

Scale Prevention on Salt Manufacturing Process by Ion-Exchange Membrane Method

S. Sugita

*Odawara Salt Experiment Station
Japan Tobacco & Salt Public Corporation
Kanagawa, Japan*

ABSTRACT

Scale formation is one of the most important problems in the salt-manufacturing process by the ion-exchange membrane method in Japan. This paper refers to our investigation of the mechanisms of scale formation in the evaporating process for salt manufacturing, and reports a new scale preventing method, developed on the basis of a number of experimental

results. This new method, which is characterized by the use of hydrochloric acid and sodium hexameta phosphate in combination, has been introduced in five factories and is contributing to the continuous stable operation with a decrease of scale formation.

INTRODUCTION

In the salt manufacturing process in Japan, scale formation is one of the most important problems. In Japan, the method for manufacturing salt was completely changed in 1972 from the traditional salt-field method to the new ion-exchange membrane method, which has converted the salt manufacturing industry from an agricultural to a chemical industry. Unlike the conventional salt-field brine, the concentrated brine obtained by electrodialysis with ion-exchange membranes varies in composition under various conditions.

This paper discusses the mechanism of the formation and its prevention of such scales as calcium carbonate, calcium sulfate and di-sodium pentacalcium sulfate during the process of heating and concentrating in the salt manufacturing process by the ion-exchange membranes. It also reports a new scale preventing method developed on the basis of experimental results.

EXPERIMENT

Preparation of the Sample

The scale formation during concentration of ion-exchange membrane brine by an evaporator is complicated because it depends on the kind of the ion-exchange membrane used, the conditions of electrodialysis and the methods used for preventing the scale formation in the electrodialysis cell.

For the purpose of investigating scale prevention, therefore, the author determined the composition of the ion-exchange membrane brine for the scale test, as shown in Table 1, and carried out the experiments with this brine and a small scale evaporating apparatus. This brine was prepared by adding reagents of Na_2SO_4 , CaCl_2 , NaCl and KCl to the original brine obtained from an experimental dialysis cell.

Analysis

Table 2 shows the methods of analysis used for the experiments.

Methods of Experiments

1) Effect of sodiumhexameta phosphate to prevent the formation of alkaline scale

The apparatus used in the experiments was a modified rotary evaporator shown in Figure 1. The apparatus was modified to a back-cooling type by cutting the rotary joint of the apparatus along a-a' in Figure 1.

TABLE 1

Constituents of Test Brine

S.G.	g/kg, brine					CaCO ₃	
	CaSO ₄	CaCl ₂	MgCl ₂	KCl	NaCl	25°C pH	ppm Alkalinity
d ₄ ²⁵ 1.194	2.43	2.33	11.80	8.00	233.50	7.6	141

TABLE 2
Analytical Methods for Samples

Component	Method
pH, alkalinity	pH-stat
Ca ²⁺ , Mg ²⁺	EDTA-method
K ⁺ , Na ⁺	Flame-photometric method
Cl ⁻	Mohr's method
SO ₄ ²⁻	Absorption spectrophotometric method or gravimetric method
PO ₄ ³⁻	Solvent chloroform + butanol extraction and absorption spectrometric method
Scale	Chemical analysis, powder X-ray diffraction and differential thermal analysis

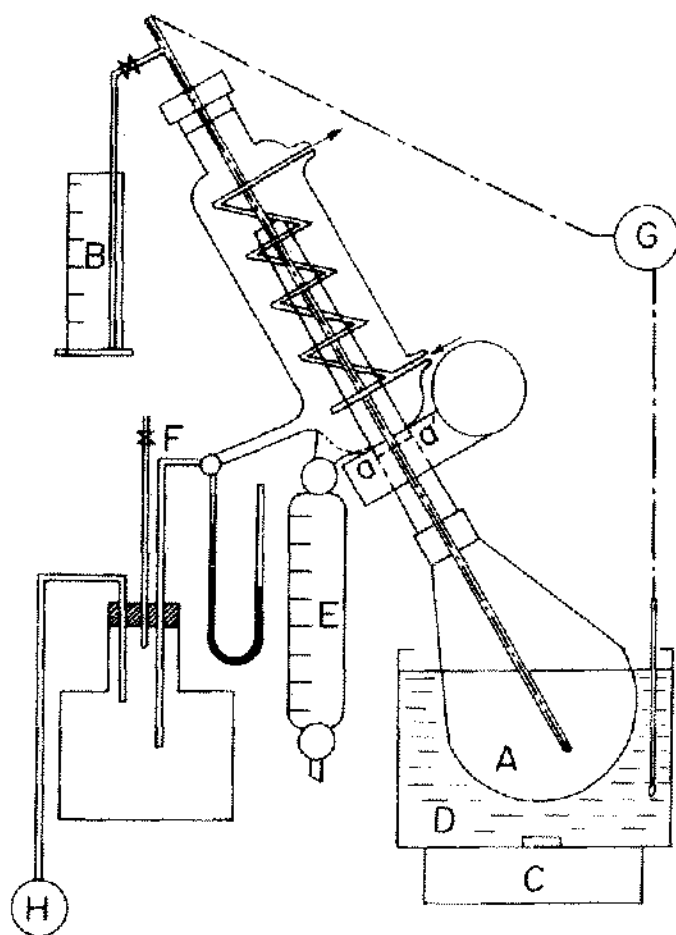


Figure 1. Apparatus

In the experiments, an evaporating flask containing two liters of brine was immersed in a glycerine bath, the pressure was reduced in advance so that the brine could boil at the experimental temperatures of 50, 75 and 100°C, and the flask was rotated at a speed of 80 rpm. The glycerine bath was kept at a temperature 20°C higher than the experimental temperature.

A similar experiment was then carried out at 50 and 100°C, in which hydrochloric acid was added to the brine to remove HCO₃⁻ and CO₃²⁻ wholly or partially (the so-called decarbonized brine).

In these experiments, the pH, alkalinity and PO₄³⁻ concentration in the brine in flask were determined each 30 or 60 minutes and the degree of alkaline scale formation was determined from a decrease in brine alkalinity.

2) Formation of calcium sulfate and di-sodium pentacalcium sulfate scale.

The apparatus used in the experiments is shown in Figure 2. It consists of 4 parts: steam generating chamber, pressure reducing chamber, heating chamber (25 × 300 mm copper tube, heating area 200 cm²) and evaporating chamber.

The brine was concentrated in a manner similar to that commercially employed for the salt manufacturing evaporator. Two liters of brine was placed in the evaporating chamber, the pressure of the chamber was reduced to a level at which the brine could boil at 75°C and the brine was heated with steam of 100°C. During evaporation, the brine was continuously fed so as to maintain constant liquid level and brine concentration while the concentrated brine was exhausted along with deposited salt crystals. Concentration tests were made at the concentration from 18 to 60 g/kg (CaCl₂ + MgCl₂).

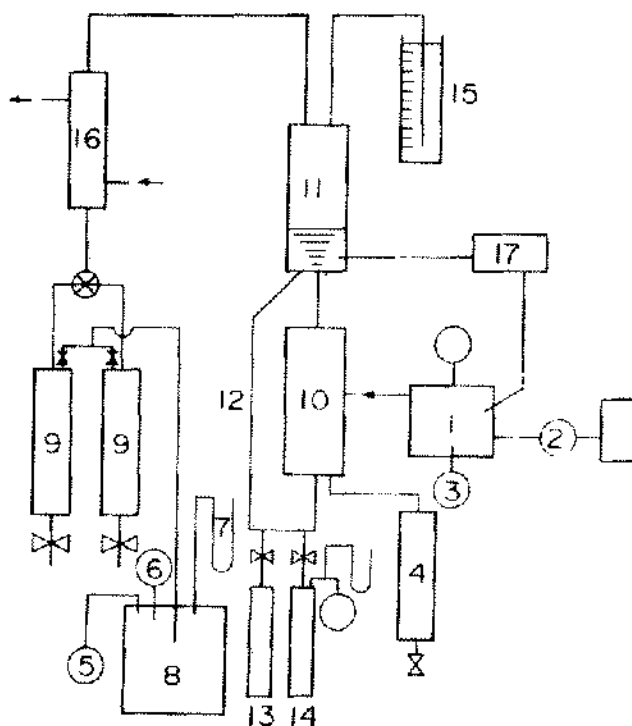


Figure 2. Apparatus

3) Effect of various additives against calcium sulfate and di-sodium pentacalcium sulfate scale formation

For scale prevention, various additives such as sodium hexametaphosphate (SHP), sodium carboxyl methyl cellulose (CMC), citric acid (CA), sodium citrate (SC), polyacrylic acid (PA), sodium polyacrylate (SPA), polyacrylamide (PAA) and Krillum (KM) were tested. The additives were introduced to the decarbonized brine, and the brine was concentrated to 35 g/kg ($\text{CaCl}_2 + \text{MgCl}_2$).

In these experiments, the pH, alkalinity, Ca^{2+} , Mg^{2+} , Cl^- and PO_4^{3-} concentration in the exhausted brine were determined. The scale deposited was dissolved in a 1 N nitric acid solution, and the composition of scale was determined by chemical analysis. The change in heat transfer coefficient was measured.

RESULTS AND DISCUSSION

Effect of Sodium Hexametaphosphate to Prevent the Formation of Alkaline Scale

It is well known that SHP is very effective in preventing scale formation. The effect of SHP to reduce the formation of alkaline scale from brine at temperatures of 50, 75 and 100°C was experimentally determined. The results are shown in Figure 3. It is apparent that in the case of SHP concentration of 20 ppm the deposition of the scale was almost completely prevented at 50°C. However, this

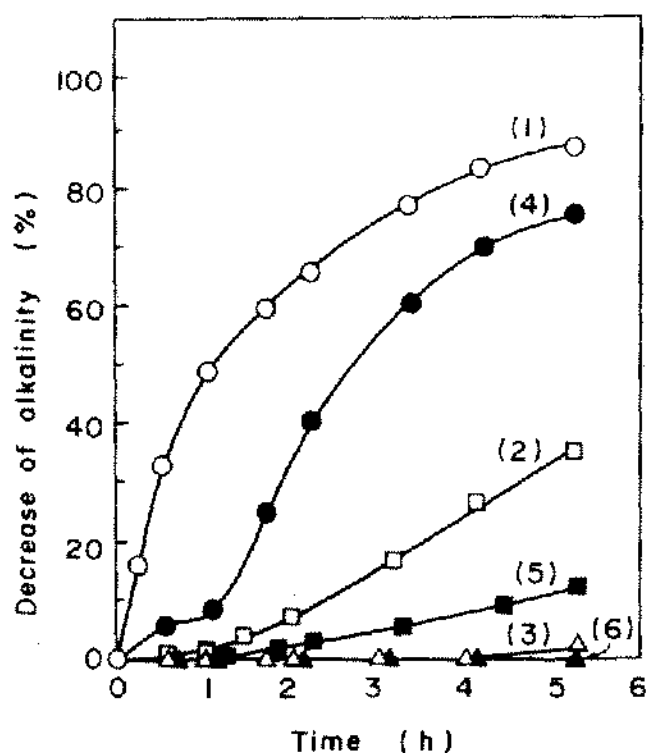


Figure 3. Decrease of alkalinity in the heating brine

effect was slightly lower at 75°C and was significantly reduced at 100°C.

To provide further evidence for this phenomenon, the degree of SHP decomposition was determined by measuring the concentration of PO_4^{3-} in heating brine. The tendency for decomposition of SHP (Figure 4) was very similar to that of the decrease in alkalinity (Figure 3). Very little decomposition of SHP took place at 50°C, more developed at 75°C, and 93% of SHP was decomposed after 30 minutes at 100°C. This result indicates that at temperatures above 75°C, at which scale formation was obviously observed in our previous paper (1972), SHP tends to decompose and to give insoluble phosphates that precipitate together with alkaline scale. It was found from the above experiment that formation of alkaline scale is closely correlated with the decomposition of SHP.

Effect of Hydrochloric Acid Treatment Against Decomposition of Sodium Hexametaphosphate

The results on decarbonized brine are shown in Figure 5. It can be seen in this figure that decomposition of SHP in the decarbonized brine was reduced from 1/10 to 1/100, compared with untreated brine, and that most of SHP remained in the solution for a long time even at 100°C. This valuable information provided the author with the starting point for the development of the new scale prevention process described later.

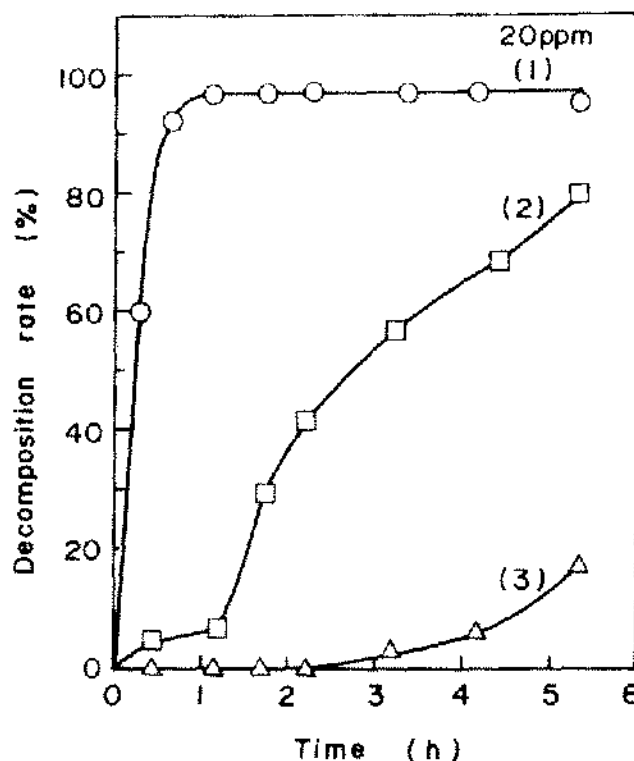


Figure 4. Decomposition of sodium hexametaphosphate added in the heating brine

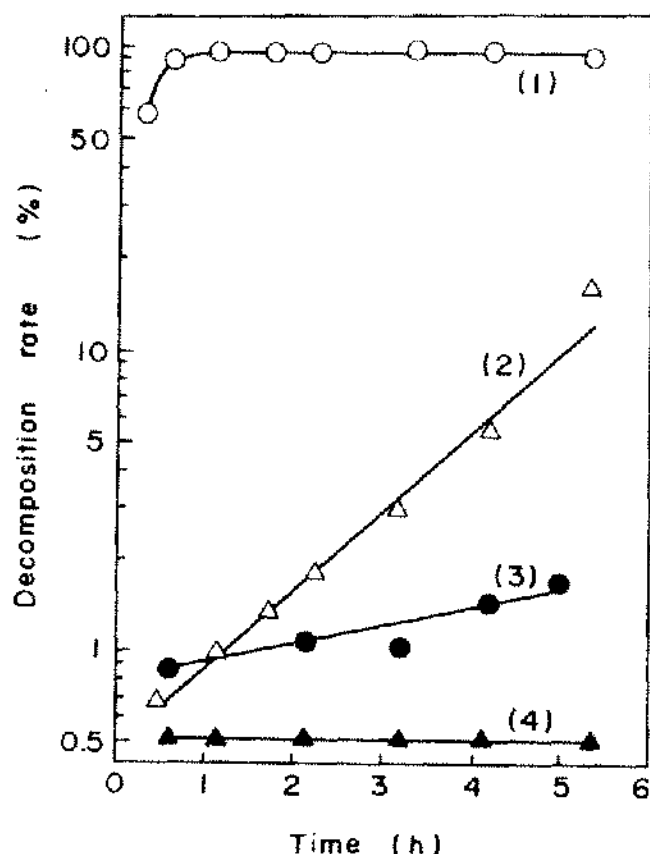


Figure 5. Decomposition of sodium hexametaphosphate added in acid treated brine

Formation of Calcium Sulfate and Di-sodium Pentacalcium Sulfate Scale

It was assumed that the formation zone of $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ existed between A and B line in Figure 6. A large number of bench-scale tests using triple effect evaporators conducted by The Japan Tobacco & Salt Public Corporation (1971), have already revealed that in a concentrating process, the scaling problems are encountered less frequently in the temperature and concentration range that causes deposition of CaSO_4 , while these troubles become marked in the hatched zone in which $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ deposits (Figure 6).

In the present study, scale formation in the latter zone was investigated in more detail by using the apparatus shown in Figure 2, at a liquid temperature of 75°C and brine concentration from 18 to 60 g/kg ($\text{CaCl}_2 + \text{MgCl}_2$). The conditions are similar to those actually employed for the second of the triple effect evaporators now in commercial operation. The results indicate that the scale is formed very rapidly at a brine concentration of about 35 g/kg (Figure 7). Both differential thermal analysis (Figure 8) and chemical analysis (Figure 7) also revealed that the scale formed is composed mainly of di-sodium pentacalcium sulfate ($\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$) and also con-

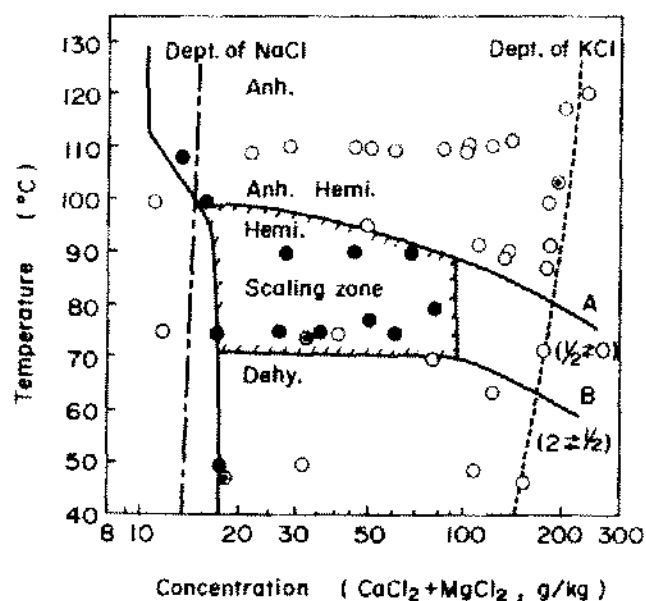


Figure 6. Adhesion behavior of calcium sulfate scales in the salt manufacturing process by ion-exchange membrane method

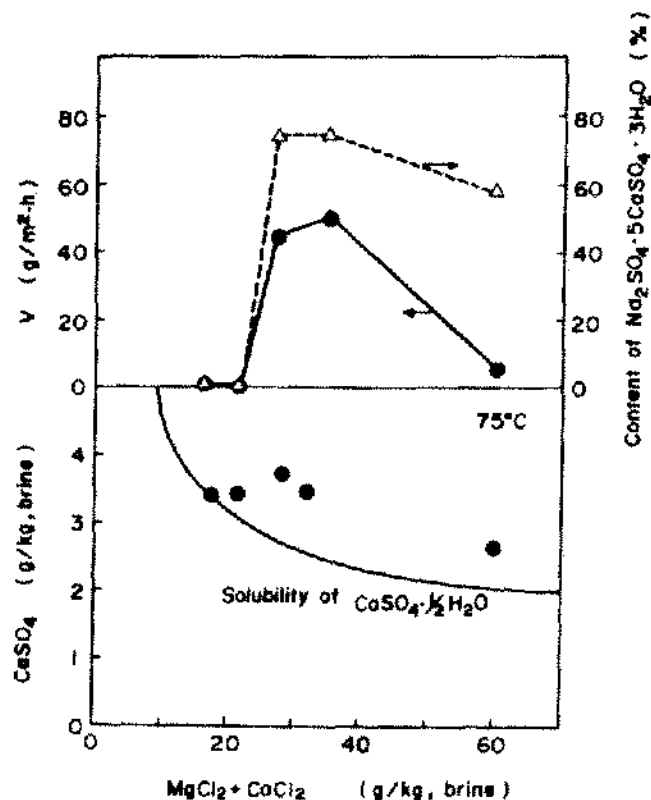


Figure 7. Relation among brine concentration, CaSO_4 concentration, adhesion rate and $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ content of scales on heating tube

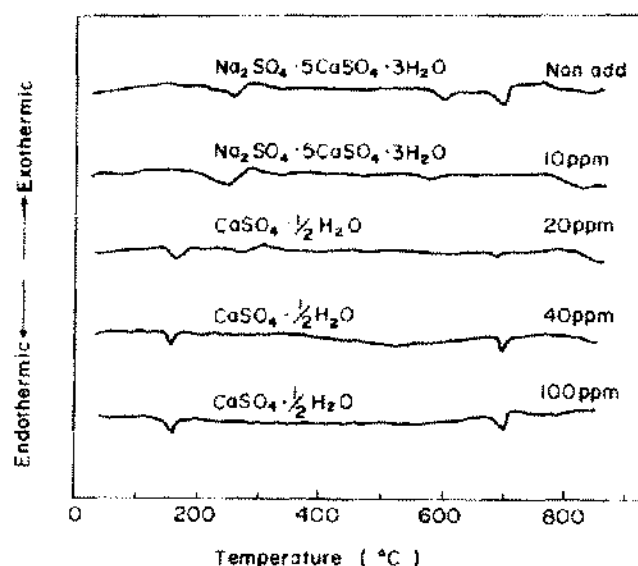


Figure 8. DTA of the crystal deposited from the brine containing sodium hexametaphosphate

tains $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$. These findings suggest that the key point for scale control is how to prevent the formation of $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$.

Effect of Various Additives Against Calcium Sulfate and Di-sodium Pentacalcium Sulfate Scale Formation

The results are summarized in Table 3. It can be seen that SHP reduced the scale adhesion rate to below 1/10 at a level of 20 ppm. Analysis of the adhered scale and the concentrated brine showed that SHP is also effective in retarding the formation of $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$. Of the

other additives tested, CMC and PAA showed some ability to decrease the scale adhesion rate, but none was found to have any effect to arrest the formation of $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$.

To learn more concerning the mechanism through which the formation of $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ is prevented, crystal form of the deposited scale was investigated by X-ray diffraction and differential thermal analysis. The relationship between the amount of SHP added and the differential thermogram of each scale can be seen in Figure 8. If SHP is added at a concentration of 20 ppm or higher, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ crystals deposit under the condition where $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ would be formed.

Conclusion of the Experiments

The combination of SHP and hydrochloric acid prevents most alkaline scale formation in the heating process and also prevents calcium sulfate and di-sodium pentacalcium sulfate scale formation in the concentrating process.

COMMERCIAL APPLICATION OF THE NEW SCALE PREVENTING METHOD

In 1975, this new method was introduced in the salt manufacturing factory with a yearly production capacity of 150,000 tons operating on backward feed type triple effect evaporators (Figure 9). In an industrial operation, brine is adjusted to pH 5-6 by the addition of hydrochloric acid, followed by the addition of 10-15 ppm of SHP and is then fed to the evaporators. Adoption of this method decreased adhesion of alkaline scale (CaCO_3) in

TABLE 3
Effect of Various Additives on Scale Formation

Additive (ppm)	pH 20°C	CaSO ₄ (g/kg)	Brine P ₂ O ₅ (ppm)	Scale on heating tube						NaCl (%)	P-salt* (%)	v (g/m ² ·h)	Heat-transfer coefficient Finish (kcal/m ² ·h·°C)
				CaCl ₂ /MgCl ₂	CaSO ₄ (%)	Na ₂ SO ₄ (%)	MgCl ₂ (%)	Ca ₃ (PO ₄) ₂ (%)	Mg ₃ (PO ₄) ₂ (%)				
Non add	7.70	3.58		0.205	80.8	12.9	2.8			3.5	74.9	84.6	1120
Decarb.	7.47	3.59		0.203	75.8	13.2	4.0			7.0	76.4	72.0	1330
CMC-20	7.39	4.04		0.200	72.9	7.1	2.6			17.4	41.2	4.8	2200
CA-20	3.55	3.63		0.207	84.6	14.6				8.0	84.7	62.0	1640
SC-20	7.45	3.65		0.205	80.1	17.2	1.6			1.1	91.0	59.5	1570
PA-20	7.24	3.58		0.206	74.4	16.9	6.2			8.1	98.0	87.0	910
SPA-20	7.25	4.30		0.199	87.8	9.7	2.3			0.2	56.0	40.1	1700
PAA-20	7.37	3.90		0.203	79.9	14.2	0.4			5.5	82.2	25.8	1510
KM-20	7.42	3.62		0.203	83.1	12.5	0.5			4.0	72.1	55.9	1520
SHP-10	7.28	4.05	10.6	0.198	89.4	1.7		3.0	0.8	5.0	10.1	15.1	1900
SHP-20	7.19	4.19	13.2	0.195	92.5			5.4	2.1			5.5	2150
SHP-30	7.48	4.28	27.8	0.195	56.4			30.5	13.1			3.5	2400
SHP-40	7.39	4.25	30.9	0.196	68.8			8.9	22.3			1.2	2200
SHP-100	4.80	4.34	69.3	0.195	4.2		75.3	9.2	11.3			0.3	2540

(Note) P-salt* indicates $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$.

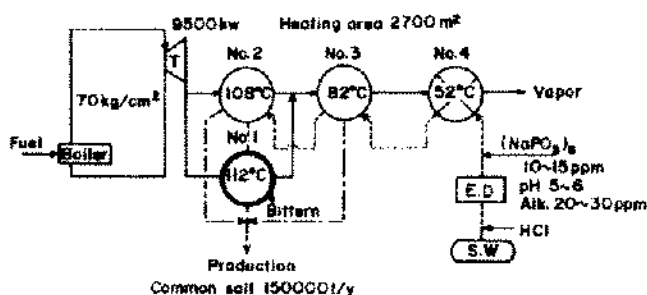


Figure 9. Flow sheet on the new preventing method

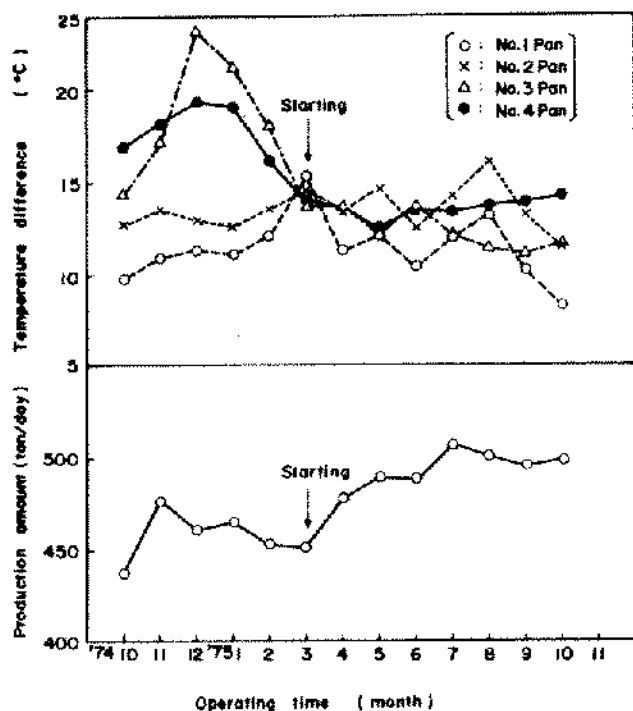


Figure 10. Effects of the new preventing method

the No. 4 evaporator as well as adhesion of $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ in the No. 3 evaporator, and also decreased "salting-up" in the No. 1 and No. 2 evaporators.

As a result, heat transfer in the four evaporators has improved significantly, leading to a 15–25% increase in salt production. SHP added to the feed brine is distributed in scale, mother liquid and product salt in proportions of 74%, 22% and 4%, respectively.

Since its introduction to five factories the new method has been contributing to the prevention of scale formation and the continuous stable operation of the plants. The new method to prevent scale formation thus established 'HCl and SHP combined treatment' was patented.

REFERENCES

- Japan Tobacco & Salt Public Corporation, Headquarters-Planning & Development edit., 1971. Studies on the salt manufacturing plant by electrodialysis with ion-exchange membrane method: pp. 108–133.
- Kaho, M., S. Sugita, T. Ishikawa, K. Soga. 1977. Concentrating method of brine by the ion-exchange membrane method; Japan patent, No. 847,454.
- Sugita, S. 1972. Formation of alkaline scale in heating the brine obtained by the ion-exchange membrane method, Jour. Chem. Sci. Japan, Chemical and Industrial Chemistry, 1972, (11): pp. 2059–2064.
- Sugita, S. 1972. Decomposition of condensed sodium phosphate in heating the brine obtained by the ion-exchange membrane method; Jour. Chem. Sci. Japan, Chemical and Industrial Chemistry, 1972, (11): pp. 2065–2070.
- Sugita, S. 1973. Formation of sodium pentacalcium sulfate scale and its prevention by the addition of additives into the brine; Jour. Chem. Sci. Japan, Chemical and Industrial Chemistry, 1973, (6): pp. 1099–1106.
- Sugita, S. 1973. Inhibition effect of condensed sodium phosphate on deposition of calcium sulfate hemihydrate and sodium penta-calcium sulfate; Bull. Sea Water Sci. Japan, v. 27 (2): pp. 106–114.
- Sugita, S. 1978. Studies on the scale formation and its prevention in concentrating process of sea water; Bull. Sea Water Sci. Japan, v. 32 (1): pp. 3–33.
- Sugita, S. 1980. Salt-manufacturing process by electrodialysis with ion-exchange membrane method, 2.5 Scale prevention on the process, Bull. Sea Water Sci., Japan, v. 34, (2): pp. 103–108.