

Solar Salt Production

Study of Evaporation—Increase of Salt Deposit

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ABSTRACT

The solar evaporation of soft water is rather well-known.

It is not the case of sea water, because the various kinds of salts act as a brake. It has been proved that the main factor which prevents evaporation on saturated brines in sodium chloride is the magnesium ion. Therefore, there is no more production of salt when the air moisture reaches a certain level, in direct relation with the quantity of magnesium in a brine.

The knowledge of such a phenomenon indicates where is the best process in order to produce the maximum of sodium chloride according to the hygrometry of the air.

Tests have been conducted on solar saltworks, and on the same way calculations have been established with a view to give a method of conducting the brine according to its density. Using a continuous flow of brine from the saturation point to a well-known level of magnesium content without any mixture, makes it possible to increase the deposit of sodium chloride.

It is also possible to obtain by that way production of salt in bad climatic conditions where it would not be possible with the usual process.

The production of salt by the natural evaporation of seawater under the combined efforts of the sun and the wind would not appear, at first sight, to raise any special difficulty.

The seawater is gradually brought from its initial concentration to saturation in sodium chloride. At this stage, the brine is let into the crystallizers or salt pans and usually the sodium chloride is

allowed to settle but at the same time avoiding any precipitation of the magnesium salts.

This operation is generally carried out by successive supplies of saturated brine which is intended to maintain a constant level in the salt pans.

Experimental findings and also theoretical studies have shown that this procedure was often prejudicial to the quality of the salt produced and did not always ensure the maximum deposit for a given evaporation.

In certain favorable regions of the globe, the conditions for evaporation are such that the preceding quantitative and qualitative phenomena appear secondary.

In other places, on the contrary, bad climatic conditions can prevent solar salt production. A special study of hygrometry may leave a hope if saturated brine is used to feed the salt pans without any mixing.

A particular analysis of the laws of evaporation on brines has made it possible to get the best out of the brine which has reached the threshold of saturation in sodium chloride.

Analysis of the evaporation of saturated sea brine, as described here, gives a theoretical explanation of the phenomenon checked by experiment.

This method can be used for the production of salts other than sodium chloride or for the concentration of different salts in brines of various chemical composition.

Evaporation on fresh water.

The evaporation, E , on fresh water is relatively well known.

Several formulas reckoning with wind velocity, V , and the difference in pressure of vapor from air

and water, D, enable one to have an approximate but nevertheless sufficient knowledge of evaporation when one has a suitable wind gauge and thermometer.

An evaporating tank is not always installed at the spot where it is desired to carry out the measuring. Installing this equipment over a very large area may prove to be costly.

On Figure 1, the various curves showing the changes in evaporation according to different authors have been traced.

The curve showing Sutton's formula is a mean curve which can be deemed sufficiently representative. It also corresponds to the mean of observations made on an evaporimeter.

Evaporation on saturated brines.

The presence of salt in brine checks the evaporation on saturated brine, as the vapor pressure of these solutions is slighter than that of fresh water placed in the same ambient conditions.

There is therefore a relation between the evaporation on brine and the evaporation on fresh water that we shall call α (alpha) by definition less than 1.

The Sutton's evaporation formula evoked in the preceding chapter is:

$$E = KV^a \left(P_B - P_C \right) \text{ for fresh water, and}$$

$$E' = K'V^a \left(P_B - P_C \right) \text{ for saturated brine,}$$

where P_C is the vapor pressure of the ambient air, and P_B and P_S the pressures of saturating vapor of fresh water and of the brine at the considered temperatures.

The value of the rate of evaporation is:

$$\alpha = \frac{P_S - P_C}{P_B - P_C} \times \frac{K'}{K}$$

The vapor pressure of the ambient air is equal to $h \times P_B$ if "h" is the hygrometrical condition of the air.

The rate of evaporation can then be expressed only in terms of saturating vapor pressures of the fresh water and the brine:

$$\alpha = \frac{P_S - h P_B}{P_B (1-h)} \times \frac{K'}{K} \quad (1)$$

Experimental determination of the rate of evaporation on saturated brine.

We have previously shown that measuring of the evaporation on fresh water could be done in any place on condition that one has easily transportable measuring instruments. The obtention of the evaporation on saturated brine could be calculated if it were possible to find a simple relation between the rate of evaporation: α and the hygrometrical condition of the air: h.

Experimental studies, bearing on different periods of the year and over several years, have made it possible to determine the value of the saturating vapor pressure of the brine, which is the unknown quantity of the preceding equation (1).

Measurements have been made on tanks of $1m^2$ section, wood outside, plastic inside and heat-insulated with glass wool. These tanks contained brine saturated in sodium chloride and variable quantities of magnesium salt. One tank contained fresh water and served as evidence (Fig. 2.)

Each of these tanks was placed on a weighing-machine of 300 k° capacity and correct to within 5 gr. As the amount of water given off due to evaporation upset the balance of the weighing-machine, this was restored by adding fresh water the quantity of which was carefully measured.

Figures 3, 4 and 5 give the figured indications which allow one to trace the values of $\log P_s$ according to T_s temperature of the saturated brine.

It is noted that the curve obtained can be likened to a straight line (Figs. 6 and 7).

Figure 8 shows the variations of $\log P_s$ according to T_E temperature of the fresh water in the test or check tank, for different concentrations in magnesium ion.

Figure 9 gives the values of P_s for the preceding contents in magnesium ion, giving to T_E the respective values of 20°C, 25°C and 30°C.

These results show us that the saturating vapor pressure of the saturated brine P_s decreases when the content in magnesium ion increases.

The preceding data make it possible to establish the formula which, founded on the experimental results, links the value of the saturating vapor pressure of the saturated brine according to the temperature of the fresh water and the content in magnesium ion.

This formula is as follows:

$$\log P_s = (a-bx) T_E + a' + b'x \quad (2)$$

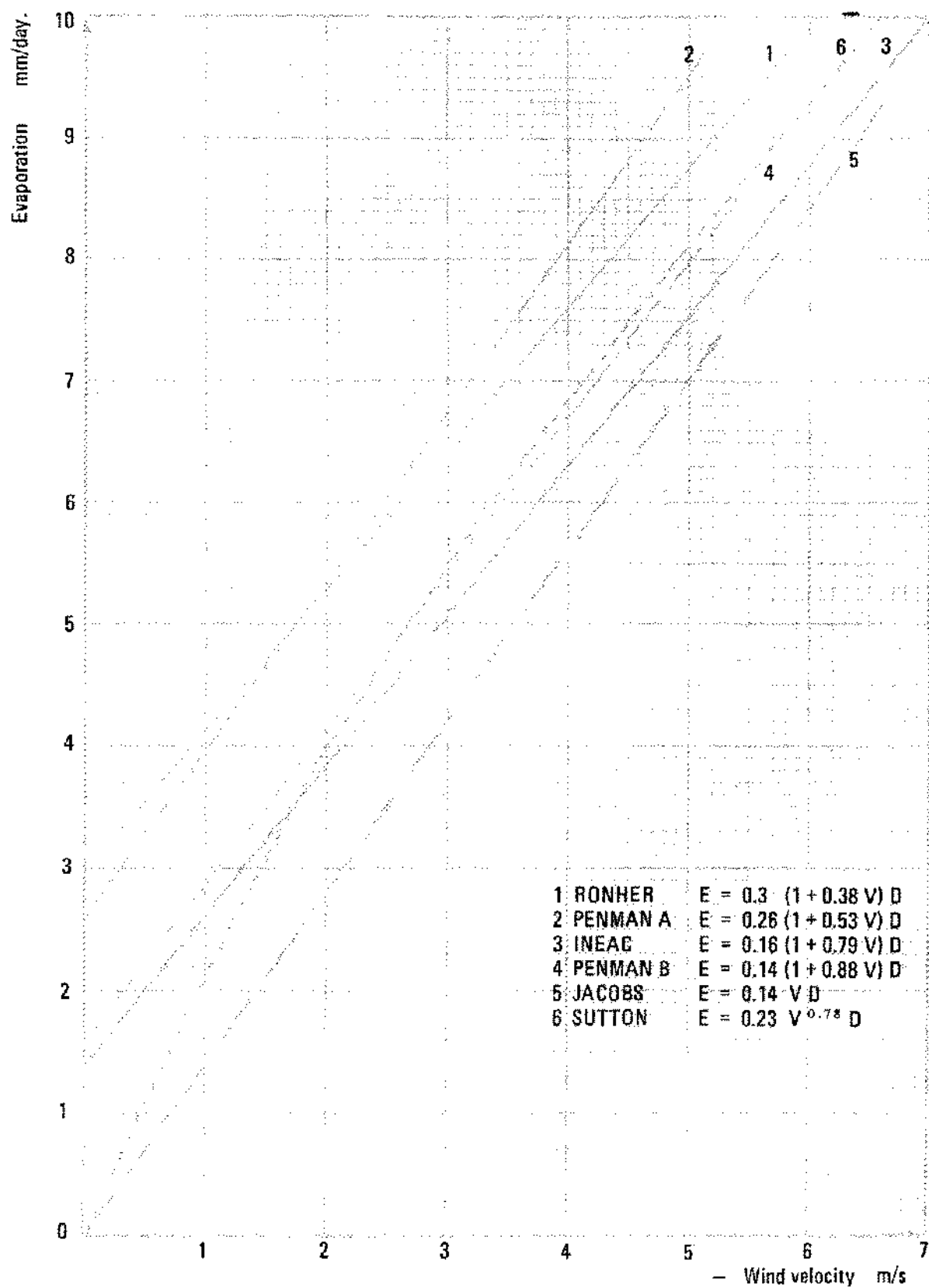


Figure 1. Evaporation on fresh water

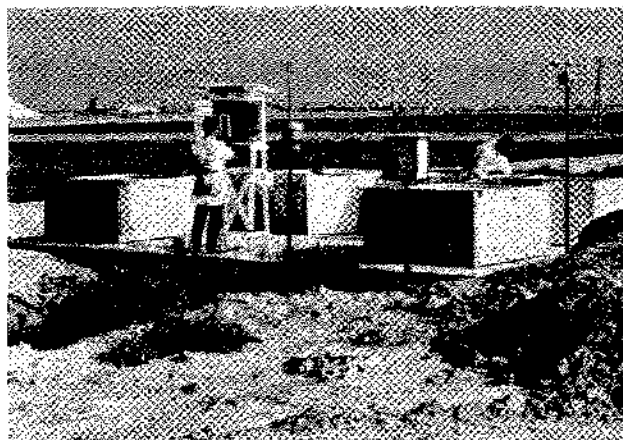


Figure 2. Experimental installation of evaporation.

Period	Time	Temperature °C		Hygrometry in %	Evaporation (mm)		P _B (in mb)	P _S	
		B ₁	B ₂		tank B ₁	tank B ₂		mb	Temperature °C
23.8.1961	8 à 14	23°3	26°3	38,2	2,29	1,66	28,41	23,58	26°3
	14 à 18	29°1	36°0	37,8	2,53	2,00	40,00	34,80	36°0
	18 à 8	15°6	23°7	64,2	2,65	1,37	17,63	14,58	23°7
24.8.1961	8 à 14	20°2	25°5	39,5	2,25	1,71	23,31	19,93	25°5
	14 à 18	27°6	33°8	49,3	2,54	1,68	36,63	30,33	33°8
	18 à 8	17°9	23°1	62,6	2,38	1,42	21,66	18,39	23°1
25.8.1961	8 à 14	20°2	25°6	49,3	2,04	1,47	23,46	15,21	25°6
	14 à 18	26°8	33°1	60,8	2,33	1,80	34,94	31,83	33°1
	18 à 8	18°5	23°3	73,7	1,82	0,70	21,15	17,79	23°3
26.8.1961	8 à 14	21°5	27°5	47,0	1,95	1,37	25,42	21,43	27°5
	14 à 18	29°2	35°6	55,5	1,78	1,25	40,23	34,88	35°6
	18 à 8	19°7	24°8	77,3	1,57	0,76	22,75	20,09	24°8
27.8.1961	8 à 14	22°9	27°9	59,3	1,00	0,54	27,65	22,48	27°9
	14 à 18	28°7	34°7	66,3	2,80	1,90	39,08	34,86	34°7
	18 à 8	20°1	24°3	83,9	0,56	0	23,31	19,56	24°3
28.8.1961	8 à 14	22°8	30°3	53,0	1,35	1,18	27,31	25,70	30°3
	14 à 18	31°0	37°2	68,5	2,19	0,68	44,56	34,89	37°2
	18 à 8	22°1	26°1	78,4	1,18	0,40	26,35	22,58	26°1

Figure 3.

Period	Time	Temperature °C		Hygrometry in %	Evaporation (mm)		P _B (in mb)	P _S	
		B ₁	B ₂		tank B ₁	tank B ₂		mb	Temperature °C
1.7.1963	8 à 14	20°6	25°7	41,6	3,92		24,05		
	14 à 18	22°1	28°0	47,5	3,91		26,38		
	18 à 8	15°9	17°6	71,9	2,89		17,95		
1.7.1963	8 à 14	21°8	26°4	45,0	3,84		25,89		
	14 à 18	23°3	28°4	50,0	3,61	2,23	28,41	22,98	28°4
	18 à 8	16°8	20°6	68,3	2,46	0,98	19,00	15,37	20°6
1.7.1963	8 à 14	19°4	24°6	50,0	1,53	0,84	22,34	17,31	24°6
	14 à 18	24°1	29°1	60,5	1,96	1,21	29,82	25,32	29°1
	18 à 8	19°2	23°1	78,1	2,41	0,97	22,07	19,18	23°1
1.7.1963	8 à 14	24°1	29°1	67,8	2,81	2,12	29,82	27,46	29°1
	14 à 18	29°5	36°1	88,5	2,80	1,51	40,93	38,76	36°1
	18 à 8	21°5	24°6	78,3	2,02	1,21	25,42	23,21	24°6
1.7.1963	8 à 14	24°5	29°1	63,0	1,94	1,26	30,53	26,59	29°1
	14 à 18	29°6	35°0	70,5	1,84	0,97	41,17	35,41	35°0
	18 à 8	21°7	25°1	66,1	2,29	1,38	25,74	22,77	25°1
1.7.1963	8 à 14	26°5	29°6	59,0	2,57	1,83	34,36	30,31	29°6
	14 à 18	30°4	37°0	67,5	2,85	1,88	43,09	38,35	37°0
	18 à 8	21°9	24°8	60,7	2,67	1,88	26,05	23,03	24°8
1.7.1963	8 à 14	24°7	29°6	38,3	2,38	1,50	30,88	23,35	29°6
	14 à 18	32°0	28°3	64,3	3,80	2,98	47,21	25,11	38°3
	18 à 8	20°4	24°8	77,0	1,85	0,60	23,75	20,07	24°8

Figure 4.

Period	Time	Temperature °C		Hygrometry in %	Evaporation (mm)		P _B (in mb)	P _S	
		B ₁	B ₂		tank B ₁	tank B ₂		mb	Temperature °C
18.9.1964	8 à 14	23°4	29°2	59,3	1,40	0,61	28,58	22,01	29°2
	14 à 18	27°8	34°4	74,0	1,84	1,10	37,07	34,07	34°4
	18 à 8	21°0	27°5	81,6	1,82	0	24,64	20,36	27°5
19.9.1964	8 à 14	23°4	28°7	56,3	1,25	0,88	28,58	24,89	28°7
	14 à 18	28°9	35°5	78,8	1,65	1,38	39,53	38,11	35°5
	18 à 8	23°3	29°1	87,8	0,95	0	28,41	24,94	29°1
20.9.1964	8 à 14	23°4	28°5	60,3	0,72	0	28,58	17,23	28°5
	14 à 18	27°9	33°4	72,0	0,90	0,63	37,28	33,92	33°4
	18 à 8	21°2	25°5	82,0	1,23	0,67	24,95	22,90	25°5
21.9.1964	8 à 14	22°3	27°0	49,5	1,62	0,86	25,14	19,18	27°0
	14 à 18	29°5	34°6	65,5	1,93	1,34	40,93	36,59	34°6
	18 à 8	21°2	26°1	79,6	1,20	0,24	24,95	20,88	26°1
22.9.1964	8 à 14	22°9	27°7	47,0	1,40	0,78	29,48	22,55	27°7
	14 à 18	28°9	34°8	51,8	2,12	1,53	39,53	34,23	34°8
	18 à 8	21°1	26°9	85,0	0,69	0	24,80	21,08	26°9
24.9.1964	8 à 14	24°6	29°7	70,5	0,66		30,70		
	14 à 18	29°5	34°9	77,0	1,78	1,00	40,93	36,80	34°9
	18 à 8	22°0	26°5	85,6	0,62		26,21	22,44	26°5

Figure 5.

T_S	$\text{Log } P_S$
20° 5	1,20763
21° 5	1,23805
22° 5	1,23045
23° 5	1,25406
24° 5	1,29336
25° 5	1,32222
26° 5	1,35526
27° 5	1,32305
28° 5	1,36530
29° 5	1,42177
30° 5	1,43521
31° 5	1,44514
32° 5	1,45697
33° 5	1,48144
34° 5	1,51957
35° 5	1,51468
36° 5	1,55145
37° 5	1,58206
$T_S = 29^\circ \text{C}$	$\text{Log } P_S = 1,38876$

Figure 6. Temperature and saturating vapor pressure of the brine.

We thus know all the factors of formula (1), which makes it possible to determine the rate of evaporation of the saturated brine. The search for this value is done from the chart in Figure 10.

As an example, let us suppose that the temperature of the fresh water is 25°C and that the magnesium content of the saturated brine is 35 gr. per liter, if the hygrometrical state of the ambient air is:

88.5% we find = 0 point C of the chart,
for 85.0% we find = 0.235 point D of the chart,
for 50.0% we find = 0.730 point E of the chart.

If the magnesium content is only 15 gr. per liter for the preceding hygrometry, points C' D' and E' of the chart are successively found.

This experimental study evidences the considerable importance played by magnesium concentration in a saturated brine which moreover, is theoretically laid down by the laws of physics for saturated solutions.

Consequences and Practical Application:

The speed of the curve which illustrates the variations in the rate of evaporation according to the magnesium ion content, gives excellent data on the salt supply from pans with saturated brine.

Let us again take formulas (1) and (2) in order to trace the curve giving variations in the rate of evaporation α according to the magnesium content of the saturated brine, x .

Let us fix the temperature of the fresh water, T_E , as well as the air hygrometry, h . Formula (2) can be expressed by the equation:

$$P_S = e^{Ax + B}$$

A and B being constants.

If we submit that: $h P_B = M$

$$\text{and: } (1-h) P_B = \frac{1}{N}$$

the rate of evaporation is expressed by the equation:

$$\alpha = N (e^{Ax + B} - M)$$

where:

$$\begin{aligned} a &= 0.027117 \\ b &= 0.0001099 \\ a' &= 0.809565 \\ b' &= 0.00135775 \end{aligned}$$

and where x is the content in magnesium ion.

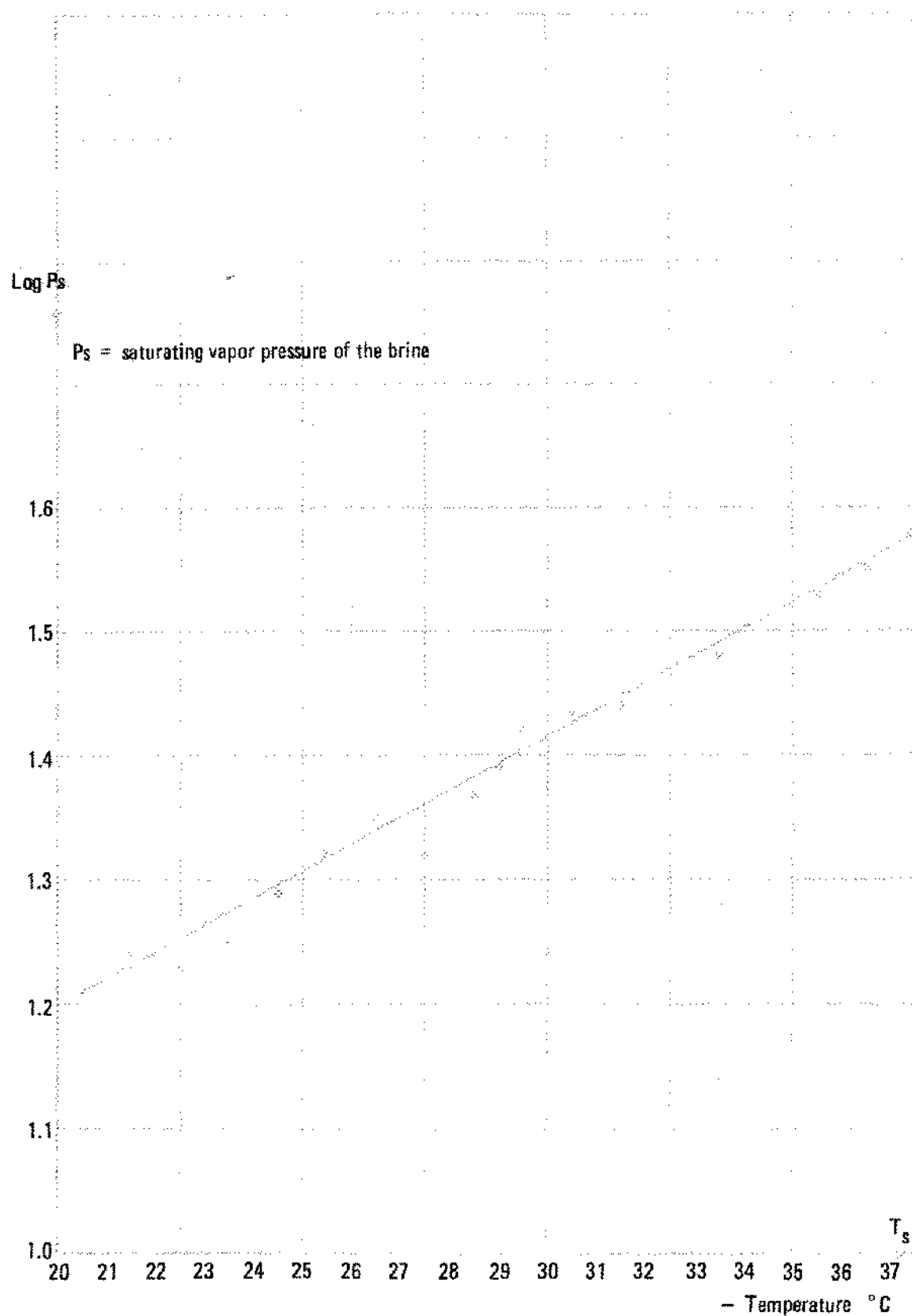


Figure 7. Temperature and saturating vapor pressure of the brine.

Mg in g/lit.	Formulas
16	$\text{Log } P_S = 0,25359 T_E + 0,83128$
24	$\text{Log } P_S = 0,024479 T_E + 0,84216$
37	$\text{Log } P_S = 0,023052 T_E + 0,85976$
40	$\text{Log } P_S = 0,022721 T_E + 0,86387$

Figure 8. Saturating vapor pressure of the brine and magnesium concentration.

Mg in g/lit.	P_S (in mb)		
	$T_E = 20^\circ \text{C}$	$T_E = 25^\circ \text{C}$	$T_E = 30^\circ \text{C}$
16	21,80	29,20	39,19
24	21,47	28,45	37,72
37	20,93	27,30	35,59
40	20,81	27,04	35,12

Figure 9. Saturating vapor pressure of the brine, temperature, and magnesium concentration.

the second derivative is:

$$\frac{d^2\alpha}{dx^2} = N A^2 e^{Ax+B}$$

This last expression is always positive, and the curve representative of the α variation according to x is a decreasing exponential having its concavity turned upwards (Fig. 11).

Let us compare two identical tanks, placed in a same spot, containing the same quantity of brine but each having a different magnesium ion concentration, x_1 and x_2 . Their rates of evaporation will be:

$$\alpha_1 \text{ and } \alpha_2.$$

The mean rate of these two tanks will be:

$$\alpha_m = \frac{1}{2} (\alpha_1 + \alpha_2)$$

Let us place at this same spot a third tank, the magnesium ion concentration of which is the mean of the concentrations x_1 and x_2 of the preceding tanks, i.e.,:

$$x_m = \frac{1}{2} (x_1 + x_2)$$

It is noted that the rate of evaporation of this solution α_m will be less than α_m .

Figure 12 shows that this difference in the rate of evaporation is far from being negligible.

This example shows that the mixture of two solutions saturated with sodium chloride, having different magnesium concentrations, diminishes the natural rate of evaporation of each of these brines taken separately but nevertheless together, and by this very fact diminishes accordingly the production of salt.

Consequently, if we feed a salt pan with successive supplies of saturated brine so as to maintain constant the height of brine undergoing evaporation, each time we lose the difference $m-s$. The algebraic sum of this difference may be important and in some cases, very considerably reduce production.

In conclusion, a crystallizing method can be advocated which would eliminate any mixture of saturated brines with different magnesium ion concentrations.

To arrive at this, it appears desirable to interconnect the salt pans, so as to create a flux of brine from the inlet of the first down to the last one. The salt pans will thus be placed in series and, as the evaporation takes place on all of the salt pans, the magnesium content will increase continually from the first to the last salt pan.

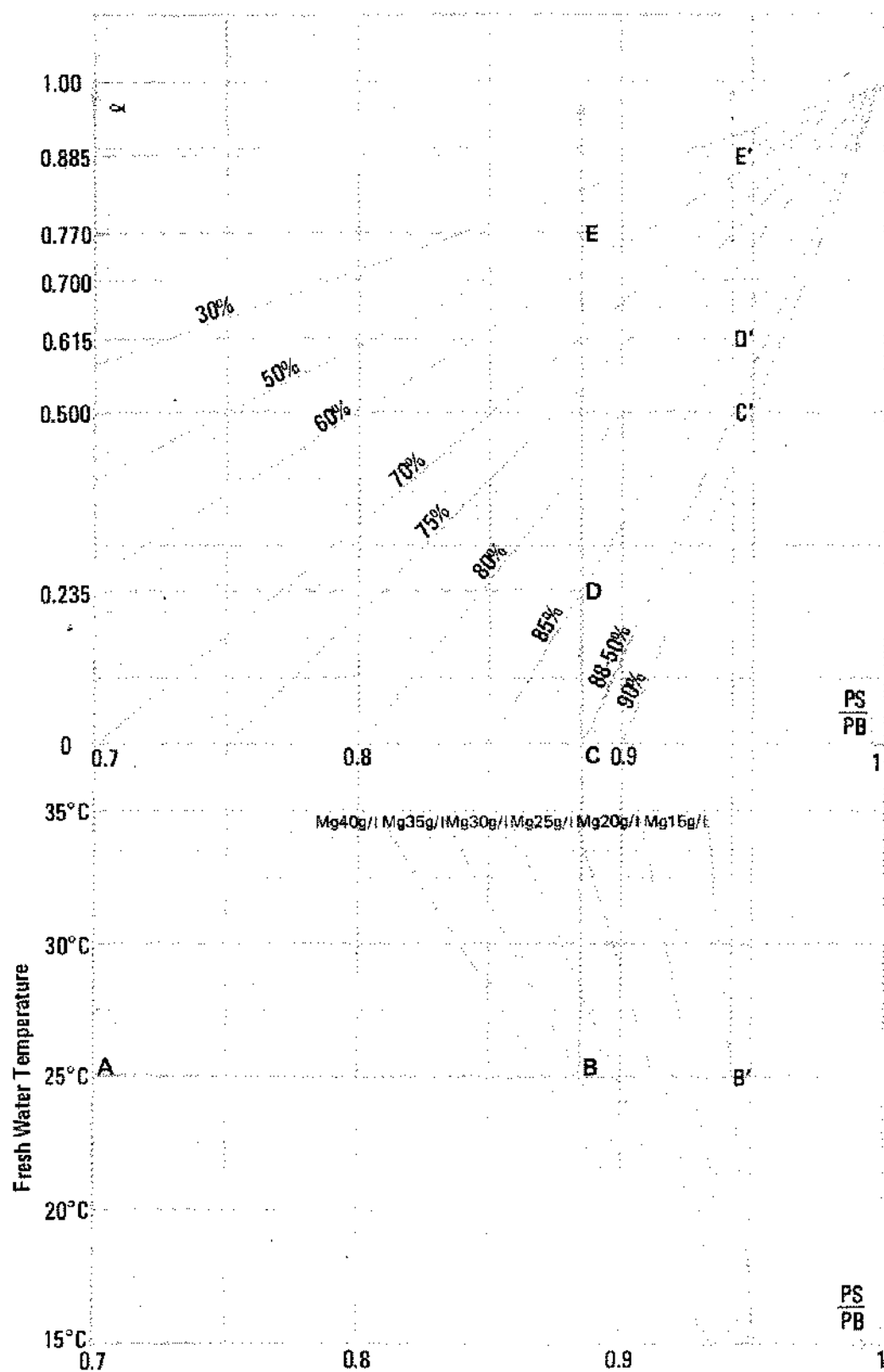


Figure 10. Evaporation ratio of brine referred to fresh water from fresh water temperature and ambient hygrometry.

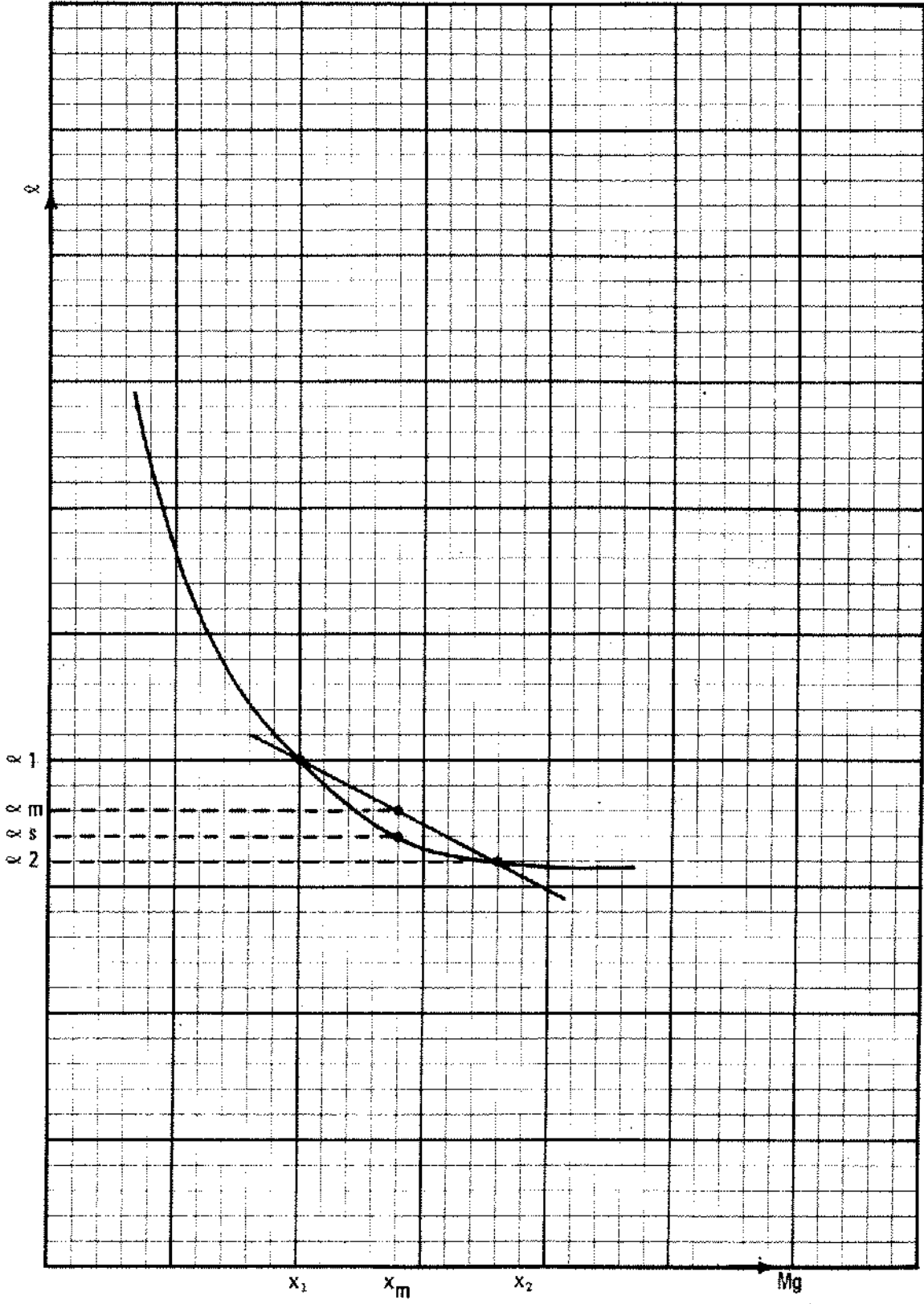


Figure 11. Rate of evaporation and magnesium ion concentration.

T_E ° C.	Hygrometry 80%				Hygrometry 90%			
	$x_1 =$ 15 gr/l $\alpha 1$	$x_2 =$ 35 gr/l $\alpha 2$	αm	$x_m =$ 25 gr/l αs	$x_1 =$ 15 gr/l $\alpha 1$	$x_2 =$ 35 gr/l $\alpha 2$	αm	$x_m =$ 25 gr/l αs
20°	0,730	0,560	0,645	0,640	0,460	0,120	0,290	0,280
25°	0,710	0,425	0,568	0,560	0,420	near of 0	0,210	0,120
30°	0,686	0,285	0,486	0,482	0,387	near of 0	0,193	near of 0

Figure 12. Rate of evaporation and mixing of brine.

The weather conditions will limit the magnesium concentration, as can moreover be shown by the preceding chart. In some areas the salt production

using this method of feeding the crystallizers has been increased up to more than 15%.