Mineral Precipitation Sequence During Evaporation of Lake Katwe Brine

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Abstract

Traditional salt mining techniques are the dominant salt extraction methods at Lake Katwe in Uganda. In this work, the effect of temperature on the mineral precipitation sequence during evaporation of lake brine was studied to foster the design of a commercial salt extraction process. Isothermal evaporation experiments at different temperatures were undertaken. PHREEQC was used to predict the precipitation sequence. The precipitates were characterised by the XRD and SEM techniques. Halite is the most abundant mineral, with Thenardite, Trona and Glaserite following, respectively. Halite will be best extracted at higher temperatures whereas the lower temepratures will favour sulphate based minerals.

Keywords: Lake Katwe, Evaporation Temperature, PHREEQC, Precipitation, Brine

Introduction

In Uganda today, salt for both domestic and industrial use is mainly imported from neighouring countries. The salt import bill is steadily increasing as the country develops which is increasingly straining the country's merger resource envelope. To avert this, the salt deposit at Lake Katwe need to be fully exploited. This salt lake has been a source of salt for a long time. However, the salt produced from the lake does not meet the required purity standards for table salt and the chlor-alkali industry(Kirabira et al. 2013; Kasedde et al. 2014).

Currently at the lake, salt is recovered by traditional means; brine is channelled from the lake into salt pans. In the salt pan, the salt crystallizes due to solar evaporation producing two salt grades of different qualities. Grade I which is averagely about 93% Halite (NaCl) is the best these rudimentally techniques can produce. Grade II is harvested after Grade I with an average composition of about 65% Halite. The third grade is obtained by hacking the lake bed with iron bars; this has a composition of about 50% halite. Due to their composition, these three salts attract low prices as the demand for them is low (Kasedde et al. 2014).

A salt plant was established for industrial processing of the Lake Katwe brine. The plant never perfomed to its design expectations and the components were heavily corroded (Driver and Tukahirwa 1990). This led to its abandonment without ever producing any meaningful products. Plans for commercial exploitation of the brine commenced with the characterisation of brine and phase chemistry experiments. The brines are highly alkaline and rich in Na^+, K^+, Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_{3-} showing an intermediate transition between Na-Cl and $Na\text{-}HCO_3$ water types (Arad and Morton 1969; Kasedde et al. 2014).

An isothermal laboratory evaporation experiment at 30°C revealed precipitation of commercial salts such as Thenardite (Na_2SO_4), Anhydrite ($CaSO_4$), Mirabilite ($Na_2SO_4 \cdot 10H_2O$), Burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$), Hanksite ($9Na_2SO4 \cdot 2Na_2CO_3 \cdot KCl$), Gypsum, Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), Halite, Nahcolite ($NaHCO_3$), Soda ash ($Na_2CO_3$), and Thermonatrite ($Na_2CO_3 \cdot H_2O$) from the brine of Lake Katwe. Moreover, the mineral salts crystallize in the order following the sequence starting with sulfates, followed by chlorides and carbonates, respectively (Kasedde et al. 2013) with a rich source of mineral salts. The present work aims at evaluating possibilities of future salt extraction from the lake deposit. An isothermal evaporation experiment was conducted on the lake brines. The precipitated salts were characterized by X-ray diffraction (XRD. Fractional crsytallisation is often times used to extract most of the aforementioned salts from brine. This, therefore necessitates investigating the precipitation sequences of minerals from Katwe brine at different temparatures in order to facilitate the design a commercial salt extraction process.

Methods and Materials

Labarotory experiments

The rainy season surface brine was sampled from Lake Katwe and stored in 1.5 L plastic bottle at room temperature prior to the evaporation study. Using 10 ml of the original brine from Lake Katwe, the polythermal evaporation experiment was run at five different temperatures (30, 40, 50, 60 & 70°C). These were chosen because they are easily achievable on a commercial scale with less material selection problems and the evaporation process is faster compared to lower temperatures. Before evaporation was started, both the biological and organic materials were filtered off using a 5 µm membrane. The filtrate was then poured into a 50 ml beaker which was then placed in a Labcon thermostatic water bath at 30°C. The formed precipitates were filtered off using a 5 µm membrane and then left to dry overnight in open air on an aluminium foil. This procedure was repeated for the other study temperatures (40, 50, 60 & 70°C).

Characterization of the precipitates

To determine the mineralogy of the precipitates, the powder X-ray diffraction method was used. A Phillips diffractometer PW3050 with a X-ray source of Cu Kα radiation (λ = 1.540598 Å) was used. The scan step size was 0.013°., the collection time 1s, and in the range 2θ CuKα from 1° to 90.5°. The X-ray tube voltage and current were fixed at 45 kV and 40 mA respectively. The Crystallography Open Database (COD) powder diffraction database was searched by *QUALX2.0* search–match identification software for phase identification (Altomare et al. 2015). The morphology of the precipitates was determined by a Zeiss Supra 55 VP Field Emission Scanning Electron Microscope (FEG-SEM); all samples were carbon coated before SEM analysis in order to make them electrically conductive.

***Table 1** Brine Composition*

pH	Brine Temp (°C)	Density (g/ml)	EC (us/m)	Major ions (g/L)								
				Na	K	Mg	Ca	Cl	Br	SO_4	HCO_3	CO_3
9.72	25.2	1.15	14109	69.6	11.6	0.0519	0.0048	44.2	0.461	32.7	18.2	38.8

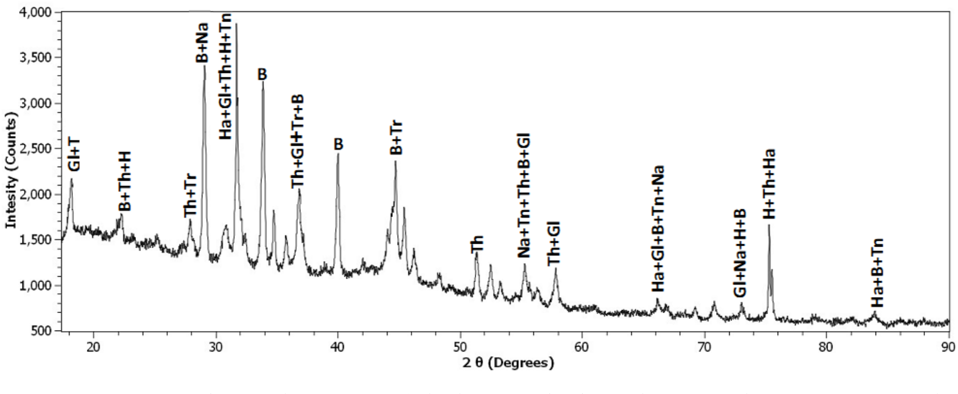

***Figure 1** XRD Pattern of mineral precipitates (Gl-Glaserite, Th-Thenardite, Ha-Halite, Tr-Trona, B-Burkeite, Na-Natron, Tn-Thermonatrite, H-Hanksite).*

***Table 2** The mineral composition of the precipitates at the different study temperatures*

	Mineral Phases			
Temp °C	Sample 1	Sample 2	Sample 3	Sample 4
30	Calcite, Magnesite, Tychite, Halite Glaserite	Calcite, Thermonatrite, Burkeite, Thenardite, Halte	Calcite, Anhydrite, Magnesium Sulphate, Burkeite, Thermonatrite, Halite, Glaserite, Sylvite	Anhydrite, Dolomite, Thenardite, Burkeite, Hanksite, Trona, Natrite, Halite, Glaserite, Sylvite
40	Calcite, Anhydrite, Magnesite, Magnesium Sulphate, Thenardite, Trona, Natron, Halite, Glaserite, Arcanite, Sylvite	Calcite, Magnesite, Halite	Magnesite, Dolomite, Thenardite, Burkeite, Thermonatrite, Halite, Glauberite, Glaserite, Sylvite	Burkeite, Hanksite, Halite, Glauberite, Sylvite
50	Anhydrite, Magnesite, Dolomite, Trona, Thermonatrite, Halite	Calcite, Magnesite, Thenardite, Trona, Halite	Calcite, Magnesite, Dolomite, Gaylussite, Burkeite, Hanksite, Trona, Thermonatrite, Natrite, Halite, Glauberite	Calcite, Anhydrite, Dolomite, Thenardite, Burkeite, Hanksite, Nahcolite, Thermonatrite, Halite, Glaserite, Sylvite
60	Calcite, Magnesite, Halite, sylvite	Magnesite, Dolomite, Halite	Calcite, Magnesite, Dolomite, Trona, Natrite	Anhydrite, Dolomite, Burkeite, Hanksite, Natron, Halite, Sylvite
70	Calcite, Magnesite, Magnesium Sulphate, Dolomite, Thenardite, Halite, Thermonatrite, Glaserite, Sylvite	Calcite, Magnesite, Dolomite, Trona, Halite, Sylvite	Calcite, Anhydrite, Magnesite, Dolomite, Halite, Sylvite	Anhydrite, Magnesite, Dolomite, Gaylussite, Thenardite, Natrite, Halite, Glauberite, Sylvite

Thermodynamic modelling

To model the precipitation sequence during the evaporation of the Lake Katwe brine, PHREEQC code (Parkhurst and Appelo 2013) version 3.4.0 was used. Due to the high concentration and ionic strength of brine, the geochemical calculations were done using the Pitzer ion interaction approach with a modified version of the pitzer.dat thermodynamic database distributed with the PHREEQC code. Evaporation was simulated in steps, 51 moles of water in 102 steps was removed (92% of the initial water was evaporated). The sequence of the modelled mineral precipitation at the study temperatures during the evaporation was noted. The major ions in Lake Katwe brine as shown in Table 1 were used as PHREEQC input (Kasedde et al. 2014).

Results and Discussion

Mineralogical analysis

Fig.1 illustrates a representative X-ray diffractogram of evaporation precipitates. X-ray diffraction results show a dominance of the carbonates and sulphates of calcium and magnesium (Calcite, Tychite, and Dolomite) in the first precipitates as predicted by Arad and Morton (Arad and Morton 1969). This is attributed to their low solubilities within the study temperature range.

Table 2 shows the mineral composition of the precipitates at the different study temperatures. Four samples are analysed at each temperature and these were collected as soon as crystals appeared. At all the study temperatures, Halite emerges as the most abundant mineral as the phase is observed in almost all the samples. This is also evident by the dominance of its microstructures in Fig.2.

At 30°C, apart from Halite, Trona is the most abundant mineral followed by Thenardite and then Natrite. Halite, Burkeite, Glaserite and then Hanksite is the order of prominence at 40°C with Thenardite appearing as a trace. The sodium carbonate and bicarbonate minerals dominate the precipitates at 50°C with traces of Arcanite and Thenardite. For 60°C as well, the sodium carbonate and bicarbonate minerals dominate the precipitates with the sulphates and chlorides of sodium precipitating as Hanksite. Natrite and Hanksite are observed to be the most dominant phases at 70°C. The XRD results are supplemented by the SEM results.

Microstructual Analysis

Fig. 2 shows the SEM micrographs of the precipitates observed during the brine evaporation. Four samples were filterd off at each study temeperature with Sample A first, followed by B and lastly C. The SEM micrographs reveal distinctive microstructures of the dominant mineral phases that precipitate out of the brine. At all the study temperatures, precipitation of Halite is observed.

The waxy massive form (Fig. 2, (70° (A)) which is due to the hygroscopic nature of the salt (Eswaran et al. 1980; Mees and Tursina 2010) and the sharp cubic crystals (Fig. 2 (60°(C))(Abdel-Wahed et al. 2015) are typical Halite morphologies. Massive forms of Halite are also observed as coatings composed of anhedral crystals (Fig. 2, (70°(B)) (Mees and Tursina 2010) on top of salt (rice) cake normally a fitting description for Thenardite crystals (Yamamoto and Zhu 1997; Warren 2016). The aforementioned is evidence of mineral stratification and co-precipitation; the latter needs to be minimised if pure salts for industrial use are to be produced. Trona is observed as blade like (Kasedde et al. 2014) and columnar massive (Warren 2016) crystals (Fig. 2 (50°(A)), on top of Thenardite (salt cake) (Fig. 2, (70°(C)) and sandwiching Halite crystals (Fig. 2 (40°(A), 50°(B) & 50°(C)). Hexagonal prismatic crystals of Hanksite are also observed as one of the precipitating mineral phases (Fig. 2, (40°(B)) (Kasedde et al. 2014; Warren 2016). Similar microstructures were identified by Kasedde and co-workers (Kasedde et al. 2013) in an isothermal evaporation study.

As temperature increases, the mineral phase stratifications become more distinct unlike at lower temperatures were phases are more mingled up. This is attributed to the increasing difference between the solubilities of the constituent minerals; as the temperature increases, the difference in the saturation with respect to the mother solution of the different minerals increases as well.

Thermodynamic modeling

At 30°C, 40°C, and 50° evaporation temperatures, the major salt precipitation sequence starts with Thenardite followed by Trona, Halite and lastly Glaserite (Fig. 3). This is in agreement with the previous isothermal evaporation study at 30°C conducted by Kasedde et al. (Kasedde et al.

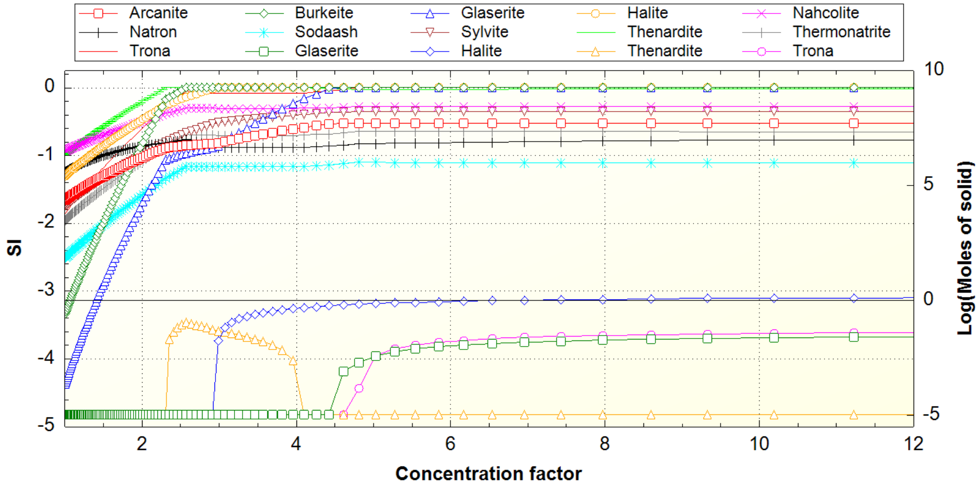

Figure 3 *Saturation Indices and Moles of solid posted during evaporation at 30°C*

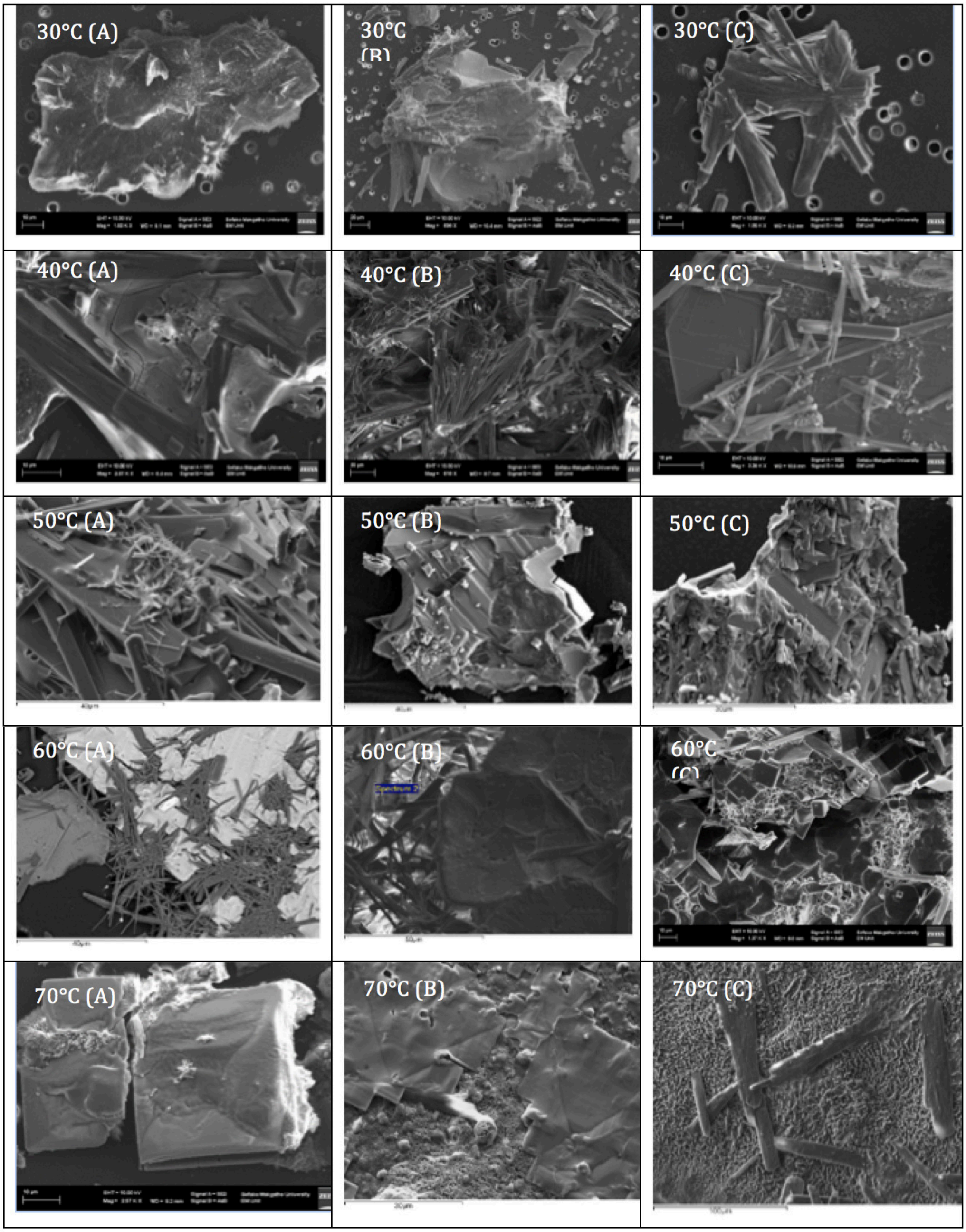

***Figure 2** SEM micrographs of the precipitated minerals from the evaporation experiments.*

2013) and Lwanyaga et al. (Lwanyaga et al. 2018). However in this study, Sylvite does not equilibrate with the brine and therefore doesn’t precipitate unlike in the previous phase developments study by Kirabira and co-workers (Kirabira et al. 2015).

When the temperature is increased to 60°C, Glaserite does not equilibrate with the solution and therefore does not precipitate. Further increase temperature to 70°C, results into the precipitation of only Thenardite and Halite. At all the study temperatures, Thenardite precipitates first and later with increasing evaporation dissolves into the solution. The Saturation Index (SI) of Soda ash, a mineral of interest in this study, increases with increasing evaporation temperature. This observation predicts precipitation of this mineral at temperatures higher than 70°C.

From the model results as seen in Fig.3, Halite posted the highest amount of precipitate, followed by Thenardite, Trona and lastly Glaserite. This is consistent with previous studies (Arad and Morton 1969; Kasedde et al. 2014; Lwanyaga et al. 2018) which ascertained that, at the salt lake, brine are comprised of more sodium, chloride, Carbonate, sulphate, Bicarbonate, & Potassium salts.

There are noticeable differences between the actual precipitated salts from the evaporation experiment and the PHREEQC results. The XRD and SEM results confirmed existence of more double salts and hydrates compared to the PHREEQC model. This variation is due to the fact that the PHREEQC model mainly considers the thermodynamic aspects and not the kinetics, yet, the actual setting considers the kinetics thus some minerals might precipitate from the model and not observed by XRD and vice versa.

Conclusions

In this work, the effect of temperature on the precipitation and crystallization sequence on the Lake Katwe brine during evaporation was investigated. Increase in temperature fostered the evaporation rate and therefore it took less time to precipitate minerals at higher temperatures than at lower ones. XRD and SEM results confirmed the presences various commercial salts. Halite is the most abundant mineral at all the study temperatures. Other minerals include, Thenardite, Trona, Burkeite, Hanksite and Natrite. carbonates and sulphates of calcium and magnesium (Calcite, Tychite, and Dolomite) precipitate first. These are in low quantities and therefore will have to be removed first in the extraction process to avoid contamination of Halite. From this study, Halite of table salt grade will be best extracted at higher temperatures (60 & 70°C).

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