THE ORIGIN OF THE "ROHR" OR ANHYDROUS SODIUM SULPHATE BEDS BELOW THE SALT PANS AT DIDWANA

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IN the January issue of *Current Science*, Dr. Dunnicliff[1] describes these Didwana sulphate deposits and explains their origin by separation of the decahydrate from the pan brine during the early colder period of the salt season, and the subsequent transformation of this decahydrate to the anhydrous salt. During a recent visit to this area I had the opportunity of examining the sulphate beds and of seeing something of the conditions under which they must have been laid down. It appears to me that an alternative explanation of their origin can be put forward, more in harmony with the facts.

QUALITY AND QUANTITY

Before discussing the origin, I would like to stress the remarkable freedom from sodium chloride of these "Rohr" deposits, especially if one remembers that they have originated by crystallisation from a solution containing three times as much chloride as sulphate. Up to the present time 200-300 tons of this material have been consumed by the Titaghur Paper Mills and this has all been carefully sampled wagon by wagon and analysed. The following figures indicate the average quality of this 200 tons:

excavated so far from four pans opened up. I understand that there are in all about 250 salt pans, and if these produce the same relative amounts of "Rohr" as the four pans excavated, there should be something in the order of 250,000 tons available at Didwana.

At the time of my visit a bed of "Rohr" two to three feet thick was exposed in one of the partly excavated pans. This bed consisted of massive interlocking crystals of the anhydrous sulphate "Thenardite".
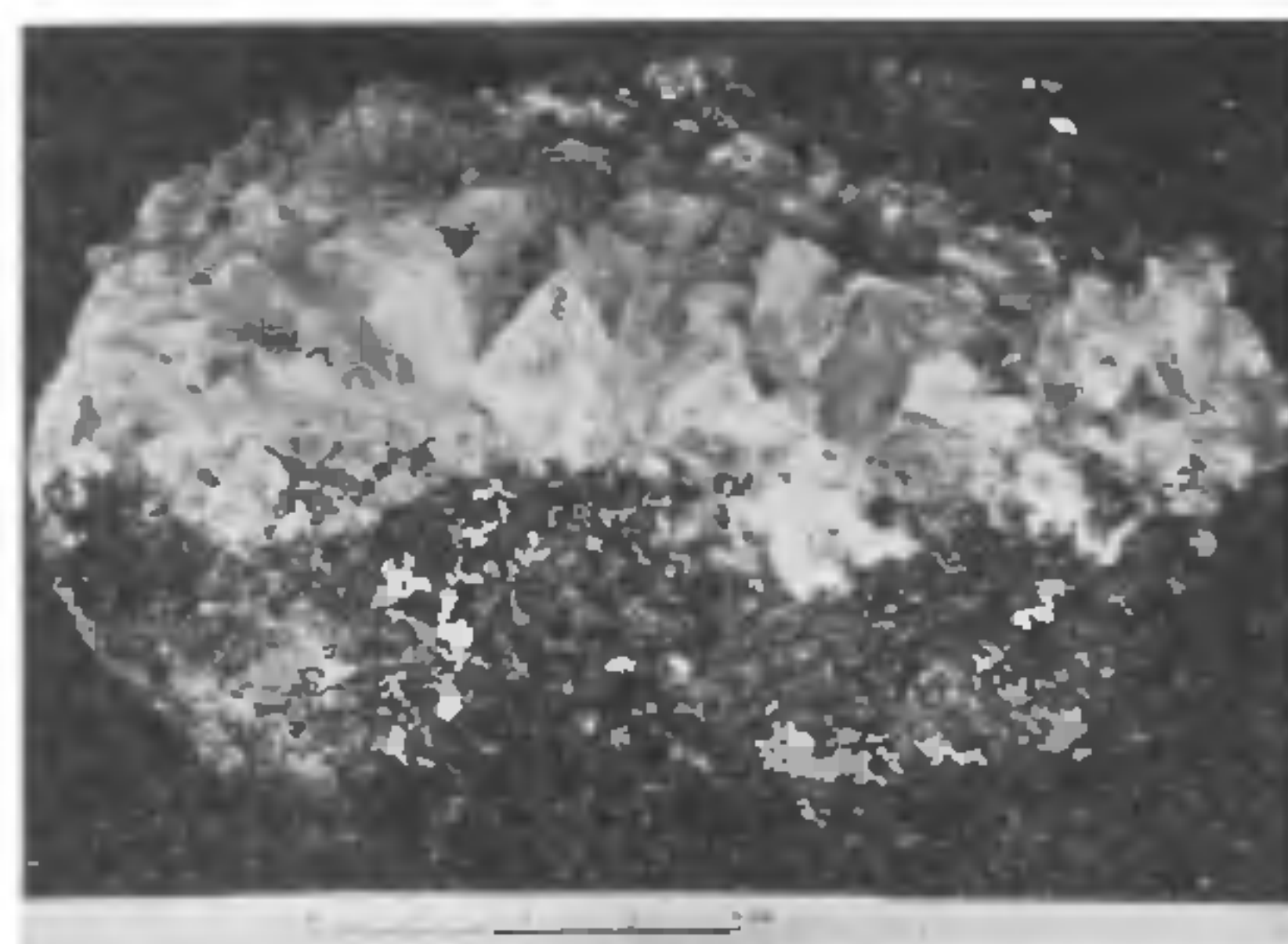

FIG. 1

	1	2	3	4	5	6	7	8
Moisture	0·15	0·15	0·10	0·20	1·13	0·88	1·82	0·74
Insolubles	5·26	4·66	6·70	5·65	11·89	5·37	6·06	9·42
Sodium sulphate	92·2	92·44	89·9	91·9	85·3	92·65	90·17	86·93
Sodium chloride	0·23	0·46	0·53	0·80	0·45	0·53	0·26	1·17
Sodium carbonate	0·21	0·10	0·10	0·10	0·21	0·16	0·22	0·17
Sodium bicarbonate	0·34	0·59	0·42	0·42	0·42	0·42	0·34	0·42
Iron and Alumina (as sulphates)	0·56	0·28	1·12	0·56	ND	ND	ND	ND
Calcium sulphate	0·36	0·24	0·24	0·24	ND	ND	ND	ND
Magnesium sulphate	0·30	0·30	0·45	0·30	0·30	0·30	0·40	0·45
	99·59	99·22	99·55	100·17	99·7	100·31	99·47	99·25

It will be seen that the average sodium chloride content runs well below one per cent., even on a basis of "silt free" material. It may be that the "Rohr" excavated from subsequent pan beds will contain more chloride, but this does not seem likely, since the above analyses probably represent a fair average of the 5,000 tons of "Rohr"

Specimens were obtained showing clusters of undamaged glass-clear crystals with individuals up to two inches in length and breadth. These are shown in the attached photographs. The crystals belong to the Orthorhombic system and are pyramidal, the principal face being a pyramid probably the Unit Pyramid (1.1.1).
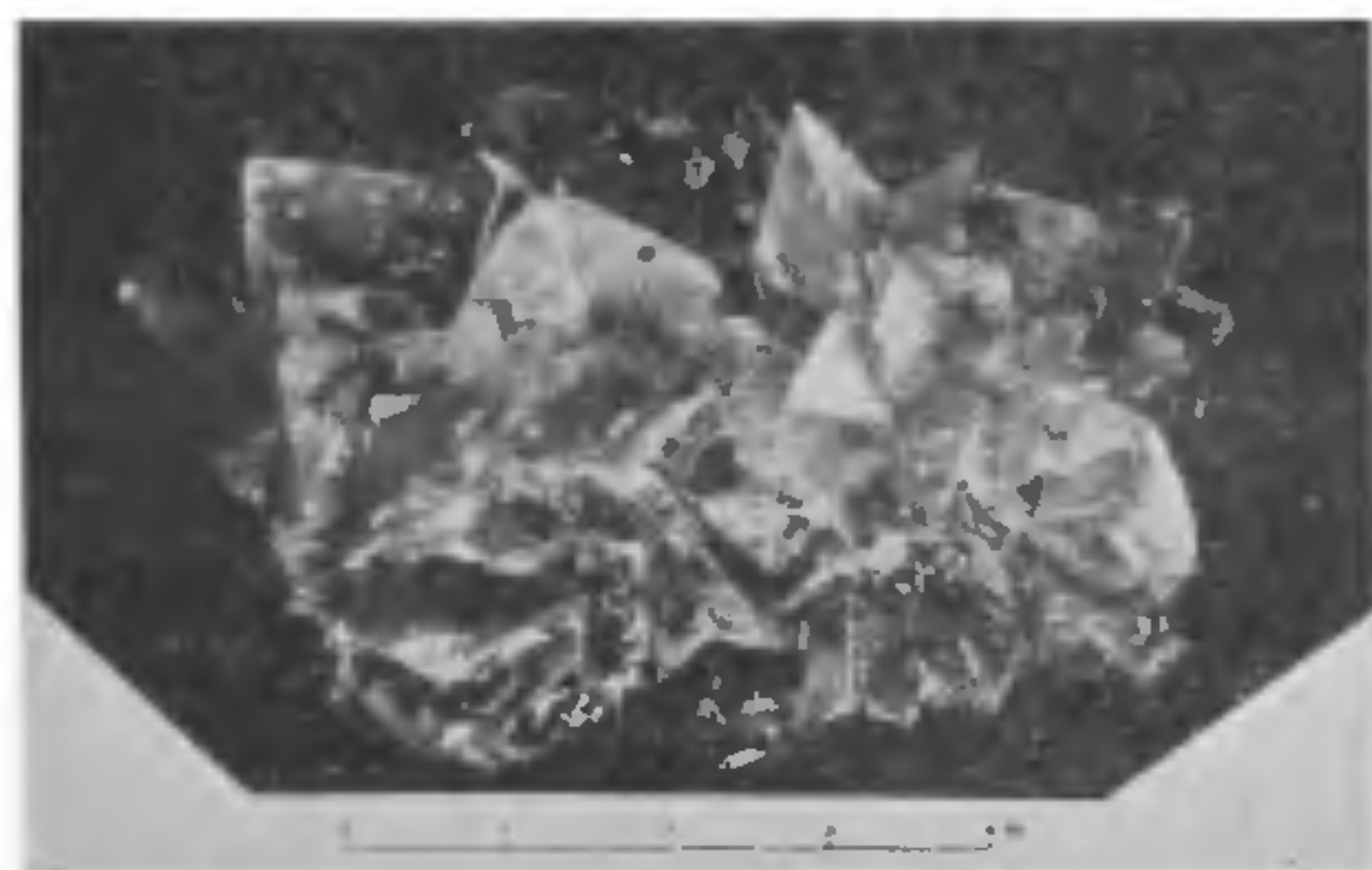
FIG. 2

ORIGIN OF THE DEPOSITS

According to Dr. Dunnicliff these "Rohr" deposits have been derived from crystallisations of the decahydrate (Na_2SO_4. $10 H_2O$) during the early cold weather period, when the pans are first filled with the well brine. The assumption is that during this period the temperature falls below the transition point for Na_2SO_4-·Na_2SO_4. $10 H_2O$ and that the decahydrate (Glauber's salt) then crystallises out. In order to understand this process and its implications, it is necessary to know something of the relative solubilities of sodium chloride and sodium sulphate and the effect of the chloride on the transition temperature of the sulphate.

· *Solubilities.*—The solubility of sodium sulphate (in the absence of sodium chloride) is fairly high but varies rapidly with the temperature as is indicated by the figures given below:[2]

Temperature	Solubility
40°F.	5%
60°	15%
80°	35%
90°	48%
93·2°	55%
100°	50%

Sodium chloride progressively decreases the solubility of the sulphate as is shown by the following solubility figures for a temperature of 90° F.

Sodium Chloride	Sodium Sulphate
5·25%	26·0%
9·45%	20·3%
16·16%	13·3%
22·0 %	7·8%

At 90° F. a solution containing 22·0 per cent. sodium chloride and 7·8 per cent. of sodium sulphate is saturated with regard to both components and if allowed to evaporate at this temperature both salts crystallise out simultaneously, the composition of the "mother liquor" remaining constant. Solutions of the two, salts on each side of this composition ratio will, on evaporation, deposit the one in excess until the above saturation ratio is reached.

Reducing the temperature of this "mother liquor" below 90° F. does not markedly reduce the solubility in respect to the sulphate (or chloride). Thus at 40° F. a solution saturated in respect to the chloride and sulphate still holds about 5 per cent. of the latter salt.[3]

Transition Temperatures.—At temperatures above 90° F. pure sodium sulphate solutions deposit the anhydrous salt (Thenardite) on evaporation. Below this temperature the decahydrate comes out. Sodium chloride depresses this transition temperature of the sulphate progressively, until in a solution saturated with respect to the chloride, the transition temperature has fallen to 64·2° F.

Practice at Didwana.—At Didwana the well brine is first fed into the pans about the middle of February. This brine contains on an average about 6 per cent. of sodium sulphate and about 18 per cent. of sodium chloride.[1,4] The maximum day temperature is then about 70° and the minimum night temperature 40° to 45° F. These are atmospheric temperatures and as indicated by Dr. Dunnicliff[1] it is probable that the ground and pan liquor temperatures may be as much as 15° F. higher than the minimum. On the coldest nights, however, the temperatures may fall occasionally below the transition point for the sulphate in which case some decahydrate would separate out. The amount could not be large, since the well brine only contains about 6 per cent. of sulphate and we have seen that 5 per cent remains in solution even at as low a temperature as 40° F.

Normal evaporation would, however, gradually increase the concentration of the sulphate (and chloride) until the saturation point had been reached. The brine would then contain about 22 per cent. of sodium chloride and about 8 per cent. of the sulphate. These conditions would be reached towards the end of February, by which

time the minimum night temperatures would have increased so as to reduce the possibility of decahydrate formation, especially in view of the temperature lag of the ground and the pan brine.

Let us assume, however, that the necessary low temperatures did obtain and that the maximum possible amount of decahydrate crystallised in this way from the saturated well brine prior to separation of the chloride. The amount so crystallised would be the difference between the solubilities at say 80°-90° F. and at 40° F., that is, 8 per cent. — 5 per cent. = 3 per cent. or only about 37 per cent. of the total sulphate in solution in the first batch of concentrated well brine fed to the pan to produce the first salt crop. From that time onwards the temperature would never again fall sufficiently low for the formation of the decahydrate in such a concentrated solution of the chloride.

During the season about five crops of salt are produced from successive additions of well brine. Hence the maximum amount of sulphate which could separate as decahydrate under the most favourable conditions would only be about 8 per cent. of the total sulphate content of the well brine fed to the pans during a season, which corresponds to about 2·5 per cent. by weight of the salt manufactured. The average annual production of salt over the past seventy years is about 13,000 tons and 2·5 per cent. of this is only 320 tons. At this rate of formation it would have taken about 800 years to accumulate these "Rohr" deposits.

A comparative study of the composition of the well brine and of the salt produced at Didwana also indicates that a much larger amount of sulphate has disappeared from the system than would be accounted for by an early separation as decahydrate. The analyses figures of Dr. Dunnicliff and others[1,4,6] show that the ratio of sulphate to chloride in the well brine is about one to three and only about one to eight or nine in the commercial salt (NaCl) produced. This represents a loss of more than 60 per cent. of the total sulphate fed into the pans, or about 8 times the amount which could have separated as decahydrate. Moreover, this sulphate must have crystallised pari passu with the salt throughout the season, otherwise the later salt crops would have been so enriched in sulphate that they would have been unsuitable for consumption. Unlike the practice at Sambhar Lake, there

is no removal of concentrated "Bittern" liquor from the crystallising pans at Didwana. As a matter of fact there would be no point in doing this, since the ratio of sulphate to chloride in the original well brine is almost as high as it is in the rejected "Bitterns" of the Sambhar Lake area. When the Didwana brine reaches crystallisation point by evaporation, it is almost saturated in respect to sulphate as well as chloride and the two salts must come out together, the only further enrichment of the "mother liquor" being in regard to the small amounts of carbonate and bicarbonate present.

Crystallisation Tests.—In an endeavour to obtain a clue to the discrepancies indicated above, laboratory experiments were carried out with saturated solutions of Didwana salt and sulphate. These were allowed to crystallise by evaporation at a temperature of about 90° F. Crops of crystals were removed periodically and examined, the mother liquor being analysed after the removal of each crop. Samples of the mother liquor were also allowed to crystallise on slides under the microscope.

It was found that when the mother liquor had reached a concentration of 22 per cent. sodium chloride and 7·8 per cent. of sulphate the two salts crystallised out simultaneously during slow evaporation, the liquor remaining constant in composition. In the shallow crystallising dish used, the chloride tended to form spongy box-shaped crystals which floated on the surface and eventually collected together in the form of a scum or layer. On the other hand the sulphate invariably crystallised as small dense double ended pyramids which separated mainly on the bottom of the dish forming eventually, a crystal layer or crust. Where crystallisation was clogged and rapid (round the edges of the dish or between the floating sodium chloride crystals) contamination with sulphate crystals occurred, but with free crystallisation as in the body of the liquor, the two salts crystallised separately. This is to be expected from the different crystallisation systems to which the two salts belong, the chloride to the cubic and the sulphate to orthorhombic system.

In one experiment, after a "crop" of chloride crystals had accumulated on the surface and had been removed, leaving a thin compact layer of sulphate crystals (with some chloride) on the bottom—the mother liquor was made up to the original

volume with a solution of the same composition but diluted slightly with water. By the time the liquor had again reached saturation point the chloride had been dissolved out from the bottom layer in the dish, leaving a thin layer of pure sulphate, which increased in thickness during the formation of the next crop of chloride crystals.

When crystallisation of the *saturated* mother liquor was observed on a slide under the microscope, it was noted that sodium chloride was *invariably* the first to crystallise, leaving a small quantity of liquor temporarily supersaturated in respect to the sulphate. The sulphate eventually crystallised as separate individuals, along with the last chloride crystals.

Interpretation of Results.—Assuming that crystallisation has taken place in the salt pans on the lines indicated above, the tendency would be for the smaller and more compact sulphate crystals to find their way to the bottom of the pan below the larger spongy salt crystals. This tendecy would be accentuated by the greater density of the sulphate than the chloride crystals (2·7 against 2·2) and by the density of the solution (1·25). It would also be greatly assisted by the raking and ridging process to which the salt crystals are subjected, in the pans. This process is carried out in order to encourage the formation of larger salt crystals (NaCl) and to prevent the tendency of the salt to form an adherent cake. There is no doubt, that with this difference in density of sulphate and chloride crystals, suspended in such a dense solution, the raking would tend to cause a gravity separation, somewhat similar to the jigging process commonly used in mining to separate minerals of different specific gravity.

After removal of each crop of salt crystals from the pan, more well brine is added and for a short period the pan liquor must be unsaturated with respect to chloride and sulphate. In becoming saturated the well brine is able to dissolve three times as much chloride as sulphate, so that the tendency would be to dissolve up any sodium chloride remaining in the pan from the residue of the salt crop, leaving the sulphate crystals in the bottom of the pan in a relatively pure condition.

This explanation would account for the difference between the sulphate contents of brine fed into the pans and that in the salt crop produced, a difference in the order

of 20 per cent. of the total weight of salt manufactured. Taking the average yearly production at 13,000 tons, 20 per cent. would represent an annual accumulation of 2,600 tons of sulphate, or 250,000 tons in about 100 years. This seems a more reasonable figure than 800 years.

It is worthy of note that without analytical help or guidance, the ancestors of these Didwana salt workers, or "Deswals" have evolved a simple and economical method of extracting a marketable salt (NaCl) from a brine so rich in sulphate. At the same time they have, unwittingly stored up, over several decades, rich deposits of nearly pure anhydrous sulphate, a salt for which there. is now an ever-increasing demand.

Sambhar Lake.—Combined to the Didwana well brine, the brine of Sambhar Lake is relatively very much richer in chloride than sulphate (and carbonate) as the following figures show.[7]

Sodium chloride—23·1 per cent.
Sodium sulphate—2·1 per cent.
Sodium carbonate—0·45 per cent.

The practice at Sambhar is to separate as much as possible of the chloride by evaporation, until the "mother liquor" approaches saturation point in respect to the other constituents, and then to discard it as "bitterns". In this way about 75 per cent. of the salt content of the brine is removed.

Average analyses[5,7] of this "bittern" liquor show that it contains approximately:

Sodium chloride—20·0 per cent.
Sodium sulphate—8 per cent.
Sodium carbonate—4 per cent.
Sodium bicarbonate—1 per cent.

If we disregard the carbonates this composition is not very different from that of the concentrated Didwana brine, and the question naturally arises whether the Didwana method of separation might not be applied to these bitterns to produce a saleable chloride, leaving the bulk of the sulphate (or sulphate-carbonate) behind at the bottom of the pans.

SUMMARY AND CONCLUSIONS

It is not disputed that Glauber's salt can be separated from Didwana well brine on the lines indicated by Dr. Dunnicliff and Saha, or that given suitable machinery for cooling and evaporation, practically the whole of the sulphate could be recovered as decahydrate from the brine, leaving the chloride in a fairly pure condition. Separation as decahydrate, however, does not

adequately explain the origin of these "Rohr" deposits, since the formation of the hydrous sulphate is only possible during the very early days of the crystallising season. The alternative explanation here put forward is that the anhydrous sulphate has crystallised, along with the chloride, throughout the salt season and that its partial separation from the latter in the form of "Rohr" at the bottom of the pan has been brought about by several factors operating together. These include:

(*a*) The tendency of the sulphate to form relatively small dense crystals and for these to find their way to the bottom of the pan by the mechanical action of stirring or "ridging".

(*b*) The tendency of the solution to become supersaturated in respect to sulphate and for this excess sulphate to crystallise at the bottom of the pan through density diffusion and where the temperature may be lower.

(*c*) The tendency of the chloride to crystallise as spongy "boxes" which float on the surface and eventually form a crust or layer.

(*d*) The removal of the salt crop and the replenishment of the pan with unsaturated well brine which dissolves out the chloride from the bottom sulphate layer, and allows the above process to be repeated again and again.

If this view is correct, a careful study of the practice at Didwana might yield information which would be of value in enabling the controlling factors to be so adjusted as to yield a still better separation of chloride and sulphate.

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1. Dunnicliff, H. B., *Curr. Sci.*, 1943, **12**, 7–12. 2. Martin, G., *Industrial and Manufacturing Chemistry*, 1917, **1**, 2, 285. 3. Robertson, J. R., *Journ. Ind. Eng. Chem.*, 1912, **34**, 133–136. 4. Auden, J. B., *Rec. Geo.. Surv. Ind.* Prof. Paper No. 1, 1942, **67**, 36. 5. *Loc. cit*, p. 33. 6. *Appendix Report—Salt Survey Committee*, Gov. Ind. Press, Calcutta, 1931, p. 100. 7. Hacket, C. A., Salt in Rajputana," *Rec. Geol. Surv. Ind.*, 1880, **13**, 3, 200.

NEPHRIDIA OF EARTHWORMS

IN a series of four memoirs recently published in the *Quarterly Journal of Microscopical Science* (Vols. 83 and 84), Prof. K. N. Bahl of the University of Lucknow, whose previous work on the nephridia of earthworms is so well known, has further added to our knowledge of this subject. In the first memoir he gives an account of the nephridia of the genus *Eutyphœus*, in which three kinds of minute nephridia—septal, integumentary and pharyngeal—can be distinguished. Of these the first two kinds open to the exterior, while the tufts of pharyngeal nephridia open into the lumen of the pharynx. He next describes the interesting nephridia of the genus *Hoplochœtella* which possesses large septal nephridia resembling those of *Lumbricus,* besides minute integumentary and tufted pharyngeal nephridia. The septal nephridia are remarkable in that they do not open separately to the exterior, but into a pair of longitudinal canals running along the parietes through the greater part of the body of the worm; these canals discharge their contents into the gut at its posterior end. The second memoir deals with three examples of multiple funnels. The South American giant earthworm *Thamnodrilus crassus* possesses nephridia, each of which possesses as many as *thirty four* functional funnels; the nephridium of *Hoplochœtella* has one large functional and 18 to 24 vestigial funnels; while the funnel of the nephridium of *Lampito* has two or three masses of cells, looking like embryonic funnels, on the neck of the single functional funnel. In the third memoir the nephridia of the different regions of the body of *Pontoscolex corethrurus* are described. This worm exhibits a very interesting condition of branching and division of the nephridia—in fact, the holonephridia are here "caught in the act of dividing up" into meronephridia, but the division is never complete, as even when hundreds of meronephridia are formed, as in the anteriormost pair of nephridia, they open to the exterior by a single bladder-like duct. In the fourth memoir the author describes the occurrence of the "enteronephric" type of nephridial system in *Megascolex cochinensis*, a type already discovered by him in four other genera of earthworms. The four memoirs form a very important contribution to our knowledge of the excretory system of the Oligochæta.   B. P.