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<u>T E C H N I C A L   R E P O R T</u>

<u>On the Visit from 5th to 9th February 1990</u>

<u>In ELPESA Factory - Managua (Nicaragua)</u>

UNECO INTERNATIONAL CHEMICAL DIVISION S.r.l.

I N D E X

Background

The Elpesa plant productions are: chlorine, caustica soda solution and some chlorinated derivatives.

The production capacities are relative to a 17.500 tons/year of chlorine.

The plant has been built by **Blaw Knox**, an engineering North American Company.

The technology comes from Olin Mathinson, a big North American chlorine producer.

Nicaragua chemical industrial development coming up in 1960 years from the intention of central American industrialized countries to create a Central American Commun Market.

In the frame of this commun market, the basis chemical production has been entrusted to Nicaragua.

Following to this decision, a chlorine caustic soda complex has been installed in Managua.

The chemical complexes built in 1960-1970 years mainly were of North American origin and the utilized technologies were not very up to date.

Begininning from 1980 year, the political problems present in Central America countries caused a worsening in technical and economical relationships with United States.

Mostly in Nicaragua from 1980 the relationships with United States were completely broken off.

Due to this political situation, the Nicaragua industries, during these ten years, were left without technical assistance and without possibility to buy spare parts from the United States' mother companies.

This fact caused a rapid and progressive deterioration of Elpesa chlorine plant; the production has dramatically fallen with a contemporary strong efficiency decrease.

PLANT BASIC TECHNICAL DATA

Technology: mercury process

Plant sections:

A) Cell room

B) Brine system

C) Chlorine handling

A) Cell room

- No. cells	= 14
- Cathode	= steel - 14,5 mq
- Anodic surface	= 14 mq
- Current density	= 9 KA/mq
- Mercury inventory	= 55 flaskes/cell
- No. metallic anodes	= 50
- Metallic anode surface	= 0,279 mq/each
- Rectifyer section	= no. 2 rectifiers
	A.C. 13.9 KV
	C.C. 0-67 Volt
	0-62.500 Amp.
- Production capacity with 95% efficiency	= 52.8 tons chlorine/day

Each electrolytic cell is connected with a vertical amalgam decomposer provided with heat exchanger for hydrogen cooling.
Copper connections between the cells and aluminium bus bars between cells and rectifyer.
Piping for brine, chlorine, hydrogen and caustic soda complete the cell room.
Intermediate storage caustic soda tanks are installed with relative pumps.

B) Brine system

Capacity	= 100 mc/hr
Saturator	= made in concrete
Settler	= made in steel $\emptyset$ 7,3 m
Filters	= no. 3 Durco precoat type
Filters surface	= 75 mq, 35 mq, 109 mq
Dechlorination system	= vacuum system consisting of a single stage, steam jet ejector with a barometric condenser

Tanks for depleted and concentrated brine with relative pumps
(titanium Durco type) and piping complete the section.

C) <u>Chlorine handling</u>

- Chlorine washing and cooling   : 1 tower with heat exchanger
circulation pumps and relevant
piping

- Drying system   : no. 3 towers with heat exchangers
for sulphuric acid cooling.
The heat exchangers are plate type
made of hastelloy C
Pumps for sulphuric acid circulation
and relative piping.

- Compression system   : no. 3 liquid ring compressors
type Nash
Capacity   : 20 tons/day each
Pressure   : 4 bar
Ring liquid : 98% sulphuric acid

- Hydrochloric acid production   : 20.000 tons/year HCl 33% solution

- Scdium hypcchlorite   : consisting of absorption tank
and titanium heat exchanger
located on recycle line
capacity: undetermined

- Calcium hypochlorite   : consisting of chlorine absorption
tank
capacity: undetermined

- Liquid chlorine section   : The liquefaction system is equipped
with 22 freon compressors and
liquefyer equipment made by Carrier
capacity: 10.000 tons/year liquid
chlorine
This sectionis completed with 3
liquid chlorine tanks.

PROCESS DATA

Comparison between actual process data (A) and standard data (B).
Considerable differences ($\triangle$)

	A	B	$\triangle$
Cell room			
Inlet brine temp.	65°C	75°C	10°C
Inlet brine PH	7-8	4	-
Brine fluorate	8 mc/hr per cell	7-8 mc/hr per cell	-
Outlet brine temp.	85°C	85°C	
Brine outlet PH	4.2-4.5	3-3.5	very high
Chlorine gas compos.	Cl_2 80%-H_2 2-4%-inerti 16-18%	Cl_2 98%-H_2 0.2%-inerti 1.6%	Cl_2 very low conc. H_2 very high conc.
Amalgam outlet conc.	0.2%	0.25%	
Amalgam inlet conc.	0.001%	0.001%	
Caustic soda conc.	48%	48%	
Chlorine pressure	+100 - 100 mm H_2O	-2/5 mm H_2O	very high instability
Operating amperage average	110 KA	125 KA	12% less
Operating voltage average	5 (5-3.2=1.8)	4 (4-3.2=0.8)	125% higher
Current efficiency	80%	96 - 97%	16 - 17% lower
Power consumption	4.720 KWH/ton Cl_2 in c.c.	3.200 KWH/ton Cl_2 in c.c	47% higher
No. cells in operation	12	13.9	1.9 less
Production	33.6 ton Cl_2/day	53 ton Cl_2/day	36.6% lower
Brine system			
Inlet brine quality			
Mg	1 - 5 ppm	1 - 2 ppm	
Ca	800 - 900 ppm	5 - 10 ppm	very high
Activated Cl_2	500 ppm	40 - 50 ppm	very very high
SO_4	1.600 ppm	6.000 - 8.000 ppm	
Fe	1 - 2 ppm	0.1 ppm max	very high
Dechlorinated brine			
Activated Cl_2	300 - 500 ppm	40 - 50 ppm	very very high
Raw materials and reagents consumption			
NaCl	2 ton/ton Cl_2	1.7 ton/ton Cl_2	+ 18%
NaOH (100% basis)	50 kg/ton Cl_2	15 kg/ton Cl_2	+ 233%
Na_2CO_3 (100% basis)	50 kg/ton Cl_2	15 kg/ton Cl_2	+ 233%
HCl (30% solution)	300 kg/ton Cl_2	60 kg/ton Cl_2	+ 400%
H_2SO_4	40 kg/ton Cl_2	25 kg/ton Cl_2	+ 60%
Cl_2 (to waste)	40 - 45% prod.	1% prod.	very high
Hg	800 gr/ton Cl_2	1 - 5 gr/ton Cl_2	very very very high

CONSIDERATIONS ON PROCESS DATA

Cell room

The main problems are in the cell room operation.

- The high PH of cell outlet brine indicates that the current
  efficiency is very low and this is confirmed by process data
  (efficiency 80% instead of 96-97%). This may be caused by the
  following reasons:

  1. Mercury low level in the decomposers, this could cause a
     vortex resulting in entrainment of caustic soda from decomposer
     to the cells through mercury flow.

  2. High hydrogen in chlorine composition, this is due to the bad
     brine quality (high iron content and may-be relative high
     concentration of heavy metals).

  3. Difficult brine mixing inside the cell due to the anodes geometry.
     This may cause a very low brine concentration in the region between
     anodes and cathode.

  4. High calcium content in inlet brine and difficult control in PH
     may cause mercury butter formation. This can provoke short circuits
     due to irregular mercury flow.

  5. The irregular chlorine suction value produces severe chlorine
     escapes from the cells cover or, alternatively, air entering
     with a striking reduction of chlorine concentration.

  6. The cells have not a centralized system for anodes adjustment.
     The copper connections between the cells are in very bad conditions
     for severe and generalized corrosions.
     Electrical contacts are in very bad conditions too.
     These elements prevent that a routine anodes adjusting operation
     takes place. Consequently the operating voltage is very high.

  7. The cells are in all their parts in very bad maintenance conditions.
     This fact, with the problem connected with butter formation and
     bad brine quality obliges frequent shutdowns for maintenance.
     The cells are not equipped with short circuit, then when one cell
     must be taken out operation, it is necessary a complete shutdown
     of the plant.
     For these reasons the average number of the cells in operation is
     very low (12 instead of 13,9).

.8. The rectifier conditions and high cells voltage do not permit
   to operate at the target amperage.
   This and shutdown of rectifier for the diodes replacement are
   the cause of low average operating amperage.

Brine system

- The main problem is represented by ineffective brine dechlorination.

   1. The outlet brine (depleted brine) high PH makes difficult the
      brine PH reduction to 2 with consequent very high consumption
      of hydrochloric acid.

   2. The brine vacuum system does not work because the steam ejector
      is out of use; for this reason the concentration of activated
      chlorine in depleted brine after dechlorination, is about 300 ppm
      and sometimes 500 ppm.

   3. This high free chlorine concentration produces severe corrosions
      in all brine system, practically increasing iron content in the
      brine.

   4. The high activated chlorine in brine produces easily the solution of
      all heavy metals held in the salt.

   5. A concentration of 300-500 ppm of activated chlorine in the brine,
      causes high difficulties in magnesium hydroxide and calcium carbonate
      precipitation. Consequently settling and filtering operations are
      very affected.

   6. The settler geometry is completely wrong; the surface of existing
      settler is 42 mq. This allowes an ascensional speed of the brine
      of 2.38 mc/hr/m. The right ascensional speed might be between 0.3 -
      0.5 mc/hr/m. Consequently the right surface of the settler had to
      be 250 mq instead of 42 mq.

Raw materials and reagents consumption

1. High consumption of salt is caused by brine losses which are coming
   from all plant sections.

2. High consumption of caustic soda and sodium carbonate are in part
   related to the salt consumption.

3. The reagents dosing system is very poor for deficiency of equipment
   and for the use of very high concentrated reagents solutions.

4. The high depleted brine PH causes an extremely high hydrochloric acid consumption to obtain the maximum dechlorination effect.

5. High voltage and low current efficiency determine the very high consumption of current.

6. The difficulties met in a good cooling system (inadequate surface of heat exchanger, shortage of cooling water) determine the high consumption of sulphuric acid, used for chlorine drying.

7. The chlorine coming from Elpesa plant has been mainly used for insecticides production. The chlorinated insecticides plant is located near to Elpesa factory, the name of the company is Ercasa. The quantity of chlorine absorbed by this company was, at the beginning, 7.200 ton/year, more than 40% of Elpesa production. Actually Ercasa have reduced, in a drastic way, their chlorine consumption to about 1.200 ton/year.
   The reasons of this reduction are connected with market and ecologycal problems.
   Due to this fact Elpesa is obliged to waste a large part of their chlorine production.
   The chlorine is wasted in form of calcium hypochlorite and this represents one of big negative ecologycal aspects of Elpesa production.

8. The high consumption of mercury is due to:

   a) high brine losses (mercury content in the brine is in the range of 10 to 50 ppm)

   b) mercury evaporation from the cells and decomposer during shut-down and maintenance operations;

   c) lack of equipment, in the plant site, for the recovery of mercury from waste water, caustic soda, hydrogen and air;

   d) very big and frequent mercury leakages from the various equipments. This mercury, due to the very poor condition of the cell room floor, enters in the depth and it cannot be recovered.

RECOMMENDATIONS

All the plant is in a very poor maintenance condition. Especially, the cell room is in so badly conditions that is very difficult and, surely not convenient, to make substantial modifications.

We limit ourselves, therefore, to suggest some maintenance and modification works only with the purpose to maintain the plant in operation till when Elpesa can take more drastic decisions.

A. **Cell room**

1. Check mercury level in each decomposer. Make sure that this level is kept the highest possible to avoid entrainment of caustic soda in the cells through mercury flow.

2. Install an automatic pressure control device on the main chlorine header to control carefully the chlorine suction in the cell room. This device might avoid the chlorine pressure fluctuations in the cell room.
   Actually, these fluctuations cause chlorine escapes producing severe equipment corrosions and making difficult and dangerous the workers operations.

3. Replace piping and valves that are in bad conditions to avoid the actual severe brine leakages. These leakages are one of the most important causes of the mercury consumption and therefore of ecologycal damage.

4. Avoid, the most possible, the individual anodes adjustment, because this practice makes impossible keeping anodes planarity and then becoming very difficult to maintain cell voltage at a right value.

B. **Brine system**

1. It is absolutely necessary to restore the dechlorination brine system. At the first approach, we suggest to install an air stripping system.
   Elpesa can do it very easily and with existing equipment.
   In second stage, we suggest the installation of a new dechlorination system based on the vacuum pumps use.

2. Caustic soda, sodium carbonate and hydrochloric acid used as reagents must be utilized in dilute solution to make easier the control of PH process.

3. Increase the excess of sodium carbonate to reduce and
   minimize calcium content in the brine.

   Install reaction and digestion vessel before the settler.

We point out that these few recommendations can help Elpesa to
keep the plant in operation, waiting for more important decisions
regarding the future of the plant.

We are persuaded that more incisive modifications cannot, at the
actual conditions of the plant, improve the plant operating at a
reasonable cost.

Elpesa must take a decision regarding to the chlorine production
technology. If they decide to carry on the mercury process, we
suggest to change entirely the cell room utilizing the same building.

The replacement of the cells can be done one by one, keeping in this
way, the plant in operaticn.

If they intend changing technology from mercury to membrane, we advise
to set up a complete new cell room in a new building located by side
of the old one.

The mercury cell plant will be able to operate till the membrane cells
will be ready for working.

Our advise is changing technology from mercury to membrane for the
following main reasons:

a) Ecologycal problems related to mercury wastes. The problem of mercury
   wastes persists, even if we install plants for mercury waste recovery.

   The mercury cell technology presents process difficulties principally
   in the treatment of the muds coming from brine filtration and settling.

   Actually, the biggest chlorine producing companies use a very pure
   crystallized salt to minimize mud problem.

   Elpesa, at present, is using solar salt. The quality of this salt
   is quite good but far from specifications of the pure crystallized
   salt which they would be compelled to import.

b) With the membrane technology the consumption of electrical
   energy is about 30% less than the consumption with mercury
   technology.
   In the case of Elpesa, energy consumption with membrane cell,
   it could be 50% less than the actual Elpesa consumption.
   At present, Elpesa consumption arises to 10.000 Kwh/hr.
   With membrane technology application, this consumption can be
   reduced to 5.000 Kwh/hr.
   In addition to the big economical saving, we have to take in
   consideration that Nicaragua suffers from electrical power
   shortage.
   The saving of 5.000 Kwh/hr can permit the development of other
   activities with very important economical and political results.

c) In the papers, which are enclosing in this report, you can see,
   more in detail, the technical and economical considerations that
   determine the choice of the membrane technology against mercury
   and diaphragm processes (see encl. no. 1 and no. 2)

CONCLUSIONS

In the industrial area of Central America, Elpesa holds a very important and strategic place.

The caustic soda and chlorine productions are utilized principally for export.

In 1977 and 1978 years, the exports value was higher than 8.7 millions US $. From 1979 the exports have undergone a constant decrease.

In 1987 Elpesa have exported products for a total of 1.9 millions US$ only. This export value is a further confirmation that the plant is working only at 35-40% of its project capacity.

In this situation, it is very important that Elpesa is put in condition to restore the initial project capacity of the plant. Only in this way, Nicaragua can keep its leadership in Central American chlorine and caustic soda market.

We advise that UNIDO might assist Elpesa in the revamping work of its industrial structure.

The immediate goal is to enable Elpesa deciding on the establishment of a new membrane cell technology for chlorine caustic soda production, and on the viability of setting up new chlorine based products to avoid chlorine wastes.

02.03.90
EB/lc

SAFETY CONSIDERATIONS
FOR
MEMBRANE PROCESS

1. **Preface**

Current generally accepted thinking regards safety as
the primary consideration in plant management and
industrial people everywhere are keen in complying
with such idea.

The ion exchange membrane process is now accepted as
superior to both the mercury and asbestos diaphragm
process in both product quality and power
effectiveness, and the general trend is to merbrane
process plant construction as well as conversion of
mercury or diaphragm process plants to the membrane
process. Hcwever, a few problems peculiar to the
membrane process are yet to be solved and performance
data remains to be accumulated. Time and efforts are
still required before the membrane process is called a
"mature technology". Above all, safety consideration
as global results of plant management is a mojor
concern.

Chlorine Engineers, as a member of the industry, has
been engaged in developing both soft and hardware for
the membrane process, including development,
designing, manufacturing and installation of
electrolyzers.

The following summarizes the safety considerations
from our performance data and operation experience.

2. **Ion Exchange Membrane Properties**

Common to all the processes, hydrogen mixed with
chlorine in the anode is a perpetual safety problem.
Table-1 shows the major causes of hydrogen gas mixing.

- 1 -

In the mercury and diaphragm processes, electrolyzer design, operation parameters, and safety standards were determined after complete study of the mercury and diaphragm properties. For the membrane process also, the primary factor in safe operation with satisfactory performance is to know the membrane properties and reflect this knowledge in process development, cell design, and plant operation.

With this in mind, the following properties of the membrane should be fully understood.

(a) Mechanical Properties

Under specific conditions, a membrane can suffer deterioration in certain qualities including tensile strength, elongation, and fatigue rate, possibly causing a break in the membrane.

(b) Chemical Properties

In particular surroundings, a weakness in the membrane exposed to chlorine, though it is manufactured using a substrate of fluorine-contained resin, can result in a degradation of membrane performance and mechanical strength.

(c) Electrochemical Properties

The effects on performance by impurities and the accumulation of impurities within the matrix of the membrane have been elucidated in many published reports. Regarding safe operation, the

membrane's sensitivity to brine feed failure
should be especially noted.

(d)   Electrical Properties

The membrane, which is a conductor when wet, can
be burnt by concentrated currents.

3.   <u>Mechanical Properties of Membranes</u>

It is natural that membranes from different suppliers
or of different brands have different mechanical
properties. All, however, as the suppliers claim, are
adequate for brine electrolysis, if folding or
abnormal loading is avoided.

Possible changes in the mechanical properties of
membranes installed in electrolyzers are among the
user's major concerns. Figure 1 shows an example of
mechanical changes in a membrane. This figure shows
that, so long as excess fatigue and the causes of
degradation shortly to be described are avoided, the
mechanical property change is not so serious as to
necessitate special attention. Although most
membranes are supported by backings which ensure
mechanical strength, unbacked membranes are also
acceptable under proper conditions.

Table-2 gives the three conditions that are essential
in mounting membranes in electrolyzers. For
electrolyzer manufacturers, how to fulfill these
conditions in the hardware is their central concern.
The Chlorine Engineers' membrane installation method,
shown in Table-3, can fulfill these three conditions

in both periods of electrolyzer operation and
shutdown, as shown in Figure 2. Somewhat more tention
is given at shutdown due to 1) increased brine
concentration resulting from the replacement by feed
brine of the anolyte containing dissolved chlorine,
and 2) membrane contraction due to the drop in
electrolyser temperature to minimize the concentration
of NaCl in NaOH.

Another problem during electrolyzer shutdown is a
decrease in the anolyte level. How much the level
lowers depends on the electrolyzer design, but the
level lowers, at least, by a portion corresponding to
the gas bubble ratio during operation. In fact, the
anolyte is replaced with brine, and therefore, the
electrolyzer can not be left with a dropping solution
level.

Table-4 shows the evaluation of stress observed when a
membrane exposed to the gas phase dries and contracts.
Generally, the anolyte level drops more than the
catholyte level and the exposed portion of the
membrane is in contact with catholyte only.
Contraction stress under such conditions was also
examined.

In the above case also, the contraction stress of the
dried membrane was 10 %, at most, of the breaking
stress, indicating no possible membrane damage at
shutdowns unless special degradation had occurred. It
should be noted, however, that the mechanical
properties of the membrane mainly depend on those of
the applied backing; improperly embedded backings give
different mechanical properties from those of the
membrane film

itself, rendering the film easily broken from any
slight stress and further spread of such breaks.

Needless to add, the membrane will break if any
irregular pressure is imposed on either the chlorine
or hydrogen side. To avoid this, care should be
exercised in the design of the associated equipment as
well as in operation.

We should mention one case of accident that we
experienced during an overseas project, caused by a
simple operating error. Feed brine was supplied to
the electrolyzer without opening a valve connecting
the manifold at the electrolyzer outlet and the header
piping. The membrane, pushed against the cathode by
the pressure of the feed brine, pressed into the
loosened seam of the cathode, and was damaged.
Fortunately, a serious situation was averted as the
membrane damage was detected during the pre-operation
inspection. This case indicates the importance of
operator training in safe plant operation.

4.   Chemical Properties of Membranes

All high performance membranes now used in brine
electrolysis have substrates of fluorine-containing
resin, giving no problems of corrosion. However, if
the membrane is in contact with chlorine gas, the gas
will disperse within the membrane and react with
back-migrating OH^-, forming NaOCl and NaCl. As a
result, the membrane will over-swell and develop
blisters.

An experiment was made using a lab cell, shown in Figure-3, in which the level of anolyte was lower than that of the corresponding catholyte. The result is shown in Photo-1. This lab cell also had an inferior current efficiency, as shown in Figure-4.

Photos-2-1 and 2-2 show a membrane sent to us from a foreign user who asked our technical advice. The membrane, removed from an electrolyzer by a certain manufacturer, had developed blisters at the top. Due to its decreased current efficiency, we had expected degradation of the membrane in the area of the chlorine gas phase at the top of the electrolyzer. The presence of the blisters proved our estimation correct. As shown in Figure-5, membrane deterioration results also in decreased mechanical properties. In the membrane with a backing, a decrease in the breaking strength was negligible, but the decrease in elongation was prominent; the membrane had become embrittled.

It should be noted that the degree of membrane degradation, which is not uniform, may be intensified with time, especially in elongation.

We believe that every hardware manufacturer pays special attention in the electrolyzer design to avoid the exposure of membranes to chlorine gas. Chlorine Engineers' design philosophy in this regard is as shown in Figure-6. In this design, the level of the solution is maintained in the frame at the top of the element so that the membrane is totally immersed in the solution. At the same time, the internal solution circulation mode contributes to a reduced bubbling

ratio and minimum formation of chlorine gas zones.
Another effective way to prevent the formation of a
chlorine gas zone is to provide a baffle plate at the
back of the anode mesh, as shown in Figure-7, to
promote flow in the pass between the plate and the
mesh.

The formation of chlorine gas zones derives from
electrolyzer design and also from the foaming of
organic substances mingled with the brine. Organic
substances capable of mingling with the brine includes
coagulants added in the brine purification process,
and chelate resin embrittled by chlorine attack.
Photo-3 illustrates an experiment to elucidate the
effects of organic substance foaming. For this reason,
feed brine quality control is important, as well as
for maintaining membrane performance.

5.   Electrochemical Properties of Membranes - brine feed
      failure

Since the electrochemical properties of membranes are
vast, the discussion here focuses only on the effect
of brine feed failure.

When the brine supply is unexpectedly disturbed, the
sodium chloride concentration of the anolyte is
decreased by continued electrolysis, causing the
membrane to be damaged eventually below a specific
allowable limit to the membrane. With further passage
of time, the extreme decrease in the sodium chloride
concentration of the anolyte and the successive heat
generation from the voltage escalation makes the brine
boil, followed by an extraordinary internal vapor

pressure rise and generation of a kind of electric
discharge on the bubble interface, causing a break in
the membrane, and, in the worst case, an explosion
initiated by hydrogen and chlorine gas mixing. Using
a lab cell, Figure-8 examines the changes of voltage
and temperature in an electrolyzer over a period after
the suspension of brine feed.

The allowable time duration from this suspension
untill the detection of brine feed failure cannot be
determined uniformly, as it partially depends on the
holdup capacity of each electrolyzer. Figure-9
represents the data obtained from a lab cell testing
the allowable safety time of our MBC(R) type
electrolyzer.

Electrolyzers are typically classified into bipolar
and monopolar types. Effects of brine feed failure on
the whole electrolyzer are the same for both types.
However, in the monopolar type, when brine feed
failure occurs only in one element, the membranes on
both sides alter from Na-type to H-type with raised
membrane resistance, decreasing the current load on
the affected element and increasing the current load
on the other elements. Figure-10 shows the results of
the simulation. Only a monopolar type electrolyzer
has a function of self-stabilization like this.

As described above, brine feed failure is dangerous.
Other processes are compared below.

Mercury process -   The brine volume retained in the
                     cell against electric current
                     capacity is small.

Asbestos diaphragm process -

> Though the brine volume retained
> in the cell against electric
> current capacity is relatively
> large, a portion of brine is
> leached out through the diaphragm.
> The top of the asbestos diaphragm
> is exposed out of the solution and
> hydrogen gas can mingle with
> chlorine gas.

Compared with other processes noted above, the
membrane process has a relatively longer time
allowance between the occurrence of brine feed failure
and the moment when a hazardous situation occurs.
Also, unless there is membrane damage, the chlorine
gas cannot mix with hydrogen gas. The membrane
process is considered to be generally safer than
others.

On the other hand, if the feed of diluted sodium
hydroxide or water to the cathode chamber fails, the
concentration of formed sodium hydroxide is increased
(with some membrane, NaOH=40%) due to the entrainment
of 3-4 mol water when Na^+ transfers from the anolyte
chamber to the catholyte chamber through a membrane.
Therefore, this failure can not lead to accidents.

6. <u>Electrical Properties of Membranes</u>

A wet membrane is conductive. At a spot where current
is concentrated, the generated heat burns the
membrane, causing a pin hole. For instance, during
electrolyser installation at a place where current is
short-circuited with a jumper switch, ii the anode

side and cathode side busbars are connected with the
electrolyte left uncharged, a short-circuited voltage
(about 0.6V) is induced between the anode and the
cathode, and a concentrated current flows through the
contact point with the membrane, burning a pin hole.
We have had such experiences in the past. The busbar
should have been connected only after the electrolyte
had been charged.

7.   Detection of Abnormal Conditions in the Electrolyzer

Abnormal pressure loading of the electrolyzer must be
avoided. At the same time, the early detection of
abnormal conditions in the electrolyzers, such as
brine feed failure is essential.

Chlorine Engineers has implemented the following
practices.

(1)   Monitoring by DDP (Data Display Processing
      System)

      To prevent serious situation from occurring, the
      minor deviation alarm (dV/dt, dT/dt) linked to
      cell voltage and temperature change, for a
      specific time range, is employed to read minute
      variations, together with the alarm indication of
      actual measurements of voltage and temperature.
      The system, automatically correcting cell voltage
      against current load at every input signal, gives
      no erroneous alarms for load adjustment.

(2) Visual Check of Overflow from Electrolyzer

Overflow condition, which can be observed through
the transparent Teflon tube shown in Photo-4, is
easily examined during periodical checks in the
cell room. Membrane damage occurs mostly during
electrolyzer shutdowns. Operation resumption
without monitoring the situation leads to
accidents. Prior to resumptions the presence of
damaged membrane can be checked after brine
chargings only to the cathode chamber through
visual inspection of overflow from the anode
chamber.

(3) Analysis of Hydrogen or Oxygen in Anodic Gas

8. Closing Remarks

As described in the Preface, the membrane process is
becoming more and more popular as a trunk technology
in the world chlorine industry. For safe operation of
plants, the acquisition of full knowledge of the
properties of different membranes as well as
sufficient understanding of hardware design
philosophy, and operation skills that utilize to their
maximum the advantageous properties of membranes and
electrolyzers will be of the highest importance.

We are happy if this report will make some
contribution to the plant safety.

TABLE-1 CAUSES OF HYDROGEN GAS MIXING
INTO CHLORINE GAS

MERCURY PROCESS

- ELECTRICAL SHORT-CIRCUITING
- AMALGAM DECOMPOSITION CAUSED BY IMPURITIES (HEAVY METALS) IN BRINE

DIAPHRAGM PROCESS

- HYDROGEN GAS TRANSFER THROUGH DIAPHRAGM CAUSED BY EXCESSIVE DIFFERENCES BETWEEN PRESSURES IN THE ANODIC AND CATHODIC CHAMBER
- CATHODIC REACTION ON THE SURFACE OF THE DIAPHRAGM CAUSED BY RUST

MEMBRANE PROCESS

- PIN HOLES OR CRACKS IN MEMRANES

FIGURE-1 BREAKING STRESS AND ELONGATION OF USED MEMBRANE AFTER 2 YEARS' OPERATION

RELATIVE RATIO AS COMPARED WITH A BRAND NEW MEMBRANE
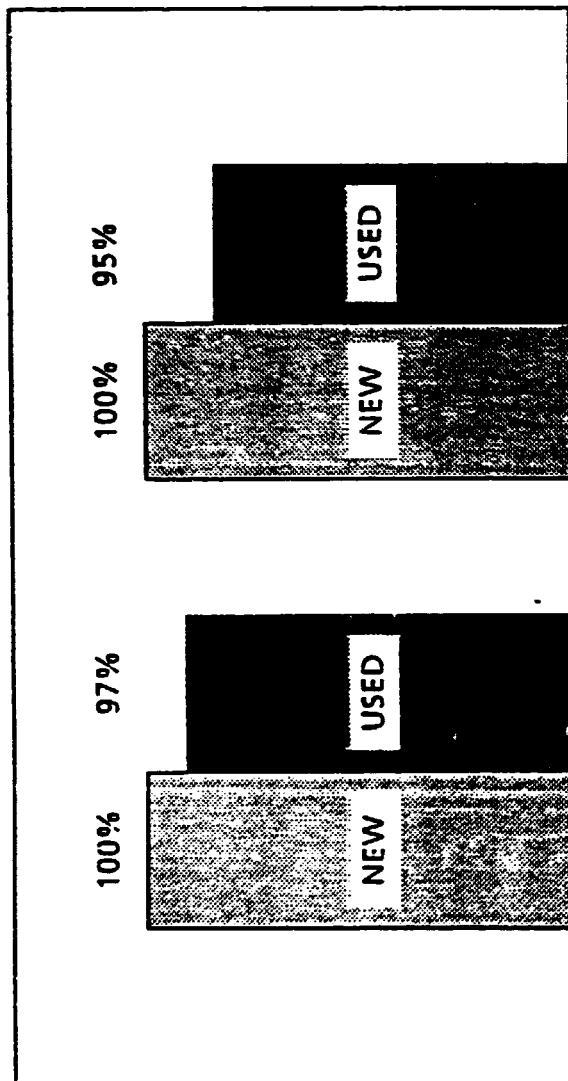
BREAKING STRESS   ELONGATION AT BREAKING

TABLE-2 NECESSARY CONDITIONS FOR MEMBRANE INSTALLATIONS ON ELECTROLYZERS

1. NO WRINKLES ON MEMBRANE

2. NO PARTIAL STRETCHING

3. NO EXCESSIVE STRETCHING

TABLE-3 CEC'S MEMBRANE INSTALLATION PROCEDURES

1. MEMBRANE IS PRE-TREATED AND PROPERLY STRETCHED.

2. MEMBRANE IS PLACED ON A HORIZONTALLY POSITIONED ANODE OR CATHODE ELEMENT WITHOUT EXCESSIVE STRETCHING AND WRINKLE.

3. AFTER REPEATING THE ABOVE OPERATION, THE WHOLE ELECTROLYZER IS CLAMPED WITH TIE RODS.

FIGURE-2 · MEMBRANE DIMENSIONAL CHANGES UNDER VARIOUS CONDITIONS

RELATIVE PERCENTAGE RATIOS

(THE MINUS FIGURE INDICATES CONTRACTIONS)

	BEFORE PRE-TREATMENT	PRE-TREATMENT	BRINE FILLING	OPERATION	SHUTDOWN
NaCl conc. (g/l)			300	200	300
NaOH conc. (wt%)			32	32	32
Temp. (°C)			70	90	30
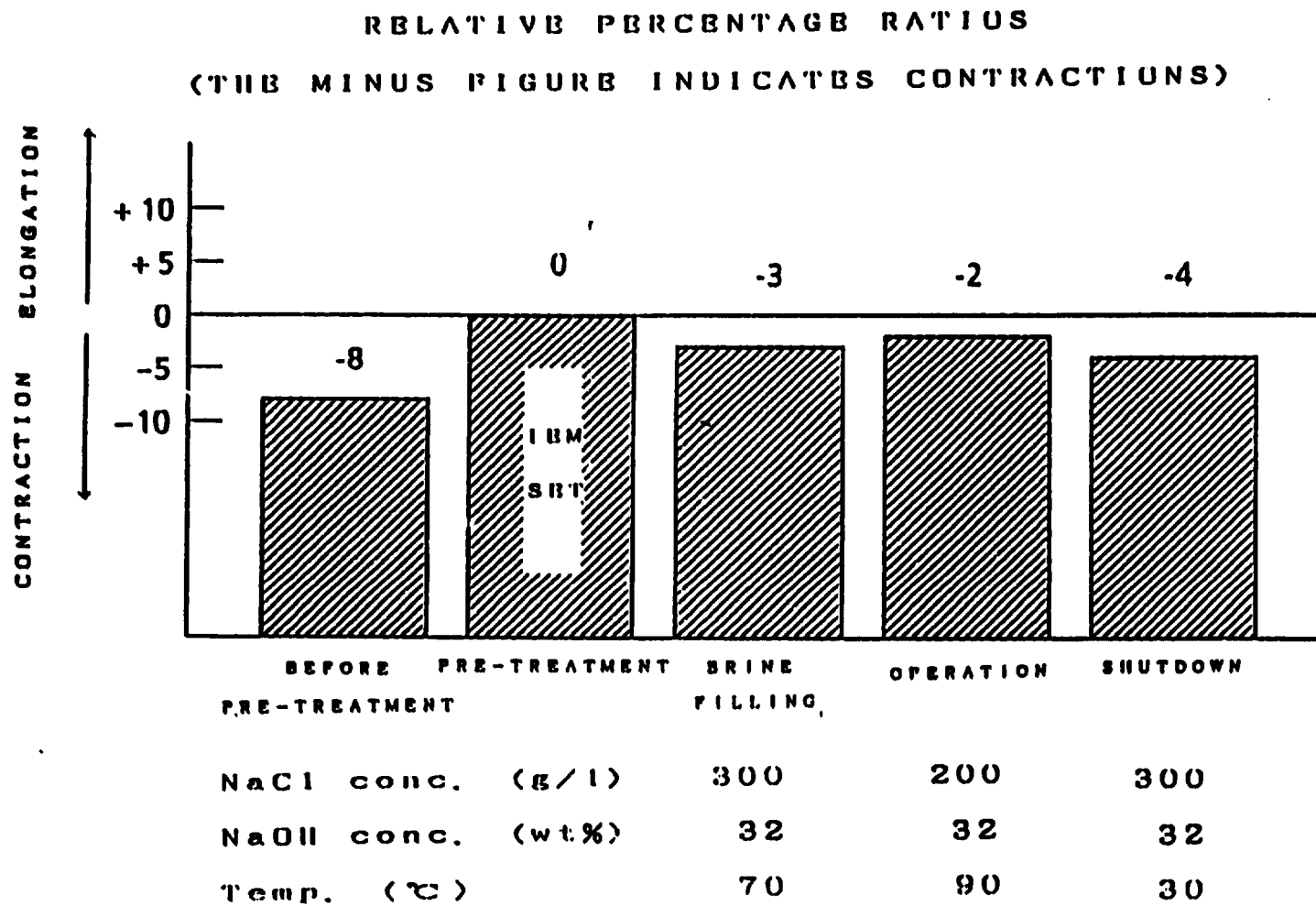
TABLE-4 CONTRACTION STRESS ON MEMBRANE IN FIXED STATE

MEMBRANE CONDITION AT SETTING	RELATIVE RATIO(%) TO BREAKING STRESS
AIR-DRIED	8 ~ 9
30% NAOH SWELLING	.10 ~ 12

NOTE:

Stress on Pre-treated Membrane from Contraction in Fixed State on the Stretching Tester.

FIGURE-3 TEST CELL HAVING A CHLORINE GAS ZONE ON THE MEMBRANE
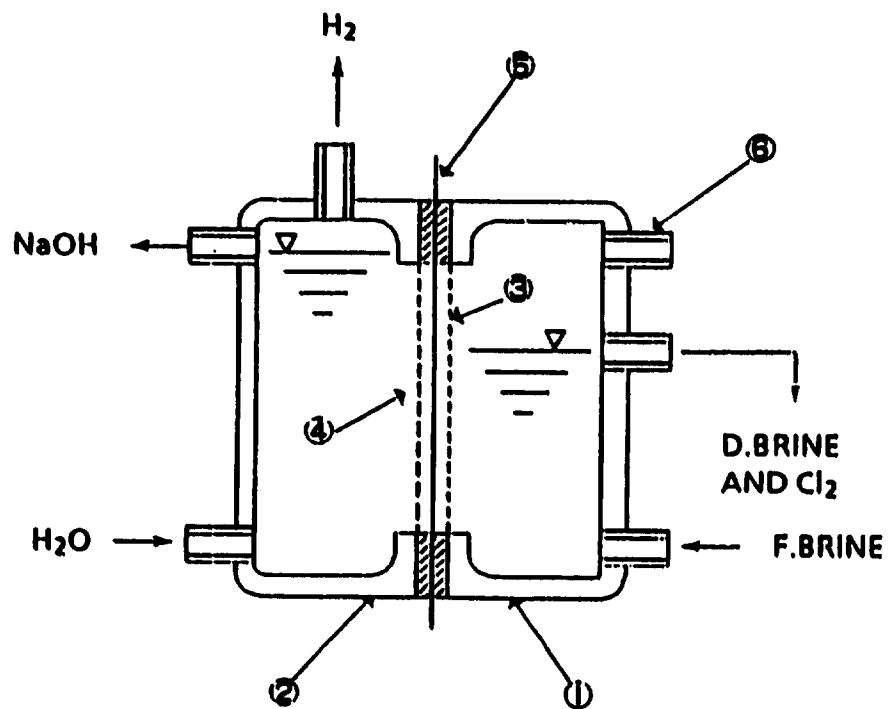
① ANODE CHAMBER

② CATHODE CHAMBER

③ ANODE   : DSA*

④ CATHODE : SUS + COATING

⑤ MEMBRANE

⑥ NORMAL DEP.BRINE OUTLET NOZZLE

PHOTO-1 BLISTERS DEVELOPED ON THE GAS ZONE
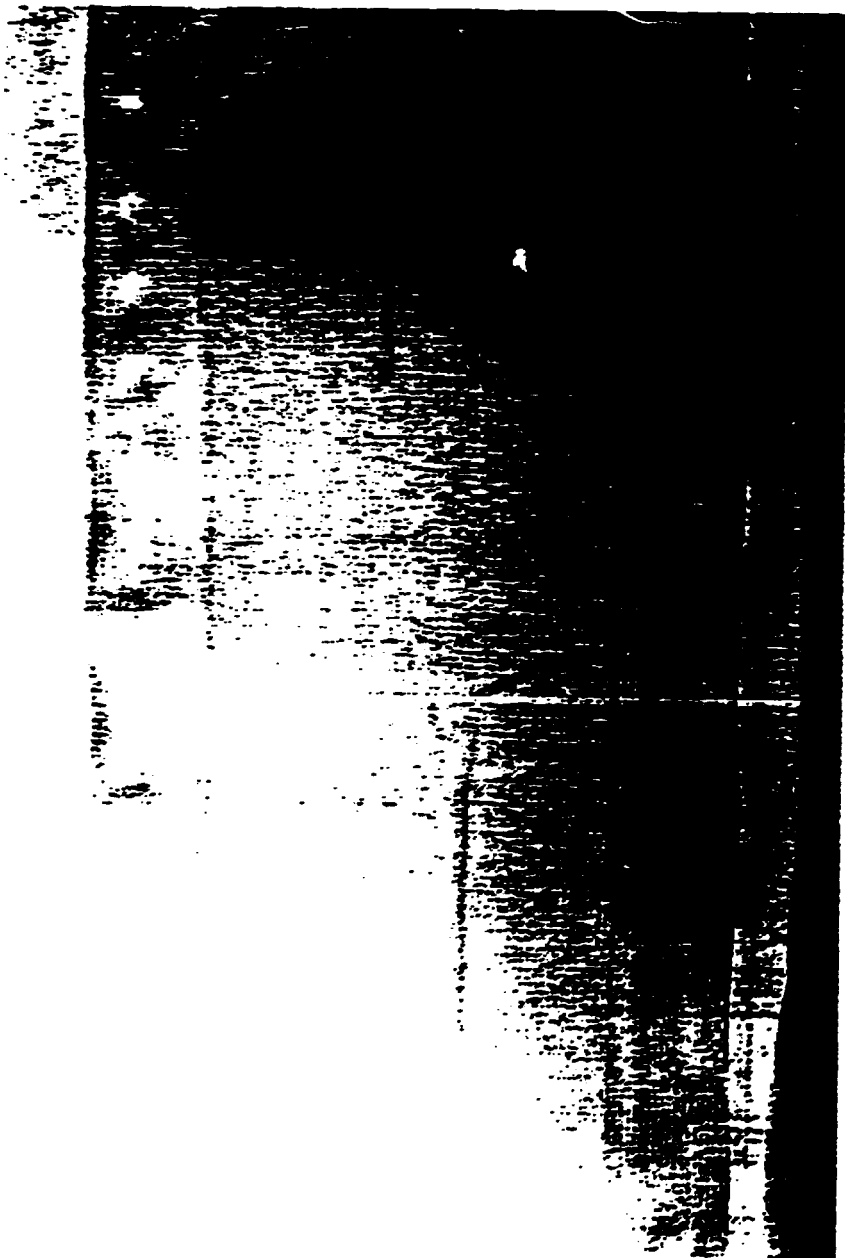
FIGURE-4 CURRENT EFFICIENCY OF A CELL WITH A CHLORINE GAS ZONE

3KA/m2,32wt%NaOH,90°C

NORMAL CELL

CELL WITH A CHLORINE
GAS ZONE

CURRENT EFFICIENCY [%]

DAYS ON LINE [DAYS]
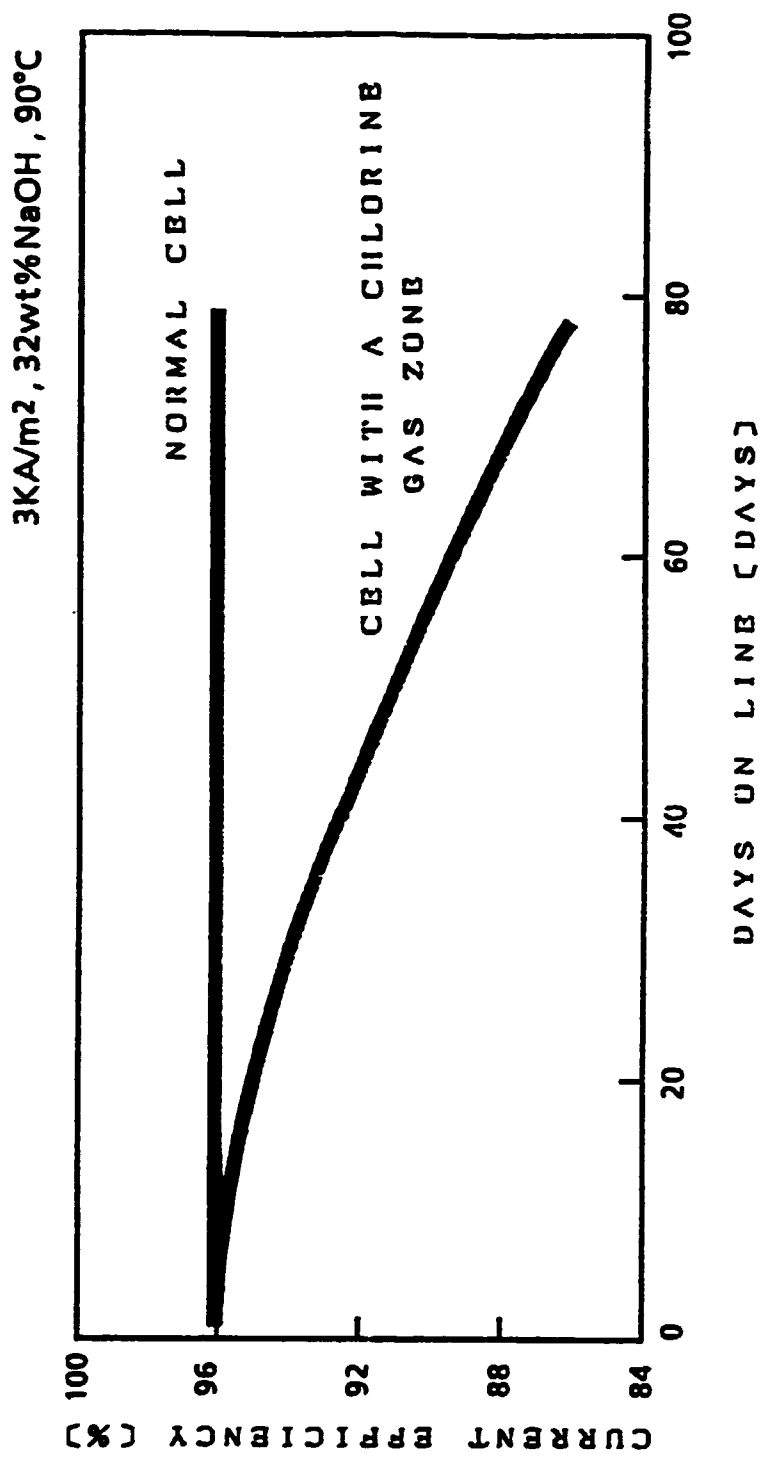
PHOTO 2-1 CHLORINE GAS ZONE
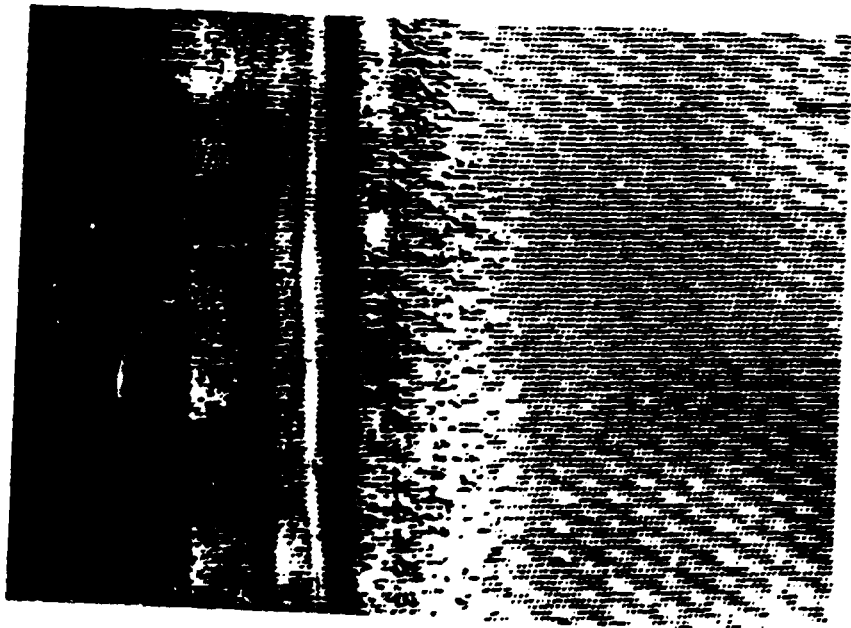
PHOTO 2-2 CHLORINE GAS ZONE
(ENLARGED)

FIGURE-5 MEMBRANE ELONGATION IN CHLORINE GAS ZONE

RELATIVE RATIO COMPARED WITH A NEW MEMBRANE
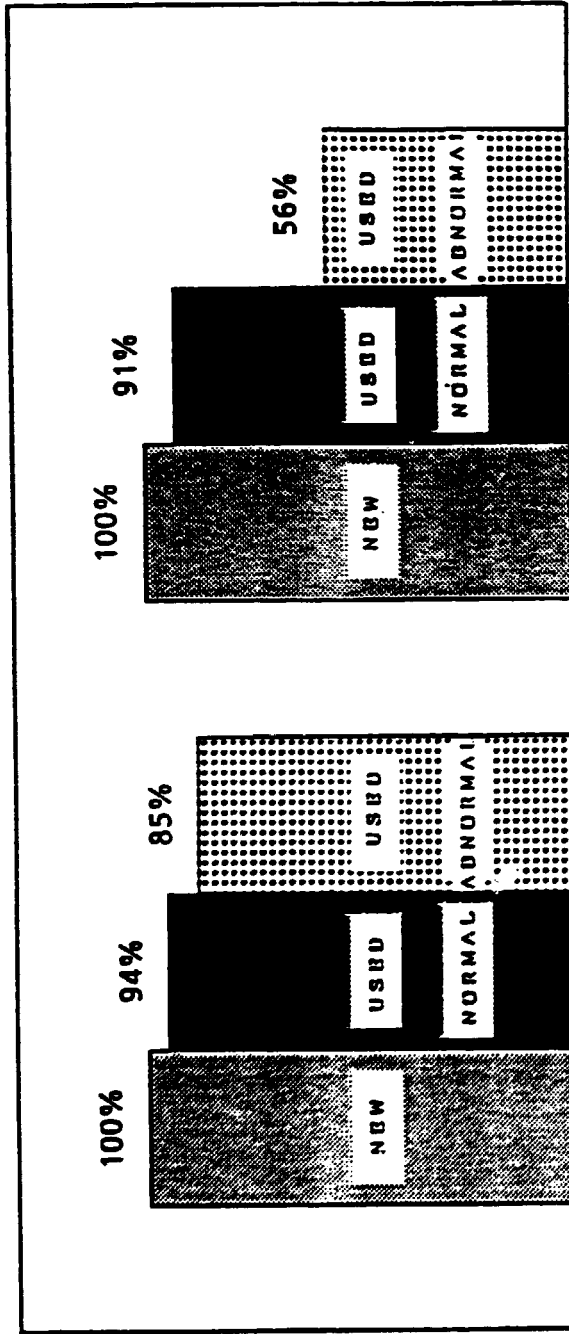
BREAKING STRESS   ELONGATION AT BREAKING

FIGURE-6 OVERFLOW MODEL
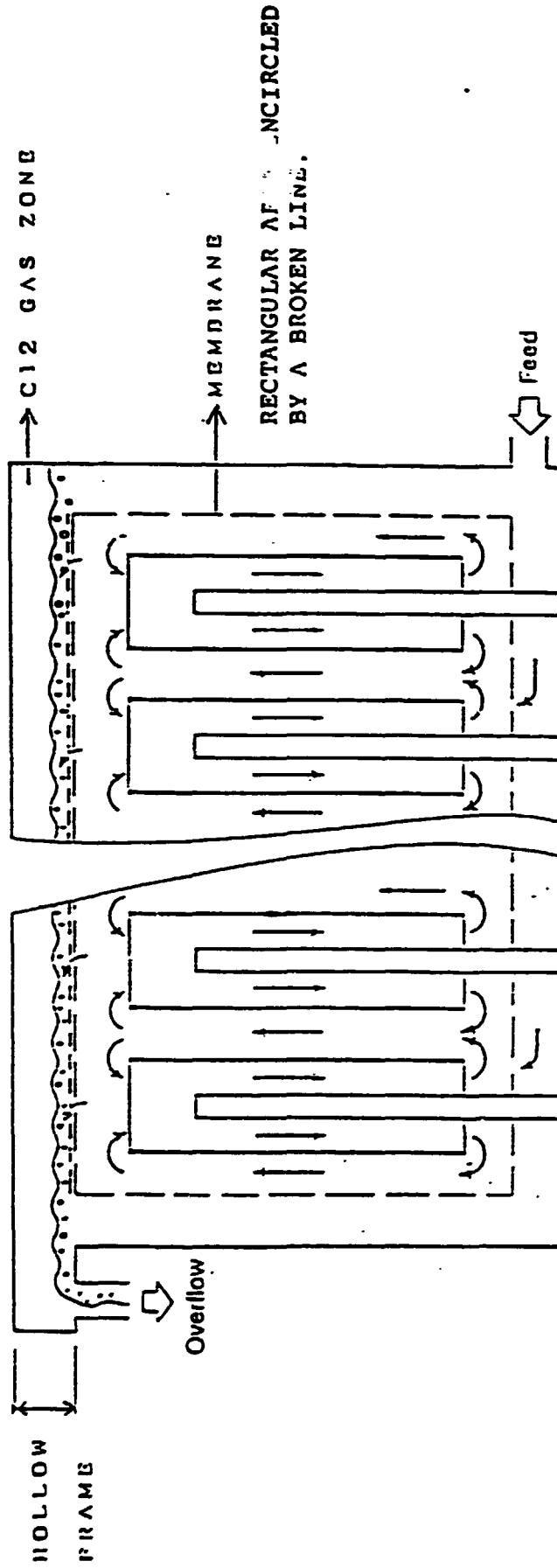
FIGURE-7 PREVENTION OF GAS PHASE
BY BAFFLE PLATE

SECTION A-A

ELECTRODE

DISTRIBUTOR

BAFFLE PLATE
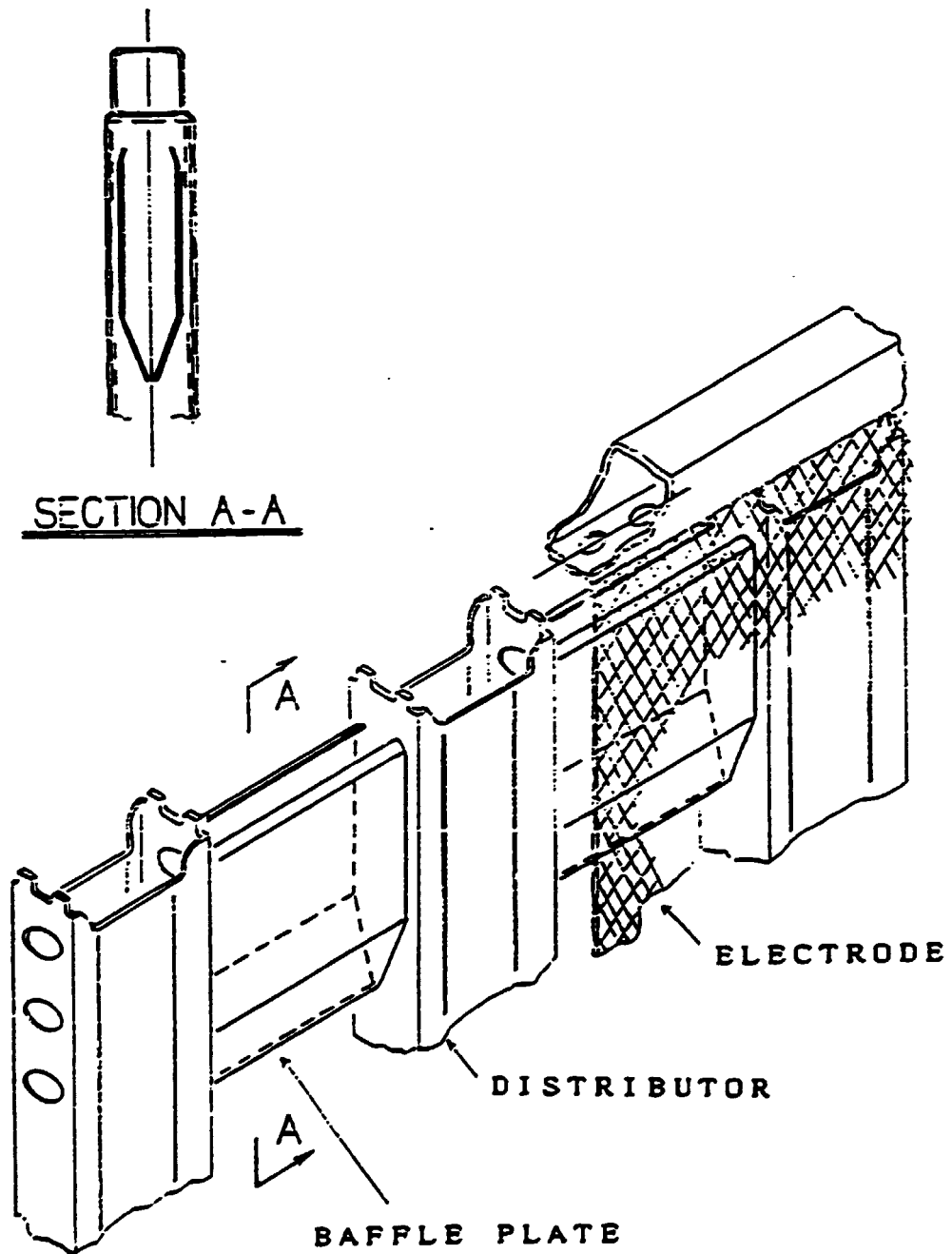
PHOTO-3 BUBBLE EFFECT CAUSED BY ORGANIC SUBSTANCE
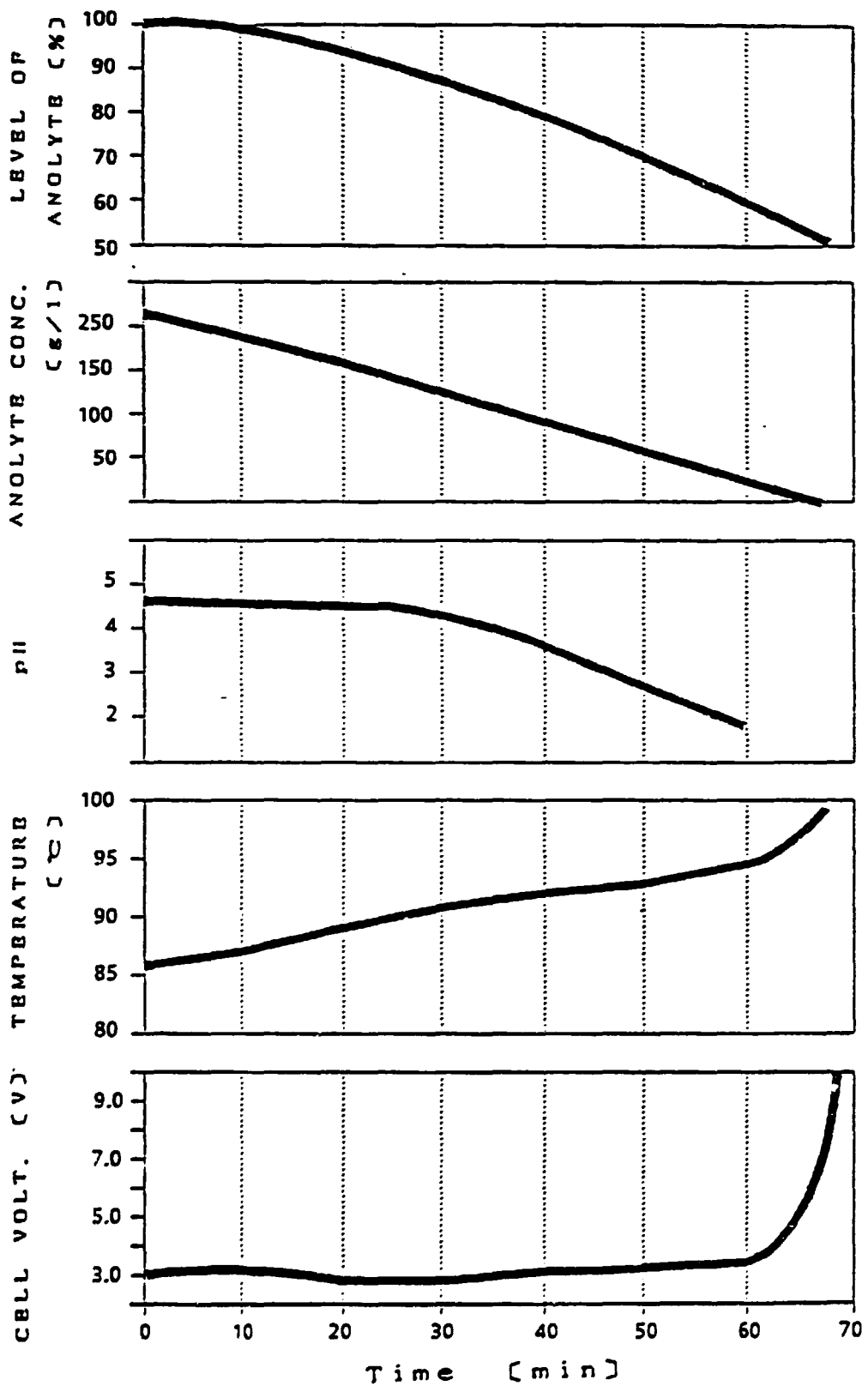
FIGURE-8 TEST OF "BRINE FEED FAILURE" IN A LAB CELL

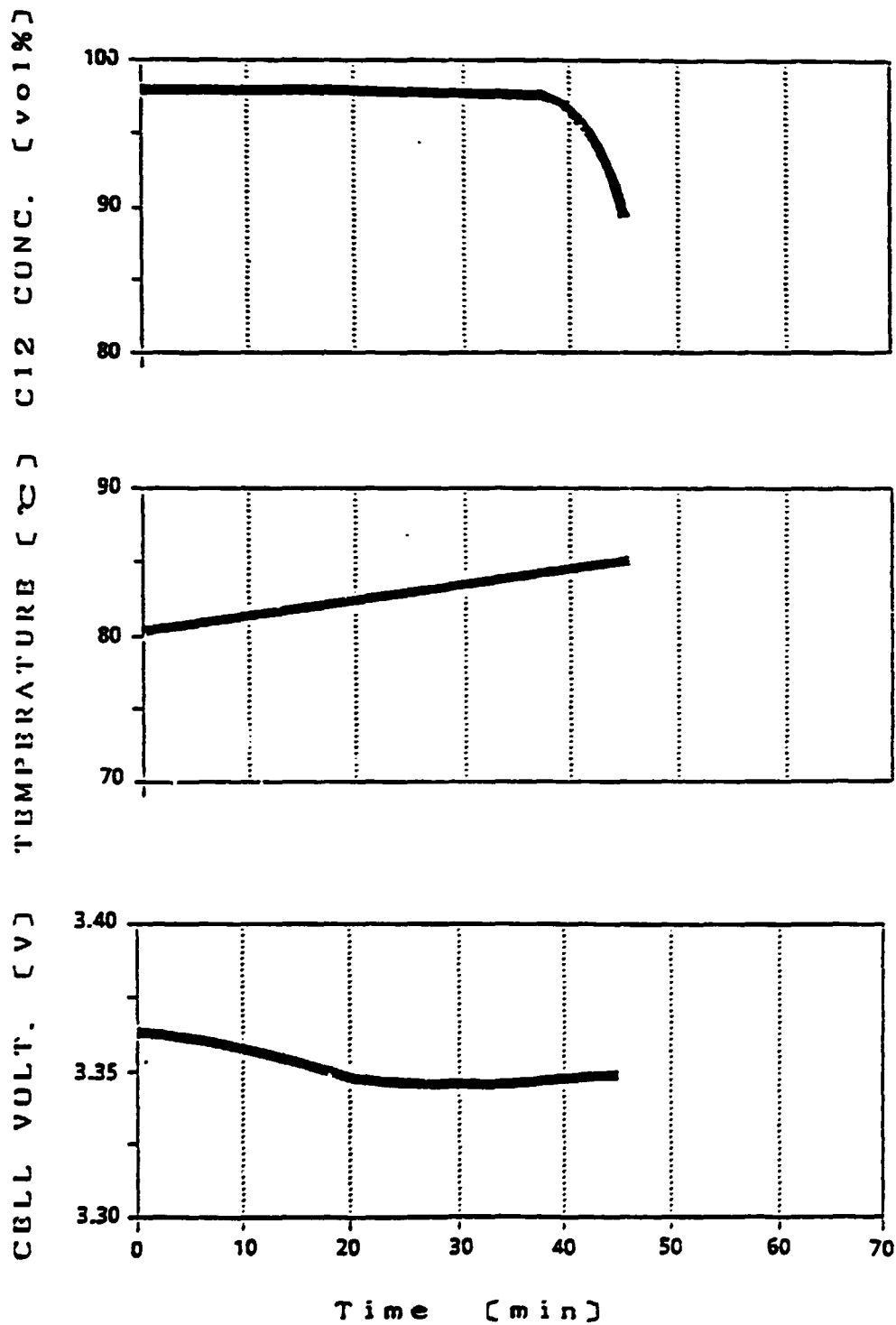# FIGURE-9 TEST OF "BRINE FEED FAILURE" ON MBC ® ELECTROLYZER

FIGURE-10 SIMULATION OF A "BRINE FEED FAILURE"BY DCM ELECTROLYZER

ELECTROLYZER   : DCM406/MONO POLAR
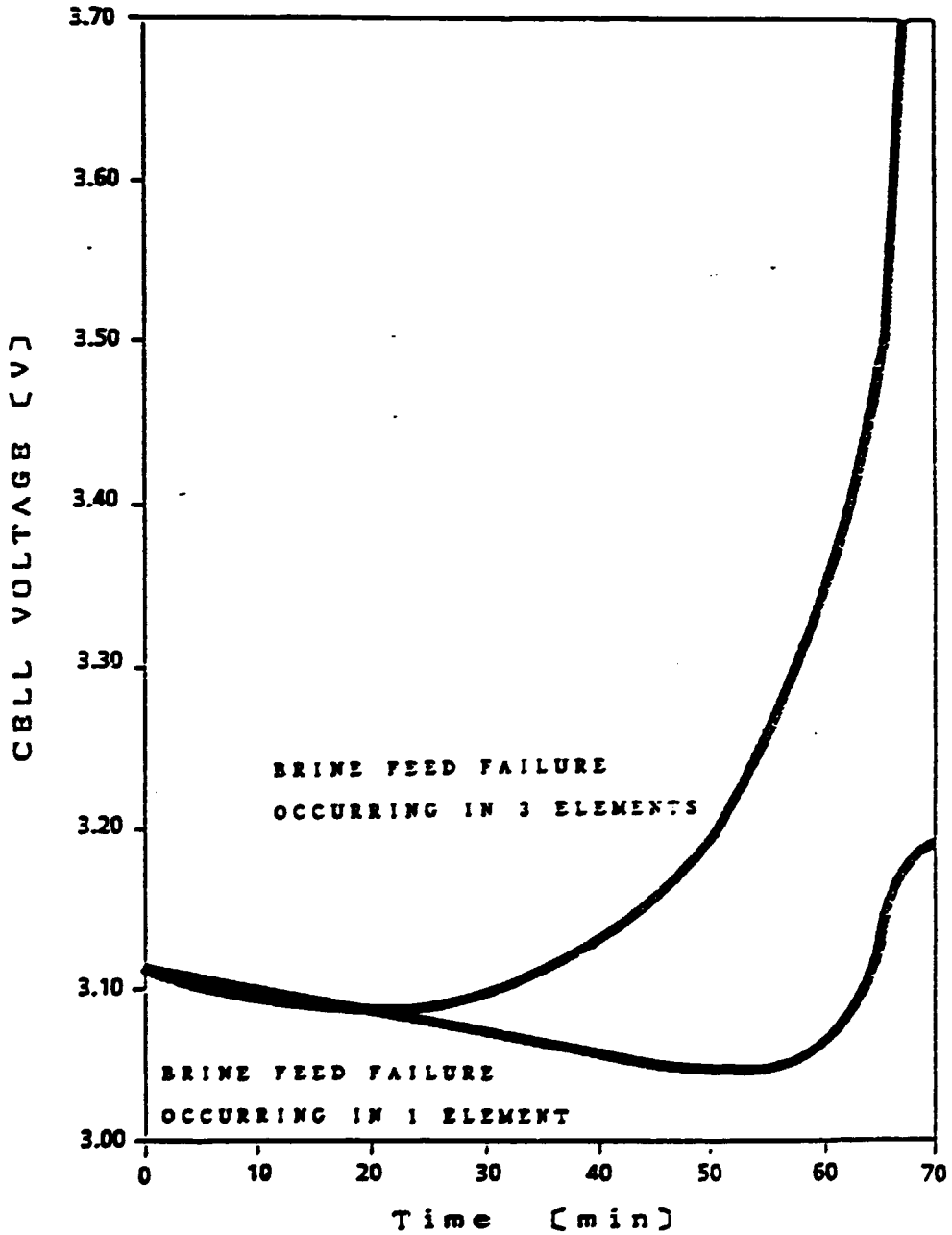CURRENT DENSITY   : 3. OKA/m²
NUMBER OF ELEMENT : 3

BRINE FEED FAILURE
OCCURRING IN 3 ELEMENTS

BRINE FEED FAILURE
OCCURRING IN 1 ELEMENT

Time [min]

CELL VOLTAGE [V]

PHOTO-4 VISUAL INSPECTION OF
OVERFLOW ELECTROLYZER

Membrane cells for chlor-alkali electrolysis

A description of the membrane process for the electrolytic production of chlorine, caustic soda and hydrogen from sodium chloride solutions is followed by a discussion of the present state of the art. This includes the development of cation exchange membranes and electrolysis cells. Finally, economic questions and trends for the future are discussed.

1. Introduction

In recent years the membrane process for the electrolytic production of chlorine, caustic soda and hydrogen has achieved a recognized position alongside the well established mercury and diaphragm processes. This development has been primarily due to the appearance on the market of perfluorinated cation exchange membranes.

The manufacture and properties of homogeneous ion exchange membranes with a high exchange capacity and high electrical conductivity were first described by Juda and McRae [1] and by Kressman [2] in 1950. The application of such ion-permselective membranes for the production of chlorine and caustic soda by the electrolysis of brine was first proposed by Ionics Inc. in 1951 [3] and 1953 [4]. At that time it was already clearly recognized that this process exhibited important advantages over the diaphragm and mercury processes [4]. Because the ion exchange membranes were made of hydrocarbon polymers with sulphonic or carboxylic acid groups, however, they were unstable in the presence of chlorine and the membrane process was therefore not suitable for chlor-alkali electrolysis. An attempt was made to protect the ion-exchange membrane from chlorine by combining it with a microporous diaphragm in a three-compartment cell [5] or by means of a perfluorocarbon membrane grafted with sulphonated styrene divinylbenzene [6].

Chemically stable ion-exchange membranes did not become available, however, until 1969. They were homogenous membranes consisting of fluorocarbon polymers with pendant sulphonic acid groups and were first used as solid electrolytes in fuel cells [7]. At the same time it was known that these ion-exchange membranes were stable to chlorine and caustic soda at temperatures up to 125°C [7], but the first report on the use of these membranes for the production of chlorine and caustic soda was only published in 1971 by Michalek and Leitz [8, 9].

In contrast to diaphragm cells, membrane cells lead to a caustic soda solution with a very low sodium chloride content, comparable to that from mercury cells. The inert perfluoropolymer membrane is used to separate the products in membrane cells; thus the use of asbestos, as in diaphragm cells, and mercury, as in mercury cells is avoided. The energy consumption and capital costs are also lower for the new process. In Table 1 it can be seen that membrane technology was introduced into commercial production in 1975. The number of membrane cells in commercial operation has increased steadily and now since the world production of chlorine is about 30 million tonnes, the share of the total now accounted for by the membrane process is about 1%. This relatively small share is mainly due to the depressed state of the chlorine market. Virtually no new capacities are being built and many plants are working well below capacity, but when existing electrolysis plants are replaced, it is by membrane plants. A further obstacle to the rapid introduction of membrane cells is the continuing rapid

Table 1. Membrane cell plants and their installed/planned capacity

Year	Total number	Total capacity NaOH ($t\,y^{-1}$)
1975	2	60 000
1976	3	120 000
1977	5	170 000
1978	8	230 000
1979	9	240 000
1980	13	282 000
1981	20	351 000
1982	27	713 000
1983	30	880 000
1984	31	933 000
1985	32	960 000
not known	34	977 000

development of the technology, including ion exchange membranes and electrolysis cells. The extent of progress in the last few years becomes apparent if the summary presented here is compared with a review published in 1977 [10]. As a result potential users of membrane electrolysis await further refinement. However one should remember that the diaphragm process and the mercury process were first used for the commercial production of chlorine and caustic soda in the last decade of the 19th century. The technology of both processes has developed steadily up to the present. It is thus no wonder that the membrane process is also undergoing constant improvement.

2. Description of the membrane process

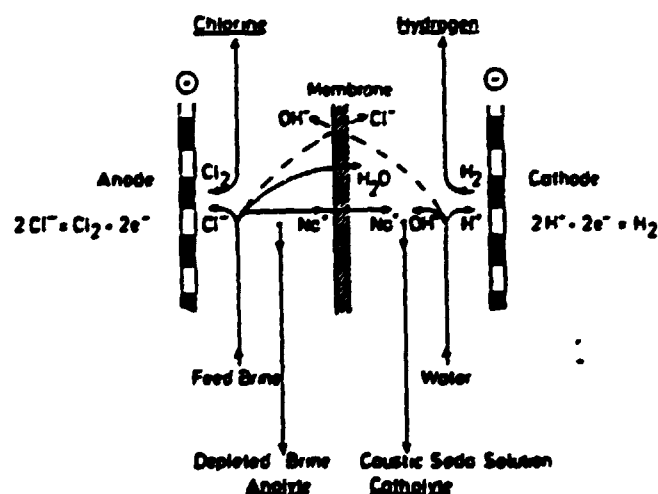Figure 1 shows schematically the basic reactions in a membrane cell. Brine enters the anode chamber and chlorine is generated at the anode; the brine depleted of sodium chloride leaves the cell along with chlorine gas. The cation exchange membrane, which divides the cell into an anode and a cathode chamber, is hydrodynamically impermeable but permits the passage of hydrated sodium ions. Water, from which hydrogen and hydroxyl ions are formed at the cathode, must be fed into the cathode chamber. Hydrogen and the caustic soda solution, concentration between 10% and 40% are drawn off from the cathode chamber.

A few side reactions are also indicated in the diagram. The most important in terms of volume is the water transport (by electroosmosis) through the membrane which accompanies the Na^+ transport. Hydroxyl ion transport from the catholyte to the anolyte must be prevented by the membrane. Otherwise there is a reduction in current efficiency, both in the anolyte chamber through loss of caustic soda and in the anode chamber through chlorate formation and also oxygen discharge at the anode [11, 12]. Finally, we should mention chloride ion diffusion from the anolyte to the catholyte which, however, occurs only at an extremely low rate owing to the high selectivity of the newer membranes.

When the membrane process is compared with the other conventional electrolysis processes for the production of chlorine and caustic soda, we can note the following differences:

1. The caustic soda solution obtained from the membrane cell is less concentrated (12-35%) than the 50% solution produced in the mercury process, but it possesses the same degree of purity

Fig. 1. Schematic picture of a membrane cell showing electrode reactions and transport processes.

(<0.01% NaCl) and no mercury is required for its manufacture.

2. In the diaphragm process the cell liquor leaving the cathode compartment contains 12% NaOH and 16% NaCl and it must be concentrated to a 50% solution in order to remove the salt. The caustic soda solution thus obtained contains about 1% NaCl. In comparison the membrane cell caustic solution can be used without being concentrated by evaporation because of its low salt content.

tent. Furthermore, no asbestos for the diaphragm is required for its manufacture.

3. Membrane cells are not adversely effected by power supply interruptions or other sudden changes in current or voltage.

4. Membrane cells do, however, require very pure brine which requires additional purification steps because the membranes are vulnerable to even temporary lapses in brine quality.
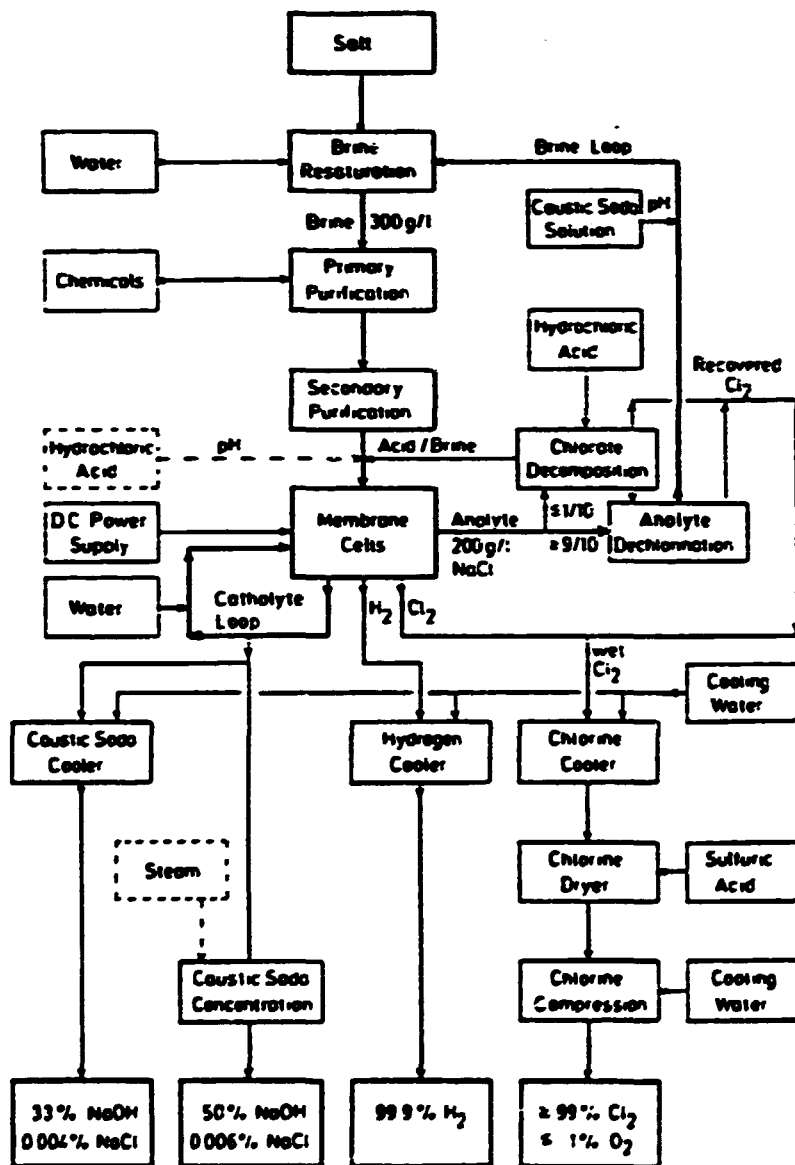
Figure 2 presents a process diagram for a mem-

Fig. 2. Flow sheet of a caustic soda–chlorine plant using membrane cells.

brine cell plant. Following brine reclamation by salt dissolution, the diagram shows conventional primary purification of the brine (which may additionally include saline precipitation by means of barium carbonate) and secondary purification by means of ion exchange resins. The depleted brine is recycled but on each loop a fraction (here 5%) is treated to remove chlorate by the reaction

$$NaClO_3 + 6HCl \rightarrow 3Cl_2 + NaCl + 3H_2O.$$

Additionally, Fig. 2 shows the caustic soda circuit. The catholyte leaving the cell is freed of hydrogen and collected in a receiver. From this receiver sodium hydroxide solution can be drawn off for direct use. More often, however, it is fed into an evaporator to yield more highly concentrated liquid caustic soda or solid caustic soda. Part of the catholyte is recycled to the cell (to act as electrolyte) after being replenished with the water required for electrolysis. The catholyte loop is used for two reasons. On the one hand this vapour circulation serves to remove the heat of reaction from the cell. The heat generated can be removed from the loop by cooling water in a heat exchanger or used for other purposes. A common purpose is the concentration of the caustic soda solution, for example in flash evaporation. The second reason for circulating the catholyte is that it simplifies the addition of water, which otherwise would have to be accomplished by the expensive process of metering small water streams into the individual electrolysis cells. Brine and catholyte circulation are completely separate from one another. One conceivable linkage, however, would be simply heating the feed brine before it enters the cell by means of heat exchangers in the caustic circuit.

3. Ion exchange membranes

3.1. Membrane composition

Membranes suitable for chlorine–caustic soda production are now being manufactured by a number of companies, some of which supply several types of cation exchange membranes for different applications. Examples include the Nafion® membranes of Du Pont [13], Flemion® membranes from Asahi Glass [14], Neosepta-F® from Tokuyama Soda [15] and Asahi Chemical membranes [16, 17]. In

1980 Du Pont opened a factory in Fayetteville, North Carolina, for the manufacture of Nafion resins and membrane. Du Pont supplies Nafion 901 for direct production of caustic concentrations of about 35% NaOH. With this membrane current efficiencies in the neighbourhood of 96% are obtained. For lower caustic concentrations the Nafion 100 series (without support cloth) and the 300 and 400 series (both with support cloth) are more suitable. The Flemion 230 supplied by Asahi Glass has properties comparable with those of Nafion 901. The Flemion 430 is suitable for lower caustic concentrations around 20% NaOH, and for KCl electrolysis Flemion 330 is the appropriate membrane. As the newest development Asahi Glass has announced the Flemion DX grades [18, 19]. Because of their hydrophilic surfaces these membranes can be operated with "zero gap", or more precisely, with minimum gap between them and the anode and cathode (cf. 3.2.). Increasingly, in 1981, Du Pont and Asahi Glass concluded an agreement covering the mutual exploitation of their patents on perfluorocarbon membranes. The prices for the membranes are governed by the type, order volume and other factors but are generally above $400 m^{-1}. In Fig. 3 it can be seen that such cation exchange copolymers are made of tetrafluoroethylene (TFE) and sulphonated or carboxylated perfluorovinyl ethers. During polymerization, the ion exchange groups are protected as sulphonyl fluorides or esters and converted to the sulphonic acid or carboxylic acid form by hydrolysis before the membrane is used. Thus the
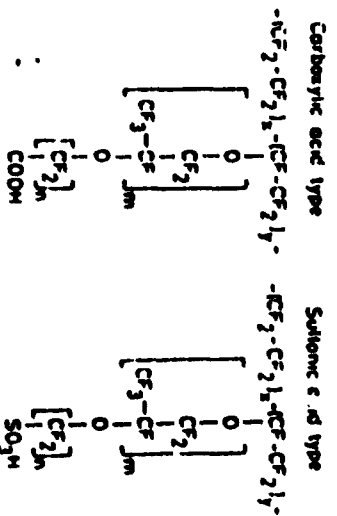
Carboxylic acid type

$$-(CF_2-CF_2)_x-(CF_2-CF_2)_y-$$
$$\begin{bmatrix} O \\ | \\ CF_2 \\ | \\ CF_3-CF \\ | \\ O \\ | \\ [CF_2]_n \\ | \\ COOH \end{bmatrix}_m$$

Sulfonic acid type

$$-(CF_2-CF_2)_x-(CF_2-CF_2)_y-$$
$$\begin{bmatrix} O \\ | \\ CF_2 \\ | \\ CF_3-CF \\ | \\ O \\ | \\ [CF_2]_n \\ | \\ SO_3H \end{bmatrix}_m$$

x : 5000 - 13500   m : 1,2,3
y : ca 1000   n : 1,2

Fig. 3. Chemical composition of perfluorinated polymer for anion-exchange membranes.

copolymers consist of a CF_2 backbone and side chains with pendant carboxyl and/or sulphonic groups. These functional groups form ionic clusters but the resin itself is not crosslinked. The most recent findings on cluster formation in ion exchange resin have been presented by Yeager and Steck [20] and by Gierke et al. [21].

The ion exchange resins are formed into films by conventional methods. These films can be used by single or multilayer membranes; in the carboxyl membranes in order to improve the selectivity or reduce the electrical resistance. The membranes are generally reinforced by being laminated on PTFE or PTFE/rayon cloth, but reinforcement with fluoropolymer fibrils has also been used. Reinforcement raises the tear-strength of the thin membranes, which have a thickness of 0.1-0.2 mm, and it helps increase the dimensional stability of the membranes. As a result of water sorption, the membrane can, on going from the dry state to various electrolyte solutions, contract or expand by a few per cent. It is important to keep these expansion and contraction processes under control because they can cause the membrane to form wrinkles in the electrolysis cell. Gaseous products of electrolysis can be trapped in these wrinkles and thus block part of the effective membrane surface, which in turn results in higher electrical resistance and higher cell voltage.

3.2. Chemical and physical properties, lifetime of membranes

The aging of the membrane, which has long been known, is attributable to the deposition of only slightly soluble metal compounds, especially calcium salts, in the membrane [22]. These cause irreversible destruction of the membrane structure by the formation of microspores, which cause a decrease in the current efficiency due to increased migration of hydroxyl ions from the cathode chamber into the anode chamber. For this reason an especially pure brine is required for the operation of the membrane cell.

Conventional methods of brine purification, such as the use of soda ash and caustic soda, yield calcium concentrations of about 5 ppm in the brine. For the membrane process the brine must be subjected to a secondary purification stage, which usually employs ion exchange resins. The result is a reduction in calcium content by a factor of about 100 to final values of <50 ppb calcium in the brine. When brine with this level of purity is used, hydroxides can no longer be deposited on the anodic side of the membrane surface. Such hydroxide coatings lead to increased electrical resistance and hence to higher energy consumption.

Let us now consider the matter of membrane service life. One can never specify the service life without also stating such relevant factors as the cost of replacement membranes and the energy costs for electrolysis. The service life is chosen so as to optimize the net effect of these factors. Membrane costs are determined by the type of membrane and the sliding scale of membrane prices in relation to order volume. The energy costs depend on the price of electric power and the power consumption; the latter depends on cell voltage and current efficiency. The cell voltage is, in turn, a function of current density, the type of cell and electrodes used and the brine quality. To achieve high current efficiency it is especially important to have uniformly high brine quality. A membrane that is guaranteed for 2 years may not last this long if a disturbance in the brine supply should occur, but the lifetime can be extended beyond this period if the brine is of especially high quality.

An interesting phenomenon to be taken into account is the transport of water molecules through the membrane. It occurs because water of hydration is transported with the sodium ions. Depending on the type of membrane and the anolyte and catholyte concentrations, 3-9 moles H_2O per mole Na^+ are transported into the cathode chamber [12]. A large part and under certain conditions even the entire quantity of water required in the cathode chamber comes from the brine in this way. Consequently the amount of maximum-purity water required to be fed into the cathode chamber is less than that calculated for water decomposition and the dilution of caustic soda. That is to say the anolyte is concen-
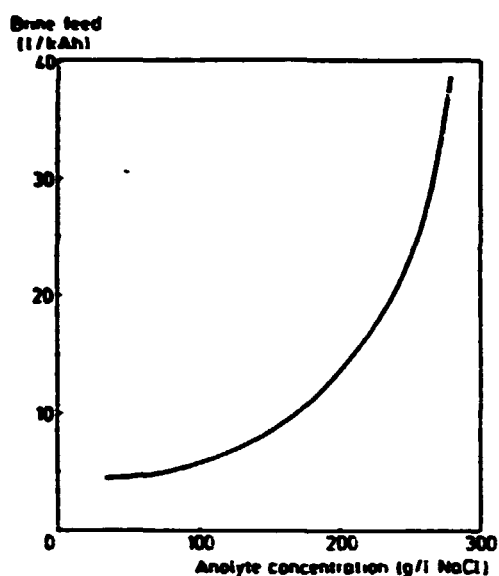
Brine feed
(1/kAh)

Anolyte concentration (g/l NaCl)

Fig. 4. Brine feed for membrane cells versus anolyte concentration.

Cell voltage (arbitrary units)

less hydrophilic membrane

hydrophilic membrane

Cathode - membrane gap (mm)

Fig. 5. Cell voltage of a membrane cell at different distances between cathode and membranes of different hydrophilicity.

trated in the anode chamber. As a result, in membrane cells, which also permit the use of much lower sodium chloride concentrations (<200 g dm^{-3} NaCl) than, for example, mercury cells (>265 g dm^{-3} NaCl), brine consumption is comparatively low. This is shown in Fig. 4, where brine feed per unit charge consumed is plotted as a function of anolyte concentration [23]. Thus, in comparison with the mercury process, the flow rate of brine into membrane cells is very low, e.g., with a membrane cell with 200 g dm^{-3} NaCl in the anolyte, the flow rate may be only 0.2-0.25 that in a mercury cell. This reduces substantially the capital expenditure for setting up membrane electrolysis since less brine need be purified and pumps, pipes etc need not be as large.

A phenomenon which can cause problems particularly when the membrane cells are operated with minimum electrode gap, or so-called 'zero gap', is the adhesion of gas bubbles to the membrane. This was revealed in studies of the interaction between the electrodes and the membrane in water electrolysis. Interestingly this effect is more pronounced with hydrogen bubbles than with chlorine bubbles. Further, it occurs less with hydrophilic perfluorosulphonic acid membranes and more with the less hydrophilic but more ion-permselective perfluorocarboxylic acid
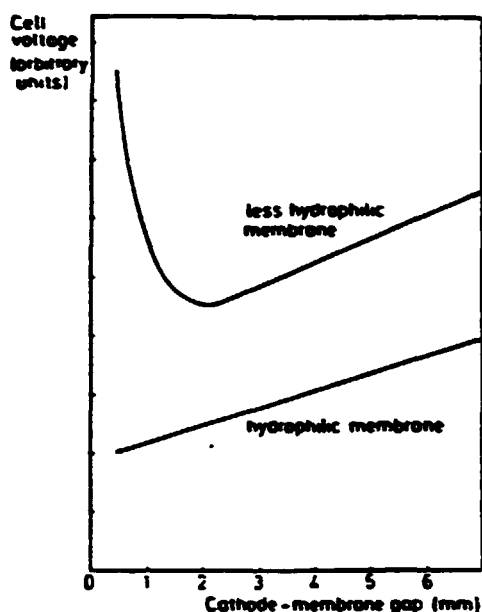
membranes. Gas blinding results in higher electrical resistance of the membrane and consequently, in increased cell voltage and energy consumption by the electrolysis. Hydrophilicity can be increased by various measures, such as the introduction of inert particles into the membrane surface [24] or mechanical roughening of the membrane [25], so that the gas bubbles no longer adhere. This effect can be demonstrated experimentally by measurement of the cell voltage of a membrane cell as one of the electrodes is moved closer to the membrane, as is shown in Fig. 5 [23]. As the cathode approaches the membrane the cell voltage falls, but contact of the hydrogen-covered cathode with the less hydrophilic membrane leads to a voltage increase. If the membrane has a hydrophilic surface this effect does not appear. With such membranes it becomes possible to operate the cell with zero or minimal gap, meaning that both the cathode and the anode are in contact with the membrane surface. This has the following advantages:

1. The voltage drop across both electrolytes, including the additional voltage drop resulting from the gas bubbles distributed throughout the electrolytes, is eliminated.

2. The voltage drop caused by the adhesion of the gas bubbles to the membrane, so-called gas blinding, is also eliminated.

3. The formation of wrinkles in the membrane is largely avoided owing to the pressure of the electrodes on both sides.

4. Because the membrane is supported on both sides by the electrodes, thinner membranes with lower electrical resistance can be used.

5. For the same reason the risk of damage to the membrane due to motion caused by pressure fluctuations or pressure surges is reduced.

The cell voltage of a membrane cell with minimal electrode gap is determined solely by the resistance of the membrane and the overvoltages on the electrodes. It can be predicted that such designs will replace the older designs with 2–4 mm electrode gaps because of their lower energy consumption and greater operational reliability.

3.3. Effects on product quality

In a discussion of product quality, interest centres on the caustic soda. The maximum caustic soda concentrations that can be achieved, even with the newer membranes, lie in the range 33–40% NaOH [18]; the optimal concentration in terms of efficient use of electrical energy probably lies between 33 and 36% NaOH. For most applications these concentrations are sufficiently high, so that only a fraction of the total output requires concentration to 50% NaOH. The melting points of 50% and 33% caustic soda solution are approximately equal (+ 11°C and + 10°C), so that the same temperature conditions apply for the transport of both grades of caustic soda. For lower caustic soda concentrations (10–25% NaOH) and caustic potash production other special membranes must be used [18]. The salt content of the caustic soda solution as it leaves the cell is around 10–50 ppm NaCl, which is even lower than that of the mercury cell caustic solution. The chlorate content of this solution has similarly low values.

Whereas the hydrogen generated at the cathode is of high purity (> 99.9% H_2), the chlorine content of the anode gas is only about 98–99%, depending on the caustic current efficiency and the anode material [11]. The remainder consists largely of oxygen (1–2%) and the hydrogen content is negligibly small. If the caustic soda current

efficiency falls it is because of OH⁻ transport through the membrane and this leads to oxygen evolution at the anode. This may be avoided by the addition of acid to the brine to neutralize hydroxyl ions that pass from the cathode chamber through the membrane into the anode chamber [11]. To achieve complete neutralization a volume, V (dm³ kA⁻¹ h⁻¹), of hydrochloric acid (37% HCl) is required:

$$V = 3.1 (1 - S_{NaOH}),$$

where S_{NaOH} is the caustic current efficiency expressed as a fraction of 1. If the acid addition to the brine exceeds this level so that the acidity of the discharged anolyte is greater than pH = 2, there is a danger that hydrogen ions will migrate through the membrane toward the cathode. This would lead to damage to the carboxyl membrane or, in the case of sulphonyl membranes, to a reduction in the caustic current efficiency.
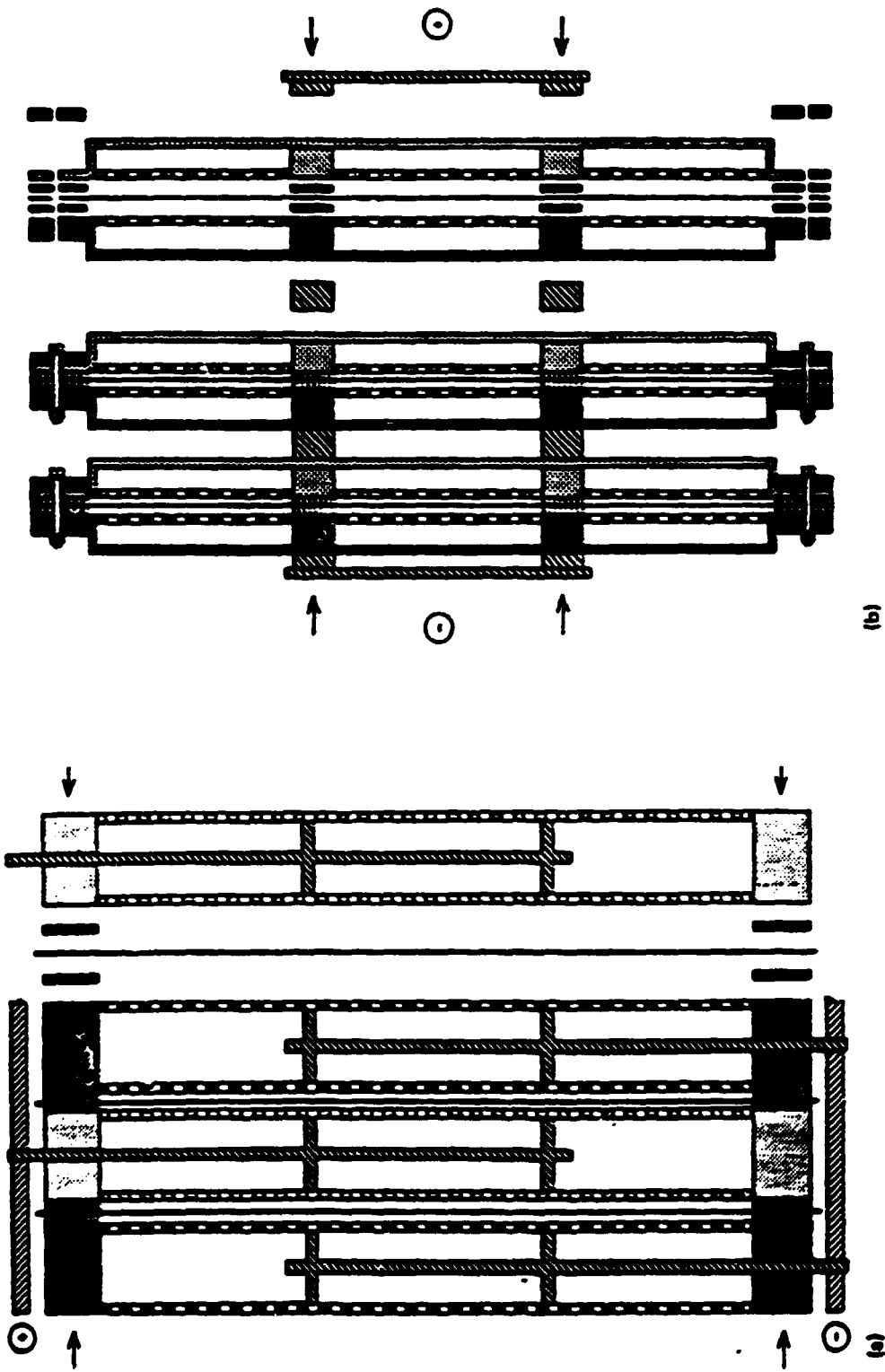
4. Membrane cells

4.1. Electrical connection

A distinction is usually made between monopolar and bipolar cells. It is based not so much on a property of the cells as on the electrical interconnection of the individual cells in an electrolyser, which can consist of 15 to 150 cells. If the cells are connected in parallel, the electrolyser is monopolar; the electrolyser current is the sum of the individual cell currents and the voltage on the electrolyser is the same as that across a single cell. If the cells are connected in series, the electrolyser is bipolar; the electrolyser voltage is the sum of the cell voltages and the total current of the electrolyser is equal to that flowing through a single cell [26]. In a system containing many cells it is obvious that monopolar electrolysers require considerable currents (50–100 kA) and bipolar electrolysers high voltages (100–400 V).

Figure 6 illustrates the construction principles of both monopolar and bipolar cells.

4.2. Electrode materials

Normally the anodes are made of titanium and the cathodes of mild steel, stainless steel or nickel [27]. The passivity of titanium under anodic conditions

Fig. 6. Schematic drawing (horizontal section) of a monopolar (a) and bipolar (b) membrane cell. Materials are marked as follow: Steel (black), titanium (dotted), copper (hatched), gasket (crosshatched).

is overcome by oxide (e.g., RuO_2/TiO_2 [28], PdO [29]) or metallic (e.g. Pt/Ir [30]) coatings containing noble metals; thus the anode overpotential is very low. The 300–400 mV overvoltage for hydrogen evolution on the above cathode materials can be reduced by catalytic (noble-metal-containing) or high-surface-area (e.g. Raney nickel) coatings [31, 32]. In contrast with the anode materials, service-life problems are still being encountered with the cathode materials. It is not expected that the answer will be found in the cathode coatings containing noble metals [27].

4.3. Cell design

The monopolar cells shown in Fig. 6 consist of square or rectangular frames, area about 1 m^2, which support on both sides expanded metal electrodes of the same type. In the anode chamber the frame and electrodes are made of titanium; the cathode material is mild or stainless steel. The current supply outside the cell is provided by copper rods or copper busbars, which penetrate the frame. In the cathode chamber they are clad with steel and in the anode chamber with titanium. As shown in Fig. 6, the frames are pressed together in an arrangement in which anode and cathode frames alternate. The division into anode and cathode chambers is provided by the ion exchange membrane, which together with gaskets is inserted between the frames. Not shown here or in the following figure are the feed pipes for brine and dilute caustic solution and the outlet pipes for chlorine/anolyte and hydrogen/catholyte. Thus each chamber, i.e., each frame, has one inlet pipe and one outlet pipe. Also not shown are the end plates which close the two open end frames of an electrolyser. An important feature of this design is that the anode and cathode chambers are separated from one another only by membranes and not by metal walls. A large number of such single frames are pressed together in a suitable device like the frames of a filter press. For this purpose one uses hydraulic presses (Asahi Glass) [33] or tie rods (Uhde) [34], or the different segments, e.g. the cathode elements, are bolted together individually (Diamond Shamrock) [35]. Metal bipolar cells of the filter press type are offered by Asahi Chemical [36] and Tokuyama Soda [37]. A bipolar cell of a different basic

design is shown in Fig. 6. The design shown here is not the filter press type, since each cell consists of half-cells or anode and cathode half-shells that are bolted together. The cathode half-shell consists of a steel frame that is closed on one side by a steel wall and on the other by the expanded metal cathode. The back wall and the cathode are connected by power-transmitting support elements of steel, which carry on the side adjacent to the membrane, spacers made of an insulating material.

The anode half-shell is similarly constructed except that this structure, consisting of a titanium back wall and a titanium anode, is provided with a steel support frame in order to save titanium. Again; in this case the anode and the back wall are connected by power-transmitting support elements of titanium and fitted with insulating spacers. After the membrane, together with gaskets, is inserted, each anode frame is bolted to a cathode frame along their periphery to form a cell. In principle a single cell of this type can be used alone for electrolysis after being hooked up to a suitable power supply. However, generally here too, a large number of single cells are mounted in a frame and pressed together by means of a single pressing device. The compressive force is transmitted through the above-mentioned insulating spacers within the cells and through copper contact pieces between the individual cells. This compression serves to facilitate current transmission from cell to cell and not the sealing of the individual cells, since this seal is provided by bolting the frames together. A system of this type has been developed by Hoechst [38].

Besides these two metal cells shown here as examples, there are also other membrane cells with plastic frames. They are constructed as bipolar filter press cells. The frame and partition wall are made of plastic; the anode and cathode of two adjacent frames are connected by power-transmitting connectors. The current conductors through the partition wall must be gas and liquid tight. Furthermore, these plastic cells have a special feature that metal cells cannot be provided with, namely channels for feeding in the electrolytes and discharging the products. These channels are formed by openings in the frames similar to those in plate heat exchangers. From these channels the anode and cathode chambers can be supplied and tapped through small openings that

are also drilled in the frame. Cells of this type are offered by Hooker [27, 39], Ionics [40] and Krebskosmo [41, 42].

A type of cell that differs greatly from those described above is the monopolar FM 21 cell from ICI [43-46]. The distinguishing features are, first of all, the size of the membrane area, only 0.21 m², and secondly, a special electrode design, which when compared with the expanded metal variety is very simple but extremely effective. The cell has electrolyte distribution and discharge channels and is thus very compact. The small size of the electrodes is advantageous in their manufacture and mounting, and in respect of the voltage drop in the electrode material. Because of their special structure the electrodes are suitable both for operation with normal electrode gap sizes (2-4 mm) and for operation with minimal or zero gap.

The newer cells with minimal electrode gap have not been described in detail. In 1980 the 'SPE' cell of the Oronzio de Nora company was introduced [47, 48]. It is a bipolar filter press cell with an electrode surface of about 1 m². It is not known whether these cells are actually solid polymer electrolyte cells, similar to those developed by General Electric [49], where porous gas and liquid permeable metallic layers are bonded to the membrane surface as catalytic electrodes. In addition to SPE technology, De Nora also describes in the patent specifications [48] the possibility of employing zero gap electrodes without the special SPE electrode-membrane composite. It is possible that in the SPE process the membrane surfaces are hydrophilized by the bonding together of the electrodes and membrane, similar to the particle embedment technique or roughing of the membrane as described in section 3.2. If the current collectors pressed against either side of the membrane can function as electrodes when the electrode-membrane bond is damaged, SPE electrolysis should convert to zero-gap operation. Under these assumed conditions the zero gap process is certainly the less expensive alternative.

The Asahi Glass Zero Gap Electrolysis Cell (AZEC) [18, 19] is not an SPE cell in the sense used above, but a configuration in which both the anode and the cathode are an integral part of the cell structure and in contact with both sides of the membrane. This design requires specially prepared hydrophilic membranes, such as the Flemion-DX type [18], as described in section 3.2.

The advantages and disadvantages of the different cell types, for example bipolar versus monopolar cells, are being constantly debated [15]. Here only two aspects will be chosen for discussion. A monopolar cell consists essentially of frame, gasket (or possibly a frame-gasket combination), electrodes and membranes. A bipolar cell has the same components, but additionally the partition wall between the anode and cathode chambers. The argument that this fact makes bipolar cells more complicated and expensive can be countered with the observation that small, isolated units operate more reliably. Nor is the argument that the leak currents in bipolar electrolysers lead to corrosion valid. There are many ways of suppressing these leak currents, which is proven by the fact that about 80% of installed membrane-cell capacity involves bipolar cells.

Currently the appearance of cells with a small electrode surface has provoked a discussion concerning their advantages and disadvantages. The advantages of small cells described above are counterbalanced by the disadvantage of the increased requirement for gasketing. Thus, for example, for a 100 t day^{-1} plant (2 kA m^{-2}): 3 m² cells have 3.8 km of gasketing, 1 m² cells have 6. km and 0.25 m² cells 15.7 km of gasketing. Which argument carries more weight? Which system is better? Only many years of operation of both cell types can decide. The selection process will then lead to a few very similar cell types, a familiar occurrence in the history of technology.

5. Economics of the membrane process

5.1. Capital costs

A comparison of the capital costs for the three electrolysis processes is extremely difficult. Hence the following discussion will only provide a rough sketch of the capital costs situation. Whereas the capital costs for the power supply, the brine supply and chlorine treatment are about the same for all three electrolysis processes, there are larger differences in the costs for the cell room, which are lower for the membrane process than for the mercury process and lowest for the diaphragm process. The cost of the caustic soda extraction is

especially high for the diaphragm process, less than half as high for the membrane process and minimal for the mercury process. On the other hand with the mercury process additional capital costs are incurred for measures to prevent mercury emission. The overall picture that emerges is as follows: if the capital costs of the mercury process are taken as 100%, the costs of the diaphragm process run to 105% and for the membrane process 90% on the same scale. Similar results have been obtained by Nagamura et al. [33]. Overall then, if the estimation error is assumed to be ± 10% and all conditions are equal, the capital costs are the same for all three processes. Important advantages accrue for one process over the others when the conditions pertaining to the feedstock or product are changed. For example, the use of solution-mined rock salt favours the diaphragm process, and if pure 35% caustic soda can be used without concentration the advantage would shift toward the membrane process [50].

Table 2 shows the operating characteristics for the processes for sodium chloride electrolysis. The differences in current density are apparent, about 10 kA m^{-2} for the mercury cell and roughly 2 kA m^{-2} for the diaphragm and membrane cells. For the membrane cell higher current densities up to 3 kA m^{-2} are used, even current densities up to 4 kA m^{-2} have been achieved. However, depending on energy, capital and other costs the optimum current density lies between 2 and 3 kA m^{-2}. Nagamura et al. [14] decided upon 2.1 kA m^{-2} as the optimum under their specific conditions. The cell voltages in Table 2 are valid for the present state of the art. The last line shows figures for expected technology in the membrane process, i.e., catalytic cathodes, thinner, hydrophilic membranes and minimal or zero electrode gap.

5.2. Energy costs

Of special interest are the energy consumption figures, shown in Table 2 as d.c. power consumption. The picture changes when the energy needed for caustic concentration are included. If 600 kWh t^{-1} NaOH (1 t steam is equivalent to 285 kWh) are added to the energy consumption figures for concentrating the caustic soda to 50% NaOH in the diaphragm process and 200 kWh t^{-1} NaOH for the membrane process, then it will be seen that the mercury and diaphragm processes are the more energy-intensive processes (cf. also Nagamura et al. [33]). Also to the advantage of the membrane process are the low energy requirements for raising the concentration of the caustic soda solution by a relatively small amount from 35% to 50% NaOH and the fact that waste heat from the electrolysis can be used in flash evaporators. As mentioned in the discussion of capital costs, the picture becomes even more favourable for the membrane process if one can omit the caustic concentration stage. It can already be said that with decreasing cell voltage in the membrane process, more efficient use must be made of waste heat [51]. Otherwise it is not even possible to maintain the cell temperature at 80–90°C without an additional heat supply if the current density is not to be increased.

Table 2. Operating characteristics of mercury, diaphragm and membrane cells

Process	Current density (kA m^{-2})	Cell voltage (V)	Current efficiency (%)	Energy consumption (kWh t^{-1} NaOH)	Caustic soda	
					% NaOH	% NaCl
Mercury	10	4.15	96	2900	50	0.006
Diaphragm	2	3.3	95	2350	(12)	(14)
					50	1
Membrane (present state of the art)	3.5	3.2	95	2280	33–35	0.004
Membrane (future technology)	4	2.9	95	2050	33–35	0.004