

THE ORIGIN OF "ROHR" AT DIDWANA

By H. B. DUNNICLIFF, C.I.E.

IN the June issue of *Current Science*, Dr. E. Spencer¹ has given an explanation of the formation at Didwana of the beds of thenardite or crystalline anhydrous sodium sulphate, locally known as 'rohr', which he claims to be more in harmony with facts than my thesis based on phase rule considerations which appeared in the January number of this *Journal*.²

In my desire to be brief, I omitted from that article much of the laboratory and field experimental evidence, part of which I now submit in support of my contention that the formation of sodium sulphate decahydrate antecedent to the development of thenardite is the normal sequence of events in the pans during that portion of the season when night and morning temperatures and the concentration of the brine in the pans make the hydrated salt alone or mixed with sodium chloride, the only possible solid phase according to accepted physical laws.

The manufacturing season commences about the middle of February, the first crop of salt being collected three or four months later. The season normally finishes at the end of April by which time about three lakh maunds of salt would have been harvested. If, however, the demand is great, as in 1942 and 1943 (4.24 lakh and 3.75 lakh maunds respectively), the season is extended to the end of May and even well into June, but the salt harvested in the latter months is discoloured through contamination with dust and contains increasingly high percentages of sodium sulphate.

In certain circumstances, the temperature conditions necessary for the separation of Glauber's salt may persist until about the middle of March.

Table I giving the maximum and minimum atmospheric temperatures at Didwana for the first three months of 1942, studied in conjunction with Table II (p. 296), supports this view. The brine would not attain these minima, the difference between atmospheric and brine temperature would vary with prevailing climatic conditions, the brine temperature being consistently higher than that of the (minimum) atmospheric temperature. The difference of 15° F. between pan and atmospheric minimum temperatures was observed in Saha's experimental eliminator pans (Ref. ², pp. 9 and 10) in which the layer of brine was far deeper (up to 10 inches) than the shallow layers of brine (1½-2 inches) used by the deswals. This led to a greater retention of heat in Saha's field experiments than in the normal process of salt manufacture in which a difference of not more than +10° F. might be expected.

Dr. Spencer's laboratory observations and conclusions have made a valuable contribution to this important subject but his experiments have not been conducted under conditions comparable with those which obtain at the salt source.

Thus, the evaporations have proceeded at an approximately uniform temperature of 90° F., which happened to be the temperature in the

TABLE I
Maximum and Minimum Temperatures at Didwana (° F.)

| | January 1942 | | February 1942 | | March 1942 | |
|----|--------------|------|---------------|------|------------|------|
| | MAX. | MIN. | MAX. | MIN. | MAX. | MIN. |
| 1 | 79 | 35 | 82 | 43 | 90 | 55 |
| 2 | 81 | 37 | 82 | 39 | 88 | 48 |
| 3 | 82 | 36 | 77 | 36 | 90 | 54 |
| 4 | 70 | 30 | 77 | 32 | 84 | 50 |
| 5 | 79 | 43 | 75 | 30 | 91 | 55 |
| 6 | 82 | 41 | 79 | 34 | 88 | 54 |
| 7 | 82 | 48 | 81 | 34 | 77 | 47 |
| 8 | 84 | 54 | 86 | 43 | 79 | 48 |
| 9 | 70 | 23 | 88 | 40 | 93 | 51 |
| 10 | 64 | 22 | 75 | 48 | 95 | 51 |
| 11 | 57 | 23 | 88 | 50 | 95 | 51 |
| 12 | 68 | 24 | 89 | 52 | 97 | 55 |
| 13 | 66 | 34 | 75 | 37 | 92 | 52 |
| 14 | 68 | 32 | 79 | 35 | 93 | 51 |
| 15 | 72 | 41 | 80 | 36 | 97 | 51 |
| 16 | 73 | 36 | 80 | 35 | 102 | 51 |
| 17 | 70 | 37 | 87 | 45 | 97 | 55 |
| 18 | 70 | 37 | 74 | 34 | 98 | 59 |
| 19 | 65 | 32 | 74 | 32 | 104 | 59 |
| 20 | 65 | 32 | 86 | 50 | 86 | 57 |
| 21 | 70 | 34 | 86 | 57 | 91 | 55 |
| 22 | 76 | 34 | 88 | 50 | 91 | 55 |
| 23 | 77 | 32 | 86 | 52 | 102 | 59 |
| 24 | 81 | 39 | 89 | 50 | 106 | 59 |
| 25 | 73 | 34 | 91 | 55 | 102 | 66 |
| 26 | 73 | 35 | 90 | 50 | 103 | 70 |
| 27 | 77 | 43 | 80 | 55 | 102 | 57 |
| 28 | 75 | 38 | 88 | 54 | 95 | 50 |
| 29 | 74 | 41 | | | | |
| 30 | 81 | 45 | | | 99 | 55 |
| 31 | 81 | 45 | | | 102 | 57 |

November 19-30, 1941: Max. 93° F.; Min. 41° F. (Max. Min. = 47° F.).

December 1-31, 1941: Max. 88° F.; Min. 35° F. (Max. Min. = 48° F.).

laboratory where the work was carried out, while, in the field, the crux of the immediate issue is not the concentration of the brine in the pans, but the difference between the relatively high temperature at which the unsaturated brine is fed into the pans, and the much lower supervening night and early morning temperatures before there has been any appreciable evaporation.

Even when some daytime evaporation takes place, fresh crystallisation occurs during the following night in the early part of the season, the deposit of Glauber's salt (which subsequently decomposes into the anhydrous sulphate) accumulating with each addition of brine.

The arguments on page 177, paras 3 and 4, and page 178, paras 1 and 2 of Dr. Spencer's

paper¹ do not appear to me to be relevant and the discussion of the phenomenon in terms of the solutions at the sodium sulphate-sodium chloride transition points is not applicable to the general proposition. Quantities of phases in conjugate solid and liquid phases formed by chilling unsaturated solutions to temperatures at which they are supersaturated cannot be calculated by the simple subtraction of percentages, for this purpose, the appropriate isothermal or polythermal diagrams are necessary.

Dr. Spencer has, however, presented a scientific and highly probable explanation of the unexpectedly low percentage of sodium chloride in the 'rohr' when conditions are such that the two anhydrous salts must separate simultaneously. This is based on the difference between the densities of the crystals of NaCl and Na₂SO₄, assisted by the strong tendency of the NaCl to form box-like floating crystals. We have discussed this problem and I am in complete accord with Dr. Spencer's views where the anhydrous sulphate is directly deposited, but I shall show that Glauber's salt, even if co-precipitated with some sodium chloride as is normally the case, will ultimately yield the anhydrous sulphate relatively free from sodium chloride.

Table II gives the solubility relationships³ for the system NaCl-Na₂SO₄-H₂O at important points.

Na₂SO₄) at which, from a solution also containing 13.6 per cent. NaCl, a mixture of Na₂SO₄, 10 H₂O and Na₂SO₄ is deposited. Between 63.5° and 77° F., however (*vide* Table II), there would be solutions having lower concentrations of Na₂SO₄ from which the mixture of Na₂SO₄ and Na₂SO₄, 10 H₂O would separate. For a detailed study of this the full polythermal diagrams and data would be necessary.

When Glauber's salt separates from 'kul' brine containing 18 per cent. NaCl and 6 per cent. Na₂SO₄ at about 27° C. by simply cooling it to 10° C., the residual brine could only contain about 3.1 per cent. of Na₂SO₄ in presence of 18 per cent. NaCl, the balance of the Na₂SO₄ (2.9 per cent.) having crystallised out as Na₂SO₄, 10 H₂O. The removal of the water as water of crystallisation automatically increases the concentration of the NaCl so that, the curve being steep, the transition point may be reached quickly and some NaCl separate with the Na₂SO₄, 10 H₂O. This effect would be intensified at 5° C. (41° F.) (*vide* Table III) and result in the separation of a still greater proportion of Glauber's salt. In my former paper,² the relationship is explained with the assistance of a diagram, but an approximate calculation will help the picture. Assuming that (unsaturated) 'kul' brine at 27° C. containing NaCl = 18 per cent.; Na₂SO₄ = 6 per cent., and H₂O = 76 per cent., is cooled to 10° C., the

TABLE II
Percent. in 100 Grams of Solution.

| 0°C. (32° F.) | | 10°C. (50° F.) | | 17.5° C. (63.5° F.) | | 25° C. (77° F.) | | Solid Phase |
|---------------|---------------------------------|----------------|---------------------------------|---------------------|---------------------------------|-----------------------------|---------------------------------|---|
| NaCl | Na ₂ SO ₄ | NaCl | Na ₂ SO ₄ | NaCl | Na ₂ SO ₄ | NaCl | Na ₂ SO ₄ | |
| 0.00 | 4.65 | 0.00 | 8.38 | 0.00 | 14.10 | 0.00 | 21.90 | Na ₂ SO ₄ , 10 H ₂ O |
| | | 3.87 | 5.80 (a) | | | | | |
| | | 8.39 | 4.16 | 8.12 | 8.51 | | | |
| 10.70 | 1.50 | 13.38 | 3.37 | 16.90 | 6.80 | 7.66 | 16.00 | |
| | | 17.35 | 3.16 (b) | | | | | |
| | | 23.27 | 3.57 | | | | | |
| 25.54 | 1.30 | 24.37 | 3.43 (c) | 22.30 | 7.31 | 13.53 | 15.42 | Na ₂ SO ₄ , 10 H ₂ O plus NaCl |
| | | | | | | 13.60 | 14.76 | Na ₂ SO ₄ , 10 H ₂ O plus Na ₂ SO ₄ |
| | | | | | | Intermediate Concentrations | | Na ₂ SO ₄ |
| | | | | | | 22.70 | 8.06 | Na ₂ SO ₄ plus NaCl |

Note: Anhydrous sodium sulphate cannot form below 17.9° C. (64.2° F.)

From these figures it will be observed that:

(i) A solution containing only, for example, (a) 9.67 per cent., or (b) 20.5 per cent. total salts can be in equilibrium with Glauber's salt.

(ii) A solution containing 18 per cent. NaCl and 6 per cent. Na₂SO₄ at 25° C. (77° F.) is unsaturated but, on concentration, the solid phase which would separate would be Na₂SO₄ or Na₂SO₄ plus NaCl. Glauber's salt can only be a solid phase at 25° C. at high concentrations of Na₂SO₄ (minimum 14.76 per cent.

residual brine could only contain about 3.1 per cent. of Na₂SO₄ in the presence of 18 per cent. NaCl (*vide* Table II and Ref. 3), the balance of the Na₂SO₄ (2.9 per cent.) having crystallised out as Na₂SO₄, 10 H₂O, simultaneously removing $2.9 \times 1.27 = 3.7$ parts of H₂O as water of crystallisation. In nature, supersaturation is not likely to occur. The residual brine should thus contain 18.0 parts NaCl 3.1 parts Na₂SO₄ and $(76 - 3.7) = 72.3$ parts H₂O or, calculated as percentages, NaCl = 19.3 per cent.; Na₂SO₄ = 3.3 per cent.; H₂O = 77.4

per cent. As a matter of fact, the solution is supersaturated with respect to $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ and the result will be that some more $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ will deposit and the point at which some NaCl also separates be attained. Accurate calculation by this method is not possible but about 50 per cent. of the sodium sulphate comes out as $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$.

In the field, when the temperature in the shallow pans rises above the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ - Na_2SO_4 transition point, the decahydrate loses water and changes into Na_2SO_4 . The water mixes with the liquid phase taking the NaCl (and some Na_2SO_4) with it, a process which is assisted by the stirring. Hence, even if originally contaminated with NaCl, the sodium sulphate deposited will be left behind considerably purified and the resultant composition of the liquid phase need have no relevance to the composition of the liquid phase at the NaCl- $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ transition point.⁶

In fact, the manufacture of high grade anhydrous sodium sulphate from Glauber's salt by adding solid common salt and heating to 20-22° C. by low pressure steam, is a commercial process.⁴

Thus, at Didwana, the water crystallised out is returned to the brine and becomes mixed with it. During the cold period, after some concentration by wind and rise of temperature, a further moiety of Glauber's salt can be deposited the following night and similarly for successive days so long as temperature and concentration conditions make $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ the only solid phase (*vide* Seidell³). The sodium sulphate will naturally be mixed with the sodium chloride crystallising out as stated by Dr. Spencer and, owing to the vertical direction of the curve, the transition point will be quickly attained after the bulk of the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ has separated.

In an actual field experiment in which masses of the decahydrate separated overnight, the unwashed but filter-paper-dried Glauber's salt analysed as follows:

- $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O} = 97.63$ per cent.;
- NaCl = 2.20 per cent.;
- $\text{Na}_2\text{CO}_3 = 0.07$ per cent.; and
- $\text{NaHCO}_3 = 0.08$ per cent.

At the daytime higher temperatures, when the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ passes into Na_2SO_4 , the water in the Glauber's salt would make a 4 per cent. solution with the sodium chloride present and some sodium sulphate would also naturally dissolve into the liquid phase to the equilibrium point.

LABORATORY EXPERIMENTS

In the laboratory experiments (Ref. 2, p. 9), the results set forth in Table III which has been condensed as far as possible by giving only the Na_2SO_4 and NaCl percentages were obtained.

Raw Didwana brine (Ref. 2, Table III, Samples 2, 3, 5 and 6) was kept in a refrigerator for sufficient time for equilibrium to be established, so far as was possible without stirring, at a temperature of about 40-42° F. (5° C.). Crystals of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, contaminated with NaCl, separated. Attention is drawn to the similarity of composition in Samples 2, 3 and

5, Table III (2), which corresponds to 6.35 per cent. NaCl on the crystal sulphate, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. This shows that the $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ -NaCl transition point was attained after the early separation of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ was completed.

TABLE III
(1) Raw Brine

| Sample No. | 2 | 3 | 5 | 6 |
|--|--------|--------|--------|--------|
| NaCl | 19.53% | 18.49% | 16.05% | 16.97% |
| Na_2SO_4 | 5.95% | 6.56% | 7.64% | 4.68% |
| NaCl: Na_2SO_4 | 3.28:1 | 2.8:1 | 2.10:1 | 3.63:1 |
| Average about 3:1 (NaCl=18%; Na_2SO_4 =6%) | | | | |

(2) Glauber's Salt Deposit Calculated on a Dry Basis

| | % | % | % | — |
|--------------------------|-------|-------|-------|---|
| NaCl | 13.11 | 13.15 | 13.15 | — |
| Na_2SO_4 | 85.09 | 85.45 | 85.78 | — |

Average proportions, Na_2SO_4 :NaCl = 6.5:1. In terms of actual components, this gives $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O} = 93.7$ per cent.; NaCl = 6.3 per cent., and the percentage composition of the crystalline mixture becomes $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O} = 91.6$ per cent.; $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O} + \text{NaCl} = 8.4$ per cent.

(3) Resultant Mother-Liquor or Purified Brine

| | % | % | % | % |
|--------------------------|-------|-------|-------|-------|
| NaCl | 21.44 | 21.44 | 18.14 | 22.90 |
| Na_2SO_4 | 1.98 | 1.45 | 1.88 | 1.75 |

(4) Purity of Salt Crystallised from Mother-Liquor

| | % | % | % | % |
|--------------------------|-------|-------|-------|-------|
| NaCl | 98.42 | 97.68 | 98.51 | 97.05 |
| Na_2SO_4 | 0.92 | 1.49 | 0.86 | 1.96 |

These figures for 5° C., seldom attained in nature, indicate a much higher order of elimination of sulphate than those quoted above for 10° C. (50° F.). This and the variable composition of the mother-liquor is due to absence of stirring and to variations of temperature which probably often fell below 5° C., as correct thermostatic conditions could not be maintained because the refrigerator had to be used for general laboratory purposes. Even with this high percentage of sodium chloride, the water in the Glauber's salt is sufficient to give about 12 per cent. sodium chloride solution on change of phase.

I hope that these details of experiments, which were not carried out under ideal labo-

ratory conditions but with an attempted approximation to natural conditions, will explain the possibility of the removal of half or more of the sulphate as decahydrate in a single stage under suitable temperature conditions which in fact exist for an appreciable part of the normal manufacturing season at Didwana. As explained above, the water of crystallisation returns to the liquid phase with some sodium sulphate but a second deposition of crystals takes place during the next cool night and so on.

CONCLUSIONS

I have discussed this problem with Dr. Spencer and we are agreed that the deposits are due to the two processes operating one after the other.

From mid-February to possibly about the middle of March, Glauber's salt separates and is subsequently dehydrated and deposited on the previous layers of thenardite.

This is succeeded by a short intermediate period when the hydrated and anhydrous sodium sulphate crystallise out together. For the rest (and greater part) of the season, the process described by Dr. Spencer¹ takes place. This is followed by the conversion of the finer deposits formed in either of the two ways into the massive form of natural crystalline sodium sulphate, thenardite.

Variations in the percentage of sodium chloride in the deposits may be due (i) to the extension of the season as in 1923 (7.49 lakh maunds); 1925 (4.02 lakh maunds); 1931 (5.34 lakh maunds), and 1932 (4.55 lakh maunds) when the demand for salt was high, (ii) to the incomplete purging from sodium chloride as described by myself, or (iii) to abnormal disturbances causing more sodium chloride than usual to separate in the process described by Dr. Spencer.

It is unfortunate that my proposal for a continuous scientific observation of the salt and 'rohr' production at Didwana was not accepted in 1941, as the results would have provided full data for the solution of this interesting phenomenon. Dr. Spencer and I are of opinion that detailed field work extending over a complete season, from November to June, including a full examination of Saha's eliminator pan proposals, is highly desirable.

SAMBHAR LAKE BITTERNS

On page 179 of his article (*loc. cit.*), Dr. Spencer makes certain suggestions regarding the separation of the components of Sambhar Lake bitterns. Elsewhere^{5,6} I have described in some detail the immense saline deposits in the East Lake Bitterns Area and have also attempted to re-construct the manner in which their stratified formation has been developed. Proposals have also been made for their commercial exploitation.

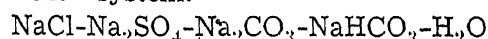
Although the NaCl:Na₂SO₄ ratio in Sambhar

kyar bitterns resembles the corresponding average ratio in Didwana brines, it is actually rather higher and the concentration of the carbonates of sodium (about 4 per cent. as Na₂CO₃) is too high to be disregarded as has been possible when discussing the crystallisation of Didwana 'kul' brines in which the carbonate percentage as Na₂CO₃ is usually of the order of 1 per cent. or under. Algal and bacterial impurities,⁸ not encountered at Didwana, also complicate the problem at Sambhar.

When allowed to crystallise out in kyars reserved for the purpose, the bitterns from the manufacture of kyar salt⁷ deposit "manufactured bitterns salt" of varied composition but averaging very roughly: NaCl = 62 per cent.; Na₂SO₄ = 22 per cent.; Na₂CO₃ = 7-8 per cent. and NaHCO₃ up to 3.8 per cent.⁶ This salt is now being produced in commercial quantities for industrial purposes.

Characteristics of the Didwana brines are, therefore, relatively low carbonate content, absence of double salt formation and the non-interference of organic matter.

Examination of the bitterns of salt deposits which have accumulated in the East Lake Area at Sambhar over a period of nearly forty years, involves the interpretation of a five-component system:



(in which CO₂ is also present) under peculiar and annually varying conditions. The progressive crystallisation and partial recrystallisation of the bitterns has yielded vast quantities of a considerable range of sodium salts together with sodium chloride. These include sodium bicarbonate, NaHCO₃; sodium sesquicarbonate or crystal carbonate, Na₂CO₃, NaHCO₃, 2 H₂O; burkeite, Na₂CO₃, 2 Na₂SO₄ (and possibly sesquiburkeite, 2 Na₂CO₃, 3 Na₂SO₄) (*vide Ref.*⁶ layers B, C and E). In 1939, careful investigation of these stratified deposits led to the discovery near the surface of a 3-4" layer of crystal salt of excellent quality. From this stratum,⁷ 13.9 lakh maunds of alimentary salt were extracted in the 1939-40 season while, in the following year, the early showers of the monsoon provided surface "washings" of concentrated brine from which 39.43 lakh maunds of kyar salt were crystallised out.

1. Spencer, E., *Curr. Sci.*, 1943, 12, 176.
2. Dunnicliff, H. B., *Curr. Sci.*, 1943, 12, 7.
3. Seidell, A., *Solubilities of Inorganic and Metal Organic Compounds*, D. Von Nostrand Inc., 1940, 1, 1234-5 and *International Critical Tables*, 1928, 4, 287.
4. Roberston, G. R., *J. Ind. Eng. Chem.*, 1942, 34, 133.
5. Dunnicliff, H. B., *Rec. Geol. Surv. Ind.* (in the Press).
6. Auden, J. B., Gupta, B. C., Roy, P. C. and Hussain M., *Rec. Geol. Surv. Ind.*, 1942, 77, 34.
7. Dunnicliff, H. B., *J. Sci. Indust. Res.*, 1943, 1, No. 4, p. 270.
8. Dunnicliff, H. B., and Padwick, *J. Ind. Chem. Soc., Indust. and News Edn.*, 1943, 6, 4.

PROF. A. V. HILL, F.R.S.

WE wish to extend a hearty welcome to Prof. A. V. Hill, F.R.S., who has just arrived in Delhi at the invitation of the Government of India. He is to study on the spot

the achievements of science and industry in India and to explore avenues of closer collaboration between Indian scientific workers and those of the United Nations.