

# Seeding Seawater to Prevent Scale in Distillation Equipment

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## ABSTRACT

*Experimental study of the operating conditions of seawater demineralization plants by high temperature distillation (150°C) without any risk of scaling, has been carried out with the collaboration of the French Atomic Energy Commission. The introduction under given conditions of Hemihydrate germs into the seawater to be treated has made it possible to operate the evaporator without any scale, even in temperature ranges from 70°C to 150°C.*

*Deposits of both calcium sulphate and calcium carbonate are prevented and the conventional elimination of calcium carbonate acidification and gas removal is unnecessary. An industrial pilot unit has operated under such conditions and remarkable results were obtained: no scale, maintenance of pH of the brine at a constant value in the vicinity of 8, reduced risk of corrosion.*

## INTRODUCTION

Studies on the germination of seawater which the Compagnie des Salins du Midi et des Salines de l'Est has conducted with the cooperation of the French Atomic Energy Commission have been carried out in two steps. In a first one, the conditions of deposition and the speed of growth of calcium sulphate crystals in synthetic seawater were studied which allowed the calculation of the activation energies. These experiments confirmed the efficiency of the prevention of calcium carbonate and sulphate deposits at 100°C by the mechanism adding calcium sulphate seeds to seawater.

During the second step, there was an attempt to develop the industrial application of the knowledge previously acquired for the continuous treatment by germination of natural seawater, with a view to its distillation at high temperatures in the neighbourhood of 150°C.

The process and the tests conducted have given very

interesting results. The seawater treated solely by germination of calcium sulphate is sufficiently decalcified to feed a conventional distillation plant, the first section of which could operate at 150°C.

## DEVELOPMENT OF THE EXPERIMENTATION

First the following parameters were studied and measured:

1. Influence of the circulation speed of the seawater in the distillation units and concentration factors.
2. Speed of precipitation and growth of the calcium sulphate at temperatures of 80°C, 100°C and 150°C.
3. Optimum quantity of suspended seeds of calcium sulphate.

This work made it possible to define the conditions which prevent deposits of calcium carbonate and sulphate at 100°C, then at 145°C and at 150°C.

## EXPERIMENTS AT LESS THAN 100°C

1—*Arrangements for the experiment were as follows:*

Seawater is circulated by pumping it inside a loop constituted by glass elements. This water is heated to the maximum temperature of 100°C and the formation of the deposits is examined on cupro-nickel tubes heated internally. Calcium sulphate seeds are mixed with seawater and circulated with it.

The parameters measured during the experiment were flow rates, concentration factors of the brine, evolution of the dissolved calcium sulphate (Fig. 1), pH, exchange coefficients (difference in temperature between the two sides of the heat exchanger tube), concentration and nature of the suspension, examination and analysis of the deposits and analysis of the magnesium and chlorine in the brine.

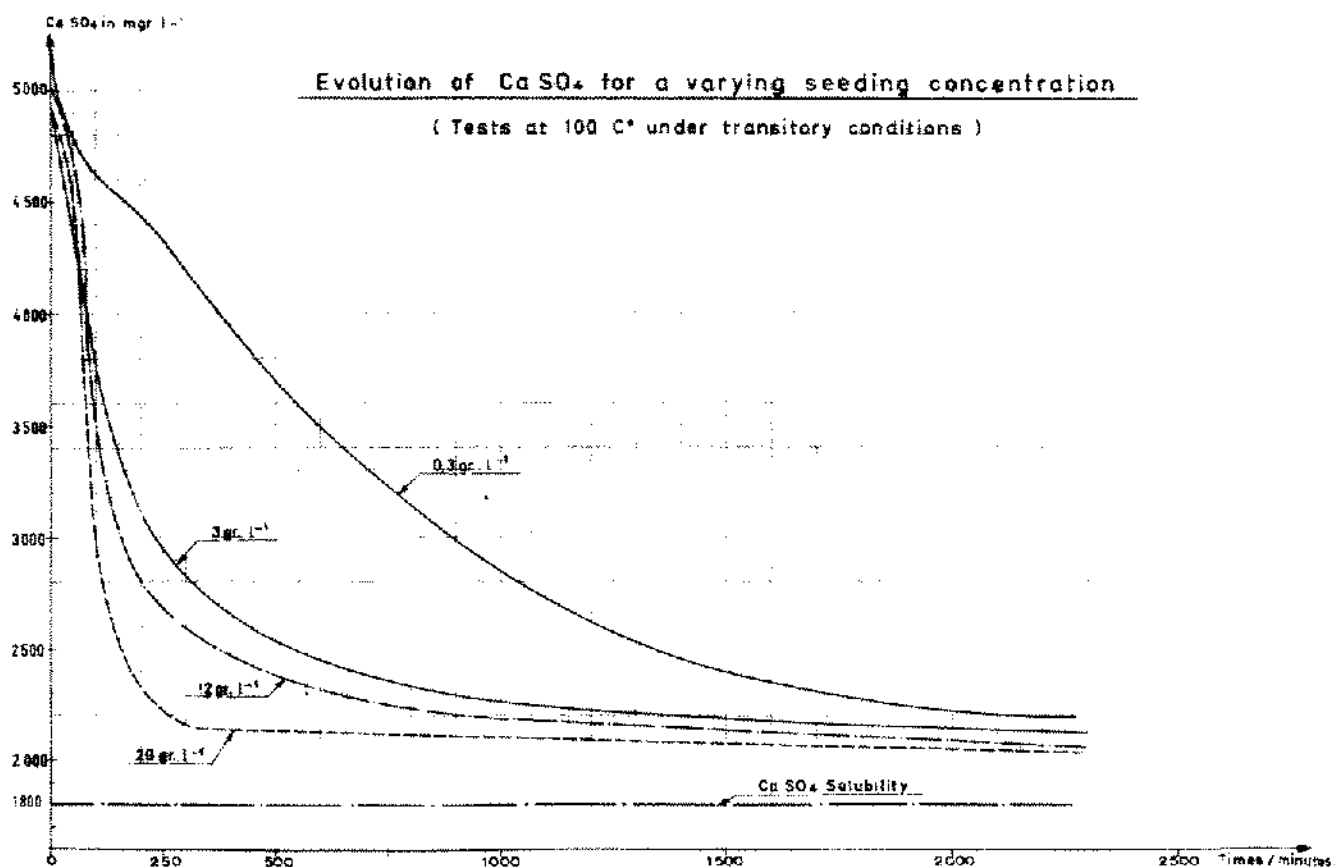


Figure 1. Evolution of  $\text{CaSO}_4$  for a varying seeding concentration (tests at  $100^\circ\text{C}$  under transitory conditions).

## 2—Precipitation rate of calcium sulphate:

Tests were made at temperatures from  $80^\circ\text{C}$  to  $100^\circ\text{C}$ , and with varied concentration factors of the brine and the seed content. The seawater used was synthetic seawater, without carbonate. Hemihydrate seeds of less than  $125\mu$  were fed into the system, then at regular intervals the reduction of calcium sulphate in the brine was measured. Samples of the seed suspension were taken at the beginning and the end of experiment and they have allowed calculation of the specific surface from the granulometric distribution of the seed in order to calculate the activation energies.

First the kinetics of the calcium sulphate precipitation law was checked in relation to the crystallized area and the constant of diffusion as follows:

$$\frac{dm}{dt} = K S \Delta C^2 \quad (1)$$

where:

$m$  = mass of calcium sulphate precipitated  
 $K$  = constant of diffusion  
 $S$  = crystallized area

$\Delta C = C - C'$  where  $C$  = effective concentration of the solution

$C'$  = saturation concentration

$V$  = volume of solution

Further it is deduced:

$$\frac{dC}{dt} = -\frac{KS}{V} \Delta C^2 \quad (2)$$

In the same way:

$$C - C' = \Delta C \quad dC = d\Delta C \quad (3)$$

which results in:

$$\frac{d\Delta C}{dt} = -\alpha \Delta C^2 \quad \text{with } \alpha = \frac{KS}{V} \quad (4)$$

By integrating this equation, we obtain:

$$\frac{1}{\Delta C} = -\alpha t + \frac{1}{\Delta C_0} \quad \text{with } \Delta C_0 = \Delta C \text{ for } t = 0 \quad (5)$$

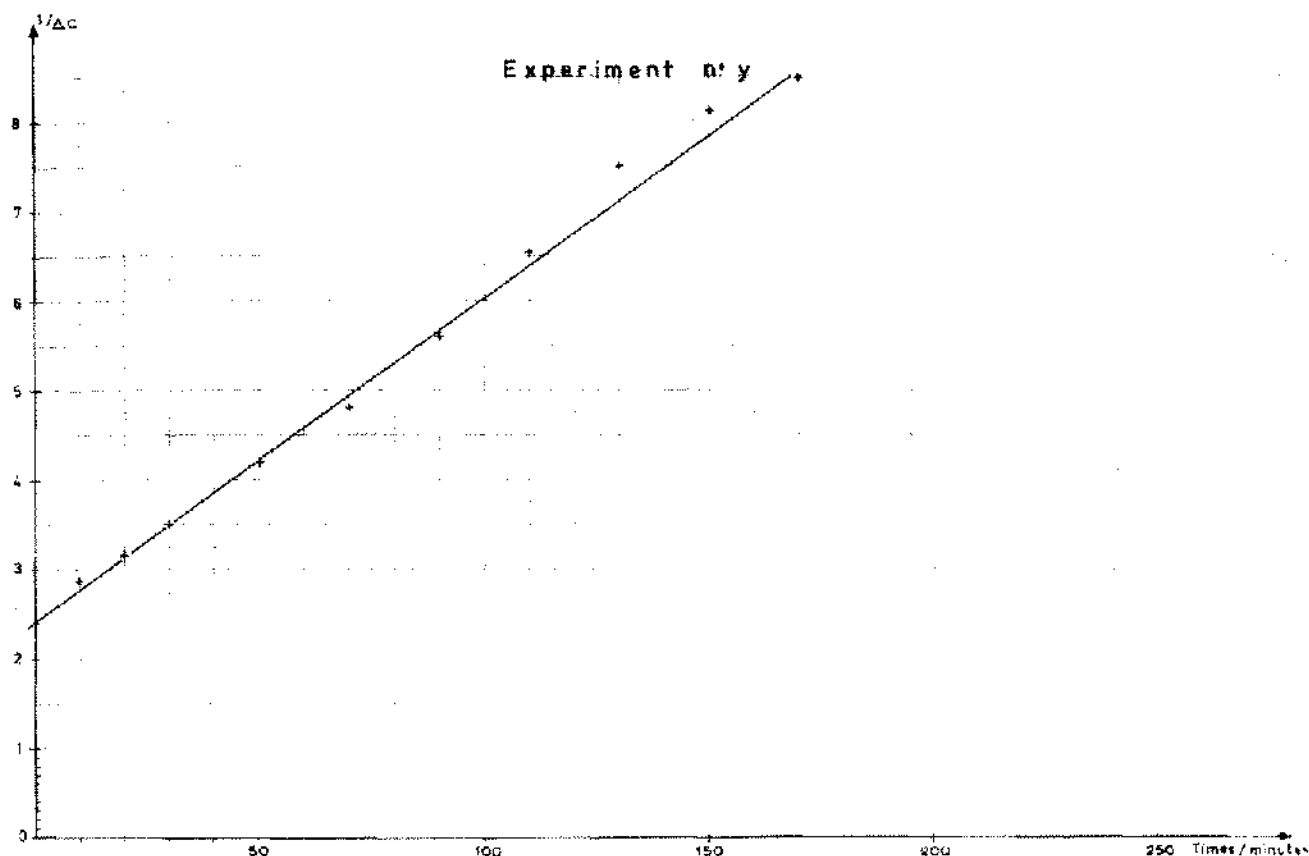


Figure 2. Experiment n° 5.

This equation could be written in the form:

$$\frac{t}{C_0 - C} = \frac{t}{C_0 - C'} + \frac{1}{\alpha(C_0 - C')^2} \quad (6)$$

The value of the  $\alpha$  constant could be determined by a two graph method more simply than by the calculation of  $dC/dt$ .

The first method consists in carrying  $1/\Delta C$  versus time and it requires the knowledge of  $C'$  (Fig. 2). The value  $\alpha$  can be determined by the slope of the straight line thus obtained.

The second method consists in tracing  $t/C^2 - C$  versus time (Fig. 3); the slope of the straight line obtained gives  $C'$  and the ordinate originally determines  $\alpha$ . The first portion of the curve which is not a straight line corresponds to an induction period.

The fact that straight lines are obtained confirms that the kinetic law is of the type expressed by the equations (1) and (2).

3—Calculation of the activation energies of the  $\text{CaSO}_4$  precipitation.

The constants of speed according to Arrhenius's law were checked:

$$K = A e^{-\frac{E}{RT}} \text{ and calculated } E \quad (7)$$

where:

$A$  = preexponential factor  
 $E$  = activation energy  
 $R$  = constant of the ideal gases (1.988 Cal. mole)

$$\log K = \log A - \frac{E}{RT} \log e$$

$$\log K_{100} = \log A - \frac{E}{R \times 373} \log e$$

$$\log K_{80} = \log A - \frac{E}{R \times 353} \log e$$

In subtracting the left and the right members of the equations:

$$\log K_{100} - \log K_{80} = -\frac{E}{R} \left( \frac{1}{373} - \frac{1}{353} \right) \log e$$

whence:

$$E = \log \frac{K_{100}}{K_{80}} \frac{20 \times 373 \times 353}{0.4343} = 3.06 \cdot 10^4 \log \frac{K_{100}}{K_{80}} \text{ cal/mole}$$

$$E = 30.6 \log \frac{K_{100}}{K_{80}} \text{ kcal/mole}$$

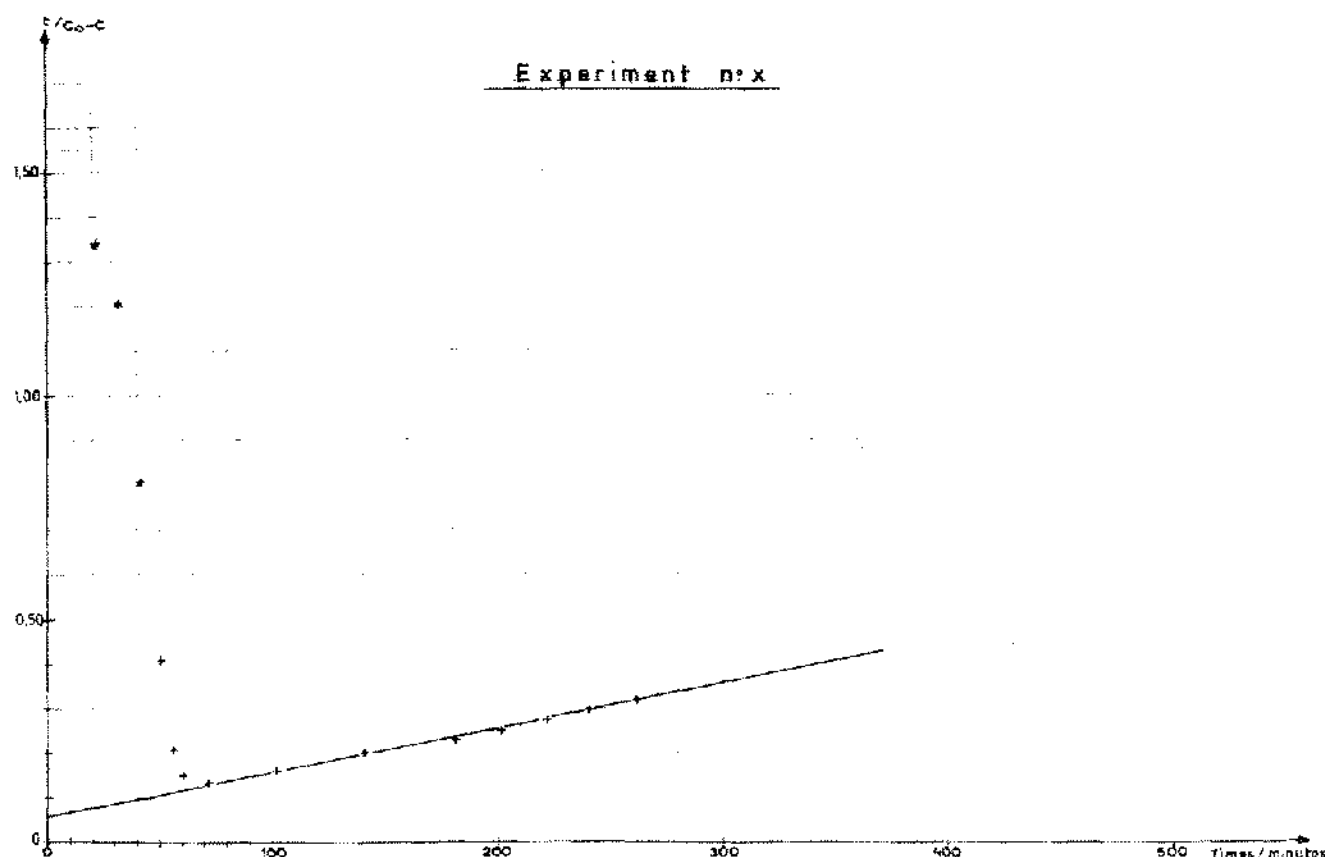


Figure 3. Experiment n° x.

The activation energies calculated from the experimental data versus the KS values and the germ area values, at 80°C and at 100°C, are closely related and round at about 35 kcal/mole (Fig. 4).

4—*Prevention of scaling by calcium carbonate and calcium sulphate at 100°C when seawater at concentration 1 is seeded by calcium sulphate.*

Prevention of the calcium carbonate:

After having brought the seawater to 60°C, a continuous supply of seawater was simulated by injection of sodium bicarbonate and calcium chloride. This addition caused the precipitation of  $\text{CaCO}_3$ . The temperature was then raised to a value slightly under 100°C to be situated under the precipitation threshold of the  $\text{CaSO}_4$ . Pilot tests, without seeds, and tests with 10 g/l of  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  seeds, have shown that in the first case, there was scaling of the heated tube ( $\Delta t$  15°C) and no deposit in the second case.

Simultaneous prevention of calcium carbonate and calcium sulphate:

During a first period, seawater without carbonate but saturated in calcium sulphate is heated to 60°C. An addition of sodium bicarbonate in solution is then added to a solution of NaCl with sufficient contact time to allow precipitation of the  $\text{CaCO}_3$ . The temperature is then

brought to 100°C and  $\text{CaSO}_4$  is injected continuously, which leads to a permanent precipitation of this element. Tests have been made without seeds and in the presence of 10 g/l of  $\text{CaSO}_4$  germs. In the first case, a great deal of scale was always obtained on the heated tubes; in the second case there was no deposit.

### EXPERIMENTS MADE AT 145°C.

The purpose of these experiments on natural seawater was to have them made under durable continuous operations and in a higher temperature range where processes already existing, such as antiscaling agent and acid treatment, are not efficient or too expensive. In addition, it involved confirming the results obtained on synthetic seawater, and showing the interesting application of seeding to inhibit deposits resulting from various scaling seawater salts.

#### 1—*Experimental principle:*

Conditions of the experiment (Fig. 5) were that a flash evaporator was fed with natural seawater preheated to temperature in the neighbourhood of 145°C. Initially about 20 g/l of Hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) is scattered into this seawater. By flashing in the evaporator, part of the brine becomes vaporized, while the part which has not been evaporated is separated from the seeds. Therefore, on

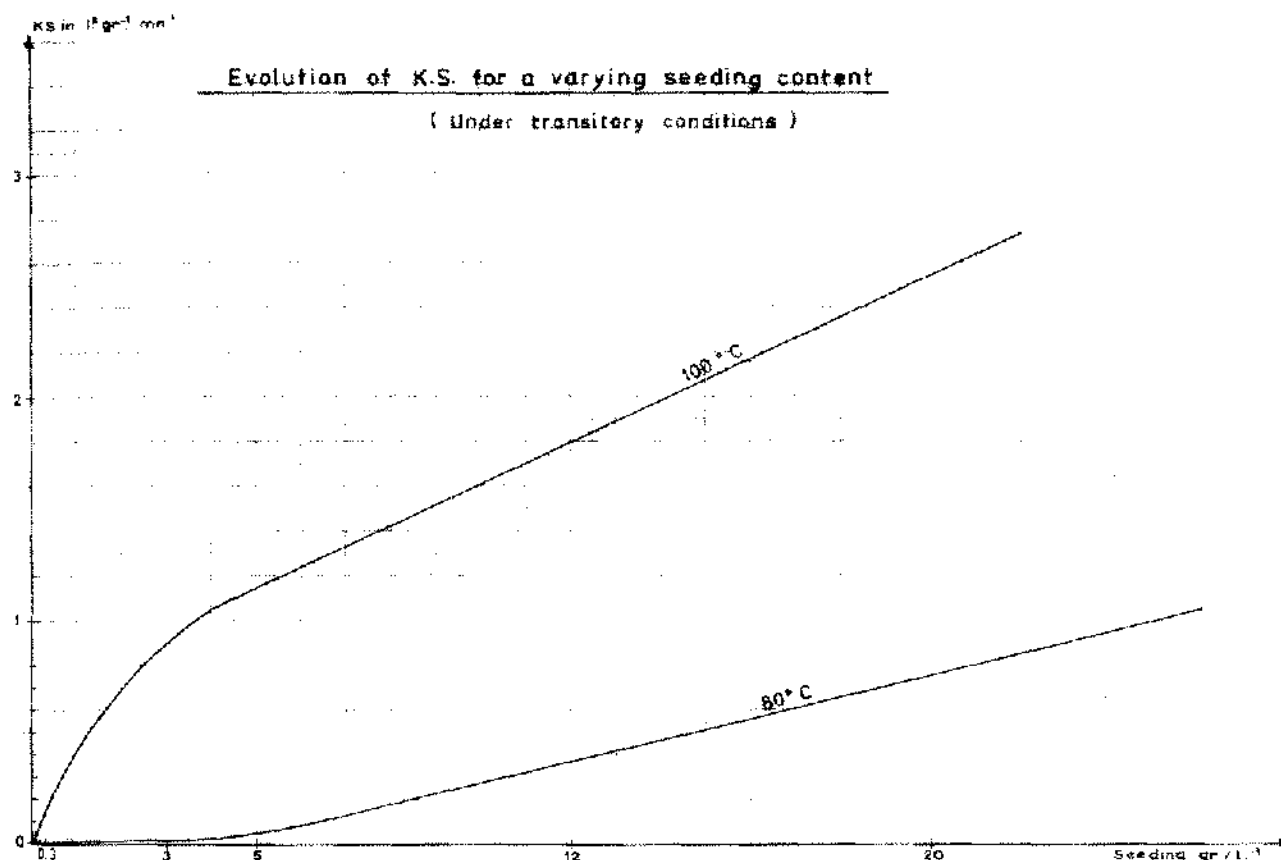


Figure 4. Evolution of K.S. for a varying seeding content (under transitory conditions).

the one hand there is production of a certain quantity of distilled water, and on the other hand production of clear brine which is evacuated to be used in some another way. The Hemihydrate seeds recovered are recycled and re-mixed with raw seawater. The discharges are regulated so as to maintain steady operation, the brine remaining at a factor of constant concentration. The brine produced the unit may constitute the feed of the first stage of a conventional distillation plant operating at a temperature close to 145°C, without any risk of scaling.

#### 2—Tests and measurements

Test conditions for the experiments are shown in Table I.

The various outputs measured included brine rejects, distilled water production and steam consumption in the heater. Hot samplings were taken in the system to measure the quantity of suspended seeds and their constitution was determined chemically and by X-ray diffraction. The concentration of the brine was checked by proportioning of the chlorides. Finally other complementary measurement of pH, AT<sup>1</sup>, CAT<sup>2</sup> and of the magnesium and calcium content were also made on the brine samplings after decantation of the germs.

#### 3—Results

During a first step (at 100°C), total inhibition of all deposits was obtained after the initial "seeding" with cal-

TABLE I

Seawater supply	Natural
Operating concentration	between 1.05 and 3
Temperatures	Heater outlet 140°C–145°C Expansion tank 135°C–140°C
Germ concentration CaSO <sub>4</sub>	> 5 g/l
Type of germs fed in	Hemihydrate (CaSO <sub>4</sub> , 1/2H <sub>2</sub> O)
Operating flow	H <sub>2</sub> O production 15 l/h Brine bleed 15 l/h Feed 30 l/h
Volume of liquid in the system	128 l
Heating capacity of electric test section	1 500 w
Period in plant	3 to 5 h

cium sulphate (Fig. 2). It was noted that the values of the pH remained constant (8–8.2). This phenomenon may be attributed to the presence of the calcium sulphate in suspension, as in all other cases of industrial or pilot plants, the pH has a tendency to increase by degassing of the CO<sub>2</sub>, and the CAT decreases from 15° to 2°.

With regard to the calcium carbonate and the magnesium salts, the first one disappears almost entirely from the system, while the second remains in solution. The calcium values in rejected brine are 1.16 to 1.36 g/l (tests

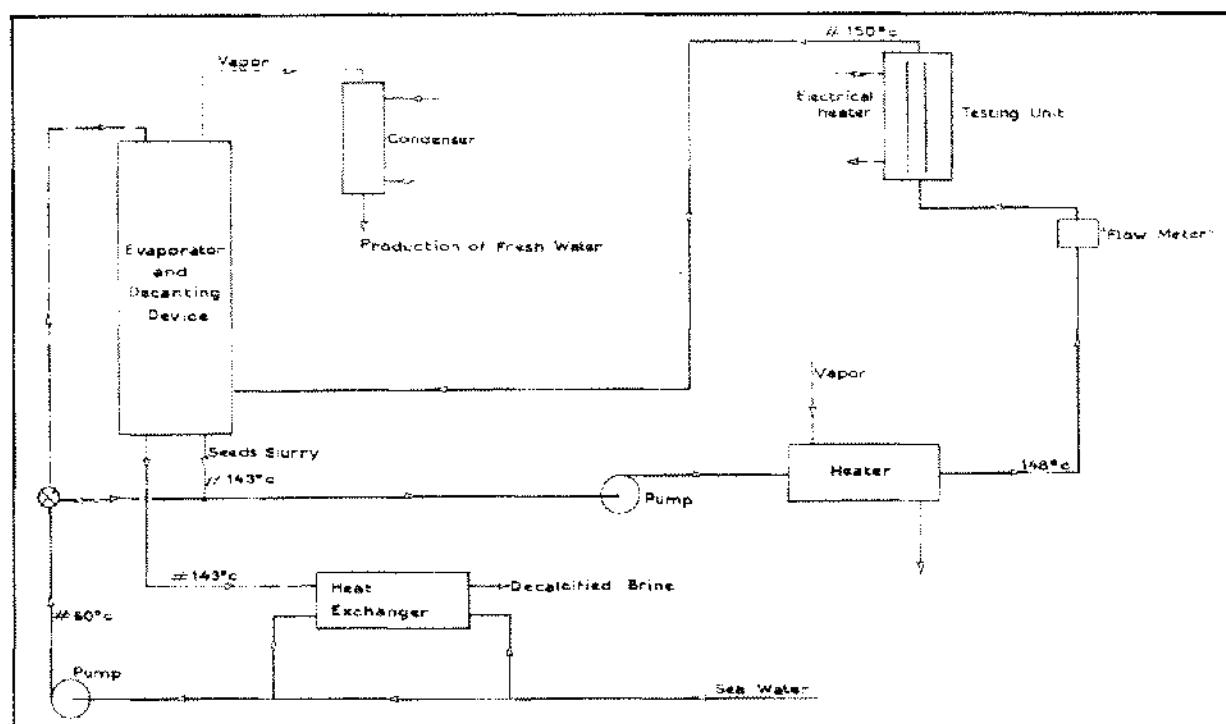


Figure 5. Pilot unit.

TABLE II

Recapitulative table of the experiments made at high temperature  
(average values after stabilization of the system)

Test n°	Period (h)	Concentration factors seawater	Temperature at heater outlet (°C)	Seed content (g/l)	CaSO <sub>4</sub> seawater (g/l)	Analysis of the brine at discharge (g/l)					Deposits
						CaSO <sub>4</sub> rem.	pH	Mg <sup>++</sup>	Cl <sup>-</sup>	CAT <sup>1</sup>	
3	68	2.03	145	18.3	1.50	1.33	8.05	2.77	43.5	2°5	No deposit
4	210	2.11	130	23	1.46	1.29	8.24	2.81	45	2°2	No deposit
5	200	1.64	153	25.6	1.50	0.78	8.15	2.20	34.4	2°6	No deposit
6	220	1.08	153	21.6	1.46	0.78	8.22	1.41	23.1	2°2	No deposit
7	300	1.07	150	20	1.53	0.81	8.17	1.45	22.9	2°1	No deposit
8	337	1.10	147	27.6	1.50	0.78	8.20	1.50	23.5	2°	No deposit

(1): 1° (alkalinity) = 10<sup>-4</sup> mole CaCO<sub>3</sub>/l

3 and 4) and correspond to the solubility limit of the Anhydrite according to Marshall and Slusher's (1968) curves.

The second step in the tests duly confirmed the efficiency of the process heated to 150°C, and at concentration factors 1.5 and 1.05, that is, no scaling.

Note: 1 - AT = simplified measurement of water alkalinity (to pH 9.0)

2 -CAT = measurement of total water alkalinity to (pH 4.0)

3 -°: 1° (alkalinity) = 10<sup>-4</sup> mole CaCO<sub>3</sub>/l

## CONCLUSION

From these results, it is clear that problems of evaporator scaling can be solved by the seeding with calcium sulphate. A substantial improvement in efficiency is obtained by the use of this process and therefore there is a cost-saving using conventional evaporators, because operating temperatures may be raised to 150°C. Additional cost-savings come from the fact that anti-scaling treatments such as additives and acidification may be avoided.

## REFERENCES

Marshall W., Slusher R., 1968. *Jour. Chem. Eng. Data*, 13, no. 1; 83