



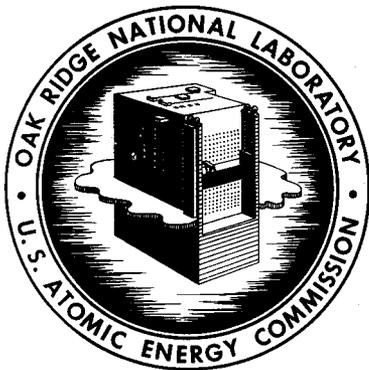
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A CLOSED-CYCLE PROCESS FOR PREVENTING  
SCALE FORMATION IN EVAPORATORS AND  
PRODUCING INDUSTRIAL CHEMICALS AT A  
NUCLEAR DESALINATION PLANT

R. E. Blanco  
W. C. Yee  
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J. M. Holmes  
R. Salmon



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Chemical Development Section B

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SEPTEMBER 1967

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## A CLOSED-CYCLE PROCESS FOR PREVENTING SCALE FORMATION IN EVAPORATORS AND PRODUCING INDUSTRIAL CHEMICALS AT A NUCLEAR DESALINATION PLANT

R. E. Blanco            W. E. Clark  
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### ABSTRACT

A closed-cycle process is proposed for removing scale-forming elements from seawater (descaling) in which all chemicals required for descaling are produced at the plant site, either directly from seawater or from recycle streams, using cheap nuclear power from the nuclear reactors. In the principal flowsheet, caustic and sodium carbonate are added to seawater to precipitate greater than 95% of the calcium as calcium carbonate at pH 9.2. After removal of the precipitate, the pH is decreased to 7 by adding hydrochloric acid to permit evaporation (to a 4X concentration) at 350 to 400°F without scale formation. Caustic, chlorine, and hydrogen are produced from concentrated seawater in a conventional industrial electrolytic cell. The calcium carbonate is calcined to produce carbon dioxide, which is combined with caustic in a recycle stream to produce sodium carbonate for further descaling. Hydrochloric acid for pH adjustment is produced by the combination of 6% of the hydrogen and chlorine. An optional feature is the production of fertilizer either (1) by combining electrolytic hydrogen and nitrogen from air liquefaction to produce ammonia or (2) by combining this ammonia with excess carbon dioxide from calcined calcium carbonate to produce urea.

The desalination plant with closed-cycle descaling could be operated jointly by a utility company and a company in the chlorine-caustic industry. The economic evaluation was based on the production of 250 million and 1 billion gal/day of fresh water. In the latter case, the private company could obtain revenue from the sale of excess chlorine and hydrogen and could provide the descaling service for a fee of 1¢/1000 gal, which is competitive with the use of sulfuric acid for scale control. With a price of 25¢/1000 scf for hydrogen, chlorine could be sold for \$39/ton, which is competitive with the current market price. This would provide a 15% return on equity after 48% Federal tax. The sale of chlorine represents 87% of the total income.

Chlorine production (3440 tons/day) is about 75% of that of another plant in the U.S. and represents about 17% of the total chlorine produced in the U.S. in 1966. In alternative flowsheets, the calcium and magnesium

are completely precipitated at pH 10-12, and the slurry is passed through the evaporator at the same pH; or the precipitate is removed, and the pH of the water is adjusted to any desired level prior to evaporation. Other variations show the recovery of magnesium, iodine, bromine, and lime.

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## 1. INTRODUCTION

The use of nuclear energy for the distillation of seawater has been proposed as a method for making desalination economically attractive.<sup>1-5</sup> Additional economies in operating costs could be achieved by providing a method for removing the scale-forming elements from virgin seawater. The evaporator could be operated more efficiently at high temperatures and/or seawater could be concentrated to a greater degree without the danger of depositing scale on the evaporator components. These improvements would increase the yield of fresh water and, thus, a greater range of water-to-power ratios would be attainable in dual-purpose nuclear desalination plants.

Traditionally designed seawater distillation plants are limited to low-temperature operation and low seawater concentration factors by scale formation in the evaporator equipment.<sup>6,7</sup> Distillation of untreated seawater coats the evaporator tubes with "alkaline" scale, calcium carbonate, and/or magnesium hydroxide, at temperatures higher than 170°F. This can be prevented by pH control, normally by sulfuric acid addition. However, the anhydrite ( $\text{CaSO}_4$ ) and the hemihydrate ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) forms of calcium sulfate exhibit a decrease in solubility with increasing temperature, which results in precipitation of either or both of these salts between 180 and 260°F. The latter is probably the upper-temperature operating limit,<sup>2</sup> unless the calcium is removed or altered either physically<sup>8</sup> or chemically.<sup>9</sup> Magnesium hydroxide precipitation is of no concern at pH 7 or lower unless a distillation temperature somewhat higher than 300°F is specified.

A number of descaling methods have been proposed, including sulfuric acid treatment,<sup>10,11</sup> phosphate-ammonia treatment,<sup>12,13</sup> ion exchange softening,<sup>14</sup> fractional crystallization of sodium chloride,<sup>15</sup> and carbonate precipitation.<sup>16</sup> The latter is a procedure which was adapted from common municipal water practice<sup>17</sup> by McIlhenny et al. for precipitating calcium and recovering magnesium from seawater,<sup>18</sup> and which was included as part of a mineral recovery process proposed by Weinberger and DeLapp.<sup>16</sup> All of these processes require purchase and shipment of chemicals into the plant site, and in some, by-products are sold to pay for the cost of descaling.

The purpose of this report is to describe a closed-cycle process in which all chemicals required for descaling are produced at the plant site. The process is based on carbonate precipitation and uses well-known chemical principles and existing industrial techniques for the principal unit operations. Many of the process features are similar to those proposed by Weinberger and DeLapp.<sup>16</sup> However, the proposed closed-cycle process differs in important aspects including (1) specificity of design for use with a nuclear reactor producing cheap power; (2) the production of all chemicals from seawater or from recycle streams using cheap nuclear power, including the carbonate required for the precipitation system and the excess carbon dioxide for production of other chemicals; (3) the option of operating the distillation system at a high pH to decrease corrosion or the possibility of passing the alkaline slurry through the distillation system; and (4) the consideration of a larger system (30 times as large) where more favorable economics should apply. The closed-cycle process should be particularly attractive for use at remotely-situated reactor complexes where transportation costs for descaling chemicals might be excessive, or in countries with unfavorable foreign exchange balances where importation is not desirable.

The closed-cycle descaling process is made economical by the sale of the by-products hydrogen and chlorine. Chlorine is expected to have an attractive growth rate of as much as 10% annually through 1970.<sup>19</sup> In this study, credits were taken only for the excess chlorine and hydrogen produced. Credits were not taken for other products such as lime and carbon dioxide. Magnesium recovery is shown in an alternative flowsheet where magnesium removal is required as part of a complete descaling

procedure. Other possible industrial by-products include hydrogen produced by electrolysis of water,<sup>20,21</sup> ammonia,<sup>20</sup> nitric acid and ammonium nitrate,<sup>22</sup> sodium chloride, bromine, and iodine. Finally, the excess carbon dioxide recovered from the seawater in the closed-cycle descaling process can be combined with ammonia to form urea where that product is desired.

Acknowledgement.--The authors are indebted to J. T. Roberts of the Chemical Technology Division for his valuable assistance in the evaluation of the process economics.

## 2. PROPOSED PROCESS FLOWSHEET

The proposed flowsheet (Fig. 1) includes precipitation of calcium carbonate from seawater by the addition of sodium hydroxide and sodium carbonate; distillation (evaporation) of the acidified supernate; fractional crystallization of sodium chloride from a small fraction of the evaporator bottoms; electrolytic generation of caustic solution from a saturated sodium chloride solution; calcination of 80% of the precipitated calcium carbonate to obtain carbon dioxide, and the dissolution of this gas in the caustic stream to form sodium carbonate; the combination of a small fraction of the electrolytically-produced gases, hydrogen and chlorine, to obtain hydrochloric acid for pH adjustment; and the treatment of additional raw seawater with these internally-produced chemicals. No external source of chemicals is required. Energy for electrolysis and calcination is furnished by the nuclear reactor that supplies power for distillation.

The composition of seawater chosen for this study is a primary standard prepared by the Hydrographic Laboratories of Copenhagen, Denmark, for use by oceanographic institutes (Table 1).<sup>6</sup> Variations in the "normal" concentrations of the major constituents are small, while those of the minor constituents are, reportedly, large.<sup>23</sup> Since this study deals with the major constituents only, there should be no significant effect due to minor changes in composition.

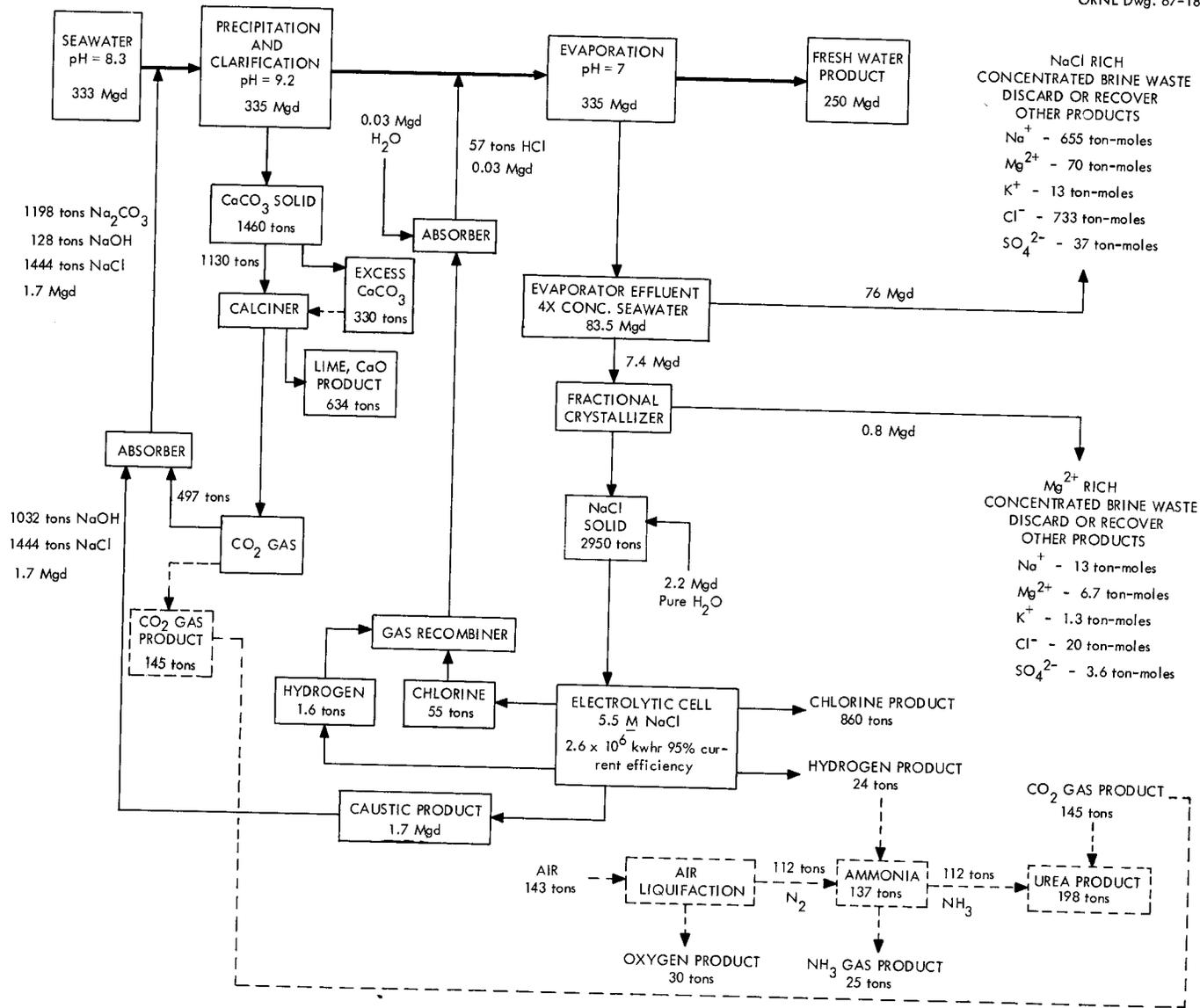


Fig. 1. Flowsheet for Proposed Closed-Cycle Descaling Process. (Basis: 250 million gal/day (Mgd) fresh water.)

Table 1. "Normal" Seawater Composition<sup>a</sup>

Component	Concentration (ppm)	(M)
Na	10,768	0.480
Mg	1,298	0.0547
Ca	408	0.0104
K	388	0.0102
Sr	14	0.00016
Cl	19,361	0.560
SO <sub>4</sub>	2,702	0.0288
HCO <sub>3</sub>	143	0.00240
Br	66	0.00084
F	1	0.00005
H <sub>3</sub> BO <sub>3</sub>	27	0.00044
I	0.05	0.00040
Si	0.02	0.00072
Others	1.3	--

<sup>a</sup>OSW Research and Development Progress Report No. 25, PB-161399.

Primary standard for "normal" seawater as given by the Hydrographic Laboratories of Copenhagen, Denmark:

Salinity	= 35.01	Total solids	= 35,175 ppm
Chlorosity	= 19.862	Weight of water	= 965 g/kg seawater
Density at 20°C	= 1.025		

Flowsheet calculations (Table 2) are based on the production of 250 million gal/day (Mgd) of fresh water. The following assumptions are made:

1. The pH of raw seawater is 8.3.
2. The concentration of bicarbonate (HCO<sub>3</sub><sup>-</sup>) is  $2.4 \times 10^{-3}$  M.
3. The amount of bicarbonate present initially in seawater is sufficient to precipitate about 25% of the calcium as calcium carbonate at pH 9.2.

Table 2. Major Ions in Liquid Streams of the Closed-Cycle Descaling Process.

Basis: 250 Mgd of fresh water produced

	"Normal" Seawater		Evaporator Effluent <sup>a</sup>		Evaporator Effluent to Frac. Cryst. (tons/day)	Frac. Cryst. Effluent <sup>b</sup> (tons/day)	Diaphragm Cell Caustic <sup>c</sup> (tons/day)
	Conc. (M)	Total Amount (tons/day)	Conc. (M)	Total Amount (tons/day)			
Na	0.480	15,400	2.05	16,500	1,450	292	1,160
Mg	0.0547	1,850	0.218	1,850	163	163	--
Ca	0.0104	585	--	--	--	--	--
K	0.0102	555	0.0405	555	47	47	--
Cl	0.560	27,600	2.30	28,500	2,510	720	876
SO <sub>4</sub>	0.0288	3,850	0.115	3,855	336	336	--
HCO <sub>3</sub>	0.00240	203	--	--	--	--	--
OH	--	--	--	--	--	--	439
Total volume		333 Mgd		83.5 Mgd	7.4 Mgd	0.8 Mgd	1.7 Mgd

<sup>a</sup>Seawater that has been concentrated by a factor of 4.

<sup>b</sup>Solution is assumed to be 20% NaCl by weight (3.9 M). See Sect. 4, Process Economics.

<sup>c</sup>Feed to the diaphragm cell is saturated brine of 5.5 M NaCl (65 to 75°C). Caustic effluent is 3.6 M NaOH and has a salt ratio (NaCl/NaOH) of 1.4. Ref.: J. S. Sconce, Chlorine, Its Manufacture, Properties and Uses, Reinhold, New York, 1962.

4. Borate ( $\text{H}_2\text{BO}_3^-$ ) ion is the only minor constituent considered in this study. Although only a portion of the borate is expected to precipitate ( $\text{pK}$  of pure boric acid = 9.24) during calcium precipitation at pH 9.2, enough acid is added prior to evaporation to redissolve the total amount present in seawater.
5. Liquid volumes given in the flowsheet are not corrected for solution that is retained on wet precipitates and sludges.
6. A diaphragm cell, typical of that used in the chlorine-alkali industry, is used for the electrolysis of brine.

Complete calcium precipitation in a 250-Mgd fresh water plant requires 128 tons NaOH and 1198 tons  $\text{Na}_2\text{CO}_3$  per operating day, while pH adjustment prior to evaporation requires 57 tons HCl. With calcium removed, the maximum brine temperature can be as high as 350 to 400°F, a brine concentration factor of four or more can be achieved, and at least 75% of the seawater treated is recovered as fresh water. The electrolysis of saturated brine (5.5 M NaCl) to produce the desired 1032 tons of caustic requires  $2.6 \times 10^6$  kwhr in a diaphragm cell of 95% efficiency. By-products include 900 tons of chlorine at the anode and 25 tons of hydrogen at the cathode. About 6% of the gases are recombined to form the hydrochloric acid required for pH adjustment. About 77% of the carbon dioxide released by calcination of the precipitated calcium carbonate reacts with 904 tons of the total caustic produced by electrolysis to yield the desired amount of sodium carbonate. Chlorine, hydrogen, lime, and calcium carbonate are produced as by-products. Credits were taken only for caustic (for descaling) (see Sect. 4) and for the sale of chlorine and hydrogen to yield a net return on investment.

Urea and ammonia fertilizer production (Fig. 1) can also be incorporated into the process (1) by calcining the excess calcium carbonate to produce 145 tons of  $\text{CO}_2$ , (2) by combining 112 tons of  $\text{N}_2$  obtained by air liquefaction with 24 tons of electrolytic hydrogen to produce 137 tons of  $\text{NH}_3$ , and (3) by reacting 112 tons of  $\text{NH}_3$  with the  $\text{CO}_2$  to produce about 200 tons of urea.

The brine concentration factor of four is arbitrarily chosen. Theoretically, with calcium removed, a concentration factor of greater than ten is possible before the brine saturation point is reached. Current evaluation of evaporation plants, however, indicates that a factor higher than six is probably not economical. Similarly, the highest practical range of distillation temperatures is said to be 350 to 400°F.<sup>24,25</sup>

The electrolytic cell used for the production of caustic is a commercial diaphragm unit which is optimized for the production of chlorine. A diaphragm cell is specified because concentrated caustic is not required in the descaling step. The elimination of the evaporation (concentration) step is a significant economic advantage in the closed-cycle system as compared to normal industrial operations where evaporation is required to produce concentrated caustic. The other type of cell used by industry, the mercury cell, produces concentrated caustic directly and could possibly be considered. Recent technological improvements in this cell have made it increasingly competitive with the diaphragm cell, especially for larger plants.<sup>26</sup> However, based on present knowledge, the diaphragm cell is preferred (see Sect. 3.2).

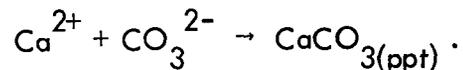
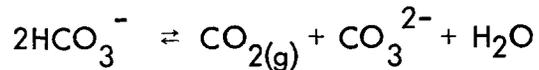
Relatively pure saturated brine is needed as feed solution to the diaphragm cell. Precipitated magnesium hydroxide, for example, decreases cathode current efficiency. The presence of high concentrations of sulfate (more than 2.5 wt % or 0.1 M) can cause rapid oxidation of the graphite electrodes.<sup>27</sup> A sulfate concentration of 0.12 M would be expected in 4X concentrated seawater. The economic trade-off between electrode oxidation rate and the extra operating steps required to minimize sulfate concentration should be studied further. For the present study, a flash crystallization unit<sup>15</sup> is used to prepare sodium chloride which, when redissolved, is assumed to constitute a satisfactory feed to the electrolysis cell. The sodium chloride remains in the caustic stream leaving the diaphragm cell, and no attempt is made to recover it for reuse. Some designers may choose to concentrate the brine to saturation in the main evaporator system, if this is practical, rather than installing a separate flash crystallizer. Others may desire a brine concentration of less than four and utilize a more dilute feed in the crystallizer.

### 3. PROCESS CHEMISTRY

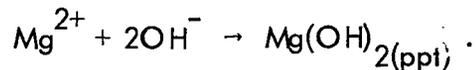
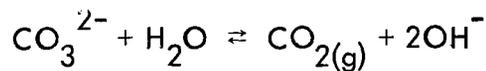
The general chemistry of each step in the process flowsheet is well known, but an exact extrapolation to the complex seawater system is difficult. Data from a literature survey and from laboratory tests were used to eliminate major areas of uncertainty and to verify the technical feasibility of the process.

### 3.1 Descaling Seawater

Removal of calcium and magnesium from seawater prior to distillation prevents the salts of these elements from depositing on the heat-transfer surfaces of the evaporator. Langelier *et al.*<sup>28-30</sup> reported that, when untreated seawater is heated, dissolved bicarbonate decomposes, carbon dioxide is released, and calcium carbonate is precipitated.



Above 180°F, the carbonate ion hydrolyzes, releasing more carbon dioxide, increasing the pH of the seawater, and precipitating magnesium hydroxide rather than calcium carbonate.



Both of these "alkaline" scales, however, can be controlled by using acid to maintain the pH at between 6.5 to 7.0.

The solid which really limits the maximum evaporator temperature and restricts the brine concentration factor is calcium sulfate. Three forms have been found as scale on evaporator components under a variety of operating conditions; these are the anhydrite ( $\text{CaSO}_4$ ), the hemihydrate ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ).<sup>31</sup> Of greatest concern are the first two forms, each of which exhibits an inverse solubility relationship with temperature. Marshall and Slusher<sup>32</sup> (Fig. 2) showed that the anhydrite and the hemihydrate precipitate when synthetic seawater (excluding carbonate and bicarbonate) is heated to 235°F and 320°F, respectively (Fig. 2). These temperatures of precipitation drop to 158 and 265°F, respectively, when seawater is concentrated by a factor of two. Additional concentration of seawater results in even lower temperatures at which precipitation occurs. The hemihydrate is found to a greater extent as scale on evaporator components than the anhydrite, even though the latter form is less soluble, indicating a decided kinetics effect.

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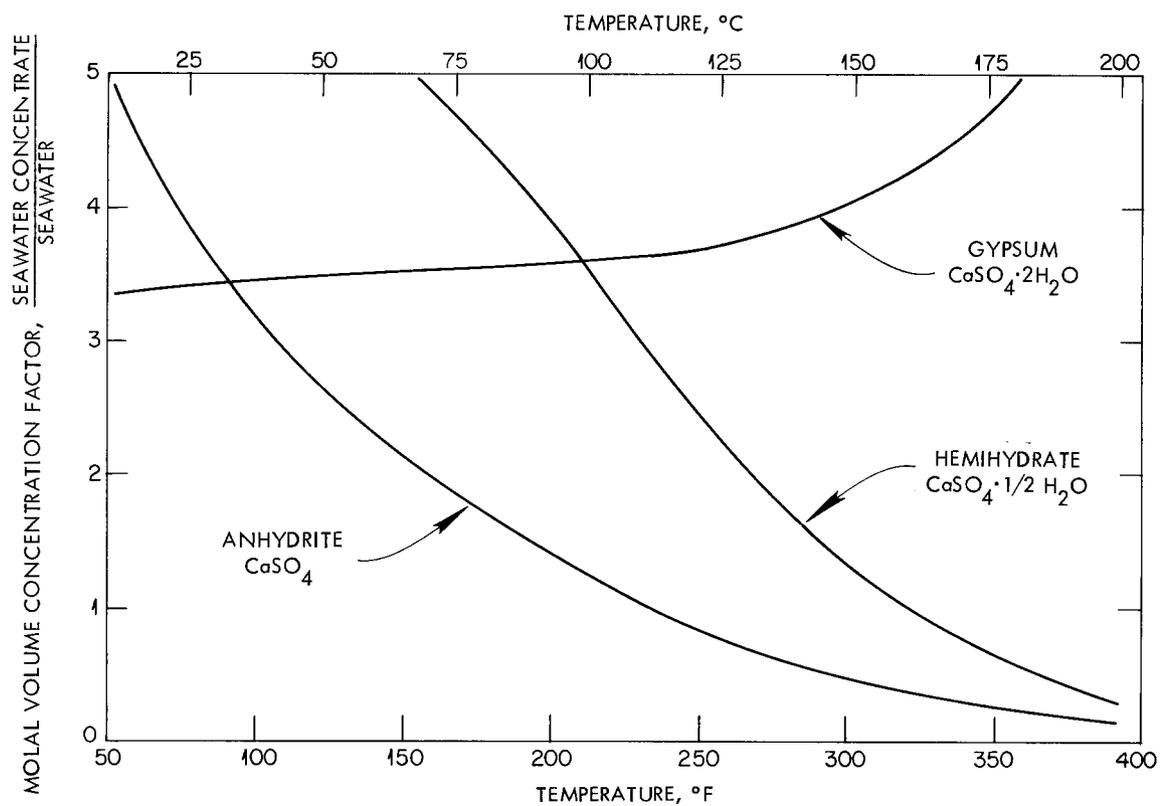
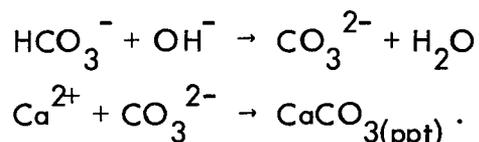


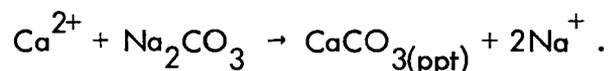
Fig. 2. Solubility Limits of Calcium Sulfate in Seawater Concentrates as a Function of Temperature. (Data of W. L. Marshall and R. Slusher, submitted for publication in J. Chem. Eng. Data, March 1967.)

In the proposed closed-cycle flowsheet, calcium is precipitated as the carbonate with alkali and soda ash in two steps:

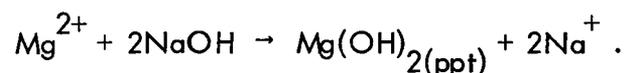
1. Bicarbonate in seawater is transformed to carbonate by increasing the pH from 8.3 to 9.2. This precipitates about 23% of the calcium as follows:



2. The remaining calcium is removed by adding carbonate in the form of soda ash:



If magnesium removal is desired, caustic is added to precipitate magnesium hydroxide at a pH higher than 9.2:



In the flowsheet variation selected for this study where selective removal of calcium is desired (Fig. 1), it was necessary to determine the pH at which calcium carbonate precipitates but magnesium remains in solution. Experiments in this work at room temperature showed that calcium precipitation is roughly proportional to the amount of sodium carbonate added and that approximately 95% of the calcium precipitated at pH 9.2 (Fig. 3). This is equivalent to a residual calcium concentration of 20 ppm. Coprecipitation of magnesium was negligible at pH 9.2 but about 90% precipitated at pH 9.7, equivalent to a residual concentration of 130 ppm  $\text{Mg}^{2+}$  in the supernate. Greater than 99% of the magnesium precipitated at pH 12, equivalent to less than 13 ppm  $\text{Mg}^{2+}$  in the supernate (Fig. 4).

These data, together with the high-temperature solubility data of Marshall and Slusher<sup>32</sup> (Fig. 2) for calcium sulfate and an extrapolation of the data of Standiford and Sinek<sup>8</sup> (Fig. 5) and Langelier *et al.*<sup>29</sup> for calcium carbonate and magnesium hydroxide, were used to determine the operating conditions for the desalination system shown in Fig. 1. In Fig. 5, the straight-line extrapolations to concentrations of calcium and

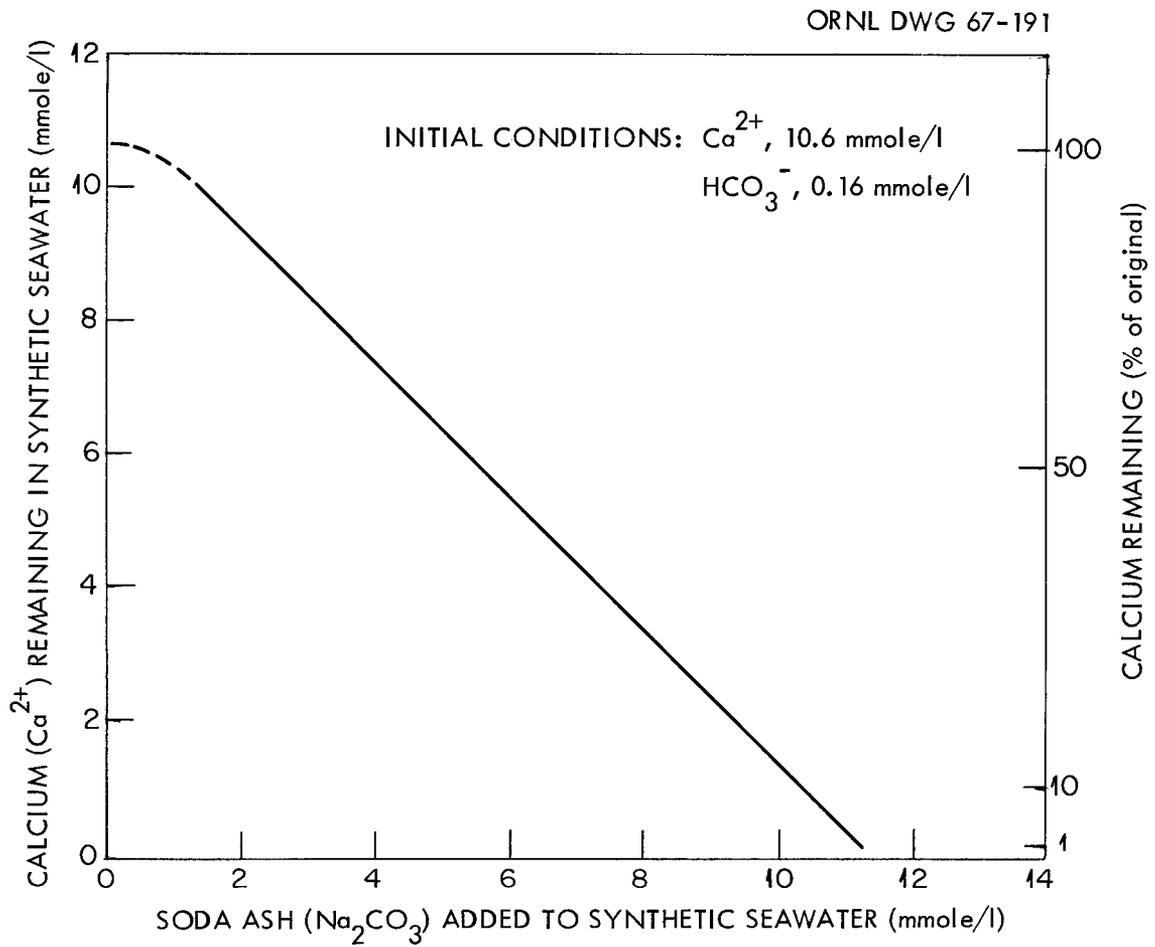


Fig. 3. Precipitation of  $\text{Ca}^{2+}$  from Synthetic Seawater is a Linear Function of Sodium Carbonate Added at pH 9.2 and at Room Temperature.

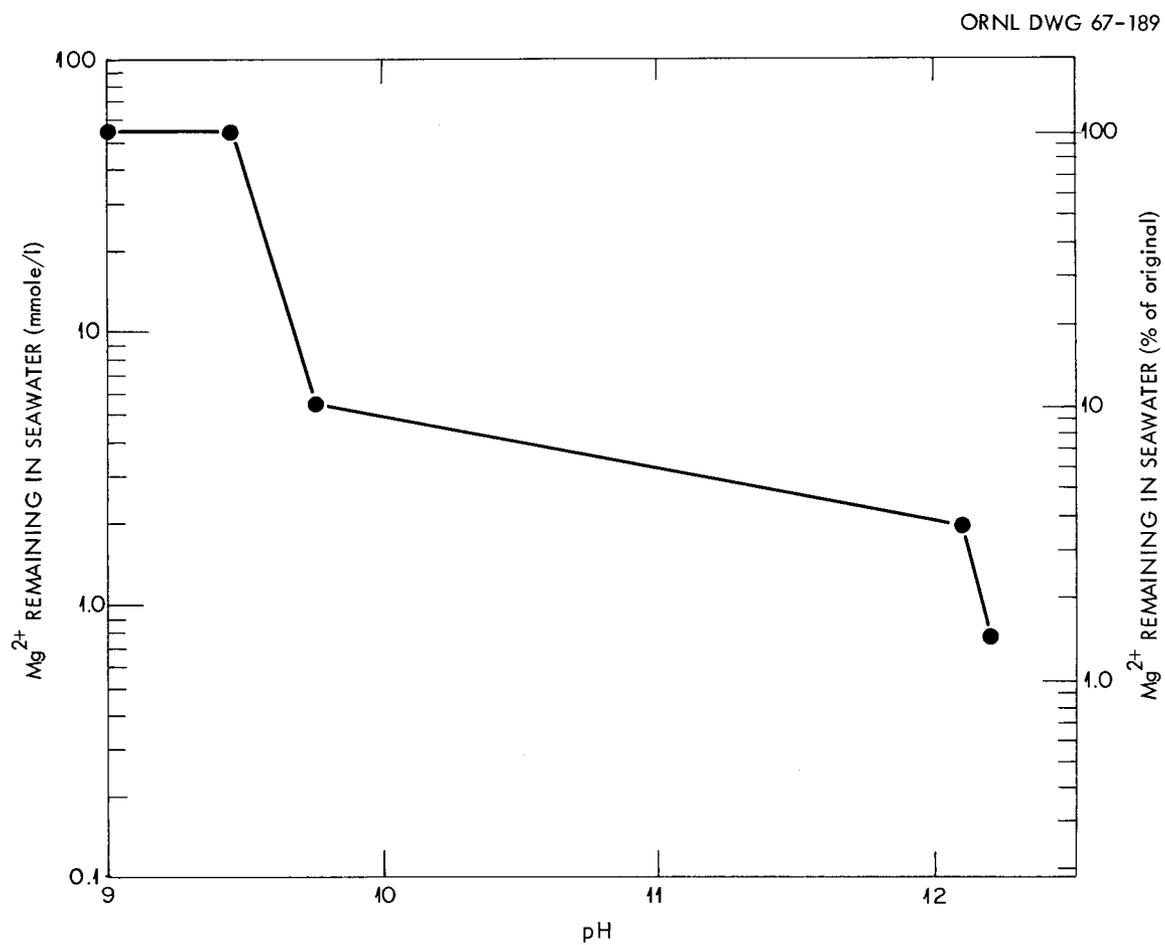


Fig. 4. Precipitation of  $Mg^{2+}$  from Seawater as a Function of pH at Room Temperature.

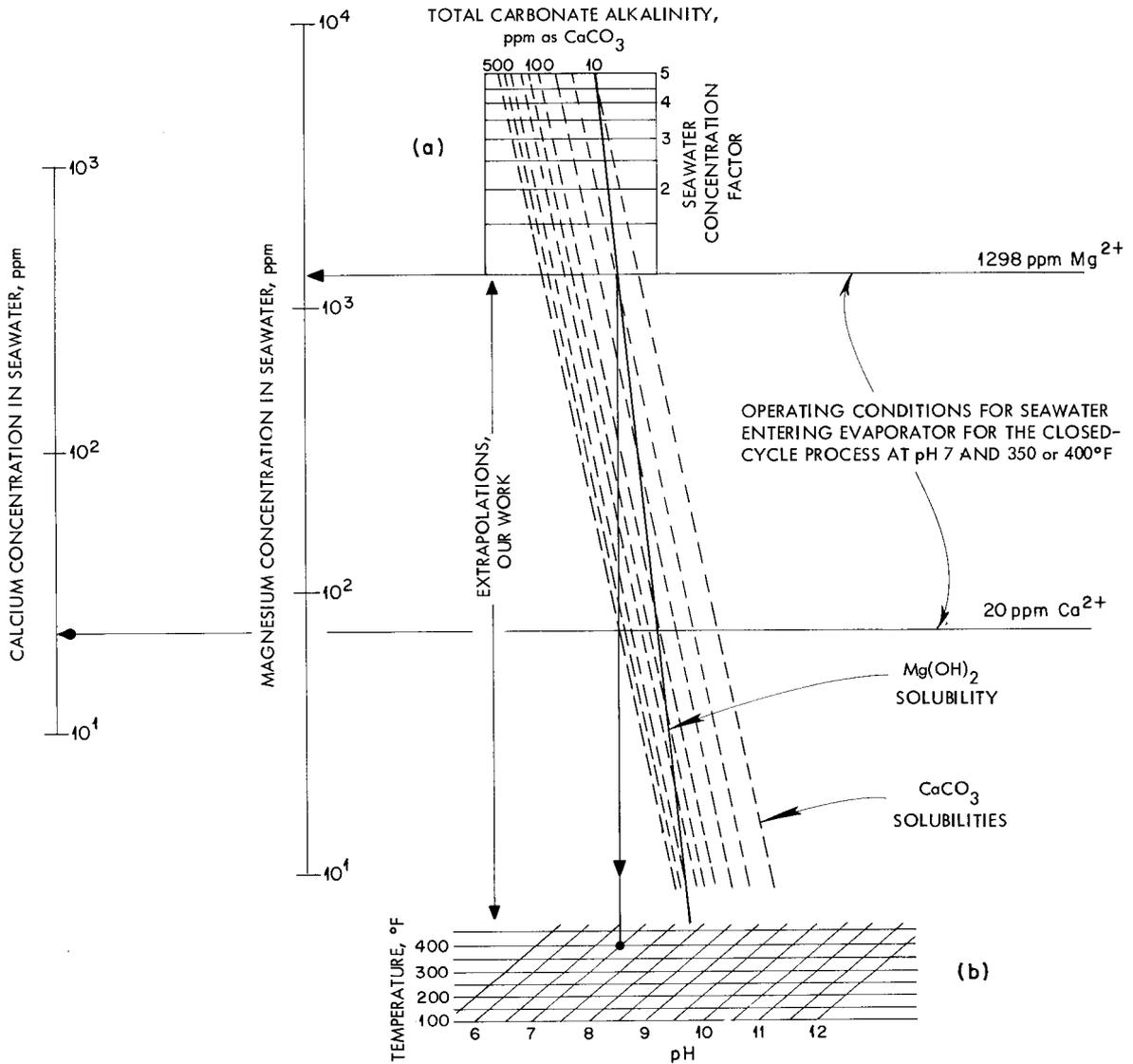


Fig. 5. Solubility of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  in Seawater Concentrates in the Closed-Cycle Process. Solubility of  $\text{CaCO}_3$  is dependent on total carbonate alkalinity, pH, and temperature. Solubility of  $\text{Mg}(\text{OH})_2$  is dependent on pH and temperature only. (a) From data of Langelier *et al.* (1950), as replotted by Standiford and Sinek (1961); (b) coordinates are those of Standiford and Sinek. (a) and (b) reduced to scale.

magnesium lower than that in normal seawater (i.e., below a concentration factor of unity) assume that the activity coefficients for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ , and  $\text{OH}^-$  are unchanged after calcium or magnesium removal. With precipitation and removal of 95% of the calcium at pH 9.2 from virgin seawater at ambient (room) temperature, no magnesium removal, and with the pH adjusted to 7 prior to evaporation, the seawater can be heated to as high as 400°F without magnesium hydroxide precipitation (Fig. 5). Also, with only 20 ppm  $\text{Ca}^{2+}$  remaining in solution, no calcium carbonate precipitation is expected unless the residual carbonate concentration exceeds 500 ppm, expressed as  $\text{CaCO}_3$  (Fig. 5). Likewise, no calcium sulfate precipitation is expected because the calcium concentration is now only 1/20 of that in normal seawater (equivalent to a concentration factor of 0.05 in Fig. 2).

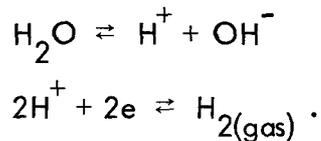
Carbonate that remains after calcium precipitation is a potential problem. Hydrolysis at elevated temperatures could lead to a carbon dioxide evolution, hydroxyl ion formation, and an upward shift in the pH of the heated solution.<sup>7</sup> As seen in Fig. 5, a small increase in the pH, from 7.0 to 7.5, would probably cause the precipitation of magnesium hydroxide at brine temperatures above 300°F. Thus, the carbonate concentration should be minimized and the pH should be maintained at 7 to attain a brine temperature of 350 to 400°F and a concentration factor of four.

If a more alkaline (less corrosive) solution and/or a higher operating temperature are desired, magnesium must be removed prior to evaporation. Normal seawater (1298 ppm  $\text{Mg}^{2+}$ ) must remain at a pH of 7 or lower to avoid precipitation of  $\text{Mg}(\text{OH})_2$  at 400°F, and 7.5 for 300°F. If 99% of the magnesium is removed by precipitation at pH 12 (13 ppm  $\text{Mg}^{2+}$  remaining in solution), the evaporator could be operated at pH 8.2 at temperatures up to 400°F (Fig. 5). Finally, the evaporator could probably be operated at the same pH as the precipitation system, in the range of 10 to 12 and at temperatures as high as 400°F, if the slurry of magnesium and calcium solids is passed through the evaporator, or if the precipitate is removed after the solution reaches the high temperature. Essentially complete precipitation of calcium along with the magnesium is expected during precipitation at ambient (room) temperature at these high pH values. Thus, the slight additional

precipitation which may occur on raising the temperature in the evaporator should cause no problem and would, in any event, be expected to adhere to the solids already in the flowing liquid stream rather than to the evaporator components.

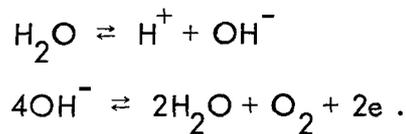
### 3.2 Caustic Production by Electrolysis

Sodium chloride crystals, a product obtained by fractional crystallization of a portion of the evaporator bottoms, are dissolved to make up a saturated brine solution which is fed to an electrolysis cell. At the cathode, hydrolysis of water occurs, resulting in hydrogen discharge and leaving an excess of alkali in the brine solution.

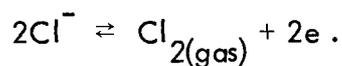


Efficiency of electrolysis is optimized by maintaining a saturated brine solution in the cell (5.5 M NaCl). The efficiency is decreased when oxidants such as dissolved oxygen, chlorine, hypochlorite, or chlorate diffuse from the anode and are reduced by peroxides and chlorides; a corresponding decrease in the yields of alkali and hydrogen occurs. If hydrogen ions diffuse from the anode, hydroxyl ions at some distance away from the cathode are neutralized, resulting in an apparent higher current efficiency for the production of hydrogen over hydroxyl ions.

At the anode, hydrolysis of water should also occur, producing oxygen and acid.



However, the activation overpotential, or overvoltage, of oxygen is appreciable for practically all materials currently used as anodes and, therefore, chlorine is the principal product discharged.



By keeping the brine saturated and by using electrodes on which the overpotential for hydroxyl ion discharge is high, the modern chlorine-caustic industry has been able to

achieve current efficiencies of higher than 95% for chlorine discharge.<sup>33</sup> Use of under-saturated brine, or use of anode materials on which the oxygen overpotential is lower than on graphite, will increase the current efficiency for oxygen production at the expense of that for chlorine. Excessive sulfate impurity (greater than 2%) in the brine has a similar effect and causes excessive oxidation of the anode.<sup>27</sup>

Two different electrolysis cells are in use today, namely, the diaphragm cell and the mercury cell. In the diaphragm cell, brine enters the anode compartment and flows out of the cathode compartment. The diaphragm prevents hydroxyl ion from diffusing back to the anode chamber. The caustic soda product is dilute, about 10% NaOH, and normally is purified and concentrated. However, these steps are not necessary in the descaling application where a crude, dilute product is acceptable.

In the mercury cell, the cathode consists of a thin moving film of mercury which flows by gravity along the bottom of the cell. Anodes, made of graphite, are placed above the flowing mercury. Brine flows through the cell, generating chlorine gas, which is collected, and sodium ion, which forms an amalgam with mercury. The amalgam flows to a decomposer, a short-circuited electrolytic cell, where water combines with the sodium released from the amalgam to form caustic and hydrogen. The caustic product is a concentrated (about 5%) solution of NaOH.

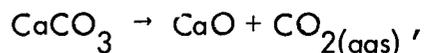
Although both technical improvements and the trend toward building chlorine plants of larger unit capacity have made the mercury cell more competitive with the diaphragm cell in the chlorine-caustic industry, it is not necessarily applicable to descaling seawater. A detailed study is warranted to determine which is better economically, the diaphragm cell without a caustic concentrator or the mercury cell with an amalgam decomposer. However, since concentrated caustic is not required and since the magnitude of operating problems that might occur through build-up of impurities from the seawater in the mercury is unknown, the diaphragm cell is preferred at present.

Closely allied with the economic choice of electrolytic cells are the tolerance limits of each type of cell for sulfate and magnesium. Instead of fractional crystallization

of evaporator bottoms to produce sodium chloride and eliminate sulfate, magnesium, and other impurities, as selected for this design study, it may be simpler and be less expensive to do the following: (1) precipitate magnesium at pH 12 from the amount of evaporator bottoms needed for caustic production, (2) further evaporate the supernate to the point of brine saturation, and (3) use this as the brine feed to the electrolytic cell. The estimated concentrations of the major ions of this saturated brine are  $5.3 \text{ M Na}^+$  and  $\text{Cl}^-$ ,  $0.1 \text{ M K}^+$ , and  $0.3 \text{ M SO}_4^{2-}$ . A combined cost study and experimental program is needed to determine if a fractional crystallization unit is really needed to extract sodium chloride from evaporator bottoms or if an anode material can be found which can tolerate  $0.3 \text{ M}$  sulfate. This and other flowsheet alternatives are shown in the Appendix as Figs. 10, 11, and 12.

### 3.3 Other Chemicals for Descaling

Soda ash is made (1) by drying the calcium carbonate sludge with steam, (2) by calcining the solids to lime and carbon dioxide using low-cost electricity from the nuclear reactor:



and (3) by absorbing the carbon dioxide in the alkali stream generated by the electrolysis of brine.

Acid is made by combining hydrogen and chlorine, the gaseous products of brine electrolysis, and by absorbing the gaseous hydrogen chloride in water. The product hydrochloric acid is used for pH adjustment of the feed to the evaporator. These operations are similar to those now in use by industry.

## 4. PROCESS ECONOMICS

The flowsheet shown in Fig. 1 was used as the basis for economic evaluation. In this system only the calcium is removed from virgin seawater, and the by-products formed are the excesses generated in the closed-cycle descaling system, namely, hydrogen, chlorine, and calcium carbonate. Credit is taken only for the sale of

hydrogen, chlorine, and caustic (for descaling). Many other flowsheet variations were considered and may prove to be practical after further investigation (see Appendix, Figs. 10, 11, and 12). One alternative (Fig. 10) involves the direct production of acid in the electrolytic cell instead of chlorine; thus, recombination of hydrogen and chlorine to furnish acid, as shown in Fig. 1, is eliminated. At the present time, however, there is no practical commercially-available electrode material having an overvoltage sufficiently low to permit production of acid and oxygen in preference to chlorine. Such a closed-cycle process, if feasible, could be of interest to a nation whose economy does not consider chlorine to be a valuable by-product.

Another modification (Fig. 11) includes (1) the passage of a slurry of calcium and magnesium through the evaporator at high pH, (2) the recovery of calcium and magnesium as a mixture from the evaporator concentrate, and (3) the production of carbon dioxide by the reaction of hydrochloric acid with calcium carbonate rather than by calcination as in Fig. 1. Recovery of the precipitate beyond that which is necessary to make the required amount of carbon dioxide is optional. An obvious advantage of this alternative is that, in a high pH environment, less corrosive conditions exist and possibly cheaper materials of construction could be used in the evaporator system. On the other hand, complete magnesium precipitation from virgin seawater prior to evaporation requires about six times more caustic than that for calcium precipitation alone. Thus, the savings in materials of construction would have to be balanced against the additional cost of preparing greater quantities of sodium hydroxide.

In a third modification (Fig. 12), magnesium is recovered in a separate precipitation step. This alternative does not appear to be feasible at the present time since the total amount of magnesium recovered from virgin seawater in a large desalination plant would exceed the current world demand for the product. About 2.4 million tons per year of magnesium would be produced in a 1 billion gal/day fresh water plant compared to a projected world production of about 0.3 million tons in 1980.

#### 4.1 Assumptions for Study

Cost estimates are made for desalination plants of two different capacities, namely, 250 Mgd and 1000 Mgd of fresh water. The former plant would be coupled to a boiling-water nuclear reactor similar to the one being built by the Tennessee Valley Authority at Brown's Ferry, Alabama.<sup>34</sup> When completed in 1971, the plant will have an electrical output of 600 Mw and a heat output of 3200 Mw. The latter plant would be coupled to a future reactor of the boiling-water type or the fast breeder type which generates about 2000 Mw of electricity and about 10,000 Mw of heat.<sup>35,36</sup> Capital costs were obtained from literature sources; these do not include the precipitation-clarification equipment (see Sect. 4.2). The cost of electrical and steam power is based on a recent study of predicted costs for power from large nuclear desalination plants by Sindt, Spiewak, and Anderson.<sup>37</sup> Two criteria determined the limits on the amount of credit allowed for the descaling service: (1) the minimum credit taken, \$0.01/1000 gal fresh water, was the estimated cost of scale prevention by sulfuric acid treatment for a 250-Mgd plant.<sup>2</sup> Acid treatment is effective only for alkaline scale control and an upper evaporator temperature limit of 260°F. (2) The maximum credit taken, \$0.04/1000 gal fresh water, was an estimate based on the sum of the credit for acid treatment plus an additional credit for the advantages that could accrue by using a maximum evaporator temperature of as high as 400°F.<sup>38</sup> Table 3 summarizes the assumptions selected for this study.

From these assumptions, estimates were made of the annual cash flow (net income) required for the recovery of investment, return on investment, interest on working capital, and Federal income taxes, using the procedure and computer code of Salmon.<sup>39</sup> This annual net income is the difference between the total income from sales and the sum of the annual operating cash expenses for all of the facilities needed for descaling seawater. Depreciation and Federal income taxes are not considered as operating expenses. Rather, they are included in the return on investment calculation. The required annual net income is shown, graphically, as a function of the return on investment desired, assuming 100% equity financing. Next, the required annual net income is shown as functions of the credit allowed for caustic descaling and the corresponding

Table 3. Assumptions for Economic Analysis

Fresh water capacity, Mgd	250	1,000
Seawater processed, Mgd	333	1,333
Chlorine production, tons/day	900	3,600
Chlorine marketable, tons/day	860	3,440
Caustic production, tons/day	1,015	4,060
Hydrogen production, marketable scfd	$8.6 \times 10^6$	$34 \times 10^6$
Calcium carbonate, <sup>a</sup> tons/day	330	1,320
Lime (CaO) production, <sup>a</sup> tons/day	590	2,350
Sodium chloride required, tons/day	2,950	11,800
Cost of electrical power, mills/kwhr	3	1.6
Cost of exhaust steam, $\$/10^6$ Btu	0.10	0.05
Credit for closed-cycle descaling, $\$/10^3$ gal fresh water	0.01-0.04	0.01-0.04

<sup>a</sup>No credit taken for selling these products.

minimum credit which can be allowed for chlorine in order to obtain the desired return on investment. The total cost of descaling is also shown exclusive of credit for the sale of hydrogen and chlorine. Finally, illustrations are given which indicate how various combinations of debt and equity financing affect the return on investment.

#### 4.2 Description of Process Equipment

##### Precipitation Equipment

Very large volumes of seawater must be handled in the precipitation equipment, and a very high throughput clarifier must be used, such as the Pfaudler Spiractor.\* This unit increases the precipitation rate of calcium carbonate by introducing granules of "catalyst", which serve as nuclei around which the calcium can precipitate. The

\* Trademark, The Pfaudler Co., Div. of Ritter Pfaudler Corp., Rochester, New York.

catalyst is usually sand; however, the crystalline calcium carbonate could probably be ground and recycled for use as the catalyst. Throughput rates as high as 500 gal/hr/ft<sup>2</sup> have been achieved in these units. The largest Spiractor ever built has a capacity of 2300 gpm (18 ft maximum diameter). One hundred one of these units would be required to handle the seawater feed to a 250-million-gal/day desalination plant. However, if the maximum diameter of the unit could be increased to 54 ft, the number of units could be reduced to about 12. Costs for these units were based on the cost of the largest unit built to date (2300 gpm).

#### Calcium Carbonate Calcination Equipment

A conventional lime kiln, heated electrically, was assumed for the calcium carbonate calcination step. Carbon dioxide from this kiln would be introduced to an absorption tower, where it would be absorbed in caustic solution to form sodium carbonate. The sodium carbonate solution would then be used in the precipitation of calcium from the virgin seawater.

Although the flowsheet of Fig. 1 shows excess carbon dioxide being produced, this economic study includes only the calcination of a sufficient amount of calcium carbonate to supply the required amount of carbon dioxide. Thus, excess calcium carbonate is produced.

#### Sodium Chloride Production Plant

The sodium chloride production facility consists essentially of an 8-stage flash crystallization plant, similar to that described by Messing (one which processes concentrated brines that contain calcium sulfate).<sup>15</sup> Since feeds to the present process will not contain calcium, the equipment might be somewhat cheaper — however, this factor was not considered in the cost analysis. Evaporation of the concentrated brine from the desalination plant is continued until about 80% of the sodium chloride has precipitated. The resulting slurry is first concentrated and then centrifuged to remove the sodium chloride crystals. The concentrated brine is then recycled to the evaporators.

Production of salt containing about 0.3% impurities is claimed for this process. For the purposes of this preliminary study, it is assumed that this is adequate for brine feed to the electrolysis cell. However, if additional purification is needed, as, for example, reducing the magnesium content from an estimated 100-150 ppm to 10-15 ppm, this could be done with commercially available equipment, such as the Higgins continuous ion exchange contactor,\* using a weak acid resin and acid and base regenerants,<sup>40</sup> which are readily available at the plant site. Additional capital investment would be less than 1%, and additional operating expenses would be comparatively nil.

### Chlorine Production Plant

The chlorine production plant includes conventional diaphragm cells such as Hooker S-4 units but omits the caustic concentrator and ancillary equipment because they are not needed. A stoichiometric yield of 1.13 tons of caustic is assumed for each ton of chlorine produced. Typically, a plant which has a captive use for chlorine and caustic (e.g., a paper mill) might have a capacity of 100 tons  $\text{Cl}_2$ /day, while one that produces chlorine for sale might have an output of 500 tons  $\text{Cl}_2$ /day. Thus, a 900 ton/day plant in conjunction with a 250-Mgd fresh-water, descaling plant is not an unreasonable size. The 860 tons/day that would be available for sale represents about 4.4% of total U.S. production in 1966 ( $7.2 \times 10^6$  tons  $\text{Cl}_2$  total);<sup>41</sup> by 1980, this could drop to about 2%, according to projected data on chlorine growth. Also, the 3600 ton/day plant associated with the 1,000-Mgd fresh-water plant is not an unrealistic size when compared to an existing chlorine plant in the U.S. which currently has a daily output approaching 5,000 tons/day.<sup>42</sup>

Hydrogen from the electrolytic cell is of high purity and, consequently, can be used for the production of ammonia directly; however, the capital cost of an ammonia facility is not included in this study. Ammonia could be produced at a rate of 130 tons/day from the 900 tons  $\text{Cl}_2$ /day plant and 550 tons/day from the 3600 tons  $\text{Cl}_2$ /day

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\* Made by Chemical Separations Corporation, Oak Ridge, Tennessee.

plant. These capacities are nominal, considering that new plants under construction have capacities ranging from 100 to 3000 tons/day.

#### 4.3 Economic Evaluation

Closed-cycle descaling of seawater in a desalination plant is separated into three sections for accounting purposes, namely, sodium chloride production, caustic-chlorine production, and seawater treatment. The total capital investment for descaling in a 250-Mgd fresh-water plant is about \$45.4 million. For 1,000 Mgd, the amount is \$158 million and is obtained by using a conservative scaling factor of 0.9 (Table 4).

The total daily cash expenses are detailed in Tables 5 and 6. For 250 Mgd, the unit cost of electric power and exhaust steam power are 3 mills/kwhr and  $\$0.10/10^6$  Btu; for 1,000 Mgd, 1.6 mills/kwhr and  $\$0.05/10^6$  Btu. All labor-associated costs — operating labor, maintenance labor, and overhead — are estimated for the larger plant by applying a conservative scaling factor of 0.8 to each corresponding labor cost of the smaller plant. A scaling factor of unity is applied to material costs. Working capital is estimated to be equal to 60 days of cash expenses. The number of operating days in a year is taken as 360 because U.S. chlorine plants have operated at 99% capacity in recent years and the announced added capacity in each of the years, 1967 and 1968, is 10%.<sup>40</sup>

Significant blocks of electrical and thermal power produced by the associated nuclear reactor, in each case, are consumed in the descaling process. In the 250-Mgd plant, 28% ( $170 \text{ Mw}_e$ ) of the electricity and 15% ( $470 \text{ Mw}_{th}$ ) of the heat produced are consumed. For the 1,000-Mgd plant, the corresponding figures are 34% ( $675 \text{ Mw}_e$ ) and 19% ( $1900 \text{ Mw}_{th}$ ).

In Figs. 6 and 7, the annual net income required is shown as a function of the weighted average return on investment,  $i_v$ , for the 250-Mgd and the 1,000-Mgd plants, respectively. If 100% equity financing is used,  $i_v$  is simply the return on equity. If the financing is a combination of debt and equity, then  $i_v$  is given by

$$i_v = (1 - k)b i_b + (1 - b)i_e ,$$

Table 4. Capital Investment for Closed-Cycle Descaling System.

	250-Mgd Plant	1,000-Mgd Plant <sup>a</sup>
Sodium chloride production	\$10,400,000	\$36,300,000
Caustic-chlorine production	20,000,000	69,700,000
Seawater treatment system		
Hydrogen-chlorine combiner	\$ 500,000	\$ 1,740,000
Calcium carbonate calcination	5,600,000	19,500,000
Precipitation and clarification <sup>b</sup>	8,000,000	27,900,000
Carbon dioxide absorber	25,000	87,000
Lime product handling	250,000	870,000
Auxillary equipment	625,000	2,180,000
	<u>15,000,000</u>	<u>52,300,000</u>
Total	\$45,400,000	\$158,300,000
(Cost of distillation system) <sup>c</sup>	(\$103,000,000)	(\$358,000,000)

<sup>a</sup>Scaled from the 250-Mgd plant using a scaling factor of 0.9 [i.e.,  $(4)^{0.9}$ ].

<sup>b</sup>Twelve 54-ft-diam Pfaudler Spiractors (installed).

<sup>c</sup>Based on a maximum brine temperature of 250°F. The capital cost would be lower if higher brine temperatures are attainable as, for example, 300 to 400°F. Does not include closed-cycle descaling cost (Ref. 2).

Table 5. Total Daily Cash Expenses for a Closed-Cycle Descaling System.  
Basis: 250 Mgd of fresh water

Item	Dollars Per Operating Day
Sodium Chloride Plant - 2950 tons/day (investment = \$10,410,000)	
Steam - $36 \times 10^9$ Btu at \$0.10/ $10^6$ Btu	\$ 3,600
Power - 201,000 kwhr at \$0.003/kwhr	603
Raw materials or chemicals	472
Maintenance materials - 0.0013% (0.5% per year) investment	135
Operating labor at \$3.25/hr - 12 men/shift - 3 shifts	936
Maintenance labor - 0.0013% (0.5% per year) investment	135
Overhead - 60% of labor	562
Taxes and insurance - 0.006% (2% per year) investment	625
	<u>7,068</u>
Chlorine Plant - 900 tons/day (investment = \$20,000,000)	
Power - $2.85 \times 10^6$ kwhr at \$0.003/kwhr	8,550
Steam - $0.9 \times 10^9$ Btu at \$0.10/ $10^6$ Btu	90
Electrodes - 6.5 lb/ton $Cl_2$ at \$0.40/lb	2,340
Other chemicals ( $H_2SO_4$ , asbestos) - \$0.35/ton $Cl_2$	315
Maintenance materials - \$1.00/ton $Cl_2$	900
Total operating labor - \$1.50/ton $Cl_2$	1,350
Maintenance labor - \$0.75/ton $Cl_2$	675
Overhead - \$4.624/ton $Cl_2$	4,162
Taxes and insurance - 0.006% (2% per year) investment	1,111
	<u>19,493</u>
Seawater Descaling Plant - 333.3 Mgd seawater (includes lime and HCl plants) (investment = \$15,000,000)	
Steam - $1.63 \times 10^9$ Btu x \$0.10/ $10^6$ Btu	163
Power - $1.01 \times 10^6$ kwhr x \$0.003/kwhr	3,030
Chemicals	0
Supplies and maintenance materials - 0.0013% (0.5% per year) investment	225
Operating labor at \$3.25/hr - 10 men/shift - 3 shifts	780
Maintenance labor - 0.0013% (0.5% per year) investment	225
Overhead - 60% labor	468
Taxes and insurance - 0.006% (2% per year) investment	900
	<u>5,791</u>
Total Daily Cash Expenses	\$32,352

Table 6. Total Daily Cash Expenses for a Closed-Cycle Descaling System.  
Basis: 1,000 Mgd of fresh water

Item	Dollars Per Operating Day
Sodium Chloride Plant - 11,800 tons/day (investment = \$36,300,000)	
Steam - $145 \times 10^9$ Btu at \$0.05/ $10^6$ Btu	\$ 7,250
Power - 804,000 kwhr at \$0.0016/kwhr	1,286
Raw materials or chemicals	1,888
Maintenance materials - 0.0013% (0.5% per year) investment	472
Operating labor <sup>a</sup>	2,838
Maintenance labor <sup>a</sup>	409
Overhead <sup>a</sup>	1,704
Taxes and insurance - 0.006% (2% per year) investment	218
	<u>16,065</u>
Chlorine Plant - 3600 tons/day (investment = \$69,700,000)	
Power - $11.4 \times 10^6$ kwhr at \$0.0016/kwhr	18,240
Steam - $3.6 \times 10^9$ Btu at \$0.05/ $10^6$ Btu	180
Electrodes - 6.5 lb/ton Cl <sub>2</sub> at \$0.40/lb	9,360
Other chemicals (H <sub>2</sub> SO <sub>4</sub> , asbestos) - \$0.35/ton Cl <sub>2</sub>	1,260
Maintenance materials	3,600
Total operating labor <sup>a</sup>	4,093
Maintenance labor <sup>a</sup>	2,047
Overhead <sup>a</sup>	12,619
Taxes and insurance - 0.006% (2% per year) investment	4,182
	<u>55,581</u>
Seawater Descaling Plant - 1,333 Mgd seawater (includes lime and HCl plants) (investment = \$52,300,000)	
Steam - $6.52 \times 10^9$ Btu x \$0.05/ $10^6$ Btu	326
Power - $4.04 \times 10^6$ kwhr x \$0.0016/kwhr	6,464
Chemicals	0
Supplies and maintenance materials - 0.0013% (0.5% per year) investment	680
Operating labor <sup>a</sup>	2,365
Maintenance labor <sup>a</sup>	682
Overhead <sup>a</sup>	1,419
Taxes and insurance - 0.006% (2% per year) investment	3,138
	<u>15,074</u>
Total Daily Cash Expenses	\$86,720

<sup>a</sup>Scaled from the 250-Mgd plant (Table 5) using a scaling factor of 0.8 [i.e.,  $(4)^{0.8}$ ].

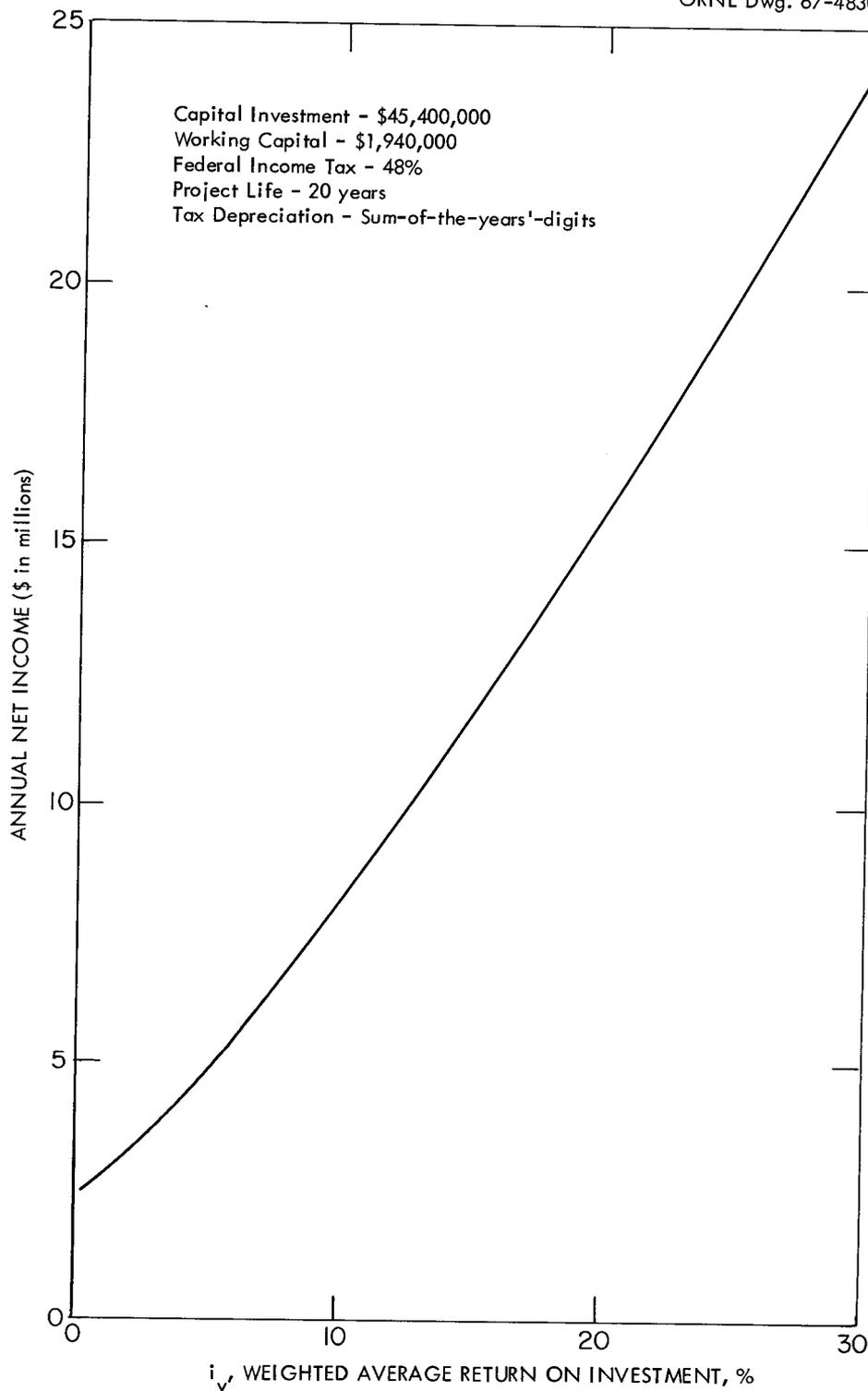


Fig. 6. Annual Net Income as a Function of Weighted Average Return on Investment. (Basis: 250 Mgd of fresh water.)

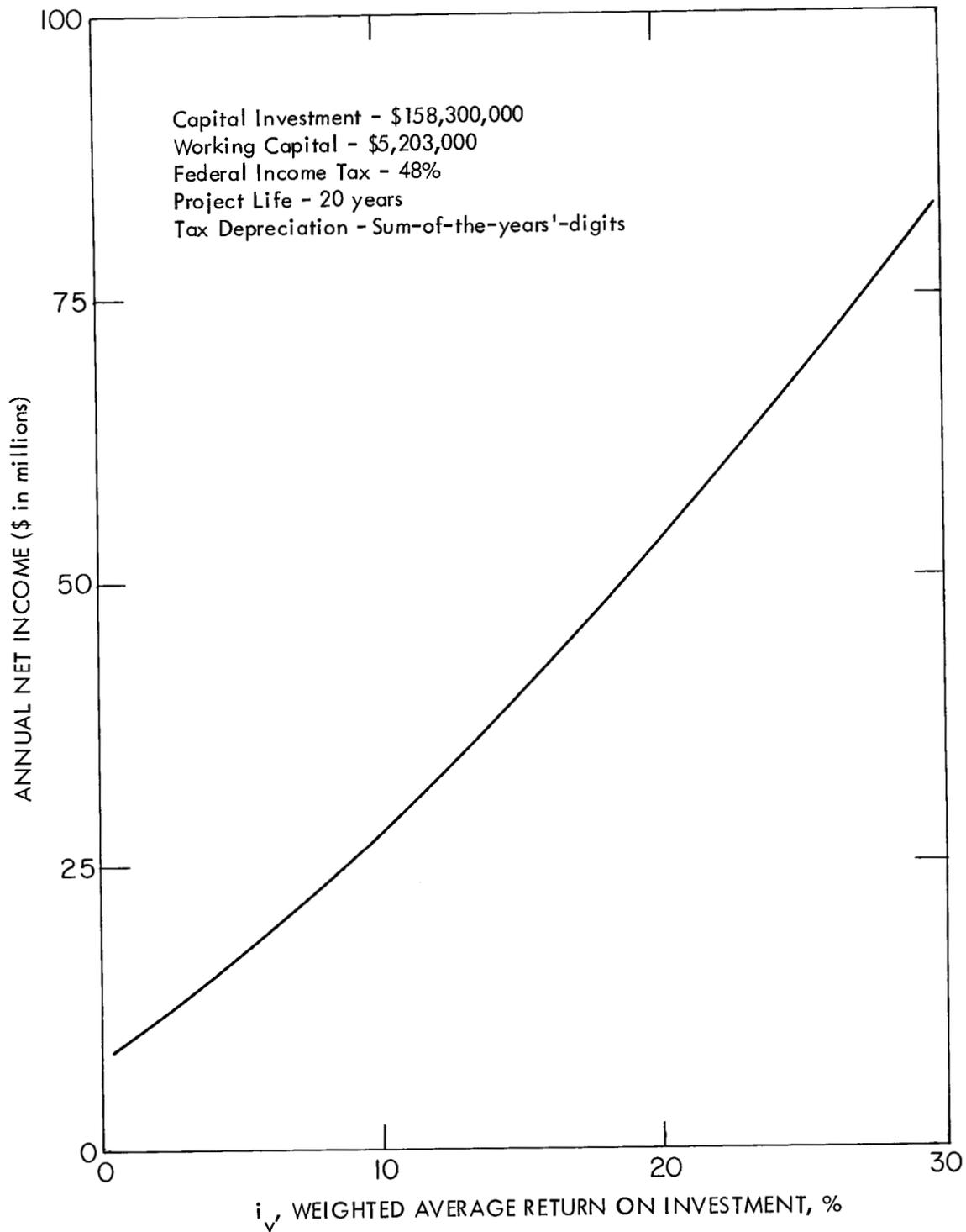


Fig. 7. Annual Net Income as a Function of Weighted Average Return on Investment. (Basis: 1,000 Mgd of fresh water.)

where

$i_v$  = weighted average return on investment

$k$  = Federal income tax rate

$b$  = fraction of capital investment in bonds

$i_b$  = interest rate on bonds

$i_e$  = rate of return on equity.

Thus, Figs. 6 and 8 can be used to find the required annual net income for any given combination of  $i_e$ ,  $i_b$ , and  $b$  ( $k$  was fixed at 48%). For any given  $i_v$ , an increase in the proportion of debt financing normally increases the return on equity, assuming that the interest rate on bonds is less than the rate of return on equity and that the ratio of debt to equity remains constant over the life of the depreciation period.

Federal income taxes were charged at the rate of 48%. Depreciation for tax purposes is calculated by the sum-of-the-years'-digits method, using a depreciable life of 20 yr. For this study, private financing is assumed, and the interest rate on bonds is taken at 6%. For a given  $i_v$ , a lower interest rate on bonds increases the return on equity.

The minimum unit prices to be charged for caustic and chlorine, respectively, in order to obtain the required annual net income, are shown as parameters in Figs. 8 and 9. In this study, the caustic price is simply the credit that would be allowed for descaling virgin seawater. The corresponding price for chlorine is a function of the caustic credit plus a credit for the electrolytic hydrogen produced which is in excess of internal plant needs —  $8.6 \times 10^6$  scfd in the 250-Mgd plant and  $34 \times 10^6$  scfd in the 1000-Mgd plant. This credit is fixed, conservatively, at \$0.25/mscf. No credit is taken for the lime and calcium carbonate produced. The costs of marketing and distribution have not been included and, therefore, the product prices or credits do not reflect these expenses.

Tables 7, 8, and 9 are generated from Figs. 6-9. They summarize the minimum credits that have to be taken for chlorine in order to obtain the required annual net income for a specified return on equity under the following methods of financing,

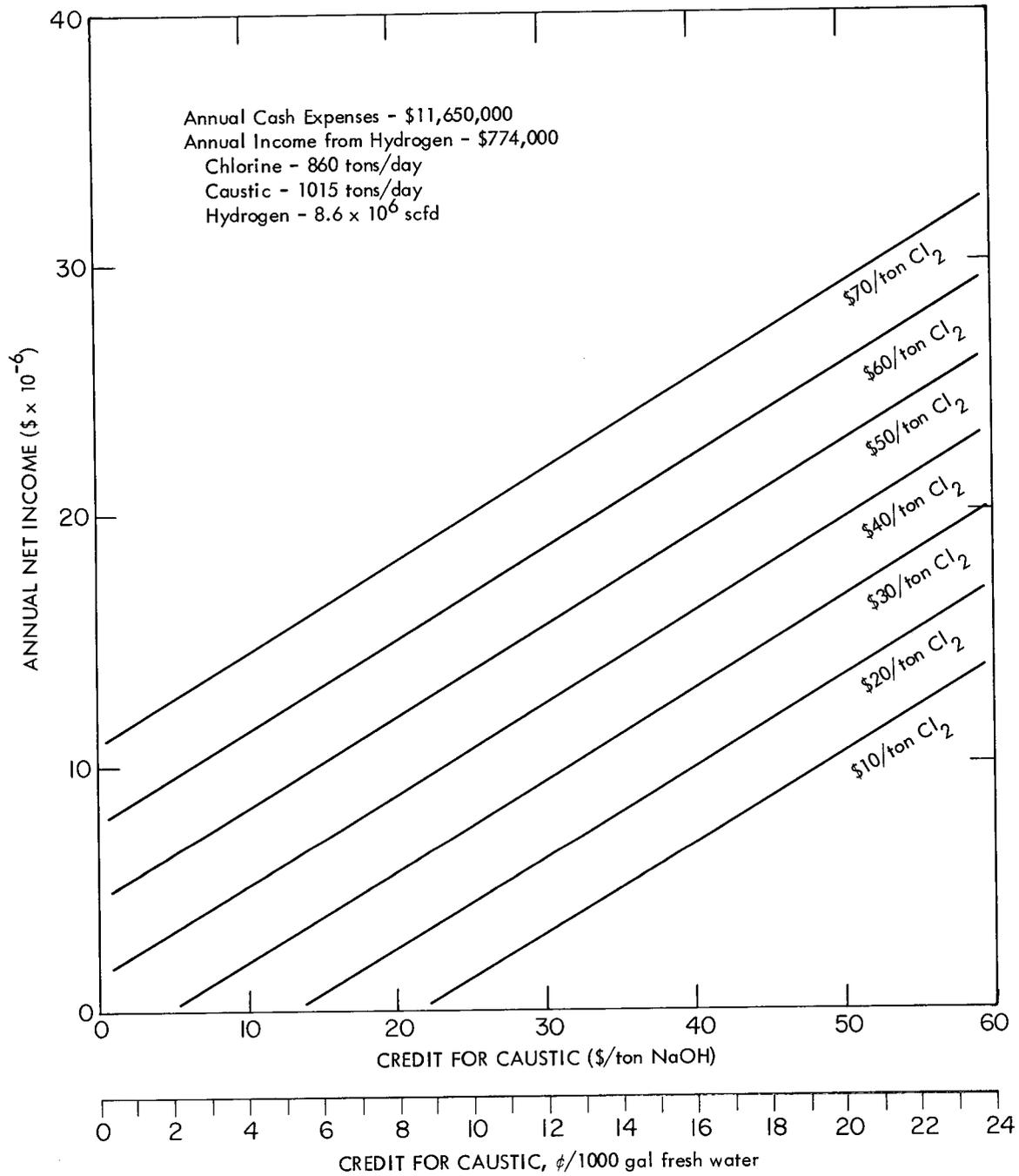


Fig. 8. Annual Net Income as a Function of Credit Allowed for Caustic and Chlorine. (Basis: 250 Mgd of fresh water.)

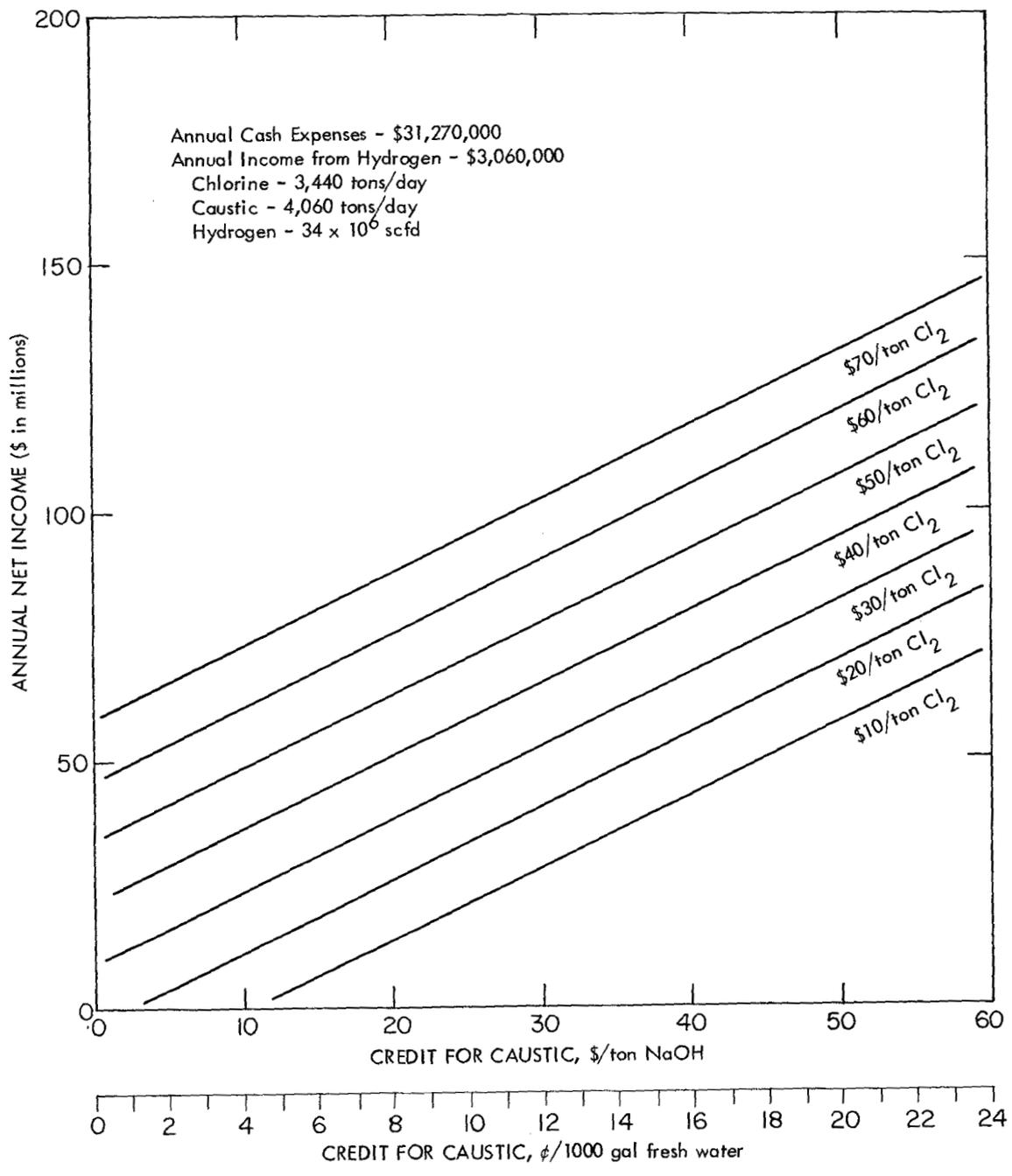


Fig. 9. Annual Net Income as a Function of Credit Allowed for Caustic and Chlorine. (Basis: 1,000 Mgd of fresh water.)

Table 7. Chlorine Price as a Function of Caustic Credit and Size of Nuclear Desalination Plant.

100% Stock Financing

Return on Equity <sup>a</sup> (%)	250-Mgd Fresh Water Plant <sup>b</sup>				1,000-Mgd Fresh Water Plant <sup>c</sup>			
	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)
	Net	Total			Net	Total		
0	2.3	14.0	2.50	40.00	7.9	39.1	2.50	26.00
4	4.2	15.9	2.50	45.50	14.6	45.8	2.50	31.60
10	8.0	19.7	2.50	57.70	27.5	58.7	2.50	41.60
15	11.7	23.4	2.50	69.70	40.0	71.2	2.50	51.60
20	15.6	27.3	2.50	82.20	53.6	84.8	2.50	63.20
0	2.3	14.0	10.00	31.60	7.9	39.1	10.00	17.00
4	4.2	15.9	10.00	36.80	14.6	45.8	10.00	22.40
10	8.0	19.7	10.00	49.10	27.5	58.7	10.00	32.80
15	11.7	23.4	10.00	61.00	40.0	71.2	10.00	42.80
20	15.6	27.3	10.00	73.60	53.6	84.8	10.00	54.00

<sup>a</sup>After Federal income tax of 48% (except for zero return). Depreciation for tax purposes is 20 years, using the sum-of-the-years'-digits method.

<sup>b</sup>Electrical power at 3 mills/kwhr, steam power at \$0.10/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>c</sup>Electrical power at 1.6 mills/kwhr, steam power at \$0.05/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>d</sup>\$2.50/ton NaOH is equivalent to \$0.01/1000 gal of fresh water produced. \$10.00/ton NaOH, \$0.04/1000 gal.

<sup>e</sup>The price needed to furnish the required total income after a credit for caustic descaling and a credit for hydrogen, fixed at \$0.25/mscf.

Table 8. Chlorine Price as a Function of Caustic Credit and Size of Nuclear Desalination Plant.

25% Bond - 75% Stock Financing

Return on Equity <sup>a</sup> (%)	250-Mgd Fresh Water Plant <sup>b</sup>				1,000-Mgd Fresh Water Plant <sup>c</sup>			
	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)
	Net	Total			Net	Total		
0	2.3	14.0	2.50	40.00	7.9	39.1	2.50	26.00
4	4.5	16.2	2.50	46.80	14.2	45.4	2.50	31.00
10	6.7	18.4	2.50	53.90	23.3	54.5	2.50	38.40
15	9.4	21.1	2.50	62.60	32.3	63.5	2.50	45.60
20	12.2	23.9	2.50	71.30	41.8	73.0	2.50	53.20
0	2.3	14.0	10.00	31.60	7.9	39.1	10.00	17.00
4	4.5	16.2	10.00	37.70	14.2	45.4	10.00	22.40
10	6.7	18.4	10.00	45.20	23.3	54.5	10.00	30.00
15	9.4	21.1	10.00	53.60	32.3	63.5	10.00	36.80
20	12.2	23.9	10.00	62.90	41.8	73.0	10.00	44.50

<sup>a</sup>After Federal income tax of 48% (except for zero return). Depreciation for tax purposes is 20 years, using the sum-of-the-years'-digits method. Debt-to-equity ratio assumed constant over depreciation period. Bond interest rate is 6%.

<sup>b</sup>Electric power at 3.0 mills/kwhr, steam power at \$0.10/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>c</sup>Electrical power at 1.6 mills/kwhr, steam power at \$0.05/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>d</sup>\$2.50/ton NaOH is equivalent to \$0.01/1000 gal of fresh water produced. \$10.00/ton NaOH, \$0.04/1000 gal.

<sup>e</sup>The price needed to furnish the required total income after a credit for caustic descaling and a credit for hydrogen, fixed at \$0.25/mscf.

Table 9. Chlorine Price as a Function of Caustic Credit and Size of Nuclear Desalination Plant.

50% Bond - 50% Stock Financing

Return on Equity <sup>a</sup> (%)	250-Mgd Fresh Water Plant <sup>b</sup>				1,000-Mgd Fresh Water Plant <sup>c</sup>			
	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)	Income Required (\$ x 10 <sup>-6</sup> /year)		Caustic Credit <sup>d</sup> (\$/ton)	Chlorine Price <sup>e</sup> (\$/ton)
	Net	Total			Net	Total		
0	2.3	14.0	2.50	40.00	7.9	39.1	2.50	26.00
4	3.9	15.6	2.50	44.80	13.5	44.7	2.50	30.40
10	5.7	17.4	2.50	50.60	19.5	50.7	2.50	35.60
15	7.2	18.9	2.50	55.50	25.0	56.2	2.50	39.30
20	9.0	20.7	2.50	61.30	30.8	62.0	2.50	44.40
0	2.3	14.0	10.00	31.60	7.9	39.1	10.00	17.00
4	3.9	15.6	10.00	35.80	13.5	44.7	10.00	21.60
10	5.7	17.4	10.00	41.60	19.5	50.7	10.00	26.40
15	7.2	18.9	10.00	46.80	25.0	56.2	10.00	31.20
20	9.0	20.7	10.00	52.30	30.8	62.0	10.00	35.60

<sup>a</sup>After Federal income tax of 48% (except for zero return). Depreciation for tax purposes is 20 years, using the sum-of-years'-digits method. Debt-to-equity ratio assumed constant over depreciation period. Bond interest rate is 6%.

<sup>b</sup>Electric power at 3.0 mills/kwhr, steam power at \$0.10/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>c</sup>Electrical power at 1.6 mills/kwhr, steam power at \$0.05/10<sup>6</sup> Btu (exhaust steam at 260°F).

<sup>d</sup>\$2.50/ton NaOH is equivalent to \$0.01/1000 gal of fresh water produced. \$10.00/ton NaOH, \$0.04/1000 gal.

<sup>e</sup>The price needed to furnish the required total income after a credit for caustic descaling and a credit for hydrogen, fixed at \$0.25/mscf.

respectively: 100% stock, 25% bonds and 75% stock, and 50% bonds and 50% stock. In these tables, zero return on equity represents only the required annual net income to refund the capital investment over a 20-yr period; no interest is paid on the capital investment and no Federal income tax is paid, since there is no taxable income. If no credits are taken for chlorine and hydrogen, the annual cost of furnishing caustic for descaling is the total income required; that is, the sum of the annual net income to refund the capital investment in 20 years plus the annual operating expenses. For a 250-Mgd plant, the total income required, annually, is \$14.0 million, and the caustic price is \$39.0/ton or \$0.156/1000 gal fresh water produced. For 1000 Mgd, the income required is \$39.1 million and the caustic price is \$27.3/ton or \$0.109/1000 gal.

In this study, however, minimum and maximum caustic credits of \$2.50 and \$10.00/ton have been allowed, corresponding to \$0.01 and \$0.04/1000 gal fresh water. At zero return on equity, a 250-Mgd plant requires an annual net income of \$2.3 million. The sum of the unit prices for caustic and chlorine, \$2.50/ton NaOH plus \$40.00/ton Cl<sub>2</sub> or \$10/ton NaOH plus \$31.60/ton Cl<sub>2</sub> is about \$42, if a credit of \$0.25/mscf is allowed for hydrogen. For the 1000-Mgd plant, the annual net income required is \$7.9 million and this sum drops to about \$28.

Characteristically, most companies in the caustic-chlorine industry strive for at least a 15% return on equity. With the capital investment supplied entirely by equity financing, 15% return can be expected if the sum of the unit price for caustic and chlorine is \$71-72 in the 250-Mgd case and \$53-54 in the 1000-Mgd case (Table 7). With 25% bond-75% stock financing, however, these sums drop to \$64-65 and \$47-48 (Table 8). With 50% bond-50% stock financing, \$57-58 and \$41-42 (Table 9). The current combined unit price for caustic and chlorine to achieve 15% return is about \$80 minimum. However, when caustic-chlorine production is integrated with a large nuclear desalination plant, large blocks of cheap electrical power can be utilized — as low as 1.6 mills/kwhr as compared with the current average cost of 5 to 6 mills/kwhr. Thus, the combined unit price for caustic and chlorine may be reduced by as much as 50% and still allow a return on equity of 15%.

With a descaling credit of \$0.01/1000 gal fresh water (\$2.50/ton NaOH) in a 1000-Mgd plant, the chlorine production cost including a 15% return on equity ranges from \$39/ton  $\text{Cl}_2$  with 50% bond-50% stock financing (Table 9) to \$52/ton  $\text{Cl}_2$  with 100% stock financing (Table 7). If only a 4% return on equity is desired, a minimum-interest-rate situation, the corresponding range of chlorine cost is \$30 to \$32/ton  $\text{Cl}_2$ . In a 250-Mgd plant, with a credit of \$0.01/1000 gal, the price range is \$56 to \$70/ton  $\text{Cl}_2$  for a 15% return and \$44 to \$45/ton  $\text{Cl}_2$  for a 4% return. However, if a credit of \$0.02/1000 gal (\$5.00/ton NaOH) is allowed, interpolation of Tables 7-9 indicates that the cost of chlorine would drop to \$53 to \$67/ton  $\text{Cl}_2$  for a 15% return and about \$43/ton  $\text{Cl}_2$  for a 4% return. It is difficult to establish what part of the combined caustic and chlorine price of \$80 is the current competitive price for chlorine; but, based on available information, it is estimated to be in the range \$35 to \$45/ton  $\text{Cl}_2$ . If this is valid, the production cost of \$30 (4% return) to \$39 (15% return) per ton  $\text{Cl}_2$  with 50% bond-50% stock financing, projected for the 1000-Mgd case, is competitive with the present price range of chlorine. At the same time, descaling is accomplished for \$0.01/1000 gal fresh water, or \$2.50/ton NaOH, which is markedly less than the estimated current price range of caustic of \$35 to \$45/ton.

Equally important, seawater descaling in conjunction with caustic-chlorine production parallels the projected demands for the two chemicals. Chlorine demand is expected to increase at the rate of 10% per year through 1970, while caustic demand is expected to level off, or, at best, grow at a much slower rate than chlorine.<sup>19</sup> The descaling operation represents a captive market for all of the caustic produced, while the chlorine produced can be readily sold. Thus, it allows for an expansion in the total inventory of chlorine to satisfy a rapidly growing market without a corresponding increase in caustic inventory.

In summary, the closed-cycle descaling process economically benefits both nuclear desalination and the manufacture of chlorine and caustic. Seawater descaling is accomplished at a cost which is competitive with sulfuric acid treatment. At the same time, chlorine can be produced at, or below, the current competitive cost, including a reasonable return on equity.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The proposed closed-cycle descaling process appears to be practical on both a technical and an economic basis. Sufficient calcium is removed to allow an evaporation temperature of 350 to 400°F. All chemicals required in the descaling process are produced from the seawater, using cheap nuclear power, thus eliminating the shipment of raw materials. These chemicals include carbon dioxide, hydrochloric acid, hydrogen, chlorine, and caustic. Excess chlorine and hydrogen are sold to provide added income. Production of the fertilizers, urea and ammonia, is optional.

An economic study shows that the descaling process benefits both nuclear desalination and caustic-chlorine manufacture, providing all caustic produced is used in descaling and the excess chlorine and hydrogen are sold. The costs for desalination plants that produce 1000 Mgd and 250 Mgd of fresh water are summarized in Table 10. In the 1000-Mgd plant, seawater is descaled at \$0.01/1000 gal fresh water, a cost that is competitive with sulfuric acid treatment. At the same time, chlorine costs \$39/ton with 50% bond-50% stock financing, which is competitive with the current price range of chlorine, \$35 to \$45/ton. Both prices reflect a 15% return on equity.

The nuclear desalination plant with closed-cycle descaling could be envisioned as a jointly-operated giant complex in which a utility company produces the power and fresh water, and a company in the chlorine-caustic industry markets the by-product chlorine and hydrogen. Pulp and paper manufacturers might also desire to share in this business venture since they consume large quantities of both caustic and chlorine and are currently building chlorine-caustic facilities for their internal needs. Generally, in making cost estimates for large industrial processes, it is not desirable to base the economics of the primary process on the sale of a substantial volume of by-product. However, there are several factors which should make this combined operation attractive to the chlorine-caustic industry. First, there is a captive market for all of the caustic produced. Second, the market for chlorine is expanding rapidly, projected at greater than 10% per year through 1970. The 860 tons per day of chlorine from the proposed 250-million-gal-per-day complex amounts to 20% of the recent two-year growth rate in the United States and should not oversupply the U.S. market.

Table 10. Cost of Descaling as a Function of Caustic Credit, Chlorine Price, Return on Equity, and Desalination Plant Size

Plant Capacity (Mgd)	Descaling Cost (\$/1000 gal fresh water)	Equivalent Caustic Credit (\$/ton)	Chlorine Price (\$/ton)	Hydrogen Price (\$/mscf)	Return on Equity <sup>c</sup> (%)
1000 <sup>a</sup>	0.11	27	0	0	0
	0.01	2.50	26	0.25	0
	0.01	2.50	30	0.25	4
	0.01	2.50	39	0.25	15
250 <sup>b</sup>	0.16	39	0	0	0
	0.02	5.00	37	0.25	0
	0.02	5.00	43	0.25	4
	0.02	5.00	53	0.25	15

<sup>a</sup>Electrical power at 1.6 mills/kwhr, steam power at \$0.05/10<sup>6</sup> Btu.

<sup>b</sup>Electrical power at 3.0 mills/kwhr, steam power at \$0.10/10<sup>6</sup> Btu.

<sup>c</sup>With 50% bond-50% stock financing, except at zero return on equity.

In order to refine the proposed descaling process, the following additional laboratory and economic studies are suggested:

1. Kinetic and equilibrium studies to determine precisely the extent of calcium precipitation as a function of time, temperature, and pH without precipitation of magnesium.
2. The change in the pH of seawater at elevated temperatures due to carbonate ion remaining after calcium removal. Data on the hydrolysis rate (hydroxyl ion production) at pH 7 as a function of brine temperature and initial carbonate concentration are required to define the temperature at which magnesium hydroxide precipitation occurs. This data would define the amounts of acid needed to maintain a pH of 7.
3. The feasibility of passing the slurry of calcium carbonate (and magnesium hydroxide) through the distillation system at pH 9.2 or higher. Limited experimental data on magnesium hydroxide precipitation under these conditions are available. The cost of clarifying equipment could be significantly reduced

if calcium carbonate could be separated from the smaller volume of evaporator bottoms rather than the raw seawater; the rate of separation is also less important in the case of the evaporator bottoms.

4. The recovery of other elements from the seawater waste streams in either macro or micro quantities. As an example, if all of the magnesium in both waste streams was recovered from a 250-million-gal-per-day plant, about 600,000 tons per year of magnesium would be produced, enough to more than saturate the current demand. Alternatively, processing of only the magnesium-rich waste stream would yield a reasonable amount, equivalent to about 4% of the total magnesium content (570,000 tons per year) of all magnesium compounds produced in the United States in 1964, or about one-third of the total magnesium metal consumed (70,000 tons per year). Other elements of interest include bromine and iodine.
5. Determination of the tolerance limits of anode materials to sulfate impurity in saturated brine under diaphragm cell and mercury cell operating conditions. Traditional electrode materials, such as graphite, and newer materials, such as platinized titanium, should be tested. If the fractional crystallization equipment for obtaining sodium chloride is not needed, a significant item of capital investment would be eliminated.
6. A detailed economic comparison of the diaphragm cell and the mercury cell is necessary to select the cell most appropriate for this flowsheet. Concentrated caustic is not required for descaling, but the daily output of chlorine is so large, at 900 tons per day, that recent improvements in mercury cell technology may favor the selection of this cell over the more traditional diaphragm cell and, at the same time, produce concentrated caustic, a more desirable product. The effect of deposition of the impurities from seawater in the mercury must be determined.

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7. APPENDIX

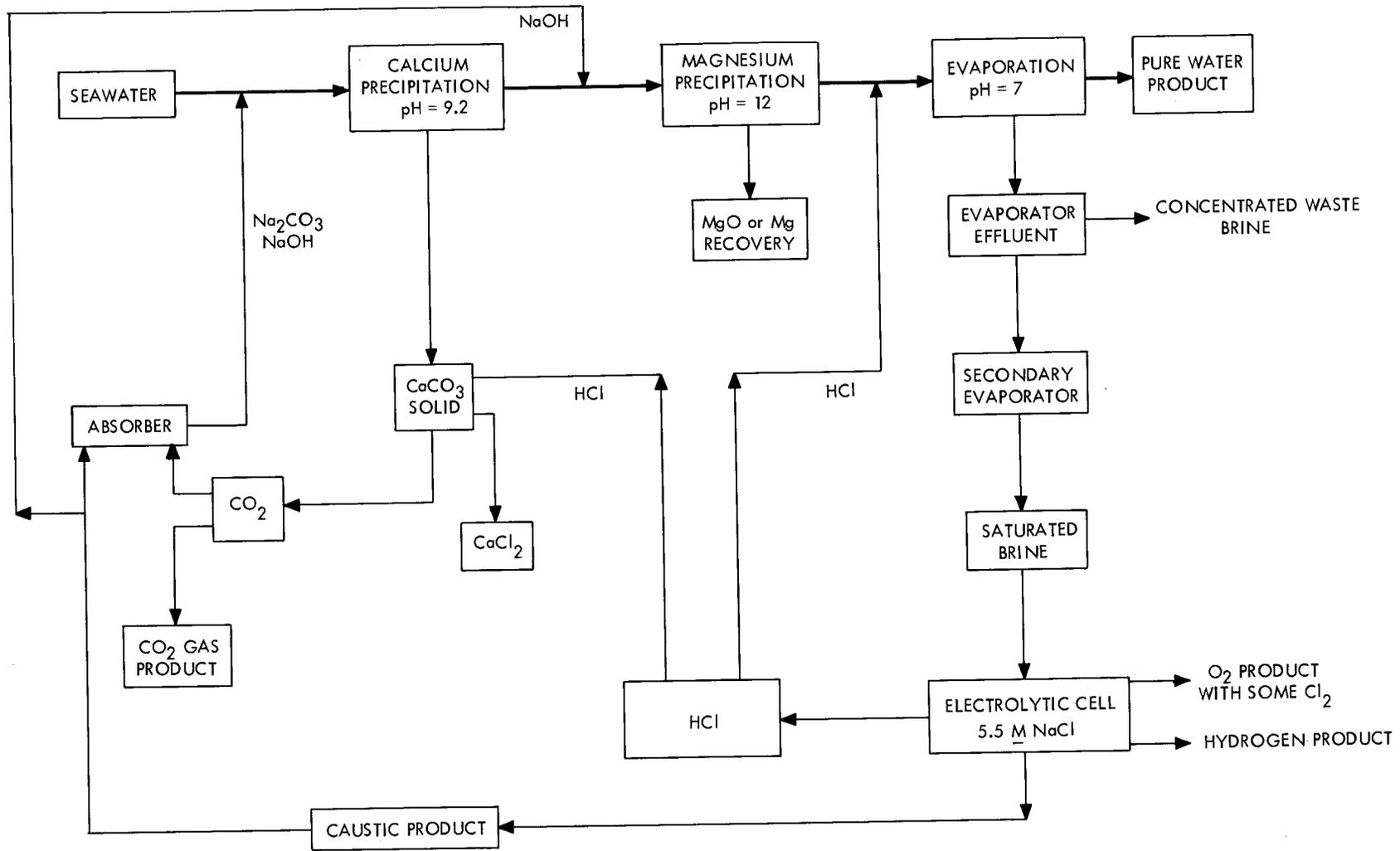


Fig. 10. Modified Flowsheet I. A closed-cycle descaling process. Hydrochloric acid is produced directly at the anode of the electrolytic cell.

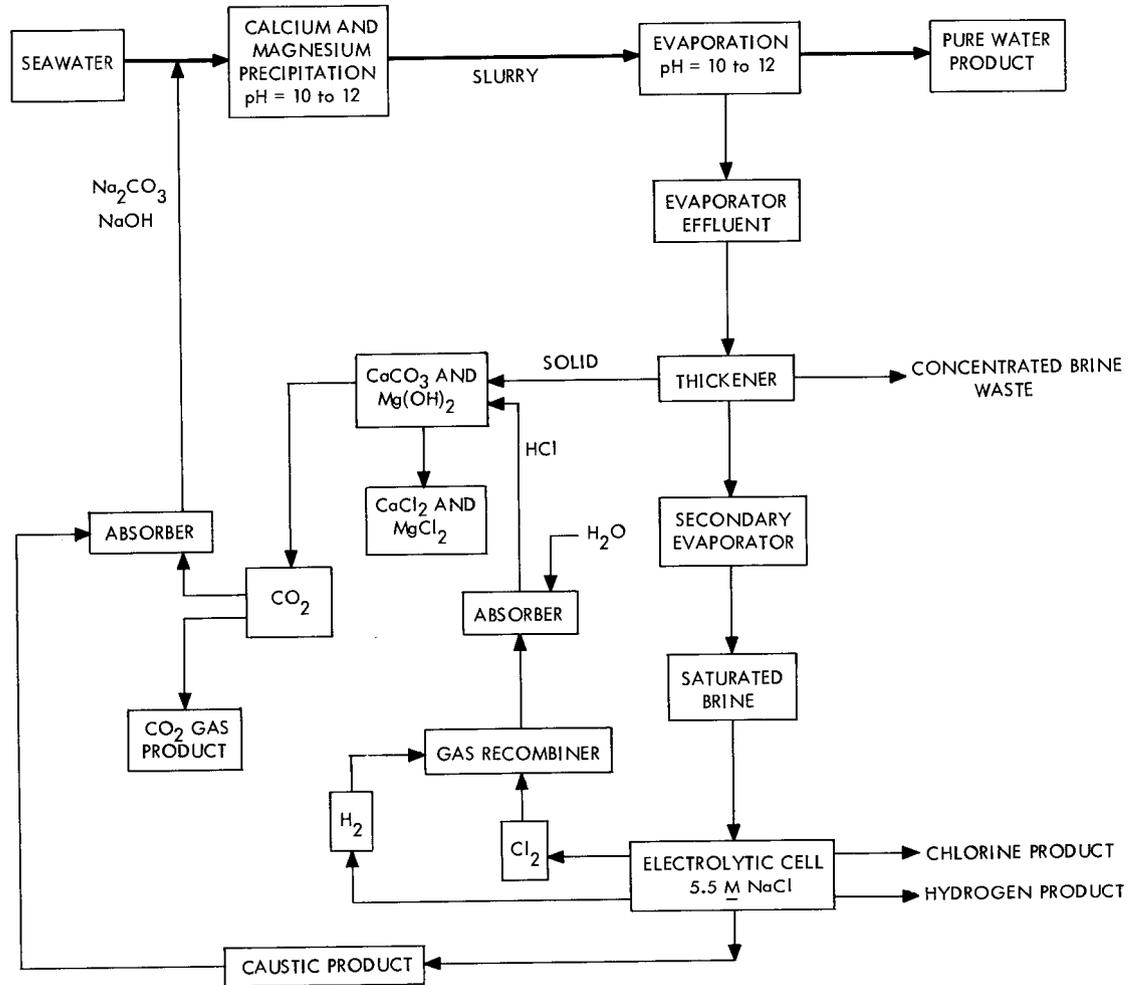


Fig. 11. Modified Flowsheet II. A closed-cycle descaling process. A slurry is passed through the evaporator at pH 10 to 12. HCl is added to a mixture of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$  to obtain  $\text{CO}_2$ .

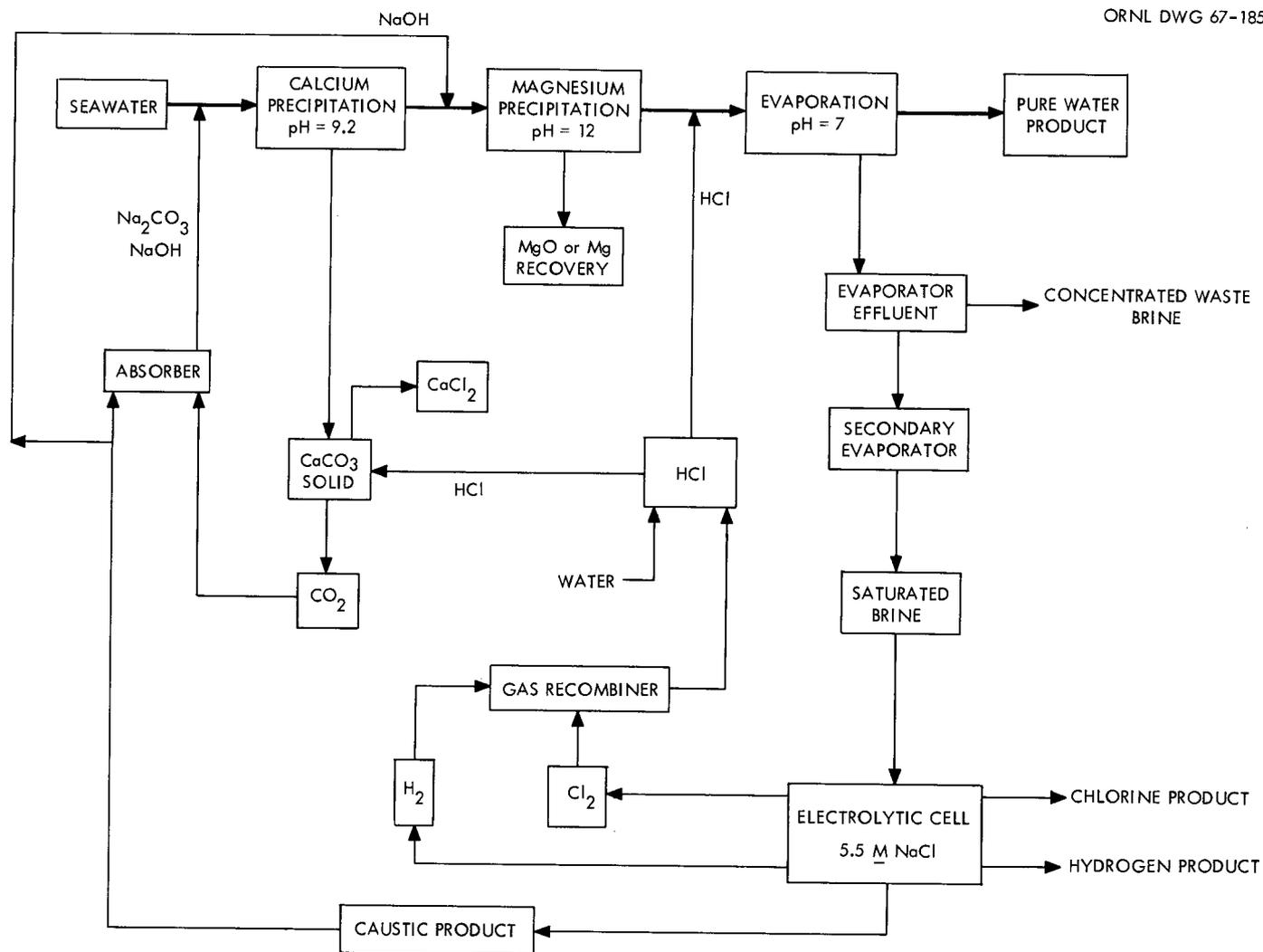


Fig. 12. Modified Flowsheet III. A closed-cycle desalting process. Magnesium is precipitated separately to recover magnesia or elemental magnesium.

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