Chlorate and oxygen formation in alkali chloride membrane electrolysis

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During the operation of an industrial-scale membrane electrolysis plant over a number of years, a record was kept of the formation of the byproduct oxygen in the anode gas and chlorate in the anolyte parallel to the decline of the current efficiencies of the main products. It was found that the current efficiencies of the byproducts increase linearly with the declining current efficiencies of the main products, chlorine and caustic soda. Of the two types of anode used, one exhibited considerably more oxygen formation than the other. The high-oxygen anode was associated with distinctly lower chlorate formation than the low–oxygen anode. The increasing oxygen contents and chlorate formation rates associated with falling caustic current efficiency are reported for both types of anode. If hydrochloric acid is used to destroy the chlorate, the amount of acid must be increased as the caustic current efficiency falls. The amounts of hydrochloric acid required for the two types of anode are calculated as examples for 96% and 93% caustic current efficiency.

1. Introduction

In an earlier publication basic questions were discussed concerning the formation of the byproducts oxygen and chlorate in alkali chloride electrolysis by the membrane process [1]. It was shown that the sum of the current efficiencies E of all products in the anode compartment is 100% (*cf*. Equation 1) and that the ratio of the current efficiencies of the byproducts $E(O_2)/E(NaClO_3)$ is dependent on the anode material.

$$E(Cl_2) + E(O_2) + E(NaClO_3) = 100\% \quad (1)$$

$$\log E(O_2) = -c\eta(O_2) - c' \quad (2)$$

It was also demonstrated experimentally that the decrease in the oxygen current efficiency $E(O_2)$ with increasing oxygen overvoltage $\eta(O_2)$ of the anodes, behaves in accordance with the empirical Equation 2 [1]. This relationship was later confirmed by Kotowski and Busse [2] and by Couper, Brooks and Denton [3] in the form of a decrease in the oxygen content of the anode gas with increasing oxygen overvoltage of the anodes.

For electrolysis plants with membrane cells this means that the choice of a type of anode with low oxygen production will result in increased chlorate formation in the anode compartment. It has recently been pointed out [4] that a substantially better chlorine quality, such as that produced in mercury cells, cannot be achieved with low-oxygen anodes. For this reason anyone undertaking to build a new membrane electrolysis plant must consider whether, and how, the byproducts oxygen and chlorate will be treated: by the addition of hydrochloric acid to the brine [4], by total liquefaction and revaporization of the anode gas, by decomposition of the chlorate in the brine-anolyte circulation or by draining off a certain amount of brine.

These considerations become increasingly important as the membrane ages because of the associated decline in the current efficiency of the main products and the resulting increase in the formation of byproducts. Formerly, one was more concerned with the increasing specific energy consumption resulting from the declining chlorine and caustic current efficiencies and, derived from this, the economic service life of the membrane [5]. Now this matter must be considered under the aspect of byproduct formation. The service life of the membrane could be limited by a certain maximum oxygen content in the chlorine or a maximum chlorate content in the anolyte, depending on the use the chlorine is put to or the location of the plant. This leads to a new definition of the service life of the membrane.

Below we report our observations of the formation of the byproducts oxygen and chlorate for two different types of anode, while the caustic current efficiency decreased to values below 90%, during the operation of industrial membrane cells over a period of years. One aim of this study was to determine whether the measured current efficiencies of chlorine, oxygen and chlorate can be plotted as a linear function of the caustic current efficiency, as had been found previously in laboratory cells (*cf*. Figs 4 and 5 in [1]). A further objective was to show the dependence of the oxygen content in the chlorine and the chlorate formation in the membrane cells on the caustic current efficiency, in order to obtain an indication for the chlorine user and for chlorate disposal.

2. Experimental details

In an experimental plant with 2.7 m² Hoechst–Uhde

Table 1. Operational data for membrane electrolysis

Membrane	Naflon® 90209
Electrode gap	3 mm
Area of anode per element	2.72 m^2
Current strength	8.2, 9.5 and 10.9 kA
Current density	3.0, 3.5 and 4.0 kA m^{-2}
Brine volume	15 dm^3 (kAh)$^{-1}$
Brine pH	10
Brine concentration	25% NaCl (300 g dm^{-3})
Anolyte concentration	18% NaCl (200 g dm^{-3})
Caustic concentration	33% NaOH
Cell temperature	88–90 °C
Chlorine pressure	25–35 mbar
H$_2$/Cl$_2$ differential pressure	15–25 mbar

membrane cells [6] with a chlorine capacity of 10 000 tonne per year, the various electrolysers were equipped with horizontally louvered titanium anodes (shown in Figs 3 and 5 of [6]) with different anode activation coatings. The coatings were made of mixtures of oxides of platinum metals and titanium dioxide. Because of various outside influences on the membranes, and as the result of experiments with the cells, the current efficiency had fallen to values below 90% within 3 years, that is to say faster than usual in production plants. In these cells the formation of the byproducts oxygen and chlorate was observed for two extreme types of anode as a function of the current efficiency. Table 1 summarizes the operational data for the membrane cells.

The current efficiencies were calculated from analytical determination of the main products and byproducts and measurement of the electrolysis current [7]. The oxygen content of the anode gas was determined by gas analysis after absorption of the chlorine in caustic solution and the oxygen in an alkaline pyrogallol solution. Chlorate analysis was performed by ion chromatography (Dionex® DX-100).

3. Results

The current efficiencies for chlorine, oxygen and chlorate, as a function of the caustic current efficiency, are shown in Figs 1 and 2. The plotting method corresponds to that used in Figs 4 and 5 of [1]. However, the current efficiencies for chlorine on the one hand, and for chlorate and oxygen on the other, are not, as in [1], all plotted together on one set of coordinates but on two part-graphs with the same abscissa and ordinate scales, in order to obtain better resolution. In the part-graphs for the chlorine current efficiencies in Figs 1 and 2, broken straight lines are used to connect the origins with the 100% points. These broken straight lines never really fit the experimental data because the chlorine current efficiency is always one or more percentage points higher than the caustic current efficiency. The reason is that only part of the hydroxide ions from the cathode compartment are transformed into oxygen and chlorate ions. The rest leave the cell as hypochlorite, hypochlorous acid and dissolved chlorine and are added to the gaseous chlorine production, thus making the chlorine current efficiency
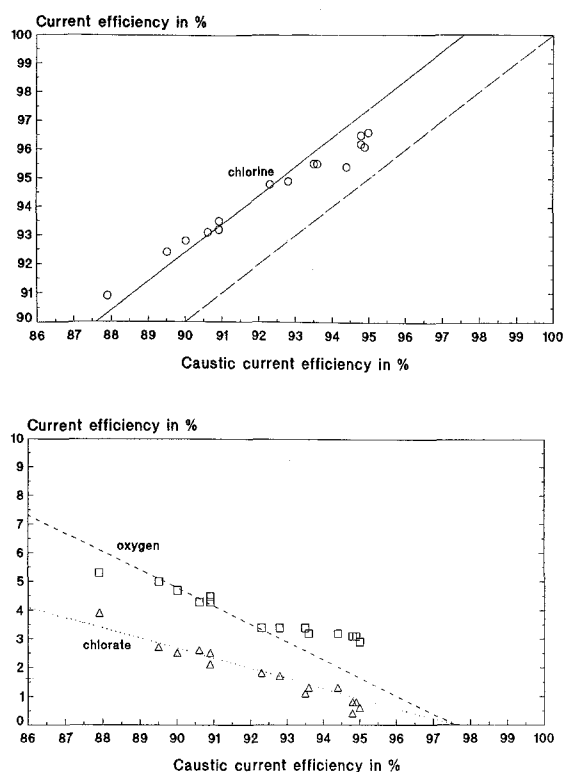

Fig. 1. Chlorine, oxygen and chlorate current efficiencies for high–oxygen anodes.

higher than the caustic current efficiency. The straight lines through the points obtained experimentally were then drawn parallel to these first lines. In Fig. 2 the straight line drawn in this way shows a good fit to the measurement points below about 94% caustic current efficiency. In Fig. 1 the fit is not quite so good. But in both cases the measurement points above about 94% caustic current efficiency seem to deviate toward the
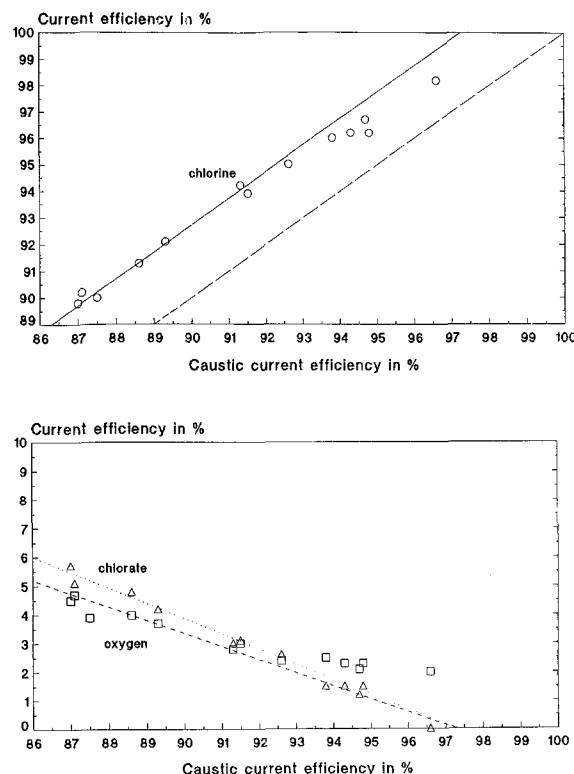

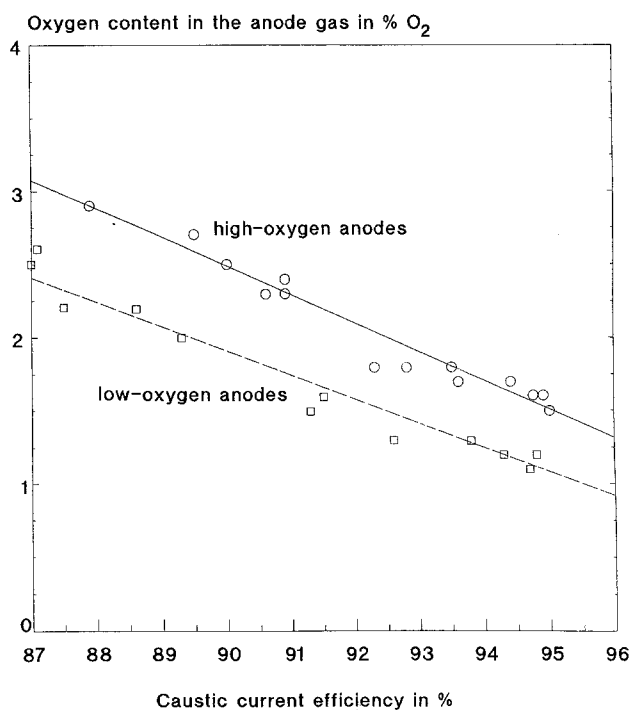Fig. 2. Chlorine, oxygen and chlorate current efficiencies for low–oxygen anodes.

Oxygen content in the anode gas in % O_2

Fig. 3. Oxygen formation as a function of the caustic current efficiency for high–oxygen and low–oxygen anodes.

broken line, that is to say in the direction of lower chlorine current efficiencies.

The straight lines for chlorate and oxygen in the lower part–graphs of Figs 1 and 2 have been drawn through the clusters of points so that they intersect the abscissa at the value of caustic current efficiency where the straight line for chlorine current efficiency attains 100%. Moreover, these lines are drawn in such a way that Equation 1, above, is satisfied by the three straight lines for chlorine, oxygen and chlorate for all values of the caustic current efficiency. In both graphs at caustic current efficiencies above 92–93%, the ex-
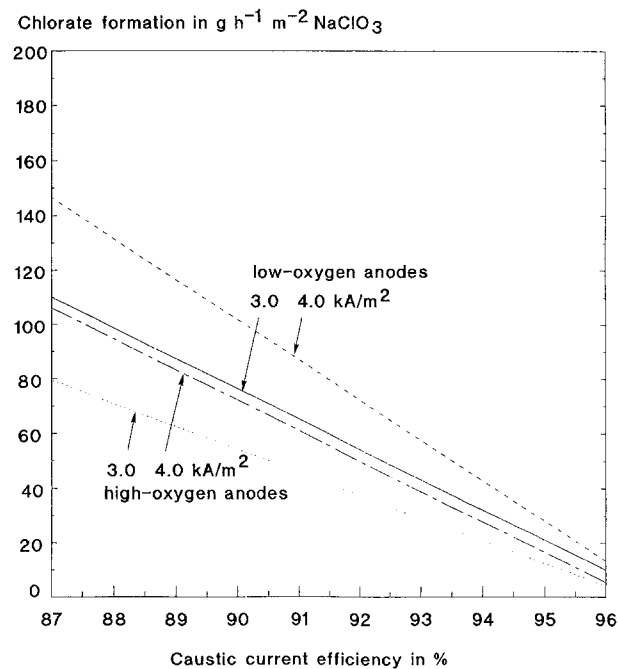

Fig. 4. Chlorate formation as a function of the caustic current efficiency for high–oxygen and low–oxygen anodes.

perimentally obtained points for oxygen deviate quite clearly from the constructed straight lines in the direction of higher oxygen current efficiencies. In Fig. 1 at caustic current efficiencies above 94–95% the chlorate measurement points appear to deviate from the straight line in the direction of lower chlorate current efficiencies. Since this behaviour is not observed in Fig. 2, these chlorate points could be due to experimental error. In fact, in Fig. 2 a better fit is found between the constructed straight lines and the measured points than in Fig. 1, as is also the case for the chlorine current efficiency.

A comparison of the two lower part-graphs of Figs 1 and 2 clearly shows that, over the entire range of the caustic current efficiencies, the one type of anode exhibits a higher and the other type a lower oxygen current efficiency. Thus we can designate the two types of anode as a high–oxygen anode and a low–oxygen anode. It is also evident from the graphs that chlorate formation is considerably lower with the high–oxygen anode than with the low–oxygen anode.

In commercial operation of electrolysis plants, however, the current efficiency figures are of less interest than the oxygen content of the chlorine and the amount of chlorate formed in the anolyte. Consequently, Fig. 3 shows the oxygen content of the anode gas for both types of anode as a function of the caustic current efficiency. It was possible to plot the measured values directly on the graph because, in accordance with Equation 3 (cf.[1]), the oxygen content of the anode gas is independent of the current density, which was varied within the range from 3.0 to $4.0 \, kA \, m^{-2}$ during trial operation. In addition to oxygen the anode gas can contain about 0.2–0.3% CO_2 from the soda added during primary brine purification and 0.1–0.2% inert gas. Figure 3 shows that the oxygen content rises linearly as the caustic current efficiency falls from 96% to 87%. For the low–oxygen anode this rise is from 0.9 to 2.4% and for the high–oxygen anode from 1.3 to 3.1%.

$$V_{O_2}/V_{Cl_2} = 0.5E(O_2)/E(Cl_2) \qquad (3)$$

$$\dot{m} = 0.00662E(NaClO_3)i \qquad (4)$$

Another way has to be found for plotting the graph for chlorate formation. In this case the analytically determined $NaClO_3$ content of the anolyte cannot simply be plotted as a function of caustic current efficiency because, on the one hand, the rate of chlorate formation is a function of the current density, i (cf. Equation 4), and on the other hand the brine flowing into the membrane cell already contains chlorate. Hence the amount of chlorate formed would have to be calculated with the use of the anolyte/brine volume ratio (0.7–0.8), which would have to be determined separately. But since the chlorate current efficiency data are available in Figs 1 and 2, the rate of formation, $\dot{m}$, of sodium chlorate in the anode compartment was calculated in $g \, h^{-1} \, m^{-2}$ in accordance with Equation 4, using a linear regression of the measurement data for chlorate current efficiencies and the

Table 2. Chlorate formation and hydrochloric acid consumption for chlorate destruction in a membrane electrolysis plant with a chlorine capacity of 100 000 tonne per year. (Example calculated for anode area of 2600 m² and current density of 3.5 kA m⁻²)

Caustic current efficiency/%	High–oxygen anode NaClO₃ formation /kgh⁻¹	HCl* amount /kgh⁻¹	Low–oxygen anode NaClO₃ formation /kgh⁻¹	HCl* amount /kgh⁻¹	Neutralization HCl† amount /kgh⁻¹
96	12	25	30	62	494
93	88	181	131	269	866

* For destruction of the chlorate in the anolyte after leaving the cell.
† For feeding into the anode compartment with the brine to reduce the formation of by-products.

current density i in kA m⁻². Figure 4 shows the graphs obtained for 3.0 and 4.0 kA m⁻². The results indicate a considerable increase in chlorate formation from 4 to 79 g h⁻¹ m⁻² at 3 kA m⁻² for the high–oxygen anode and from 10 to 110 g h⁻¹ m⁻² for the low–oxygen anode.

Table 2 gives calculated data for conditions closely resembling those encountered in normal operation, in which the current efficiency of an industrial electrolysis plant (100 000 tonne chlorine per year) falls from the initial level of 96% to 93%. For a high–oxygen anode the NaClO₃ formation increases from 12 to 88 kg h⁻¹ and for a low–oxygen anode from 30 to 131 kg h⁻¹. The chlorate accumulates in the brine circulation system if it is not destroyed or removed. If chlorate is destroyed with hydrochloric acid in accordance with Equation 5, at least the stoichiometric amount of HCl indicated in Table 2, but in practice excess HCl, must be added to the anolyte.

$$NaClO_3 + 6HCl = 3Cl_2 + NaCl + 3H_2O \quad (5)$$
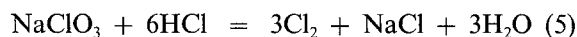
These amounts of HCl in the 3rd and 5th columns of Table 2 are compared with the amount in column 6, which would be required to suppress the formation of byproducts through the addition of HCl to the feed brine and, thus, through neutralization of the hydroxide ions in the anode compartment [4]. This amount is considerably larger than that required to destroy the chlorate formed. It must be borne in mind, however, that the addition of acid to the brine also greatly reduces oxygen formation [4].

4. Discussion

The reason why the straight lines are plotted in Figs 1 and 2 for the current efficiencies of the products in the anode compartment is given in [1]. There the values of the efficiencies for chlorine, oxygen and chlorate, in the very much larger range of caustic current efficiencies from 45% to 96%, fit the straight lines well, although here too, there is a slight indication of deviation of the measurement points from the straight lines at high caustic current efficiencies. The deviations of the measurement points from the solid straight lines drawn in Figs 1 and 2 are in the same direction, for chlorine downwards and for one by-product, here oxygen, upwards. As a result of this fact Equation 2 retains its validity despite these deviations, which probably, therefore, do not stem from measurement errors.

Parallels can be seen with brine acidification to suppress byproduct formation. In the present case the number of hydroxide ions in the anode compartment is reduced by the decreasing penetration of the membrane as the caustic current efficiency rises. In the case of brine acidification [4] the number of hydroxide ions in the anode compartment is reduced by the increasing proton supply to the brine at a higher acid content. From Fig. 7 in [4] it can be seen that the oxygen current efficiency is still at a rather high level when the chlorate current efficiency has already fallen to zero. A noticeable oxygen current efficiency is still present, even in a very strongly acid environment.

The curves of the chlorine and oxygen efficiencies in Figs 1 and 2 in the region near 100% caustic current efficiency cannot, however, be predicted from the measurements presented here. But two possibilities can be discussed. In the first instance the curves can run parallel to the caustic current efficiency axis, which would make $E(Cl_2) < 100\%$ and $E(O_2) > 0\%$ at 100% caustic current efficiency. The alternative case would be a transition of the chlorine efficiency data points from the solid straight line to the broken straight line in Figs 1 and 2 and the corresponding behaviour of the oxygen current efficiency data points. In this case $E(Cl_2) = 100\%$ and $E(O_2) = 0\%$ at 100% caustic current efficiency. The latter possibility is the more likely one because equation 29 in [1] states that $E(Cl_2) = E(NaOH)$ if no hydroxide ions are transformed into HClO and no hydroxide ions are neutralized by H⁺ ions. That seems to be possible at high caustic current efficiencies with no acid addition to the brine. Unfortunately, this question cannot be resolved experimentally because membranes with 100% selectivity are not available.

Acknowledgements

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