SYNOPSIS

India is favoured with a long coastal line and a climate suitable to utilize solar energy for recovery of common salt and byproducts from sea water, a raw material, which is also available freely. However, besides production of common salt and gypsum, no chemicals are known to be produced from this source on a large scale. It is known that sea water is a complex aqueous system of almost all the known elements present in their ionic form. The major ions in sequence to their concentration are $\text{Cl}^-$, $\text{Na}^+$, $\text{Mg}^{++}$, $\text{S}^-$, $\text{Ca}^{++}$, $\text{K}^+$, $\text{Br}^-$ etc. With all these favourable points, it is only gypsum and sodium chloride which are recovered commercially even though salts of all the remaining ions present in it are still today imported in India. Import figures for potash as $\text{K}_2\text{O}$ and sulphur are about 7 lakh and 10 lakh tonnes respectively and that for bromine is about 400 tonnes per year. India produces about 8 million tonnes of common salt of which about 90 per cent is recovered from sea brine and remaining from saline lake and subsoil brines. As most of the ions saturate after the maximum of sodium chloride crystallisation and have effect on each other's solubility, these salts cannot be obtained in pure form by simple solar evaporation of sea brine. The equilibrium in such a multi-component system can be theoretically arrived by employing Phase Rule which is relating to degrees
of freedom of a system, the number of components and the number of phases present. It is better represented by a simple equation \( F = C - P + 2 \) where \( F \) is the number of degrees of freedom, \( C \) the number of components and \( P \) the number of phases. Equilibrium data mostly in the form of phase diagrams are employed during process developed for any chemical at one stage or the other. Applications of phase diagrams particularly for complex systems demand ingenuity and insight of a Scientist. For easy interpretation of the complex data, different methods of its representation are in vogue. In the present thesis, it is attempted to employ phase diagrams to develop simple and novel processes by help of which byproducts from sea brine concentrates can be recovered.

Sulphur is present in sea water as a sulphate ion. It can be recovered as a salt of calcium, magnesium, sodium and potassium. Calcium sulphate has very low solubility. It crystallizes out to the extent of 80 per cent from sea brine by solar evaporation prior to crystallization of sodium chloride. Remaining sulphate ions concentrate in bittern, an end liquor of common salt manufacture. Similarly, potassium and magnesium salts also start exerting their presence on the equilibrium of the system barring their production in pure form by simple solar evaporation. Thus, by evaporation of bittern from 1.255 sp.gr. (29.5°Be')
to 1.309 sp.gr. (34°Be') it is only impure common salt which is obtained. As the ions saturate one after another, they start crystallizing along with the salts which are already saturated and crystallizing out. Magnesium sulphate gets saturated at about 1.312 sp.gr. (34.5°Be') of the bittern. It then starts separating on further evaporation in the form of different hydrates along with sodium chloride which is already crystallizing. Thus a salt fraction rich in sulphate content is obtained. It is known as Sels Mixtes. Sodium sulphate has many industrial uses and has very high demand. It is therefore advantageous to convert the above raw material to sodium sulphate by developing a suitable process technology.

Similarly, on further evaporation bittern gets saturated with potassium salts at about 1.324 sp.gr. (35.5°Be'). It starts crystallizing in the form of Kainite (KCl, MgSO$_4$·3H$_2$O) along with already separating sodium chloride and hydrates of magnesium sulphate. It is known as mixed salt and is a raw material for recovery of salts of potassium.

Thus it is possible to recover sulphur in the form of sulphates of calcium and magnesium and also potash in the form of kainite (KCl, MgSO$_4$·3H$_2$O). For every 100 tonnes of salt produced 2.2 tonnes of sulphur and 0.7 tonnes of potassium are recoverable in this way.
Sodium sulphate is produced in India as a byproduct during Rayon and Dichromate manufacture. Present production of sodium sulphate is 70,000 tonnes. It does not satisfy the present demand of about 1 lakh tonnes. If sodium sulphate is recovered as a byproduct of salt industry it will be helpful in satisfying the demand to some extent.

Similarly against the import of 0.7 million tonnes of potash as $K_2O$, 0.075 million tonnes of potash ($K_2O$) is present as reserve in the sea bittern produced at a level of 6.6 million tonnes of sea salt produced during 1982. It will reduce the burden on foreign exchange, if potash is recovered from the source.

Studies were therefore undertaken to develop new technologies for recovery of sodium sulphate and potassic chemicals (potassium chloride and potassium sulphate) as byproducts of salt industry by application of phase diagrams.

This thesis is divided into four Chapters as follows:

Chapter I: Introduction
Chapter II: Recovery of raw materials for marine chemicals from sea brine.
Chapter III: Recovery of sodium sulphate from salts mixtes.
Chapter IV: Recovery of potassium chloride and potassium sulphate from mixed salt.

Chapterwise summaries are given below:
Chapter I : Introduction

In this chapter, phase rule is explained with definition of the terms involved viz. number of phases, number of components and number of degrees of freedom. To understand different forms of graphical representations, simple as well as more complex systems with reference to number of components are dealt with. Typical system of each class/form is taken as an example and has been explained thoroughly with the help of phase diagram. The systems and phase diagrams explained are as follows:

<table>
<thead>
<tr>
<th>Type of system</th>
<th>System component</th>
<th>Type of diagram</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>One component system</td>
<td>Water</td>
<td>Rectangular Coordinate pressure &amp; temperature diagram.</td>
<td></td>
</tr>
<tr>
<td>Two component system</td>
<td>i. KCl-H₂O</td>
<td>Rectangular Coordinate temperature &amp; concentration</td>
<td>No hydrate is formed.</td>
</tr>
<tr>
<td></td>
<td>ii. NaCl-H₂O</td>
<td>-do-</td>
<td>Hydrate formed, solubility increases with rise in temperature.</td>
</tr>
<tr>
<td></td>
<td>iii. Na₂SO₄-H₂O</td>
<td>-do-</td>
<td>Hydrate formed, solubility decreases with increase in temperature.</td>
</tr>
<tr>
<td>Three component system</td>
<td>i. NaCl-KCl-H₂O at 20°C</td>
<td>Rectangular Coordinate concentration of KCl and NaCl in g/100g</td>
<td>No double salt formed.</td>
</tr>
<tr>
<td>Type of System</td>
<td>System Component</td>
<td>Type of Diagram</td>
<td>Remarks</td>
</tr>
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<tr>
<td>i. MgSO₄-NaSO₄-H₂O at 15°C</td>
<td>Triangular Coordinate</td>
<td>Formation of two hydrates.</td>
<td></td>
</tr>
<tr>
<td>ii. MgSO₄-Na₂SO₄-H₂O at 50°C</td>
<td>-do-</td>
<td>Formation of one double salt which does not decompose on addition of water and formation of one hydrate.</td>
<td></td>
</tr>
<tr>
<td>iii. MgSO₄-K₂SO₄-H₂O at 35°C</td>
<td>Triangular Coordinate</td>
<td>Formation of a double salt which decomposes on addition of water and formation of one hydrate.</td>
<td></td>
</tr>
<tr>
<td>iv. K₂SO₄-MgSO₄-H₂O at 55°C</td>
<td>-do-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Four component system:

| Na₂SO₄-K₂SO₄-MgSO₄-H₂O at 25°C | Jähncke's method of representation | Formation of three double salts and there are 4 quaternary invariant points. |

Five component system:

| Na⁺, K⁺, Mg²⁺-Cl⁻, SO₄²⁻-H₂O at 25°C | Both by Löwenherz method and Jähncke's method of representation | Oceanic salt system. |

Different processes represented in the literature for recovery of marine chemicals especially those of sodium, potassium and magnesium chemicals are reviewed. It has been
tried to locate their disadvantages resulting in not being adopted by the industry. The processes are complex and energy intensive. The aim was set to satisfy the need for simple and novel processes to recover sodium sulphate and potassium chloride and potassium sulphate by interpreting and employing phase diagrams.

Chapter II : Recovery of raw materials for marine chemicals from sea brine:

In this chapter methods for recovery of common salt are first reviewed. The two methods of charging brine in crystallizers viz. series and parallel feeding are explained and discussed the advantages of series feeding system for recovery of good quality salt and increase in the yield. Laboratory experiment was first carried out for evaporation of brine and bittern in cement pan to avoid their losses and to determine the exact volume reductions. The quantities of salt separated at different ranges of densities were also determined. On the basis of the data collected in this laboratory experiment, field experiment was carried out. It is further explained in details the way the crystallizers were prepared for field trials; the way the crystallizers were fed and the manner in which the salt was collected, heaped and weighed. Results of analyses of bitterns at different stages, product composition and finally comparison of data of laboratory and field experiments are discussed.
The area distributions for different ranges are calculated and compared with the actual requirement of areas and reasons for the variations are discussed.

Chapter III: Recovery of sodium sulphate from sels mixtes:

After discussing the uses of sodium sulphate, its recovery from natural sources and chemical reactions are explained. Its recovery from naturally found astracanite by different methods is discussed. All these processes however involved chilling of the astracanite solution at one stage or the other. For a tropical country like ours, processes involving chilling to low temperatures are uneconomical.

Sea brine is a perennial source of sulphate ions for manufacture of sodium sulphate. It has been explained on the phase diagram why sodium sulphate cannot be obtained by direct evaporation of sea brine or bittern. It can only be recovered from sea brine by chilling to \(-6^\circ C\). But it is uneconomical. It has been further discussed in the chapter that sodium sulphate can be recovered from sulphate rich solar evaporite of sea bittern called sels mixtes either via astracanite at ambient temperature or via vanthoffite at higher temperature.

i. Recovery of sodium sulphate from sels mixtes via astracanite:
It was found by tracing the composition of sels mixtes on the Jänecke's diagram of Na⁺, Mg²⁺, Cl⁻, SO₄⁻ at 25°C that it falls in the astracanite field. Process based on the phase diagram was explored to get maximum conversion of sulphate to sodium sulphate in the form of astracanite with the help of calculation based on the law of mass action. Composition for getting maximum conversion of astracanite was established. Experimental studies based on these theoretical deductions were carried out. Physico-chemical parameters were also investigated and established to obtain anhydrous sodium sulphate from recovered astracanite. It has been for the first time established that through a new and simple route sodium sulphate can be obtained from marine evaporite sels mixtes. Based on these experimental results, a novel process has been evolved. The process has an advantage of being adoptable by the salt manufacturers in the coastal area where the steam or electricity is difficult to obtain.

ii. Recovery of sodium sulphate from sels mixtes via vanthoffite:

In the salt works, where it is possible to adopt, a process using steam or electricity, an another route involving vanthoffite (3Na₂SO₄·MgSO₄) formation for recovery of sodium sulphate was investigated. The process was first evolved theoretically with the help of phase diagram and then investigated experimentally in laboratory to obtain
technical data. This alternative process has an advantage of getting a concentrated intermediate vanthoffite.

For both the processes, flow sheets have been prepared and the detailed process steps have been described.

Chapter IV: Recovery of potassium chloride and potassium sulphate from mixed salt:

After discussing how the demand for potash is increasing every year, uses of important potassium compounds are given. In absence of any potash deposits in India, we have to solely depend on imports. India's imports of potash have increased from 28,000 tonnes $K_2O$ in 1961-62 to 6,77,030 tonnes $K_2O$ in 1982-83.

Sea brine contains 0.039% of potassium per 100 ml. Total reserve of potash if all the bittern is processed is 65,000 tonnes. Recovery of potassium rich solid fraction from bittern called mixed salt containing potassium as kainite ($KCl, MgSO_4 \cdot 3H_2O$) alongwith hydrates of magnesium sulphate, magnesium chloride and sodium chloride is discussed. Two important processes for recovery of potassium chloride and potassium sulphate from mixed salt were investigated with the help of phase diagrams of the oceanic salt system $Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$ - H O at 25°C.

1. Recovery of potassium chloride from mixed salt via carnallite:
It was observed that if mixed salt is kept immersed in bittern of composition falling in carnallite field, kainite in mixed salt gets converted to carnallite. The carnallite obtained this way is decomposed by water and recrystallized to pure potassium chloride. The process is a novel one which earlier workers were not able to establish even though theoretically it was thought possible.

ii. Recovery of potassium sulphate from mixed salt via glaserite:

To make the process simple and attractive to the salt manufacturers avoiding complicate processes, a room temperature process was investigated based on the formation of leonite by addition of water. Leonite so obtained was converted to glaserite which finally yielded potassium sulphate on reacting with potassium chloride. Equilibrium compositions of the solution were calculated on the basis of the phase diagram of the oceanic salt system \( \text{Na}^{+}, \text{K}^{+}, \text{Mg}^{2+}, \text{Cl}^{-}, \text{SO}_{4}^{2-} \) - \( \text{H}_2\text{O} \) at 25°C. The process was established experimentally in the laboratory by optimising different parameters.

For both the processes of recovery of potash, flow diagrams and detailed process steps have been given.