Production of pure potassium salts directly from sea bittern employing tartaric acid as a benign and recyclable K+ precipitant

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ARTICLE

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Shortage of land and vulnerability to climate change expose future production of potash from sea bittern through evaporite route to greater risks. Potash recovery through selective extraction from bittern is an attractive alternative. Unfortunately, previous attempts in this direction have suffered from one drawback or another. The present study reports a viable scheme employing tartaric acid as a benign and recyclable K^+ precipitant. The key steps in the scheme were (i) selective precipitation of potassium bitartrate in 81.2% yield with respect to magnesium tartrate used, (ii) decomposition of the bitartrate salt into potassium nitrate with regeneration of magnesium tartrate, and (iii) recovery of residual tartaric acid from K^+-depleted bittern as calcium tartrate, from which tartaric acid was regenerated and reused. The process was made further viable through co-production of Epsom salt (0.30 t/t of KNO_3) and ammonium sulphate (1.47 t/t of KNO_3). Spent bittern, containing < 50 ppm of tartaric acid, was the only effluent. The overall energy requirement for a 1 TPD KNO_3 plant was estimated to be ca. 38.31GJ/t of KNO_3 production, along with the associated products, comparing reasonably with the computed figure of 34.80 GJ based on available data from a standard database. A simplified version of the above scheme yields a K-N-S compound fertilizer currently under evaluation.

1 Introduction

Potassium (K), along with nitrogen (N) and phosphorus (P) are the three primary plant nutrients.[1] Seawater, containing 0.39 g L^{-1} K^+, is a universal source of potassium. Its progressive evaporation crystallizes out gypsum followed by NaCl, and further evaporation of the mother liquor (bittern) yields kainite ($KCl.MgSO_4.3H_2O$), albeit contaminated with NaCl and other salts. Kainite is converted into schoenite ($K_2SO_4.MgSO_4.3H_2O$) and, eventually, into potassium sulphate.[2] Relative humidity (RH) is an important climatological parameter that controls the extent to which brine can be concentrated through solar evaporation (Figure S1).[3-4] Apart from dry climatic condition, evaporite-based processes demand large tracts of land for evaporation. Moreover, excessive and unseasonal rains pose serious threats to sustainable operation. Extraction of potash directly from bittern, without recourse to evaporite production, is an attractive means of addressing the problem.

Dipicrylamine anion (DPA^-) has been employed previously for selective separation of potassium from bittern.[5] KDPA was obtained as a precipitate in 98% yield. Its decomposition with a suitable acid regenerated DPA for reuse whereas pure potassium salt was left behind in aqueous solution. Although the scheme was attractive, it was not amenable to scale up due to the toxic and hazardous nature of the reagent. Another precipitant reported is pentaborate ($B_{10}O_{16}^{2-}$).[6] Yield of precipitated $K_2B_{10}O_{16}$ was 65%. The main drawback of the process was the conversion of the reagent to boric acid during decomposition of the precipitate, necessitating tedious steps to regenerate pentaborate. Another difficulty was the high retention of precipitant in bittern. Thus a practically implementable scheme has remained elusive.

Potassium bitartrate ($KC_4H_5O_6$) (KHT), commonly referred to as cream of tartar, crystallizes during fermentation of grape juice. The structure comprises alternating layers of bitartrate anion (HT^-) and K^+, each cation being surrounded by eight O atoms from seven $C_4H_5O_6^-$ moieties.[7] The utility of bitartrate ion as an analytical tool for the estimation of K^+ has been demonstrated previously.[8] However, no attempt seems to have been made to apply the knowledge toward recovery of potash from bittern. Suffice it to say that, besides selective precipitation of K^+ in high yield, any viable scheme for this purpose must insure cost-effective isolation of the desired potassium salt and ease of recyclability of tartaric acid (H_2T) with minimal losses. Efforts in this direction are reported in the present study.[9]

2 Experimental section

2.1 Materials

For selectivity study of tartaric acid, all chemicals (NaCl, KCl, $MgCl_2$, $CaCl_2$, NaOH and DL-tartaric acid) used were of AR grade. Tartaric acid used in the process was of commercial grade (DL, 98% purity). Magnesium hydroxide used was of high purity (>99.5%) which was generated in the Institute. Concentrations of liquor ammonia, nitric acid and sulphuric acid used were 17.5 N, 15.8 N and 36.8 N, respectively. Bittern used in this study was sourced from M/s Tata Chemicals Limited, Mithapur, India. Its composition is given in Table S1 (27.97 °Bé virgin bittern). 50 L of this bittern was subjected to solar evaporation up to a density of 32.42 °Bé. Composition of this concentrated bittern is provided in Table S1.

2.2 Methods

Ionic compositions of liquids and solids were measured using established methods in the literature.[10] Mg^{2+} and Ca^{2+} were estimated by complexometric titration with EDTA. K^+ and Na^+ were estimated by flame photometry (Cole-Parmer Instrument Company Chicago, Model 2655-00, Digital flame Analyzer). High-performance liquid chromatography (Waters; Breeze 2; SUPELCOGEL™ C-610H Column) was used for tartaric acid estimation. Basis of reporting constituent concentration for solid and liquid samples were "*w/w*" and "*w/v*" respectively. Powder X-ray diffraction (XRD) measurements were performed on Empyrean machine (PANalytical from Netherlands) using CuKα radiation operating at 40 KV and 30 mA. Data were collected in the range of 5 to 50° 2θ . Search match analysis was performed with high score plus software using ICDD-JCPDF data base.

2.3 Selectivity studies with H_2T

0.4 M H_2T was prepared and divided into 2 sets. The pH of the first set was maintained at 3.5 and that of the second at 6.5 by adding required quantity of NaOH solution to each set, while monitoring the pH. Selectivity studies were carried out by adding 10 mL of pH-adjusted H_2T solution into an equal volume of (i) aqueous solution containing 0.4 M each of NaCl, KCl and $MgCl_2$ and (ii) aqueous solution containing 0.4 M each of NaCl, KCl, $MgCl_2$ and $CaCl_2$ at room temperature. The contents were stirred with magnetic stirrer for 24 h. The precipitates obtained from the four sets of experiments were filtered, washed with small aliquot of water to remove adhering mother liquor, dried at 70 °C and analysed for the ions.

2.4 KHT precipitation

Epsom salt was first recovered from 32.42 °Bé concentrated bittern (Table S1) in 58.4% yield (sulphate basis) following literature procedure.[11] 1 L (0.63 mol of K^+) of the resultant $MgSO_4$-depleted bittern (Table S1) was taken in a jacketed glass beaker and chilled to 5±1 °C. 148.54 g (0.57 mol; 90.5 mol% with respect to K^+) of MgT pre-dispersed in 100 mL of water was added into the bittern under mechanical stirring. 15.2 mL (0.28 mol) of H_2SO_4 was added gradually thereafter. Stirring was continued for 12 h while maintaining the temperature. Final pH of the reaction mixture was 0.87 at 5 °C. 1.055 L of filtrate (K^+-depleted bittern), containing 0.13 mol of K^+ and 0.08 mol of H_2T was obtained upon filtration. The residue was washed with 100 mL of water and dried to obtain 87 g of product containing 21.65% K and 77.01% H_2T against the theoretical values of 20.74% and 79.79%, respectively, for pure KHT. Mg^{2+} and Na^+ were also estimated and found to be 0.27% and 0.20%, respectively. KHT yield was computed with respect to both K^+ in bittern and added MgT. Residual tartrate in the K^+-depleted bittern was recovered as described in 2.6 below, while the washings were recycled in a subsequent batch of concentrated bittern.

2.5 Decomposition of KHT

200.0 g (1.12 mol K^+) of KHT was taken in 400 mL of water and reacted with 70.3 mL (1.11 mol) of HNO_3 and 65.0 g of $Mg(OH)_2$ (1.11 mol) under stirring for 4 h. Final temperature of reaction mixture was maintained at 35±1 °C. Upon filtration of the resultant slurry and washing of the residue, 250.0 g (1.02 mol) of MgT was obtained (9.65% Mg; 58.30% H_2T). The filtrate contained 28.18% KNO_3, which was further chilled to recover KNO_3 as pure solid. The mother liquor was used in subsequent batches of KHT decomposition.

2.6 Precipitation of residual tartaric acid from K^+-depleted concentrated bittern

1.08 g (0.011mol) of $CaCO_3$ and 3.72 g (0.021 mol) of gypsum were dispersed in 150 mL of seawater under stirring. The resultant slurry was added under stirring into 150 mL of K^+-depleted bittern having 1.08% (10,800 ppm) residual tartrate. The reaction was continued under stirring for 12 h, maintaining the temperature at 5±1 °C. The reduction in the tartrate concentration over time was monitored and the final pH was ensured to be in the range of 6.0-6.5 prior to filtration. 5.375 g of crude CaT was obtained while the spent bittern was found to contain only 95 ppm of residual tartaric acid after 3 h and < 50 ppm after 12 h. Tartaric acid was regenerated from CaT following literature procedure.[12]

2.7 Preparation of magnesium hydroxide/magnesium carbonate from magnesium sulphate with co-production of ammonium sulphate

200.0 g (0.81 mol) of magnesium sulphate obtained in **2.4** above was dissolved in 400 mL of water and reacted with 110 mL (1.93 mol) of liquor ammonia under stirring. Stirring was continued for 2 h, maintaining the temperature at 25±1 °C. The wet residue obtained upon filtration was washed with 500 mL of water and dried to obtain 24.5 g (0.42 mol) of magnesium hydroxide. Thereafter CO_2 gas was purged through the filtrate for 3 h to effect magnesium carbonate precipitation (51.9 g, 0.374 mol). The filtrate contained 0.71 mol ammonium sulphate with only 0.017 mol of residual Mg^{2+}.

3 Results and discussion

3.1 Ion Selectivity

Being diprotic, DL-tartaric acid (in water) has two pK_a values: $pK_{a1} = 3.03$; $pK_{a2} = 4.37$.[13] At low pH (<1) it exists mainly in un-dissociated form (H_2T), at about pH 3.5 the primary species is bitartrate ion (HT^-), and at pH > 6.5 tartrate ion (T^{2-}) predominates (Figure S2). When an aqueous solution containing 0.4 M each of Na^+, K^+ and Mg^{2+} was treated with a solution of H_2T, partially neutralized to a pH of 3.5 (control of the pH of tartaric acid solution was of critical importance), a precipitate was obtained containing mainly K^+ (Figure 1A).

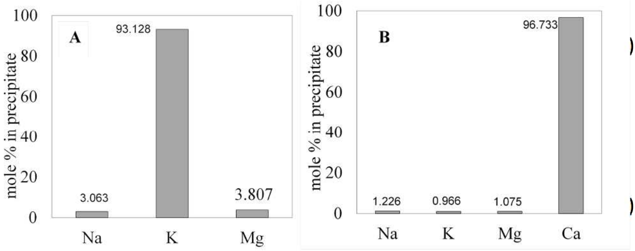


Figure 1. Ion selectivity of tartaric acid at pH 3.5 in the presence of equimolar concentrations (0.4 M) Na^+, K^+, and Mg^{2+} (A) and in the presence of equimolar (0.4 M) concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} ions (B).

Powder XRD studies confirmed the formation of KHT as the predominant phase (Figure S3). The pH of the supernatant measured ~ 3.3. When the same experiment was repeated with inclusion of 0.4 M Ca^{2+}, the solid obtained showed dominance of Ca^{2+} (Figure 1B), while the pH of the supernatant dropped to ~1.3. This was ascribed to the precipitation of Ca^{2+} as calcium tartrate ($CaC_4H_4O_6.4H_2O$) (CaT) (Figure S4) with concomitant build-up of H_2T in the solution. Figure 2 provides data on ion selectivity in presence of T^{2-} at pH 6.5.

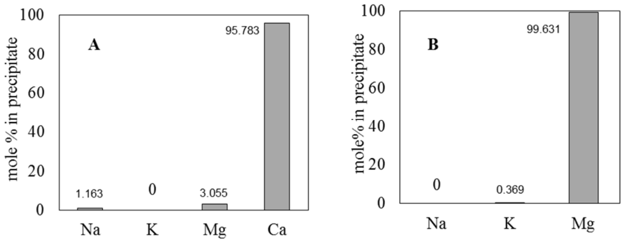


Figure 2. Ion selectivity of tartaric acid at pH 6.5 in the presence of (A) equimolar concentrations (0.4 M) Na^+, K^+, Mg^{2+} and Ca^{2+} ions and (B) equimolar (0.4 M) concentrations of Na^+, K^+, and Mg^{2+}.

It can be seen that when all the four cations were present, precipitation of Ca^{2+} dominated (Figure 2A). The precipitate was confirmed to be CaT (Figure S5). When Ca^{2+} was absent, Mg^{2+} precipitated preferentially as magnesium tartrate ($MgC_4H_4O_6.5H_2O$) (MgT) (Figure 2B) as confirmed by powder XRD (Figure S6). These findings were consistent with the 0 °C solubility values of 0.003% and 0.62% of CaT and MgT, respectively.[14]

3.2 Studies with Sea bittern

Seawater contains similar concentrations of Ca^{2+} and K^+ (ca. 0.01 M each). However, in view of the ca. 2.6:1 ratio of $[SO_4^{2-}]$: $[Ca^{2+}]$ in seawater, the concentrations of these ions follow different trajectories upon evaporation, due to precipitation of gypsum (Figure S7). $[K^+]$ in the 27.9 °Bé virgin bittern employed in the present study was 0.336 M – similar to the K^+ concentration taken for the ion selectivity studies above – whereas $[Ca^{2+}]$ was only 0.004 M [Table S1 (virgin bittern)]. As a result, Figure 1B was largely irrelevant for this composition. Further, the data of Figure 1A suggested the possibility of selective K^+ recovery from bittern, with the caveat that $[Na^+]$ and $[Mg^{2+}]$ are much larger than $[K^+]$ in this case [Table S1 (virgin bittern)]. A practical scheme would additionally require that the KHT be converted into useful potassium salts, with regeneration of the tartaric acid in desirable form for recycle. The data of Figures 1A and 2B were utilized to devise such a scheme based on the approach outlined below:

(i) Precipitate K^+ selectively from bittern as sparingly soluble KHT;
(ii) Convert KHT to MgT with release of potassium salt into solution;
(iii) Recycle MgT as source of HT^- for KHT precipitation;
(iv) Take advantage of the very low solubility of CaT to mop up residual HT^- in K^+-depleted bittern.
(v) Regenerate H_2T from CaT and recycle along with MgT.

3.2.1 KHT PRECIPITATION

From the above ion selectivity studies, eqn. 1 was proposed as the basis of potash recovery from virgin bittern (Table S1), with recycle of H_2T in the form of MgT.

$$K^+_{(aqs.)} + MgT_{(s)} \underset{\text{Near neutral pH}}{\overset{\text{Acidic pH}}{\rightleftharpoons}} KHT_{(s)} + Mg^{2+}_{(aqs.)} \qquad (1)$$

Under acidic conditions, KHT precipitation from bittern would be expected. Subsequently, the isolated KHT may be decomposed by the reverse reaction, regenerating MgT for recycle in a fresh batch of bittern.

Using 0.9 and 0.45 molar equivalents of MgT and H_2SO_4, respectively, experiments were conducted with 0.5 L of virgin bittern at 25 °C and 5 °C. It can be seen from Figure 3 that 57.6%

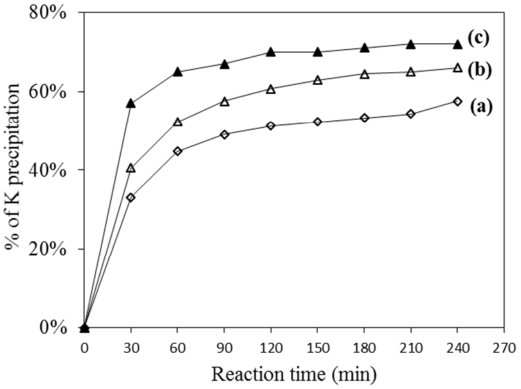


Figure 3. Percent precipitation of Potassium from bittern as a function of time following addition of 0.9 molar equivalent of HT^- into 27.97 °Bé virgin bittern [(a) 25 °C; (b) 5 °C] and 32.42 °Bé concentrated $MgSO_4$-depleted bittern at 5 °C (c).

(trace a) and 66.1% (trace b) of initial K^+ precipitated out at 25 °C and 5 °C, respectively, after 4 h of reaction time. Further experiments were carried out at 5 °C. However, to reduce energy consumption, virgin bittern was first concentrated through solar evaporation to a density of 32.42 °Bé. Upon chilling, Epsom salt ($MgSO_4.7H_2O$) was obtained in ca. 58% yield (with respect to available sulphate) while the $MgSO_4$-depleted bittern had the composition shown in Table S1.[11] The bittern, containing 2.42% (0.633 M) K^+, was chilled to 5 °C and treated with 0.9 molar equivalent of MgT and 0.45 molar equivalent of H_2SO_4 to promote HT^- formation and, in turn, the precipitation of KHT. Precipitation of the potassium salt followed the trace c in Figure 3. Analysis of the precipitate indicated satisfactory mass balance and its powder XRD matched reasonably the simulated powder XRD pattern generated from single crystal KHT data (Figure 4). KHT yields computed with respect to K^+ in bittern and added MgT were 73.1% and 81.2%, respectively, assuming pure product.

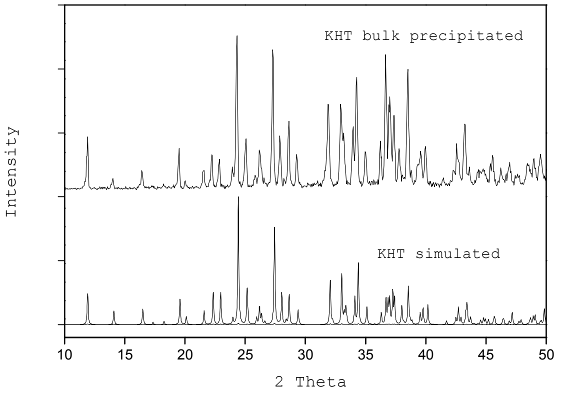


Figure 4. Powder XRD of precipitate obtained from bittern and simulated powder XRD generated from the single crystal XRD data of DL-KHT (CCDC 236651).

KHT is reported to have a solubility of 0.37% at 0 °C and 0.61% at 25 °C in pure water.[14b] MgT was taken in sub-stoichiometric amount (90% with respect to K^+) in the above studies in the expectation that residual tartrate level in the bittern would be very low in that case. However, even for sub-stoichiometric usage, 13-15% of the tartrate originally present in MgT remained in the K^+-depleted concentrated bittern. Interestingly, whereas the initial bittern pH was 6.2 and pH of MgT/ H_2SO_4 slurry was 3.5, the resultant pH upon mixing was 1.4. It is reported that the solubility of KHT is considerably higher under acidic conditions, which may explain the substantial presence of tartaric acid in the K^+-depleted bittern.[14b] The shift of the pH towards higher acidity can be ascribed to the high ionic strength (10.1 M) of the bittern which increased the proton activity, and consequently reduced the pH (Section S3). The computed pH was 1.14, the value being surprisingly close to the measured pH considering the likely errors in applying the Davies equation to the prevailing high ionic strength conditions.[15]

Since a part of the $MgSO_4$ in concentrated bittern separated out on chilling, a study was carried out to ascertain any effect its removal might have had on KHT precipitation. An experiment was conducted at 25 °C using the concentrated bittern composition of Table S1 directly. As before, added HT^- (constituted from 1:1 MgT and H_2T) was 90% with respect to K^+ amount taken. In another experiment the concentrated bittern of Table S1 was chilled to remove $MgSO_4.7H_2O$, the filtrate was then allowed to warm to 25 °C, and HT^- was introduced in the same manner as above. In the first experiment [K^+] reduced from 2.2% to 1.3% over 12 h whereas in the second experiment the reduction was to 0.7% over the same duration. Thus removal of $MgSO_4$ through chilling was beneficial for KHT precipitation, likely on account of the reduced ionic strength. Chilling of bittern and recovery of Epsom salt from chilled bittern led to other benefits also. Since the Mg^{2+} in MgT was lost in K^+-depleted bittern in the KHT forming reaction (eqn. 1), a constant supply of outsourced $Mg(OH)_2/MgCO_3$ was required to effect the reactions of eqn. 2 ($X = Cl^-, SO_4^{2-}, NO_3^-$, etc.).

$$KHT_{(s)} + Mg(OH)_{2(s)} + HX \longrightarrow MgT_{(s)} + KX_{(aqs.)} \tag{2a}$$

$$KHT_{(s)} + MgCO_{3(s)} + HX \longrightarrow MgT_{(s)} + KX_{(aqs.)} + CO_{2(g)} \tag{2b}$$

It occurred to us that the Epsom salt itself can be utilized to produce these compounds.[9b] Thus the major portion of the recovered Mg salt was reacted with ammonia to yield $Mg(OH)_2$ in ca. 50% yield (eqn. 3a), the balance magnesium presumably remaining in the filtrate in the form of an ammonia complex. The filtrate, upon further reaction with CO_2, gave magnesium carbonate quantitatively (eqn. 3b).

$$MgSO_{4\,(aqs.)} + 2NH_4OH \longrightarrow \sim 0.5Mg(OH)_{2(s)} + \text{Filtrate} \tag{3a}$$

$$\text{Filtrate} + CO_{2(g)} \longrightarrow \sim 0.5MgCO_{3\,(s)} + (NH_4)_2SO_{4\,(aqs.)} \tag{3b}$$

This approach enabled $Mg(OH)_2$ / $MgCO_3$ essential in the scheme to be internally generated, while yielding ammonium sulphate as useful by-product.

3.2.2 DECOMPOSITION OF KHT

KHT derived from the concentrated bittern was decomposed with nitric acid and magnesium hydroxide/magnesium carbonate

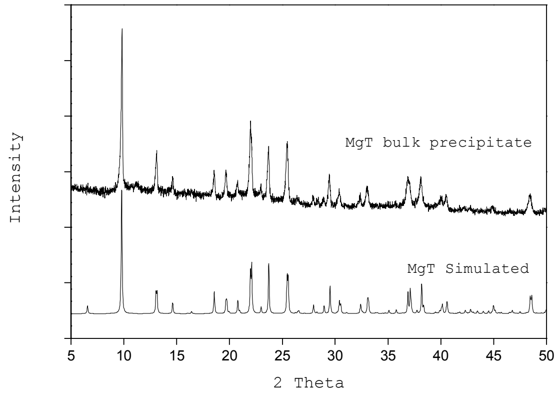


Figure 5: Powder XRD of precipitated MgT obtained from KHT decomposition reaction and simulated powder XRD from the single crystal X-ray data of DL-MgT (CCDC 631939).[16]

(eqn. 2a / 2b) to yield MgT residue (Figure 5) and filtrate containing KNO_3. Conversion was quantitative. The filtrate was chilled to crystallize KNO_3 in > 99.5% purity on dry basis, while the mother liquor was recycled in the subsequent batch of KHT decomposition. The MgT was conveniently recycled in the forward reaction of eqn. 1. An alternative method to decompose KHT was considered to simplify the overall process. KHT was reacted with Epsom salt and ammonia, resulting in the reaction of eqn. 4. Such an approach dispenses with the processes under eqn. 3, and may be attractive for manufacture of a K-N-S compound fertilizer.[9b]

$$KHT_{(s)} + MgSO_4 + NH_4OH \longrightarrow [K(NH_4)SO_4]_{(aqs.)} + MgT_{(s)} \qquad (4)$$

3.2.3 RECOVERY OF RESIDUAL TARTARIC ACID

As discussed above, a substantial amount of tartrate originally present in the added MgT remained in K^+-depleted bittern after the precipitation of KHT. Its recovery is essential for overall viability of the scheme and compliance with environmental regulations. The very low solubility of calcium tartrate (0.003% in water), and the high selectivity with which it was formed in Figure 2A, suggested that this may be a useful approach to adopt for recovery of tartaric acid from K^+-depleted bittern. The bittern was neutralized with $CaCO_3$ (eqn. 5) to a pH of 6.5 which was followed by the forward reaction of eqn. 6, taking advantage of the much lower solubility of CaT than $CaSO_4$ at lower temperatures (Figure S8).[14,17]

$$2HT^-_{(aqs.)} + CaCO_{3(s)} \longrightarrow CaT_{(s)} + T^{2-}_{(aqs.)} + CO_2(g) \qquad (5)$$

$$T^{2-}_{(aqs.)} + CaSO_{4(s)} \underset{18\ N\ H_2SO_4;\ 75\ ^oC}{\overset{\text{Neutral pH; } 5\ ^oC}{\rightleftharpoons}} CaT_{(s)} + SO_4^{2-}{}_{(aqs.)} \qquad (6)$$

It was possible to reduce the tartaric acid concentration by a factor of ca. 56 within 3 h, the residual amount being only 95 ppm (Figure 6).

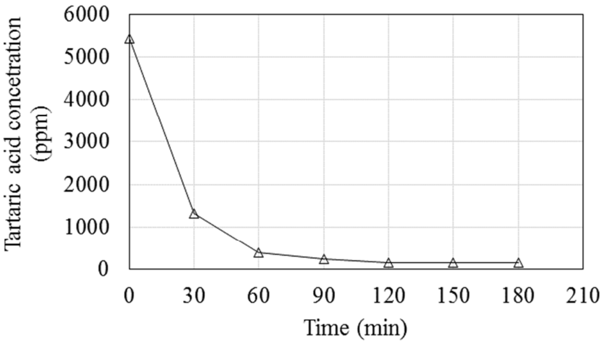
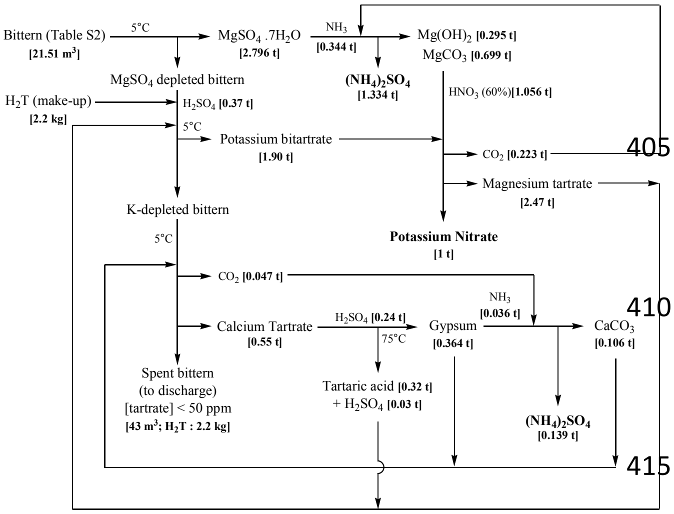


Figure 6: Residual Tartaric acid recovery as CaT from K^+-depleted bittern at 5 °C. The bittern was diluted with equal volume of seawater for effective removal of CaT

Its concentration reduced to < 50 ppm when the reaction was continued for 12 h. The CaT residue obtained in the process was digested with excess H_2SO_4 at 70-75 °C to effect the reverse reaction of eqn. 6.[12] The resultant H_2T solution was recycled along with MgT, make up H_2T and H_2SO_4 for HT^- formation by the forward reaction of eqn. 1. A part of the by-product gypsum was recycled in the forward reaction of eqn. 6 and the remaining part was subjected to the Merseberg reaction (eqn. 7) to generate calcium carbonate required in eqn. 5. Ammonium sulphate was the co-product.

$$CaSO_{4(s)} + 2NH_4OH + CO_{2(g)} \longrightarrow CaCO_{3(s)} + (NH_4)_2SO_{4(aqs)} \qquad (7)$$

Scheme 1 shows the overall integrated process for KNO_3 production. Total energy input toward production of 1 t KNO_3, along with 1.47 t $(NH_4)_2SO_4$ and 0.3 t $MgSO_4.7H_2O$ in a 1 tpd capacity plant, amounted to 38.31 GJ of which 14.64 GJ was used in the process and the remaining accounted for the energy consumption for production of the input raw materials (Tables S2-S4).[18] While the above figure is ca. 10% higher than the corresponding figure for mass production through conventional technology (Table S2), it is expected that the energy requirement of the process of the present study will reduce at higher scale of operation.



Scheme 1. Process scheme, along with mass balance, for the production of potassium nitrate (1 t basis) and allied products through KHT precipitation from concentrated sea bittern.

4 Conclusion

Preparation of pure potassium nitrate from 32.4 °Bé sea bittern was successfully mediated by tartaric acid. The scheme revolved around two equilibrium processes, one involving the KHT/MgT pair and the other involving the CaT/H_2T pair. These were conveniently manipulated by changing pH and temperature. In this manner, KNO_3 was obtained in ca. 80% yield with respect to tartaric acid and there was only nominal loss (<0.2% per cycle) of the reagent in the spent bittern stream. Chilling of the bittern required energy but it was justified by the manifold gains. Whereas the results of laboratory studies have been presented herein, the process has also been successfully demonstrated at 300 L bittern batch^{-1} scale. The total energy input in the process was found to be close to the database figure for production through conventionally practiced technologies. The specific energy requirement is expected to reduce with enhanced scale of operation. Besides KNO_3, other potash fertilizers (KCl, K_2SO_4) too can be obtained in pure form from KHT. A variation of the theme was the synthesis of a K-N-S compound fertiliser with gains in terms of process simplification. The present approach offers greater flexibility of potash production in as much as sea bittern can be utilized directly without recourse to evaporite formation.

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Notes and references

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Electronic Supplementary Information (ESI) available: Section S1: Figure S1 – S8; Section S2: Table S1 – S4 and Section S3: computation of pH. See DOI: 10.1039/b000000x/

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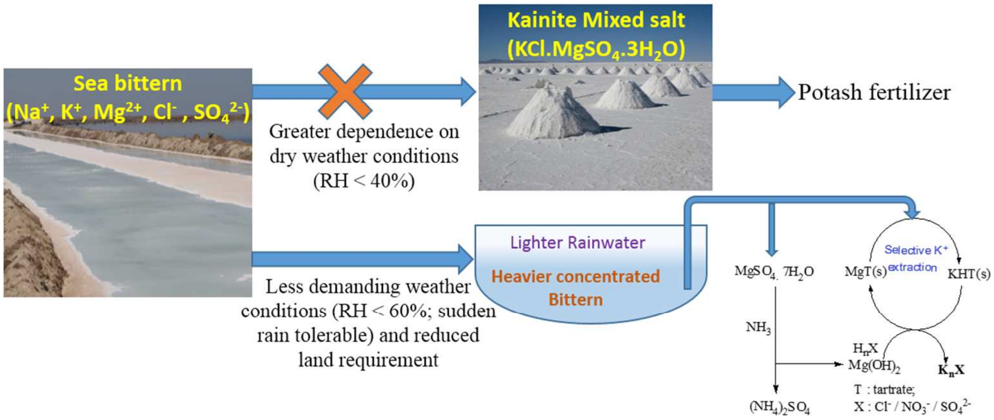

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