

# Effect of Manganese in Solar Salt Works

G.C. Jain

D.S. Datar

Council of Scientific and Industrial Research  
New Delhi, India

Central Salt and Marine Chemicals Research Institute  
Bhavnagar-2 (Gujarat), India

## ABSTRACT

*Common salt due to its use by all people regularly and being a substance available cheaply, forms a good base for the inclusion of trace nutrients like calcium, iron, phosphorus, iodine, manganese, zinc etc. Processes have been developed in this Institute for the inclusion of majority of these trace elements with common salt, during the course of its manufacture in solar salt works.*

*In the process of calcium fortification, advantage has been taken of the crystalline structure of sodium chloride where gypsum particles are entrapped in the agglomerates of common salt crystals in the natural course of solar evaporation of brine concentrates. Five to six percent fortification with calcium sulphate (or other insoluble salts of calcium viz. calcium carbonate, calcium phosphate, calcium tartarate) is required, so as to provide 200-300 mg of calcium for the average consumption of 12-15 g. of common salt needed per day. In this process, crushed gypsum is added to the crystallizers after a small layer of salt is formed. The crop is raked occasionally. Similarly, insoluble salts of iron, zinc etc., can be simultaneously impregnated with common salt.*

*The processes developed are simple and cost of inclusion of these trace elements with common salt is that of their cost, while no other cost is involved and at the same time crystalline structure of fortified salt is retained.*

In some inland brines in India there are trace quantities of manganese which affect the solar evaporation characteristics of the brine and the crystal growth of the salt. The objective of this

work was to study the behavior of manganese in solar evaporation. It was observed that on the addition of a manganese salt to a saturated brine first a white, flocculant, colloidal manganous hydroxide is formed. This changes to a buff colored precipitate of  $MnO(OH)$  which settles; again manganous hydroxide is formed and this is oxidized and settles. This cyclic process, which is completed in a definite period depending on the initial manganese content, continues as long as manganese is present in the brine. There is an increase in the evaporation rate of brine during the period manganous hydroxide is in suspension.

The crystals of common salt formed in the presence of manganese are cubical, hard and compact. The addition of 0.008 percent manganese to the brine is sufficient for the formation of perfectly cubical crystals. The salt produced with manganese is purer, having less adhering mother liquor and also substantially less mother liquor included within the crystals.

The salt contains a trace of manganese, which if desired for use in the chemical industry, can be removed by conventional lime (or caustic soda)—soda ash treatment followed by an ammonia treatment.

Hou (1942) reported that the use of a trace quantity of manganese added to saturated brine increases the rate of evaporation to the extent of 10 percent and claimed that addition of 0.06 percent (w/w basis) of manganous sulphate improves the quality of salt to 95-96 percent. He reported that no manganese salts are found in the salt crop obtained. Acharya and Tondon (1961) on the other hand suggested the use of manganous sulphate at a lower level of 0.01 percent to prevent

the salt crop from being colored. They claimed that when the crop obtained is washed with 5-6° Be' brine, the purity of washed salt is acceptable for the chemical industry. Surasiti and Sandell determined the approximate amount of manganese salt required to obtain minimum moisture content in the salt crop. Egli, Yamanto (1931) and Booth (1951) investigated the use of manganese salts for obtaining transparent and pure crystals of salt in solar salt works.

The salt obtained from the sub-soil high density brine in the Rann of Kutch (India) is hard and compact when compared with sea salt crystals. This has been attributed by Jain (1966, 1968) to the presence of a higher level of manganese in the brine, presumably derived from the neighboring soil strata of variegated coloration such as yellow, green and blue. The manganese content of salt from inland and marine solar salt works varies from 0.1-7.0 ppm Mn.

In Bangkok (Ecafe Seminar, 1962), papers were presented recommending the use of manganese salts for the alteration of crystal structure; the use of manganous sulphate up to 0.06 percent (w/w basis) to the saturated brine was suggested for obtaining an increased rate of evaporation and compact salt crystals, but it was pointed out that traces of manganese might prohibit the use of such salt for the manufacture of caustic soda by the electrolysis of brine, due to poisoning effect of manganese in the cells.

An attempt is made in this paper (a) to study the mechanism by which addition of manganese salts to the brine causes an increase in the rate of evaporation, (b) to determine the optimum quantity of manganese required to cause re-orientation of the sodium chloride crystals and (c) to show how manganese present in the salt crop can be removed in order to make the salt acceptable for the manufacture of caustic soda.

#### *Methods of analysis salt and brine.*

Samples of salt and brine were analyzed for calcium, magnesium, chloride, insoluble matter and moisture. Calcium and magnesium were determined volumetrically by E.D.T.A. Sulphate was determined gravimetrically as barium sulphate. Chloride was determined volumetrically with silver nitrate according to Mohr's method. Insoluble matter in salt was determined by dissolving it in water and filtering through a tared filter paper. Moisture in salt was determined by drying at 140°C for 4 hours. The periodate method suggested by Willard

and Luclean (1917) was used for the estimation of manganese, in trace quantity in brine and salt.

#### *Hardness of crystals.*

The well formed crystals obtained on slow evaporation of saturated brine by addition of various percentage of manganese salts were tested for hardness on 'Modified Vicar Needle' (1 mm<sup>2</sup>).

#### *Microscopic examination.*

Microphotographs (x 30) of salt crystals were taken under a microscope fitted with a camera.

#### *Experimental procedure.*

Manganous sulphate (MnSO<sub>4</sub> · H<sub>2</sub>O-B.P.) was used. A standard solution of manganous sulphate was prepared in distilled water depending upon the percentage of manganese required. The exact quantity was transferred with a burette to the brine. The standard solution was normally prepared fresh and preserved for short durations in the dark to avoid its oxidation. The evaporation studies of brine containing manganese were carried out as follows: To 25 ml beakers of the same make, 20 ml portions of brine were added. Periodically, and at the same time, the beakers were weighed on an analytical balance. The difference in two weights for the same beaker indicated the loss of water due to evaporation for the test period.

#### *Discussion increase in rate of evaporation by addition of manganese.*

On subjecting the brine containing a trace quantity of manganese to solar evaporation, the rate of evaporation initially decreases and then shows an increase after a definite time interval, as compared with its 'blank.' However, the rate of increase of evaporation is not constant, but it is found to increase to a certain stage and thereafter, the rate of evaporation diminishes.

In the experiment, the sea brine concentrate containing 0.04 percent manganese was exposed to (1) direct sun light, (2) a laboratory condition in the shade, and (3) a dark condition. Their respective 'blanks' were exposed alongside in the identical conditions. For sunlight exposure an open terrace was used, while the sample in the shade was kept in the laboratory. The third sample was kept in a dark locker and was exposed to light only for a short duration while making the weighings. The data on these evaporation tests are given in Table 1.

It is interesting to note that initially the rate of evaporation decreased in comparison with the

Table 1. Variation in the Rate of Evaporation of Brine Containing 0.04 Percent of Manganese

Cumulative time in hours	Intermittently exposed to sun's rays		% increase + or decrease ( - ) in the rate of evaporation in comparison with their blanks		
	Sunny hours	Non-Sunny hours	On Exposure as shown in Col. 2 & 3	During the total period as shown in Col. 2 & 3	
				In room condition	In dark condition
1	2	3	4	5	6
16	—	16	-29.61	-30.84	-40.37
24	8	—	+1.7	-6.57	-1.90
40	—	16	2.12	-10.53	-2.07
48	8	—	0.6	-16.62	-5.09
64	—	16	8.47	+2.92	-13.47
184	—	120	22.71	9.57	-9.21
232	—	48	1.48	2.25	-5.00
240	8	—	1.52	0.98	-0.28
256	—	16	2.37	7.76	-2.14
264	8	—	14.22	4.14	-1.91
280	—	16	13.98	15.75	-4.31
288	8	—	14.61	4.13	+2.49
360	—	72	—	3.11	+0.39
456	—	96	—	—	+1.24

'blank,' and increased at the time coinciding with the formation of a white, colloidal flocculant precipitate. This precipitate subsequently settled down as a buff colored compound. During the first 24, 48, and 288 hours in sun, room and dark conditions respectively, the evaporation was less, but gradually approached the evaporation rate of their 'blanks.'

In another set of experiments, to the saturated brine, 0.002, 0.006, 0.014, and 0.04 percent of manganese were added and subjected to direct sunlight, without permitting the water vapor to escape from the brine. Colorimetric readings were taken at 450 mu using a Bausch & Lomb instrument. The readings were taken as a measure of the formation of colloidal manganese hydroxide. The data are plotted in Figure 1 and show an initial period of increasing formation of manganese hydroxide (indicated by decrease in transmittancy). This is followed by a decrease in manganese hydroxide,

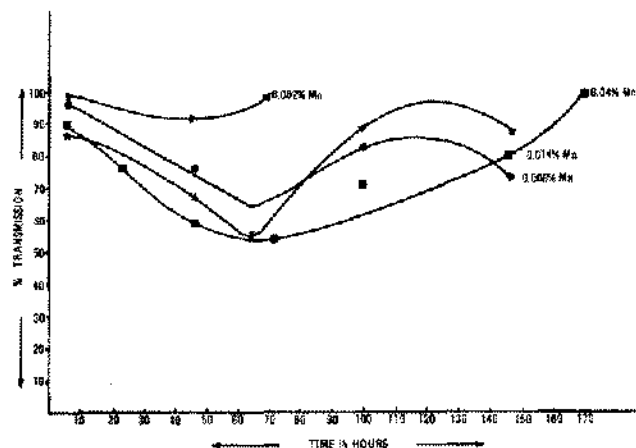


Figure 1. Time required for formation and complete settling of manganese hydroxide from brine on addition of manganese in varying concentrations.

and in some instances another increase. This cycle is repeated until all the manganese is removed from the brine. Table 2 shows the effect of initial manganese level on the time required for formation and settling of manganese hydroxide.

The non-uniform evaporation of brine containing varying levels of manganese is thus attributed to the appearance of a colloidal white precipitate of manganese hydroxide, followed by the complete

settling of a buff colored oxidation product of the initial white precipitate.

Based on the above observations, field experiments were conducted by adding various percentages of manganese salts to the saturated brine, for longer duration, to work out the average increase in rate of evaporation. Small size crystallizer pans prepared in the conventional way and of the size of 3 m X 3 m in our salt farm were prepared to conduct the field trials. In all the pans, saturated brine was charged to a depth of 15 cm and a solution of manganous sulphate prepared in saturated brine was added to the extent desired, keeping a few pans of the same size as 'blanks' for comparison. The results presented in Table 3 show that the level of manganese for obtaining the optimum increase in rate of evaporation is 0.01 to 0.02 percent, and the increase in evaporation is about 10 percent.

The white, flocculant colloidal precipitate and its oxidation product were analyzed. The analysis given in Table 4 shows that the former has the composition of  $Mn(OH)_2$ , while the latter has the composition of  $Mn_2O_3 \cdot H_2O$ .

**Table 2. Time Required for Formation and Complete Settling of Manganese Hydroxide from Brine on Addition of Manganese in Varying Concentration**

Percentage of manganese added to saturated brine	Hours
0.002	70
0.006	110
0.014	130
0.04	170

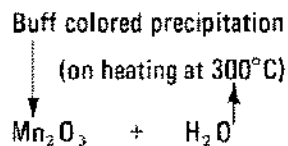
**Table 3. Increase in the Rate of Evaporation on Addition of Varying Amounts of Manganous Sulphate to Saturated Brine**

Manganous Sulphate added (as percent Mn)			Percent increase in evaporation
Below		0.01	5 - 7
0.01	to	0.02	8 - 10
0.02	to	0.06	9 - 11

**Table 4. Probable Composition of White and Buff Colored Precipitate on Analysis**

Description of precipitate	Percent Mn on theoretical basis	Expt. 1	Difference of Col. 2 & 3	Expt. 2	Difference of Col. 2 & 5
		Percent $\pm$ Mn		Percent Mn	
1	2	3	4	5	6
White colloidal precipitate dried at 90° C.	61.77	61.54	-0.23	61.37	-0.4
Buff colored precipitate on heating at 300° C.	69.61	69.59	-0.02	70.01	+0.4

The above reaction may be explained as follows:



*Effect of addition of manganese on the salt crystal.*

A systematic crystallographic study was conducted by adding manganese ranging from 0.0005 to 0.06 percent, to saturated sodium chloride

solution under similar conditions. The crystals were formed in glass troughs having 6 litres capacity, with slow precipitation under room conditions. The crystals were stirred slowly with a glass rod once each 3-4 days so as to permit all the faces of the crystals to grow uniformly. It was observed that first the corners of the hopper shaped crystals normally obtained in solar evaporation of sodium chloride become rounded and the apex is flattened. At 0.008 percent of manganese added to the brine, the crystals obtained are perfectly cubic. Enclosed microphotographs (photos 1 to 4) show the flattening of the crystals on addition of manganese and formation of perfectly cubic salt crystal. Further addition of manganese causes the formation of more compact crystals while the salt

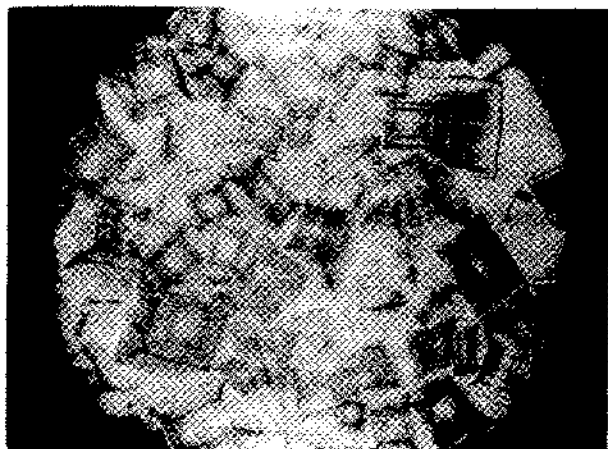


Photo 1. Crystals of sodium chloride (No manganese added to brine).

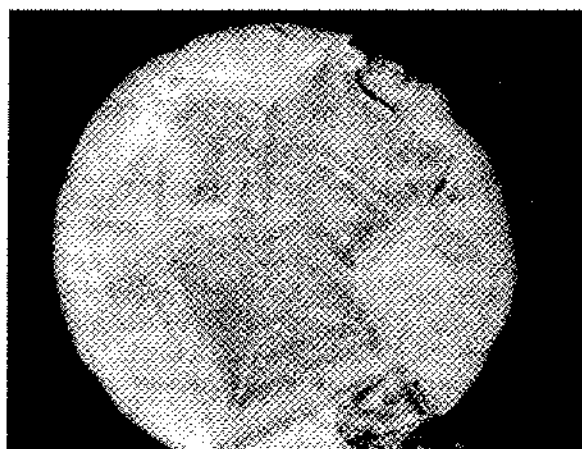


Photo 2. Crystals of sodium chloride (with 0.004% manganese added to brine).



Photo 3. Crystals of sodium chloride (with 0.008% manganese added to brine).



Photo 4. Crystals of sodium chloride (with 0.04% manganese added to brine).

obtained gets colored dirty yellow, at 0.06 percent manganese concentration hard and compact salt crystals obtained are highly colored. Hardness of salt crystals increases as can be seen from results on Vicar needle plotted in Figure 2. The increasing

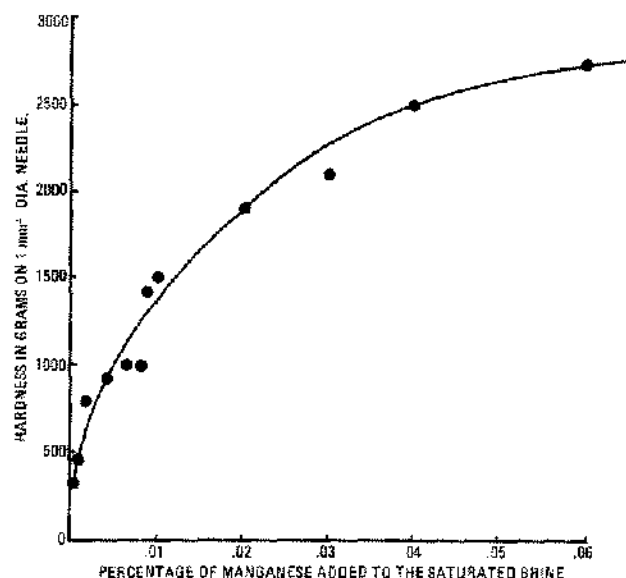


Figure 2. Relationship of hardness of the salt crystals with the manganese added to the saturated sodium chloride solution.

clarity of the crystals also definitely show a decrease in included mother liquor with increasing manganese.

#### *Absorption of manganese by the salt crystals.*

Various workers have explained that manganese is absorbed on the developing (111) plane, due to a good fit. Experiments conducted have revealed that the various faces of a well developed salt crystal containing manganese, absorb manganese almost uniformly over all its faces. However, the proportion of manganese removed from the brine with the salt by absorption is a function of the initial manganese level in the brine. This is shown in Table 5. It is seen that the percentage absorption of manganese with the separating salt crystals is more when present in the range of 0.0005 to 0.01 percent manganese in the brine, and above this level of manganese the trend reverses.

#### *Improvement in quality of salt with addition of manganese.*

In the compact and cubical salt crystals obtained by the addition of manganese in the brine, the adhering and included mother liquor will be less and therefore the salt will be purer with respect to magnesium salts. Also, in the well formed compact crystals, the moisture content will be reduced considerably. A study conducted on the addition of various percentages of manganese to the saturated brine in the crystallizers, under identical conditions, has shown that the purity of salt has improved gradually from 92.52 percent NaCl to 96.78 percent NaCl at 0.06 percent manganese addition, due to reduction from 5.18% to 1.78% of

Table 5. Inclusion of Manganese in Salt Crystals on Evaporation Of Brine Containing Various Percentages of Manganese

No.	Percent of manganese added to saturated brine	Percent of manganese retained in salt	Percent of manganese retained with bittern at 30°Be'
1	0.0005	79.80	20.20
2	0.0007	70.11	29.89
3	0.002	65.06	34.94
4	0.004	59.98	40.02
5	0.006	56.93	43.07
6	0.008	55.04	44.96
7	0.009	53.01	46.99
8	0.02	48.00	52.00
9	0.040	35.05	64.95

magnesium chloride and from 1.46% to 0.52% magnesium sulphate. However, the calcium sulphate impurity is not affected in any way. Similarly, the moisture content has been reduced from 10.47 percent to 3.51 percent at 0.06 percent manganese addition, accounting for a reduction of almost one third, which is very appreciable. The results of the experiments are shown in Table 6. The purity of salt is a matter of great consideration, as the demand for salt is increasing considerably for the chemical industries, which need salt of high purity.

For a commodity as cheap as common salt which is required in large quantities, the transportation charges are the deciding factor for long distances. The unnecessary moisture which is normally accompanied to the extent of 4-6 percent, accounts for a major transportation cost factor. Therefore, any reduction in the moisture content of salt will make corresponding savings in the cost of salt delivered.

#### *Hard crystallizer bed.*

Taking advantage of the formation of hard and compact salt crystals by the addition of manganese, a crystallizer bed has been prepared by adding 0.06 percent of manganese. This gave 40 percent increased bearing strength, as compared with a bed with common salt under identical conditions. The process adopted in the preparation of a hard bed is to add 0.06 percent manganese (as manganous sulphate) to a small depth of brine in

the crystallizer in the initial stage and permit the formation of about 1-2 cm thick crust of hard crystals. It may be mentioned that in solar salt works, where the salt crop is harvested manually, a permanent layer of 2-3 cm thick is prepared in the beginning of the salt manufacturing season, so as to avoid the contamination of mud impurities picked at the time of harvesting the salt crop. Also, due to low solubility of hard and compact salt layer prepared by the addition of manganese, the salt manufacturing operations may be continued during monsoons in regions of moderate rainfall such as Saurashtra, Kutch and Tuticorin, without this salt layer being dissolved.

#### *Removal of manganese from brine solution.*

While the trace quantity of manganese retained by the separating salt crystals, is considered as an "essential nutrient" when such salt is used for edible purposes, its presence is objectional for the salt based chemical industries, more particularly for the manufacture of caustic soda by brine electrolysis, due to its poisoning effect on the cells. Similarly, over a certain limit, the presence of manganese is considered undesirable in the Solvay process for the manufacture of soda ash.

The salt obtained in solar salt works, due to presence of magnesium, calcium and sulphate is subjected to soda ash-lime (or caustic soda) treatment, whereby calcium and magnesium are removed as calcium carbonate and magnesium

Table 6. Analysis of Salt Crystals Separated from Brine at 30° Be in Presence of Manganese (on Dry Basis)

Percentage of Manganese added To Brine														
Constituents	Blank	Blank	0.0005	0.001	0.002	0.004	0.006	0.008	0.009	0.01	0.02	0.03	0.04	0.06
WEIGHT PERCENT														
NaCl	92.52	92.65	92.85	93.17	93.35	93.61	93.86	94.23	94.45	95.68	95.68	96.30	96.58	96.78
MgCl <sub>2</sub>	5.18	5.17	5.18	4.73	4.66	4.46	4.27	4.04	3.94	3.29	2.97	2.33	2.05	1.78
MgSO <sub>4</sub>	1.46	1.36	1.24	1.27	1.16	1.07	0.96	0.85	0.84	0.70	0.54	0.56	0.53	0.52
CaSO <sub>4</sub>	0.64	0.63	0.64	0.66	0.71	0.71	0.78	0.74	0.68	0.69	0.73	0.77	0.77	0.77
Insolubles	0.20	0.18	0.12	0.16	0.12	0.12	0.13	0.11	0.09	0.19	0.11	0.04	0.07	0.15
Moisture	10.47	10.63	8.81	8.47	7.32	6.96	6.91	6.13	6.37	6.10	5.29	4.8	3.7	3.51
PPM Mn in salt			2.9			3.6				6.8		6.95	7.1	

hydroxide. It is found that manganese is also removed to an extent of about 79.00 percent by this treatment and another 19 percent by further treatment with soda ash. Thus about 98 percent of the manganese present is removed with the precipitating magnesium and calcium salts. By further treating the brine with a very small percentage of ammonia, manganese is removed almost completely due to the formation of a manganese-ammonia complex. This simple and economic process of removal of manganese from the saturated brine solution makes the use of manganese possible for the salt required for industrial uses.

In summary, the use of a cheap substance like manganous sulphate for solar salt manufacture is recommended on a large scale. For edible purposes, manganese to the extent present is considered desirable as an "essential nutrient." The high bulk density of the salt will require less packaging material (jute bags), the cost of which is several times higher than the cost of the salt packed. Also, lower moisture content of the salt will be helpful in reducing the cost of transportation. In the majority of cases, salt has to be carried over long distances in India. Chemical industries consuming salt on a large scale will have salt of high purity with respect to magnesium salt which will permit lower costs for the treatment of brine with soda ash-lime. For export, a major cost is trans-

portation, and this could be reduced to the extent that the salt crystals will have lower moisture content.

## REFERENCES

- Acharya, C.S., and Tondon, S.P., *J. Sci. Indus. Res.*, V. 20D, (Dec. 1961), p. 464-5.
- Booth, A.H., 1951, *Trans. Faraday Soc.* 47, p. 633-40.
- Ecafe's seminar report, *Chemical Age of India*, (Nov.-Dec. 1962) p. 440.
- Hou, T.P., *Manufacture of soda*, 1942, (Reinhold Publishing Corp. N.Y.) p. 58.
- Jain, G.C., Patel, J.M., Bhatt, R.M., Bhatt, R.B., 1966, *Salt Res. & Ind.* 4, p. 146.
- Jain, G.C., *Salt Res. & Ind.* 3, 1966, p. 116-20.
- Jain, G.C., Thesis for Ph.D., Gujarat University (India), 1968, p. 102-8.
- Surasiti, G., and Sandell, E.B., *Nature*, 203 (July 4th, 1964) p. 60-61.
- Willard, H.H., and Luclean, H., 1917, *Amer. Chem. Jr.*, v. 39, no. 11, p. 2366.
- Yamamoto, 1931, *Bull. Inst. Phy. Chem. Res.* (Tokyo), 10, p. 52-60.