SYNOPSIS

In the days of dwindling mineral resources and energy crisis, one has to look for inexhaustible resources of mineral as well as energy. The nature has provided us with respect to both in the form of oceans and in the form of sun respectively. The oceans contain almost all the elements useful to mankind in the form of a very dilute solution which can be concentrated by the use of solar energy. Oceans and sun have remained untapped to full extent till today bearing few exception. Time has come for us to be ready with a suitable technology to utilize these resources.

The concentration of elements in seawater ranges from $10^{-4}$ to $10^{-15}$ ppm. Based on the concentration, the elements in seawater easily can be classified as major, minor and trace elements. Out of the major elements, some of them crystallize out as pure salts during its evaporation. Thus calcium carbonate, gypsum and common salt are obtained. The remaining elements concentrate in the bittern. On further evaporation, no salt separates out in pure form because the solubilities overlap and they are obtained as a mixture of individual salts or double compounds or mixture of both of them. In this thesis
the study is carried out to separate them in pure form by a physical method as employed in ore dressing. When the substance is placed in an inert liquid medium having a density intermediate between the densities of two constituents of the substance, one being a lighter floats and the other sinks resulting in the desired separation. The above principle of physical separation by sink and float method has been applied to recover the marine salts.

The thesis is divided into three chapters. Chapter one and two deal with the separation of marine salts by sink and float method. Chapter 3 deal with the study of estimation and recovery of minor constituents boron and iodine from seabrine.

(1) INTRODUCTION:

First chapter of the thesis deals with the introduction of marine salts, various chemical methods for recovering them, different physical methods of separation of substances and sink-float method employed for separation of coal and ore dressing. It also explains the function, properties and uses of surface active agents in separation of salts and minerals by flotation.

It is reported that German research workers have studied the physical methods of separation for Stassfurt deposits, which contains halite (NaCl),
Sylvite (KCl) and carnallite. They have tested various physical methods like differential grinding, electrostatic separation, air separation, vibrating plate separation and flotation. But due to some technical reasons, the methods except flotation did not stand. Physical methods of sink and float separation is widely and successfully used in ore dressing. It is based on the differences of specific gravities of different constituents of the mineral. The marine salts are also having the same constituents possessing difference in density and the method may be found applicable.

(2) SEPARATION OF CONSTITUENTS OF SEABRINE EVAPORITES (MARINE SALTS) BY PHYSICAL METHOD.

RECOVERY OF SEPS MIXT AND MIXED SALT FROM SEA BITTERN

Second chapter deals with the study of separation of marine salts obtained during different stages of evaporation of 29°Be° bittern by sink float method. When bittern is evaporated, the salts mixt separates out between 34° and 35°Be° which contains epsom salt and sodium chloride. On further evaporation the mixed salt separates out which is a mixture of potassium chloride and sodium chloride, magnesium sulphate and magnesium chloride. The study is carried out to separate these salt fractions as well as carnallite and a mixture of sodium chloride and potassium chloride, obtained during processing of these fractions as raw materials.
STUDIES ON PHYSICAL SEPARATION OF SALT FROM SELS SELS MIXT AND MIXED SALT, ETC., BY SINK AND FLOAT METHOD.

All the parameters affecting the separation of salt by sink-float method were first studied with artificial salt mixture. Afterwards the study was carried out with natural salt fractions. The separation of all these salts was carried out in an inert liquid medium of carbon tetrachloride and ethylene dibromide. The density of liquid medium was adjusted to intermediate between the densities of two salts by suitably varying the ratio of carbon tetrachloride and ethylene dibromide. Sels mixt is a mixture of epsom salt and sodium chloride. The epsom salt has a density of 1.72 and sodium chloride has a density of 2.075. So the liquid medium was prepared by 300 ml carbon tetrachloride (density = 1.60) and 100 ml ethylene dibromide (density = 2.18) to adjust the density 1.745 for 100 g. of sels mixt. So epsom salt can float and sodium chloride can sink. Carnallite (KCl·MgCl₂·6H₂O, density = 1.64) was containing 10-15 percent sodium chloride as impurity. For separation of carnallite liquid medium was prepared from 300 ml carbon tetrachloride and 50 ml ethylene dibromide which gave a density of medium 1.68. However, the separation of salts into sink and float did not take place due to adhesion forces existing between two salt crystals, so that the crystals of salts aggregated through out the medium. So the study of effect of surface active agents in separation of salts was carried out.
STUDIES ON EFFECT OF SURFACE ACTIVE AGENTS.

The surface active agents played an important role in separation of salts by overcoming the forces of adhesion. For each salt fraction, the different surface active agent was effective. In separation of salts mixt the surface active agent - Teepol was found suitable. In case of carnellite and mixed salt, the surface active agents Armac-C and a mixture of Oleic acid and pine oil respectively were found suitable. In case of NaCl-KCl mixture number of surface active agents were tried but no one was found suitable. The surfaces play an important role in separating salts from each other in aggregates. As a measure of the surface activity, the heat of adsorption was measured.

(3) STUDY ON ESTIMATION AND RECOVERY OF LESS COMMON ELEMENTS LIKE BORON AND IODINE.

Chapter 3 deals with the study of estimation and recovery of boron and iodine as representatives of minor and trace element group. Section one of this chapter deals with the estimation and recovery of boron and section two deals with the estimation and recovery of iodine.

ESTIMATION AND RECOVERY OF BORON.

Boron has been reported as a useful trace element for the plant life. It is also reported that
the presence of boron in the refractory material improve the physical characteristics. 2 & Kilolo litres of seawater contain 1 tonne of boron. No study is reported on its concentration or separation from seawater. Hence the study in detail has been taken up on estimation of boron in micro quantity colorimetrically on spectrometer using carminic acid. Carmine acid reacts with borate to form a blue complex. Boron content in stage-wise fractions obtained during solar evaporation of seawine to bittern and various phosphoric and potash fertilisers recoveries from seawine and bittern has been measured. The co-precipitation of boron with magnesium hydroxide has been studied using different precipitating agents. Among the reagents tested sodium hydroxide has been found most effective.

ESTIMATION AND RECOVERY OF IODINE

Section two deals with the estimation and recovery of iodine from algae. Seawater contains only 0.05 ppm of iodine but certain algae possesses the capacity to concentrate the iodine within their cell structure, with vast seacoast, India abounds in different species of seaweeds. As no attempt has been reported in literature regarding utilization of this source in India, the study with respect to estimation of iodine, burning of seaweed to ash, extraction of iodine from ash, concentration of the extract and precipitation of iodine has been carried
Literature has indicated that several methods have been suggested for estimation of iodine in presence of organic matter. The different methods have been reviewed. But it also made clear that the estimation was very difficult and each and every method suggested has certain drawbacks. The study was carried out to standardize a method for adoption. The following methods have been tested, (i) Oxidation of algae in KMnO$_4$, (ii) Fusion of algae with nitrate decomposition mixture, that is KNO$_3$, K$_2$CO$_3$ and Na$_2$CO$_3$, (iii) Digestion with alcoholic potash, (iv) Oxidation with sulphuric acid and hydrogen peroxide, (v) Burning in closed flask at 600-650°C, and (vi) Digestion with sodium carbonate solution and burning at 500°C. The last two methods have been found to give reproducible results within the limits of experimental errors.

The beneficiation of indigenous iodine raw material, algae, was studied. Study on burning of iodine was carried out to reduce the losses of iodine during burning. It was found out that by controlled burning of algae the loss of iodine by volatilization could be reduced from 75 percent to 40 percent. The ash was extracted with water. The extract was evaporated to concentrate iodine and precipitation of iodine was done from concentrated extract. During evaporation of extract, potash salts were separated out. The full data are presented. Based on these results the process
is suggested for the recovery of iodine/potash salts. Based on these data it was calculated that about 2.7 tonnes of *Sargassum* seaweed would yield 1 Kg of iodine and about 225 Kg of potash salts.

The studies on wet extraction of algae and their further treatment for alginic acid revealed that iodine was lost during processing in the waste liquors as well as waste solid residue. A method was studied to recover iodine lost in the alginic acid waste. From the results it was established that about 67 percent of iodine could be recovered from waste liquors by oxidizing with bromine and liberating free iodine by sodium bisulphite. Based on the available estimate on brown seaweed, it would be possible to recover 800 Kg of iodine from this source. At present estimates available source, iodine required for iodised salt for Gaitre controlled can be met (approximate requirement 1000 Kg iodine per annum).

Published paper on (i) determination of potassium as tetraphenyl boron (ii) arsenic content of marine algae (iii) arsenic content in Indian solar salt and marine products are attached as appendix.