SYNOPSIS

Introduction

This investigation relates to a method for the recovery of anhydrous sodium sulphate from, (i) solid bittern available in India from the salt works in Rajasthan containing sodium sulphate and considerable quantities of sodium chloride, (ii) sodium sulphate bearing materials available from any other sources. The solid bittern is obtained either by solar evaporation or by forced evaporation from liquid bittern of 29° to 30° Be' from the salt works.

The introductory part of the thesis surveys, (i) the history of the development of the flotation process, (ii) natural, homogeneous deposits in India, containing anhydrous sodium sulphate and sodium chloride, (iii) flotation of soluble salts of sodium. It also deals, in brief, with the following theoretical considerations: (i) contact angle and surface tension - the measures of flotability, (ii) fatty acids as collector, (iii) the role of a modifier, (iv) effect of pH on flotation, (v) size and flotability of particles and (vi) pulp density.

Solar evaporation study of Sambhar liquid bittern.
bittern was carried out to find out the composition of the solid bittern being thrown out during concentration. It is observed that a major portion of solid bittern is thrown out on the per cent reduction in volume of the liquid bittern from 0 to 79.3 and this fraction of the solid bittern on the dry basis shows the average composition: $\text{Na}_2\text{SO}_4$ 25 to 26, $\text{NaCl}$ 57 to 59, $\text{Na}_2\text{CO}_3$ 15 to 17 per cent. This fraction contains about 85 per cent of total sodium sulphate initially present in the liquid bittern. It is also observed that, during solar evaporation, Sambhar liquid bittern, from initial to 93.8 per cent reduction in volume, indicates different percentage compositions, its per cent sodium sulphate content gradually decreasing, its per cent sodium carbonate content gradually increasing, while its per cent sodium chloride content remaining fairly constant (22 to 23 per cent) upto 79.3 per cent reduction stage in volume and then onwards decreasing gradually to 18.3 per cent.

**X-ray study of Sambhar solid bittern:** The X-ray powder diffraction pattern of Sambhar solid bittern was taken and was examined for the existence of a chemical species of burkeit ($2\text{Na}_2\text{SO}_4; \text{Na}_2\text{CO}_3$) along with other constituents. The standard X-ray powder pattern of ASTM 2.0840 was used for identification. The solid
bittern shows the presence of a chemical species of burkeit along with other excess impurities.

**Direct recovery of anhydrous sodium sulphate:**
The conventional process for the recovery of sodium sulphate from liquid bittern is by chilling the bittern at 0°C, whereby crystals of Glauber salt (Na\textsubscript{2}SO\textsubscript{4}·10H\textsubscript{2}O) are separated out. The crystalline slurry is then centrifuged and the crystals are dehydrated to produce anhydrous sodium sulphate.

Eliminating chilling and dehydration operations, as required in the conventional process, a method yielding direct recovery of anhydrous sodium sulphate has been investigated, in which the flotation is used for the separation of anhydrous sodium sulphate, which separates out in concentrate from other ingredients like sodium chloride which goes as raffinate. The anhydrous sodium sulphate recovered by this method is of technical grade suitable for use in paper and textile industries.

**Contact angle and surface tension - measures of flotability:** The physico-chemical understanding of the mechanism of flotation requires the use of conceptions of contact angle, surface tension and polarity. The processes of hydration essentially determine the wettability of minerals in water. The relation between
wettability and flotability of a mineral has been studied in this investigation.

The hydration of the surfaces of anhydrous sodium sulphate and of sodium chloride by the saturated solution of anhydrous sodium sulphate and sodium chloride at room temperature has been investigated by measurement of the contact angle. Such data for anhydrous sodium sulphate and sodium chloride have not been reported in literature. This study has indicated that a small contact angle shows water-avidity and non-flotability of the material, while a large contact angle shows water repellancy and flotability of the material. In this investigation, it is clearly stressed that the flotation reagents affect the flotation of anhydrous sodium sulphate and of sodium chloride by changing the hydration of their crystals.

If solid and gas bubbles are individually suspended in water, subsequent attachment of particles to bubbles reduces the solid-liquid and the liquid-gas interfaces by an area $S$, but increases the solid-gas interface by the same area $S$. The reduction in the potential energy of the system ($\Delta W$) per square centimeter of solid surface is given by,

$$\Delta W = E_{aw} (1 - \cos \theta)$$
where, $E$ denotes the surface energy at the air-water interface and $\theta$ is the contact angle measured through water. Numerically, $T_{aw}$, the surface tension of the solution, can be substituted for $E_{aw}$ since they are numerically equal. The quantity $\lambda$ is also known as the work of adhesion and is a measure of the tendency to float. The surface tension of the flotation liquor was measured by "the rise in capillary" method. Knowing the values of the surface tension and the contact angle, $\lambda$ was calculated, which gives a measure of flotability.

Actual flotation experiments under the identical conditions, during this investigation, have fully supported all the derivations from the above-mentioned theoretical study and thus it has been established that a theoretical study should easily and necessarily precede a flotation operation to assess the optimum conditions.

Preparation of surface for contact angle measurement: The contact angle was studied by placing a small drop of the flotation liquor on a plane, less porous surface of the material. Instead of the usual method being followed for the preparation of a surface of a soluble salt for the contact angle measurement by spreading a uniform layer of the pulverized material on a paraffin-coated surface, an alternate easy method has been deviced and employed for the same purpose in this
investigation. The salt surface is obtained either in a fused-form (if no chemical reaction takes place upto the fusion temperature) or in a hard tablet-form.

Design of direct reading contact angle measurement: For the contact angle measurement, the surface, as mentioned above, of anhydrous sodium sulphate and of sodium chloride were conditioned at room temperature in saturated solution of sodium sulphate and sodium chloride, employing varying amounts of reagents as required. The contact angle for each surface was first measured by a direct reading instrument devised by the investigator, and based on the principle of observation of the reflected light at the front edge surface of a small drop of liquid resting on the material surface. This value of the contact angle, when each time checked by the conventional horizontal plate method employing a travelling vernier microscope, was found to be fairly coinciding. The contact angle value for the conditioned surface of the material proportionately denotes its flotability under the corresponding conditions. The contact angle measurement by this instrument is easy, quick, direct and accurate.

Natural and acquired flotability: To start with, the natural flotability of anhydrous sodium sulphate and of sodium chloride was studied. Sodium chloride
was found to possess more natural flotability than anhydrous sodium sulphate. Using oleic acid as a collector, the acquired flotability of both these salts was investigated at the same pH of the conditioning liquor. The acquired flotability of anhydrous sodium sulphate was found to be greater than that of sodium chloride. Thus it was established that oleic acid acts as a selective collector for anhydrous sodium sulphate.

**Particle size:** The material must be ground to a point of complete liberation. Particles of various sizes do not float equally well. An increase in the upper size limit of flotable particles is of economic significance. By the actual flotation experiments, the optimum coarse particle size limit for the selective flotation of anhydrous sodium sulphate from a crystalline mixture of anhydrous sodium sulphate and sodium chloride was investigated. It was found to be < 295 microns (i.e. -52 B.S. mesh).

**Modifier:** The acquired flotability, obtained through collectors, is selective in a broad sense. Further selectivity in the acquired flotability is obtained by the addition of other reagents, grouped as "modifiers". The use of calcium chloride as a modifier was found to be advantageous to increase the selective
flotability of anhydrous sodium sulphate. It is interesting to note that, during this study, the optimum amounts of calcium chloride as a modifier and of oleic acid as a collector are in the stoichiometric proportion to form calcium oleate.

**PH effect:** The collector ions are adsorbed in the form of an oriented film with the polar ends attached to the mineral and the non-polar ends away from it. Since the adsorbing ion is replacing hydrogen, hydroxyl or other more strongly attached ions from the surface, and also since ionization of the collector is necessary, pH is an important factor to be controlled; pH of the flotation liquor was varied in the range of 5 to 9 by addition of either sulphuric acid or soda ash (or caustic soda). Alkaline pH in the range of 7 to 8 was found to be optimum. It is also noticed that a shift of pH by a unit or so on either side of the optimum range creates an adverse effect on the flotation results, inspite of other conditions remaining constant.

**Collector:** Keeping all other experimental conditions constant, the optimum amount of calcium chloride as a modifier and that of oleic acid as a collector were determined one after the other. As already mentioned, these were found to be in the stoichiometric proportion to form calcium oleate. Next, the form of oleic acid to
to be used as collector was investigated. Oleic acid in the form of 5 to 10 per cent solution in rectified spirit was found to be most efficient.

Having established that oleic acid acts as a collector for anhydrous sodium sulphate, several other suitable collectors were also tried under the similar conditions, but none of them was found to be a better substitute to oleic acid.

The selective flotability of anhydrous sodium sulphate as derived from the contact angle and the surface tension readings using different collectors at the optimum pH, was found to be identical with that arrived at by knowing only the contact angle under the similar conditions.

Pulp density: In a flotation process the pulp density is important in both chemical and mechanical considerations. It determines relative time and quantity of reagent required to give desired reagent concentrations. A few variations in the pulp density, during this study, established that the pulp density, solid phase : liquid phase :: 1:4 is optimum.

Optimum conditions: The following optimum conditions have been arrived at, during this investigation, for the selective flotation of anhydrous sodium sulphate
from a crystalline mixture of anhydrous sodium sulphate and sodium chloride:

(i) Particle size: The maximum coarse particle size of the crystalline mixture of \( \leq 295 \) microns (i.e. \(-52\) B.S. mesh).

(ii) Collector: Oleic acid in the form of 5 to 10 per cent solution in rectified spirit at the rate of 0.5 to 1.0 g/l kg crystalline material/4 l flotation liquor.

(iii) Modifier: Calcium chloride in the form of 5 per cent aqueous solution at the rate of 0.1 to 0.2 g/l kg crystalline material/4 l flotation liquor.

(iv) Flotation liquor: A clear, saturated solution (28° to 28.5° Be' at room temperature) of sodium chloride and sodium sulphate.

(v) pH: The pH of the flotation pulp in the range of 7 to 8 throughout the flotation experiment.


(vii) The order of addition: First the modifier followed by the collector to the pH adjusted pulp.

(viii) Conditioning period: (a) the pulp dispersed for 5 minutes, after the pH adjustment, (b) followed by addition of the modifier and conditioning for 5 minutes
(c) followed by addition of the collector and conditioning for 5 minutes, and (d) followed by the actual flotation for about 10 minutes.

Under these optimum conditions, 80 to 85 per cent of the total anhydrous sodium sulphate from Sambhar solid bittern is floated, the percentage purity of the floated sodium sulphate being 75 to 80 on the dry basis.

As it is very likely that the composition of the crystalline mixture of anhydrous sodium sulphate and sodium chloride can vary in different samples, the effect of variation in the composition of the raw material on the flotation results was investigated. It was found that the percentage purity and the yield of anhydrous sodium sulphate, both go on increasing as the ratio by weight of $\text{Na}_2\text{SO}_4 : \text{NaCl}$ changes from 1:1.74 to 1:0.79.

**Scale up experiments:** Several large scale experiments, each time taking 80 kg raw material for the flotation of anhydrous sodium sulphate, indicated the reproducibility of the laboratory results.

**Leaching of sodium chloride impurity:** A saturated solution of sodium sulphate and sodium chloride, at room temperature, would show the composition: $\text{Na}_2\text{SO}_4$ 8 to 9, $\text{NaCl}$ 27 to 28 per cent, meaning thereby that the solubility of sodium sulphate is highly depressed in the presence of sufficient amount of sodium chloride. Utilizing this fact,
during this investigation, the flotation concentrate was further enriched for its anhydrous sodium sulphate content by removing its sodium chloride impurity by leaching at room temperature with a calculated amount of the saturated solution of sodium sulphate. The finished product, anhydrous sodium sulphate, was found to conform to Indian Standard Specifications for anhydrous sodium sulphate, technical grade B. Over-all percentage recovery of anhydrous sodium sulphate was about seventy. The leachate from this step can be utilized to replenish the loss in the flotation liquor during the flotation operation.

De-sliming of Sambhar solid bittern: During this investigation it was found that if the raw material (Sambhar solid bittern) used to contain three or more per cent insoluble matter, the flotation results were adversely affected and the final product, anhydrous sodium sulphate, did not conform to the Indian Standard Specifications for anhydrous sodium sulphate, technical grade B. Under such circumstances, the preliminary desliming of the raw material by its counter-current washing in its own, clear, saturated solution at room temperature was investigated. It was found that this operation eliminates about 70 per cent of the total insoluble matter, there being about 5 per cent loss in the recovery of anhydrous sodium.
The results of sieve analysis of the material before and after desliming show that a major portion of the insoluble matter resides in the finer particle size portion of the pulverized raw material. Thus it is indicated that the insoluble matter, present in Sambhar solid bittern, is superficial and not intersticial and that most of it is present in the finer particle size portion of the pulverized material.

Summary

(i) A process for the direct recovery of anhydrous sodium sulphate from a crystalline mixture of anhydrous sodium sulphate and sodium chloride or from anhydrous sodium sulphate bearing material has been developed.

(ii) An instrument has been devised and utilized to directly measure the wettability of a mineral surface by a liquid, by measuring the contact angle of a small drop of the liquid resting on the surface of the mineral. With this instrument the contact angle measurement is easy, quick, direct and sharp.

(iii) It has been established that the wettability of a mineral surface, as derived either by the contact angle measurement or by the contact angle and the surface tension measurements is a direct proportionate measure of its flotability under the similar conditions. This
conclusion has also been verified at each stage by carrying out the actual flotation experiments under the identical conditions. Such theoretical data for anhydrous sodium sulphate and sodium chloride system is still not available in literature.

(iv) An approach has been investigated wherein it has been established that a theoretical study should easily precede an actual flotation operation to assess the optimum conditions for the same.

(v) An easy method has been investigated for the preparation of the surface of a soluble salt to measure the contact angle.

(vi) In the present investigation, the effects of the following factors on a flotation operation have been extensively studied and discussed; (a) Natural and acquired flotability; (b) Particle size; (c) Role of modifier, its form and concentration; (d) Role of collector, its form and concentration; (e) pH of the flotation pulp; (f) Comparative effect of various suitable collectors; (g) Pulp density; (h) variation in the composition of the raw material; (i) Presence of insolubles and slimes.

(vii) De-sliming of Sambhar solid bittern has been investigated, whereby about 70 per cent of the insoluble
mattered has been eliminated. It has also been indicated that most of the insoluble matter present in the solid bittern is superficial and not interesticial, and is present in the finer particle size portion of the pulverized bittern.

(viii) This investigation has shown that it is possible to enrich anhydrous sodium sulphate content of a material also containing sodium chloride by leaching out the latter at room temperature with a calculated amount of water or a saturated solution of sodium sulphate.

(ix) The solar evaporation study of Sambhar liquid bittern has brought forward the following facts:

a) A major portion of the solid bittern is thrown out on the per cent reduction in volume of the liquid bittern from 0 to 79.3.

b) The solid bittern, as thrown out in (a), shows the average composition: \( \text{Na}_2\text{SO}_4 \) 25 to 26, \( \text{NaCl} \) 57 to 59, \( \text{Na}_2\text{CO}_3 \) 15 to 17 per cent.

c) About 85 per cent of the total sodium sulphate initially present in the liquid bittern is recovered in the solid bittern, as thrown out in (a).

d) During concentration, Sambhar liquid bittern, from initial to 93.8 per cent reduction stage in volume
indicates different percentage compositions, its per cent sodium sulphate content gradually decreasing, its per cent sodium carbonate content gradually increasing, while its per cent sodium chloride content remaining fairly constant (22 to 23 per cent) upto 79.3 per cent reduction stage in volume and then onwards decreasing gradually to 18.3 per cent.

(x) The X-ray study of Sambhaf solid bittern has indicated the presence of a chemical species of burkeit \((2\text{Na}_2\text{SO}_4; \text{Na}_2\text{CO}_3)\) in solid bittern, along with other ingredients.