

THERMODYNAMIC MODELING OF PHASES EQUILIBRIUM IN AQUEOUS SYSTEMS TO RECOVER POTASSIUM CHLORIDE FROM NATURAL BRINES

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ABSTRACT

Chemical fertilizers, such as, potassium chloride (KCl), potassium sulphate (K_2SO_4), monoammonium phosphate (MAP or $NH_4H_2PO_4$), diammonium phosphate (DAP or $(NH_4)_2HPO_4$) and ammonium nitrate (NH_4NO_3), and other chemical products, like sodium hydroxide (NaOH) and soda ash (Na_2CO_3), are produced from electrolyte solutions or brines with a high content of soluble salts. Some of these products are manufactured by fractional crystallization, process where several salts are separated as solid phases with a high degree of purity (>90%) by evaporation of water present in the solutions. Due to the high world demand for the products, it is necessary to have a good knowledge about the thermodynamic models used to estimate the compositions of salts and brines obtained by fractional crystallization. The Pitzer and Harvie's model was used to calculate the composition of crystallized salts after remove water from multicomponent electrolyte solutions or brines representing the quinary system NaCl-KCl-MgCl₂-CaCl₂-H₂O at 293K. The temperature of 293K represents the medium brine temperature in saline deposits located in South America, especially in Salar de Atacama in Chile. Initially, the mineral solubilities of binary systems (NaCl-H₂O, KCl-H₂O and MgCl₂-H₂O) and ternary system (KCl-MgCl₂-H₂O) were calculated at 293K and compared with literature data. The results show that Pitzer and Harvie's model represents well the binary and ternary systems. The phase diagrams of solutions with high ionic strength were also plotted against the experimental data from tests with natural brine representative of quinary system NaCl-KCl-MgCl₂-CaCl₂-H₂O at 293K. The results show that the Pitzer and Harvie's model can be used to estimate the chemical composition of the salts produced during fractional crystallization and to do a material balance in the solar pond with the objective to recover potassium chloride from natural brine containing several salts dissolved, for instance, NaCl, KCl, MgCl₂ and CaCl₂.

KEYWORDS: quinary system; natural brine; potassium chloride; Pitzer and Harvie's model and fractional crystallization.

RESUMO

Os fertilizantes químicos, tais como, cloreto de potássio (KCl), sulfato de potássio (K_2SO_4), fosfato monoamônio (MAP ou $NH_4H_2PO_4$), fosfato diâmonio (DAP ou $(NH_4)_2HPO_4$) e nitrato de amônio (NH_4NO_3), além dos produtos químicos, soda cáustica (NaOH) e carbonato de sódio (Na_2CO_3), são produzidos a partir de soluções eletrolíticas ou salmouras contendo altas concentrações de sais dissolvidos. Alguns dos produtos mencionados são obtidos por cristalização

fracionada, processo onde os sais são separados como fases sólidas com alta pureza (>90%) a partir da evaporação do solvente presente nas soluções eletrolíticas ou salmouras multicomponentes. Devido à grande demanda mundial por esses produtos, há necessidade de que haja um bom conhecimento dos modelos termodinâmicos usados para estimar as composições dos sais e das salmouras obtidas por cristalização fracionada de soluções eletrolíticas ou salmouras multicomponentes. O modelo de Pitzer e Harvie foi usado para determinar as composições dos sais cristalizados após diferentes quantidades de solvente, presentes em uma salmoura multicomponente NaCl-KCl-MgCl₂-CaCl₂-H₂O a 20°C, serem evaporadas. A temperatura de 20°C foi usada pelo fato de ser a temperatura média das salmouras multicomponentes processadas nas piscinas de evaporação solar usadas nos depósitos salinos localizados no norte da América do Sul, em especial no Salar de Atacama no Chile. O modelo de Pitzer e Harvie foi validado por meio da comparação com os dados da literatura dos sistemas binários NaCl-H₂O, KCl-H₂O e MgCl₂-H₂O e do sistema ternário KCl-MgCl₂-H₂O a 20°C, mostrando-se adequado para ser usado para estimativa das solubilidades dos sais nesses sistemas binários e ternário. Os diagramas de fases para soluções com elevada força iônica foram construídos a partir dos dados experimentais de ensaios realizados com polpas sintéticas e salmoura natural, representantes do sistema multicomponente NaCl-KCl-MgCl₂-CaCl₂-H₂O a 20°C em estudo. Os resultados obtidos nos experimentos realizados com polpas sintéticas e nos ensaios de evaporação forçada da salmoura natural e os valores calculados pelos modelos de Pitzer e Harvie não apresentaram diferenças significativas, indicando que o modelo pode ser usado para estimar as composições químicas dos sais obtidos durante a cristalização fracionada de uma salmoura multicomponente: NaCl-KCl-MgCl₂-CaCl₂-H₂O. O modelo de Pitzer e Harvie é uma importante ferramenta para a determinação do balanço de massa em piscinas de evaporação solar, usadas para recuperação de cloreto de potássio por cristalização fracionada de salmoura contendo vários sais dissolvidos em água, entre eles NaCl, KCl, MgCl₂ e CaCl₂.

1. INTRODUCTION

The prediction of the solubility of electrolytes in aqueous solutions is important for a variety of applications such as brines and seawater desalination systems, drowning-out crystallization and liquid-liquid extraction in chemical, mineral and hydrometallurgical industries (YANG at al., 2013). For example, the high evaporation rates and minimal rainfall at brines located in northern regions of Argentina and Chile allow using solar evaporation ponds to produce saleable salts like potassium chloride, potassium sulphate and lithium salts (ZUVIC at al., 1983). However, the resulting multicomponent brines have to be processed to deliver the individual salts with purities compatible with market-grade products. Thermodynamic models are then used to design the facility to produce the desired salts. The process is based on the separation of inorganic salts from a multicomponent system using fractional crystallization (SONG and YAO, 2003). To this end, Pitzer's ion-interaction model (PITZER, 1973) and its extended Harvie and Weare's model (HARVIE and WEARE, 1980, HARVIE and EUGSTER, 1982 and HARVIE at al., 1984) are suitable tools, because they are reliable for predicting the mineral solubility of multicomponent salt systems in natural waters with high ionic strengths over a wide range of temperatures (0 to 300°C) (PALABAN and PITZER, 1987, SPENCER at al., 1990 and MARION and FAREEN, 1999). The objective of this study is to understand better the equilibrium in the quinary system NaCl-KCl-MgCl₂-CaCl₂-H₂O. Solubility data measured at 293K and the predicted counterparts based on Pitzer's ion-interaction model are presented. The motivation behind this study is to obtain data to help in evaluating the technical and economic feasibility to start operations in natural occurring brines.

2. MATERIAL AND METHODS

Chemicals and experimental apparatus: Batch crystallization experiments with a natural brine from a salar located in north of Argentina were performed in a 2 liters jacketed glass crystallizer. The temperature was controlled by an electric heating system at 85±3°C. Stirring was provided by a mechanic stirrer at 250 RPM, using a 45° pitched blade impeller. Table 1 shows the mass composition of the natural brine investigated.

Table 1. Natural brine density and chemical composition.

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)
1.198	183.91	18.34	30.07	62.37	0.19

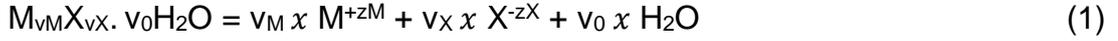
Experimental method: The natural brine sample was divided in four recipients, concentrated by forced evaporation and cooled to 293K. After 24 hours in contact with the solid phase at 293K, the equilibrium brines were separated from the salts by filtration. Sodium, potassium, magnesium, calcium and chloride contents were analyzed in the solution and in the wet salts.

Analytical method: The chloride concentrations in the liquid and solid phases were determined by titration with a standard solution of AgNO₃ in the presence of drops of 0.1% (w/v) K₂CrO₄ as an indicator. The solutions were diluted and the respective wet salts dissolved in doubly deionized water to determine the sodium, potassium,

magnesium and calcium contents by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3. RESULTS AND DISCUSSION

Calculation of the solubility by the Pitzer and Harvie's model: The solubility equilibrium constant, K_{SP} , at a specified temperature and pressure for a hydrated salt ($M_{vM}X_{vX} \cdot v_0H_2O$) is expressed by equation 1 and equation 2.



$$\ln K_{sp} = -(v_M x \mu^\circ_M + v_X x \mu^\circ_X + v_0 x \mu^\circ_{H_2O})/RiT + (\mu^\circ_S)/RiT \quad (2)$$

Where the chemical potentials of solids (μ°_S), water ($\mu^\circ_{H_2O}$) and ions in aqueous solution (μ°_M and μ°_X) at a given temperature (T) and standard state conditions are indicated. R is the universal gas 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 and solvent standard states were taken to be the respective pure phases at the pressure and temperature of interest.

The saturation index (SI) for a given salt is calculated from the ionic product (IP) and the solubility product as exemplified in equation 3 and equation 4 for potassium chloride (KCl) and for a generic salt represented by equation 1, respectively.

$$SI_{KCl} = \frac{IP_{KCl}}{K_{SP_{KCl}}} \text{ and } \frac{IP_{M_{vM}X_{vX} \cdot v_0H_2O}}{K_{SP_{M_{vM}X_{vX} \cdot v_0H_2O}}} \quad (3)$$

$$IP_{KCl} = a_{K^+} x a_{Cl^-} \text{ and } IP_{M_{vM}X_{vX} \cdot v_0H_2O} = (a_{M^{+zM}})^{v_M} x (a_{X^{-zX}})^{v_X} x (a_{H_2O})^{v_0} \quad (4)$$

Where $a_{K^+} = m_{K^+} x \gamma_{K^+}$, $a_{M^{+zM}} = m_{M^{+zM}} x \gamma_{M^{+zM}}$, $a_{Cl^-} = m_{Cl^-} x \gamma_{Cl^-}$ and $a_{X^{-zX}} = m_{X^{-zX}} x \gamma_{X^{-zX}}$, a_i are the ionic activities, m_i are the molal concentrations and γ_i are the activity coefficients for single ions, where $i=K^+$, Cl^- , M^{+zM} or X^{-zX} . The Pitzer and Harvie's model calculates the activity coefficients (PALABAN and PITZER, 1987). If $SI=1$ the solution is saturated, if $SI<1$ the solution is unsaturated and if $SI>1$ the solution is supersaturated. The activity of water (a_{H_2O}) is related to the osmotic coefficient, ϕ , by the equation 5.

$$a_{H_2O} = \exp(-\phi x \frac{\sum m_i}{55,51}) \quad (5)$$

Where $\sum m_i$ is the sum of molalities of species in the solution. The osmotic coefficient, Φ , is calculated from ion-interaction described by PALABAN and PITZER, 1987.

Validation of the solubility model: In order to check the Pitzer's ion-interaction model, the solubility of the binary systems NaCl-H₂O, KCl-H₂O, MgCl₂-H₂O and the ternary system NaCl-KCl-H₂O were calculated at 293K and the values were compared with the data from PALABAN and PITZER, 1987. The Figure 1 (a) and (b) show that the molalities calculated by the Pitzer and Harvie's model compare well with experimental measurements from PALABAN and PITZER, 1987 for the binary

systems NaCl-H₂O, KCl-H₂O and MgCl₂-H₂O at different temperatures and for saturated solutions in the ternary system NaCl-KCl-H₂O at 293K.

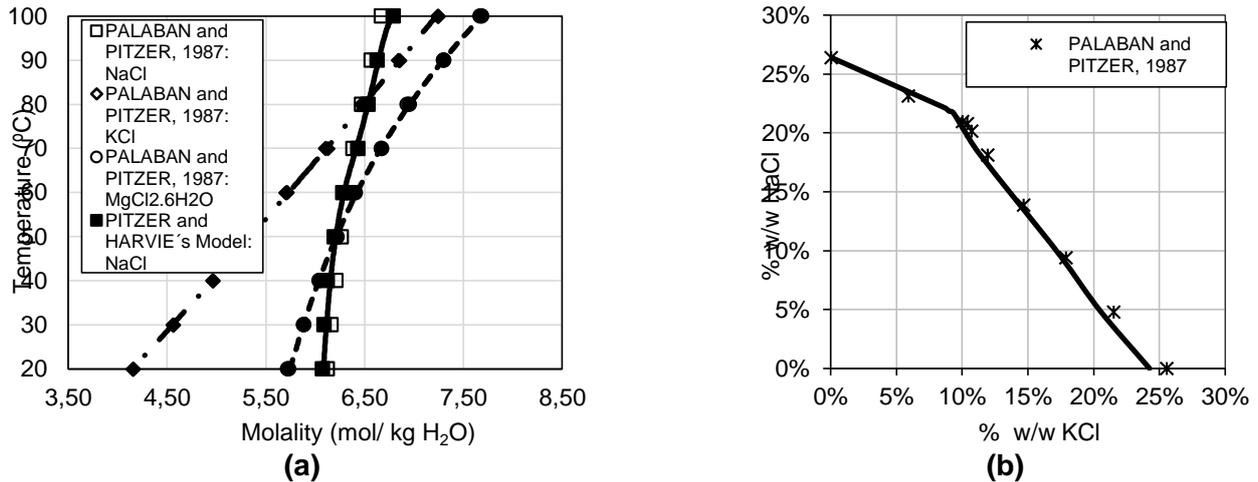


Figure 1. Comparison of the Pitzer and Harvie's model and data from PALABAN and PITZER, 1987 for the binaries systems NaCl-H₂O, KCl-H₂O and MgCl₂-H₂O at various temperatures and the ternary system NaCl-KCl-H₂O at 293K.

Predictability of the solubility model – Natural Brine: Figure 2 shows a comparison between the compositions of equilibrium brines at 293K calculated by Pitzer and Harvie's model and obtained by the tests for NaCl, KCl, MgCl₂ and CaCl₂.

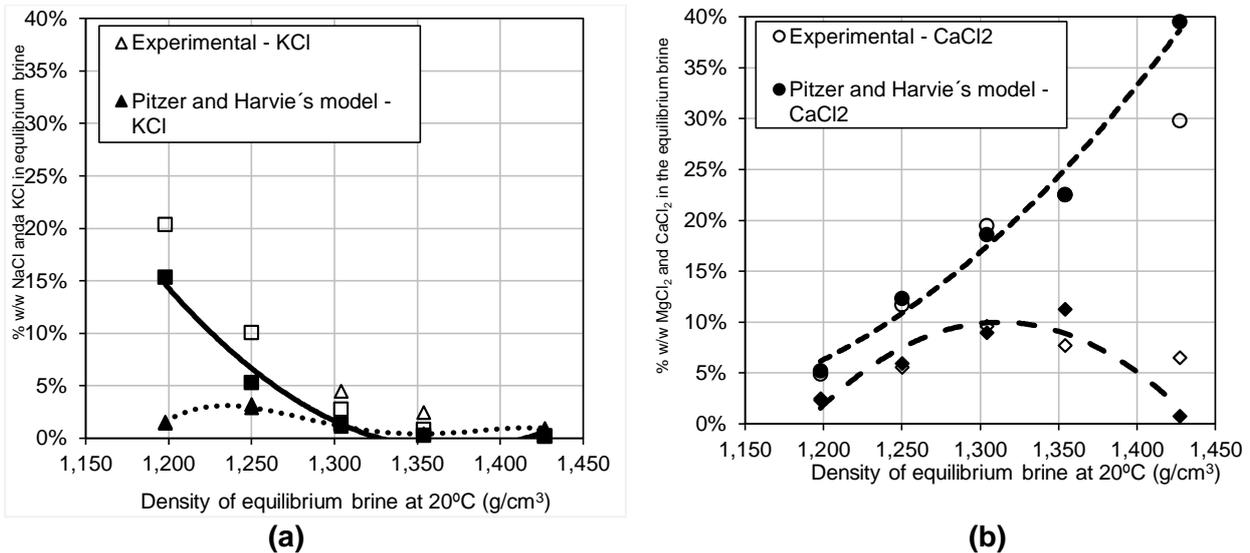


Figure 2. Comparison of Pitzer model and experimental data for system NaCl-KCl-MgCl₂-CaCl₂-H₂O at 293K: NaCl (a), KCl (b) MgCl₂ (c) and CaCl₂ (d) with natural brines.

Applicability of Pitzer and Harvie's mode to extract saleable salts from natural brine: Solar evaporation process has been designed for the extraction of potassium chloride from brine deposits of salares, like Salar de Atacama in northern Chile. The basic stream for a 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 is a function of pond area (MARION and FARREN, 1999). It was assumed a leakage of 0.011 kg/day/m²; (ii) Evaporation is the water evaporated from the pond and is usually expressed in mm/day or kg/day/m². For steps 1, 2 and 3, it was assumed 3.5, 2.8 and 2.0 kg of

evaporated water per day per m². (iii) Entrainment is the brine that is lost within the salt deposit. As the salt crystals grow or accumulate on the pond floor, there are voids created and some brine is trapped therein. The quantity of entrainment is a function of the quantity and type of salt deposited. The entrainment is generally expressed as a weight percent of the combined salt deposit and entrained brine. It was assumed 15% of entrainment lost in salt deposited in steps 1, 2 and 3. Salts plus entrainment is denominated impregnated salts.

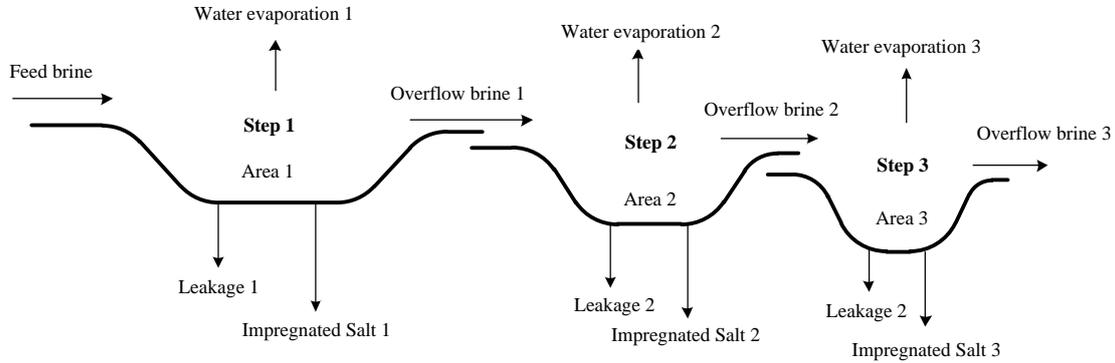


Figure 3. Basic streams of a solar pond for Step 1, 2 and 3.

Generally, the brine concentration throughout the solar pond is uniform and equal to the respective exit brine concentration. This observation is a key assumption in the pond material balance. The leakage, the entrainment and the exit brine will have the same concentration, so these streams can be created as a single stream to simplify the material balance.

For fixed feed and end brine concentrations, the pond material balance becomes a system of five variables: feed brine, end brine, evaporation, salts and pond area. Of these five variables, only two are independent. By establishing the value of any two of these variables, the pond is totally defined and the other three variables can be calculated.

The overflow brine from Step 1 feeds the Step 2 and overflow brine from Step 2 feeds the Step 3. The overflow brine from Step 3 is called bittern brine, rich in most soluble salts, like, MgCl₂, CaCl₂. The Table 2 shows the material mass balance for Step 1, Step 2 and Step 3 using solar evaporation process to crystallize the desired salts and Table 3 shows the composition of feed and overflow brines.

Table 2. Material mass balance results in solar ponds.

	Step 1	Step 2	Step 3
Pond area (m ²)	3050	937	980
Feed brine (kg/h)	1000.00	378.69	231.48
Water evaporation (kg/h)	444.77	109.31	81.68
Leakage (kg/h)	1.40	0.43	0.45
Impregnated salts (kg/h)	175.14	37.47	38.20
Entrainment (kg/h)	26.27	5.62	5.73
Not impregnated salts (kg/h)	148.87	31.85	32.47
Overflow brine (kg/h)	378.69	231.48	111.15
% accumulated evaporated water	59%	74%	84%
Composition of impregnated salts (%w/w)			
NaCl	76.14	45.37	7.32

KCl	2.44	22.30	5.75
MgCl ₂	1.43	4.67	21.42
CaCl ₂	2.96	9.69	46.86
CaSO ₄	0.02	0.01	0.01
Total water	17.02	17.96	18.65
Composition of not impregnated salts (%w/w)			
NaCl	87.65	49.63	5.99
KCl	2.33	24.31	0.00
KCl.MgCl ₂ .6H ₂ O	0.00	0.00	17.46
MgCl ₂ .6H ₂ O	1.33	7.81	21.89
CaCl ₂ .6H ₂ O	1.71	10.05	47.41
CaSO ₄ .2H ₂ O	0.12	0.04	0.02
Free water (% w/w)	6.88	8.16	7.23
% w/w of feed KCl crystallized (accumulated)	28	82	97
% w/w of feed KCl crystallized (in the respective Step)	28	54	15

Table 3. Composition of initial and overflow brines (% w/w).

Component	Feed	Overflow Step 1	Overflow Step 2	Overflow Step 3
NaCl (%w/w)	15.35	5.30	1.33	0.26
KCl (%w/w)	1.53	2.90	1.14	0.40
MgCl ₂ (%w/w)	2.51	5.95	8.96	11.25
CaCl ₂ (% w/w)	5.21	12.34	18.58	22.49
Continue Table 3				
CaSO ₄ (% w/w)	0.02	0.01	0.00	0.00
Total water (% w/w)	75.39	73.50	69.99	65.61
Density at 20°C (g/cm ³)	1.198	1.250	1.304	1.354
KCl (g/L)	18.34	36.31	14.88	5.39
MgCl ₂ (g/L)	30.07	74.33	116.78	152.77
Total soluble solids (g/L)	295	331	391	466

According to the Pitzer and Harvie's model results and the material balance, a sequence of three stages could be defined for the crystallization of halite salts (87.65%w/w of NaCl) in the Step 1, sylvinite salts (49.63% w/w of NaCl + 24.31% w/w of KCl) in the Step 2 and mixed of halite (5.99% w/w of NaCl), carnallite (17.46% w/w of KCl.MgCl₂.6H₂O), bischofite (21.89% w/w of MgCl₂.6H₂O) and calcium chloride (47.41% w/w CaCl₂.6H₂O) in the Step 3.

The feed brine is saturated in NaCl and in CaSO₄, but not saturated in others salts. The first salts to be crystallized are halite (NaCl) and calcium sulphate (CaSO₄) and the saturation in KCl is achieved in the overflow brine from Step 1 that feed the Step 2. The overflow brine from Step 1, saturated in KCl (36.31 g/L of KCl), is concentrated in additional solar ponds (Step 2 and Step 3) to crystallize rich KCl salts (sylvinite and carnallite salts). Considering the amount of evaporated water in Step 1 (444.77 kg/h) and an evaporation rate of 3.5 mm/day, it will be necessary a pond area of about 3,050 m². The halite salts crystallized in Step 1 will be harvested and discarded. The brine density at 20°C changes from 1.198 to 1.250 g/cm³, crystallizing approximately 394 kg of halite salts per 1,000 kg of evaporated water. Around 28% of entering potassium will be lost by impregnated brine in the salts.

The sylvinite salts crystallized in Step 2 could be harvested and fed an industrial KCl Plant. The brine density at 20°C changes from 1.250 to 1.304 g/cm³, crystallizing

approximately 343 kg of salts per 1,000 kg of evaporated water. About 54% of entering potassium will crystallize. Considering the amount of evaporated water in Step 2 (109.31 kg/h) and an evaporation rate of 2.8 mm/day, it will be necessary a pond area of about 937 m².

The mixed of halite, carnallite, bischofite and calcium chloride salts crystallized in Step 3 could be harvested and fed in an industrial KCl Plant as well. The brine density at 20°C changes from 1.304 to 1.354 g/cm³, crystallizing approximately 468 kg of salts per 1,000 kg of evaporated water. About 15% of entering potassium will crystallize. Considering the amount of evaporated water in Step 3 (81.68 kg/h) and an evaporation rate of 2.0 mm/day, it will be necessary a pond area of about 980 m².

The amount of total soluble solids in the brine increases from 295 g/L in the initial brine to 466 g/L in the overflow brine of Step 3. The content of most soluble salts in the brine, calcium chloride, CaCl₂, increases from 5.21% w/w to 22.49% w/w. It is expected to crystallize only magnesium and calcium salts above brine density of 1.354 g/cm³. The total KCl recovery in the solar pond is 69%, 54% in the step 1 plus 15% in Step 3. The KCl in the salt obtained in Step 1 is not recovered due to the low KCl content. Considering a KCl recovery of 70% and an on-stream factor of 90% to process the salts in an industrial KCl Plant, it will be generated per ton of KCl 60% K₂O about 22.5 ton of solid residues and 10.6 m³ of bittern brine. It will be also evaporated per ton of KCl 60% K₂O about 82 ton of water. It will be necessary about 73 m² of solar pond to produce a ton of KCl 60% K₂O per year. Considering a KCl recovery of 69% in the solar pond and 70% in industrial KCl plant, the overall KCl recovery will be about 48% and it would be necessary a pond area of 98 km² to produce about 1,350,000 t/year of KCl 60% K₂O.

4. CONCLUSIONS

Experimental solubility data for various electrolyte systems were obtained and compared to Pitzer and Harvie's model predictions at 293K. The Pitzer and Harvie's model agrees well with literature data on the binary systems (NaCl-H₂O, KCl-H₂O, MgCl₂-H₂O) and ternary systems (NaCl-KCl-H₂O) at 293K considered in this study. From these results, the single-salt Pitzer parameters of sodium, potassium, magnesium and calcium chlorides were calculated, as well as the mixing ion-interaction parameters for the quinary NaCl-KCl-MgCl₂-CaCl₂-H₂O system. The experimental data on the quinary system NaCl-KCl-MgCl₂-CaCl₂-H₂O also compared well with the Pitzer and Harvie's model. The model predicted the crystallization path found experimentally. This result will be useful for solubility prediction for more complicated systems and supply a theoretical basis for the extraction of salts from naturally occurring brines.

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6. REFERENCES

HARVIE, C., EUGSTER, H., WEARE. J. Mineral equilibria in the six-component seawater system, Na-K,-Mg-Ca-SO₄-Cl-H₂O at 25°C II: Compositions of the saturated solutions. *Geochimica et Cosmochimica Acta*; Vol. 46, p. 1603, 1982.

HARVIE, C., MOLLER, N., WEARE. J. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochimica et Cosmochimica. Acta* Vol. 48, p. 723-751, 1984.

HARVIE, C, WEARE J.H. The prediction of mineral solubilities in natural waters: the Na-KMg-Ca-Cl-SO₄-H₂O system from zero to high concentration at 25°C. *Geochimica et Cosmochimica. Acta.* Vol 44, p. 981 – 997, 1980.

MARION, G.M., FARREN, R.E. Mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O system: A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model. *Geochimica et Cosmochimica, Acta* Vol. 63, No. 9, p. 1305–1318, 1999.

PABALAN, R.T., PITZER, K. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high temperatures for mixtures in the system Na-K-Mg-Cl-SO₄-OH-H₂O. *Geochimica et Cosmochimica. Acta* Vol. 51, p. 2429-2443, 1987.

PITZER, K.S., *J. Phys. Chem.* 77, p. 268, 1973.

PERRY, R, GREEN, D. *Perry's chemical engineering handbook*, McGraw-Hill, Co., Inc., New, York, 2008.

SPENCER, R., MOLLER, N. e WEARE, J. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25°C; *Geochimica et Cosmochimica. Acta*, Vol. 54, p. 575-590, 1990.

SONG, P.; Yao, Y. *CALPHAD*, 27. p. 343-352, 2003.

ZUVIC, P., PARADA, N., VERGARA, L. Recovery of Potassium Chloride, Potassium Sulfate and Boric Acid from the Salar de Atacama Brine Sixth International Symposium on Salts, Vol. II, 1983.

YANG, J., PENG, J., DUAN, Y., TIAN, C., PING, M. The Phase Diagrams and Pitzer Model Representations for the System KCl+MgCl₂+H₂O at 50 and 75°C. *Russian Journal of Physical Chemistry*, p. 1930-1935, 2012.