

Combination of the amalgam cell and the membrane cell processes for chlor-alkali production*

F. HINE†

4-4-6 Jinnan, Ikaruga, Nara 636-01, Japan

A. J. ACIOLI MACIEL

Salgema Industrias Quimicas S.A., Maceio, AL, Brazil

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The combined operation of amalgam cells and membrane cells is feasible for increasing the production capacity of existing amalgam cell plant. The membrane cell caustic of 30% NaOH concentration can be utilized as the feed to the amalgam decomposer for producing 50% caustic. A part of the purified brine in the amalgam cell plant is bypassed to the membrane cell plant, dechlorinated completely, then treated further to remove traces of impurities.

1. Introduction

The production capacity of the amalgam cell process is large, especially in Europe. Additionally, membrane cell technology has been developed rapidly for the last two decades, and is now recognized as the most energy efficient, and, hence, economical route for producing high quality caustic soda. The combined operation of amalgam cells and membrane cells is therefore desirable for increasing the production capacity to meet the demand for chlorine and caustic. This paper deals with the modification of the flowsheet for the combination of a membrane cell facility with an existing amalgam cell plant.

The flowsheet and the material balance of an amalgam cell plant and a membrane cell plant are described in detail in previous publications [1, 2]. In an amalgam cell plant, polished brine is fed to the cell and the depleted brine is chlorinated to prevent precipitation of mercury compounds. Brine depletion is in the range of 10–15% to keep the energy efficiency high.

Sodium amalgam of about 0.2% Na concentration by weight is decomposed to produce 50% NaOH solution. This caustic solution is filtered to remove impurities, mainly carbon particles, iron oxide, and mercury.

The operating conditions of the membrane cell plant are as follows: brine feed 300–310 g dm⁻³ NaCl; brine return 170–230 g dm⁻³ NaCl; and brine decomposition 30–50% with a product caustic of 30–35% NaOH. Although the brine flowsheet resembles that in the amalgam cell plant, the filtered brine is polished further with chelating resin to remove unwanted magnesium and calcium impurities to the desired level. This is called the secondary treatment.

Product caustic solution is 30–35% NaOH in concentration and contains NaCl in the range of 20–

30 mg dm⁻³. This catholyte liquor can be used directly in various applications, or evaporated to 50% concentration for the merchant market.

2. Addition of a membrane cell facility to an existing amalgam plant of comparable size

It is possible to utilize a membrane cell caustic of 30–35% in concentration as the feed to the amalgam decomposer where sodium amalgam reacts with caustic solution to produce 50% caustic and byproduct hydrogen.

Figure 1 shows the material balance in an amalgam decomposer having a capacity of 100 tons day⁻¹ (t/d hereafter) NaOH on a dry basis. The decomposer requires 45 t/d water for reaction and about 100 t/d water for dilution. Also, 5–10 t/d water is evaporated with the hydrogen depending on the catholyte concentration and the operating temperature. The figure indicates the maximum utilization of the membrane cell caustic solution. Of course, a certain amount of water can be supplied to the amalgam decomposer if the capacity of the membrane cell facility is small.

Amalgam decomposition is exothermic and the reaction heat is about 20% of the total heat, the second largest factor after the sensible heat of the mercury [3]. Also, the rate of amalgam decomposition depends greatly on the operating temperature. Thermal insulation reduces the heat loss through the wall, though it is only 0.1% of the total output

The sensible heat of the caustic liquor affects the heat balance since the flow rate of solution is large compared to the conventional process using water. The contribution of the sensible heat of solution in the decomposer utilizing water is 2% of the input and 6% of the output. It is preferable to supply the mem-

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† To whom all correspondence should be addressed.

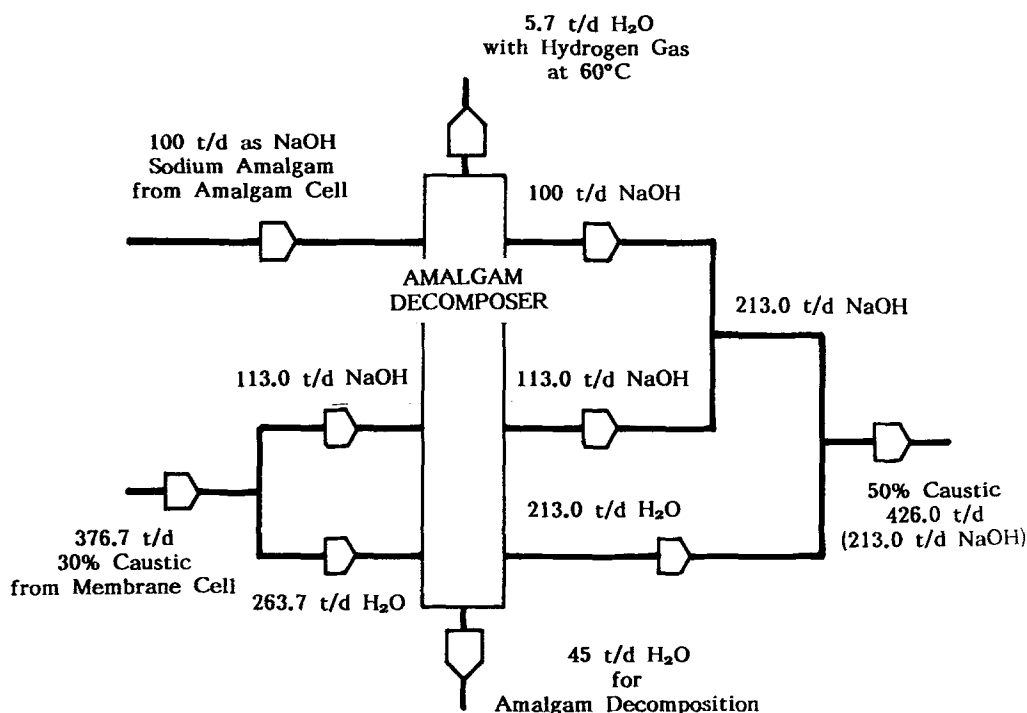


Fig. 1. Material balance of the amalgam decomposer. Basis: 100 t/d as 100% NaOH from the amalgam cell plant.

brane cell caustic to the amalgam decomposer at high temperature.

The size of the amalgam decomposer, especially its diameter, is determined strictly by the flow rate of mercury since the mass transfer coefficient in the tower depends greatly on the mercury flow [4]. In the author's experience, the solution flow rate is a minor factor for a tower operated in a regular manner. Flooding can occur, however, when a large amount of 30% caustic solution is supplied. The graphite packing size has to be increased to enlarge the space for solution flow. The inlet and outlet piping must be modified accordingly.

A combined flowsheet on the basis of 100 t/d (as dry caustic) with the amalgam cell process is shown in Fig. 2. Construction of a separate facility for the membrane cells is feasible when the capacity of the new plant is comparable to that of the existing plant. The membrane cell caustic is sent to the amalgam decomposer where 50% caustic of combined production is produced. The equipment and piping of the downflow from the decomposer are modified to handle product caustic in large volume if necessary.

The concentration and the flow rate of the membrane cell caustic to be fed to the amalgam decomposer are adjusted by the addition of water to the catholyte reservoir.

3. Increase of capacity with membrane cells of relatively small size

The amalgam decomposer is able to produce 60% NaOH solution without any modification or difficulty. Only the feed water flow rate must be adjusted. Therefore, membrane cell caustic of 30% NaOH concentration can be added to the storage tank containing 60% caustic to obtain 50% NaOH solution. This

procedure may be employed to increase the amalgam plant capacity by 50% with membrane cells.

The process is advantageous since only a large storage tank, and a mixing tank if necessary, need be installed. No other modification or conversion of the caustic cooler, the polishing filter or the piping in the amalgam cell plant is required.

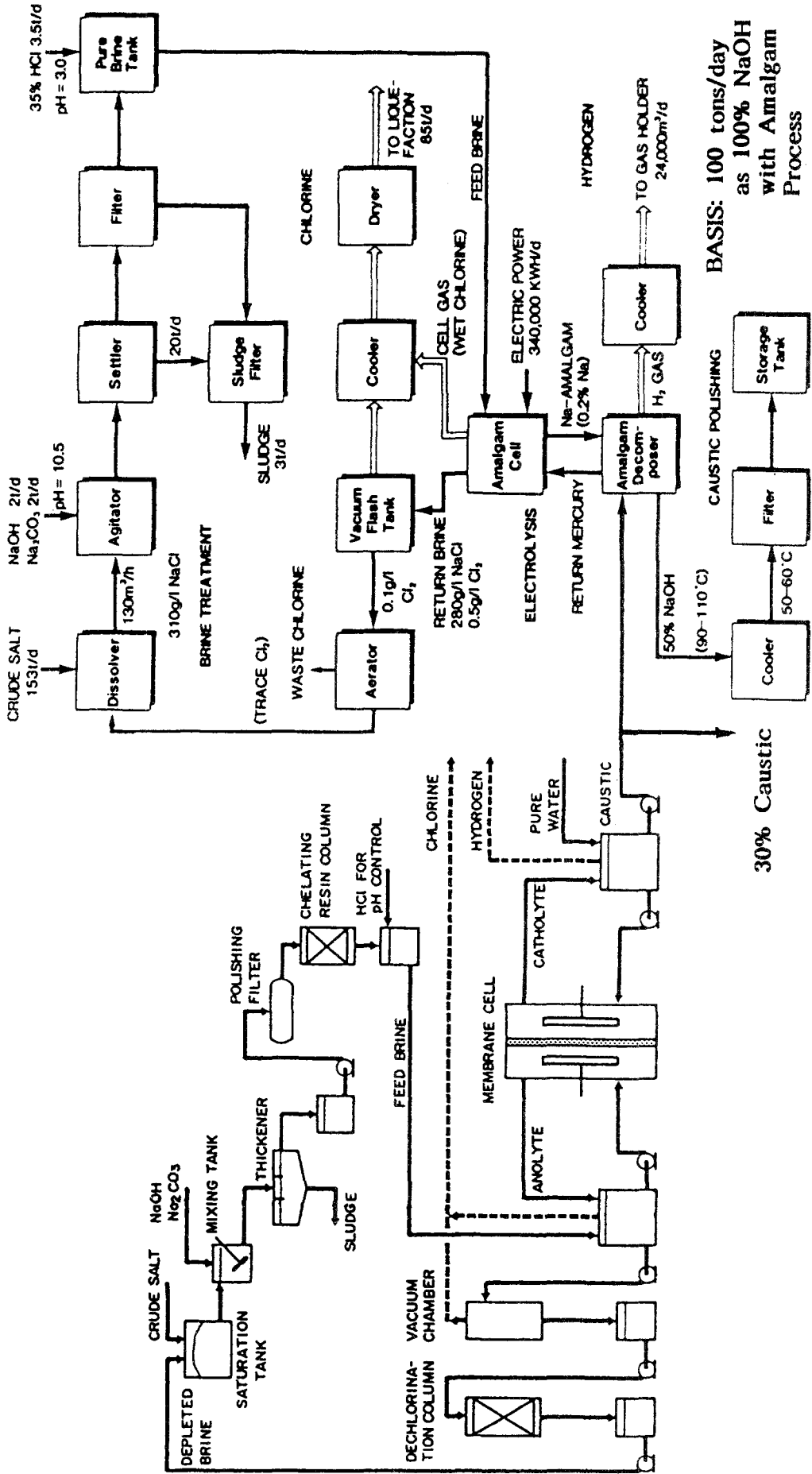
In the flowsheet shown in Fig. 2, dilute but pure caustic solution produced by the membrane cell is sent to the amalgam decomposer, which contaminates the solution with carbon particles and mercury that must be removed before shipment.

Although caustic solution of 50% by weight in concentration is produced by the amalgam decomposer for the market in general, it is possible to produce more concentrated NaOH liquor such as 70% by weight with no evaporation. One of the authors (F.H.) has designed amalgam decomposers for producing 70% caustic for several plants many years ago. Of course, the design and the operating conditions of these towers differed from those of conventional decomposers. Feed of membrane cell caustic of 20–30% NaOH in concentration into the amalgam decomposer for producing 70% caustic would be applicable or rather preferable since the reaction is stimulated and the operating temperature is kept high.

4. Hydrogen and chlorine

Hydrogen gas generated in the amalgam decomposer is cooled to remove moisture, caustic mist, and mercury and is sent to the polishing tower packed with specially designed resin to eliminate traces of mercury [5].

On the other hand, hydrogen generated in the membrane cell is free from mercury. Therefore, the gas is



BASIS: 100 tons/day as 100% NaOH with Amalgam Process

30% Caustic

Fig. 2. Flowsheet of an amalgam process plant combined with a membrane process plant.

just washed and dried in the regular manner and sent to the gas holder.

Mercury or its compounds are not found in the chlorine of the amalgam process plant, and hence the chlorine can be combined with that from the membrane cell plant. The oxygen content must be checked since chlorine generated at the anode in the membrane cell contains some oxygen.

5. Brine treatment and flowsheet

The brine in the amalgam process plant contains dissolved chlorine (about 0.1 g dm^{-3}) and mercury compounds, and is acidified prior to sending it to the cell. In the membrane cell plant, on the other hand, the depleted brine has to be dechlorinated perfectly, otherwise expensive ion-exchange resin in the polishing tower will be damaged. Therefore, separate treatment of brine as shown in Fig. 2 is advisable in the combined chlor-alkali plant.

In a large amalgam cell plant, for example, it would be preferable to utilize a side stream of saturated brine for a membrane cell facility having a relatively small capacity to minimize the investment and the operating cost for brine treatment. In this case, the side stream is dechlorinated, then treated with resin to remove heavy metal ions.

Construction of an integrated treatment facility for the feed brine to be sent to both the amalgam process and the membrane process plants is worthwhile if it is necessary to modify or renew the existing facility extensively.

A recommended flowsheet is illustrated in Fig. 3. A part of the primary treated brine is bypassed to the membrane cell plant where it is dechlorinated and filtered to remove dissolved chlorine and mercury compounds, and sent to the resin column to eliminate the brine hardness. The depleted brine, together with the return brine from amalgam cell plant, is sent to the vacuum flash tank to recover chlorine, and is brought to the salt dissolver. Hydrogen generated at the cathode in the membrane cell is sent to the integrated hydrogen holder directly since the gas is free of mercury.

6. A case history

The combined process has been demonstrated at Companhia Quimica do Reconcavo (C.Q.R.), a subsidiary of Salgema Industrias, in Brazil. The plant is producing caustic soda of 52 000 t/y with the DeNora $14 \times 3\text{F}$ amalgam cells. A part of the caustic solution is evaporated to produce 99% flake while 70% caustic is also produced directly by the amalgam decomposer.

The combined operations of the membrane cells have been tested twice in this plant. A part of the saturated brine in the amalgam cell plant was sent to the membrane cell after removal of mercury with chelating resin to an acceptable level. Membrane cell caustic solution of 30–40% in concentration was fed to the amalgam decomposer packed with graphite

lumps containing iron of 0.6% by weight to produce 50% NaOH solution. Sodium amalgam could be decomposed without any difficulty, and the sodium content in the mercury stream after decomposition was sufficiently low. Table 1 is an example of the test results.

Mercury in the decomposer effluent was in the range 3–4 p.p.m. in concentration. It was removed by activated carbon to nearly 0.05 p.p.m. The process does not require expensive evaporation equipment. With these test results, the combined process was considered to be suitable for the expansion program.

After strict feasibility studies, the company has decided to expand the plant capacity by 200 000 t-NaOH/y with Uhde membrane cells combined with the existing amalgam-cell facility by 1993. The brine treatment facility will be constructed to meet the additional production capacity and evaporated salt from the diaphragm-cell plant of Salgema will be utilized as feedstock. The flowsheet is essentially the same as in Fig. 2 to avoid any problem with mercury contamination. As stated above, production of 70% caustic with the combined process has been successful at C.Q.R.

The flowsheet of an amalgam process plant combined with a membrane process plant depends greatly on the plant situation and size. The installation of a new facility of the membrane cell process with own brine treatment yard such as shown in Fig. 2 would be preferable when an existing amalgam cell plant and a new membrane cell plant are comparable in size with each other.

On the other hand, polished brine in the amalgam process plant is bypassed and further treated by a resin column prior to sending to the membrane cells when the capacity of the membrane cell process to be added is relatively small and the size of existing brine treatment yard is sufficiently large. Anolyte effluent of membrane cells is sent to the vacuum flash tank in the amalgam cell plant and chlorine gas is recovered together with chlorine produced by amalgam cells. Hydrogen generated at the cathode of membrane cell is also mixed with the gas coming from amalgam decomposers. Consequently, the plant capacity is increased with minimum investment. This case is illustrated in Fig. 3.

Membrane cell caustic liquor is either delivered directly to the user or sent to the amalgam decomposer depending on the plant situation and the market.

The investment of the combined chlor-alkali plant varies greatly with the plant size, the depreciation or the age of existing facility, the plant layout, the marketability of products, and other factors. However, concentrated caustic soda solution, either 50% or 70% by weight, can be produced without expensive evaporator for concentrating membrane cell caustic.

7. Conclusion

The combined operation of amalgam cells and membrane cells is feasible for increasing the production

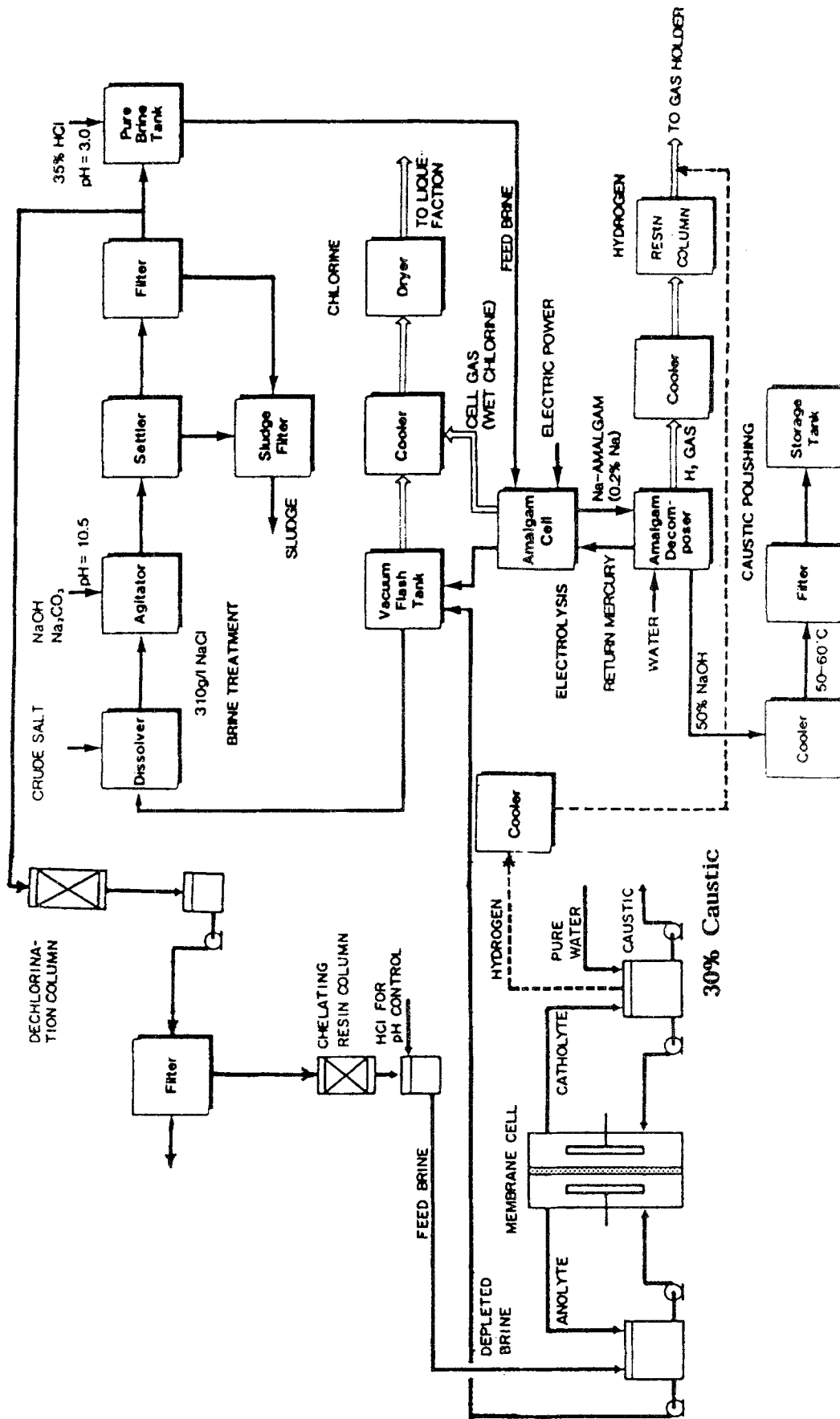


Fig. 3. Flowsheet in the combined chlor-alkali plant.

Table 1. Test results of combined operation of the membrane cell and the amalgam cell

Run number	1	2	3	4
Feed to decomposer				
Concentration/wt %	33.42	35.01	42.38	42.10
Flow rate/dm ³ hr ⁻¹	650	600	1100	1100
Temperature/°C	77-67	73-69	73-71	77-76
Impurities/p.p.m.				
Cl	52.00	33.10	39.90	67.30
Fe	9.00	7.50	8.80	8.50
Hg	2.30	2.40	2.40	2.76
Effluent from decomposer				
Concentration/wt %	50.50	50.29	49.47	50.20
Temperature/°C	103-98	109-103	104-101	107-101
Impurities/p.p.m.				
Cl	36.80	34.70	42.60	64.00
Fe	6.30	1.20	2.90	0.90
Hg	7.90	5.50	5.10	3.96
Amalgam concentration/wt %				
Inlet	0.284	0.222	0.296	0.310
Outlet	0.036	0.080	0.023	0.032
Cell load/kA	119	120	118	115

capacity and/or for the modernization of an existing amalgam cell plant. The ratio of the production capacity of the membrane cell plant to the amalgam cell plant is an important factor for the project.

Membrane cell caustic of 30% NaOH concentration is utilized as the feed of the amalgam decomposer. Since the resulting solution is contaminated with mercury, it must be polished by using a fine filter coated with activated carbon.

The depleted brine of the membrane cell plant is sent to the salt dissolution yard together with the brine from the amalgam cell plant, and the saturated solution is brought to the primary treatment. A part of

Table 2. Cost evaluation for a 200 000 tons per year plant

	Capital cost/\$	Running cost/ \$ (ton NaOH) ⁻¹
Regular membrane cell process		
Evaporator	19 000 000	7.00
Combined process		
Mercury treatment	100 000	0.07
Utilities, additional		5.60
Difference	18 900 000	1.33

the brine thus treated is bypassed to the membrane cell plant, and dechlorinated perfectly. It is filtered to remove suspended solids, mostly mercuric compounds, prior to sending to the resin column, where traces of brine hardness and mercury are removed.

Chlorine from the two processes can be handled together by a conventional method since no mercury is found in the gas. Since hydrogen generated at the amalgam decomposer contains mercury, it must be polished before being combined with hydrogen from the membrane cell.

The water balance in the brine flowsheet for the membrane cell process and the amalgam cell process, as well as the combined process plant, is of great importance, since the water output or consumption is minor. This problem is solved if purified salt is used. That is, the combination of the membrane cell with the diaphragm cell is feasible through the utilization of recovered salt in the diaphragm cell process. The depleted brine in the membrane cell plant is saturated using the recovered salt, and the saturated brine is treated by the resin column.

The plant test has been conducted successfully, and the combined operation of the membrane cells in the amalgam cell plant has been decided upon for expansion of plant capacity in Brazil. The start-up of its unique plant is scheduled for 1993.

In conclusion, there are many possible combinations of membrane cell plant with conventional process plant, either the amalgam cell process or the diaphragm cell process.

Acknowledgement

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