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Reduction of by-product formation in alkali chloride membrane electrolysis

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To obtain higher chlorine purity hydrochloric acid can be added to the feed brine of membrane cells in alkali chloride electrolysis. During the electrolytic process hydroxide ions migrate from the cathode compartment into the anode compartment. Hydrochloric acid neutralizes these hydroxide ions and, hence, formation of the by-products (oxygen in the anode gas and sodium chlorate in the anolyte) is reduced. With laboratory membrane cells the effects of varied amounts of hydrochloric acid on concentrations and current efficiencies of these by-products have been studied. Under normal operating conditions (with pH of feed brine between 2 and 11) the formation of by-products is not influenced by the addition of acid. Effects can only be observed at brine pH values < 1. Maximum effects occur if the brine pH is 0.1 and the anolyte pH is 2. The latter value is the limiting pH given by the membrane suppliers. At this point 6.3 dm^3 hydrochloric acid (37% HCl) per 1 m^3 of the feed brine have to be added in order to obtain an anode gas with 0.4% oxygen by volume. The formation of sodium chlorate is completely suppressed. Problems connected with this process and its application to industrial electrolysis are discussed.

1. Introduction

It has long been known that in alkali chloride electrolysis with membrane cells [1, 2] oxygen and sodium chlorate production are reduced by the addition of acid to the brine. Experiments have proved that this measure increases the chlorine current efficiency without changing the current efficiency of the caustic solution [3]. In normal operation, that is without the acid addition, the total amount of these by-products is determined by the permeability of the membrane to hydroxide ions which react according to Equation 1, whereas the ratio of sodium chlorate to oxygen is determined by the type of activation coating on the titanium anode [4].

Meanwhile there have been more recent investigations of this subject, for example by Kotowski and Busse [5] and by Bork [6]. These studies have determined that oxygen is formed largely by reaction (2) at the anode [5] and that the formation of sodium chlorate proceeds 'chemically' in accordance with Equation 3, and that probably no 'anodic' sodium chlorate formation takes place. Rather, sodium chlorate is more likely to be decomposed to Cl_2 or ClO_2 in the acid diffusion layer of the anode [6]. However, these findings do not change the basic idea that the type of the anode coating determines the amount of oxygen which is formed from hydroxide ions that have migrated through the membrane into the anode compartment, and that sodium chlorate is formed from the remaining hydroxide ions.

$$Cl_2 + OH^- = HClO + Cl^- \qquad (1)$$

$$HClO + H_2O = 3H^+ + Cl^- + O_2 + 2e^- \qquad (2)$$

$$2HClO + ClO^- = ClO_3^- + 2Cl^- + 2H^+ \qquad (3)$$

Although the addition of acid to the brine to neutralize hydroxide ions and thus suppress side reactions in the anode compartment is often mentioned, for example by Seko [7] and Austin [8], the industrial application of this technique does not appear to be common practice. It is probably difficult to determine the dosage rate of hydrochloric acid that is correct for all membranes in an electrolysis plant and there is the danger of damage to the membrane caused by an overdose of acid. Therefore a large anolyte recirculation rate is applied in plants which employ acid addition to the brine. So the acid is diluted before entering the cells and damage as mentioned above is thus avoided.

Simmrock *et al.* [9] in their Fig. 16 describe the formation of active chlorine and sodium chlorate in the anolyte and oxygen in the anode gas as a function of the hydrogen ion concentration in the anode compartment. These data are based on work by Jörissen [10], who also discusses the calculation of the amounts of hydrochloric acid required and the technical aspects of the hydrochloric acid addition. His experiments were conducted with Nafion® 355 and our own [3] with Nafion® 390, that is with membranes that carry only strongly acid functional groups ($-SO_3H$) and exhibit only poor current efficiencies ($\leqslant 90\%$ with 20% NaOH) compared with the most modern membranes. Hence it was necessary to conduct trials with the new types of membrane, which have a fluoropolymer layer with COOH groups on the cathode side and, consequently, achieve considerably higher current efficiencies ($\geqslant 95\%$ with 33% NaOH). Furthermore, the laboratory trials described below have been

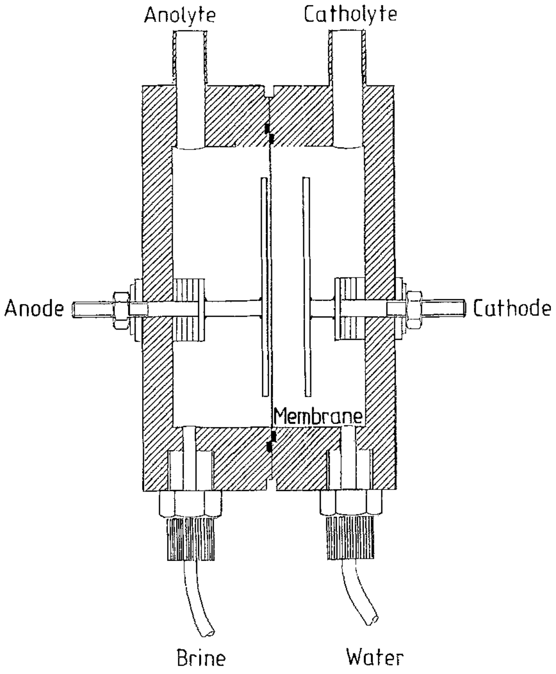

Fig. 1. Sectional drawing of the 36 cm^2 membrane cell.

conducted and presented in such a way that the results can be applied directly to practical plant operation.

2. Experimental details

Fig. 1 shows the cylindrical laboratory cell (12.8 cm in diameter) used for the electrolysis experiments. It consisted of an anode half-cell made of polypropylene and a cathode half-cell of acrylic glass. The electrode half-cells were sealed with O-rings placed between the membrane and both half-cells. Electrolyte and water were fed through connecting pipes in the underside of each half-cell. The electrolysis products left each half-cell through one of the three connection pieces in the top. The cell was heated by a glass-jacketed heating element introduced via the second connection piece in the top of the anode half-cell. Temperature regulation and heating cutout in response to excess temperatures were mediated by two contact thermometers in the third connection piece of the electrode half-cells.

The circular expanded-metal electrodes were welded to current supply bars which projected through the side walls of the half-cells, where they were sealed in suitable gaskets. Each electrode was 36 cm^2 in area. The titanium anode was coated with a Pt–Ir mixture (50 : 50 % wt). The nickel cathode carried an activation coating produced by the thermal decomposition of nickel and ruthenium salts. The membrane used in all experiments was of Nafion® 901 from the DuPont company, a fabric-reinforced two-layer membrane with carboxyl and sulphonyl fluoropolymers. It was built into the cell in such a way that it was stretched taut in contact with the anode. The distance from the membrane to the cathode, that is, the electrode gap was 3 mm.

Fig. 2 shows the flow chart for electrolysis with this laboratory cell. Brine with 300 g NaCl dm^{-3} and demineralized water was fed to the cell by metering pumps. The brine was prepared with vacuum salt containing no anticaking agent, adjusted to pH 10 with NaOH solution and freed of calcium and magnesium ions with a chelate ion exchange resin (for example, Bayer's Lewatit TP207 or Sumitomo Q10R). Electrolysis was run at 90° C and a current density of 3.0 kA m^{-2} (equivalent to 10.8 A). The anolyte concentration amounted to 200 g NaCl dm^{-3} and the catholyte concentration was 33% NaOH.

The caustic current efficiency E(NaOH) was determined by weighing the amount of NaOH solution produced, acidimetric determination of the NaOH concentration and measurement of the current strength during electrolysis.

To determine the chlorine current efficiency $E(Cl_2)$ the anode gas was absorbed in caustic soda solution. The sodium chlorate and active chlorine contents of

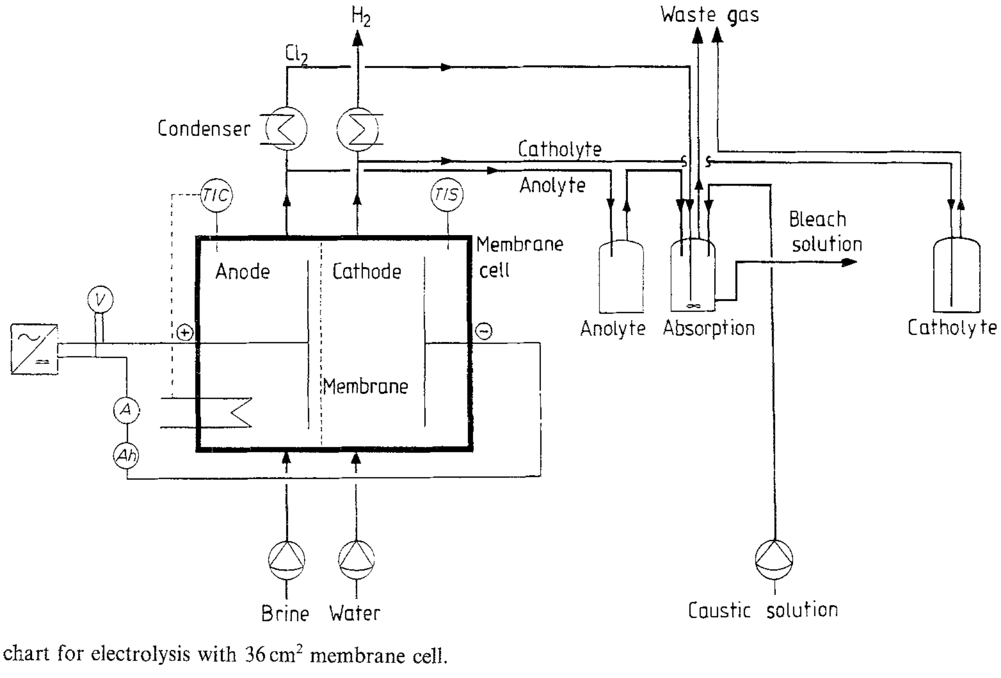

Fig. 2. Flow chart for electrolysis with 36 cm^2 membrane cell.

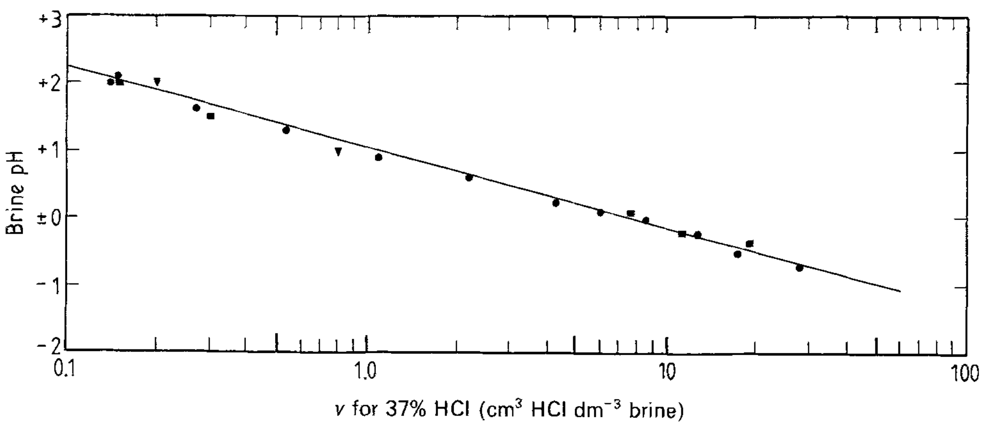

Fig. 3. Relationship between acid added to brine and brine pH.

the discharged anolyte were determined oxidimetrically and then the chlorine is blown out of the anolyte after acidification to pH 2 and also absorbed in the caustic soda solution. This permitted determination of the entire amount of chlorine produced and hence determination of the chlorine current efficiency $E(Cl_2)$. The sodium chlorate current efficiency $E(NaClO_3)$ was calculated from the sodium chlorate concentration in the anolyte and the amount of anolyte.

The oxygen content of the anode gas was determined by gas analysis, that is, by absorption of the chlorine in caustic soda solution followed by absorption of the oxygen in an alkaline pyrogallol solution. Analysis of the entire amount of gas discharged confirmed that the anode gas contained practically only chlorine and oxygen. Then the oxygen current efficiency $E(O_2)$ was calculated as follows:

$$E(O_2) = E(Cl_2) \times 2V(O_2)/(100 - V(O_2)) \quad (4)$$

where $V(O_2)$ is the oxygen content of the anode gas in vol %. An electrolysis trial under constant experimental conditions lasted about one week. Over a period of 10 months 36 trials were conducted. These were divided into four series each of which began with a new membrane because the previous membrane had been damaged in the preceding trial. The symbols ●, ■, ▲ and ▼ are used in the graphs to depict the results of the first, second, third and fourth trial series, respectively.

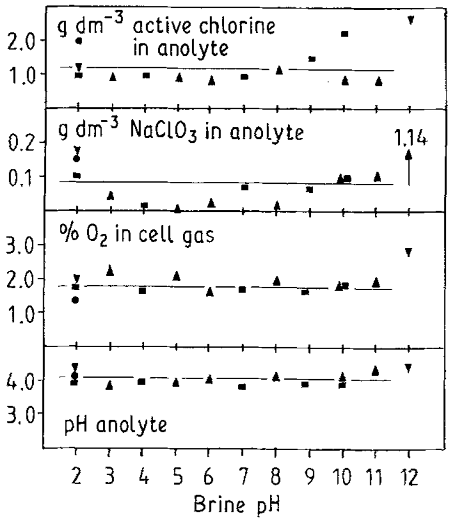

Fig. 4. Product and by-product contents in anolyte and chlorine in brine pH range 2 to 12.

3. Results

3.1. *Correlation of pH with acid addition to the brine*

In the accompanying graphs the pH of the brine is always given as the reference quantity. To show the relation between pH and the amount of hydrochloric acid added to the brine, the brine was purified with an ion exchange resin at pH 10, concentrated hydrochloric acid (37% HCl) was added, and the pH was measured with a pH measuring device and a pH electrode after two-point calibration with buffer solutions. The results are shown in Fig. 3. The equation of the fitted straight line is

$$\log v = (1.024 - \mathrm{pH})/1.153 \quad (5)$$

where v is the volume ratio representing cm^3 hydrochloric acid to dm^3 brine. Equation 5 is valid only for the brine preparation used here. If other brines are used, for example one purified by precipitation with caustic soda solution and soda ash, Equation 5 may be different.

3.2. *Normal working range: brine pH 2 to 11*

In Fig. 4 the active chlorine and sodium chlorate contents and pH of the anolyte and the oxygen content of the anode gas are plotted against the brine pH in the range 2 to 12. It is apparent that despite a wide scatter in some instances all values are constant within the range 2 to 11, while larger by-product contents are found at pH 12.

Figure 5 shows the experimentally determined current efficiencies as a function of brine pH in the range 2 to 12. Here again we note the constancy of the values between pH 2 and 11, despite the instances of wide scatter, which are ascribable to analytical inaccuracy, and the divergent values at pH 12.

Table 1 summarizes the means of the contents and current efficiencies, with their standard deviations, from Figs 4 and 5. The sum of the current efficiencies

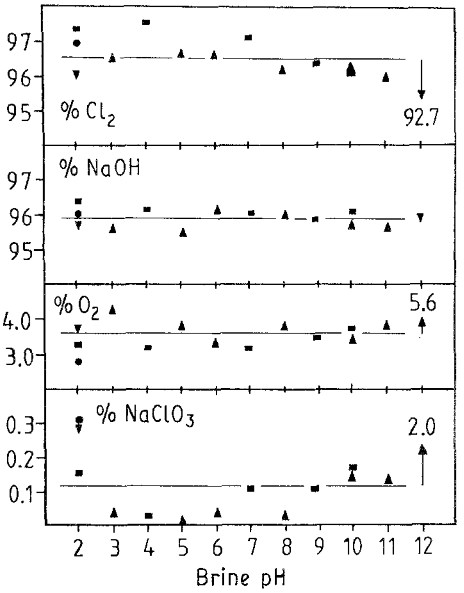

Fig. 5. Current efficiencies of products and by-products in brine pH range 2 to 12.

in the anode compartment, $E(Cl_2) + E(NaClO_3) + E(O_2) = 100.32\%$, can be considered as reasonable in view of the relatively large standard deviations of the individual values.

3.3. *Acid addition to the brine: brine pH 2.0 to −0.8*

Figure 6 shows a plot of the active chlorine and sodium chlorate contents in the anolyte, oxygen content in the anode gas and anolyte pH against brine pH in the range −0.8 to +2.0.

The active chlorine content appears to exhibit no obvious dependency on brine pH, but this is due to the experimental design, in which anolyte is collected in a vessel outside the membrane cell, where it always maintains the same active chlorine saturation at room temperature (*cf.* Fig. 2). The mean of all values lies at $1.3 \pm 0.8\,\mathrm{g\,dm^{-3}}$ and is thus very similar to the value in the brine pH range 2 to 11 (*cf.* Table 1). The other three quantities exhibit a distinct decline at brine pH < 0.6. The slopes of the declining curve segments differ from one another, with $NaClO_3$ attaining a minimum at pH +0.2, O_2 at pH 0 and anolyte pH only at about pH − 0.7. Because of the blocking of the COOH groups at low anolyte pH as mentioned above, membrane manufacturers give +2 as the lower limiting value of the anolyte pH. It can be seen in Fig. 6 that the anolyte pH reaches +2 at brine pH +0.1 and that then the $NaClO_3$ content of the anolyte is already zero and the O_2 content of the anode gas has fallen to about 0.4% by volume.

Figure 7 shows the current efficiencies. It is interesting that because of proton penetration of the membrane the caustic soda solution current efficiency does not begin to fall until a brine pH of −0.1, that is, in a range in which the chlorine current efficiency has already attained its maximum and the oxygen and sodium chlorate current efficiencies their minima. For this reason the minimum anolyte pH of +2 (at brine pH +0.1; see Fig. 6) recommended by the membrane manufacturers is a safe limit at which no danger of damage of the membrane due to proton penetration can appear.

Table 2 summarizes the results of Figs 6 and 7 for brine pH +0.1. It represents the conditions under which the least possible formation of by-products occurs in practice, namely when the discharged anolyte is at the prescribed pH limit of 2. For brine pH 0.1 Equation 5 yields the hydrochloric acid requirement of $6.3\,\mathrm{dm^3}$ (37% HCl) per $1\,\mathrm{m^3}$ brine (*cf.* $12\,\mathrm{dm^3}$ hydrochloric acid per $\mathrm{m^3}$ brine for Nafion® 390 [3]).

4. Discussion

In the membrane process [1, 2] the pH of the anolyte discharged from the anode compartment always lies between 4 and 5 regardless of the pH of the feed brine entering the anode compartment, as long as the latter lies within the normal working range of pH 2 to 11. This phenomenon is ascribed to the buffering capacity of the two coupled relations chlorine hydrolysis (Equation 1) and the dissociation of hypochlorous acid (Equation 6)

$$HClO + OH^- = ClO^- + H_2O \qquad (6)$$

Additionally, however, another determinant quantity for anolyte pH must be taken into account, namely hydroxide ion migration from the cathode compartment through the membrane into the anode compartment. Simple calculations show that this quantity of hydroxide ions is considerably larger than the quantity of hydrogen ions or hydroxide ions introduced

Table 1. Results of electrolysis for brine pH 2 to 11

	Content	*Current efficiency (%)*
NaOH in caustic solution	(33%)	95.9 ± 0.3
Cl_2 in anode gas and anolyte	(98.2% by vol.)	96.6 ± 0.5
Active chlorine in anolyte	$1.2 \pm 0.4\,\mathrm{g\,dm^{-3}}$	–
$NaClO_3$ in anolyte	$0.08 \pm 0.05\,\mathrm{g\,dm^{-3}}$	0.12 ± 0.09
O_2 in anode gas	1.8 ± 0.2% by vol.	3.6 ± 0.4
Anolyte pH	4.1 ± 0.1	–

Table 2. Results of electrolysis for brine pH +0.1 and anolyte pH 2

	Content	*Current efficiency (%)*
NaOH in caustic solution	(33%)	96.1
Cl_2 in anode gas and anolyte	(99.6% by vol.)	99.8
Active chlorine in anolyte	$1.3\,\mathrm{g\,dm^{-3}}$	–
$NaClO_3$ in anolyte	$0.0\,\mathrm{g\,dm^{-3}}$	0.0
O_2 in anode gas	0.4% by vol.	0.7
Anolyte pH	2.0	–

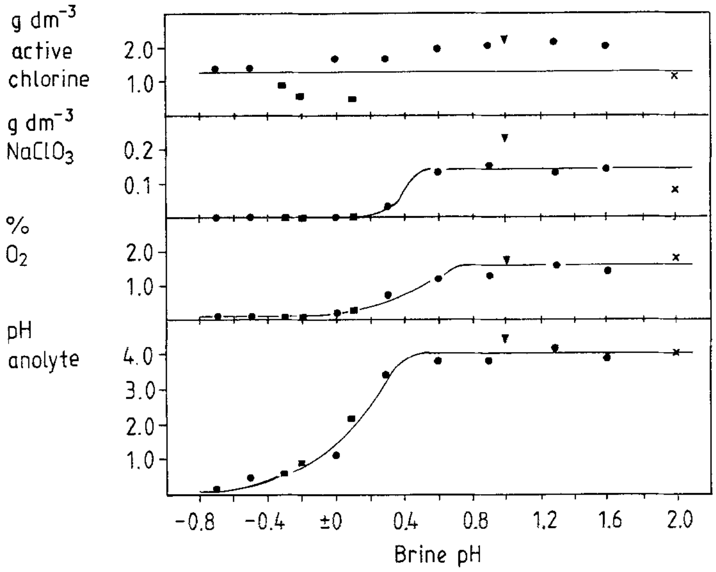

Fig. 6. Product and by-product contents in anolyte and chlorine in brine pH range −0.8 to 2.0. The points (x) at pH 2 correspond to the means of Fig. 4.

into the anode compartment with the brine if the brine pH lies within the range of 2 to 11. The anolyte pH is determined by the brine pH only if the hydroxide ions originating from the cathode compartment are neutralized with hydrochloric acid. In this case the brine pH will be 1 or less. An overdosage of acid in the brine can cause the anolyte pH to fall to 2 or lower. Then it must be assumed that the charge transport through the membrane is, in part, taken over by hydrogen ions instead of sodium ions. If these protons enter the cathode compartment, part of the caustic soda solution will be neutralized, that is the amount of caustic soda solution produced will be decreased and the caustic soda solution current efficiency will fall. Since the newer ion exchange membranes (Aciplex® from Asahi Chemical Co., Flemion® from Asahi Glass Co., and Nafion® of Dupont Co.) have a layer of carboxyl-containing fluoropolymers on the cathode side, the hydrogen ions transported toward the cathode when the anolyte is strongly acid will convert the carboxyl groups into the undissociated state. The result is an increase in the membrane's electrical resistance associated with strong heat generation, which finally leads to destruction of the ion exchange membrane, by, for example, blistering.

In this connection it must be noted that the types of membrane that carry carboxyl groups on the anode side are unsuitable for operation with strongly acidic brine. If in such cases the anolyte is acidic, the blocking action of the membrane will also occur in the anode compartment.

In an earlier paper [4] the relative concentrations of the species Cl_2, HClO and ClO^- with reference to the active chlorine content of the anolyte were calculated with the help of the equilibrium constants for Equations 1 and 6. The same data were used to calculate the curves of Fig. 8, from which the following conclusions can be drawn:

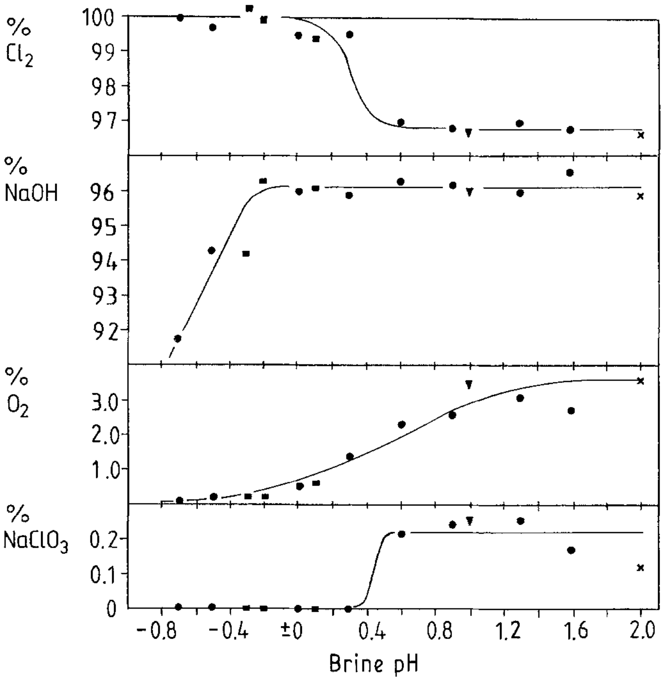

Fig. 7. Current efficiencies of products and by-products in brine pH range −0.8 to 2.0. The points (x) at pH 2 correspond to the means of Fig. 5.

(i) In the pH range 4 to 5 the predominant active chlorine species, with 80% to 96%, is HClO. Chlorine molecules are present in greater numbers than ClO^- ions.

(ii) The ratio of the concentrations $[Cl_2]/[HClO]$ is ten times larger at pH 4 than at pH 5. This also follows from the equilibrium constants of Reaction (1), because the chloride ion concentration is practically constant and ten times as many hydroxide ions are present at pH 5 than at pH 4.

In a membrane cell 26.8 Ah is required to form 1 mol NaOH, or 37.3 mol hydroxide ions are produced per kAh. At a caustic soda solution current efficiency of $x\%$, the fraction $(100 - x)/100$ of the hydroxide ions produced migrates from the cathode compartment through the membrane into the anode compartment. This method was used to calculate the values of hydroxide ion penetration in Table 3 for current efficiencies between 90% and 98%.

At a mean brine feed rate of $14\,dm^3\,(kAh)^{-1}$ about 0.014 mol $OH^-\,(kAh)^{-1}$ enters the anode compartment at a brine pH of 11 and $0.14\,mol\,H^+\,(kAh)^{-1}$ enters it at a brine pH of 2. Together with the hydroxide ion penetration of the membrane the resulting quantities of hydroxide ions per kAh shown in columns 3 and 4 of Table 3 are obtained.

The following conclusions can be drawn from Table 3:

(i) Reduction of the current efficiency from 98% to 90% causes the quantity of hydroxide ions in the anode compartment to increase by a factor of 5. But for the pH to change from 4 to 5 requires an increase by a factor of 10. Hence the anolyte pH remains within the range of 4 to 5 even when the current efficiency drops.

(ii) Use of brine with pH 11 instead of pH 2 increases the quantity of hydroxide ions only by a factor of 1.04 to 1.25. Thus the brine pH has no substantial influence on the anolyte pH, as is also evident from Fig. 4.

If electrolysis takes place with a brine pH of 0.1 and an anolyte pH of 2 (*cf.* Table 2), the hydroxide ions in the anode compartment that have passed over from the cathode compartment are only partly neutralized. A caustic soda solution current efficiency of about 96% (*cf.* Table 2) yields, according to Table 3, a quantity of hydroxide ions of $1.49\,mol\,(kAh)^{-1}$ in the anode compartment. For the quantity of brine of $14\,dm^3\,(kAh)^{-1}$ we obtain, with the help of Equation 5, a brine pH of −0.06, at which all hydroxide ions in the anode compartment are neutralized. From these considerations it can be seen that when a strongly acidic brine is used in membrane electrolysis, the recommended minimum value of 2 for the anolyte pH has been very cautiously chosen. With automatic control techniques the addition of hydrochloric acid to the brine can be carried out without any problems, for example through the determination of brine pH and brine volume with monitoring of the anolyte pH. A precondition is that unusual situations such as start-up, shut-off and stoppage of electrolysis are kept under control so that the anolyte does not become overacidic. In large electrolysis plants, acidification will not be carried out centrally in the brine system but at individual electrolysis cells or groups of cells in which the membranes installed are alike in respect of type and service age.

Table 3. Influence of brine pH on the quantity of hydroxide ions present in the anode compartment of a membrane cell

Caustic current efficiency (%)	*Hydroxide ion penetration of membrane (mol (kAh)⁻¹)*	*Resulting quantity of hydroxide ions (mol (kAh)⁻¹)*	
		Brine pH 2	*Brine pH 11*
98	0.75	0.61	0.76
96	1.49	1.35	1.50
94	2.24	2.10	2.25
92	2.98	2.84	2.99
90	3.73	3.59	3.74

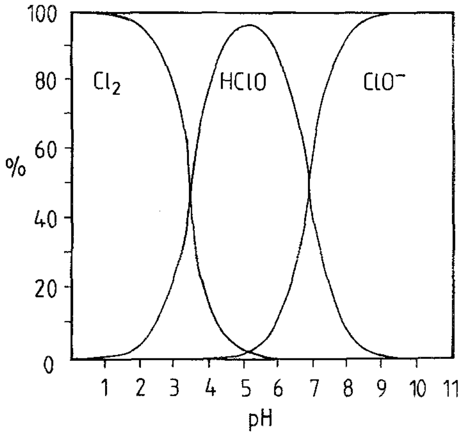

Fig. 8. Percentages of active chlorine species Cl_2, HClO and ClO^- as a function of anolyte pH at 90°C and $200\,g\,NaCl\,dm^{-3}$.

The question concerning the reduction in by-products, especially the oxygen in the anode gas, is only of interest to consumers of gaseous chlorine directly from electrolysis, because in the case of liquid chlorine [13] the oxygen is separated out on liquefaction. If gaseous chlorine containing more than 1% oxygen is used for chlorination reactions, yield losses or catalyst damage may occur. These problems have long been familiar in diaphragm electrolysis and are solved, if need be, by total liquefaction of the chlorine. In such cases the entire amount of chlorine produced is first liquefied and then vapourized again, which yields chlorine of very high purity. Consequently, where a new membrane electrolysis plant is to be built, total liquefaction of the chlorine is recommended, especially when partial liquefaction for storage purposes is desirable in any case. The difference in cost between partial and total liquefaction is generally acceptable. A more difficult case is found where production must be converted from the mercury-cell process to membrane-cell electrolysis, only plant for partial liquefaction is available and the chlorine gas consumers are accustomed to chlorine with a low oxygen content (< 1%). In this case considerably larger capital expenditures for a total liquefaction plant would be required. The problem cannot be resolved with special anode coatings that produce less oxygen. First, the oxygen content is reduced only minimally, secondly, sodium chlorate formation is increased and, thirdly, oxygen formation at the anodes rises as the membrane ages because of increased hydroxide ion penetration. Consequently, the only alternative is to add acid to the brine to reduce by-product formation.

Acknowledgements

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References

[1] D. Bergner, *J. Appl. Electrochem.* **12** (1982) 631.

[2] D. Bergner, M. Hartmann and R. Staab, *Chem. Ing. Techn.* **59** (1987) 271.

[3] D. Bergner, *Chemiker Ztg.* **101** (1977) 433.

[4] *Idem, ibid.* **104** (1980) 215.

[5] S. Kotowski and B. Busse, *Dechema Jahrestagung*, Frankfurt (1984); and *idem.* in [12], p. 310.

[6] R. Bork, Diplomarbeit, Department of Chemical Engineering, University of Dortmund (1981).

[7] M. Seko, A. Yomiyama, S. Ogawa and H. Ono, in [11], p. 87.

[8] J. H. Austin, in [12], p. 131.

[9] K. H. Simmrock, E. Griesenbeck, J. Jörissen and R. Rodermund, *Chem. Ing. Techn.* **53** (1981) 10.

[10] J. Jörissen, Dissertation, Department of Chemical Engineering, University of Dortmund (1982).

[11] 'Modern Chlor-Alkali Technology', vol. 2 (edited by C. Jackson), Ellis Horwood, Chichester (1983).

[12] 'Modern Chlor-Alkali Technology', vol. 3 (edited by K. Wall), Ellis Horwood, Chichester (1986).

[13] H. Hund and F.-R. Minz, in 'Chemische Technologie' (edited by H. Harnisch, R. Steiner and K. Winnacker), vol. 2, *Anorganische Technologie I*, Carl Hanser, München (1982) p. 424.