

Thermodynamic Modeling of Lake Katwe Brine for Industrial Salt Extraction

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Salt Production

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Abstract

Lake Katwe is a saline lake located in the western arm of the East African rift valley system in Western Uganda. The extraction of commercial mineral salts from the lake brine requires thorough knowledge of the brine phase chemistry. Solution chemistry and solid–liquid (phase) equilibrium play a very important role in the design, synthesis and analysis of crystallization-based separation processes involving electrolytes. In this paper a solubility software (PHREEQC) has been used to predict which salts, their respective yield and the order in which they can crystallize from Lake Katwe brine. The brine solution was evaporated to supersaturation by removing 51 moles of water at 27.6°C. Thereafter, supersaturated solution was subjected to temperature variations ranging from -30° to 130°C. After removal of 31 moles of water, Thenardite equilibrates with the solution followed by Trona (33 moles), Burkeite (35.5 moles), Halite (36 moles) and lastly Glaserite (41.5 moles). Halite posts the highest yield of about 0.783mols/kg followed by Thenardite (0.16 mols/kg), Burkeite (0.13 mols/kg), Glaserite (0.02 mols/kg), and Trona (0.0195 mols/kg). The pH averaged at 9.73 until the first mineral equilibrated with the solution, after this it dropped with increasing evaporation to 9.58 at supersaturation. At subzero temperatures, Mirabilite emerged with the highest Saturation Index (SI) followed by sylvite and Halite. The Saturation Indices of Mirabilite and sylvite reduced with increasing temperature while that of Halite slightly increased. Burkeite, natron and Thenardite registered positive SIs at 28°C, Glaserite at 15°C, natron at 99°C and thermonatrite at 91°C. The brine pH decreased with increasing temperature -30°C to 0°C and thereafter increases steadily with increasing temperature. During evaporation, the PHREEQC model predicts a mineral precipitation sequence that starts with Thenardite followed by Trona, Burkeite, Halite and Glaserite. Based on the yield results, Halite, Thenardite, Burkeite, Glaserite, and Trona are the feasible salts that can be extracted, the latter being the least feasible. The ideal parameter ranges of pH, alkalinity, temperature, brine concentration factor and ionic strength were determined.

Introduction

Lake Katwe is an explosion crater in western Uganda and is one of eight craters which contain a rich supply of natural salt (Figure 1). There are about 22.5 million tons of commercially viable common salt in Lake Katwe according to a study by the Uganda Development Corporation (UDC) in 1997[1].

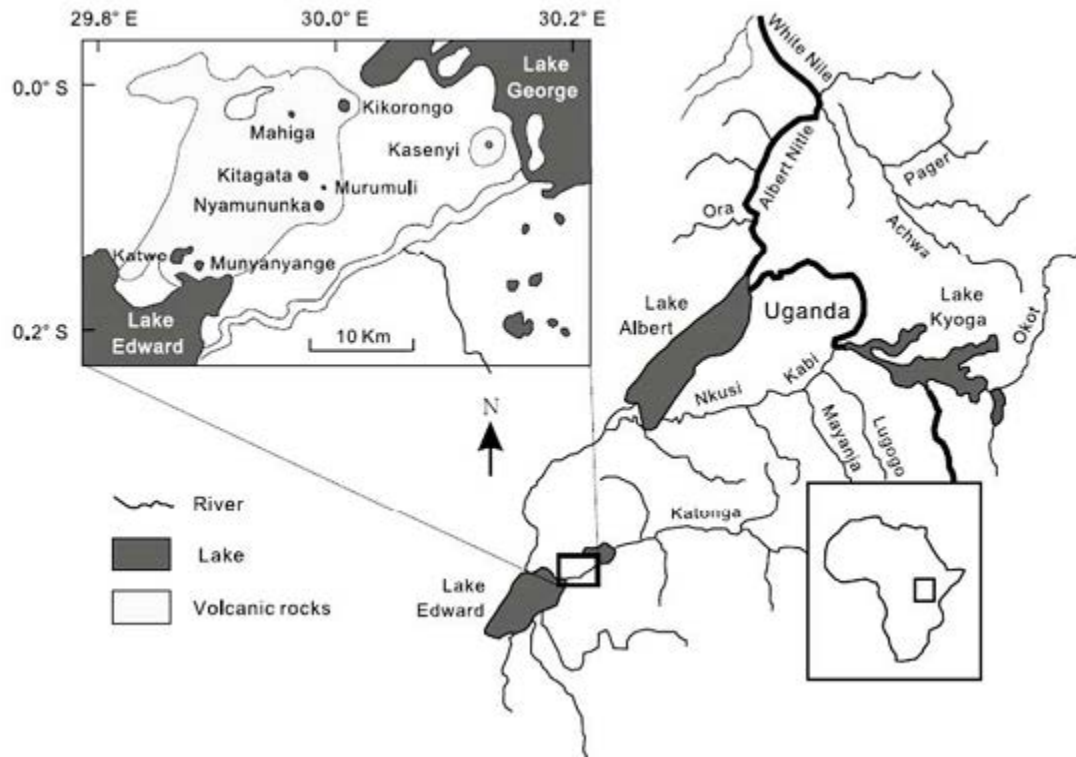


Figure 1: Location of Lake Katwe and the other saline crater lakes within the Katwe-Kikorongo volcanic field [2]

In Uganda today, nearly all the salt consumed domestically and by the related industry are imported from the neighboring countries. Yet, Uganda is gifted with commercial salt reserves evident in the brines and evaporite deposits of Lake Katwe. The traditional salt mining and processing techniques that salt winners have employed at Lake Katwe for centuries have yielded salt that is both impure and in low quantities[3]. This salt is normally used as an animal feed supplement and is neither suitable for both human consumption nor for industrial use. The latter requires salt with purity of over 95% and in large quantities hence the severe need for salt imports in the country.

In order for Uganda to reduce her dependence on imports for salt supplies and be able to satisfy her domestic and industrial salt demand, a clear methodology needs to be developed to support commercial extraction of industrial salts from the lake. Positive developments in field studies, experimental, and thermodynamic modeling methodologies have been achieved in previous studies [3], [4] seeking to develop a much improved technique for salt purification to standards safe for domestic and commercial applications. The studies have characterized the salt lake raw materials and have shown they contain substantial amounts of salt which can be developed into commercial production. From other studies[4], [5], various types of economic

salts such as Thenardite, anhydrite, Mirabilite, Burkeite, Hanksite, Gypsum, Trona, Halite, Nahcolite, Soda ash, and Thermonatrite precipitate from the brine of Lake Katwe.

Kasedde and coworkers [6] reported that to spin off full exploitation of the natural resource, thermodynamic and the related phase equilibria studies of the brine are critical. They, however, did not investigate the effect of temperature and other physico-chemical brine parameters on the crystallization process in their study.

From the foregoing, it is clear that Lake Katwe brine is of a complex nature and therefore various commercial salts cannot be extracted by simple means[3]. This, therefore, necessitates the development of an extraction process to effect an efficient separation process. Solution chemistry and solid–liquid (phase) equilibrium play a very important role in the design, synthesis and analysis of crystallization-based separation processes involving electrolytes[7]. Before the separation process is attempted, it is prudent to investigate the brine phase chemistry to ascertain the crystallization fields of the constituent brine components.

In this paper a solubility software (PHREEQC) based on the Pitzer's ion-interaction model [8]–[10] is a suitable tool because it is reliable for predicting salt's solubility in multicomponent aqueous systems with high ionic strength over a wide range of temperatures (0°–300°C)[11], [12]. The major aim of this study was to predict the effect of temperature and other physico-chemical brine parameters on the salt(s) extraction process. Information provided by this study will be important for the design of an extraction process for the commercial salts from Katwe brine.

Materials and methods

In this study, PHREEQC program version 3.0 [13], a geochemical software was used to model the thermodynamics of Lake Katwe brine. Aqueous equilibria simulations were performed with the mean brine composition of the two seasons (rainy and dry) [4] shown in Table 1 as the initial input. Brines of Lake Katwe are highly concentrated and therefore the Pitzer database was chosen because of its suitability for highly concentrated solutions, due to a term of long range interactions between the ions and a virial term for the short range interactions between solute species[11]. However, the database had to be modified to incorporate thermodynamic data for Soda ash and Thermonatrite from the SIT (Specific ion Interaction Theory) data base in PHREEQC.

Table 1: Brine Composition

Season	pH	Brine Temp (°C)	Density (g/ml)	EC (us/m)	Na	K	Mg	Ca	Cl	Br	SO ₄	HCO ₃	CO ₃
Rainy	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
Dry	9.69	30.0	1.19	15127	87.3	14.8	0.0613	0.0046	50.8	0.561	40.4	22.1	46.5
Mean	9.705	27.6	1.17	14618	78.5	13.2	0.0566	0.0047	47.5	0.511	36.6	20.2	42.7

As aforementioned, in this study, the thermodynamic modelling of the brine aimed at predicting which salts and their sequence of precipitation and an estimation of the amounts that can be harvested. PHREEQC simulation returns the saturation index (SI) of all possible salts. Therefore, PHREEQC can be used to predict the sequence in which the salts crystallize from the brine [14]. SI was utilized to estimate the supersaturation of a precipitate phase in solution.

The SI is the ratio of the Ion Activity Product (IAP) to the Solubility product (K_{SP}) as shown in Equation 1[15].

$$SI = \frac{IAP}{K_{SP}} \quad (1)$$

The value of the SI indicated whether the solution is in equilibrium ($SI=0$), under-saturated ($SI<0$), or supersaturated ($SI>0$). Under-saturated meant that the mineral will remain dissolved in solution whereas supersaturated meant that the salt will precipitate as a crystal from the solution under favorable reaction kinetics. The thermodynamic driving force of a chemical reaction is the Gibbs free energy (ΔG), as elaborated in Equation 2, whose value indicates whether a particular reaction is in equilibrium ($\Delta G=0$), impossible ($\Delta G>0$) or spontaneous ($\Delta G<0$)[16].

$$\Delta G = \frac{RT}{n} \ln \frac{IAP}{K_{SP}} \quad (2)$$

R is the ideal gas constant, T is the absolute temperature, n is the number of ions in a formula unit. The relationship between ΔG and SI has been expressed in Equation 3.

$$\Delta G = -\frac{2.303RT}{n} SI \quad (3)$$

The modelling was based on an open system which meant that the system was in equilibrium with atmosphere and therefore with the atmospheric carbon dioxide and pressure. First, the mean brine composition was subjected to a speciation analysis in PHREEQC; all possible minerals and their respective saturation indices were posted. The brines are highly alkaline and rich in Na^+ , K^+ , Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^- . Moreover, they contain trace amounts of Mg^{2+} , Ca^{2+} , Br^- , and F^- . Ions and their respective minerals with the highest concentration and of major commercial interest were considered in the subsequent simulations. These were allowed to react to a specified saturation index during the batch-reaction calculation whether they were initially present or not in the solution.

The brine solution was concentrated due to evaporation by cumulatively removing 0.5 moles of water at each reaction step up-to 51 moles of water in 102 steps. This enables the prediction of the precipitating salts, sequence and their respective yields. This was followed by subjecting the evaporated brine to a temperature variation of $-30^\circ C$ to $130^\circ C$ cumulatively in 161 steps. This being an open system, the atmospheric carbondioxide was equilibrated with solution. At the end of this simulation, the temperature at which the respective minerals precipitated where computed.

Results and discussion

Brine Concentration

PHREEQC speciation analysis using brine composition as reported in Table 1 returned several minerals listed in Table 2.

Table 2: Saturation Indices that are obtained through the thermodynamic modeling using brine composition

Phase		SI
<i>Arcanite</i>	K_2SO_4	-1.65
<i>Burkeite</i>	$Na_6CO_3(SO_4)_2$	-3.40
CO_2	CO_2	-3.47
<i>Glaserite</i>	$NaK_3(SO_4)_2$	-2.15
H_2O	H_2O	-1.48

<i>Halite</i>	NaCl	-1.31
<i>Kalicinite</i>	KHCO ₃	-2.71
<i>Mirabilite</i>	Na ₂ SO ₄ · 10H ₂ O	-0.62
<i>Misenite</i>	K ₈ H ₆ (SO ₄) ₇	-67.68
<i>Nahcolite</i>	NaHCO ₃	-0.83
<i>Natron</i>	Na ₂ CO ₃ · 10H ₂ O	-1.08
<i>Soda ash</i>	Na ₂ (CO ₃)	-2.57
<i>Sylvite</i>	KCl	-1.73
<i>Thenardite</i>	Na ₂ SO ₄	-1.03
<i>Themonatrite</i>	Na ₂ CO ₃ · H ₂ O	-2.15
<i>Trona</i>	Na ₃ H(CO ₃) ₂ · 2H ₂ O	-1.76

Ions with the highest concentrations were considered despite the fact that carbonates of calcium and magnesium were supersaturated with respect to the solution [14]. From the speciation results, sulphates, carbonates and chlorides of potassium and sodium emerged as the predominant minerals. Calcium and magnesium based salts were therefore considered trace elements. From the posted saturation indices of the different minerals, it is evident that all the salts are under-saturated with respect to the solution. This, therefore, necessitated concentration of the solution by removing water a process mimicking evaporation. The sequence of the salts precipitating from the brine is represented in Figure 2.

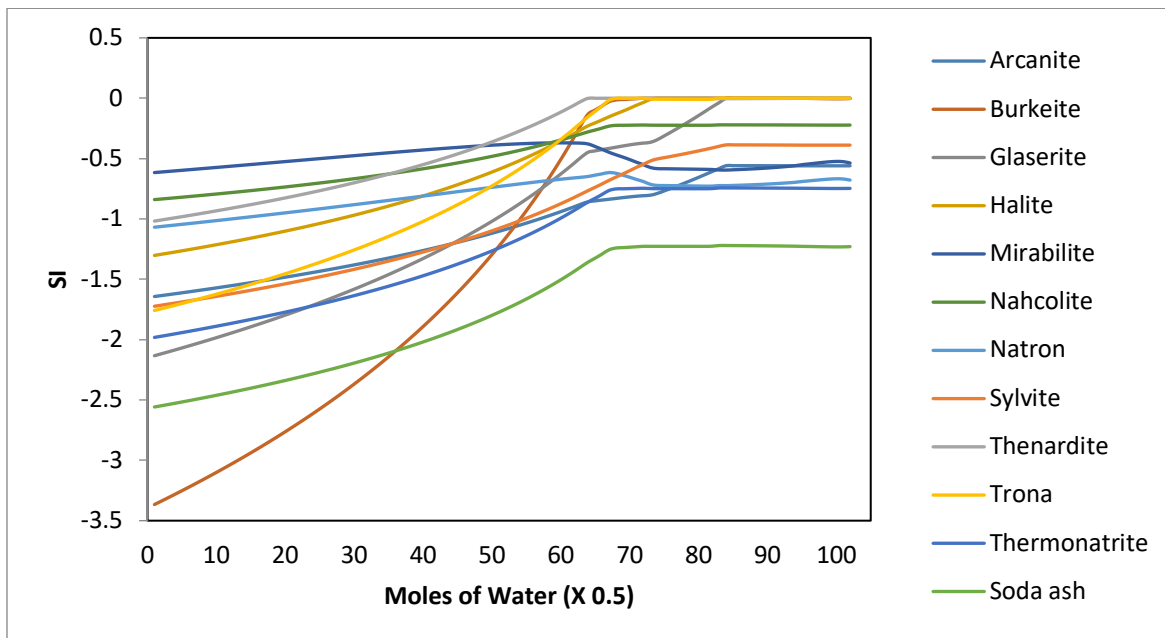


Figure 2: Brine Concentration

Figure 2 shows that Thenardite equilibrates first with the solution after removing 32 moles of water, and yielded 5.287×10^{-3} moles. The Thenardite yield increased with increasing solution concentration up-to 5.161×10^{-2} moles after the removal of 33.5 moles of water. Trona is the next mineral to equilibrate with the solution but this time together with Thenardite. This happens after the removal of 34 moles of water; Trona yielding 5.521×10^{-3} moles and Thenardite 9.112×10^{-2} moles. At 36 moles, Burkeite as well equilibrates with the solution together with both Thenardite and Trona posting 4.176×10^{-2} moles. As the solution continues to be concentrated, Trona gets undersaturated with the solution after the removal of 36.5

moles of water from the solution. With increasing solution concentration, Halite (4.176×10^{-2} moles) equilibrates with the solution at 37 moles. At this point Halite together with Thenardite and Burkeite are in equilibrium with the solution. The moles in assemblage of both Burkeite and Halite increase with increasing solution concentration while Thenardite's decreases until it becomes under-saturated at 41 moles. Trona re-equilibrates with the solution at 41.5 moles and at 42 moles, Glaserite equilibrates with the solution together with the other three minerals. At 47.5 moles, Thenardite re-equilibrates with the solution as Burkeite becomes under-saturated.

The results reported in this section indicate that the minerals likely to precipitate are predominantly; Thenardite, Trona, Burkeite, Halite and Glaserite. Like in previous studies[6], the minerals precipitate in a sequence of sulphates followed by chlorides and carbonates. As seen in Figure 3, Halite posts the largest amount and therefore the most abundant mineral.

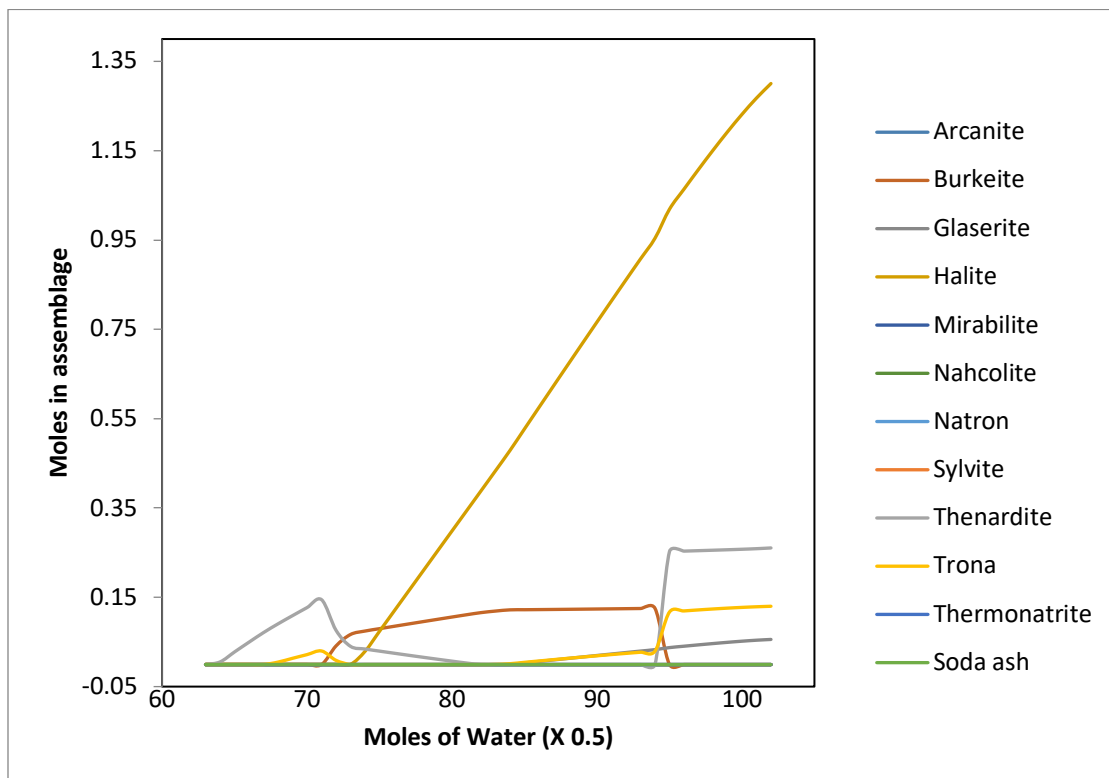


Figure 3: Mineral yield variation with brine concentration

Alkalinity and pH modeling

Figure 4 shows that, the pH initially maintained constant values as brine concentration increased. Before decreasing, the pH posted a maximum value of 9.745 after the removal of 33.5 moles of water. Alkalinity exponentially increased with increasing brine concentration up to a maximum value of 1.043 (eq/kg) and then sharply decreased before gradually decreasing with increasing brine concentration.

Comparing Figures 2 and 4, the pH and alkalinity increased with increasing SIs of the different minerals and decreased when they equilibrated with the solution. At high concentration factors, molality of the constituent minerals increased therefore increasing both the pH and alkalinity. At equilibration, moles of the minerals are precipitated from the solution, reducing the

molality and subsequently the pH and alkalinity. A concentration factor range of 65 – 101, pH 9.745 – 9.095 and alkalinity of 0.15 – 1.5 (eq/kg) are the ideal conditions for salt extraction of Lake Katwe brine.

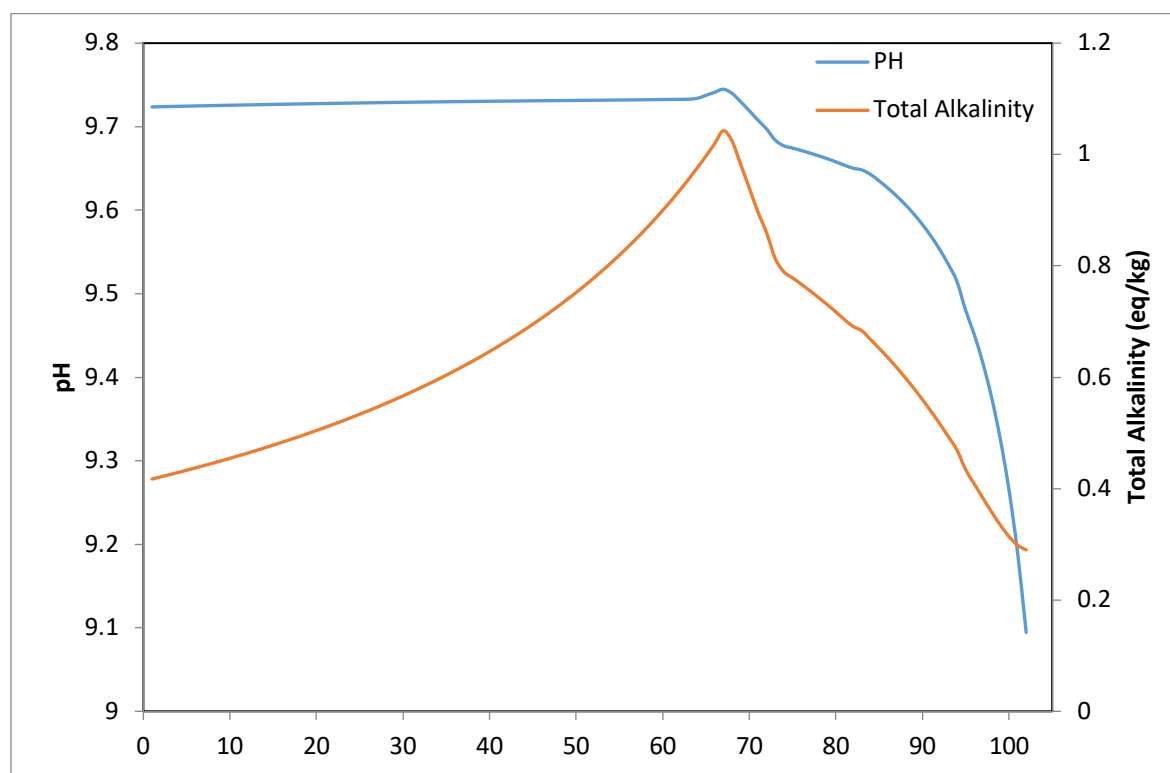


Figure 4: pH and Alkalinity variation with brine concentration

Ionic Strength Modeling

Figure 6 shows that, the solution ionic strength steadily increased with increasing brine concentration. When the minerals started to equilibrate with the solution, the ionic strength levelled off; the rate of increase of ionic concentration equaled rate of ionic removal from the solution. Comparing Figures 2 and 5, the ionic strength increased with increasing SIs due to the increase ionic concentration. Between concentration factors of 95 to 101, the ionic strength increases exponentially; this is due to the ions that remain in solution despite further evaporation. The solution ionic strength range of 8.9 – 9.0 (mol/kgw) and a corresponding concentration factor range of 65 – 95 are the ideal salt extraction conditions.

The thermodynamic modeling here only considers thermodynamic aspect and not the solution kinetics. The observed results here exhibit a degree of uncertainty due to the difficulty in the modeling of aqueous electrolyte systems caused by; the formation of unknown species in the brine solution, the dissolution of inorganic substances that ionize to varying degrees in the brine and precipitation of the ionic species in the brine.

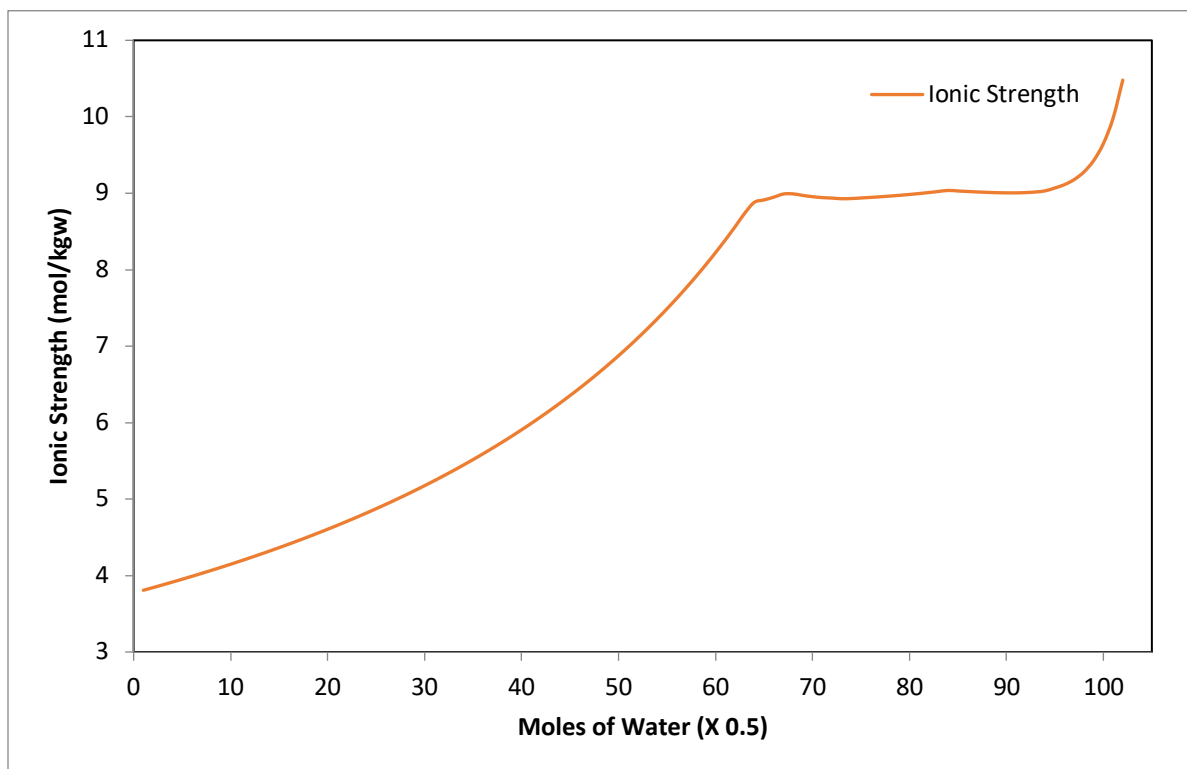


Figure 5: Ionic strength variation with brine concentration

Solubility dependence on temperature

Figure 6 shows that, at subzero temperatures [-30°, 0°C], Mirabilite is the predominant mineral that is most likely to precipitate followed by sylvite. As the temperature increases, their saturation indices decrease; sylvite equilibrates with the solution at -12°C and Mirabilite at 12°C. Halite equilibrates with the solution at 2°C, mildly gets supersaturated at 5°C and re-equilibrates with the solution at 24°C. Between 30°C and 54°C Burkeite, Thenardite and Trona are the only salts that are supersaturated with respect to the solution. Other sodium salts later attain supersaturation status; thermonatrite at 57°C, natron at 60°C, and Soda ash at 65°C. At 101°C, the saturation indices of these minerals start to decrease with increasing temperature therefore reducing the supersaturation of the minerals.

Since most of the minerals are sodium based, separating them with the use of temperature as the only parameter in fractional crystallization seems difficult. It is only at subzero temperatures were a potassium based salt (sylvite) can be precipitated. For an optimal extraction process, a temperature range of 20°– 65°C will be required for the brines of Lake Katwe. This range is easily achievable in practice and most of the minerals of interest are highly soluble within it, this makes it very favorable.

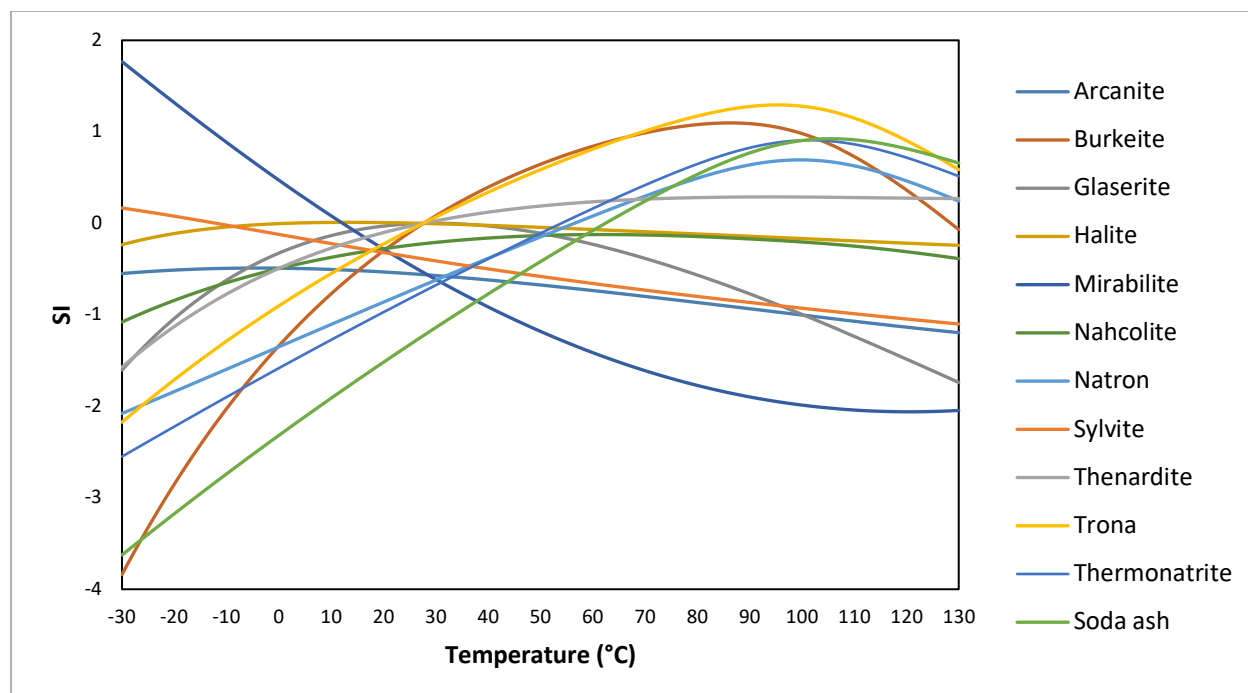


Figure 6: Effect of temperature on mineral solubility

Conclusions

To foster industrial salt Production Lake Katwe brine, a thermodynamic modeling study was undertaken and the following conclusions were drawn:

Gradual concentration of brine showed that Thenardite, Trona, Burkeite, Halite, and Glaserite are the feasible salts that could be extracted at industrial scale. Halite is the most abundant mineral and therefore most viable.

For industrial production of Mirabilite, temperature is important because, it is the predominant mineral at subzero temperatures. Between 20° – 24°C, Halite can be separated from the brine solution without any other mineral co-precipitating with it. The other minerals can be best extracted at a temperature range 30° – 65°C. Considering the brine composition for this study, the following parameter ranges are favorable for the commercial salt extraction process; concentration factor (65 – 95), pH (9.745 – 9.095), alkalinity (0.15 – 1.5 (eq/kg), and ionic strength (8.9 – 9.0 (mol/kgw))

Ionic strength, pH, alkalinity and temperature, each affects the solubility of the minerals differently. This, therefore, means that a separation process that can specify a combination of these parameters for a particular mineral salt will have a high chance of extracting the salt. Experimental investigation need to be undertaken to ascertain the model results and as well determine the mineral crystallization kinetics for better process control. This will be very handy in designing an extraction process for the potential commercial salts at Lake Katwe.

Acknowledgements

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