potassium chloride (KCl) accounts for most of the potassium (K) used in world agriculture and represents 96% of the world potash capacity. The other 4% includes potassium sulfate (K₂SO₄), potassium nitrate (KNO₃) and potassium-magnesium based salts. In this sense, the prediction of the solubility of electrolytes in aqueous solutions is important to provide data for processes that extract potassium salts from multicomponent brines. In this work, Pitzer’s and Harvie’s models were used to calculate the amount and composition of crystallized salts after water evaporation. The process involved four crystallization steps starting from multicomponent brines represented by the quinary Na-K-Ca-Mg-Cl aqueous system at 20°C. The temperature of 20°C was chosen because it is the average process brine temperature in many dry salt lakes. The Pitzer’s and Harvie’s models allowed performing a material balance in solar ponds producing saleable salts like sodium, potassium, magnesium and calcium chlorides.

Keywords: Crystallization; Potassium; Quinary Na-K-Ca-Mg-Cl Aqueous System.

1 INTRODUCTION

The knowledge of solubility of electrolytes in aqueous solutions is essential for the development of many processes such as brines and seawater desalination, salting-out crystallization and liquid-liquid extraction in chemical, mineral and hydrometallurgical industries [1]. For example, high evaporation rates and minimal rainfall in northern regions

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RECOVERY OF SALEABLE SALTS FROM OCCURRING NATURAL BRINES REPRESENTING THE QUINARY AQUEOUS SYSTEM Na-K-Mg-Ca-Cl

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RECUPERAÇÃO DE SAIS COMERCIAIS A PARTIR DE UMA SALMOURA NATURAL REPRESENTATIVA DO SISTEMA QUINÁRIO Na-K-Mg-Ca-Cl

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Resumo

O cloreto de potássio (KCl) é uma das principais fontes de potássio (K) usada na agricultura e corresponde a 96% do consumo mundial desse nutriente. Os outros 4% incluem o sulfato de potássio (K₂SO₄), nitrato de potássio (KNO₃) e os sais duplos de potássio e magnésio. A previsão da solubilidade dos eletrólitos em soluções aquosas é importante na estimativa dos parâmetros de processos da rota de processo a ser usada na extração seletiva dos sais de potássio presentes em salmouras multicomponente. Nesse sentido, os modelos de Pitzer e Harvie foram usados nas estimativas das quantidades e das composições dos sais cristalizados após evaporação da água. A rota de processo envolve quatro etapas de cristalização de uma salmoura representativa do sistema aquoso quinário Na-K-Mg-Ca-Cl na temperatura de 20°C. A temperatura de 20°C foi escolhida por ser a temperatura média das salmouras verificadas nos salares Andinos. Os resultados obtidos com os modelos de Pitzer e Harvie permitiram a elaboração do balanço de massa e energia das piscinas de evaporação e obtenção dos sais comerciais: cloretos de sódio, potássio, magnésio e cálcio.

Palavras-chave: Cristalização; Potássio; Sistema Aquoso Quinário Na-K-Ca-Mg-Cl.

1 INTRODUCTION

The knowledge of solubility of electrolytes in aqueous solutions is essential for the development of many processes such as brines and seawater desalination, salting-out crystallization and liquid-liquid extraction in chemical, mineral and hydrometallurgical industries [1]. For example, high evaporation rates and minimal rainfall in northern regions
of Argentina and Chile allow solar evaporation ponds to produce commercial salts from natural brines, like potassium chloride, potassium sulfate and lithium salts [2].

The processing of brines from Qarhan Salt Lake (China) containing K\(^+\), Na\(^+\), Mg\(^{2+}\) and Cl\(^-\) follows the crystallization sequence: NaCl → NaCl + KCl → NaCl + KCl + MgCl\(_2\) + 6H\(_2\)O → NaCl + MgCl\(_2\) + MgCl\(_2\) + 6H\(_2\)O. In this process, during carnallite (KCl,MgCl\(_2\), 6H\(_2\)O) formation step, NaCl is always associated with carnallite as mixed crystals. Therefore 12-25% w/w NaCl has to be separated first in order to produce pure KCl by carnallite decomposition [3]. Similarly, all resulting multicomponent brines have to be processed to deliver the individual salts with purities compatible with market-grade products.

Thermodynamic models are a usual tool to design and evaluate the facilities that produce salts with market-grade purities. For example, the Pitzer and Harvie’s model agrees well with literature data on both: the binary systems (NaCl-H\(_2\)O, KCl-H\(_2\)O and MgCl\(_2\)-H\(_2\)O) and on the ternary systems (NaCl-KCl-H\(_2\)O) at 20°C as already published [4]. The process is based on the separation of inorganic salts from a multicomponent system using fractional crystallization [5]. To this end, Pitzer’s ion-interaction model [6] and its extended Harvie and Weare’s model [7,8] are suitable tools, because they are reliable in predicting the mineral solubility of multicomponent salt systems in natural waters with high ionic strength (0 to 6 molal), over a wide range of temperatures (0 to 300°C) [8-10].

A complete study for the system Na-K-Mg-Ca-HCl-SO\(_4\)-OH-HCO\(_3\)-CO\(_3\)-CO\(_2\)-H\(_2\)O was carried out at 25°C by Harvie et al. [7]. The authors used the salts solubilities in the ternary ion system to obtain the mixture parameters and also to determine the chemical potentials of some of the solid phases. A similar procedure was used to predict the solubilities of the Na-K-Mg-SO\(_4\)-OH-H\(_2\)O system at several temperatures [9]. The equations for the calculation of the solubilities of halite, sylvite and carnallite, individually or combined, have been set up by Marcus and Soffner [11] for the quinary system NaCl-KCl-MgCl\(_2\)-CaCl\(_2\)-H\(_2\)O at 25°C.

Thus, the objective of this study is to understand the equilibrium of the quinary aqueous system Na-K-Mg-Ca-Cl, using synthetic pulps with different amounts of NaCl, KCl, MgCl\(_2\), 6H\(_2\)O and CaCl\(_2\), 2H\(_2\)O analytical grade salts. To this end, solubility data measured at 20°C for liquors and solids in equilibrium, representing the aqueous Na-K-Mg-Ca-Cl system, were compared with the solubilities calculated based on Pitzer’s and Harvie’s ion-interaction models. The idea was to verify the capability to predict the behavior of the system after the removal of different amounts of water by evaporation. The motivation behind this study is to obtain data to help in evaluating the technical and economic feasibility of operations in natural occurring brines, representing the aqueous Na-K-Mg-Ca-Cl system. The purpose would be to obtain saleable salts, like magnesium and calcium chlorides, as well as sodium and potassium chlorides, at grades matching market specifications.

### 2 METHODOLOGY

Phase equilibrium at 20°C in the quinary system was studied using the isothermal dissolution method [12]. Batch crystallization experiments with synthetic pulps were conducted using a thermostatic shaker from Innova 44 model New Brunswick, with temperature controlled to 0.02K. Analytical grade salts from Merck: sodium chloride (NaCl, 99.5 wt%), potassium chloride (KCl, 99.5 wt%), magnesium chloride (MgCl\(_2\), 6H\(_2\)O, 99.5% wt%) and calcium chloride (CaCl\(_2\), 2H\(_2\)O, 99.5% wt%) and double-deionized water were used to prepare the various slurries. Stirring was provided by a mechanical stirrer at 200 RPM, using a 45° pitched blade impeller. Table 1 shows the amount of salts used to prepare the exploratory five synthetic pulps. All pulps were saturated with NaCl. The difference of the three first pulps was the amount of water to evaluate the effect of water in the crystallization by evaporation. The fourth pulp had a reduced amount of NaCl in order to evaluate the behaviour of KCl, MgCl\(_2\), and CaCl\(_2\), and, in the fifth, the amounts of NaCl and KCl were reduced to analyse the behaviour of MgCl\(_2\) and CaCl\(_2\).

The pulps were distributed in five recipients and stirred for 48 hours at 200 RPM in order to achieve equilibrium. The pulps in equilibrium at 20°C were vacuum filtered using 0.22 µm membranes. The temperature of 20°C was chosen because it is the average process brine temperature in most salt lake operations [2].

The liquid phases were diluted with double-deionized water to determine the sodium, potassium, magnesium and calcium contents with a GBCPlus Atomic Absorption Spectrometer. The chloride concentrations in the liquid phases were determined by titration with a standard solution of AgNO\(_3\) in the presence of drops of 0.1% (w/v) K\(_2\)CrO\(_4\) as an indicator.

Solids samples for X-ray diffraction were ground below 200 # TYLER MESH and analyzed on a PANalytical Model X’Pert PRO MPD (PW 3419) with a PW3050/60 (0/0) goniometer, X-ray ceramics tubes, anode of Cu (K\(\alpha\) = 1.540598 Å) and PW3373/00 model (2000 W-60kV). Diffraction patterns were acquired from 5° to 75°, 20 at 0.02 steps. The identification of all minerals was done with X’ Pert High Score version 2.1b software from PANalytical.

**Table 1. Amounts of salts and water used to prepare the five synthetic pulps**

<table>
<thead>
<tr>
<th>Test Number</th>
<th>NaCl (g)</th>
<th>KCl (g)</th>
<th>MgCl(_2), 6H(_2)O (g)</th>
<th>CaCl(_2), 2H(_2)O (g)</th>
<th>H(_2)O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57.47</td>
<td>4.05</td>
<td>14.16</td>
<td>18.23</td>
<td>188.02</td>
</tr>
<tr>
<td>2</td>
<td>57.47</td>
<td>4.05</td>
<td>14.16</td>
<td>18.23</td>
<td>88.02</td>
</tr>
<tr>
<td>3</td>
<td>57.47</td>
<td>4.05</td>
<td>14.16</td>
<td>18.23</td>
<td>68.02</td>
</tr>
<tr>
<td>4</td>
<td>0.70</td>
<td>4.05</td>
<td>14.16</td>
<td>18.23</td>
<td>28.02</td>
</tr>
<tr>
<td>5</td>
<td>0.70</td>
<td>0.05</td>
<td>14.16</td>
<td>18.23</td>
<td>8.01</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The results are shown in two separate sections. In the first, the solubilities of interest are calculated using the thermodynamic models and the experimental data are compared to the solubilities calculated by the models. In the second section, a material balance for a solar evaporation pond is developed to estimate the production of market-grade salts.

3.1 Solubility Predicted by Pitzer’s and Harvie’s Models

The theory used to calculate the salts solubilities was described by Silva et al. (2016) according to reference [278]. Experimentally determined equilibrium compositions of liquid and solids phases from five synthetic pulps are shown in Table 2 and Table 3. The Pitzer’s and Harvie’s models results are presented in Table 4.

From Table 2 and Table 4, it is seen that the liquid phases obtained from tests 1, 2 and 3 are all saturated with NaCl, while the low NaCl contents, in the solid salts from tests 4 and 5, could be due to their respective impregnated liquid phases. The high amount of solids in equilibrium with the respective brine was founded in test 4, 11% w/w of brine and 89% w/w of solids. The equilibrium liquid phase from test 5 is saturated with respect to several salts, as indicated in Table 3 and Table 4. It is noticed the presence of the most soluble salts, carnallite and calcium chloride included, in the solid phases of test 4 and test 5, respectively. Table 4 presents the values of activities of water (aw), calculated by equation 6 from reference [11], for the five liquid phases in equilibrium with the solids in each test. It is possible to check a reduction of water activity with the increase of total soluble solids.

Figure 1 shows a comparison between the compositions of equilibrium brines at 20°C calculated by Pitzer’s and Harvie’s models and obtained by the tests with synthetic pulps.

The simulated and experimental results of the synthetic pulps for the experimental concentrations of 2-2 electrolytes are shown in Figure 1a. Magnesium chloride (MgCl₂) and calcium chloride (CaCl₂) are in the equilibrium as well as...
Recovery of saleable salts from occurring natural brines representing the quinary aqueous system Na-K-Mg-Ca-Cl

3.2 Use of Pitzer and Harvie’s Model to Evaluate the Separation of Saleable Salts from Brines Represented by the Na-K-Mg-Ca-Cl System

The Pitzer’s and Harvie’s models [7,9] were used to simulate the process to obtain saleable salts from natural brine containing Na-K-Mg-Ca-Cl. The composition of liquid phase obtained in the Test 1 was assumed as the same of feed brine due to its saturated condition in NaCl, commonly seen in most brines used to produce KCl.

A solar evaporation process has been designed for the extraction of potassium chloride from brines. The basic streams for the material balance around a single solar pond is shown in Figure 3 where: (i) leakage is the brine lost from the pond through porous dikes and floors. The quantity of leakage is usually described in kg per day and it is a function of the pond area [13]. According proposed by Butts [14], it was assumed a leakage of 0.011 kg/day/m$^2$; (ii) the water evaporated is usually expressed in mm/day or kg/day/m$^2$. For steps 1, 2, 3 and 4, it was assumed 3.5, 2.8, 2.0 and 1.50 kg of water evaporated per day per m$^2$; (iii) entrainment is related to the brine that is lost attached to the salts deposit. As the salt crystals grow or accumulate on the pond floor, voids are created and some brine is trapped therein. The quantity of entrainment is a function of the quantity and type of salt deposited. It was assumed an entrainment loss of 15% in all steps. Salts combined to entrainment are here denominated impregnated salts.

Generally, the brine concentrations throughout each solar pond are uniform and equal to the concentration in the brine that leaves each step. This observation is a key assumption for the pond material balance. It was assumed that the leakages and the exit brines have the same concentration, so these streams can be created as a single stream to simplify the material balance.

For fixed concentrations at the entrance and exit points of the pond, the material balance is represented by a system of five variables: flowrate of feeding brine, flowrate of exit brine, evaporation rate, amount and composition of salts formed and pond area. The brines and salts compositions were calculated by the Pitzer and Harvie’s model [7,9], and it is described in item 3.1. Of these five variables, only two are independent. By establishing the value of any two of these variables, the system may be solved and the material balance is obtained.
The overflow brine from Step 1 feeds the Step 2, the overflow brine from Step 2 feeds the Step 3 and the overflow brine from Step 3 feeds the Step 4. The overflow brine from Step 4 is called bittern brine, rich in the most soluble salts, like, MgCl$_2$ and CaCl$_2$. Table 5 shows the results of the material balance for Step 1, Step 2 and Step 3 using solar evaporation process to crystallize the desired salt. Table 6 shows the composition of feed and overflow brines.

According to the solubility calculated by the Pitzer and Harvie’s model [7,9] and the material balance, a sequence of four stages could lead to the crystallization of following salts:

- Step 1: halite (84% w/w of NaCl);
- Step 2: sylvinit (58% w/w of NaCl + 16% w/w of KCl);

![Figure 2. X-ray diffractograms for crystallized salts produced in (a) Test 1, (b) Test 2, (c) Test 3, (d) Test 4 and (e) Test 5.](image)
Recovery of saleable salts from occurring natural brines representing the quinary aqueous system Na-K-Mg-Ca-Cl

The feed brine in Step 1 is saturated in NaCl, but it is not saturated in other salts (KCl, MgCl$_2$, and CaCl$_2$), so this is the first salt to be crystallized in Step 1. Considering the amount of evaporated water (356 kg/h) and an evaporation rate of 3.5 mm/day, it will be necessary a pond area of about 2,442 m$^2$. Halite crystallized in Step 1 could be harvested and fed to an NaCl Industrial Plant. The brine density at 20ºC changes from 1.200 to 1.215 g.cm$^{-3}$, crystallizing approximately 451 kg of halite per 1,000 kg of evaporated water. Around 5% of entering potassium chloride is lost by impregnated brine in the salts.

Saturation in KCl is achieved in the overflow brine from Step 1 that feeds Step 2 (36.60 g/L of KCl). In the solar ponds of Step 2, KCl-rich salts (sylvinite) crystallize. The sylvinite crystallized in Step 2 is collected and fed to an industrial KCl Plant. The brine density at 20ºC changes from 1.215 to 1.230 g.cm$^{-3}$, resulting in the crystallization of approximately 433 kg of salts per 1,000 kg of evaporated water. About 30% of entering potassium will crystallize in this Step. Considering the amount of evaporated water in Step 2 (68 kg/h) and an evaporation rate of 2.8 mm/day, a pond area of about 579 m$^2$ will be necessary.

A mixture of sylvinite, carnallite and bischofite crystallizes in Step 3. This mixture could be harvested and fed to an industrial MgCl$_2$ Plant as well. The brine density at 20ºC changes from 1.300 to 1.370 g.cm$^{-3}$, crystallizing approximately 470 kg of salts per 1,000 kg of evaporated water. About 7% of entering potassium will crystallize in this Step. Considering the amount of evaporated water in Step 3 (58 kg/h) and an evaporation rate of 2.0 mm/day, a pond area of about 693 m$^2$ will be necessary.

A mixture of sylvinite, carnallite and calcium chloride crystallizes in Step 4. This mixture could be harvested and fed to an industrial CaCl$_2$ Plant as well. The brine density at 20ºC changes from 1.300 to 1.370 g.cm$^{-3}$, crystallizing approximately 696 kg of salts per 1,000 kg of evaporated water. About 20% of entering potassium will crystallize in this step. Considering the amount of evaporated water in
3 CONCLUSIONS

The experimental solubility data for Na-K-Mg-Ca-Cl aqueous systems compared well with the Pitzer’s and Harvie’s models. The models predicted the crystallization path found experimentally and was used to design a fractional crystallization process with four evaporation steps. This result will be useful for solubility prediction in more complicated systems and supply a theoretical basis for the extraction of salts from aqueous solution representing the Na-K-Mg-Ca-Cl aqueous systems, for instance, NaCl, KCl, KCl·MgCl$_2$·6H$_2$O, MgCl$_2$·6H$_2$O, MgCl$_2$·CaCl$_2$·12H$_2$O and CaCl$_2$·6H$_2$O.

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