British Journal of Applied Science & Technology
11(4): 1-7, 2015, Article no.BJAST.20598
ISSN: 2231-0843

SCIENCEDOMAIN *international*
www.sciencedomain.org

SCIENCEDOMAIN

Phase Developments during Natural Evaporation Simulation of Lake Katwe Brine Based on Pitzer's Model

John Baptist Kirabira[1*], Hillary Kasedde[1,2], Matthäus U. Bäbler[3] and Thomas Makumbi[4]

[1]*Department of Mechanical Engineering, College of Engineering, Design, Art and Technology, Makerere University, P.O.Box 7062, Kampala, Uganda.*
[2]*Department of Materials Science and Engineering, KTH, Royal Institute of Technology, Brinellvägen 23, SE-100 44 Stockholm, Sweden.*
[3]*Department of Chemical Engineering and Technology, KTH, Royal Institute of Technology, Teknikringen 42, SE-100 44 Stockholm, Sweden.*
[4]*Department of Electrical and Computer Engineering, College of Engineering, Design, Art and Technology, Makerere University, P.O.Box 7062, Kampala, Uganda.*

Authors' contributions

This work was carried out by collaboration between all authors. Author JBK initiated the idea, assisted in its development, offered technical guidance during the study and wrote the manuscript. Author HK developed the idea, selected the materials and methods for the study, participated in data collection and writing the manuscript. Author MUB assisted in data analysis as well as giving technical guidance during the study while author TM assisted in data collection, providing information sources as well as editing the manuscript. All the authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2015/20598
Editor(s):
(1) Verlicchi Paola, Department of Engineering, University of Ferrara, Via Saragat 1, Ferrara, Italy.
Reviewers:
(1) Alexandre Gonçalves Pinheiro, Universidade Estadual do Ceará, Quixadá, Brazil.
(2) Anonymous, Nanjing University of Aeronautics and Astronautics, China.
Complete Peer review History: http://sciencedomain.org/review-history/11221

Original Research Article

Received 31st July 2015
Accepted 22nd August 2015
Published 1st September 2015

ABSTRACT

Lake Katwe is the largest of the eight saline crater lakes in the pleistocene Katwe-Kikorongo volcanic field situated in the western arm of the great East African Rift system in southwestern Uganda. The salt lake is hydro-chemically of a carbonate type with its brines representing an important source of mineral salts of high economic value. In the present work, the geochemical

---

**Corresponding author: E-mail: makumbitom@yahoo.com;*

simulation of the crystallization route of the natural evaporation of the lake brine in PHREEQC based on Pitzer's thermodynamic model was done. The precipitation sequence of the different mineral salts that crystallized step by step from the brine during natural evaporation at 30ºC was obtained. The results show that the mineral salt precipitation sequence following the saturation data is: Sulfates, chlorides and carbonates. During the evaporative concentration process, the brines become enriched in Na^+, K^+, HCO_3^- + CO_3^{2-}, and depleted in Cl^- and SO_4^{2-} with massive halite precipitation. The study provides the basis for the future comprehensive utilization of the natural brine resource in Lake Katwe.

Keywords: Brine; crystallization sequence; Lake Katwe; PHREEQC modeling; pitzer models.

ABBREVIATIONS

SI:	*Saturation Index; XRD: X-ray Diffraction;*
Sida:	*Swedish International Development Agency.*

1. INTRODUCTION

The future hydrological and geochemical evolution of closed natural saline basins depends very strongly on water evaporation and mineral salt precipitation from these basins [1]. Interactions between ions in natural waters have a great effect on the rates of mineral solubility. Models describing the variation of activity coefficients with ionic strength, temperature, and solution composition are required to quantify these effects and hence can be used to make many thermodynamic calculations such as aqueous speciation of elements, mineral crystallization sequence, mixing of aqueous solutions and phase equilibria of mineral-solution. In the past few decades, the progress of geochemical modeling dealing with concentrated electrolyte solutions allowed the application of up-to-date approaches to understanding the geochemical aspects of natural phenomena. The ion-interaction model, developed by Pitzer in 1973 [2], has not only advanced the development of the theory of concentrated electrolyte solutions, but also provided a valuable tool for the realization of a more accurate description of saline crystallization sequences observed in several present day saline systems.

The applicability of the ion-interaction approach to modeling geochemical processes involving natural brines has been well established. Successful applications have included models accounting for mineral sequences produced by evaporating sea water [3], deposition of trona on Lake Magadi, Kenya [4], formation of boron rich evaporation products at Searles salt Lake, California [5] and halite solubility in the Dead Sea in Israel [6]. Further studies involved simulated evaporation of natural waters [7,8] and estimation of the quantities of salts obtained from evaporation of brines from disposal basins [9].

In this work, Lake Katwe brine deposits were investigated; the lake is the largest among the eight saline crater lakes within the pleistocene Katwe-Kikorongo volcanic field north of Lake Edward in southwestern Uganda. At an elevation of 885 m, the lake occupies a maximum area of 2.5 km^2, circumference of 9 km, and a depth ranging from 0.4 to 1.6 m. The lake natural brine is hydro-chemically of a carbonate type, forming a mineral assemblage characterized by alkaline mineral salts rich in Na^+, K^+, Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^-. In a previous investigation, the mineral recovery from the lake brine using experimental evaporation under isothermal laboratory conditions at 30°C was reported. According to those investigations, the mineral salt precipitation sequence from the brine, which was monitored over a period of 50 days, can be summarized by: sulfates→chlorides→carbonates [10]. In the present study, further work was initiated to model the physico-chemical relationship between Lake Katwe brine evaporation and mineral salt precipitation. The main goal is to provide additional information needed to get a better understanding of the evolution of the brines and mineral salts that form upon evaporation of the lake brines.

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this study included a brine sample (pH = 10.2), PHREEQC 3.0 software package for simulating the natural brine evaporation and Microsoft excel for analysis of the results.

2.2 Methods

2.2.1 Thermodynamic modeling

For the simulation of the natural brine evaporation, a thermodynamic modelling package, PHREEQC 3.0 was used [11]. PHREEQC is an interactive modeling code with an extensive thermodynamic database. It is based on Pitzer's ion-interaction model which accounts for the non-ideality of aqueous solutions. It iteratively calculates mineral-solution-gas equilibria in complex brine systems. Due to the high ionic strength of the solutions in this study, the Pitzer database was used. In this database, the temperature dependence of the appropriate mass-action law constants and Pitzer mixing parameters for the calculation of activity coefficients in aqueous solutions of high ionic strength are implemented. The simulations were made using the chemical composition of a brine sample (pH = 10.2) from Nambawu saltpans at Lake Katwe summarized in Table 1 [10]. The ions with the highest concentration were used as input parameters in the code since interest is in the bulk of the precipitation of the major evaporite minerals at 30°C. Moreover, 30°C is the mean temperature for the dry and rainy seasons in the lake basin.

Table 1. Analytical data used as input for the modeling

Ion	Composition (g/l)
Na^+	137
K^+	39.1
Mg^{2+}	0.00143
Ca^{2+}	0.005
Cl^-,	124
SO_4^{2-}	43
HCO_3^-	3.39
CO_3^{2-}	61
F^-	0.082

To simulate brine evaporation in a series of sequential steps, PHREEQC was constrained to reduce the original water mass of the brine by 10% in the first evaporation step, and then reduce the resulting new water mass by 10% in the second evaporation step, and so on while allowing mineral salt precipitation. After 6 evaporation steps, 60% of the original water mass (33.3 moles) was depleted without replenishment from outside sources such as rainfall. The original brine mass was 1 kg or 55.508 moles. Output from the model lists the new brine volume and the resulting composition from each evaporation step. It also identifies the mineral species that precipitate at each step. Brine composition in terms of water, major ions, and precipitated mineral species from each evaporation step is expressed in moles. PHREEQC uses the brine composition from the previous evaporation step as input to calculate the brine composition for the next evaporation step. The step-wise process continued until brine compositions were calculated for all the 6 evaporation steps.

During evaporation, PHREEQC calculates several brine parameters including the mineral saturation indices (SI), ionic evolution, and number of moles of precipitated mineral salts. The modeling does not take into account kinetic factors such as those caused by day-night temperature changes and the time to reach equilibrium which affect the crystallization path. Furthermore, the modeling does not provide information on the fate of trace elements in the mineral salts.

3. RESULTS AND DISCUSSION

3.1 Saturation State of the Brine

The saturation state of the analyzed brine solutions are shown in Fig. 1. Positive values of SI indicate that the solution is supersaturated and hence, mineral precipitation will occur. Negative values indicate mineral dissolution.

The results in Fig. 1 show that the sulfates of sodium and potassium have SI greater than 0 while carbonate salts have low SI, less than 0. The thermodynamic potential for mineral salts to precipitate from solution is often expressed in terms of SI. The results above imply that upon brine evaporation, the sulfate minerals precipitate before the other salts. The carbonate salts precipitate last from the brines. However, it should also be noted that SI values exceeding 0 do not automatically result in the precipitation of a mineral phase, because precipitation kinetics can be very slow. The development of the saturation indices for the most important mineral phases was further modeled to show which mineral phases dominate in the solution and to estimate the point at which the precipitation of certain minerals begin during brine evaporation (Fig. 2). At each stage of precipitation, the mineral phase with the largest SI is predicted to precipitate. Most often, observations show that amorphous phases precipitate first, followed by a slow maturation to more crystalline, less soluble phases.

When considering the recovery of mineral salts from brine, the first step is the evaporation of the solution where different salts precipitate stepwise according to their solubility product. This gives a rough understanding of the processes occurring during the evaporation of the brine. The results from the evaporation simulations in Fig. 2 indicate that glaserite, thenardite, sylvite and halite are slightly over saturated in the original brine solution and hence have high saturation indices. This also explains the existence of the three minerals in the salts from the mineralogical analysis by XRD [12]. The precipitation of these mineral salts is dominant during the concentration of the brine. The evaporation simulations also show that the composition of the brine during concentration is controlled primarily by the precipitation of sulfate and chloride mineral phases. Therefore, the point of brine concentration when a certain mineral begins to precipitate is moved towards a higher concentration. The saturation indices of the carbonate salts reduce during the evaporation and do not reach saturation at higher degrees of evaporation. This implies that most carbonates have very high solubilities in the brine. The evolution of the saturation indices is in good agreement with previously reported results from earlier laboratory evaporation experiments [10]. The mineralogical analysis of the recovered salts could not detect some of the mineral phases as observed from the model calculations. To explain this, we note that the model calculations only consider ideal thermodynamic conditions which do not exist in a natural setting. Under natural conditions, the influence of kinetic factors and the formation of over saturated solutions explain the delayed precipitation of some minerals or their absence from solution.

3.2 Brine Ionic Evolution

Furthermore, the ionic evolution of the brines is modeled at different degrees of evaporation with the assumption that, the considered mineral phases precipitate from solution as soon as reaching a positive SI (Fig. 3).

Results show that until an evaporation rate of 10%, sodium, chloride, potassium, and sulfate show a decrease in concentration. Thereafter, these ions behave differently. Sodium and potassium show a conservative behavior during further evaporation while chloride and sulfate concentrations decrease further during the later stages of evaporation. The continuous depletion of sulfate and chloride is explained by the continuous precipitation of thenardite and halite respectively. Carbonate and bicarbonate concentrations show a steady increase in concentration with a constant slope. The conservative behaviour of these ions indicates that the carbonate and bicarbonate bearing-mineral phases stay in solution until a high

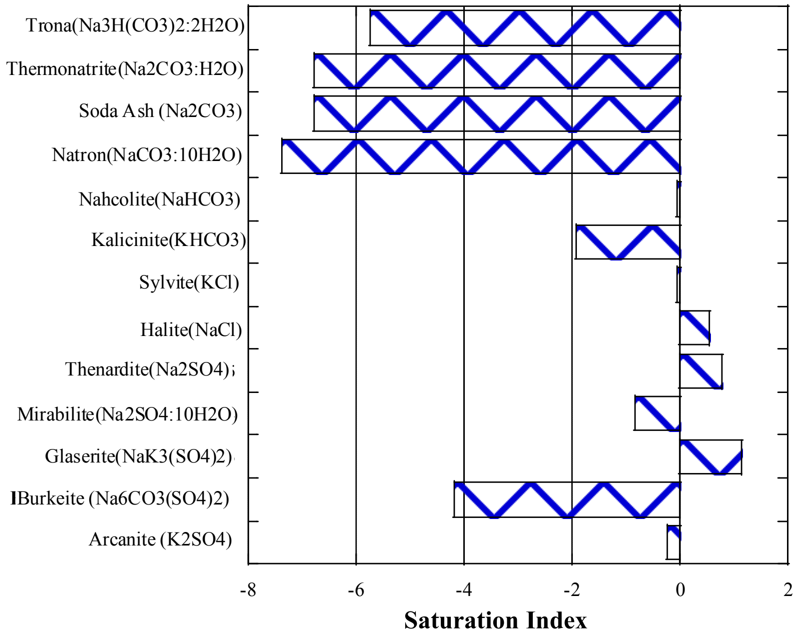

Fig. 1. Saturation indices of the major mineral phases obtained through the thermodynamic modeling using as input the brine composition of Nambawu salt pans at a concentration factor equal to 1

degree of evaporation due to their high solubility in the brines. It should also be noted that the (HCO_3^- + CO_3^{2-}) concentration is not significantly lowered during the evaporation because of the high alkalinity of Lake Katwe brines.

3.3 Mineral Evolution

The results from the geochemical modelling of the mineral evolution during brine evaporation are shown in Fig. 4.

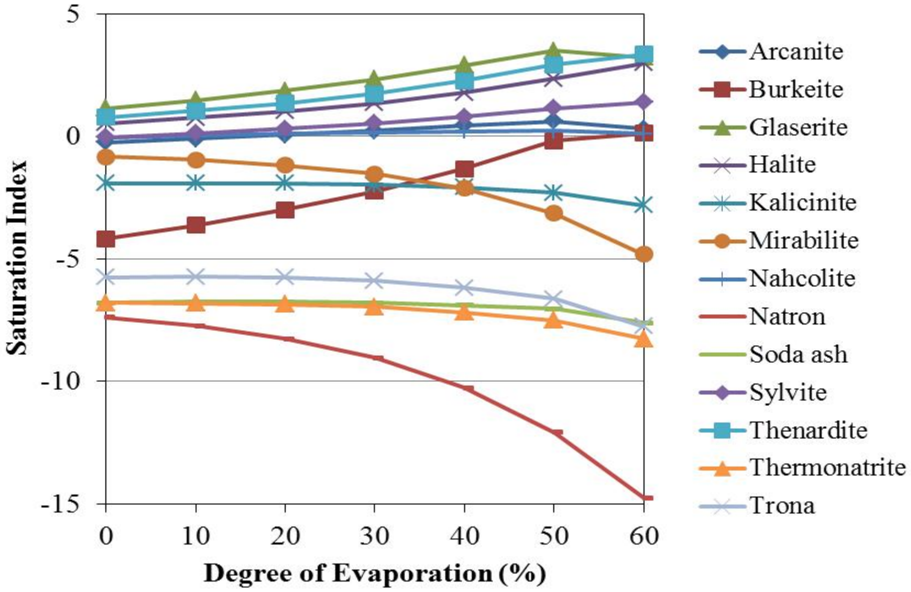

Fig. 2. Development of the saturation indices for the major mineral phases with increasing evaporation of the brine from Nambawu salt pans as modeled with PHREEQC

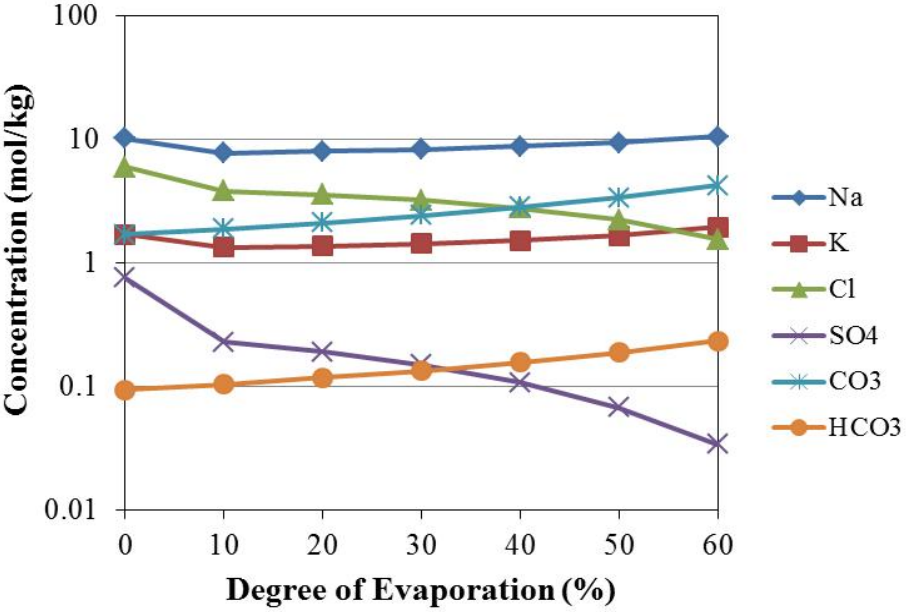

Fig. 3. Evolution of the major ion species with increasing evaporation of the brine as modeled in PHREEQC

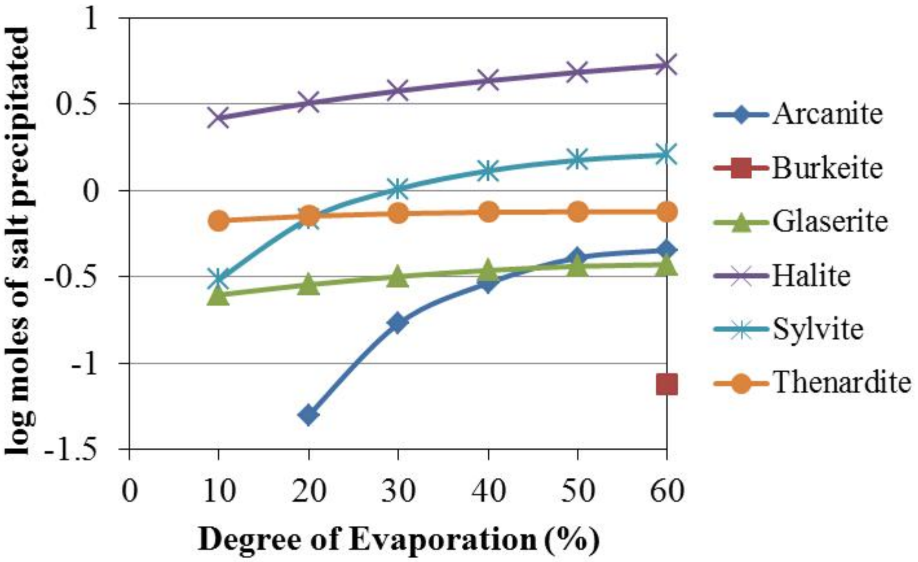

Fig. 4. Evaporative concentration of Nambawu salt pan brine showing the masses of major mineral salts precipitated as a function of evaporated water

The geochemical evolution of brines in closed saline basins is primarily controlled by inflow composition, selective removal of solutes and evaporite precipitation. Modeling of the brine evolution pathways assumes that inflow waters evolve into brines which is controlled by evaporative concentration followed by mineral precipitation. The simulation results in Fig. 4 above carried out at 30°C show that as evaporation progresses, new mineral salt species are precipitated at the expense of some previously precipitated salts, which are reabsorbed back into solution. Once the least soluble minerals begin to precipitate, a chemical divide is created where the composition of the remaining solution changes as minerals are removed from the system. The solution therefore evolves along a new pathway until the next mineral phase reaches saturation before a new chemical divide is established [13]. In contrast with the other minerals predicted to precipitate from the brines, only arcanite, burkeite, glaserite, halite, sylvite, and thenardite were predicted by PHREEQC to precipitate from the brines with halite being the predominant mineral formed. Because of their high solubility in the brines, all carbonate bearing minerals contained in these brines remain in solution even after 60% of the water is evaporated.

4. CONCLUSIONS

Simulated evaporation of Lake Katwe brines provides the following conclusions.

- Thenardite, halite, sylvite, glaserite, and arcanite are the first mineral phases to precipitate from solution. Halite precipitates more massively and hence, contributes most of the salt mineral mass.
- Carbonate-bearing mineral precipitates (trona, soda, kalicinite, nahcolite, and thermonatrite) do not appear in the early stages of the evaporation. They remain in solution even after 60% of the water mass is evaporated.
- The evolution of the saturation indices is in good agreement with the mineral determinations carried out on the solid experimental samples, and hence interprete the evaporative evolution of the lake brines.
- During the evaporative concentration process, the brines become enriched in Na^+, K^+, and HCO_3^- + CO_3^{2-}. Cl^- and SO_4^{2-} concentrations are lowered because of halite, thenardite, sylvite, glaserite, arcanite, and burkeite precipitation.

For most simulations, the predicted results match closely with those observed from earlier experimental investigations. Since thermodynamics can only suggest final equilibrium phases and cannot specify neither geochemical path nor time to reach equilibrium, further studies should investigate the kinetics of mineral salt precipitation from Lake Katwe brines.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Krumgalz, BS. Application of the Pitzer ion interaction model to natural hyper-saline brines. Journal of Molecular Liquids. 2001; 91:3-19.
2. Pitzer KS. The thermodynamics of electrolytes 1: Theoretical basis and general equations. Journal of Physical Chemistry.1973;77:268-277.
3. Harvie CE, Moller C, Weare JH. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_2-H_2O system to high ionic strength at 25°C. Geochimica Cosmochimica Acta. 1984;48:723-751.
4. Monnin C, Schott J. The determination of the solubility products of sodium carbonate minerals and an application to trona deposition in Lake Magadi (Kenya). Geochimica et Cosmochimica Acta. 1984; 48:571-581.
5. Felmy AR, Weare JH. The prediction of borate mineral equilibria in natural waters, application to Searles Lake, California. Geochimica et Cosmochimica Acta. 1986; 50:2771-2783.
6. Krumgalz BS, Millero FJ. Halite solubility in dead sea waters. Marine Chemistry.1989;27:219-233.
7. Risacher F, Clement A. A computer program for the simulation of evaporation of natural waters to high concentration. Computers and Geosciences. 2001;27: 191-201.
8. Ma L, Lowenstein TK, Russel JM. A brine evolution model and mineralogy of chemical sediments in a volcanic crater, Lake Kitagata, Uganda. Aquat Geochem. 2011;17:129-140.
9. Aral H, Sparrow GJ. Estimation of the Quantities of salts that may be obtained from the disposal basins. CSIRO Minerals. Report DMR-2378D; 2004.
   Available:https://www.waterconnect.sa.gov.au/Content/Publications/DEWNR/dwlbc_techrpt_2009_12.pdf
   (Accessed 05th May 2014).
10. Kasedde H, Bäbler MU, Kirabira JB, Tilliander A, Jonsson S. Mineral recovery from Lake Katwe brines using isothermal evaporation. Reliable Mine Water Technology. 2013;2:855-860.
11. Parkhurst DL, Appelo CAJ. Description of input and examples for PHREEQC version 3. A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Techniques and Methods; 2013.
    Available:http://pubs.usgs.gov/tm/06/a43
    (Accessed 20th January 2014).
12. Kasedde H, Kirabira JB, Bäbler MU, Tilliander A, Jonsson, S. Characterization of brines and evaporites of Lake Katwe, Uganda. Journal of African Earth Sciences. 2014;91:55-65.
13. Eugster HP. Geochemistry of evaporitic lacustrine deposits: Annual Review. Earth Planet Science. 1980;8:35-63.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/11221