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Detection of damaged membranes in alkali chloride electrolysers

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Holes in cation exchange membranes of alkali chloride cells can have a number of different causes. They do not represent a source of great danger during operation of a membrane electrolyser as long as their number is limited or their combined diameter does not exceed a certain size. Of the different methods for detection of holes in membranes, two procedures are described in detail: the cell voltage test and the leak test with measurement of the gas flow through the holes. The cell voltage test is performed with low time consumption during start-up of an electrolyser. It mainly shows the large membrane holes in a cell. In contrast to this, with the leak test all holes in a membrane are detected. However, the procedure is time consuming and is possible only with a totally drained electrolyser. It is recommended to perform these tests immediately after installing new membranes and then from time to time in order to avoid damage to the cells or to the plant chlorine system.

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1. Introduction

Pores, pin-holes or tears in cation exchange membranes for alkali chloride electrolysis can cause loss of current efficiency, damage due to corrosion of cell components or explosions resulting from mixing of chlorine and hydrogen. Therefore, it is very important to know if holes are present in a membrane and it is equally important to know where the damaged membrane is located in the electrolyser. Only then is it possible to find the right place for membrane renewal in the row of unit cells.

There are various reasons for the presence of holes in membranes. The first is faults in the membrane manufacture process. Provided that the quality control of the membrane suppliers is good, pores or holes are unlikely to be present in membranes delivered to the customer. More likely is the perforation of the membranes by insufficiently trained personnel during handling and installation into the electrolysers. Piercing with tools and severe creasing must be avoided. A third possibility for pores is bad cell design or poor cell manufacture; for example, expanding gaskets can produce tears along the rim of a cell or sharp points and edges on electrodes can pierce membranes. The fourth and most probable source of pores and pin-holes is the formation of voids, blisters and delamination of the membrane due to faults in start-up and shut-down procedures and by contaminated electrolytes. A fifth possibility for the formation of holes is abrasion by membrane movement towards the electrode as a result of pressure fluctuations. This can be avoided by sufficient hydrogen overpressure to maintain the membrane in contact with the anode.

The effects of holes depend on their size and number, on their location, whether in the liquid, foam or gas phase, on the state of the cell, whether in operation or during shut-down, and on operating errors by the plant personnel. Usually, pin-holes are not even recognized during normal operation of membrane cells. But in other cases corrosion has taken place by caustic attack on the titanium anodes or even explosions have damaged cells or parts of the gas purification system when a source of ignition of the gas mixture was present. As mentioned above, during normal operation a differential pressure between cathode and anode compartment is always maintained by the higher density of the caustic solution compared to the anolyte, and by keeping the hydrogen pressure at a higher level than the chlorine pressure. Therefore, only caustic and hydrogen can enter the anode compartment. Under these circumstances it is impossible for chlorine and anolyte to enter the cathode chamber. Only during shut-down, especially when the cell is drained, by malfunction of valves or errors by the cell operators, can chlorine enter the cathode compartment. Since both compartments are usually vented with nitrogen during draining, no greater damage can take place with chlorine in the cathode compartment. Nevertheless, dangerous situations can occur when two faults or more coincide.

In general, the presence of one or a few pores or pinholes does not necessarily represent a state of great danger, as shown by Groszek and Moomaw [1]. They describe electrolysis tests with a single membrane cell with holes punched into the membrane. In the first test, one of the two holes of 3 mm diameter each was located 7.5 cm below the top of the cell and the other was positioned near the bottom of the cell. This means that the upper hole was in the area with high gas content in the foam and the lower hole was in the area of negligibly low gas content. For the second test, one hole with 1.6 mm diameter

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was punched into the membrane 1 cm below the top of the cell where accumulations of the gases were possible. Groszek and Moomaw [1] conclude: "Holes in membranes are not a catastrophic problem. This is particularly true for multi-cell electrolyzers where the inefficiencies and impurities are diluted over a large number of cells. Even with the fairly large holes used in the tests above, hydrogen concentrations are quite low as compared to other chlor-alkali technologies (i.e. mercury and diaphragm cells)."

Nevertheless, a close observation of the anolyte pH and even the caustic content of the anolyte is recommended by the authors [1] before start-up of electrolysers in order to avoid loss of current efficiency or damage to the cells.

2. Detection of damaged membranes by cell voltage measurement during start-up

2.1. *Basic considerations*

The electrode reactions of an alkali chloride membrane cell are:

$$\begin{array}{ll} \text{Anode} & 2\,\mathrm{Cl^-} = \mathrm{Cl_2} + 2\,\mathrm{e^-} \\ \text{Cathode} & 2\,\mathrm{H_2O} + 2\,\mathrm{e^-} = \mathrm{H_2} + 2\,\mathrm{OH^-} \\ \hline \text{Total} & 2\,\mathrm{Cl^-} + 2\,\mathrm{H_2O} = \mathrm{Cl_2} + \mathrm{H_2} + 2\,\mathrm{OH^-} \end{array}$$

The decomposition voltage of the total reaction at 80 °C and with the normal electrolyte concentrations is about 2.2 V. During start-up of an electrolyser the cell voltage is normally in the range 2.2–2.6 V at current densities of up to 0.3 $\mathrm{kA\,m^{-2}}$.

Sometimes, especially with electrolysers in operation for a long time, it is observed that one or more single cells, at low current densities, show cell voltages well below 2.2 V. This is not possible with the reactions described above taking place. Therefore it is likely that water splitting in alkaline solution is caused by caustic penetrating the membrane towards the anode. The electrode reactions are then as follows:

$$\begin{array}{ll} \text{Anode} & 2\,\mathrm{OH^-} = \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} + 2\,\mathrm{e^-} \\ \text{Cathode} & 2\,\mathrm{H_2O} + 2\,\mathrm{e^-} = \mathrm{H_2} + 2\,\mathrm{OH^-} \\ \hline \text{Total} & \mathrm{H_2O} = \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2} \end{array}$$

According to Sandstede [2] the reversible voltage of this reaction is about 1.2 V and the cell voltage of a membrane cell for water splitting is about 1.5 V at 3 $\mathrm{kA\,m^{-2}}$. In alkali chloride membrane cells this low voltage is never observed at higher current densities, i.e. 2–4 $\mathrm{kA\,m^{-2}}$. But while increasing the current density from zero during start-up low cell voltages may be observed initially. These low values of less than 2.2 V are being adjusted during further increase of current density to the normal level of cell voltage for the chlorine evolution, i.e. to more than 2.2 V. This may be explained by the increasing turbulence produced by the chlorine bubbles. This removes the relatively small quantities of caustic from the anode surface by forming hypochlorite. For a cell having a low cell voltage of less than 2.2 V at relative high current density, for example at more than 1 $\mathrm{kA\,m^{-2}}$, the caustic transport must be considerable and, accordingly, the size of the membrane hole or tear must be large. This also holds for the rare case of a wide tear when all the chlorine produced reacts with the entering caustic. In addition to the voltage effect there is no greenish chlorine colour to be seen in the outlet pipes if these are transparent or translucent.

2.2. *Procedure and results*

During start-up of an electrolyser the cell voltages of the single cells are usually closely monitored. On the recommendation of the membrane suppliers the current density is increased stepwise from zero to full load over a certain time, e.g. one to two hours. At the single current density levels, the cell voltage print-outs are checked for cells with unusual behaviour. As an example Fig. 1 is presented with data from an 1.25 $\mathrm{m^2}$-electrolyser of the membrane cell pilot plant in Frankfurt-Hoechst. Figure 1 is showing three unit cells b–d at the lowest load level with abnormal low voltages of below 2.2 V and cell a for comparison with 2.5 V, i.e. above the decomposition voltage for the chlorine evolution. At the second step only the two cells c and d remain in the critical area. As the current density increases further, the cell voltages of all cells come more and more into line. Above 1.2 $\mathrm{kA\,m^{-2}}$ no more voltage differences are observed between these four cells. At this point the chlorine production is strong enough to disperse the small caustic streams coming through the membrane from the cathode compartment.

In Fig. 2 the cell voltages of a 2.7 $\mathrm{m^2}$-electrolyser of the pilot plant with 16 single cells at low current density are displayed. With two exceptions, all cells behave normally, i.e. their cell voltages are well above 2.2 V. Only cells 4 and 8 show voltages of below 2.2 V. This means that cells 4 and 8 have an abnormally high degree of caustic penetration into the

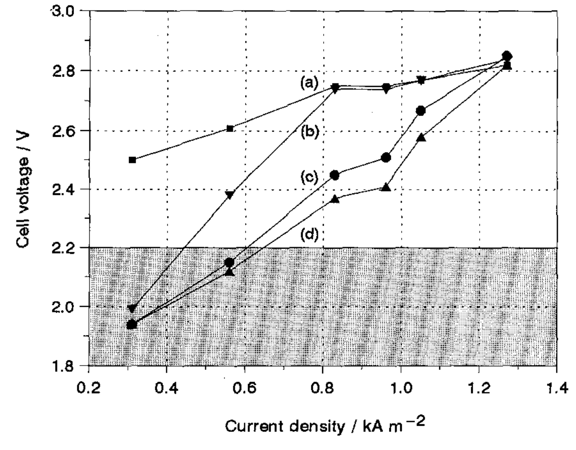

Fig. 1. Cell voltages of membrane cells at low current densities with one intact membrane (a) and three damaged membranes (b, c, d).

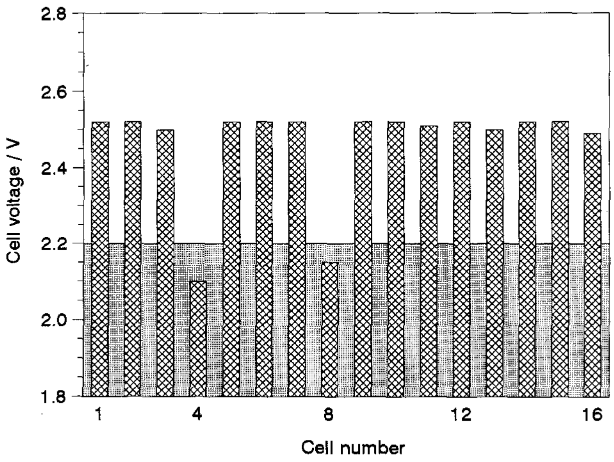

Fig. 2. Membrane electrolyser with 16 single cells at 0.3 kA m^{-2}. Cells 4 and 8 contain damaged membranes.

anode compartment, caused by deterioration of the membrane, in the worst case by one or more holes. From our experience it is not absolutely necessary to stop the start-up procedure and to replace the membrane by a new one. But it is advisable to watch this particular electrolyser closely during operation with regard to anolyte pH and hydrogen content in the anode gas. Normally no unusually high value due to mixing of the products of cells 4 and 8 with the products of the other 14 cells will be found. But it is also recommended to observe all measures against explosions extremely carefully, for example flooding the electrolyser with nitrogen during shut-down. At the next convenient time, during a shut-down of the plant, or during a repair job on the electrolyser system, a leak test should be performed.

3. Detection of damaged membranes by a leak test

3.1. *Description of the method*

The usual method of detecting pores, pin-holes or tears in membranes is performed by imposing a nitrogen pressure onto the membranes from the cathode side. This is possible only when the electrolyser has been drained completely. As shown in Fig. 3, nitrogen is introduced via the inlet or the outlet pipes into the cathode compartment of one or several individual cells of an electrolyser. The second opening of the cathode compartment is closed by a stopper or a flange. By maintaining a certain pressure, for example 100 cm head of water by means of a liquid seal, the nitrogen is forced through holes in the membrane. The nitrogen leaking through the membrane leaves the cell either via the inlet or outlet pipe of the anode compartment while its other opening is closed. The escaping gas can be collected in a calibrated cylinder by simultaneously measuring the time of collection or it can be measured directly by use of a flowmeter.

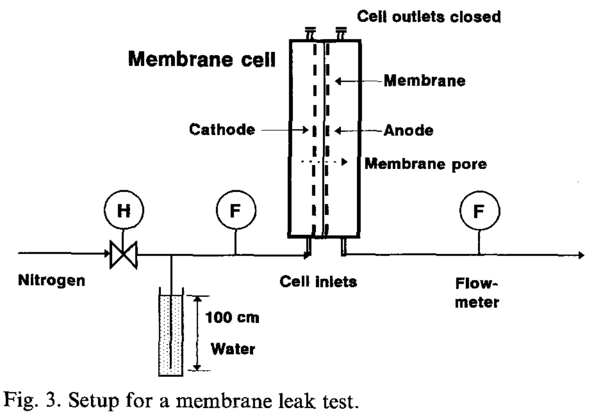

Fig. 3. Setup for a membrane leak test.

While applying nitrogen pressure onto the membrane over more than 30 min gas bubbles were observed in the collecting device even if no pores were present in the membrane. It is believed that the wet membrane is flattened out slowly by the nitrogen pressure and flows into the openings of the anode structure. Thereby the gas in the anode compartment is pressed bubble by bubble into the water used as seal in the pneumatic trough. In order to keep the time for the test as short as possible the leak rate is measured after a certain time, for example 10 min after turning on the nitrogen stream. Then a limiting amount of gas flow in dm^3 h^{-1} has to be defined, the exceeding of which represents a severe membrane damage. Kucinski and Gerner [3] have set this limiting leak rate to a value of 20 dm^3 h^{-1}. This limiting nitrogen flow may be adjusted to a lower value for small scale electrolysers. But according to our experience, this is a value for safe operation of membrane electrolysers of 1 m^2 and above, provided that the usual precautions for handling of chlorine and hydrogen are taken. However, if the leak rate is higher than 20 dm^3 h^{-1} the membrane should be replaced. On the other hand it is possible to repair the membrane by placing special membrane patches over the damaged area and by using a heat seal technique [4].

3.2. *Results of the leak test*

In the following example the 16-cell electrolyser of Fig. 2 was checked by the leak test (see Fig. 4). Surprisingly, four single cells were found with rather high gas leaks with the highest being cells 4 and 8.

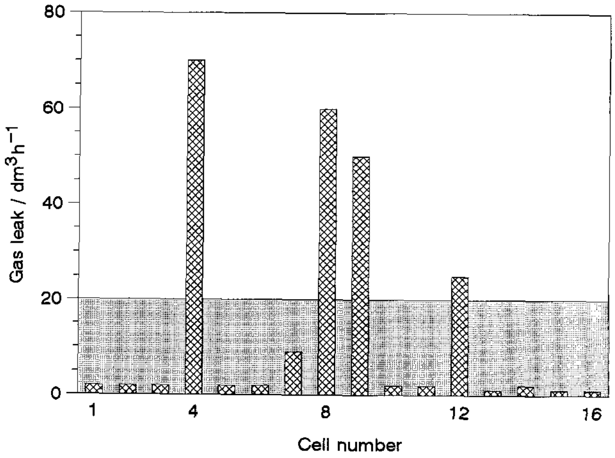

Fig. 4. Result of a leak test with a membrane electrolyser with 16 single cells (cf. Fig. 2). Cells 4, 8, 9 and 12 contain damaged membranes.

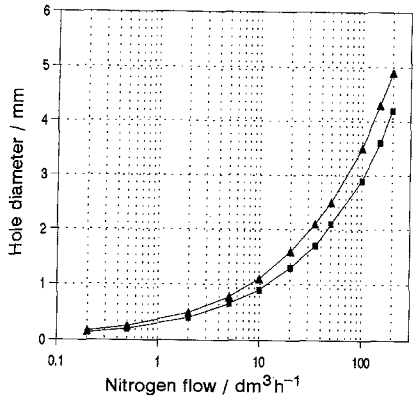

Fig. 5. Hole diameter calculated as a function of the nitrogen flow rate through the holes. Nitrogen pressure is 50 cm (▲) and 100 cm head of water (■).

During the preceeding operation of the electrolyser no abnormally high hydrogen content in the anode gas was observed. The values of 0.8% for the oxygen content and 4.4 for the anolyte pH were also in the normal range. The caustic current efficiency of this particular electrolyser was about 95%, which is also normal. These operational results show that even four damaged membranes have no detrimental effect on the operation of a membrane electrolyser.

The reason for detecting only two damaged membranes by the cell voltage test is that the differential pressure caused by the density differences of catholyte and anolyte increases from top to bottom of the cell. If the differential pressure is large, enough caustic can penetrate through small holes in order to develop oxygen at the anode. In the case of large holes at the top of the cell, these too will be detected by the cell voltage test. Therefore, only cells 4 and 8 with the highest nitrogen leak rate in Fig. 4 show abnormal behaviour in the cell voltage test in Fig. 2.

After the cells are disassembled, pores or holes are often not found by visual inspection. Shrinking processes of the membrane during drying may close pores. On the other hand a large number of small pores cannot be detected simply by looking at the membrane. Sometimes one observes a small white spot of corrosion on the black anode coating or even a bright spot of titanium corrosion by caustic attack. In such cases it is often possible to find a pin-hole in the membrane opposite to the anode defect.

To determine the hole size by means of the leak rate, Fig. 5 presents the hole diameter calculated as a function of the nitrogen flow rate. For example, a nitrogen flow of 10 $dm^3 h^{-1}$ means a pore of 1 mm diameter and 70 $dm^3 h^{-1}$ nitrogen represents one hole of 2.5–3.0 mm diameter or several holes of an equivalent combined diameter. Figure 5 also shows that changes of nitrogen pressure of between 50 and 100 cm head of water have only a minor influence on the results of this semiquantitative test. Therefore, this leak test can also be performed with 50 cm head of water nitrogen pressure. As our experience shows and the tests of Groszek and Moomaw [1] confirm, chlorine can be safely produced with a membrane leak rate of below 20 $dm^3 h^{-1}$ nitrogen flow corresponding to a pore size in the order of 1.3 mm diameter. However, to avoid explosions, all precautions have to be observed which are also usual in other technologies, i.e. amalgam and diaphragm technology.

4. Discussion

In Table 1 are shown the different methods for the detection of holes in membranes. The first two methods can be easily performed within a short space of time. In some plants online measurement of the gas contents or of the caustic content in the anolyte are available. But since the measurable effects of one or a few small holes are diluted by the many cells without damaged membranes in the electrolyser or in the electrolysers, the detection is not very reliable. Therefore only very large holes can be detected.

The cell voltage test can be performed during the start-up procedure simply by viewing cell voltage print-outs. But cell voltage measurements on single cells can be made only on bipolar electrolysers, where the single cells are connected electrically in series [5]. Then it is possible to locate the damaged membranes in the electrolyser, preferably if the holes are not too

Table 1. Different methods for the detection of pores, holes and tears in membranes

Method of detection	*Advantages*	*Disadvantages*
Gas analysis of hydrogen and oxygen in the anode gas	Possible during cell operation Use of online analysers Locates damaged electrolyser	Dilution by anode gas of other cells Detects very large holes only Does not locate damaged membranes
Titration of anolyte caustic content	Low time consumption Use of online analysers Locates damaged electrolyser	Only possible during shut-down Dilution by anolyte of other cells Detects very large holes only Does not locate damaged membranes
Cell voltage measurement at low current density	Low time consumption Locates damaged membranes Detects large holes	Only possible during start-up Only possible with bipolar electrolysers
Determination of nitrogen flow through membranes	Locates all damaged membranes	Only possible with drained electrolysers Single cells must be accessible High time consumption

small. This test should always be performed when there is a short shut-down for repairs, during power failures or the like. Then the operator is able to judge the state of the membranes and has an indication of whether further investigations should be carried out.

The best, but also the most time consuming, method is the leak test by passing nitrogen through membrane holes. This test is only possible on electrolysers with single feed lines and/or single discharge lines to and from the individual cells, i.e. with an external manifold system [5]. It is also possible only when the electrolyser is totally drained. But then all holes and even small pores can be detected.

It should be mentioned that another method of pinhole detection exists. In this method either the cathode compartment is filled with demineralized water or the anode compartment with diluted brine. In both cases the other compartment is then empty. The liquid leaks through available pinholes and may be collected from the inlet hoses of the empty compartments. In the case of an internally manifolded electrolyser, inspection of the manifolds, for example by an endoscope, will disclose the site of the membrane damage. This method has several disadvantages compared to the nitrogen flow method: filling the electrolyser with liquid is more time consuming than with gas; small pores are not easily detected; the hydrostatic pressure affects the leak rate depending on the vertical position of the pore in the cell. Therefore, this method should only be employed when the nitrogen flow method cannot be used, for example in electrolysers with an internal manifold system.

In view of the potential damage which pores, holes and tears can cause it is necessary to use the methods of Table 1 whenever the particular situation allows. It is also very useful to perform a leak test after installation of new membranes into an electrolyser. Although the time consumption is high for this test, it is much higher if an electrolyser has to be disassembled because one large hole or a wide tear has been discovered after putting the electrolyser into operation.

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