CATHODIC AND ANODIC EFFICIENCY LOSSES IN CHLORATE ELECTROLYSIS*

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Abstract—In chlorate electrolysis, chlorine, formed at the anode, and alkali, formed at the cathode, react in the bulk of the electrolyte to form hypochlorite which reacts further chemically to form chlorate. However, part of the hypochlorite is lost through cathodic reduction to chloride ions and anodic oxidation with oxygen evolution. Furthermore, some chlorate is reduced cathodically.

These current efficiency losses have been investigated experimentally. It was found that the cathodic or reduction loss is directly proportional to the hypochlorite concentration ($ClO^- + HClO$), inversely proportional to the current density, increases with temperature to the extent of about 3% per °C, decreases with an increase of the NaCl concentration and, at higher hypochlorite concentrations, also decreases with an increase of the $NaClO_3$ concentration. Finally, the reduction loss is independent of pH between 6·5 and 10·5 if the total hypochlorite concentration is kept constant. All these effects are explained by the assumption that the rate of reduction of hypochlorite is limited by convective diffusion of hypochlorite to the cathode surface. The effects of the NaCl and $NaClO_3$ concentrations are explained by their influence on the viscosity of the electrolyte and hence on the diffusion constant.

According to the experimental data, the anodic or oxidation loss is directly proportional to the hypochlorite concentration, inversely proportional to the c.d., increases with temperature at about 2% per °C and is independent of pH between 6·5 and 10·5 at a constant hypochlorite concentration. These effects show that also the anodic oxidation of hypochlorite is governed by convective diffusion.

Résumé—Dans l'électrolyse des chlorates, le chlore engendré anodiquement réagit au sein de l'électrolyte sur l'alcali engendré cathodiquement, pour former de l'hypochlorite, se transformant à son tour chimiquement en chlorate. Mais une partie de l'hypochlorite est détruite par réduction cathodique en chlorure, ainsi que par oxydation anodique libératrice d'oxygène gazeux. De plus, une partie du chlorate est conjointement réduite cathodiquement. Les rendements de courant correspondant à ces pertes ont été établis expérimentalement. La perte cathodique est proportionnelle à la concentration d'hypochlorite ($ClO^- + HClO$), inversement proportionnelle à la densité de courant, croît avec la température à raison d'environ 3 pour cent par °C, est fonction décroissante de la concentration en NaCl et de la concentration en $NaClO_3$ (aux hautes teneurs en hypochlorite). Elle est indépendante du pH entre 6,5–10,5 si la teneur en hypochlorite est maintenue constante. Ces effets s'expliquent en admettant que la vitesse de réduction de l'hypochlorite est limitée par sa diffusion convective vers la cathode, NaCl et $NaClO_3$ modifiant d'autre part la viscosité de la solution, dont dépend le coefficient de diffusion. Par ailleurs, la perte anodique est proportionnelle à la concentration d'hypochlorite, inversement proportionnelle à la densité de courant, croît avec la température d'environ 2 pour cent par °C, est indépendante du pH entre 6,5–10,5 à concentration constante d'hypochlorite. Ces effets peuvent dès lors s'interpréter aussi par une diffusion convective régulatrice de l'hypochlorite.

Zusammenfassung—In der Chloratelektrolyse reagiert in der Hauptlösung des Elektrolyten an der Anode gebildetes Chlor mit dem kathodisch gebildeten Alkali. Dabei entsteht Hypochlorit, welches chemisch weiter reagiert und Chlorat bildet. Ein Teil des Hypochlorits geht jedoch durch kathodische Reduktion zu Chlorid-Ionen und durch anodische Oxidation mit Sauerstoffentwicklung verloren.

Diese Verluste in der Stromausbeute sind experimentell untersucht worden. Man fand, dass der kathodische oder Reduktionsverlust der Hypochloritkonzentration ($ClO^- + HClO$) direkt proportional ist, zur Stromdichte umgekehrt proportional ist, bei steigender Temperatur mit ungefähr 3% per °C steigt, bei steigender NaCl-Konzentration abnimmt und, bei hohen Hypochloritkonzentrationen, auch mit steigender $NaClO_3$-Konzentration abnimmt.

Schliesslich ist der Reduktionsverlust unabhängig vom pH zwischen 6,5 und 10,5, wenn die totale Hypochloritkonzentration konstant gehalten wird.

Auch der anodische oder Oxidationsverlust ist der Hypochloritkonzentration direkt proportional, der Stromdichte umgekehrt proportional, nimmt bei steigender Temperatur mit rund 2% per °C zu, und ist bei konstanter Hypochloritkonzentration unabhängig vom pH zwischen 6,5 und 10,5.
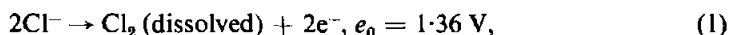
Alle diese Effekte werden durch die Annahme, dass die Geschwindigkeit der kathodischen Reduktion und der anodischen Oxidation des Hypochlorits durch die konvektive Diffusion des Hypochlorits zu den Elektroden begrenzt wird, erklärt.
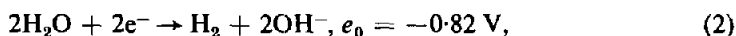
MAIN REACTIONS IN CHLORATE ELECTROLYSIS

CHLORATE is manufactured by electrolysis of a neutral solution of sodium chloride between graphite anodes and steel cathodes or between bipolar graphite electrodes. The primary products of the electrode reactions, chlorine and alkali, react in the bulk electrolyte between the electrodes to form hypochlorite, which is subsequently transformed to chlorate by chemical auto-oxidation (disproportionation). The latter reaction is favoured by a large electrolyte volume and is often carried out in specially provided compartments of the cells or even in a separate reactor after the electrolysis cells.

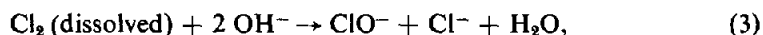The main reactions in the chlorate electrolysis process can thus be written:

at the anode

$$2Cl^- \rightarrow Cl_2 \text{ (dissolved)} + 2e^-, e_0 = 1 \cdot 36 \text{ V}, \tag{1}$$

at the cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, e_0 = -0 \cdot 82 \text{ V}, \tag{2}$$

between the electrodes

$$Cl_2 \text{ (dissolved)} + 2 OH^- \rightarrow ClO^- + Cl^- + H_2O, \tag{3}$$

in the bulk electrolyte

$$2HClO + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+, \tag{4}$$

or

$$HClO + 2ClO^- \rightarrow ClO_3^- + 2Cl^- + H^+. \tag{5}$$

That the primary product at the anode is chlorine according to reaction (1) is shown by the formation of solid chlorine hydrate by electrolysis at a low temperature, and even if the electrolyte is alkaline.[1]

The dissociation constant of hypochlorous acid is given by various authors[2-5] as $3 \cdot 0$, $3 \cdot 6$, $5 \cdot 0$ and $6 \cdot 8 \times 10^{-8}$. Accepting the mean $4 \cdot 6 \times 10^{-8}$ or $10^{-7 \cdot 3}$, we find that reaction (4) has a maximal reaction velocity at $pH = 7 \cdot 3 - \log 2 = 7 \cdot 0$, while the optimum pH for reaction (5) is $7 \cdot 3 + \log 2 = 7 \cdot 6$. The reactions have about the same velocity constants and so the optimum pH in the cell would be $7 \cdot 3$ at 25°C, corresponding to $7 \cdot 0$ at 40–50°C.[4]

In writing the main reactions above and the subsidiary reactions below, the standard states were chosen taking account of the fact that the anode film is acid, the cathode film alkaline. Accordingly, the hypochlorite is written as HClO at the anode and as ClO⁻ at the cathode. The standard electrode potentials given after the reactions were derived from thermodynamic data.[6] As a comparison the potential of a non-impregnated graphite anode in a chlorate cell was found to be $+1 \cdot 5$ V and the potential of a steel cathode in the presence of chromate in the electrolyte $-1 \cdot 2$ V, both values measured at a c.d. of 5 A/dm² and relative to the standard hydrogen electrode.

In the chlorate electrolysis cell a number of subsidiary reactions occur, reducing the current efficiency of the process. These loss reactions can be divided into cathodic or reduction losses and anodic or oxidation losses.
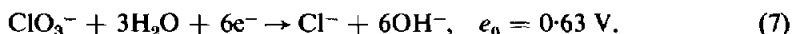
<div align="center">SUBSIDIARY REACTIONS</div>

Cathodic loss reactions

The cathodic or reduction efficiency losses occur on the cathode surface and are due to

1. *Reduction of hypochlorite*

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-, \quad e_0 = 0.89 \text{ V} \tag{6}$$
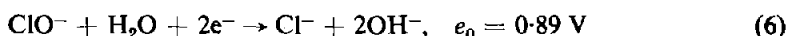
and, to a small extent, to

2. *Reduction of chlorate*

$$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-, \quad e_0 = 0.63 \text{ V}. \tag{7}$$

In accordance with the well-known chemical properties of these ions, hypochlorite is much more easily reduced than chlorate.

The cathodic losses were studied recently by Nagai and Takei.[7] Their results indicate that these losses are governed by diffusion of hypochlorite towards the cathode surface. However, such important variables as hypochlorite concentration and pH were not controlled in the study mentioned.
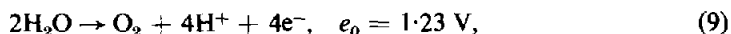
Anodic loss reactions

In principle, the following anodic or oxidation loss reactions have to be considered:
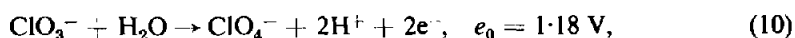
A. *Anodic reactions other than chloride ion discharge.* (a) Oxygen evolution from hypochlorite, which reaction will also yield chloride ions and seems to be accompanied by chlorate formation. This electrode process is usually described by the following resultant reaction:

$$6HClO + 3H_2O \rightarrow \tfrac{3}{2}O_2 + 4Cl^- + 2ClO_3^- + 12H^+ + 6e^-, \quad e_0 = 1.14 \text{ V},$$
$$\tag{8}$$
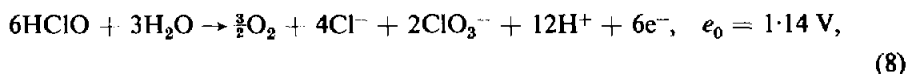
(b) Oxygen evolution from water

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \quad e_0 = 1.23 \text{ V}, \tag{9}$$

(c) Oxidation of chlorate to perchlorate.

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-, \quad e_0 = 1.18 \text{ V}, \tag{10}$$

B. *Chlorine losses in the cell gases*

$$Cl_2 \text{ (dissolved)} \rightarrow Cl_2 \text{ (gas)}. \tag{11}$$

C. *Decomposition of hypochlorite in the electrolyte*

$$2HClO \rightarrow 2HCl + O_2. \tag{12}$$

As shown by the results, reaction (9) is of small importance in concentrated chloride solutions. While some perchlorate is formed according to reaction (10) at magnetite anodes, which have a high oxygen overvoltage, it is negligible at graphite anodes. So are the chlorine losses according to equation (11), if the electrolyte is not allowed to become acid. The decomposition of hypochlorite according to reaction

(12) is catalysed by heavy metal ions, such as cobalt from graphite anodes impregnated with linseed oil, containing cobalt compounds as siccatives. In pure electrolytes, however, this loss reaction can also be neglected. This means that the main oxidation loss will be oxygen evolution according to equation (8).

PLAN OF EXPERIMENTAL INVESTIGATION

In the present investigation, an experimental study was made of the efficiency losses, consisting of the reduction losses according to equations (6) and (7) and the oxidation losses due to anodic evolution of oxygen according to reactions (8) and (9). The experimental conditions were such that other loss reactions would be negligible. Furthermore, since the hypochlorite concentration was known to be of prime importance for the efficiency losses, special care was taken to study the influence of this variable. It was thus desirable to vary the hypochlorite concentration between fairly wide limits (0–250 mmole ($HClO + ClO^-$)/l.) and to keep it practically constant during each run. These conditions can be fulfilled if the consumption of hypochlorite due to chemical formation of chlorate according to reactions (4) and (5) is suppressed. This can be done either by electrolysis at a very low temperature ($0°C$) or at a high pH (>9). Most of the experiments were carried out at high pH and normal temperatures. Some runs were made at a low temperature in solutions of lower pH, however. The electrolysis factors, whose influence on the efficiency losses were studied were: current density, temperature, concentrations of hypochlorite, chloride and chlorate, pH and electrode material.

In industrial chlorate electrolysis, chromate is added to the electrolyte to suppress reduction of hypochlorite at the cathode, corrosion inhibition and pH buffering being further advantages of the chromate addition. The action of the chromate is explained by the formation on the cathode surface of a thin film, probably consisting of chromium oxides, which reduces the effective cathode surface area and thus the reduction of hypochlorite. The same effect can be attained in chromate-free electrolytes by using a chromium-plated cathode.[7,8]

Preliminary experiments showed, however, that an addition of chromate to the electrolyte led to bad reproducibility in studies of cathodic reduction losses. In the experiments reported below no such addition was made, therefore, but the action was simulated by using a small cathode area, i.e. a high cathodic c.d.

Apparatus

The electrolyte cell consisted of a 3000-ml flask with round bottom and a wide neck. It was closed by a rubber stopper carrying the electrodes, a thermometer, a contact thermometer and a gas outlet. The anode consisted of a cylindrical tube of inner diameter 50 mm and height 60 mm. The cathodes, consisting of steel, or in some experiments of graphite, were cylinders of diameter 32·00, 21·05, 14·03, 7·06, 3·22, 1·94 and 1·00 mm, thus allowing the cathodic c.d. to be varied between wide limits (6·6–212 A/dm^2) at a constant anodic c.d. (usually 4 A/dm^2) and a constant ratio of current to electrolyte volume (ca. 1·3 A/l). The position of the electrodes to each other was fixed by PVC plates, serving also to reduce edge effects. The electrode arrangement is shown in Fig. 1.

The electrolysis cell was placed in a thermostat bath. Temperatures below room temperature were maintained by means of an alcohol bath, the alcohol being circulated

through a refrigerator by a pump, regulated by the contact thermometer. To maintain soloution homogeneity a magnetic stirrer was provided at the bottom of the cell. The stirrer did not influence the flow conditions at the electrodes, which were determined mainly by gas evolution.
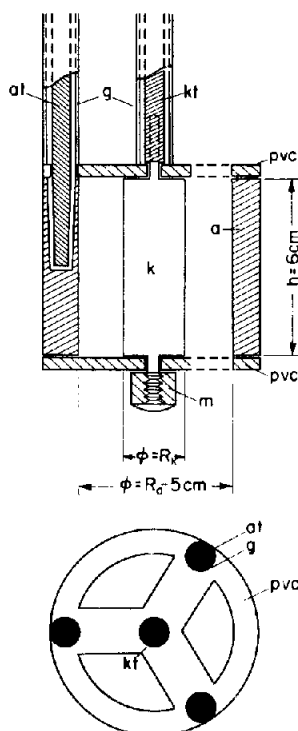

FIG. 1. Electrode arrangement in electrolysis cell

a anode (graphite)
k cathode (steel or graphite)
at anode conductors (3, graphite)
kt cathode conductor (steel)
g insulating glass tube
pvc plates of polyvinyl chloride
m nut of polyvinyl chloride

The efficiency losses were obtained from the amount and composition of the cell gas, which was collected in a gas burette, provided with a tube for absorbing oxygen in alkaline pyrogallol solution. From the volume of total cell gas, a, the volume of oxygen in it, b, and the gas volume, c, evolved in a gas coulometer connected in series with the electrolysis cell, the efficiency losses were obtained:

$$\text{Reduction loss} = P_{\text{red}} = \frac{(2c/3) - (a - b)}{(2c/3)} \cdot 100\%, \tag{13}$$

$$\text{Oxidation loss} = P_{\text{ox}} = \frac{b}{(c/3)} \cdot 100\%. \tag{14}$$

Experimental procedure

The electrolyte solutions were prepared by dissolving reagent grade sodium chloride

and sodium chlorate in distilled water. The desired concentration of hypochlorite was obtained by adding the equivalent amount of sodium hydroxide and bubbling through chlorine gas until pH reached a value between 9 and 10. Due to small changes in composition during the relatively short electrolysis experiments, the same electrolyte could usually be used in several successive runs. The pH of the solution was determined by a glass electrode and its hypochlorite concentration by iodometric titration. The electrolyte was run into the electrolysis vessel and brought to the desired temperature.

The iron cathodes usually used were degreased and cleaned with emery paper, inserted in the electrode assembly, which was connected to a 12-V battery in series with a variable resistor and then quickly lowered into the electrolyte. From this point the electrolysis time was measured by a stop watch. The electrolyte volume was chosen in such a manner that the gas volume between the electrolyte level and the rubber stopper was practically nil. The cell gas therefore reached equilibrium composition very quickly. After about 10 min a gas analysis was made. This was repeated in certain cases. After 15–30 min electrolysis, the current was broken and the total time of electrolysis read off from the stop watch. A check of the amount of electricity passed in a run was obtained from an Ah-meter in series with the cell. Finally, pH and hypochlorite concentration were again determined.

RESULTS AND DISCUSSION

Experimental conditions and results obtained are recorded in Tables 1–4 and Figs. 2–6.

From experiments 22–27, see Table 4 and Fig. 6, carried out at 0°C it is evident that the efficiency losses are independent of pH between 6·5 and 10·5. Hence the study of the losses at higher temperatures at pH-values around 10 is justified. The independence of pH also shows that HClO and ClO⁻ react in the same way at the electrode and furthermore, that oxygen evolution from water according to reaction (9) is negligible under the conditions studied.

Considering first the *reduction* loss, we find that P_{red}

(1) increases proportionally to the hypochlorite concentration (HClO + ClO⁻), Figs. 2 and 3
(2) Is approximately inversely proportional to the current density, Figs. 7 and 8
(3) Increases slowly (about 3 % per °C) with temperature, Fig. 5
(4) Decreases with an increase of the NaCl concentration and, at higher hypochlorite concentrations, also with an increase of the NaClO₃ concentration.

All these effects are explained by the assumption that the rate of reduction of hypochlorite is limited by convective diffusion of hypochlorite to the cathode surface. This assumption seems reasonable, since the hypochlorite is apparently formed in the bulk electrolyte by reaction between dissolved chlorine from the anode and alkali from the cathode. In the cathode film the hypochlorite concentration is low, however. Furthermore, even in the bulk electrolyte the hypochlorite concentration is low (ca. 0·1 M) compared to the concentrations of NaCl and NaClO₃.

For the limiting current, I_{lim}, of hypochlorite reduction we have

$$I_{lim} = 2F \cdot A \cdot D \cdot \frac{c_{hyp}}{\delta}, \tag{15}$$

TABLE 1. INFLUENCE OF HYPOCHLORITE CONCENTRATION ON ANODIC AND CATHODIC EFFICIENCY LOSSES AT 25°C AT VARIOUS CATHODIC CURRENT DENSITIES. ANODIC CURRENT DENSITY, $i_a = 4$ A/dm². ELECTROLYTE: 150 g/l NaCl (2·56 M), pH 10 (9·5–10·5)

Expt. No.	Cathodic c.d. i_c(A/dm²)	[NaClO] before (mmole/l)	after	P_{red} (%)	P_{ox} (%)	$F.V.\Delta c_{hyp}/Q$	x
1a	14·5	52·0	—	16·7	16·7	+0·122	2·52
1b	14·5	—	54·5	12·8	19·7	+0·122	2·24
2a	14·5	52·2	—	17·4	22·4	+0·121	1·61
2b	14·5	—	55·7	16·9	25·4	+0·121	1·32
3a	14·5	108·7	—	19·8	33·4	+0·003	1·39
3b	14·5	—	108·8	20·3	33·1	+0·003	1·39
4a	14·5	160·4	—	34·4	43·2	−0·291	1·89
4b	14·5	—	152·3	33·3	43·3	−0·291	1·86
15	14·5	201·4	192·9	53·2	57·5	−0·602	1·91
5a	14·5	259·2	—	58·0	60·5	−0·681	1·95
5b	14·5	—	235·4	49·2	55·2	−0·681	2·39
10	29·0	54·4	56·3	8·78	18·3	+0·136	2·50
56*	29·0	—	99·2	16·2	44·1		
11	29·0	111·9	110·8	16·2	31·8	−0·078	2·13
12	29·0	165·9	161·1	20·6	46·5	−0·336	2·16
14	29·0	208·2	201·4	31·0	54·5	−0·481	2·04
13	29·0	216·1	208·1	37·7	52·3	−0·548	2·28
6a	63·0	56·1	—	5·26	14·5	+0·221	2·40
6b	63·0	—	62·3	7·89	16·8	+0·221	1·89
7	63·0	115·9	115·5	11·2	31·3	−0·027	2·01
8	63·0	170·3	166·3	13·5	46·4	−0·286	2·10
9	63·0	220·4	214·5	18·8	53·2	−0·425	2·13
18	105·0	57·8	60·7	3·85	18·8	+0·206	1·92
57	105·0	99·2	—	8·50	24·0		
21	105·0	184·3	180·0	13·8	49·8	−0·302	1·94
17	204·0	55·0	57·7	5·26	16·5	+0·178	2·58
19	204·0	60·7	62·6	3·76	18·8	+0·137	2·67
20	204·0	189·3	184·3	12·8	49·3	−0·344	2·16
16	204·0	192·9	188·2	11·6	49·1	−0·330	2·14
33a†	29·0	161·0	158·5	30·1	41·6		
33b†	29·0	158·5	154·8	27·6	40·7		
33c†	29·0	154·8	150·0	27·2	39·5		
31†	29·0	169·2	165·0	39·4	43·0		
30†	29·0	174·5	169·2	47·4	43·4		
32†	29·0	165·0	161·0	33·2	42·4		

* $i_a = 1$ A/dm².

† Graphite cathode.

with A = electrode surface (cm²), D = diffusion coefficient (cm²/sec) of hypochlorite, c_{hyp} = hypochlorite concentration ($\Sigma HClO + ClO^-$) (moles/cm³), δ = thickness of Nernst diffusion layer (cm), F = Faraday's constant.

The effects 1–4 above are explained in the following way:

1. According to equation (15), P_{red} in the absence of chlorate should be directly proportional to the hypochlorite concentration. Fig. 2 shows that within wide limits this is really the case. In the presence of chlorate (cf. Fig. 3) there is a certain reduction loss also at hypochlorite concentration nil, evidently corresponding to reduction of chlorate according to reaction (7). The reaction loss still increases linearly with hypochlorite concentration, although more slowly. As shown below, this is due to decrease of the diffusion coefficient caused by the higher viscosity in the presence of chlorate.

TABLE 2. Influence of hypochlorite concentration on anodic and cathodic efficiency losses at 25°C at various cathodic current densities. Anodic current density, $i_a = 4$ A/dm². Solution: 150 g/l NaCl, (2·56 M), 273 g/l NaClO₃, (2·56 M), pH 7–10

Expt. no.	Cathodic c.d. i_c(A/dm²)	[NaClO] before (mmole/l)	after (mmole/l)	P_{red} (%)	P_{ox} (%)	F.V.$\Delta c_{hyp}/Q$	x
37	14·5	0·0	4·05	8·6	3·65	+0·390	2·67
40	14·5	12·9	17·1	9·21	5·85	+0·402	0·78
42	14·5	119·0	118·6	17·3	31·3	−0·042	1·91
44	14·5	—	176·6	15·7	40·8		
45	14·5	176·6	174·1	15·9	41·0	−0·222	2·13
39	29·0	8·6	12·9	3·09	4·48	+0·415	2·10
43	29·0	118·6	118·9	7·33	28·8	−0·028	2·02
46	29·0	174·1	172·6	11·0	39·3	−0·158	2·07
47	29·0	172·6	171·2	10·8	36·2		
38	105·0	4·05	8·6	2·21	2·66	+0·418	4·34
41	105·0	118·9	119·0	5·96	26·7	+0·007	2·47
48	105·0	∼170·0	∼170·0	4·33	36·4		
49	105·0	—	169·0	4·90	37·0		

TABLE 3. Influence of temperature on anodic and cathodic efficiency losses at 0·1 M/(HClO + ClO⁻) (values at this concentration calculated from experimental data). Anodic current density, $i_a = 4$ A/dm², cathodic current density, $i_c = 63$ A/dm². Solution: 150 g/l NaCl (2·56 M)

Temperature (°C)	P_{red} (%)	P_{ox} (%)
0	4·7	19·0
25	9·0	26·0
45	12·0	33·0
45	12·0	34·0
45	15·0	38·0

TABLE 4. Influence of pH at 0°C on anodic and cathodic efficiency losses. Anodic current density, $i_a = 4$ A/dm², cathodic current density, $i_c = 63$ A/dm². Solution: 150 g/l NaCl (2·56 M), 149–179 mmoles/l (HClO + ClO⁻)

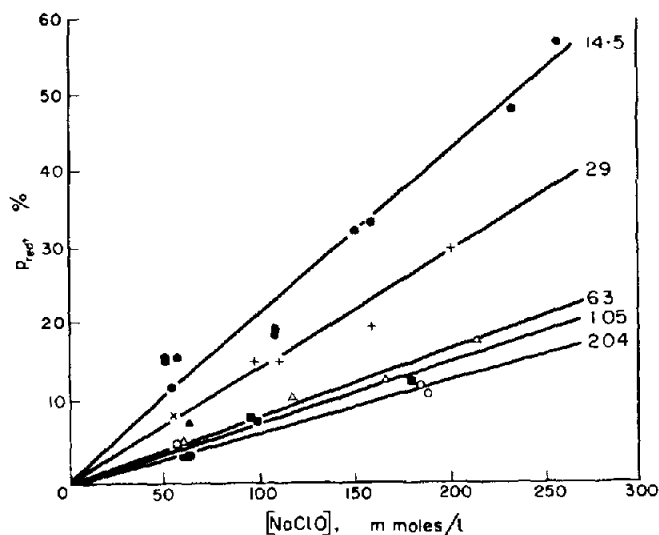| Expt. no.	pH before	pH after	[NaClO] (mmoles/l)	P_{red} (%)	P_{red} at 0·1 M NaClO (%)	P_{ox} (%)	P_{ox} at 0·1 M NaClO (%)
27	6·30	6·35	149·0	6·88	4·6	32·9	22·1
26	6·77	6·82	156·3	9·53	6·1	29·8	19·0
25	6·47	7·42	165·0	7·90	4·8	31·5	19·1
24	8·00	8·07	174·4	7·86	4·5	32·8	18·8
23	9·57	10·22	177·0	7·24	4·1	31·9	18·0
22	9·50	10·50	178·7	8·30	4·6	35·0	19·6

FIG. 2. Reduction loss vs. hypochlorite concentration at 25°C and various cathodic c.d's ● 14·5; × 29; Δ63; ■ 105; ○ 204 A/dm²). Steel cathode. Solution: 150 g/l NaCl, 0 g/l NaClO₃, pH 10, no chromate addition. Anodic c.d. 4 A/dm².
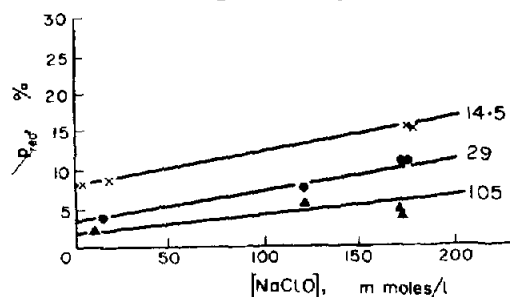

FIG. 3. Reduction loss vs. hypochlorite concentration at 25°C and various c.d's (× 14·5; ● 29; ▲ 105 A/dm²). Steel cathode. Electrolyte: 150 g/l NaCl, 273 g/l NaClO₃, pH 10, no chromate addition. Anodic c.d. 4 A/dm².
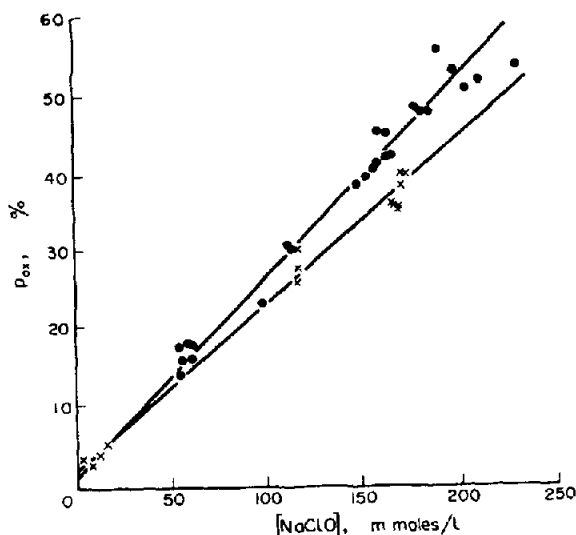

FIG. 4. Oxidation loss vs. hypochlorite concentration at 25°C, 150 g/l. NaCl, anodic c.d. 4 A/dm². ● 0 g/l NaClO₃, × 273 g/l NaClO₃.
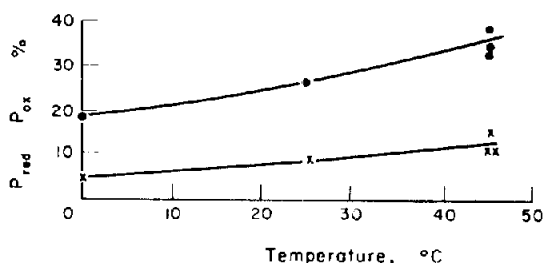
Fig. 5. Reduction (×) and oxidation (●) loss at 0·1 M (HClO + ClO⁻) vs. temperature, 150 g/l NaCl and 0 g/l NaClO₃. Anodic c.d. 4 A/dm², cathodic c.d. 63 A/dm².
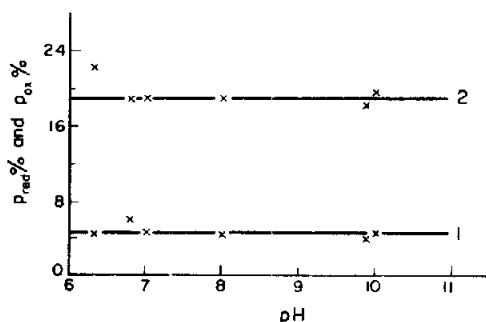
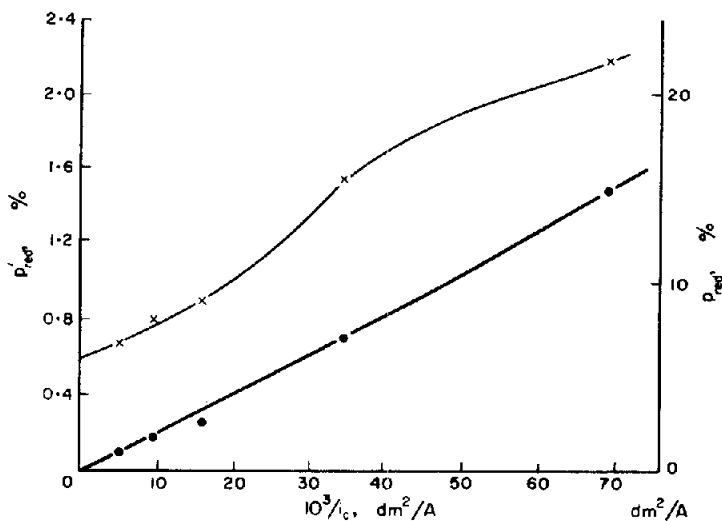Fig. 6. Reduction (1) and oxidation (2) loss at 0·1 M (HClO + ClO⁻) vs. pH at 0°C, $i_c = 63$ A/dm², $i_a = 4$ A/dm², 150 g/l NaCl, 0 g/l NaClO₃.

Fig. 7. Reduction loss at 0·1 M (HClO + ClO⁻) vs. reciprocal of cathodic c.d. at 25°C, 150 g/l NaCl and 0 g/l NaClO₃. × P_{red} (experimental values), ● P'_{red} (calculated equivalent reduction loss at constant thickness of diffusion layer according to equation 18).
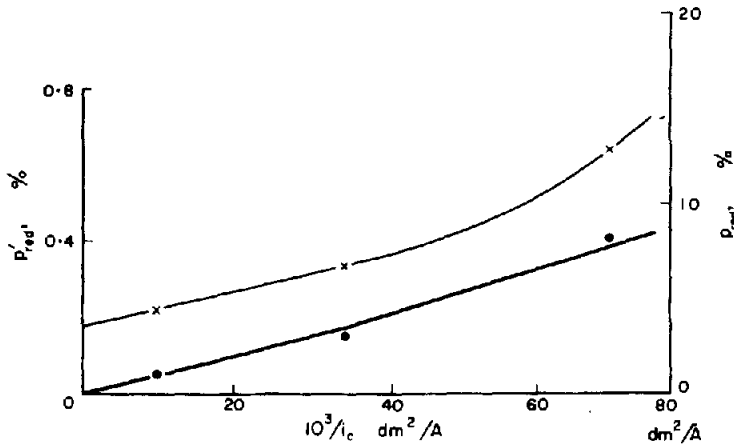
FIG. 8. Reduction loss at 0·1 M (HClO + ClO⁻) vs. reciprocal of cathodic c.d. at 25°C, 150 g/l NaCl and 273 g/l NaClO₃. × P_red (experimental values), ● P′_red (calculated equivalent reduction loss at constant thickness of diffusion layer according to equation 18).
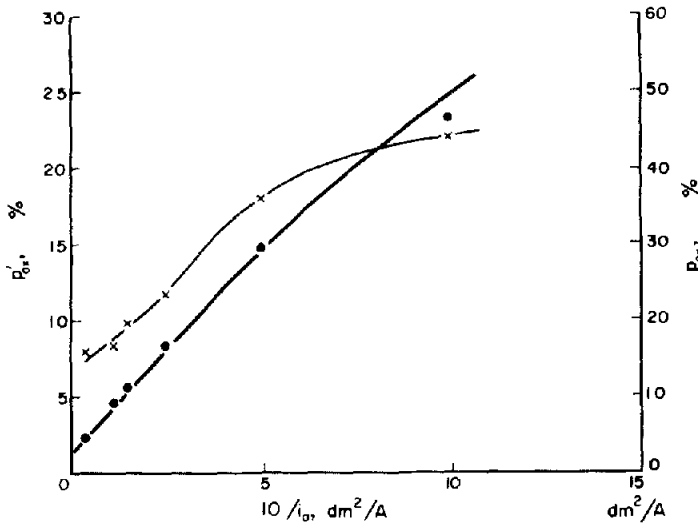

FIG. 9. Oxidation loss at 0·1 M (HClO + ClO⁻) vs. reciprocal of anodic c.d. at 25°C, 150 g/l NaCl and 0 g/l NaClO₃. × P_ox (experimental values), ● P′_ox (calculated equivalent reduction loss at constant thickness of diffusion layer according to equation 18).

2. The diffusion limiting current, I_{lim}, for the reduction of the hypochlorite ion is, according to equation (15), directly proportional to the cathode surface area A but, to a first approximation, is independent of the total cathodic current, I_c. The diffusion c.d., i_{lim} is therefore independent of the cathodic c.d., i_c and so P_{red} is inversely proportional to i_c. Figs. 7 and 8 show that this is approximately true. Deviations are observed at high cathodic current densities. On

the assumption that convective diffusion of the hypochlorite ion to the cathode surface is the rate-controlling step, we write

$$P_{red} = \frac{2FDc_{hyp}}{i_c \delta_1} \tag{16}$$

Under steady state natural convective flow conditions, at any point in the cathode plane, δ_1 should be constant. This is only truly valid when there is no gas evolution from the cathode surface. According to Venczel,[9] the Nernst diffusion layer thickness δ_1, varies with the rate of gas evolution V in cm^3/cm^2 min according to the empirical relationship

$$\delta_1 = 1{\cdot}5 . 10^{-3} . V^{-0{\cdot}5} \text{ cm.} \tag{17}$$

Equation (17) appears to hold for varying electrode size and shape. For the particular electrolyte system studied by Venczel, when $V = 0$, $\delta_0 = 0{\cdot}024$ cm. Using this empirical data, we recalculate the reduction loss by writing

$$P'_{red} = P_{red} \cdot \frac{\delta_1}{\delta_0} = \frac{2FDc_{hyp}}{i_c \delta_0} . \tag{18}$$

A similar relationship is proposed for P_{ox}. The evolution rates of hydrogen and oxygen are

$$V_{H_2} = V_{H_2}^{100} . (1 - P_{red}), \; V_{O_2} = V_{O_2}^{100} . P_{ox}. \tag{19}$$

where the superscript indicates 100 per cent hydrogen or oxygen evolution. The results of some typical calculations are given in Table 5. If the above reasoning is correct, then

TABLE 5. CATHODIC AND ANODIC EFFICIENCY LOSSES CORRECTED ACCORDING TO EQUATION (18)

P_{red} (%)	i_c (A/dm²)	$V_{H_2}^{100}$ cm³/cm² min	$V_{H_2} = V_{H_2}^{100} . (1 - P_{red})$ cm³/cm² min	$\delta_1 . 10^4$	$10^3 . \delta_1/\delta_0$	P'_{red} (%)	$10^3/i_c$ dm²/A
(a) Cathodic efficiency losses (absence of $NaClO_3$).							
21·8	14·5	1·10	0·86	16·29	67·87	1·48	69·0
15·5	29·0	2·21	1·87	10·81	45·04	0·70	34·5
9·0	63·0	4·80	4·37	6·92	28·83	0·26	16·0
8·0	105·0	7·99	7·35	5·27	21·96	0·18	9·5
6·7	204·0	15·54	14·50	3·71	15·46	0·10	5·0
(b) Cathodic efficiency losses (273 g/l $NaClO_3$, 2·56 M)							
13·0	14·5	1·10	0·96	15·45	64·38	0·84	69·0
6·7	29·0	2·21	2·07	10·30	42·92	0·29	34·5
4·4	105·0	7·99	7·62	5·18	21·58	0·095	9·5

(c) Anodic efficiency losses (absence of $NaClO_3$)

P_{ox} (%)	i_a (A/dm²)	$V_{O_2}^{100}$ cm³/cm² min	$V_{O_2} = V_{O_2}^{100} . P_{ox}$ cm³/cm² min)	$\delta_1 . 10^4$	$10^3 . \delta_1/\delta_0$	P'_{ox} (%)	$10^3/i_a$ (dm²/A)
44·5	1·01	0·0384	0·0171	127·5	531·25	23·64	990·0
36·5	2·02	0·0767	0·0280	98·26	409·42	14·94	495·0
24·0	4·05	0·1538	0·0369	85·20	355·00	8·52	246·9
20·0	7·08	0·2689	0·0538	69·75	290·62	5·81	141·2
17·5	9·07	0·3445	0·0603	65·67	273·63	4·79	110·2
16·5	30·00	1·1390	0·1879	36·09	150·38	2·48	33·3

a plot of the corrected reduction and oxidation losses versus the reciprocal electrode current density should be linear, even at high current densities. Figs. 7–9 show this to be the case.

3. The increase of P_{red} with temperature according to Fig. 5 corresponds to the decrease of viscosity and the resultant increase of the diffusion coefficient D with rising temperature. This effect is 2–3% per °C. If the activation polarization were rate-determining, a greater dependence on temperature would be expected.

4. A comparison of Figs. 2 and 3 will show that, at higher hypochlorite concentration, the reduction loss is decreased by an addition of chlorate to the solution. This is explained by the resultant rise of the viscosity of the electrolyte and the consequent decrease of the diffusion coefficient D according to the relation $D\eta = $ const. At small hypochlorite concentrations, the simultaneous reduction of chlorate is dominating. However, also an increase of the sodium chloride concentration alone will lower the reduction loss to a degree that is explained by the viscosity effect. This is illustrated by data in Table 6 below.

TABLE 6. REDUCTION LOSS P_{red} PER 0·1 M HYPOCHLORITE AS A FUNCTION OF NaCl CONTENT AND VISCOSITY AT 45°C, AND 63 A/dm² CATHODIC C.D.

NaCl (g/l.)	Relative viscosity	Reduction loss. P_{red} (%)	ηP_{red}
150	1·33	12·1	16·1
225	1·58	9·9	15·6
300	1·88	8·3	15·6

The *oxidation loss*, in its dependence on electrolysis variables, shows a clear analogy with the reduction loss. Hence, P_{ox} is proportional to the hypochlorite concentration (Fig. 4), approximately inversely proportional to current density (Fig. 9) and increases slowly (at ca. 2% per °C) with temperature (Fig. 5). Fig. 4 shows that the oxidation loss is also decreased by an addition of chlorate, as would be expected from the viscosity effect referred to above. These effects suggest, therefore, that the oxygen evolution due to equation (8) is also governed by convective diffusion according to eqn. (15). In this case, i_{lim} means the limiting c.d. for diffusion of hypochlorite to the anode surface. In the anode film, pH is apparently too low for hydrolysis of chlorine according to equation (3) to occur. This point is discussed thoroughly in a recent paper by Ibl.[10] The results confirm, furthermore, that oxygen evolution from water according to reaction (9) is negligible, since this reaction would not give limiting current characteristics.

Reaction (8) for the anodic evolution of oxygen with a simultaneous anodic disproportionation of hypochlorite to chlorate deserves a special consideration in view of the experimental results. The reaction was suggested by Foerster and Müller[11] and Foerster,[12] who based it on extensive experimental investigations including the electrolysis of solutions of hypochlorous acid. It is usually referred to as electrochemical or anodic formation of chlorate. It should be observed that the oxygen is equivalent to the water involved and hence hypochlorite undergoes no net oxidation, since 6HClO are disproportionated to $2ClO_3^-$ and 4 Cl⁻ in the same way in chemical formation of chlorate according to equations (4) and (5). In the steady state electrolysis,

involving a constant concentration of hypochlorite in the solution, and if no chemical formation of chlorate occurs reaction (8) will give an anodic loss of 6/18 = 33·3 per cent.

Rius and Llopis[13] assume the electrochemical chlorate formation to occur according to

$$5HClO + 8H_2O \rightarrow 2O_2 + 2Cl^- + 3ClO_3^- + 21H^+ + 16e^-. \qquad (20)$$
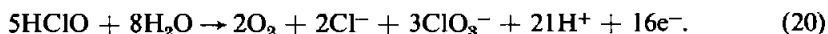
This reaction involves oxygen evolution from $4H_2O$ and an electrochemical formation of chlorate at 100 per cent current efficiency according to

$$5HClO + 4H_2O \rightarrow 3ClO_3^- + 2Cl^- + 13H^+ + 8e^- \qquad (21)$$
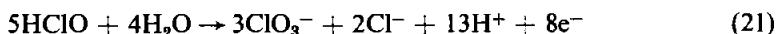
In the steady state the anodic loss according to this reaction would be 8/26 = 30·8 per cent, i.e. hardly experimentally distinguishable from that of the Foerster–Müller mechanism.

Reactions of such high orders are very improbable and must certainly proceed in several steps. De Valera[14] in his studies of the theory of chlorate electrolysis considers the assumption of such complicated reactions as that of Foerster and Müller to be superfluous and finds it sufficient to state that reactions other than chlorine ion discharge and involving oxygen evolution and current efficiency losses occur at the anode surface. Along this reasoning attempts were made in the present study to explain the anodic loss by simpler reactions. Oxygen evolution at the anode is directly connected with the hypochlorite concentration of the electrolyte and involves formation of chloride ions. The simplest reaction fulfilling these requirements would be
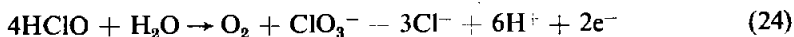
$$HClO + H_2O \rightarrow O_2 + 3H^+ + Cl^- + 2e^-, \quad e_0 = 0.96 \text{ V.} \qquad (22)$$
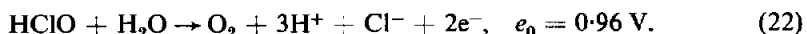
Formation of chlorate at the anode could occur according to a simultaneous reaction

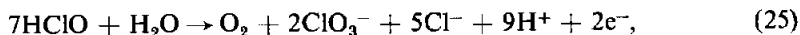$$HClO + 2H_2O \rightarrow ClO_3^- + 5H^+ + 4e^-, \quad e_0 = 1.43 \text{ V.} \qquad (23)$$
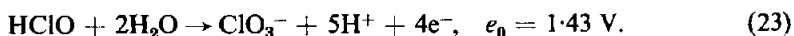
It is possible to test the applicability of these reactions by comparing the change of hypochlorite concentration with the amount of electricity passed during an experiment. Such data exist for thirty-six of the experiments listed in Tables 1 and 2. They show conclusively that the electrochemical chlorate formation under oxygen evolution can *not* be described by equations (22) and (23). The consumption of hypochlorite during electrolysis is much higher than these equations can explain. Hence one is led to the conclusion that the anodic oxygen evolution and the anodic formation of chlorate are coupled in such a way that a certain, rather high ratio between hypochlorite consumption and oxygen evolution exists.

Still, reaction (22) might be the primary step in such a reaction, furnishing on the electrode surface the hydrogen ions, perhaps in an activated state, that seem to be necessary for chlorate formation according to equations (4) and (5). A tentative combination of equation (22) with (4) or (5) suggests the possibilities

$$4HClO + H_2O \rightarrow O_2 + ClO_3^- - 3Cl^- + 6H^+ + 2e^- \qquad (24)$$

and

$$7HClO + H_2O \rightarrow O_2 + 2ClO_3^- + 5Cl^- + 9H^+ + 2e^-, \qquad (25)$$

with anodic efficiency losses of 40 and 25 per cent respectively.

An amount of hypochlorite equivalent to the anodically evolved oxygen is lost because it is never formed or decomposed to oxygen and chloride ions. However, an additional amount of hypochlorite disappears through the accompanying oxidation to chlorate. The ratio between this *additional* loss of hypochlorite equivalents to the oxygen equivalents evolved anodically is, for the equations (8), (20), (24) and (25), found to be $12/6 = 2$, $18/8 = 2\cdot25$, $6/4 = 1\cdot5$ and $12/4 = 3$ respectively. Assuming now this ratio to be unknown (x), we make the following balance of the change of the amount of hypochlorite during a run:

Amount of electricity passed through electrolyser during
  run $= Q$ As.

Amount of hypochlorite formed, if anodic current efficiency
with respect to hypochlorite formation were 100 per cent $+\dfrac{Q}{2F}$ mole

Percentage of anodic current used for oxygen evolution $= P_{\text{ox}}$
  per cent.
Amount of hypochlorite thereby never formed, or lost $-\dfrac{Q}{2F}\cdot P_{\text{ox}}$ mole

Additional decrease of hypochlorite due to accompanying chlor-
ate formation $-x\cdot\dfrac{Q}{2F}\cdot P_{\text{ox}}$ mole

Percentage of cathodic current spent on reduction of hypochlo-
rite according to equation (6) $= P_{\text{red}}$. Loss of hypochlorite
due to P_{red} $-\dfrac{Q}{2F}\cdot P_{\text{red}}$ mole

Increase of hypochlorite concentration during run $= \Delta c_{\text{hyp}}$.
Electrolyte volume $= V$
Hence, we find for the actual increase of hypochlorite during run

$$\frac{Q}{2F}\left[1 - (1 + x)\,P_{\text{ox}} - P_{\text{red}}\right] = V\cdot\Delta c_{\text{hyp}} \tag{26}$$

and thus

$$x = \frac{1 - P_{\text{red}} - [2F\cdot V\cdot\Delta c_{\text{hyp}}]/Q}{P_{\text{ox}}} - 1 \tag{27}$$

In Tables 1 and 2, values of

$$\frac{F\cdot V\cdot\Delta c_{\text{hyp}}}{Q}$$

and of x are listed. From twenty-seven experiments where no reduction of chlorate is involved we obtain $x = 2\cdot06 \pm 0\cdot06$.

From this it seems justified to conclude that equation (8) according to Foerster and Müller gives a good description of the anodic efficiency loss reaction in chlorate electrolysis. It takes account of the fact that the anodic evolution of oxygen is accompanied by an anodic disproportionation of hypochlorite to chlorate and chloride ions. Furthermore, it gives a better expression of the quantitative relation between oxygen evolution and hypochlorite consumption than similar formulae with other coefficients. It cannot, therefore, be considered superfluous.

2

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