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Recovery of Mineral Salts and Potable Water from Desalting Plant Effluents by Evaporation. Part II. Proposed Simulation System for Salt Recovery

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Abstract

Salt recovery from rejected brines of the Al-Khobar Water Desalination Plant, Saudi Arabia, is studied through the simulation of a modified MSF system. Two phases of concentrations are planned: Phase I will concentrate the main effluent from 6.4 wt% total salt to 28.8%, while Phase II will use the effluents from Phase I as a feed to undergo further evaporation and cooling. NaCl and water are produced throughout this phase, while the end residue product will be essentially $MgCl_2$, since it is the most soluble. A mathematical model is developed and used to perform stage-to-stage material and heat balance calculations. Concentrations of NaCl and $MgCl_2$ in the streams entering and leaving a stage are determined by using the solubility correlation developed in Part I. Simulation results show that by using 5210 tons/h brine as a feed for Phase I, we can recover 4430 tons/h fresh water, 277 tons/h NaCl, and 502 tons/h bitttern (in which the ratio of $MgCl_2/NaCl$ is increased to 12) as the very final products of the integrated scheme. This bitttern provides 30 tons/h $MgCl_2$ as an end product.

1. SALT RECOVERY FROM SEAWATER: STATE OF THE ART

Desalination plants do not remove all of the water available in a given amount of seawater; they remove only about half of it. Thus, the effluents

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from these plants are about equal in volume to the amount of potable water produced, and they have about twice the concentration of the original seawater. Effluents are therefore more valuable as a source of minerals than average seawater. The recovery of mineral salts from desalination plants effluents has recently assumed new importance as a possible route to reduce the overall cost of water conversion through the profitable sale of valuable minerals as well as reducing the pollution of seawater. The Kingdom of Saudi Arabia with its large number of desalination plants would be best suited for the recovery of mineral salts from desalination plant effluents.

The recovery of the major salts from seawater is usually carried out by different methods described in the literature (1-6). These methods are identified as precipitation, electrolysis, electrodialysis, adsorption, ion exchange, chelation, oxidation, chlorination, solvent extraction, and solar evaporation.

Thus, the trends in recovering salts from seawater are mainly devoted to chemical separation methods. However, the current commercial method to obtain sodium chloride from seawater is by solar evaporation (7). Magnesium chloride, on the other hand, is recovered commercially by the Dow Chemical Process (7, 8) where $MgCl_2$ is extracted from seawater by a series of chemical treatments and fed to electrolytic cells to produce magnesium metal. More than 90% of magnesium metal used in the United States is produced by this method (5).

The recovery of valuable minerals from concentrated brines by the physical separation approach appears particularly attractive, since no raw materials are needed except the brine itself. Added to that is the fact that additional fresh water is obtained during the evaporation process.

Abdel-Aal and co-workers (1, 2, 6) proposed a preferential separation technique to separate $MgCl_2$ from seawater. Solar energy was used in evaporating a dynamic stream of seawater across an inclined long channel evaporator.

Glassett (9) proposed a recovery process to obtain valuable minerals. The process involves solar evaporation at room temperature to 1.27 specific gravity with subsequent dilution with fresh water and cooling.

The production of potable water along with sodium chloride from seawater was practiced in Kuwait and described by Messing (10). In this process a three-stage forced-circulation evaporator was used for sodium chloride recovery. It was built as a subsequent stage to a flash evaporator plant. The purity of the sodium chloride produced is 99.68%.

The current practice in multistage flash evaporators (MSF) desalina-

tion plants normally produces effluent brines in which the concentration of the salts reaches 2 to 3 times the initial seawater concentration.

This work is aimed at vaporizing these desalting effluents for further concentration in a series of MSF units with the objectives of coproduction of fresh water and mineral salts (sodium and magnesium chlorides), as well as reducing the pollution of seawater by the discharge of untreated effluents. In a country like Saudi Arabia, where some of the world's largest commercial desalting plants have been built and where most of present day desalting capacity is located, operating these MSF plants represents an attractive approach for economic reclamation of valuable mineral salts and additional potable water (11).

2. MODIFIED MSF SCHEME

The simulated MSF scheme aimed at evaporating the brines exiting the desalination plants consists of two phases: Phase I, in which potable water is the only product, evaporated by a series of MSF evaporators; and Phase II where potable water, NaCl, and a highly concentrated MgCl₂ bittern are obtained. Thus, arrangement is provided in Phase II to have separators (coolers) along with the MSF evaporators to bring about the separation of the NaCl salt. A simplified outline for the proposed process is shown in Fig. 1.

2.1. Formulation of Mathematical Model Equations

Phase I: MSF Evaporator

The mass and energy balances around one stage (see Fig. 2A) are as follows.

Mass Balance

$$F = B + D \quad (1)$$

$$x_F F = Bx_B + Dx_D \quad (2)$$

$$x_F = (1 - R)x_B + Rx_D \quad (3)$$

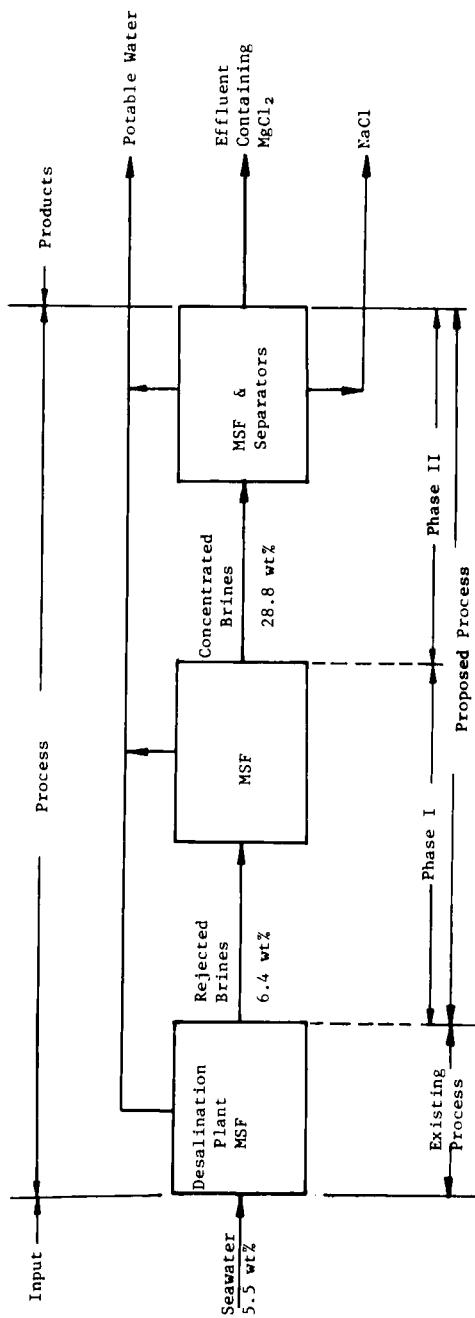
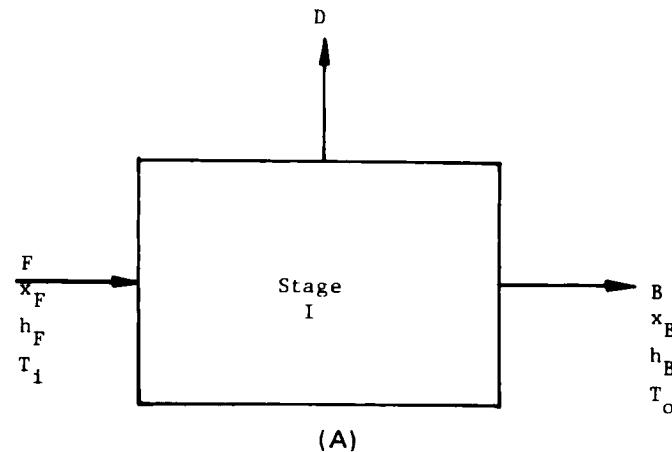
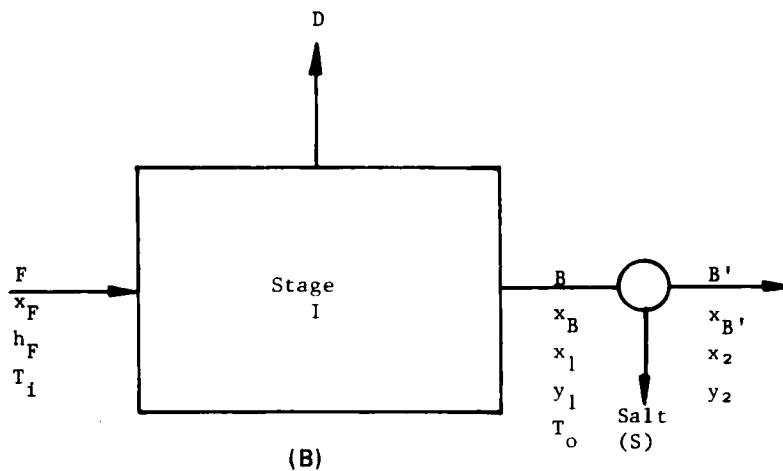


FIG. 1. Proposed desalting scheme for the coproduction of mineral salts and potable water.



(A)



(B)

FIG. 2. (A) Simplified diagram for MSF calculations. (B) Simplified diagram for Phase II calculations around the separator.

$$x_B = \frac{x_F - Rx_D}{(1 - R)} \quad (4)$$

where $R = D/F$.

Heat Balance

$$h_F F = DH + Bh_B \quad (5)$$

$$h_F = RH + (1 - R)h_B \quad (6)$$

$$F = \frac{h_F - h_B}{H - h_B} \quad (7)$$

The calculation procedure for the MSF scheme was programmed as shown in Fig. 3.

Phase II: Separator

The mass balances around the separator (see Fig. 2B) are given as follows.

Overall Mass Balance

$$B = S + B' \quad (8)$$

where B' is the blowdown flow rate after the separator and S is the NaCl salt solution flow rate.

MgCl₂ Balance

$$y_1 B = y_2 B'$$

$$y_1 = y_2 \left(1 - \frac{S}{B}\right) \quad (9)$$

$$y_2 = \frac{y_1}{(1 - w)} \quad (10)$$

where $w = S/B$.

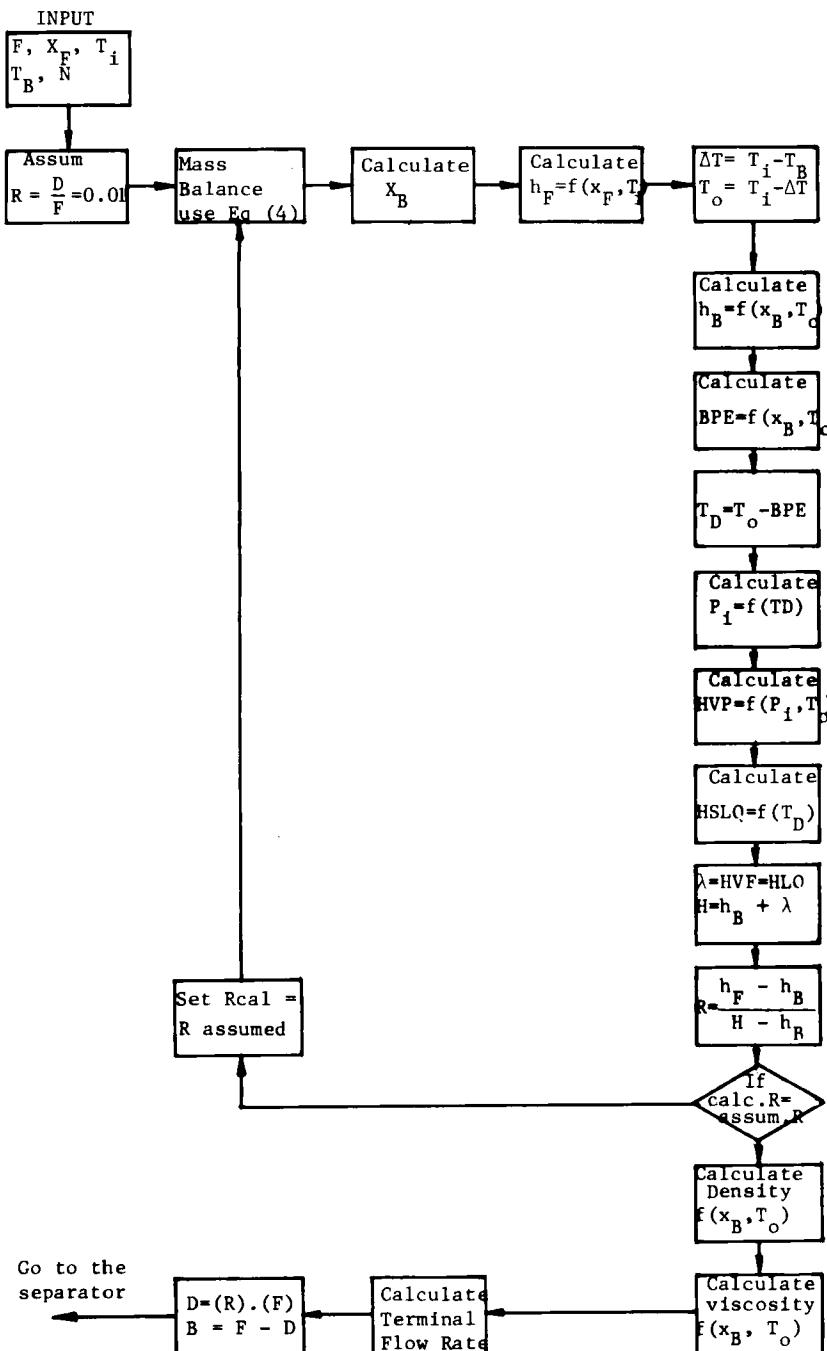


FIG. 3. Block diagram for MSF calculations.

NaCl Balance

$$x_1 B = B' x_2 + S \quad (11)$$

$$x_1 = (1 - w)x_2 = w \quad (12)$$

$$w = \frac{(x_1 - x_2)}{(1 - x_2)} \quad (13)$$

The calculation procedure for the separator is shown in Fig. 4. This involves the simultaneous solution of the mass balance equations—as shown in Fig. 5—along with the equilibrium solubility correlation.

Figure 6 represents a simplified diagram showing how the phase equilibria data are used in the separation of salts for Phase II.

2.2. Computation Method

The calculation is performed by the main program which includes the input and output. It calculates the heat and material balance of the whole plant (all stages). This program calls Subroutine (CALC) which calculates the heat and material balance of each stage and finds the composition of each stream using the solubility correlation. Subroutine (CALC) calls several short subroutines to perform physical properties calculations. These subroutines are described below:

- (a) ENTH: This subroutine is used to calculate the enthalpy of brine as a function of temperature and concentration.
- (b) BPE: This subroutine is used to determine the boiling point elevation of brines as a function of temperature and concentration.
- (c) VIS: This subroutine calculates the dynamic viscosity of brines as a function of temperatures and concentration (correlation was presented in Part I).
- (d) DEN: This subroutine computes the density of seawater as a function of temperature and concentration (correlation was presented in Part I).
- (e) SPVOL: This subroutine calculates the specific volume of superheated steam as a function of temperature and pressure.
- (f) SOLUB: This subroutine calculates the solubility of sodium chloride in magnesium chloride solutions as a function of temperature and

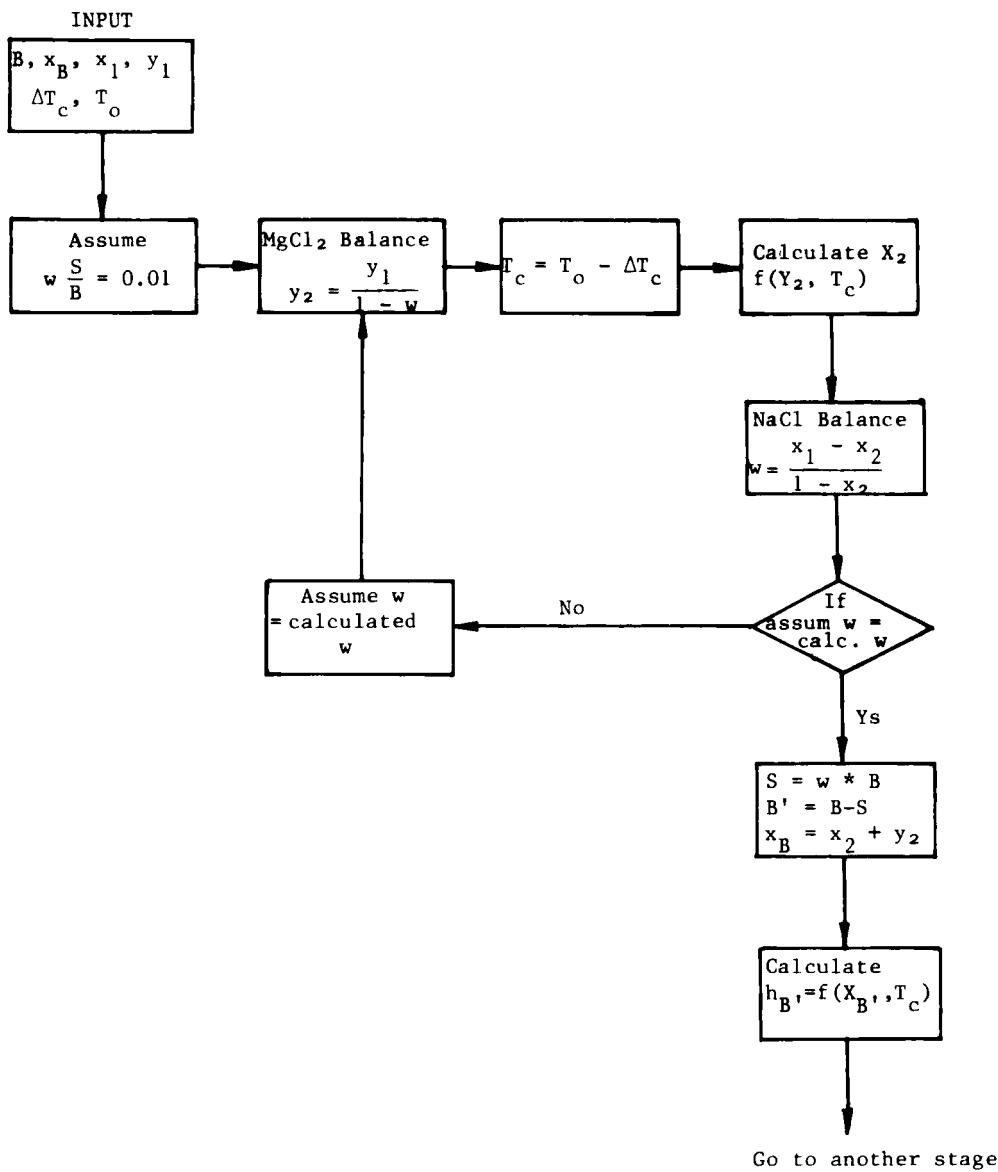
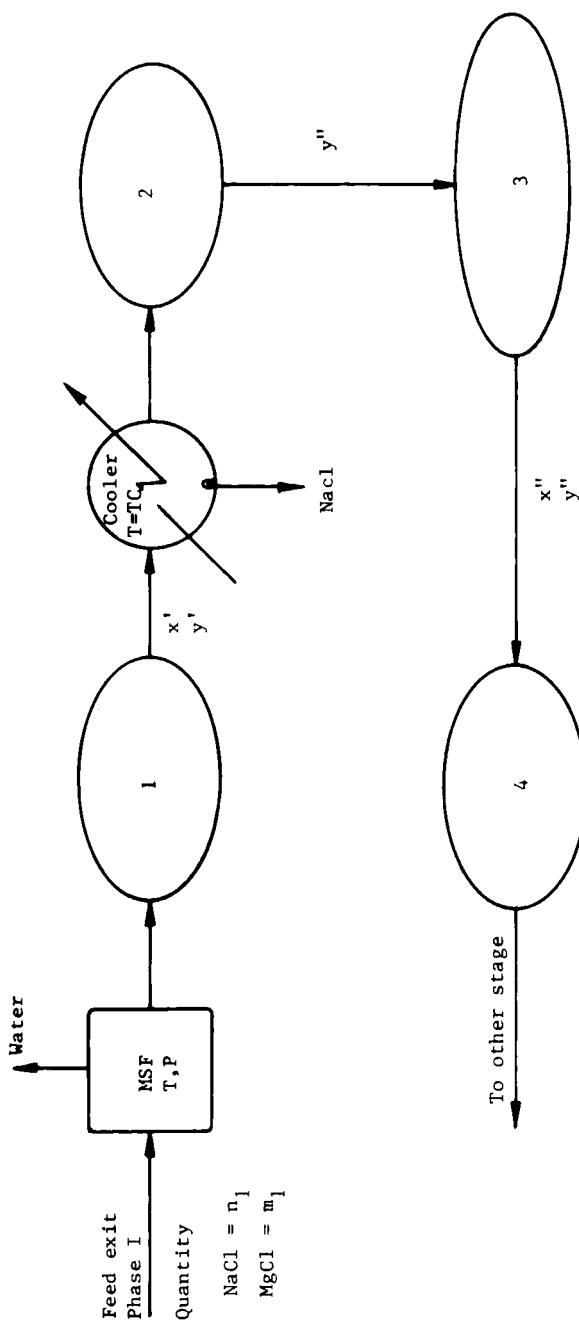


FIG. 4. Block diagram for Phase II calculations around the separator.



Basis : $m_1 = \text{constant}$

Step 1 = Using Mass & Heat Balance, calculate the concentration of NaCl & MgCl₂. (x' , y')

Step 2 = Using Mass Balance calculate, MgCl₂ concentration around the cooler (y'')

Step 3 = Using Solubility Correlation at T_c , calculate NaCl concentration (x''), $x'' = f(T_c, y'')$

Step 4 = a) Using Mass Balance, calculate the quantity of NaCl soluble with MgCl (n_2),
b) NaCl separated (n_3), $n_3 = n_1 - n_2$

FIG. 5. Block diagram for mass balance calculation in Phase II.

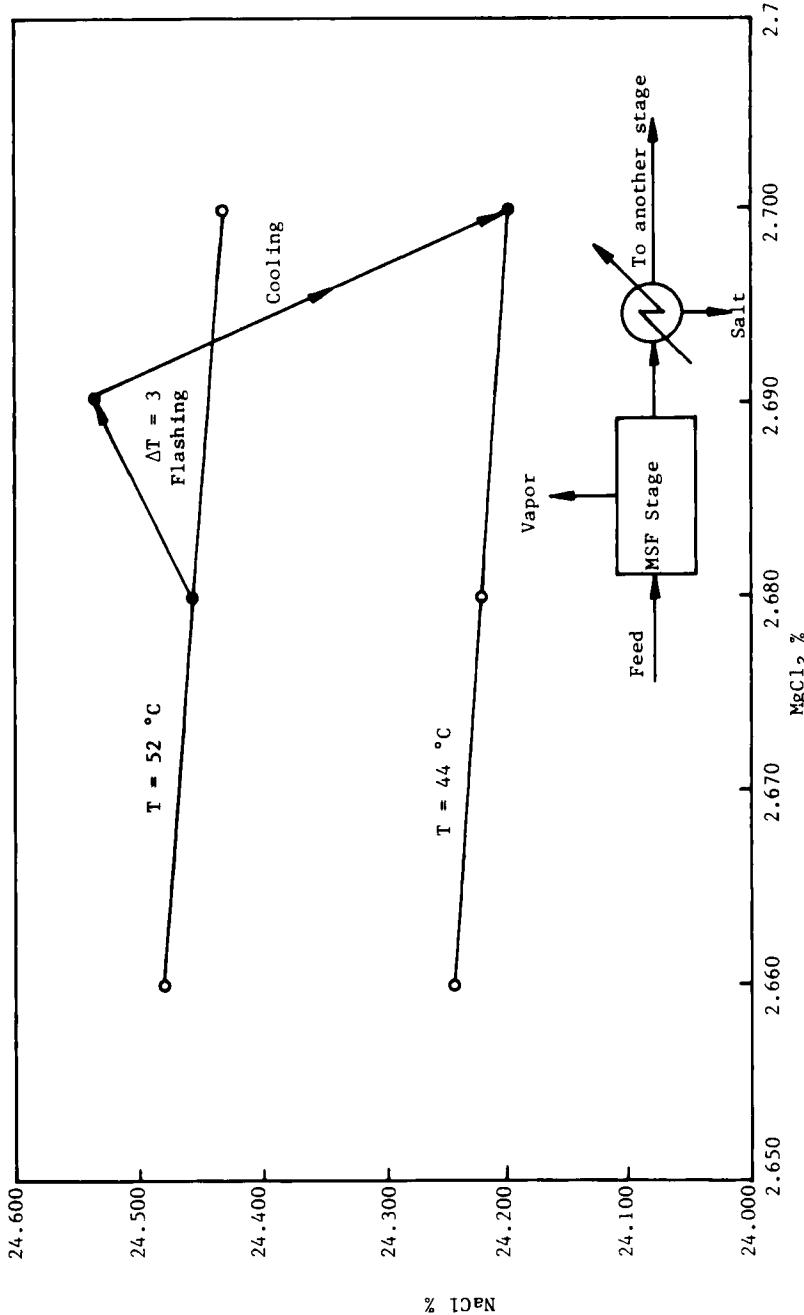


FIG. 6. Simplified diagram representing the phase equilibria for the separation process in Phase II.

magnesium chloride concentration (solubility correlation was developed for the full range in Part I).

- (g) HV: This subroutine calculates the enthalpy of superheated stream as a function of temperature and pressure.
- (h) HSLQ: This subroutine calculates the enthalpy of saturated stream as a function of temperature.
- (i) PRESS: This subroutine calculates the pressure of saturated stream as a function of temperature.
- (j) EXTR: This function is called by any subroutine to extrapolate the value of any physical property outside the limited range of this property.

3. RESULTS AND DISCUSSION

Phase I

Currently, the Al-Khobar Desalination Plant gives 5210 tons/h of effluents having 1.2 times the original concentration of the Arabian Gulf water. This amount is used as a feed to Phase I of the proposed salt recovery process. Conditions and design parameters of the initial phase of work are given in Table 1. Results show that 4080 tons/h is produced as potable water as a consequence of stage-to-stage calculations which are given in Table 2. The total number of stages is 20. As a result of concentrating the brine, 78.31% of the feed is obtained as fresh water.

TABLE 1
Design Parameters of Phase I

Total number of stages = 20
Desalination effluents temperature = 35°C
Top brine temperature = 140°C
Blowdown temperature = 60°C
Salinity in feed = 6.44%
Salinity after recirculation = 26.3%
Salinity of blowdown = 28.8%
Salinity of distillate = 0.01%
Feed rate = 5210 tons/h
Distillate rate = 4080 tons/h
Blowdown rate = 1130 tons/h
Recirculation rate = 42,490 tons/h
Average stage decrement temperature = 4.0°C

TABLE 2
Stage-to-Stage Calculations for Phase I

Stage no.	Brine flow (tons/h)	Distillate (tons/h)	Blowdown (tons/h)	Concen- tration (%)	Pressure (bar)	Inlet tem- perature (°C)	Outlet tem- perature (°C)	Boiling point evalution (°C)	Distillate tem- perature (°C)
1	47,700	230	47,470	26.4	2.533	140	136	7.7049	128.295
2	47,470	220	47,250	26.6	2.251	136	132	7.5705	124.43
3	47,250	220	47,030	26.7	1.995	132	128	7.4365	120.544
4	47,030	220	46,810	26.8	1.763	128	124	7.303	116.697
5	46,810	220	46,590	26.9	1.554	124	120	7.1701	112.830
6	46,590	210	46,380	27.1	1.365	120	116	7.0378	108.962
7	46,380	210	46,170	27.2	1.196	116	112	6.9062	105.094
8	46,170	210	45,960	27.3	1.045	112	108	6.7754	101.225
9	45,960	210	45,750	27.4	0.909	108	104	6.6454	97.355
10	45,750	200	45,550	27.5	0.789	104	100	6.5164	93.484
11	45,550	200	45,350	27.7	0.682	100	96	6.3883	89.612
12	45,350	200	45,150	27.8	0.587	96	92	6.2611	85.739
13	45,150	200	44,950	27.9	0.504	92	88	6.1351	81.865
14	44,950	190	44,760	28.0	0.431	88	84	6.0102	77.990
15	44,760	200	44,560	28.2	0.366	84	80	5.8865	74.114
16	44,560	190	44,370	28.3	0.311	80	76	5.7639	70.236
17	44,370	190	44,180	28.4	0.262	76	72	5.6427	66.357
18	44,180	190	43,990	28.5	0.220	72	68	5.5228	62.477
19	43,990	180	43,810	28.6	0.184	68	64	5.4043	58.596
20	43,810	190	43,620	28.8	0.153	64	60	5.2872	54.713

Phase II

With the effluents of Phase I having a specific gravity of 1.20, Phase II uses these effluents as a feed for further concentration. For the separation of the salts (NaCl), the effect of changing the cooling temperature at the separator was considered as an important parameter in our study.

Two cases were studied to investigate the effect of changing the cooling temperature on the salt recovery.

Case 1. Here, the cooling temperature is chosen to be 5° less than the outlet temperature of the stage as shown in Fig. 7 for a feed rate of 1130 tons/h.

In this case 20.59 tons/h salts and 14.07 tons/h of potable water are obtained. This is accomplished in 4 stages. Tables 3 and 4 summarize the results of this case. Figures 8 and 9 illustrate the change in fresh water and salt recovered with stage number, respectively. The recovery ratio of $MgCl_2/NaCl$ is shown in Table 5.

Case 2. The cooling temperature is chosen to be 2° less than the outlet temperature of the stage.

In this case, again for a feed input of 1130 tons/h, 22.31 tons/h salt is produced along with 21.03 tons/h of distillate, and this is achieved in 6 stages.

Tables 6 and 7 show the results of this case, and Figs 9, 10, and 11 illustrate the change in potable water and salt recovery with the number of stages. For this case, one can conclude that changing the cooling temperature drop from 5 to 2°, while keeping other operating conditions constant, will produce more salts and water; however, more stages are needed. This consequently requires a higher operating and capital cost.

CONCLUSIONS

1. The data used in this research to simulate the MSF evaporation were obtained from an actual desalination plant.
2. The evaporation of the brine exit of the desalination plant is carried out in two consecutive phases. In Phase I, where the $MgCl_2/NaCl$ ratio is about 0.1, the brine is concentrated from a specific gravity of 1.04 to 1.2 using 20 MSF stages. Potable water is the only product. In Phase II the concentration of the feed is carried out in 32 repeated cycles of 4 stages

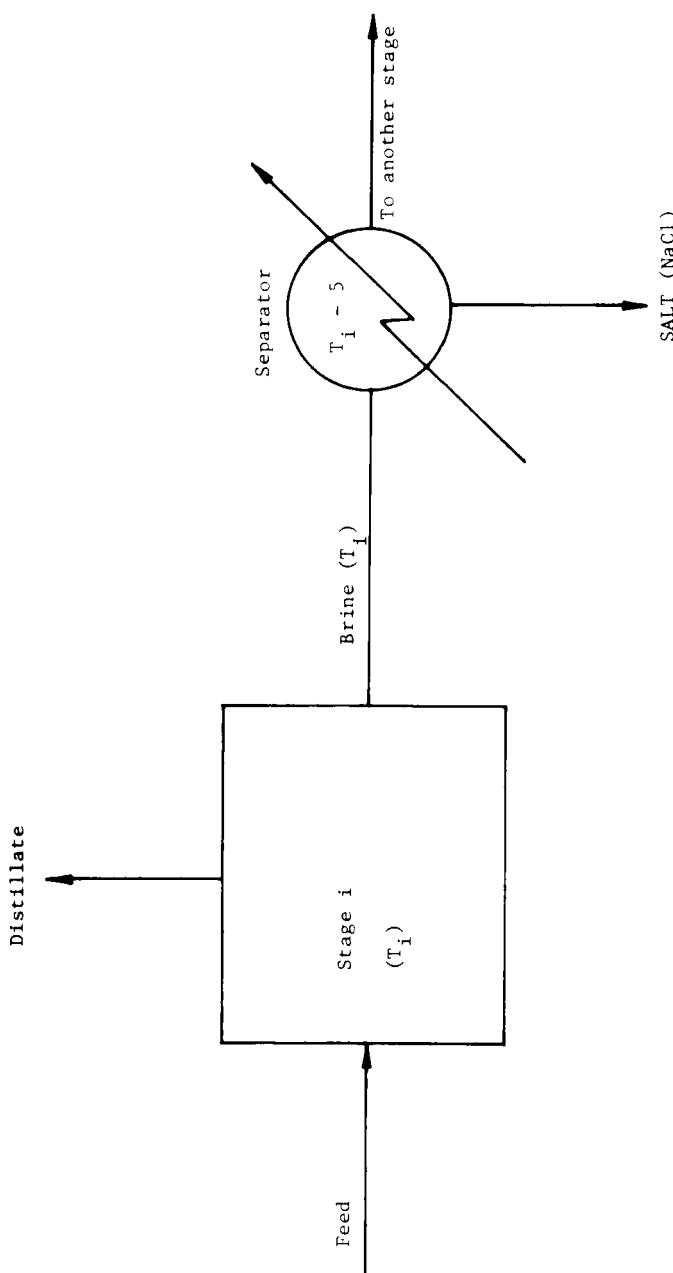


FIG. 7. A typical stage plus a separator.

TABLE 3
Design Parameter for Case 1 (Phase II)

Number of stages	4
Desalination effluents temperature	60°C
Top brine temperature	60°C
Blowdown temperature	28°C
Salinity in feed	28.80%
Salinity in blowdown	26.42%
Salinity in distillate	0.01%
Stage decrement temperature	3.0°C
Cooling decrement temperature	5.0°C
Feed rate	1130 tons/h
Distillate rate	14.07 tons/h
Salt recovery	20.59 tons/h
Blowdown rate	1095.34 tons/h

each to obtain potable water, sodium chloride salt, and a highly concentrated $MgCl_2$ bittern in which the $MgCl_2/NaCl$ ratio increases to 12.

3. The proposed process of flashing the effluents of desalination plants leads to the production of fresh water, $NaCl$, and a highly concentrated bittern rich in $MgCl_2$. This paper shows that MSF evaporators along with the proposed coolers/separators can theoretically be adopted for the co-production of mineral salt and fresh water from desalination plants effluents. However, it has to be emphasized that further studies have to be undertaken to investigate the influence of highly viscous fluid handling as well as the effect of high salinity on the materials of construction of the piping and equipment used in such a process. Dilution with fresh water is one way of overcoming some of these problems, which is recommended for further work.

4. The ratio of $MgCl_2/NaCl$ has increased from 0.10 to 12 after 32 repeated cycles of evaporation (each is 4 stages) in Phase II. This is equivalent to the removal of 98% of $NaCl$ by this process.

NOMENCLATURE

B blowdown mass flow rate
B' blowdown mass flow rate leaving separator for Phase II
D distillate mass flow rate

TABLE 4
List of Stage-to-Stage Parameters for Case 1

Stage no.	Brine flow (tons/h)	Distillate (tons/h)	Blowdown (tons/h)	Concen- tration (%)	Pressure (bar)	Inlet tem- perature (°C)	Outlet tem- perature (°C)	Boiling point elevation (°C)	Distillate tem- perature (°C)	Salt recovery (tons/h)
1	1130	3.54	1120.52	27.14	0.133	60.0	52.0	5.20821	51.792	5.94
2	1120.52	3.56	1111.95	26.89	0.0916	52.00	44.00	4.606	44.394	5.01
3	1111.95	3.51	1103.56	26.66	0.0609	44.00	36.00	4.314	36.686	4.88
4	1103.56	3.46	1095.34	26.42	0.0394	36.00	28.00	4.0385	28.961	4.76

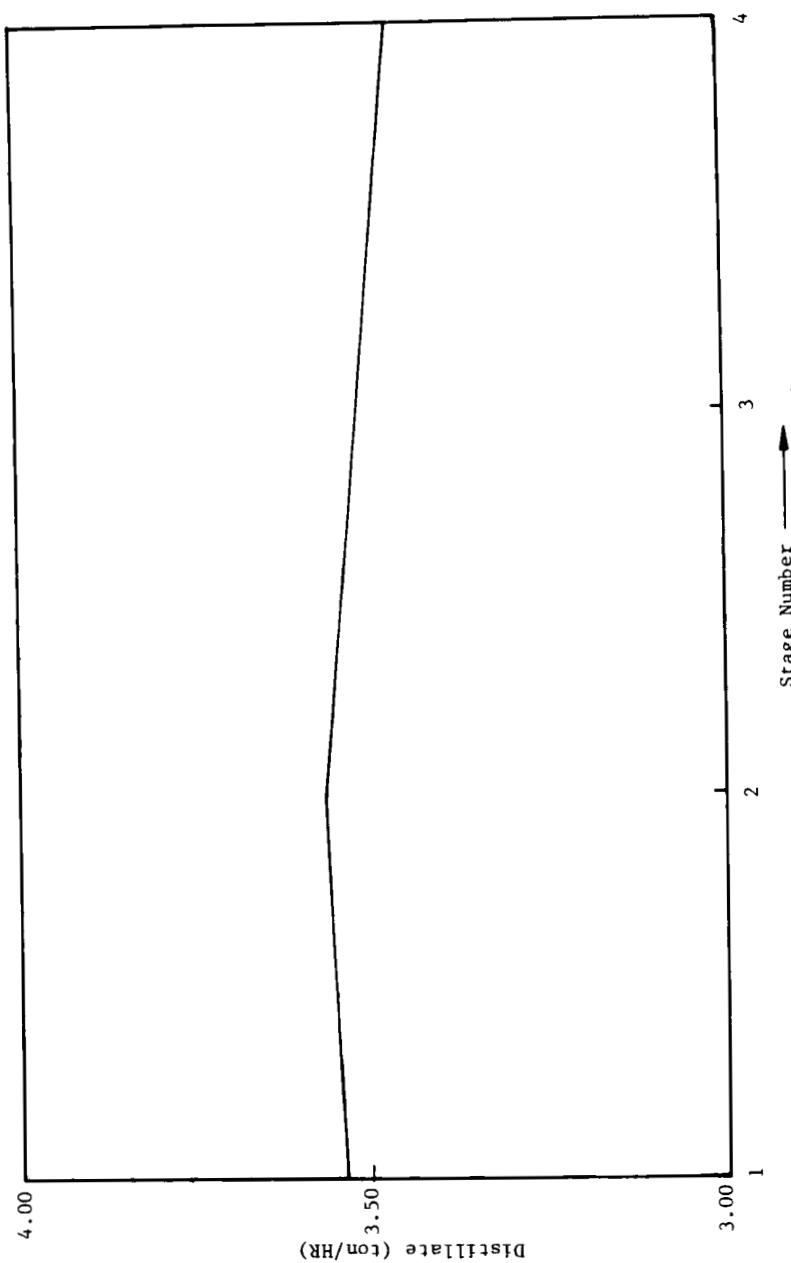


FIG. 8. Change of distillate flow rate with stage number (Phase II, Case 1).

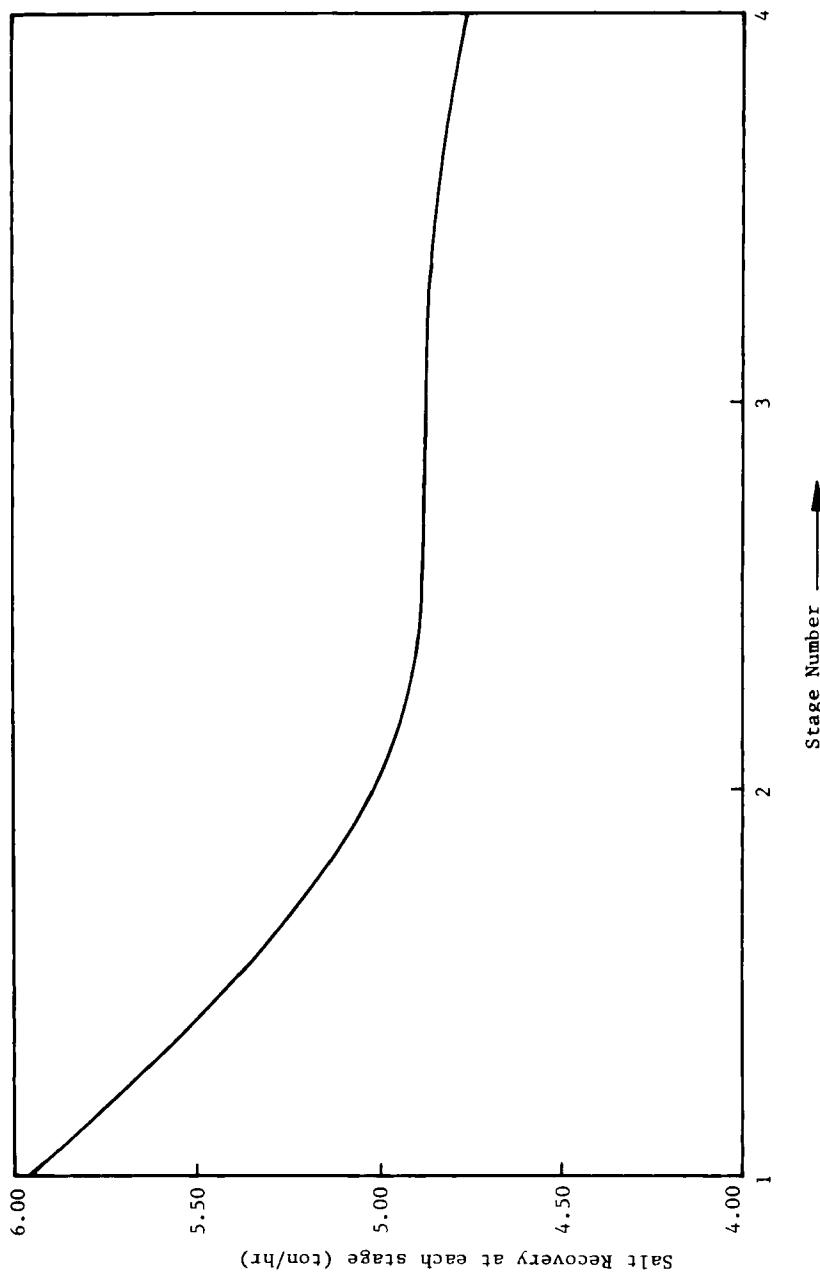


FIG. 9. Change of salt recovery with stage number (Phase II, Case 1).

TABLE 5
Summary of Feed Input and Product Output for a Typical Case of Salt Recovery

	Feed	Exit Phase I	Exit Phase II (Case 1)	Exit after 32 repeated cycles of Phase II (Case 1)
Flow (tons/h)	5210	1130	1095.35	529.4
H ₂ O (tons/h)	4900	820	805.93	469.85
NaCl (tons/h)	280	280	259.41	2.55
MgCl ₂ (tons/h)	30	30	30	30
$R = \frac{\text{MgCl}_2}{\text{NaCl}}$	0.1	0.1	0.12	11.77

TABLE 6
Design Parameters for Case 2 (Phase II)

Number of stages	6
Desalination effluents temperature	60°C
Top brine temperature	60°C
Blowdown temperature	30.0°C
Salinity in feed	28.8%
Salinity in blowdown	26.47%
Salinity in distillate	0.01%
Stage decrement temperature	3.0°C
Cooling decrement temperature	2.0°C
Feed rate	1130.00 tons/h
Distillate rate	21.03 tons/h
Salt recovery	22.31 tons/h
Blowdown rate	1086.66 tons/h

TABLE 7
Stage-to-Stage Calculations for Case 2 (Phase II)

Stage no.	Brine flow (tons/h)	Distillate (tons/h)	Blowdown (tons/h)	Concen- tration (%)	Pressure (bar)	Inlet tem- perature (°C)	Outlet tem- perature (°C) elevation (°C)	Boiling point (°C)	Distillate tem- perature (°C)	Salt recovery (tons/h)
1	1130	3.54	1121.92	27.23	0.1330	60.0	55.0	5.20821	51.792	4.55
2	1121.92	3.57	1114.67	27.07	0.1062	55.0	50.0	4.71882	47.281	3.68
3	1114.67	3.53	1107.53	26.92	0.0829	50.0	45.0	4.53072	42.469	3.61
4	1107.53	3.50	1100.47	26.77	0.0641	45.0	40.0	4.3490	37.651	3.56
5	1100.47	3.46	1093.52	26.62	0.0492	40.0	35.0	4.17361	32.826	3.49
6	1093.52	3.43	1086.66	26.47	0.0373	35.0	30.0	4.0044	27.996	3.43

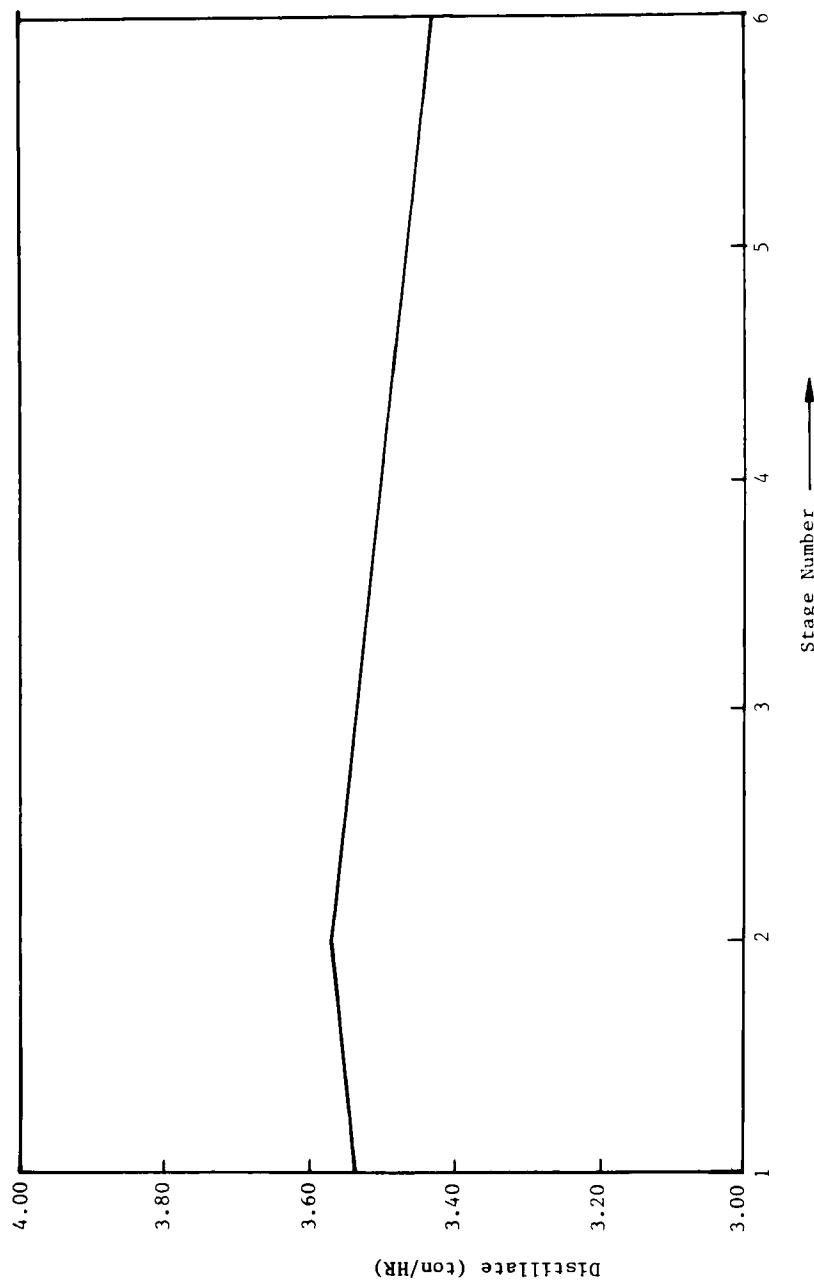


FIG. 10. Change of distillate flow rate with stage number (Phase II, Case 2).

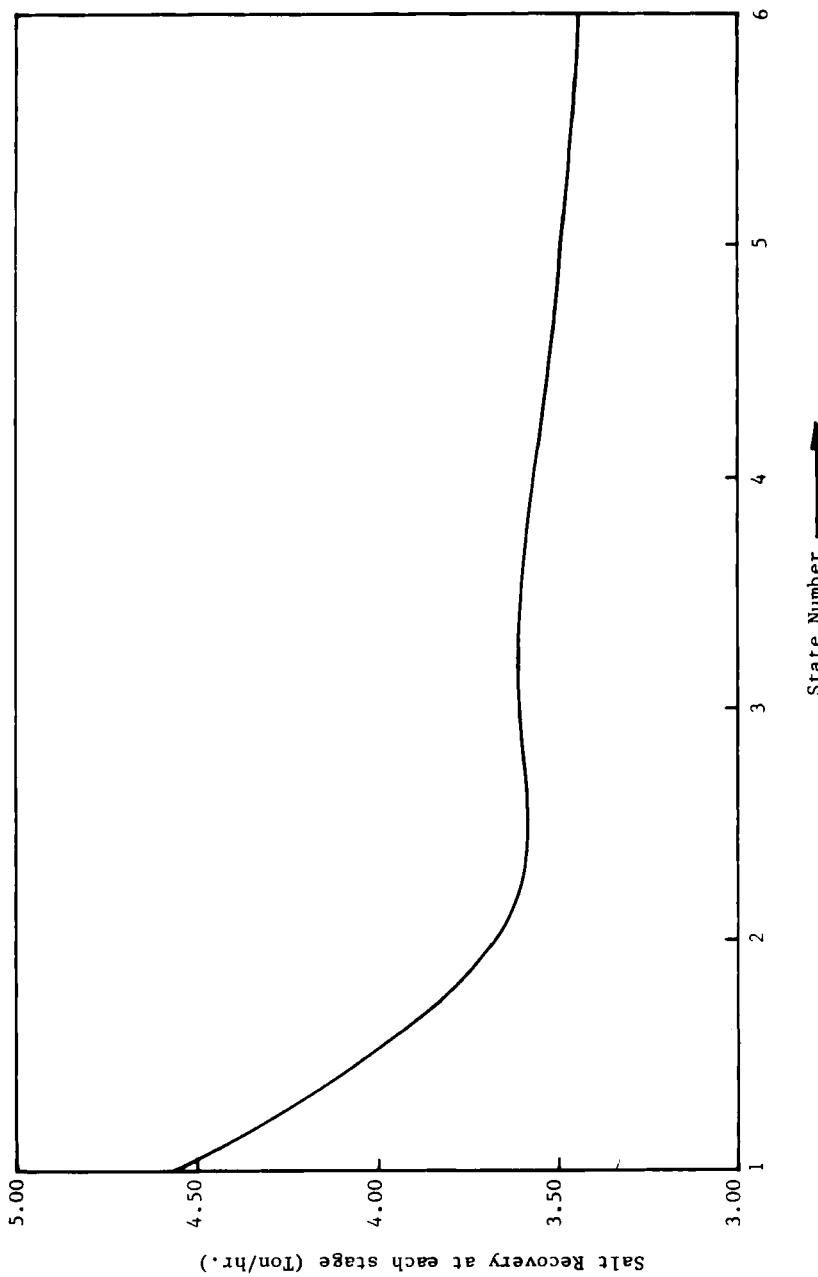


FIG. 11. Change of salt recovery with stage number (Phase II, Case 2).

<i>F</i>	feed mass flow rate
<i>H</i>	enthalpy of vapor (distillate) leaving a MSF unit
<i>h_B</i>	enthalpy of liquid (bottom) leaving a MSF unit
<i>h_F</i>	enthalpy of feed (both Phases I and II)
<i>N</i>	number of stages
<i>R</i>	ratio defined as <i>D/F</i>
<i>S</i>	quantity of salt separated
<i>T</i>	operating temperature for a MSF unit
<i>T_C</i>	cooling temperature drop
<i>T_i</i>	feed temperature for a MSF unit
<i>T₀</i>	blowdown temperature
<i>w</i>	ratio defined as <i>S/B</i>
<i>x_B</i>	blowdown composition
<i>x_D</i>	distillate composition
<i>x_F</i>	feed composition
<i>x₁</i>	composition of NaCl in the separator inlet
<i>x₂</i>	composition of NaCl in the separator outlet
<i>y₁</i>	composition of MgCl in the separator inlet
<i>y₂</i>	composition of MgCl in the separator outlet

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