Mineral recovery from Lake Katwe brines using isothermal evaporation

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Abstract Lake Katwe is a saline lake within the East African Rift system in Western Uganda, 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) and scanning electron microscopy (SEM) methods. Various economic salts such as thenardite, gypsum, mirabilite, burkeite, hanksite, anhydrite, trona, halite, nahcolite, thermonatrite, and soda ash precipitate from the lake brines. The experiments also reveal the sequence of mineral salt precipitation in the order sulfates→chlorides→carbonates.

Keywords Lake Katwe; Brine; Isothermal Evaporation; Sulfate salts; Chloride salts; Carbonate salts; XRD; SEM.

Introduction

Lake Katwe is a closed saline lake on the northern side of fresh water Lake Edward within the western branch of the East African Rift valley system, and about 15 km below the equator in western Uganda. The lake lies at an elevation of about 885 m, with a maximum area of 2.5 km², depth of less than 1.5 m, and measuring 9 km in circumference. The natural salt lake brines are highly alkaline and rich in Na⁺, K⁺, Cl⁻, CO₃^{2–}, SO₄^{2–}, and HCO₃⁻ with lesser amounts of Mg²⁺, Ca²⁺, Br⁻, and F⁻. The surface brines are hydro-chemically of a carbonate type and represent an important source of mineral salts that are of great economic value. The salinity and density of the lake brines varies from 140 to 150 g/L and 1.15 to 1.23 g/mL respectively and depend on seasonal variations (Kasedde et al. 2012 submitted). The meteorological conditions in this region are generally semi-arid, with little rainfall, and a great capacity for evaporation. Because of these conditions, traditional solar pond evaporation techniques are currently used to extract salts

from the surface brine resources of the lake. These salt extracts are composed of halite mixed with other impurities.

Since the 1960s, studies have been developed to exploit and utilize the lake's mineral resources. Besides the study of the geological setting of the region and chemistry of the lake brines (Arad and Morton 1969), investigations were extended to studying the feasibility of salt extraction through estimation of the salt reserves (Morton and Old 1968, Dixon and Morton 1970, Morton 1973, UDC 1997), and the mineralogical composition of the evaporites (Nielsen 1999). Further studies involved devising techniques and concepts of improving salt mining and extraction from the lake resources (Kirabira et al. 2013) and characterization of the mineral salt raw materials from the salt lake deposit (Kasedde et al. 2012 submitted).

In the present investigation, an isothermal evaporation experiment was performed to determine the nature of mineral salts that can be recovered from Lake Katwe brines, and to study the sequence of their precipitation. The study is essential for evaluating the possibilities for future comprehensive and sustainable utilization of the salt-lake brine resources.

Materials and methods Apparatus and reagents

An FP12 thermostatic water bath (Julabo Labortechnik, GmbH, Seelback, Germany) was used for the isothermal evaporation experiment. The precision of temperature control was ±1 °C. The density of the liquid phase was measured by a portable densito-meter (DMA 35 Anton Paar, Graz Österreich, Austria) with an accuracy of ± 0.001 g/cm³. The salinity and electrical conductivity were measured by an electrode probe meter (HANNA instruments HI 98360, Woonsocket, RI, USA) with an accuracy of ±0.5 %. The pH value of the liquid phase was determined by a PC Titrator (Mantech). The mineralogy of the precipitated salts at each stage of evaporation was identified by Xray diffractometry (XRD) using a D2 Phaser benchtop XRD system (Bruker Corporation, Massachusetts, USA) with a copper K_{α} radiation (λ = 1.5405 Å) operating at a voltage and current power of 30 kV and 10 mA. A diffraction interval between 2θ -10°-80° with step increments of 0.01° and a scan speed of 0.5 seconds were used. The morphology of the salts was examined by a Field Emission Gun Scanning Electron Microscope (FEG-SEM) using a LEO 1530 Gemini (Zeiss, Oberkochen, Germany) with settings at a voltage of 15 kV and aperture 60 µm. The images were taken with a secondary electron detector. A gold sputter coater (Emitech K550) was used to prepare the mineral salt samples before SEM analysis to make them electrically conductive. Double distilled water having a conductivity of 0.0182 S/m at 25 °C was used in the experiment.

Experimental methods

The dry season surface brine was sampled from Nambawu salt pans at Lake Katwe in August 2012 and was stored in plastic bottles at room temperature prior to the present study

in October 2012. The brine had not been saturated since no solid precipitates were observed. For the isothermal evaporation experiment, one liter of the natural brine was filled in a glass beaker. The beaker was placed in a thermostatic water bath which was maintained at 30±1 °C. The evaporation conditions were close to those existing at Lake Katwe. The brine was left to evaporate without stirring in a ventilated environment at 30±1 °C with a continuous air flow of 1 m/s. The evolution of the brine evaporation was monitored on a daily basis for newly precipitated solid salts. When a sufficient amount of the solid salts appeared, they were separated from the solution by filtration. The salts were then dried and stored in small plastic sample bags and subsequently characterized with X-ray diffraction and scanning electron microscope techniques. At the same time, a 10 mL brine sample was taken from the liquid phase, diluted with distilled water to a final volume of 50 mL, then measurement of its physical properties were taken. The isothermal evaporation experiment was repeated for each sample until all the brine dried up.

Results and Discussion

The brine sample used in the evaporation experiment was the original brine from Lake Katwe. It's chemical composition in g/L was 137 Na⁺, 39.1 K⁺, 0.00143 Mg²⁺, 0.005 Ca²⁺, 124 Cl⁻, 43 SO₄²⁻, 3.39 HCO₃⁻, 61 CO₃²⁻, and 0.082 F⁻. In the course of the isothermal evaporation experiment, twelve liquid and twelve solid samples were collected. The physico-chemical parameters of the original brine (sample L₀) and the mother liquors (sample Ln, n representing the corresponding evaporation stage) are presented in Table 1.

The evolution of density and conductivity as given in Table 1 is shown graphically in Fig. 1. The original brine (sample L_0) is undersaturated and hence, upon evaporation of water from the original brine, both density and conductivity increase until the first salt precipitate is harvested at sample L_1 . Thereafter, density

Sample	Evaporation Time(days)	Electrical Conductivity (mS/cm)	рН	Salinity (g/L)	Density (g/cm³)		
Lo	0	140.1	10.2	70.0	1.306		
L_1	6	147.3	10.7	73.8	1.315		
L_2	12	138.3	10.7	69.2	1.316		
L_3	15	133.5	10.7	66.6	1.322		
L_4	20	132.3	10.7	66.1	1.326		
L_5	25	134.5	10.8	67.4	1.320		
L_6	29	130.5	10.9	65.3	1.325		
L_7	33	123.6	10.9	62.1	1.336		
L_8	36	116.6	10.8	58.4	1.343		
L9	40	99.6	11.1	49.8	1.360		
L ₁₀	43	95.2	11.1	47.4	1.361		
L_{11}	47	93.0	11.2	44.0	1.355		
L ₁₂	50	-	-	-	-		

Table 1 Physico-chemical parameters of the liquid brine samples.

and conductivity follow a different trend: while density tends to increase, conductivity gradually decreases. This indicates a change in the ionic composition of the brine as different ionic species contribute differently to density and conductivity. Furthermore, the local maxima of density, respectively the local minima of conductivity, observed for sample L₄ indicates a change in the precipitation sequence, as confirmed by analysis of the precipitates as outlined below.

The inset in Fig. 1 shows the evolution of pH during evaporation. After a sharp increase when moving from the original brine to the first sample, the pH assumes a constant value that lasts until sample L_4 after which a further

increase is observed. This second period of increase culminates in a local maximum at sample L_6 and L_7 , followed by a local minimum at sample L_8 . Thereafter, a third increase is observed leading to plateau at sample L_9 and L_{10} . Likewise to the local extrema in density and conductivity, the different regions in the evolution of pH relate to the precipitation sequence.

The mineralogical composition of the recovered solids were analyzed by XRD and SEM. These measurements indicate the presence of various solid phases in each sample. A typical XRD measurement showing several characteristic peaks is shown in Fig. 2. Analyzing the XRD spectra allowed for identifying the solid





Fig. 1 Evolution of brine density (square symbols), conductivity (circles), and pH (inset).

Fig. 2 X-ray diffraction (XRD) results for salt sample S1 (Then-Thenardite, An-Anhydrite)

Mineral phase	Sample												
		S_1	S_2	S_3	S_4	S_5	S_6	S ₇	S_8	S9	S_{10}	S_{11}	S_{12}
Thenardite (Then)	Na ₂ SO ₄	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Mirabilite (Mir)	$Na_2SO_4 \cdot 10H_2O$		Х			Х		Х		Х		Х	
Burkeite (Bur)	2Na ₂ CO ₃ ·Na ₂ SO ₄		Х	Х		Х	Х	Х	Х				
Hanksite (Han)	9Na ₂ SO ₄ ·2Na ₂ CO ₃ ·KCl		Х	Х		Х		Х	Х	Х		Х	
Gypsum (Gy)	CaSO ₄ ·2H ₂ O			Х		Х	Х	Х		Х			
Anhydrite (An)	CaSO ₄	Х			Х								
Trona (Tr)	$Na_3(CO_3)(HCO_3) \cdot 2H_2O$					Х	Х		Х	Х	Х	Х	Х
Nahcolite (Nah)	NaHCO ₃											Х	Х
Thermonatrite (Th)	Na ₂ CO ₃ ·H ₂ O												Х
Soda ash (S)	Na ₂ CO ₃											Х	
Halite (Ha)	NaCl						Х	Х	Х				

 Table 2: Mineralogical composition of the solid salts
 Particular
 Particular

phases in each sample. Table 2 gives an overview of the identified solid phases.

From the data in Table 2 we can identify several precipitation stages. A first stage lasting from sample S_1 to S_4 is dominated by the precipitation of sulfates only, *i.e.* the XRD of the first four samples indicated the presence of the sodium sulfates thernardite and mirabilite, the carbonate containing sulfates burkeite and hansite, as well as the calcium sulfates gypsum and anhydrite. The corresponding mother liquors (sample L_1 to L_4 in Fig. 1) had a constant pH of 10.7, while the density and conductivity were increasing, respectively decreasing.

SEM micrographs of the salt sample in this first stage are shown in Fig. 3 (S1 to S4). Well faceted crystals with either elongated or platelet like shape together with long tubular crystals are seen in sample S1. Similar shape and sizes are seen in sample S2 which additionally contains some smaller less developed structures. Comparing the XRD measurements of the first two samples, the additional structures seen in the SEM of sample S2 can be related to the presence of hanksite, burkeite, and mirabilite in this sample. Considering sample S3 and S4, it is observed that the crystal sizes decreases while well faceted and elongated crystals together with platelets are also seen in these samples.

In a second precipitation stage, lasting from sample S_6 to S_8 , sodium chloride crystal-

lizing as halite precipitates together with sulfate minerals. In the physico-chemical parameters of the brine shown in Fig. 1, this stage is characterized by a strong increase in liquid density combined with a weak decrease in conductivity. The pH during this second stage goes through a local maximum as seen in the inset of Fig. 1. SEM micrographs are shown in Fig. 3 (S6 to S8). Small hexagonal crystals together with needles and some less well developed particles are observed. The typical cube like crystal shape of pure halite was not observed.

A third precipitation stage, lasting from sample S₉ to S₁₂, is characterized by the formation of sodium carbonates precipitating together with sulfates. Several sodium carbonates were identified by XRD, namely trona, nahcolite, thermonatrite, and soda ash. The mother liquors at this precipitation stage assumed fairly high densities, i.e. around 1.36 g/cm³ (Table 1), which can be explained by the relatively high solubility of the involved salts. On the other hand, conductivity was low while pH assumed values larger than 11. SEM micrographs of this last precipitation stage are shown in Fig. 3 (S9 to S12). While sample S₉ still shows many small crystals of various shape, sample S₁₀ shows few large crystals together with some bulky material, identified as thenardite and trona, respectively. Sample S₁₁ shows small prismatic crystals together with



Fig. 3 SEM micrographs of the recovered salts (S_1 - S_{12}) during the isothermal evaporation experiment. Scale bars = 10 μ m.

large indistinguishable crystals which we relate to nahcolite and trona, respectively.

Conclusion

From the isothermal evaporation experiment of Lake Katwe brine, the following conclusions are drawn:

Precipitates show a rich variety of different mineral salts, *i.e.* upon evaporation of lake brines thenardite, anhydrite, mirabilite, burkeite, hanksite, gypsum, trona, halite, nahcolite, soda ash, and thermonatrite are formed. Thenardite precipitates during the entire evaporation process and its crystals were observed to be present in all samples.

The mineral salts precipitating from the lake brines follow the sequence sulfates \rightarrow chlorides \rightarrow carbonates. The evaporation pathway of Lake Katwe brines thus differs from that of modern sea water evaporation sequence.

The salts produced at Lake Katwe by traditional and artisanal techniques are composed of several mineral phases with limited production rates. The results from the present study can provide an important reference in the development of technologies for the extraction of various pure mineral salts from the natural brines of Lake Katwe. Understanding the sequence of salt precipitation from the brine helps to control its evolution during concentration and hence will lead to an improved operating design scheme of the current extraction process. However, to fully exploit the lake's brine resource, further work is required in studying its thermodynamics and the related phase equilibria.

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References

- Arad A, Morton WH (1969) Mineral springs and saline lakes of the Western Rift Valley, Uganda Geochimica et Cosmochimica Acta 33:1169–1181
- Dixon CG, Morton WH (1970) Thermal and Mineral Springs in Uganda. U.N Symposium on the Development and Utilization of Geothermal Resources, Pisa 1970. Vol. 2, Part 2

- Kasedde H, Kirabira JB, Bäbler MU, Tilliander A, Jonsson S (2012) Characterization of brines and evaporites of Lake Katwe, Uganda. Manuscript submitted to Journal of African Earth Sciences
- Kirabira JB, Kasedde H, Semukuuttu D (2013) Towards the improvement of salt extraction at Lake Katwe. International Journal of Scientific and Technology Research 2: 76–81
- Morton WH, Old RA (1968) A composition and tonnage survey of the salt reserves of Lake Katwe. Uganda Geological Survey. Unpublished Report No. WHM 6/RAO 7
- Morton WH (1973) Investigation of the brines and evaporite deposits of Lake Katwe, western Uganda. Overseas Geology and Mineral Resources, No. 41, Institute of Geological Sciences, 107–118.
- Nielsen JM (1999) East African magadi (trona): fluoride concentration and mineralogical composition. Journal of African Earth Sciences 29:423–428.
- UDC (1997) Feasibility study of the rehabilitation of Lake Katwe Salt Project. Uganda Development Cooperation, Republic of Uganda.