

Beneficiation of Salts Crystallized from Lake Katwe Brine

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Abstract

A salt extraction process to enhance the quality and quantity of salt produced at Lake Katwe in Uganda is presented. To validate the designed process, laboratory experiments were conducted. The techno-economic analysis of the process flow sheet was modeled and simulated by SuperPro Designer. Halite of purity >98% was obtained by floating burkeite and trona which co-precipitate with it during evaporation. The other feasible products of the process are soda ash and sodium sulfate. With a net present value of US\$25,077,817, the proposed process is economically viable.

Keywords: Salt Extraction, Lake Katwe, Sodium Chloride, Soda Ash, Sodium Sulfate, SuperPro Designer

Introduction

In Uganda, Lake Katwe is the major source of brine containing valuable minerals (Kirabira et al. 2013). The reserve contains about 22.5 million tonnes of crystalline salts (UDC 1997). At the deposit, salt mining has been taking place since precolonial times using rudimentary methods. As a result, the mined salt is of low quality (55.8 – 94.8% halite content) (Kasedde et al. 2014) and quantity thus, fetching small prices on the market. Due to this, Uganda imports over 90% of the salt from neighbouring countries (Chopra 2020).

The government of Uganda in the 1970's established a salt processing plant which failed within a few months without posting any results (UDC 1997). The process involved heating brine by steam in a series of evaporators operating at different temperatures. Additionally, cyclones, centrifuges, and filters were employed to separate crystals from the mother liquor. The expected primary product of this process was halite with potassium chloride as the secondary product. The failure of this process could be attributed to lack of the requisite phase chemistry knowledge of the raw

material that resulted in severe corrosion of the plant equipment.

Kasedde et al. (2014) characterised the raw material and determined that the brine constituted mainly Na⁺, Cl⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻ with lesser amounts of K⁺, Mg²⁺, Ca²⁺, Br⁻, and F⁻ ions. Several thermodynamic studies followed (Kasedde et al. 2013; Lwanyaga et al. 2018, 2019b,a) 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) that established the major evaporites as halite, burkeite, trona, and thenardite. These phase equilibrium studies have reported the mineral crystallization sequence as generally sulfate, halides and lastly carbonates. Furthermore, the evaporites co-precipitate with each other (Lwanyaga et al. 2019b,a) 40, 50, 60 and 70 and therefore, cannot be separated by simple techniques. From the above-mentioned studies, it was found that Lake Katwe brine composition is different from sea water and other notable salt lakes (e.g. Magadi, Dead

Sea, and Searles Lake). Therefore, a unique salt extraction process has to be tailored/customised to suit the brine at hand.

It is upon the knowledge of the aforementioned phase chemistry that the existing single solar pond system at Lake Katwe can be improved. The climate at Katwe is semi-arid with ambient temperatures ranging between 24 – 38 °C, an annual evaporation rate of 2160 mm/yr, and a precipitation of 860 mm annually (Kasedde et al. 2014). The foregoing conditions, coupled with low energy, capital and labour costs, make Lake Katwe a suitable place for solar salt production (Hocking 2005). Thus, the present study aims at developing a conceptual design for a commercial salt extraction process at Lake Katwe for the recovery of common salt and its co-products with solar as the main source of energy. SuperPro Designer v10 (Intelligen Inc 2019), a computer aided process design and simulation tool was used to conduct a techno-economic evaluation of the proposed process.

Process Development and Description

The proposed process employs sequential solar evaporation ponds as crystallizers for the readily processable salts from the brines of Lake Katwe. The evaporation ponds operate at atmospheric pressure and at an average ambient temperature of 30 °C (Kasedde et al. 2015). The brine residence time in a particular pond is determined by the brine density and pH. In the first pond, the brine is concentrated to precipitate calcite and magnesite. The brine is further concentrated in the second pond to precipitate sodium chloride with minimum contamination from burkeite and trona. By employing the flotation technique, the burkeite and trona crystals are separated from the sodium chloride (halite) slurry. The halite slurry is then dried in an open tray to produce common salt. The second pond filtrate is carbonated to precipitate the insoluble sodium bicarbonate, also known as nahcolite, in a NaCl saturated solution. The nahcolite is then calcined to produce sodium carbonate (soda ash). The supernatant from this step is processed first by freezing it in a cooling crystallizer to produce mirabilite

also known as Glauber's salt. The mirabilite is further dehydrated in an evaporative crystallizer to produce thenardite, a useful raw material in the glass and paper industries. The rest of the liquid is discarded as waste.

Methods and Materials

Laboratory experiment

A 3 L natural brine sample obtained from the surface of Lake Katwe during the rainy season was used in the experiment. The chemical composition of the brine is shown in Table 1. The brine solution was evaporated sequentially in a thermostatic water bath (Model 207, Lenton Furnaces, South Africa) at a temperature of 85 °C under atmospheric conditions for 12 h until a pH of 9.74 and density of 1.282 g/cm³ were attained. A high temperature of 85 °C was employed in order to reduce the time needed to concentrate the brine to the desired brine conditions. Upon the start of crystallization, the brine was cooled down to 30 °C, which is the average ambient temperature at Lake Katwe (Kasedde et al. 2015). The subsequent evaporation processes were handled under the same conditions of temperature and pressure.

The precipitates from the first evaporation step were filtered off using a vacuum filter (Model LVS 300 Z, Welch, Germany) and discarded. The filtrate from the first evaporation step was further concentrated to a density of 1.302 g/cm³ and the crystallised solids ground to -35 mesh particle size and later mixed with water at a ratio of 1:2 before loading the mixture on a laboratory froth flotation machine (D12 (VFD-L), Denver, USA). The flotation was done in the presence of octadecylamine surfactant at a concentration of 500g/ton for 30 min. The froth was discarded and the clarified material dried in a desiccator at 70 °C for 3 h. This was followed by evaporating the filtrate from the second evaporation step to dryness. The resulting solids were dissolved and carbonated in a jacketed reactor at 50 °C for 3 h to produce sodium bicarbonate. The sodium bicarbonate was filtered and calcined in a muffle furnace (Model KLS 03/10/M, ThermConcept, Germany) at 200 °C for 1 h to form soda ash. The filtrate from the carbonation process was cooled in a cooling

Table 1 Brine chemical composition.

pH	Brine Temperature (°C)	Density (g/mL)	Major ions (mg/L)								
			Na	K	Mg	Ca	Cl	Br	SO ₄	HCO ₃	CO ₃
10.4	25	1.12	4350	766	3.08	1.44	33600	390	21700	1710	4330

crystallizer at -2 °C for 30 min and later dehydrated in an evaporative crystallizer at 50 °C for 45 min.

Analyses

The mineralogy of the solids was determined using an X-ray diffractometer (Model, Malvern PANalytical Aeris 300W, Netherlands) operated with a PIXcel detector and fixed slits with Fe filtered Co-K α radiation ($\lambda = 0.1540$ nm, operating at 40kV and 7.5 mA). The XRD data was collected from 5 to 80° (2 θ) in a continuous scan mode with a scanning step size of 0.02°. The phases were identified using X'Pert Highscore plus software that runs with the ICDD database. The relative phase amounts (weight %) were estimated using the Rietveld method. For the liquid samples, the anion composition of Br⁻, Cl⁻, SO₄²⁻, CO₃²⁻, and HCO₃⁻ in the liquid phase were determined using the ion chromatography method. The cations in the aqueous phase were determined using the ICP-OES technique. The pH was measured by an Ohaus starter 300 pH meter and the density of the liquid samples was determined gravimetrically using a pycnometer and a weighing scale.

Results and Discussion

Process scheme validation

In the first evaporation step, the mineral composition of the precipitates after concentrating raw brine from a density of 1.12 to 1.282 g/cm³ comprised calcite and magnesite at 30 °C. The brine pH decreased from 10.4 to 9.74. At this stage, according to the thermodynamic calculations performed

by PHREEQC (Parkhurst and Appelo 2013) a Pitzer specific-ion-interaction aqueous model, and the SIT (Specific ion Interaction Theory, about 56% of the initial free water had been evaporated. The precipitates from this step were not processed further due to their low quantities and thus low economic importance. The filtrate saturated with sodium chloride from the first evaporation step was concentrated further to a density of 1.302 g/cm³ in the second evaporation step. To get to this point, 76% of the initial free water was evaporated. This resulted into the precipitation of salts that weighed 273.514 g which comprised mainly halite contaminated by trona and burkeite as seen in Table 2 (sample 1). In the third evaporation step, the filtrate from the second evaporation step was evaporated to dryness producing burkeite with traces of trona, halite and calcite as seen in Table 2 (sample 2). These precipitates weighed 150.771 g. It should be noted that, glaserite was not present as predicted by PHREEQC. The reason for this is that, the PHREEQC model only accounts for thermodynamic aspects yet at the deposit, both the thermodynamics and kinetics aspects affect the mineral crystallization (Lwanyaga et al. 2019a). As a result, some minerals precipitating from the model might not precipitate in the actual setting and vice versa (Lwanyaga et al. 2019a).

The precipitates from the second evaporation step were subjected to a flotation process using octadecylamine as the surfactant to float burkeite and trona thus leaving purer halite. The froth presumably containing burkeite and trona was discarded. The clarified material was dried in an open

Table 2 XRD Quantitative analysis of evaporites from the second and third evaporation steps (wt%)

Sample ID	Trona	Burkeite	Halite	Calcite
1	5.8	2.6	91.6	0
2	10.6	84.8	4.3	0.3

pan and a sample of the solids characterised. The XRD qualitative analysis as shown in Fig. 1 reported halite as the only crystalline material remaining thus confirming the removal of burkeite and trona. It, however, reported a 10.1wt.% composition of amorphous material. This could be due to an error in the determination of the quantity of the amorphous material which was reported to be about ± 15 weight %. Halite was reported to be 89.9wt.% and the amorphous material, 10.1wt.%. However, the amorphous content was higher than expected.

A sample of the precipitate from the carbonation process was characterised. The XRD analysis revealed that 81.6% was nahcolite (sodium bicarbonate) contaminated by burkeite and trona with traces of halite. The reported amorphous phase composition of 5.6wt.% is within the margin of error. The crystalline precipitate (majorly sodium bicarbonate) from the carbonation step were calcined at 200 °C for 1 h. This produced crystalline solids constituting mainly natrite (soda ash) contaminated by burkeite and thermonatrite with traces of halite. There is a big composition (38.1wt%) of the amorphous phase in the posted results. This could be due to the presence of some impurities like clay. It is worth noting that all the nahcolite from the carbonation process was converted into soda ash and thermonatrite. However, the burkeite

composition remained constant since the calcination process was not intended to decompose it into its constituent compounds.

The supernatant from the carbonation process was frozen at -2 °C for one hour; a white emulsion was observed. The XRD analysis shows that burkeite is the dominant phase followed by nahcolite, trona, natrite, thermonatrite and halite. The purpose of this step was to crystallise out mirabilite and thereafter dehydrate it to produce thenardite. The results posted here deviate from the expected results. This could be attributed to the variation in temperature of the sample during transportation to the storage facility at the XRD lab. The presence of burkeite attests to the presence of sulfate which were the target of the process. The presence of nahcolite and other carbonates of sodium may be due to the incomplete precipitation process during the carbonation process or vacuum filtration inefficiency. In a well controlled environment, the suggested unit procedures are expected to produce thenardite.

Process flow sheet simulation

In this study, a flowsheet based on the laboratory experiment and PHREEQC software was simulated. As seen in Fig. 2, the raw brine (Table 1) is concentrated at 85 °C in the first reactor (R-101)/ Pond 1 for 12 h to precipitate carbonates and sulfate of

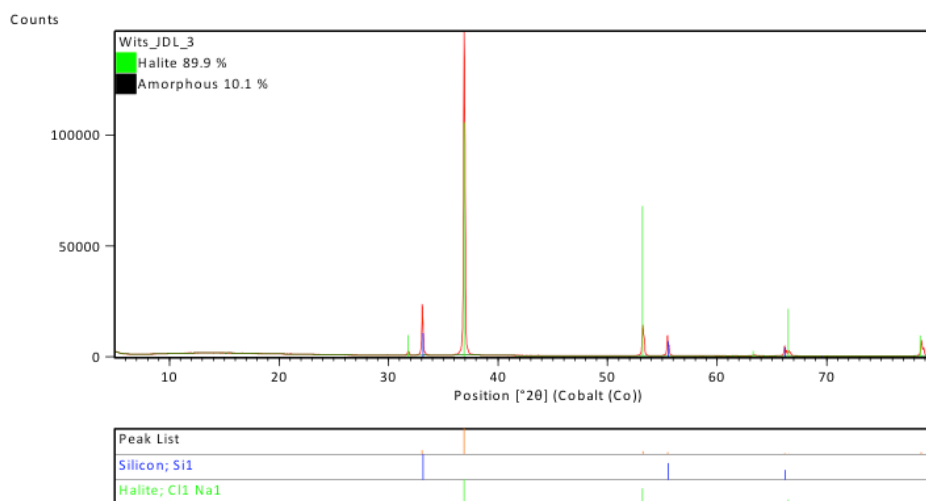


Figure 1 XRD analysis of purified halite

calcium and magnesium. These are filtered off (P-2/ PFF-101) and discarded. The solar pond is presumed to behave like a reactor where both evaporation and crystallization take place. The filtrate from the first pond is further concentrated in the second reactor (R-102)/Pond 2 to mainly precipitate halite contaminated by burkeite and trona. The precipitates are filtered off (P-4/ PFF-101) and the cake subjected to flotation (FL-101). The froth presumably constitutes mainly burkeite and trona which are discarded. The halite is the clarified material that is dried at 70 °C in the tray drier (TDR-101)/grainer pan to form common salt of over 99% purity. It was noticed that instead of evaporating the filtrate from pond 2 before carbonation, it was better to carbonate it in order to avoid formation of complex minerals such as burkeite and trona (Garrett et al. 1975). Therefore, the filtrate from Pond 2 was carbonated (R-103) at 50 °C for 4 h to form sodium bicarbonate. The bicarbonate was further calcined (Garrett et al. 1975) (GBX-101) at 200 °C for 45 min to form soda ash. The supernatant from the carbonation process was cooled at -2 °C in a crystallizer (CR-101) to form mirabilite. The formed mirabilite is dehydrated in an evaporative crystallizer (CR-101) at 50 °C to form sodium sulfate (Garrett et al. 1975).

Cost analysis and Economic evaluation

The economic feasibility of the proposed process was modeled using SuperPro Designer. For design purposes, the simulation was set to design mode to automatically size the equipment and the size of the equipment determined its purchase cost. An extra 20% on the equipment budget was factored in for contingencies such as the minor equipment which was not enlisted in the process flow sheet. The costs arising from building, installation and piping were integrated into the total investment cost.

A number of economic evaluation parameters for the entire project were assumed; year of analysis and construction as 2020, and a project lifetime of 20 years. Out of the 365 days in a year, the plant will be operated for a period of 243 days annually because the other 122 days are not suitable for solar salt production due to the rainy season. Therefore, the rainy season will be used for plant maintenance.

A minimum of 500,000 L of raw brine per batch is needed for economic viability of the venture. A total of 41 batches are executed annually requiring 52.47 h per batch. From this, 63,729 kg, 10,499 kg, and 8,239 kg per batch of common salt, soda ash and sodium sulfate respectively are expected to be produced. As

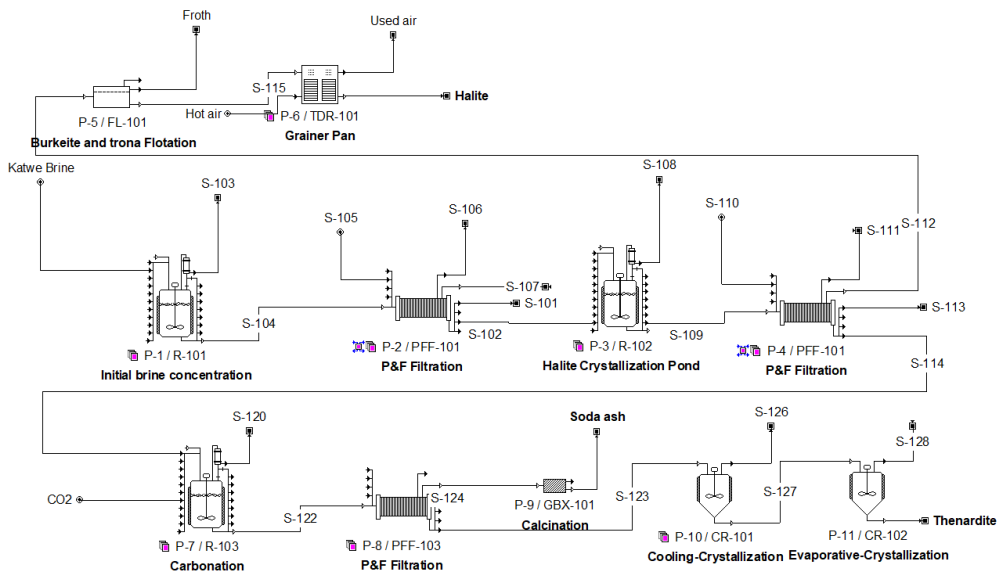


Figure 2 Process flow sheet for the extraction of halite, soda ash and thenardite from Lake Katwe brine.

a result, a total investment worth US\$7.5m is required to start the project. Between 30% and 40% of the annual operating cost will be spent on maintaining the plant. On average, the annual salt imports in Uganda for the year ended December 2019 was UGX. 94.7 billion shillings (US\$25 million) (Chopra 2020). An average cost of capital of 10% was used as per the Uganda Development Bank that can support the financing of the plant (Khisra 2020). All the profitability indices are positive with a payback period of 18 years, Return on Investment of 10.54%, an Internal rate of return of 6.955 and a net present value of US\$25,077,817.30 without inflation consideration. Therefore, it is economically feasible to exploit Lake Katwe brine which in turn will reduce Uganda's dependency on imported salt.

Sensitivity Analysis

A differential sensitivity analysis was performed with the aim of studying how changes in the project economic variables would influence the economic viability of the project. Sensitivity margins are computed and summarised in Table 3.

From Table 3, the total annual revenue/salt revenues, has the lowest sensitivity margin (i.e. 0.518) as compared to other parameters. This implies that if the salt sales are decreased below 51.8%, then the process plant will cease to be economically viable. Salt being a domestic necessity, such a fall in revenue isn't expected unless other competitors join the market. The sensitivity results also show that,

the project will not be economically viable should the annual operating costs increase beyond 295%. The sensitivity margins in Table 3, suggest a sound process design simulation in Fig. 2. For the plant investment to break even, the cost of capital should not be beyond 16.87%. A headline inflation rate of 2.8% was adopted to adjust the annual revenues while an inflation rate of 6.2% for energy, operating, production and maintenance costs was used (UBOS 2020). Table 4, indicates the effect of change in the inflation rate on payback period and net present value (NPV). A double digit (high-end) inflation rate of 10% still indicates that the designed process is still economically viable with an NPV of US\$ 18,872,444.23.

Conclusions

An improved solar salt extraction process is presented as an alternative technique to foster the purity and quantity of salt extracted at Lake Katwe. The method is based on solar evaporation coupled with flotation and drying for the production of common salt of purity >98%. Soda ash is produced by carbonation and calcination after the extraction of halite. Lastly, successive cooling and evaporative crystallization processes lead to the production of sodium sulfate. An economic analysis conducted in SuperPro Designer revealed that the salts can be produced at a cost that is competitive on the market.

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Table 3 Sensitivity Margins for economic variables.

Item	Amount US\$	PV US\$	Sensitivity Margins
Direct Investment cost	6,204,320	(6,204,320.0)	4.042015843
Indirect Investment cost	1,523,826	(1,523,826.0)	16.45723313
Annual operating cost	998,336	(8,499,433.4)	2.950544894
Annual Energy cost	33,267	(283,222.0)	88.5452607
Equipment purchase cost	751,250	(751,250.0)	33.38164357
Annual Direct Production Cost	427,369	(3,638,448.7)	6.892486792
Indirect Production cost	71,228	(606,406.7)	41.35501752
Annual Maintenance Cost	215,679	(1,836,204.7)	13.6574965
Total Annual Revenues/Sales	5,687,271	48,419,150.4	0.517934733
Salvage	12,926	1,920.8	13055.97289

Table 4 Sensitivity analysis of change in inflation rate on economic viability.

	Without inflation	Single digit inflation	Double digit inflation
Payback period (years)	4.61	5.48	6.01
NPV US\$	25,077,817.30	26,914,589.01	18,872,444.23

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References

- Chopra A (2020) Annual salt import grow to Shs 94.7 billion. Dly. Monit.
- Garrett DE, Kallerud MJ, Chemtob EM (1975) Beneficiation of Salts Crystallized for Searles Lake Brine. 6.
- Hocking MB (2005) Handbook of Chemical Technology and Pollution Control. Elsevier.
- Intelligen Inc (2019) SuperPro Designer, User Guide. Scotch Plains, NJ, USA.
- Kasedde H, Bähler MU, Kirabira JB, et al (2013) Mineral recovery from Lake Katwe brines using isothermal evaporation. In: Brown A, Figueroa L, Wolkersdorfer C (eds) Reliable Mine Water Technology. Publication Printers, Denver, Colorado, USA, pp 855–860.
- Kasedde H, Kirabira JB, Bähler MU, et al (2014) Characterization of brines and evaporites of Lake Katwe, Uganda. J African Earth Sci 91:55–65. doi: 10.1016/j.jafrearsci.2013.12.004.
- Kasedde H, Lwanyaga JD, Kirabira JB (2015) Optimization of Solar Energy for Salt Extraction from Lake Katwe, Uganda. Glob NEST J 16:1152–1168. doi: 10.30955/gnj.001367.
- Khisa I (2020) Uganda Development Bank to cut lending rates. Indep.
- Kirabira JB, Kasedde H, Semukuuttu D (2013) Towards The Improvement of Salt Extraction At Lake Katwe. Int J Sci Technol Res 2:76–81.
- Lwanyaga JD, Kasedde H, Kirabira JB (2018) Thermodynamic Modeling Of Lake Katwe Brine For Industrial Salt Production. Int J Sci Technol Res 7:31–37.
- Lwanyaga JD, Kasedde H, Kirabira JB (2019a) Effect of Temperature on Mineral Precipitation Sequence of Lake Katwe Brine during Evaporation. Curr J Appl Sci Technol 33:1–12. doi: 10.9734/cjast/2019/v33i630104
- Lwanyaga JD, Kasedde H, Kirabira JB (2019b) Mineral Precipitation Sequence During Evaporation of Lake Katwe Brine. In: Khayrulina E, Wolkersdorfer C, Polyakova S, Bogush A (eds) IMWA2019 -Mine Water:Technological and Ecological Challenges. International Mine Water Association, Perm, Russia, pp 515–521.
- Parkhurst DL, Appelo CAJ (2013) Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. In: U.S. Geological Survey Techniques and Methods, book 6, chapter A43. p 497.
- UBOS (2020) Uganda consumer price index: 2009/10=100. Kampala.
- UDC (1997) Feasibility study of the rehabilitation of Lake Katwe Salt Project. Kampala.