SYNOPSIS OF THESIS ON POTASSIUM CHEMICALS FROM SEA WATER

There are no potash deposits in India and requirements of potash fertiliser and chemicals are mostly met by imports. The only important and perennial source for the manufacture of potassium chloride is bittern from marine and sub-soil brines which is now going waste. About 40,000 tonnes of potassium chloride can be manufactured annually on the basis of practical recovery whereas the estimated reserve from the salt industry will be of the order of 1.5 lakh tonnes.

The thesis is divided in two sections. The section two on recovery of potassium chemicals from sea water is divided in five chapters: 1) Recovery of mixed salt by solar evaporation of bitterns, 2) Utilisation of mixed salt to obtain potassium chloride, magnesium sulphate and sodium sulphate, 3) Recovery of potash alum from mixed salt, 4) Corrosion studies to select suitable materials of construction, 5) Recovery of potassium as potassium nitrate from sea water and bitterns, by the use of selective reagent calcium dipicrylamine. Laboratory studies have been extended to field scale trials in harvesting mixed salt in solar salt works. The pilot plant study and corrosion experiments have been carried out to collect additional data and to find out the economic feasibility of the developed processes and are described separately in each chapter.

Chapter 1 deals with evaporation of 29° Be bittern to obtain mixed salt a fraction rich in potassium chloride. The normal composition of mixed salt is 32 - 35 per cent

$MgSO_4$, 6-8 per cent $MgCl_2$, 15 - 20 per cent NaCl and 18-20 per cent KCl and the yield of mixed salt per 100 gallons or 455 litres is approximately 39 to 40 kg. Studies on various factors effecting mixed salt separation are discussed. Acceleration of evaporation by utilising dyes and studies on direct and mixed bittern evaporation by addition of magnesium chloride in the form of 36° Be bitterns are described. Normally major separation of potassium chloride takes place at 38° Be density which is difficult to obtain by solar evaporation at all places. The present studies have established that addition of magnesium chloride (by addition of byproducts 35 per cent magnesium chloride bitterns) 70 - 80 per cent of potassium chloride along with other marine salts can be separated at lower densities between 34 - 36° Be' instead of 36 to 38° Be. The process uses solar heat to further concentrate the bitterns of salt works to obtain a mixed salt, a solid material 10 times concentrated than that of the parent source of bitterns, l~~i~~eaving behind a concentrated bitterns of 36° Be' containing mainly magnesium chloride. It has been observed on field scale trials that by addition of required quantities of magnesium chloride and solivap green, the period of evaporation can be substantially reduced from 20 days to 9 days to reach 36° Be bitterns stage. It is also observed that control of bittern evaporation can be easily carried out by density or using a flame photometer and by determining only KCl-NaCl concentrations. In absence of flamephotometer, methods are developed to control the evaporation by noting the density against total chloride and total magnesium concentrations. Some observations on mixed salt and high density bittern storage are also described.

Chapter 2 deals with utilisation of mixed salt for the production of potassium chloride and recovery of byproducts namely epsom salt and sodium sulphate. The process consists of treating mixed salt with 36° Be bittern and heating the mixture to 110°C. The hot filtered extract on cooling to room temperature gives carnallite. Carnallite a double salt of potassium chloride and magnesium chloride is decomposed with water to obtain crude potassium chloride; crude potassium chloride is further recrystallised with NaCl - KCl saturated solution to obtain pure potassium chloride. The filtered cake (sel's mixts) obtained after extraction of mixed salt is dissolved in water to saturation and then chilled to 10°C to obtain epsom salt. The solution left after epsom salt separation is once again saturated with sodium chloride and chilled to -5°C to obtain sodium sulphate. 8 tonnes of mixed salt yields one tonne of potassium chloride, 2.4 tonnes of epsom salt and 1.2 tonnes of anhydrous sodium sulphate. Pilot plant studies are carried out to obtain technical data for large scale plants.

Some of the improvements carried out over the previously developed processes are (1) In recrystallisation of impure potassium chloride, the recrystallising solution which attains a certain concentration of magnesium chloride after certain number of cycles, requires treatment with sodium carbonate to remove magnesium salt as magnesium carbonate. In the improved procedure the solution, instead of treatment with sodium carbonate, is used directly for decomposition of fresh carnallite. Thus, the potassium chloride in the solution is recovered and the costlier treatment with sodium carbonate is avoided. (2) Sodium sulphate decahydrate is converted to anhydrous sodium sulphate by melting the product above 32°C and evaporating the solution to approximately half the volume (force evaporation). The end liquor containing sodium sulphate and sodium chloride is recycled in the process. In the modified procedure, anhydrous sodium sulphate is precipitated at 50°C from the melted solution of sodium sulphate decahydrate by addition of calculated quantity of powdered sodium chloride. Thus the modified procedure has avoided evaporation of a large volume of solution and the difficulties of hard scale formation on the evaporator during evaporation. The method has also additional advantage that the purity of the product can be easily controlled.

Chapter 3 deals with utilisation of mixed salt, ~~and~~ indigenous and cheap raw material for potassium industries in the country for the manufacture of valuable chemical potash alum. Solid potash alums can be obtained practically free from other salts directly by addition of mixed salt in a saturated solution of aluminium sulphate. The mixture is stirred and heated to 110°C and filtered hot using pressure filter. The hot clear extract on cooling to room temperature separates potash alum. In the above treatment potassium chloride is converted to potassium sulphate at the expense of magnesium sulphate which is also present in the mixed salt. Potash alum obtained is pharmaceutical grade. One tonne of mixed salt gives 1.2 tonnes of potash alum.

The process confers certain positive advantages (1) It is better and cheaper than the conventional process of manufacture of potash alum. 2) Recovery of potassium from mixed salt is over 90 per cent. 3) It is suitable for cottage scale industries; thus transportation and collection of mixed salt by small scale salt works from nearby area is all avoided. 4) Process is simple using almost inexpensive equipment available in the country and the price obtained per unit K_2O as alum is high. It fulfils the natural deficiency as potash alum does not occur in the mineral form of alunite or kalinite in India as it occurs in several other countries.

Thus application of solubility data on oceanic salts has been utilised to evolve two novel processes 1) preparation of mixed salt and its utilisation for the manufacture of potassium chloride, magnesium sulphate and sodium sulphate, 2) utilisation of mixed salt for obtaining potash alum. Both the processes use indigenous raw material and equipment. Based on the first process a commercial plant producing 3 tonnes of potassium chloride and 7 tonnes of epsom salt has been set up and commissioned at Kandla.

Chapter 4 deals with corrosion studies at the reaction temperature and selection of suitable material of construction for the two developed processes.

Chapter 5 deals with the recovery of potassium at room temperature either as potassium nitrate or potassium sulphate directly from sea water and bitterns. Hexanitrodiphenylamine (dipicrylamine) is used as precipitating agents. Dipicrylamine forms soluble salt with calcium and magnesium while alkali salts are relatively insoluble. The calcium salt of the reagent is used for precipitation of potassium ion from sea water, brines and bittern solutions. It is observed that recoveries of potassium from sea water 3.5° Be' and concentrated brines such as 14 and 23° Be and bittern of 29° Be density are 70,80, and 92 per cent at room temperature. The addition of excess of reagent over the stoichiometric ratio (1:1.6) is required in case of sea water to obtain good recoveries. The study shows that in case of concentrated brines and bitterns excess of reagent addition is not essential. The concentration of reagent left out in the end liquor decreases substantially with saturation of other salts in solution. The contamination due to sodium and calcium which increases with the concentration of brines and bitterns is washed easily either on buchner or in centrifuge operation.

Normally 5 to 6 times the theoretical amount of acid of not less than 7 normal strength is required for decomposing the precipitates. A new procedure has been worked out which utilises minimum quantities of acetone and the theoretical amounts of acid upto 4 normal strength for decomposing the precipitate and to obtain 6 to 10 per cent potassium nitrate or sulphate in solution. The potassium salt solution in the

filtrate is further subjected to solar evaporation to recover pure salt. The study shows that recycling of the reagent is possible and the acid requirement can be reduced. Methods such as absorption of the reagent from the large bulk of end liquor by active carbon and eluting it with acetone or extraction of the reagent from the end liquor by using normal butanol are described. Solubilities of potassium dipicrylaminate and free amine are determined to obtain concentrated potassium salt in solution and to reduce the losses of the reagent and are reported.