PREFACE

Potash and sulphur are both vital for the economic growth of a country like India. Presently, demand for these chemicals is fully satisfied through imports. Sea water can become a main source for satisfying this demand. Therefore, with an idea of developing simple processes for the recovery of sulphur as sodium sulphate and potassium as potassium chloride and potassium sulphate from sea water concentrates, these investigations were taken up.

The work recorded in this thesis includes:

1. Studies on recovery of raw materials like (i) sels mixtes, a mixture of magnesium sulphate and sodium chloride which is useful for sodium sulphate manufacture and (ii) mixed salt, a potassium chloride rich fraction of bittern evaporite which is the only source at present for recovery of potassium chemicals in the country.

2. Studies on recovery of sodium sulphate from sels mixtes (i) via astrakanite (Na₂SO₄·MgSO₄·4H₂O) and (ii) via vanthoffite (3Na₂SO₄·MgSO₄) from sels mixtes.

3. Studies on (i) recovery of potassium chloride by conversion of kainite (KCl·MgSO₄·3H₂O) in mixed salt to carnallite (KCl·MgCl₂·6H₂O) at ambient temperature and (ii) recovery of potassium sulphate from mixed salt via glaserite (3K₂SO₄·Na₂SO₄).
The entire investigation presented in this thesis is my original contribution to the advancement of knowledge. The following new facts have been found out during the course of investigation.

1. During salt manufacture from sea brine, mother liquor that remains is known as bittern. I have recovered for the first time crude salt, sels mixtes and mixed salt from bittern in series with salt manufacture in the field employing phase diagrams for controlling compositions at each stage. It has been proved that series feeding can be continued upto crude salt stage. Sels mixtes and mixed salt crystallizers can however be charged in continuation from the crude salt and sels mixtes crystallizers respectively by keeping proper ratios between the areas of these three crystallizers without affecting series feeding upto the crude salt stage. The relations for the ratios required between the areas for crude salt, sels mixtes and mixed salt were obtained.

2. I have initiated the use of phase diagram for conversion of sels mixtes to astracanite and vanthoffite. I have further developed processes for recovery of sodium sulphate from the same. I have worked out the compositions for getting maximum conversions by employing data available from the phase diagrams of the reciprocal salt pairs (Na^+, Mg^{++}, (Cl^-, S0_{4}^{2-})-H_{2}O at 25°C.
3. A novel method for conversion of kainite in mixed salt to carnallite at ambient temperature was worked out by me for the first time. Potassium chloride separates as kainite in the mixed salt. I developed a method to get sulphate reduced bittern, the composition of which would fall in carnallite field in the diagram of oceanic salt system \((\text{Na}^+, \text{K}^+, \text{Mg}^{++})-(\text{Cl}^-, \text{SO}_4^{2-})-\text{H}_2\text{O}\) at 25°C. By contacting mixed salt with this bittern at ambient temperature, I had been able to convert kainite in mixed salt to carnallite. This carnallite could be processed by conventional process to get technical grade potassium chloride.

I also developed a process for recovery of potassium sulphate from mixed salt via glaserite. The kainite in mixed salt was first converted to leonite \(\text{K}_2\text{SO}_4\cdot\text{MgSO}_4\cdot\text{H}_2\text{O}\) by contacting with water. The equilibrium compositions for the same were calculated on the basis of the phase diagrams of the oceanic salt system \((\text{Na}^+, \text{K}^+, \text{Mg}^{++})-(\text{Cl}^-, \text{SO}_4^{2-})-\text{H}_2\text{O}\) at 25°C. Conditions for conversions of leonite to glaserite were then worked out. Potassium sulphate was obtained from glaserite by conventional means for which conditions were arrived at on the basis of the data for the system \((\text{Na}^+, \text{K}^+)-(\text{Cl}^-, \text{SO}_4^{2-})-\text{H}_2\text{O}\) at 25°C.

The results, discussions and conclusions are based on the research carried out by me and are entirely original.
Sources on which this work is based are quoted in the text. Details of these references are given in the bibliography.

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