Phase Diagram Modeling of a Multicomponent Aqueous Solution of Katwe Salt Lake, Uganda

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Abstract

A methodology is developed to compute the phase diagram of a hexary system and to determine the mineral precipitation sequence upon removal of water. The methodology is applied to construct the phase diagram and precipitation sequence of the system $(Na^{+}, K^{+})(Cl^{-}, SO_4^{2-}, CO_3^{2-}\ \&\ HCO_3^{-})$ in water. The thermodynamic model chosen is the Extended UNIQUAC. A 3D grid is constructed in order to solve this model in MATLAB. On the basis of this grid, a 3D phase diagram is calculated and a Jänecke projection is obtained. The precipitation sequence due to evaporation is calculated thus obtaining the coordinates of the solution along this path as well as the order of precipitation. The numerical model is also able to calculate all these steps for temperatures 0-110°C. In addition, the number of ions and the composition of the system can be varied in order to model other elective systems. The obtained results are well suited to be used for the design of sustainable salt extraction processes for both Sea and Lake brines.

Keywords: Evaporation, Extended UNIQUAC, Precipitation, Phase diagram, MATLAB

1. Introduction

Lake Katwe, a crater lake in south western Ugandan has for a long time been a major source of salt of various grades the people of Katwe and neighboring areas. The lake brines however constitute a complex multicomponent system comprising mainly of $\boldsymbol{Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-}}\ \&\ \boldsymbol{HCO_3^{-}}$ ions (Kasedde et al. 2014). As a result, a number of salts coprecipitate during evaporation from these brines thus yielding impure products (Kasedde et al. 2013; Lwanyaga et al. 2019). To improve on both the quality and quantity of the salts currently produced at lake Katwe, an extraction process that is based on the phase chemistry of the brine is vital. Every brine is unique and therefore understanding the solid liquid equilibrium of a particular system is a prerequisite in the design and analysis of crystallization-based separation processes of multicomponent systems (Takano et al. 2002). It's upon the background that a theoretical phase equilibrium study was undertaken to calculate the phase diagram and determine the mineral precipitation sequence during brine evaporation. This in turn will foster the sustainable exploitation of the salt reserve since it is a renewable resource due to its geological setting.

2. Methods

In this study, the isothermal phase diagram of the hexary system was calculated numerically. The Extended UNIQUAC (Sander et al. 1986) thermodynamic model was deployed in MATLAB for calculation of saturation surfaces, post processing for visual representation of the phase diagram and calculation of the precipitation path. Regions of interest on the phase diagram where refined and others with a less node density to ensure minimal computational time. Furthermore, suitable projections and cuts were applied as was the case in previous studies (Kwok et al. 2008). The model results were compared to solubility data in literature (Seidell and Linke 1941; Henry et al. 1979).

3. Results and Discussion

The program is structured in such a way that the user only has to modify the inputs. The user can also decide up to what degree the program should run; the solution calculation, and the various data processing are divided into different parts but can easily be called individually form the main program.

A 3D phase diagram derived from the most abundant ions in the brines of Lake Katwe was calculated as shown in Figure 1. It can be seen from Figure 1 that the order of precipitation of the salts and the possible dry up points can be estimated. The constituent phases coprecipitate with each other upon evaporation thus yielding an impure phase. To alleviate this, the precipitation sequence path due to evaporation needs to be calculated such that infeasible process paths are avoided depending on the target product.

Projecting the 3D phase diagram parallel from the infinity z direction (Figure 1, water coordinate) on the x-y planes results in the Jänecke Diagram. The Jänecke plot is often times used in the design of salt extraction processes. It allows for easy and quick controls of calculated operating points and process schemes. The Jänecke plot at 25°C revealed the existence of one double salt (glaserite), a hydrate (mirabilite) and other salts namely, halite, arcanite, thernadite and sylvite. On this phase diagram, glaserite has the largest crystallization field and sylvite the smallest. This means that glaserite is more likely to crystallize out of the lake brine compared to other salts and the reverse is true for sylvite due to differences in their solubilities.

The mineral precipitation sequence due to evaporation was calculated and illustrated on a Jänecke diagram. A starting point (0.3, 0.4, 0.8) was selected from which the evaporation process commenced upto the dry up point. The order of precipitation was observed to be $K_2SO_4 \rightarrow NaK_3(SO_4)_2 \rightarrow KCl \rightarrow NaCl$.

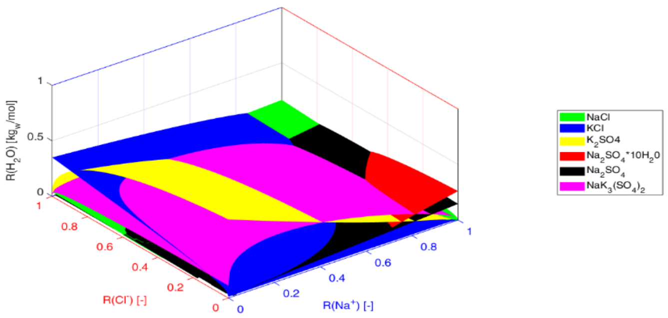

Figure 1. Saturation surfaces of the quaternary system $(Na^+, K^+)(Cl^-, SO_4^{2-}) - H_2O$ at 25°C

The developed code is flexible in that it can be used for different temperatures. The approach in this study is isothermal, therefore, data for different temperatures has to be calculated independently. To ascertain this, a Jänecke plot at 100°C was calculated. It was observed that the Mirabilite field on the plot disappeared at this temperature as predicted by Nicolaisen and coworkers (Nicolaisen et al. 1993). The invariant points as well on the predicted phase diagrams fitted well with the experimental data. From the foregoing, the data posted by the code is in tandem with phase diagrams in literature. Thus, the developed program in this study is suitable for the calculation of phase diagrams of the Lake Katwe brine system. The code however has to be validated with other experimental data, salt composition and at different temperatures.

One short coming for this approach is the need for more computer memory for higher dimensional systems with increased accuracy. Thus, it is prudent to rethink the numerical approach for large systems on a detailed grid. The applied physical model is still valid and many parts of the code can be kept.

4. Conclusions

The solid liquid (phase) equilibrium of the Katwe brines was calculated by Using the Extended UNIQUAC in the MATLAB environment. The precipitation sequence of the salts due to evaporation was determined. A 3D phase diagram and several 2D Jänecke projections (without the water coordinate) were drawn. With these diagrams, it is now clearer on how to proceed on the design of the salt extraction process. The code was also tested at temperatures different from 25°C; the results fit well with experimental data in literature. This model should be validated experimentally for different electrolytes and temperatures. Sufficient computer memory should be planned for when modelling systems of higher dimensions in the future.

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