

DISCOVERY OF DEPOSITS OF SODIUM SULPHATE AT DIDWANA

BY

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WHEN the author was on a visit to Sambhar Lake in November 1940 in connection with an investigation into the possibility of exploiting the sodium sulphate and sodium carbonate deposits in the East Lake Bitterns Area,¹ the General Manager, Rajputana Salt Sources gave him a sample of 'pan scale' from Didwana, a salt source in Jodhpur State, about forty miles north-west of Sambhar.

'Pan scale', also called 'papri', is formed by the evaporation to dryness of the bitterns which remain after the manufacture of edible salt from subterranean brine at that place and it contains a high percentage of sulphate. When the General Manager received the analysis of this pan scale (Table I, Sample I) showing 85 per cent. of sodium sulphate, he expressed considerable surprise stating that the last reported analysis (*ibid.*, Sample II) in 1933 showed a much lower sulphate content and he suggested that another sample should be examined. The writer reported on this in January 1941 (Sample III) and expressed the view that this material might provide a good source of sodium sulphate for which there is a considerable and constant demand in India.

The matter was reported to the Central Board of Revenue and when Mr. R. K. Nehru, I.C.S., Collector, Central Excises and Salt, North-Western India, visited Didwana in the following March, he sent a number of samples of 'papri', collected from different pans, for analysis. These samples which varied very widely in sulphate content were mixed, the average analysis being shown in Table I, Sample IV.

TABLE I
Didwana Papri

	Sample I %	Sample II %	Sample III %	Sample IV %
Insolubles ..	0.27	2.80	0.56	3.14
Sodium chloride ..	13.05	69.8	19.26	63.04
Sodium sulphate ..	85.22	20.28	78.00	29.50
Sodium carbonate ..	0.70	6.78	0.58	0.35
Sodium bicarbonate	0.76	0.08	0.84	0.41
Undetermined and moisture ..	—	0.68	0.76	1.56

This very wide range of composition of papri or pan scale is not unusual, individual samples collected containing from 18 to 80 per cent. of sodium sulphate. This is explained by the method of formation of the papri which will be clearly understood from the description of Didwana salt manufacture given later, and the subsequent discussion.

The Collector proposed to ascertain if some industrial use could be found for papri of which, at the present scale of salt manufacture, about 15,000 to 20,000 maunds would be available annually. Mr. J. M. Saha, M.Sc., C.R.C.S., Chemical Examiner, Central Excises and Salt, North-Western India, expressed the view that a salt having the composition of Sample No. IV, Table I, would be very suitable for curing hides and skins. The Collector asked him to submit a further report on the possibilities of Didwana papri and, with this object in view, he visited the Didwana Salt Works in May 1941.

Although by this visit Saha did not improve on his previous report on 'papri', he made a valuable contribution to India's industrial development in the discovery of a plentiful source of high grade, naturally occurring sodium sulphate and, in reconstructing its genesis, devised an improved method for the manufacture of high quality salt from Didwana brine.

Saha observed that the beds of the crystallising pans were formed of a thick crust of a very hard crystalline substance called "rohr" which was reported to be as much as three feet deep in some places.

Samples drawn from two different pans had the following composition.

TABLE II
Didwana Pan-bed Crust or 'Rohr'

	I (%)	II (%)
Inorganic insolubles	11.90	5.98
Organic insolubles	0.52	0.30
Sodium sulphate	82.74	93.17
Sodium chloride	4.50	0.40
Undetermined	0.34	0.15
Sodium sulphate on water soluble components	94.84	99.56

According to Saha's most recent calculations, over fifty lakh maunds and possibly a crore maunds of rohr are available for recovery.² About 3,000 tons of the rohr, very rich in anhydrous sodium sulphate, have recently been excavated from a few pans with a view to commercial exploitation, and Table III gives analyses of samples from different depths of a particular deposit.

TABLE III
Didwana Pan-bed Crust or "Rohr"

	Top sample %	Middle sample %	Bottom sample %
Insolubles	0.40	1.08	0.35
Sodium chloride	1.10	1.10	1.46
Sodium sulphate	98.11	97.50	97.50
Sodium carbonate	0.11	0.13	0.13
Sodium bicarbonate	0.11	0.21	0.34
Moisture	0.16	0.21	0.31
TOTAL	99.99	100.23	100.09

The Government of India are operating the Didwana Salt Works for the manufacture and sale of salt on lease under a treaty with the Jodhpur State to whom the area belongs, and the State is making arrangements for marketing this new and valuable source of salt cake.

PRESENT METHOD OF MANUFACTURE OF
SALT AT DIDWANA

Salt has been manufactured at Didwana in Jodhpur State, Rajputana, from times

immemorial. The salt source is an oval-shaped depression, about 4 miles long and 1½ miles broad, which generally remains dry, except for a short time during the annual monsoon.

The total area developed so far for the production of salt is 92 acres or less than 5 per cent. of the total available. Wells about 6 feet in diameter and 16 feet in depth are sunk in the depression. Kul (well) brine of unusually high density (Table IV) is found at a depth of about six feet from the surface and the supplies are said to be inexhaustible.

Round the wells, shallow evaporating pans are made of varying size and about one foot deep. Originally they had clay beds. The warm brine is taken from the wells by means of earthenware pots attached to the ends of lever lifts (chaunch).

The brine is run into the pans and is concentrated by solar evaporation and deposits salt, the multiple accretion system of manufacture being followed. The pans are charged to a depth of 1" to 2" with brine drawn from the wells. Evaporation and crystallisation take place and the pans are again charged, the same process being repeated until, after a few weeks, a thick crust of salt has been obtained. Much of the sulphate crystallises with the salt and naturally the quality of the product is poor [Table V, (a) and (b)]. Underneath this salt and in course of salt manufacture extending over many years, a hard crystal-

TABLE IV
Didwana 'Kul' (well) Brine

Density ^o , Be'	26.9 ^o 37.5 ^o C. %	26 ^o 39 ^o C. %	25 ^o 39 ^o C. %	24 ^o 39 ^o C. %	23 ^o 37.5 ^o C. %	20.9 ^o 37.5 ^o C. %
Sodium chloride	32.99	19.53	18.49	18.27	16.05	16.97
Sodium sulphate	5.80	5.95	6.56	5.37	7.64	4.68
Sodium carbonate	0.51	0.87	0.42	1.04	0.48	0.62
Sodium bicarbonate	0.53	0.56	0.37	0.63	0.53	0.58
Total solids	29.88	26.91	25.84	25.31	24.70	22.85
Water	70.12	73.09	74.16	74.69	75.30	77.15
<i>The above results expressed in terms of dry matter are given below.</i>						
Sodium chloride	76.93	72.56	71.55	72.18	64.98	74.31
Sodium sulphate	19.41	22.11	25.39	21.21	30.93	20.44
Sodium carbonate	1.71	3.23	1.63	4.11	1.94	2.71
Sodium bicarbonate	1.95	2.10	1.43	2.50	2.15	2.54
	100.00	100.00	100.00	100.00	100.00	100.00
Percentage ratio of sulphate to chloride	25.23	30.52	35.49	29.42	47.61	27.51

crystalline bed of sodium sulphate has formed cumulatively on top of the clay bed.

The manufacturing season starts at the beginning of February and continues until the middle or end of May and sometimes even later. The mother liquor (bitterns) left in the pans after the extraction of salt subsequently dries and forms into a thick scale called 'papri' (v.s.). After each monsoon, it is only necessary to remove the mud and the papri from the pans and they are again ready for the manufacture of salt.

As ordinarily manufactured, Didwana salt is very dull and unattractive in appearance; the composition of two typical samples [Table V, (a) and (b)] indicate its poor quality, the principal contaminant being sodium sulphate.

TABLE V
Didwana Salt

	As manufactured by the usual process (%)		As manufactured by Saha's process (%) (vide below)	
	(a)	(b)	(c)	(d)
Insoluble matter ..	0.66	0.61	0.17	0.38
Sodium chloride ..	88.76	85.61	98.24	97.52
Sodium sulphate ..	9.45	12.79	0.85	1.40
Sodium carbonate ..	0.27	0.11	0.05	0.21
Sodium bicarbonate	0.13	0.08	0.08	0.08
Moisture and undetermined ..	0.73	0.80	0.61	0.41

An examination of the composition of typical samples of brine from which the salt is manufactured (Table IV) will show that the indifferent quality of the salt made by the current method is not unexpected. The brines are of remarkably high density and the proportion of sodium sulphate to sodium chloride is very high, approximately 25 to 48 per cent.

SAHA'S THEORY OF THE FORMATION OF THE BED CRUST

On cold winter nights in February at the beginning of the annual manufacturing season, when the temperature of brine falls low, the solubility of the sodium sulphate falls sharply while that of the sodium chloride is not much affected. The solubility of the sodium sulphate is also further reduced by the presence of the sodium chloride so that, in cooling from over 80° F. (27° C.) to the cold weather temperature of about 36-40° F., sodium sulphate

crystallises out as the decahydrate, Na₂SO₄·10H₂O and deposits on the pan bed. This probably goes on night after night until the brine is sufficiently concentrated to deposit sodium chloride, by which time a large proportion of the sodium sulphate will have probably crystallised out. Saha thought that, up to a certain point, this separation of sulphate was specific, the hydrated salt losing water due to rise in temperature at a later stage. His conjecture was based on the composition of the samples of bed crust (rohr) which consist mainly of anhydrous sodium sulphate, remarkably free from the chloride and carbonates of sodium. The existing bed crust must have been formed by the sulphate thus separated only from the first few charges of brine fed into the pans each year. It has, therefore, taken generations to attain its present thickness. The sulphate separated in the later charges of the pans would deposit on the existing crystals of salt and thereby lower its purity.

LABORATORY EXPERIMENTS

Working on this theory of the formation of the bed crust, he conducted experiments at the Central Revenues Control Laboratory, New Delhi, on samples of impure brine brought from Didwana, which yielded very satisfactory results and confirmed the theoretical reasoning.

Using artificial refrigeration, he showed that the separation of the sulphate and purification of the brine were most satisfactory at temperatures of from 36° F. to 42° F. The brine thus purified yielded samples of beautifully clear crystalline salt having as high a purity as 98 per cent. [vide Table V, (c) and (d)], while, from the crystalline Glauber's salt, anhydrous sodium sulphate separated when the laboratory temperature rose to summer heat.

On the results of these experiments, Saha proposed a scheme of manufacture calculated both to improve the quality of salt and to produce the valuable by-product, sodium sulphate, in commercial quantities. He suggested that the manufacturing season at Didwana should commence from the beginning of November and continue until February or March, i.e., so long as the minimum night temperatures fell below 60° F. The method proposed that a certain number of pans to be called "eliminators" should be set apart for the separation of

sulphate, the resultant purification of the brine being assisted by natural agency of the low atmospheric night temperatures prevailing at Didwana. The eliminator pans, fully exposed to the cold atmosphere, should be charged to a depth of about 4 to 5 inches and, when the maximum amount of sulphate has separated but before the crystallisation of salt has commenced, the brine thus purified should be transferred in the early morning to a separate set of "crystallising pans" where, by the day-time heat and breezes, it would be evaporated for the manufacture of salt.

The separated decahydrate would be dehydrated before marketing.

FIELD WORK AT DIDWANA

Experiments on a large scale were next conducted at Didwana in the months of December and January, 1941-42, using specially selected existing pans and also pans newly constructed for the purpose. The author accompanied Saha on one of his visits and was much impressed with the success of his experiments, the only major difficulty encountered being that the temperature of the hot brine never fully fell to the lower atmospheric temperature anticipated. It was observed that the desired low temperatures actually occur at Didwana during November to February but, while the minimum temperature attained at one time was as low as 21.5° F., it usually varied between 32° and 40° F., while the brine temperature always remained about 15° F. higher than the minimum atmospheric temperature recorded. As a result of this and in spite of the very low range of atmospheric temperatures, the separation of sulphate and the purification of the brine were not so effective as Saha expected nor as complete as was promised by his laboratory experiments. He is of opinion that this is due to the fact that the natural temperature of the ground is high and that its radiation prevents the temperature of the brine from falling to the atmospheric level. In order to circumvent this difficulty, he has suggested that the eliminator as well as crystallising pans should be constructed on a special type of bed.

On the whole, however, the results obtained were very satisfactory and the process is undoubtedly workable and easy of operation even by the illiterate local salt manufactur-

ers (deswals). Thus, apart from the discovery of this rich and plenteous source of sodium sulphate which should be sufficient to meet India's entire demand for some decades to come, the new method devised for the production of an improved quality of alimentary salt would simultaneously ensure the annual production of sodium sulphate on a large scale.

It has been found that, for every lakh maunds of salt produced, 15 to 20 thousand maunds of anhydrous sodium sulphate will be available. The average purity of the salt and the sulphate thus produced will be 97-98 and 97 per cent. respectively.

Saha's process has the great merit of simplicity in execution and in the words of the Collector "it kills several birds with one stone". A better quality of salt could be placed on the market, the season could be extended resulting in higher production and unemployment amongst the deswals would be relieved. Didwana would also increase in importance as a source of alimentary salt, the dependence on Sambhar for salt in the North of India being thereby considerably reduced and a valuable and much wanted industrial bye-product would be obtained in quantities. This annual supply of sodium sulphate would be supplementary to the rohr deposits mentioned earlier in the paper and the total output should satisfy India's entire demand for salt cake.

This scheme of salt manufacture will not interfere in any way with the normal recovery of the ordinary quality salt. This, as in current practice, should be started in February or March using the same pans after the winter manufacturing season is over. The deswals will thus remain employed for the greater part of the year to their great economic benefit.

THE THEORETICAL EXPLANATION OF THE DIDWANA DEPOSITS AND SAHA'S PROCESS

Ignoring the small percentage of carbonates present, in terms of the phase rule, the simple system involved is $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ and it is complicated only by the possible existence of the hydrates of sodium sulphate. Of these, the only one of any consequence is the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

The observed facts are explained as follows.

At the temperature of 37.5° C. at which the brine is drawn from the well, the solution is only rarely saturated with respect to the salts. It is usually unsaturated, though a study of the International Critical Tables will show that analysis No. 1 in Table IV practically corresponds with that of a saturated solution at the $\text{Na}_2\text{SO}_4\text{-NaCl}$ transition point at 37.5° C., the hydrates of sodium sulphate being incapable of existence at that temperature.

The presence of sodium chloride has the effect of lowering the $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ — Na_2SO_4 transition point, the lowering being greater the higher the concentration of sodium chloride until a minimum transition point of 17.9° C. is reached, the transition point for the pure salt being 32.3° C. at atmospheric pressure.

In the circumstances described, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ is likely to separate at temperatures of 20° C. (68° F.) and lower which prevail in the cooler weather.

While the solubility curve of the decahydrate is fairly steep (considerable increase of solubility with rise in temperature), the anhydrous salt has a "negative" solubility curve. The separation of the decahydrate from the solution effects a concentration of the liquid phase with respect to sodium chloride by removing from the solution water amounting to 1.27 times the weight of the sodium sulphate itself. This may involve the partial co-precipitation of some sodium chloride but, as will be observed from the brine analyses (Table IV), the ratio of sodium sulphate to sodium chloride is such that the sodium chloride can still stand some increase in its concentration owing to the removal of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ before its saturation point is reached. The tendency of the sodium chloride to separate is to some extent counterbalanced by the removal of sodium sulphate, the presence of which lowers the solubility of sodium chloride. The separation of the sodium chloride will thus be relatively small but the temperature range over which Glauber's salt crystallises out will be somewhat increased. It is of course possible that some anhydrous sodium sulphate will crystallise out from the hot brine but this is of no consequence because it would ultimately change to the hydrated salt in contact with the aqueous solution at the lower temperature.

The brine, partly denuded of its sodium

sulphate at night and early morning cold weather temperatures in the eliminator pans, can now be run into the (salt) crystallising pans for solar concentration at higher temperatures. This rise in temperature permits a greater concentration of sodium sulphate in solution before becoming saturated with respect to it and results in the separation of a crust of sodium chloride reasonably free from sulphate, because the solubility of sodium chloride does not vary much with temperature and so will speedily come to saturation on simultaneous evaporation and rise in temperature.

These relationships are shown in Fig. 1 which is only diagrammatic. The presence of small quantities of the carbonates of sodium does not materially affect the system and has been ignored.

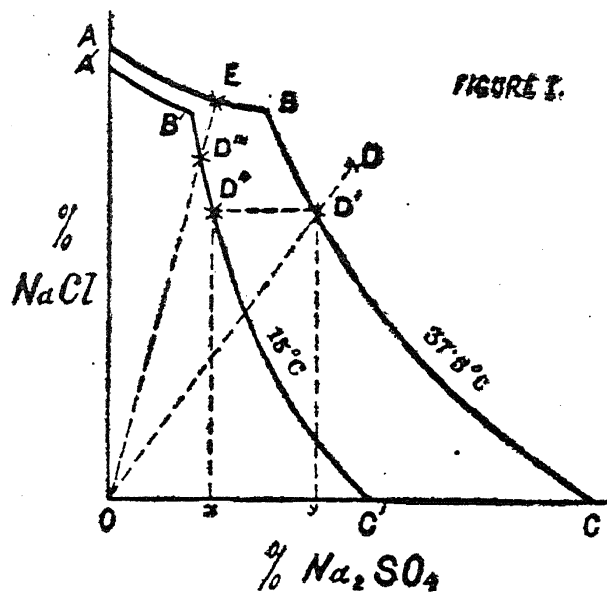


FIGURE 1.

A-B-C is the $\text{Na}_2\text{SO}_4\text{-NaCl}$ solubility curve at 37.5° C. and A'-B'-C' is the corresponding solubility curve for 15° C.

For convenience, sodium sulphate is plotted in terms of Na_2SO_4 though the solid phase for the lower curve (15° C.) is the decahydrate, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$.

Suppose the brine drawn from the well has the (unsaturated) concentration D. This will correspond with a point D' on the 37.5° C. saturation curve A-B-C. The solid phase in contact with this solution would be anhydrous sodium sulphate. Now imagine that this solution is cooled quickly to 15° C. Assuming that the concentration of the sodium chloride remains approximately the same, the corresponding point on the 15° C. curve would be D' and a considerable amount of sodium sulphate, corresponding with the difference in the concentration, y-x

on OC would have separated. But, at 15° C. this sodium sulphate which separates as decahydrate would actually have taken with it 1.27 times its weight of water and this would increase the concentration of the sodium chloride so that the composition of the liquid phase actually attained may be taken as D". On further concentration, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ could separate until point B' is attained but only cooling takes place in the eliminator pans and not solar evaporation. At D" therefore the brine is run off from the deposited $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ into the crystallising pans. Here the temperature rises and, on the Na_2SO_4 -NaCl curve at 37.5°, the point attained (assuming no separation of solid phase to have taken place) will be E on the line joining O to D" and produced to cut the curve AB.

The effect of this is that the solid phase in equilibrium with the solution, abruptly changes from $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to NaCl. Now solar evaporation can proceed, the concentration of the liquid phase increasing along the composition curve EB with deposition of sodium chloride until composition B is attained. At this point Na_2SO_4 would also separate. Before this happens, either more brine must be added from the eliminators or the mother liquor must be run away so that contamination of the salt crust may be obviated.

FORMATION OF ROHR

In the process as practised for many generations, much decahydrate obviously separated at the bottoms of the pans. The

temperature subsequently rose beyond that at which $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ can exist and this salt lost water and became converted into anhydrous salt, assisted by the presence of the sodium chloride. The anhydrous sodium sulphate was left at the bottom of the pan and the sodium chloride which may have been deposited with the Glauber's salt passed into solution and diffused into the supernatant brine eventually adding its quota to the salt crust. The finely divided sodium sulphate slowly changed into the larger crystals obtained on excavation at a later stage. This process continues adding its quota to the bed annually, and the high percentage of sodium sulphate in the rohr, contaminated by wind-borne dust and sand, is accounted for on a scientific basis.

PAPRI

After crystallisation is over and the salt removed, the residual mother liquor is left in the pans to dry out and is recovered as "pan scale" or "papri", *vide* Table I.

Theoretically, the proportion of sodium chloride and sulphate in "papri" should correspond with that in the liquid phase at the transition point at the final temperature attained but, owing to the conditions including variable temperatures under which the drying out occurs, such a theoretical composition for papri cannot be expected and the widely differing compositions recorded are not anomalous.

1. *Records of the Geological Survey of India* (in the press). 2. I. B. Audea, B. C. Gupta, P. C. Roy and Mehdi Hussain, *Ann. Geol. Surv. Ind.*, 1942, 77, 36; 42.

OBITUARY

Prof. Richard Willstatter

READERS of *Current Science* will note with regret the death of Prof. Willstatter, one of the great masters of organic chemistry, on August 3, 1942, in Switzerland, a few days before his seventieth birthday, and three years after narrowly escaping a concentration camp when he was at Munich.

Starting with his brilliant work on alkaloids, he passed on to a variety of problems on catalysis, etc., and thence to intensive studies of natural colouring

matters, principally chlorophyll, carotenes, and anthocyanins. The last phase of his work was another series of intensive investigations on the isolation, reactions and constitutions of enzymes, carried out with a brilliant band of collaborators. Willstatter was the first to develop the technique of selective adsorption in the preparation and separation enzymes. He was awarded the Nobel Prize in 1920.