SYNOPSIS
OF Ph.D. THESIS ON
STUDIES ON IMPURITY ASSOCIATION AND REMOVAL,
HYGROSCOPICITY, CAKING AND DISSOLUTION
CHARACTERISTICS OF SOLAR SALT

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This investigation pertains to various studies on salt obtained by solar evaporation of sea water and inland brines and aims at improving the quality of salt by indicating the salient points, to be borne in mind at the time of manufacture of salt and finding out the easier and cheaper methods for upgrading the salt. Other physico-chemical processes like moisture absorption and desorption by salt containing impurities at different relative humidities, caking of salt under various conditions and rate of dissolution of salt in water, which have an important bearing on salt and salt based industries have also been studied.

The survey of the quality of salt produced in the country shows that, though it is suitable for edible purpose, most of the salt samples contain more impurities than specified by Indian Standard Specifications for "Salt for chemical industries". Therefore, present work was planned to study the improvement of Indian salts, selecting five representative samples.

ASSOCIATION AND DISTRIBUTION OF IMPURITIES IN SALT

The theoretical study on "Crystal growth and association of impurity" has been made and on the basis of this study, explanation of association of impurities in common salt is given. This is followed by experimental work on two typical salt samples viz. inland salt from Kharaghoda and sea salt from Bhavnagar.
The preliminary experiments gave idea about the distribution of impurities in various particle size ranges but did not show whether the impurities are trapped or superficial. For this the various size ranges of salt were contacted with neutral and acidic saturated salt solution (from A.R. sodium chloride) to remove the superficial impurities and analysing the samples after this.

Analysis of various layers of Kharaghoda salt aggregates revealed that calcium impurity is deep seated and irregularly distributed throughout. Analysis after contacting the salts with saturated salt solution, and calculating statistically the analytical data, showed that 43 per cent of calcium, 39 per cent of magnesium, 46 per cent of sulphate and 33 per cent of insoluble matter in Kharaghoda salt and 37 per cent of calcium 48 per cent of magnesium and 45 per cent of sulphate in Bhavnagar salt are in trapped conditions. Association of impurities was confirmed by taking microphotographs of salt crystals showing trapped calcium sulphate and cavities showing trapped magnesium salts in the form of mother liquor.

The association of calcium impurity was also confirmed by radioactive tracer technique in which salt crystals were grown from sea brine of 24°Be' to which Ca^{45} isotope was added. From the activity measurements in brine and salt crystals, it was found that calcium
impurity was irregularly distributed in sodium chloride crystal matrix and it starts depositing or entering, after the salt crystal achieved the size of approximately 1 mm.

The association of magnesium impurity in salt is due to the adherence of mother liquor. This was proved by calculating the ratio of residual $SO_4^{2-}:Mg$ ions in salt as well as in mother liquor of various densities which was constant in both viz. 1.2 - 1.4. This has also been shown by correlating the bulk densities of different salts with their magnesium content.

**WASHING OF SALT**

Literature survey showed that washing of salt in large scale has been adopted by many countries as well as India but published informations on washing of salt in general and Indian salt in particular are not available. The object of this work was to obtain experimental informations on washing of Indian salts which may be useful to salt based industries.

Experimental portion has been divided into laboratory scale experiments and pilot plant experiments. Laboratory scale experiments have been carried out on batch as well as continuous method.

**Laboratory scale experiments**: Effect of time of contact, solid:liquid proportion, particle size and concentration of magnesium ion in wash liquor, on the washing of salt
was studied on batch scale. On the basis of 65 - 75 per cent magnesium and 40 - 50 per cent calcium removal, the optimum conditions were, time of contact 1 - 2 minutes, solid: liquid ratio 1:1 - 1:2, particle size -18 B.S. mesh and Mg²⁺ concentration in wash liquor 19 - 20 gms per litre.

Laboratory scale experiments in continuous method were carried out in a "Disperse column washery unit" of 10 - 15 Kg per hour capacity, specially designed and developed for this purpose. Washing of Kharaghoda and Bhavnagar salt was carried out to study the effect of particle size and brine flow rates. Results of these experiments have shown that good quality washed salt is produced from Bhavnagar salt while Kharaghoda salt improves to considerable extent.

Pilot Plant experiments: From the series of experiments on 1 - 2 tonnes per hour scale, using screw conveyor washery unit, the following general conclusions have been drawn. Though the removal of impurities depends upon the nature, physical characteristics, particle size and distribution of impurities, the marine salt samples studied showed similar trends in washing. Solid:liquid ratio 2:1 was considered better, both from the impurity removal point as well as practical view point. Results of cocurrent and counter current washing did not differ significantly. Decrease in rpm did not help much, it was therefore considered desirable, to work with high rpm, so as to
increase the capacity of plant. Removal of impurity in average sea salt samples was calcium 30 - 50 per cent, magnesium 60 - 75 per cent, sulphate 40 - 65 per cent and insoluble matter 40 - 70 per cent and corresponding loss of salt was 8 - 10 per cent.

Screw-conveyor type washery unit is not suitable for Kharaghoda salt and therefore a bigger, "Disperse column washery unit" of 60 - 75 kg per hour capacity was designed and constructed on the basis of smaller unit. Washing of Kharaghoda salt and Bhavnagar salt was carried out on this unit which confirmed that good quality washed salt can be prepared from Bhavnagar salt. Kharaghoda salt can be improved to considerable extent and a quality close to Indian Standard Specification for "Salt for chemical industries" can be obtained.

MOISTURE ABSORPTION BY SALT

This study pertains to the absorption and desorption of moisture by salt, containing magnesium chloride and/or magnesium sulphate in proportions usually present in sea salt, synthetically prepared for the purpose and to moisture absorption by pure sodium chloride, magnesium chloride and magnesium sulphate at relative humidities in the range of 50 - 90 per cent at room temperature.

Moisture absorption by pure salts at 50 - 90 per cent relative humidities: Moisture absorption by NaCl, MgSO$_4$.7H$_2$O, MgSO$_4$.H$_2$O, MgCl$_2$.6H$_2$O and MgCl$_2$.2H$_2$O was studied. This study revealed that NaCl is stable up to 70 per cent relative humidity and becomes hygroscopic
at 80 and 90 per cent relative humidities. MgSO$_4$·7H$_2$O converts to MgSO$_4$·H$_2$O at 50 per cent relative humidity which is stable at this humidity. MgSO$_4$·H$_2$O converts to MgSO$_4$·6H$_2$O at 60, 70 and 80 per cent relative humidity. MgSO$_4$·7H$_2$O also converts to MgSO$_4$·6H$_2$O at 60 per cent relative humidity. MgSO$_4$·7H$_2$O is stable at 90 per cent relative humidity but MgSO$_4$·H$_2$O first converted to MgSO$_4$·6H$_2$O at this humidity which is hygroscopic. MgCl$_2$·6H$_2$O and MgCl$_2$·2H$_2$O are hygroscopic at all humidities.

Moisture absorption by salt (sodium chloride) containing magnesium chloride or magnesium sulphate or both (together): At 50, 60 and 70 per cent relative humidities all the samples attained equilibrium with respect to moisture within 48 hours of exposure. At 80 and 90 per cent relative humidities, NaCl becomes an active participant in moisture absorption process and therefore the samples absorbed considerable moisture at the rate of 0.9 - 1.5 gms and 3.5 - 4.0 gms H$_2$O per 100 gms of salt per day, at 80 and 90 per cent relative humidities respectively. Equilibrium conditions were not reached at these humidities after an exposure for 30 days.

Moisture absorption increased with the increase in humidity but was not directly proportional to it. Salt containing magnesium chloride absorbed more moisture than those containing magnesium sulphate upto 70 per cent relative humidities after which absorption was practically similar.
When per cent moisture absorption after 48 hour's exposure was plotted against per cent magnesium chloride or magnesium sulphate content of salt, linear relationship was obtained at all humidities. Empirical equations were derived to correlate the moisture absorption and impurity content at various humidities.

It was found that moisture absorption was not proportional to the calculated surface area of particles but to the weight of salt and exposed surface of the container in which it was placed.

Salt containing both magnesium chloride and magnesium sulphate showed similar trends of moisture absorption as shown by salt containing either of them, at all humidities. From magnesium chloride and magnesium sulphate content of these salt samples, per cent moisture absorption was calculated with the help of empirical equations. The calculated values were in close agreement with actual moisture absorption by these salts.

Equations have been derived by earlier workers to calculate the vapour pressures of two or multicomponent systems containing Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻ ions at various concentrations in solution. It was possible to calculate the concentrations of unknown solution, containing the above ions in two component system, if vapour pressure of this solution was known. Thus, in the moisture absorption experiments from the known humidity and magnesium impurity content in salt, it was possible to calculate in the first instance, the concentration of
solution which can remain in equilibrium at particular humidity and from this, the amount of water required to be absorbed to reach that concentration. When moisture absorption by salts samples containing magnesium impurity was calculated by this method, calculated values showed good agreement with observed values, at 70 per cent relative humidity.

In an another method, results of equilibrium moisture absorption by MgCl$_2$·6H$_2$O and MgSO$_4$·H$_2$O were utilised, to calculate the moisture absorption by salt containing magnesium chloride and magnesium sulphate respectively at 50, 60 and 70 per cent relative humidities. Here the agreement between calculated and observed values was better, at 50 and 60 per cent relative humidities than at 70 per cent humidity.

**DESORPTION OF MOISTURE FROM SALT**

When moist sodium chloride was exposed to 50-70 per cent humidities, it was found that, moisture desorption decreases with the increase in moisture content and relative humidity. Thus, salts containing 1.5 and 10.0 per cent moisture lost 83 to 17 per cent, 76 to 13 per cent and 20 to 6 per cent of initial moisture at 50, 60 and 70 per cent relative humidities respectively after 4 hour's exposure. With 48 hour's exposure at 50 and 60 per cent relative humidities, 90 - 95 per cent of initial moisture was lost and residual moisture content in salt was in the range of 0.15 and 0.38 per cent, while to desorb the same amount at 70 per cent relative humidity, it took 4 to 5
days and residual moisture was 0.4 - 0.5 per cent.
Comparing these equilibrium moisture contents, with
those found during moisture absorption studies, it was
observed that, they are higher i.e. some portion of
moisture is held very tenaciously by salt.

Desorption results on moist salts containing
impurities, supported the above observations. Desorption
by moist salt of similar magnesium chloride content but
different particle size supported the previous observation
made during moisture absorption experiments. Thus, desorption
also was not proportional to the calculated surface area
of particles but was proportional to the weight of sample
and exposed area of container.

CAKING OF SALT

Initial portion deals with the literature study
on the mechanism of caking and effect of various factors
affecting it. Quantitative data on the caking of salt
are scanty.

Various methods were tried and tested and finally
the method of mechanical moulding of salt water mix into
a block of definite size, followed by drying and testing
its compression strength was devised and it gave good
results. Effect of various factors on caking was studied
by this method.

Effect of moisture: Caking of salt increased with the
increase in the initial moisture content of salt block,
in the range of 2 - 7 per cent moisture and was directly
proportional to it. From the graph of initial moisture
content against the compression strength, which showed a linear relationship, an empirical equation was derived.

Effect of impurities: Upto 1.5 per cent of magnesium impurity expressed as magnesium chloride caking of salt with or without addition of impurity was practically same but with increase in the impurity content from 1.5 to 2.2 per cent, the corresponding decrease in caking, was 3.4 to 19.5 per cent, compared to the blank salt used for the caking.

Effect of particle size (on caking): When caking of salt of various particle size ranges containing 3.75 per cent moisture was studied, it was found that caking increases with the decrease in particle size, but was not directly proportional to it. Compared to the coarsest size used in these experiments, the gradual decrease in mean particle size was in the range of 20.8 - 87.6 per cent while the corresponding increase in compression strength was in the range of 30 - 1300 per cent. When reciprocal of the logarithm of mean particle size against the logarithm of compression strength was plotted, a straight line was obtained. An empirical equation was derived from this.

Effect of pressure: The effect of pressure is to increase the compaction, bulk density and points of contact between the adjoining particles. Such effect was produced by compacting the salt block by application of a number of
blows (2 to 14) with a hammer. The resulting salt blocks showed increase in compression strength from 25 to 50 kg per sq.cm.

**Effect of humidity and temperature:** Increase in the humidity decreases the caking. Thus the salt blocks exposed to 5, 30, 50, 60 and 70 per cent humidities, showed the decrease of 45 to 74 per cent in compression strength compared to that at 5 per cent humidity.

Effect of temperature is to remove the moisture from salt blocks at rates depending on temperature. If the temperature of drying is low, evaporation is slower, as a result, the microcrystalline bridges formed are bigger in size but their number is small. Conversely, if the temperature is high the evaporation is faster and the microcrystalline bridges are smaller in size, but their number is large. The increase in temperature from 30°C to 110°C and 140°C showed corresponding increase in caking and compression strengths of salt blocks were 100 and 125 per cent higher than those at 30°C.

**Effect of anticaking agent:** Effect of different anticaking agents was studied by adding suitable proportions of such agents to salt and then moulding the salt into blocks. From the compression strength of the resulting salt blocks, it was found that, calcium silicate reduced caking to the extent of 31 per cent and was best amongst the dry, solid, and finely powdered anticaking agents, while sodium
ferrocyanide added in form of solution, in the proportion of 10 ppm reduced the caking to 71 per cent and was the best of all studied.

RATE OF SOLUTION OF SALT

In soda ash and caustic soda chlorine industries, salt is dissolved to obtain the solution of required concentration prior to processing it further. Comparative study on the dissolution rates of five Indian salts was carried out under known experimental conditions, which may provide useful informations to these industries. Attempt was also made to correlate the rate of dissolution with bulk density, particle size distribution, hardness and calculated surface area of the salts. The results of these experiments showed that Kharaghoda salt, either as composite sample or of fixed particle size, in batch or continuous method dissolved slowly compared to rest of sea salt samples. The rates of dissolution, agreed very well with respective bulk densities and particle size distribution of different salt samples, however, hardness of salts and their calculated surface area could not be correlated.

Relevant literature on this subject has been reviewed and two equations derived by previous workers have been tried in this study to calculate the diffusion coefficient of salt. One of the equations was applicable to the results of rate of dissolution, particularly of finer particle size of salt. The inapplicability to coarser sizes, is supposed to be due to high irregularity of shape
and porous nature of crystals in case of sea salt compared to the regular shape, compact and non porous nature of rock salt crystals upon which the equations have been derived.