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Studies on electrochemical disinfectant production using anodes containing RuO_2

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Abstract

The present work contains results for artificial water electrolysis in discontinuous operation using laboratory reactors without separators. Rotating anodes with mixed oxide coatings containing IrO_2/RuO_2 were used. The experimental parameters were the chloride concentration, current density, rotation rate, cathode material, pH and water composition. Active and total chlorine concentrations and current efficiencies were obtained. It was shown that even for very low chloride concentrations, chlorine formation occurs, but side effects and side reactions significantly lower the efficiency in this case. Nitrite and ammonia formation was found to reduce the efficiency of chlorine formation. Partial polarization curves were obtained in kinetic experiments using solutions containing chloride and sulphate ions.

Abbreviations

Δ	difference
κ^0	initial value of specific conductivity, S cm^{-1}
Λ	equivalent ionic conductivity, m^2 A V^{-1} mol^{-1}
Φ	electrical potential, V
	current efficiency, %
AC	active chlorine
c	concentration, mg dm^{-3}
D	coefficient of diffusion, m^2 s^{-1}
diss.	dissolved
E	electrode potential, V vs SHE
F	Faraday constant, A s mol^{-1}
i	current density, mA cm^{-2}
I	current, A
j	component j
M	Molaric mass, g mol^{-1}
N	molaric flux, mol s^{-1} m^{-2}
n	number of electrons
rpm	revolutions per minute
SHE	standard hydrogen electrode, V
t	time, s, min
V	electrolyte volume, dm^3
w	velocity, m s^{-1}
x	coordinate, m
z	charge number

1. Introduction

There are many enterprises for developing and selling disinfection technologies based on the direct electrochemical treatment of drinking water. These technologies use the natural presence of chloride ions. Thus, active chlorine (considered as hypochlorite ions, hypochlorous acid and dissolved chlorine) and total chlorine (the sum of active and bonded chlorine, mainly as chloramines) are the main products. By-product formation has been insufficiently studied [1]. The chemical character of the disinfection process was discussed recently by the authors [2].

The product and by-product spectra obtained in an electrochemical disinfection depend significantly on the use of a separator. The anodic current efficiency of chlorine production can be reduced by cathodic reduction. Dissolved oxygen can be reduced cathodically to hydrogen peroxide. Calcareous deposits can cover the cathode. The use of a separator between anode and cathode may shift the pH to lower values. Thus, more HOCl is produced which is known for having higher efficiency in killing microorganisms than hypochlorite. The electrolysis of water for disinfection generates hydrogen and oxygen, which can be dissolved or outgas, accelerates pipe corrosion or causes other effects. Due to inappropriate cell application and the wide variety of water qualities and process parameters, more research is needed for better health risk assessment.

Many electrode materials have been studied for the electrochemical water disinfection treatment, which is completely different in terms of the applied potentials and killing mechanisms from the electrochemical treatment of microorganisms artificially adhered to electrodes before electrolysis [3]. Results from studies with anodes containing RuO_2 were first reported in work comparing activities of several anode materials such as DSA® for chloralkali electrolysis, magnetite, graphite, platinum and boron doped diamond [4, 5]. Several authors tested IrO_2 anodes [2, 6]. We demonstrated [7] that IrO_2/RuO_2 anodes have a higher chlorine efficiency than IrO_2 anodes.

Electrochemical processes may form organic and inorganic by-products in more or less complex reactions during direct water treatment. Whereas many hundreds of organic disinfection by-products were identified for water chlorination [8, 9], no detailed studies are reported for water electrolysis. Czarnetzki and Janssen [10] studied the mechanism of chlorate formation in an electrolytic cell with relatively low chloride concentration. Chlorate is also a well-known product of electrochemical or chemical reactions in disinfection solutions [11]. The anodic reaction of hypochlorite on platinum was studied by Tasaka and Tojo [12]. Kinetic considerations of chloride reduction were summarised by Trassatti [13] but this and other research was carried out for conditions not typical for drinking water, without reliable online-analysis and adequate product analysis [14].

After analysing literature data and studying disinfection electrolysis in initial experiments [5], we classified groups of inorganic by-product problems as follows: chlorine dioxide, chlorite, chlorate, hydrogen peroxide, ozone and nitrite. The relevance of these problems depends at least on the chlorine formation rate or chloride concentration level because many by-products can react with active chlorine [15]. Several authors have discussed the formation of by-products such as ClO_2[16], ozone [17] or hydrogen peroxide [18]. When ozone and hydrogen peroxide are present in the treated water the formation of radicals is possible:

$$H_2O_2 + 2O_3 \rightarrow 2OH^* + 3O_2 \qquad (1)$$

Radicals generated by reaction 1 may have longer life times in the bulk of electrolyte than those generated directly at the anode in an electrochemical reaction as reported for diamond electrodes [19]:

$$H_2O \rightarrow OH^* + H^+ + e \quad 2.59\,V \qquad (2)$$

Another problem is the possible formation of nitrite by cathodic nitrate reduction [20] if the cell is not divided.

There are many indications that electrolysed water has a higher disinfecting activity compared to normal commercially available hypochlorite solutions but the comparison is difficult, due to the adjustment of equal starting conditions such as pH and initial active chlorine concentrations. The analysis of components is an additional problem in solutions of the so-called mixed oxidants with the potential for fast reactions [21].

It is the aim of this work to present product and by-product formation studies during the discontinuous electrolysis of water systems with an IrO_2/RuO_2 anode.

2. Experimental conditions

2.1. *Apparatus and experimental methods*

Discontinuous experiments were carried out using a thermostated dark beaker cell with 0.150 dm^3 of electrolyte (artificially prepared water). The working temperature of 20 °C was adjusted with a *Lauda* potentiostat model *RM*6. Cathodes of different shape and material in several experiments (extended Ti mesh disk activated with an IrO_2 layer, Ti plate with central hole of 4 mm diameter, stainless steel plate, the latter both $35 \times 40 \times 2$ mm^3) were located 25 mm above the base of the beaker at a distance of 4 mm below the rotating anode. The anode was rotated using a *MLM MR25/Medingen* unit and contacted through a *Mercotac* contactor (Figure 1). The anode, a disc of 35 mm diameter, was made from titanium with an active layer containing IrO_2 and RuO_2 (*DeNora Germany*).

For studies of non-IR corrected polarization curves, an *EG&G* potentiostat model 283 together with a rotating disc electrode stand (model 616) were used. The anode was a 1 cm^2 Ti disc activated with IrO_2/RuO_2. A mercury sulphate reference electrode in an outer beaker connected with a salt bridge containing 0.25 M Na_2SO_4 was used to measure the anode potential. The cathode was a platinum sheet of 15×30 mm^2 size. The anode was polarized to an end potential of 2.2 V (SHE) by linear scanning starting from a set potential of 0.4 V (SHE), after 30 s of nitrogen purging and holding the electrode at current-less potential for 15 s. Chloride from

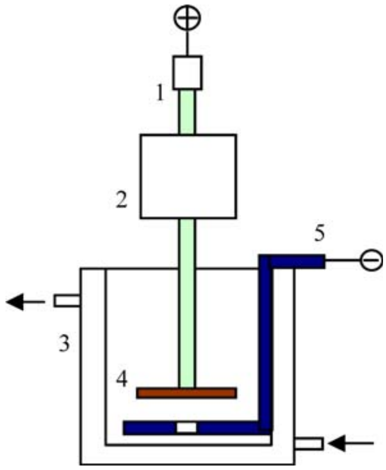

Fig. 1. Electrolysis cell with rotating anode (1 – rotating contact, 2 – electronically controlled stirrer, 3 – thermostated beaker, 4 – rotating anode, 5 – cathode with central hole, $V = 0.150$ dm^3).

NaCl stock solution was added and the experiment repeated correspondingly.

The pH was measured using a *WTW* pH meter *pH 340*, specific conductivity with a conductometer *Cond 340i* from *WTW*. *Statron* rectifiers were used for electrical power supply in the constant current mode. The exact cell current was checked using a multimeter (*MY-64*, *Conrad Electronic*). A UV/vis spectrophotometer (*Specord 40*, *Analytik Jena*) was used for special spectroscopic studies in the UV range. Quantitative analysis was carried out using a spectrophotometer (*Nanocolor D100*, *Macherey & Nagel* or *CADAS 40*, *Dr. Lange*).

2.2. *Chemicals*

Chemicals of analytical pure grade with relatively low impurity influence in UV spectra from *Roth* (Na_2CO_3), *Baker* ($NaNO_3$), *Fisher Scientific* (NaCl, Na_2SO_4) and of ultra-pure grade from *Merck* (HCl) were taken for preparing artificial electrolytes. Chemicals were partially treated twice by fractional crystallisation (Na_2SO_4, NaCl) at different temperatures. The deionised water for preparing the artificial drinking water systems was produced in a unit combining reverse osmosis and ion exchange (*USF/Seral*). A specific conductivity less than 0.1 μS cm^{-1} was measured at the outlet.

2.3. *Analytical methods*

Samples were directly transferred into covered spectrophotometric cells or partially diluted in the dark and analysed within an average time of 30 s. Analysis sets based on the DPD method (*N*,*N*-diethyl-1,4-phenylene diamine) were used for quantifying active and total chlorine. In this method, DPD is firstly oxidised by active chlorine giving a red colour for spectrophotometrical analysis at 540 nm. After this, total chlorine can be analysed adding KI solution. Bonded chlorine will reduce the iodide to iodine, which also reacts with DPD in the same proportion. Nitrate was analysed applying the spectrophotometrical *Dr. Lange* method LCK 339 reacting nitrate with 2,6-dimethylphenol to 4-nitro-2,6-dimethylphenol. The nitrite analysis was carried out by photospectroscopy using the *Dr. Lange* test LCK 341 (sensitivity 0.002 mg dm^{-3}) and partially by a second method after adding defined volumes of acetic acid, sulphanilic acid and α-naphtol to samples and measuring peaks at 476 nm (sensitivity 0.001 mg dm^{-3}).

3. Results and discussion of chlorine formation

3.1. *Influence of cathode material and water composition for a fixed chloride ion concentration*

In a series of experiments, the cathode material was varied. Additionally, the content of water was changed and the chlorine concentrations during discontinuous experiments were measured as described by data in Table 1.

For comparison, the limiting values in mg dm^{-3} allowed by German law are: 250 for chloride, 240 for sulphate and 50 for nitrate ions. The pH must be between 6.5 and 9.5 but inside a treatment cell it can be higher or lower.

The measured values of total chlorine concentration vs reaction time are given in Figure 2. It is surprising that for relatively smaller reaction time intervals, the differences are relatively small. Obviously, the influence of the counter electrode is not significant in the studied range of concentrations. For higher time intervals, differences between the values become bigger in some cases. It is assumed that chemical and electrochemical side reactions are affecting the chlorine concentration. A more precise discussion is only possible after obtaining more analytical data with respect to several species in the treated water.

Table 1. Initial parameters of used water systems (anion concentrations in mg dm^{-3}, sodium salts; system F was prepared from NaCl and HCl)

Water system:	A	B	C	F
[Cl^-]	125	125	125	125
[SO_4^{2-}]	240	240	240	240
[NO_3^-]	10	10	0	0
[CO_3^{2-}]	50	2.5	2.5	0
pH^0	10.0	7.3	7.1	3.02
κ^0 in μS cm^{-1}	1200	1000	970	1113

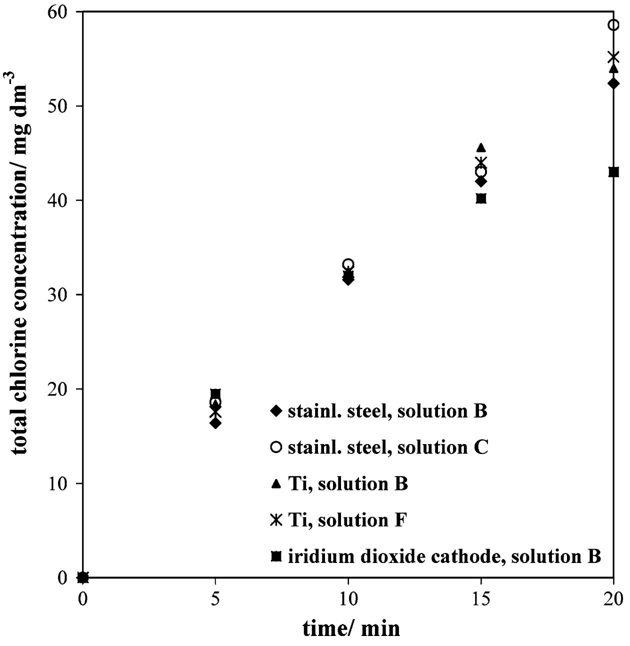

Fig. 2. Total chlorine formation in experiments with variation of water composition (Table 2) and counter electrode (temperature 295 K, current 300 mA, rotation rate 300 rpm, $V = 0.150$ dm^3).

3.2. *The influence of chloride concentration*

According to the accepted theory [13], chloride ions react in a complex manner at active Ru sites to adsorbed and dissolved chlorine, which reacts with hydroxide ions or water to hypochlorous acid and hypochlorite (Equations 3–6). The mass distribution between the three main active chlorine components is strongly dependent on pH.

$$2Cl^- \rightarrow Cl_2 + 2e \quad 1.358\,V(SHE) \tag{3}$$

$$Cl_2 \rightarrow Cl_{2,diss.} \tag{4}$$

$$Cl_{2,diss.} + OH^- \rightarrow HOCl + Cl^- \tag{5}$$

$$Cl_{2,diss.} + H_2O \rightarrow OCl^- + H^+ + Cl^- \tag{6}$$

The adsorption of chloride ions competes with the adsorption of other species, mainly anions. This fact is an essential problem for anodic kinetic studies since numerous water components may affect the mechanism. The electrochemical reaction of chlorine formation competes with the formation of oxygen in the two main reactions (Eqs 7 and 8), which both lie in the pH range of drinking water.

$$H_2O \rightarrow 0.5O_2 + 2H^+ + 2e \quad 1.229\,V(SHE) \tag{7}$$

$$2OH^- \rightarrow 0.5O_2 + H_2O + 2e \quad 0.401\,V(SHE) \tag{8}$$

Due to these reactions, the pH of the anodic electrolyte layer can significantly differ from that of the bulk and lead to different chemical reactions.

There is no information about the influence of chloride ion concentration on the effectiveness of active chlorine formation. A minimum chloride concentration of 10–20 mg dm^{-3} is reported as sometimes necessary for chlorine formation [22]. In general, these questions can be answered only by multiple parameter studies. Figure 3 shows only representative results from studies at the rotating anode in an aqueous solution of sodium chloride and sodium sulphate. The method did not allow the demonstration of anodic activities for very small chloride concentrations (5 mg dm^{-3}). Also, adsorption effects for the chloride ions occur, as can be seen from the polarization curves, in the potential range between 0.9 and 1.3 V. Figure 4 shows, in addition to the curve for the blank solution, differential polarization curves obtained by subtraction. There is clear electrode activity starting at potentials near 1.4 V. This activity can be correlated with the expected formation of chlorine. Higher chloride concentrations enhance the partial current density at the same potential. The simplest explanation for this is the better migration of chloride ions to the active electrode sites (see also Section 3.3). In accordance with the well-known equation 10, migration depends almost linearly on concentration. The predominating influence of migration is also expected due to the strong influence of current density (or potential gradient at the anode) on the chlorine production rate [6]. Mass transfer differences play a secondary role (Section 3.4).

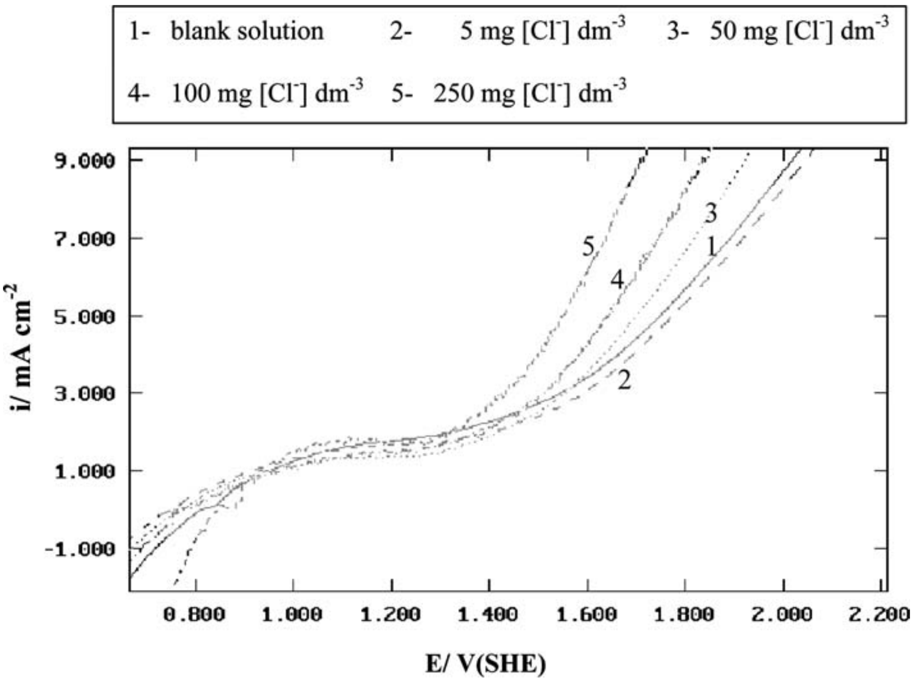

Fig. 3. Polarization curves on IrO_2/RuO_2 in blank solution (240 mg $[SO_4^{2-}]$ dm^{-3} as Na_2SO_4) and in $Na_2SO_4/NaCl$ solutions of differing chloride ion content given in mg dm^{-3}, rotation rate 500 rpm, $T = 298$ K.

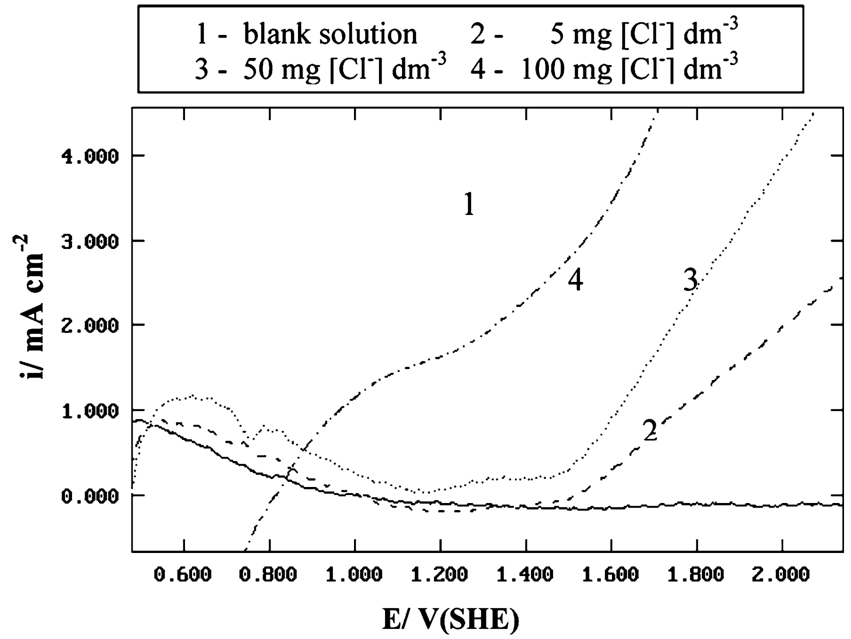

Fig. 4. Polarization curves on IrO_2/RuO_2 in blank solution (240 mg $[SO_4^{2-}]$ dm^{-3} as Na_2SO_4) and differential polarization curves in Na_2SO_4/NaCl solutions of differing chloride ion content given in mg dm^{-3}, rotation rate 1000 rpm.

Figure 5 includes results for discontinuous electrolysis of synthetic waters with sulphate, nitrate, carbonate/bicarbonate and chloride ions as sodium salts. Even the results for the smallest chloride concentration of 1 mg dm^{-3} were measured as being higher than for the blank solution (actually 0.1 mg $[Cl^-]$ dm^{-3}). The response for the blank solutions can be caused by traces of chlorine or ozone as the DPD method is also sensitive to these. Side effects can prevent a continuous increase of chlorine concentration as shown in Figure 5. Typical side effects which lower the chlorine concentration may be:

- Stripping of chlorine by the evolving oxygen from the electrode surface.
- The electrochemical reaction of active chlorine in consecutive reactions at the anode [12].
- Chemical reaction of active chlorine in the bulk electrolyte.
- Cathodic reduction of active chlorine.

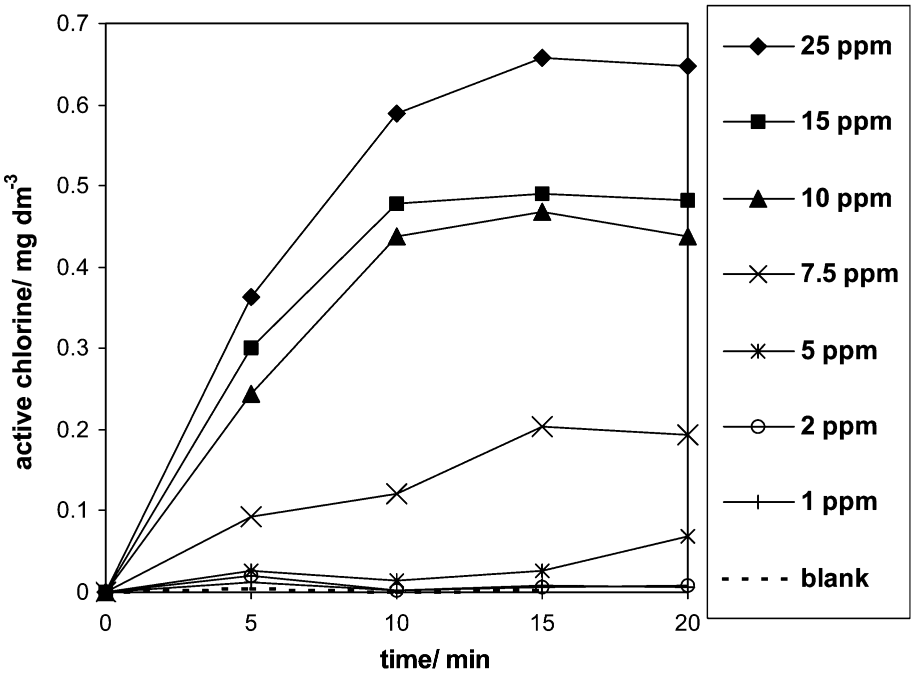

Fig. 5. Active chlorine concentration vs time in discontinuous experiments with varying chloride ion concentration in mg dm^{-3} indicated as ppm (current 100 mA, rotation rate 300 rpm, temperature 20–22 °C, $V = 0.150$ dm^3, IrO_2 cathode, sulphate – 240 mg dm^{-3}, nitrate – 10 mg dm^{-3} and carbonate – 50 mg dm^{-3}, as sodium salts).

Previous discontinuous experiments (not presented here) showed a decrease in chlorine concentration for longer electrolysis times for waters with higher Cl^- concentration. As noted above, our spectrophotometric measurements demonstrated the formation of ClO_2, H_2O_2 and products resulting from cathodic nitrate reduction depending on the chosen electrolysis conditions. Table 2 includes the measured values of active chlorine, total chlorine and current efficiency calculated from the uncorrected active chlorine data:

$$\varphi = \frac{\Delta c_{\mathrm{AC}} nFV}{I \Delta t M_{\mathrm{Cl}}} 100 \tag{9}$$

It is apparent that a significant increase of measured chlorine starts at a chloride concentration of 7.5 mg dm^{-3}. Below this value, the chlorine concentration is negligible and in agreement with the above-mentioned statement in the literature about a necessary minimum chloride concentration for the formation of active chlorine. However, the formation of chlorine components is evident even in the case of extremely low chloride concentrations. Figure 6 includes results from experiments with still higher adjusted starting chloride concentrations. Because the influence of the efficiency lowering effects is obviously smaller than for chloride concentrations shown in Figure 5, the chlorine concentration increases steadily with time. The relationship of chlorine concentration to the chloride concentration is nearly linear.

3.3. *The influence of current density*

In an electrolytic process, ion transfer can proceed by different mechanisms. At a planar electrode, the one-dimensional mass transfer of a component j in the direction x may be expressed by Equation (10) for the cross section related molar flow N_j:

$$N_j = wc_j - D_j \frac{dc_j}{dx} - c_j \frac{\Lambda_j}{zF} \frac{d\Phi}{dx} \tag{10}$$

Usually, in low concentration systems with a supporting electrolyte, diffusion is the limiting factor. However, drinking water is a very low concentration solution and a maximal specific conductivity of only 2500 μS cm^{-1} is permitted (German regulations for drinking water). Thus, a significant amount of migration in the ion transport is to be expected. A simple calculation underlines this. The following working conditions are assumed: current density 150 A m^{-2} at a cell voltage of 20 V for a water conductivity of 500 μS cm^{-1}. The rotation rate of the anode is 300 min^{-1}. Furthermore, a typical mass transfer coefficient of 5×10^{-5} m s^{-1} is calculated from the Sherwood number equation for the rotating disc electrode using a Cl^- diffusion coefficient of 2.03×10^{-9} m^2 s^{-1} [23]. A chloride concentration of 35.5 mg dm^{-3} (1×10^{-3} mol dm^{-3}) and a typical current efficiency of 6.7% (calculated from data in Figure 6) are assumed. With these data, the partial current density with respect to transported chloride ions is about 10 A m^{-2}. Calculating the limiting diffusion current density from the second term in Equation 10, we obtain 5.4 A m^{-2} and, correspondingly, 4.6 A m^{-2} for the remaining migration part neglecting convection. Thus, the migration current density is of the same order of magnitude as the maximal diffusion-based current density. Consequently, a higher current density should improve electrochemical chlorine production but not necessarily the current efficiency. This is evident from Figure 7, where the production of chlorine and the cell current are only weakly correlated.

The right-hand graph (b) in Figure 7 shows the calculated integral current efficiency vs the current. The integral current efficiency was calculated from Equation 9 using the change of active chlorine concentration Δc_{AC} during the time period Δt with current I for treated volume V. The graph predicts an optimum current density. This was confirmed in a further series of experiments. The occurrence of the optimum can be explained by the competition of chlorine and oxygen evolution starting at several potentials with different slopes.

3.4. *The influence of hydrodynamics*

It was shown above that migration is not a negligible mechanism in the mass transfer of chloride ions, and only a small influence from improved hydrodynamic conditions can be expected.

Figure 8 summarises the effect of rotation rate on chlorine formation. It can be seen that lower rotation rates increase chlorine production to a small extent (the influence of by-product formation has not yet been studied).

3.5. *The influence of nitrate ions in the non-divided cell*

The nitrite concentration in drinking water is limited by regulations, so that the conditions of nitrite formation should be a subject of special studies. But even if the measured concentration is lower than the limit concentration, it must be made clear whether nitrite (or other

Table 2. Measured values of active and total chlorine concentration and calculated current efficiency dependent on the chloride concentration (in mg dm^{-3}) for the 5 min

Chloride concentration:	0	1	2	5	7.5	10	15	25
Active chlorine (mg dm^{-3})	0.006	0.009	0.012	0.027	0.092	0.245	0.3	0.363
Total chlorine (mg dm^{-3})	0.011	0.019	0.022	0.03	0.104	0.268	0.335	0.406
Current efficiency (%)	–	0.024	0.033	0.073	0.25	0.666	0.815	0.986

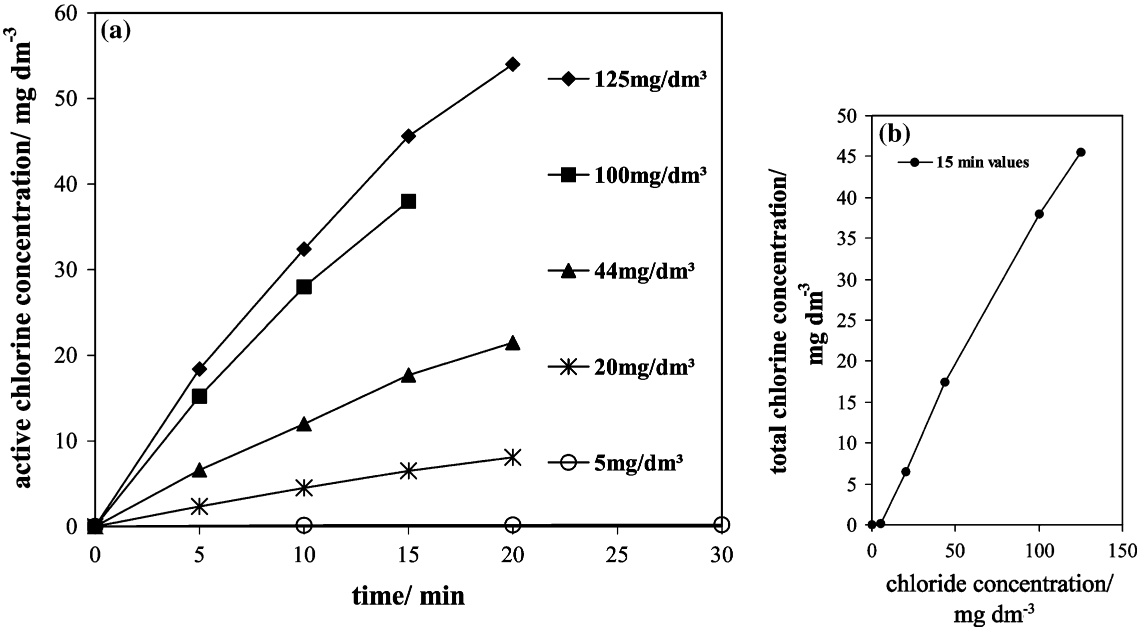

Fig. 6. (a) Active chlorine concentration vs time in discontinuous experiments with varying chloride concentration, (b) 15 min values of total chlorine concentration, (current 300 mA, rotation rate 300 rpm, temperature 20–22 °C, V=0.150 dm^3, Ti cathode, sulphate – 240 mg dm^{-3}, nitrate – 10 mg dm^{-3} and carbonate – 50 mg dm^{-3}, as sodium salts).

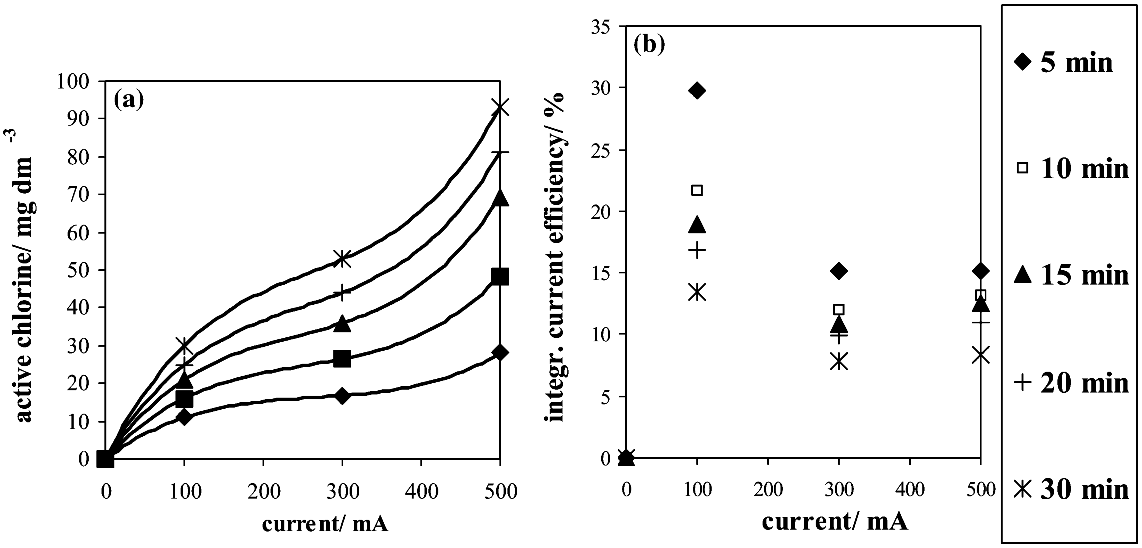

Fig. 7. (a) Active chlorine concentration vs cell current, added trend lines, (b) calculated integral current efficiency vs current, discontinuous experiments (current 300 mA, temperature 22–23 °C, rotation rate 500 rpm, stainless steel cathode, V=0.150 dm^3, sulphate – 240 mg dm^{-3}, nitrate – 10 mg dm^{-3}, chloride – 125 mg dm^{-3} and carbonate – 50 mg dm^{-3}, as sodium salts).

nitrogen containing components) can lower the disinfection efficiency. Nitrate can react in weakly alkaline solution [20] as summarised in Equations 11–13.

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad 0.008\,V \qquad (11)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \; -0.165V \qquad (12)$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \; -0.100V \qquad (13)$$

Our experiments working with a current density of 300 A m^{-2}, a Ti cathode and water containing only 200 mg [NO$_3^-$] dm^{-3} resulted in clearly measurable 476 nm peaks and nitrite concentrations of more than 10 mg dm^{-3} after electrolysis of 45 min.

In practice ammonia is the most prevalent end product in alkaline nitrate reduction. This means that it can take part as a chlorine consumer in a series of reactions forming chloramines (similar to the so-called breakpoint phenomenon [24] in conventional water disinfection with chlorine). Chloramines are mostly less effective or even forbidden disinfectants and conse-

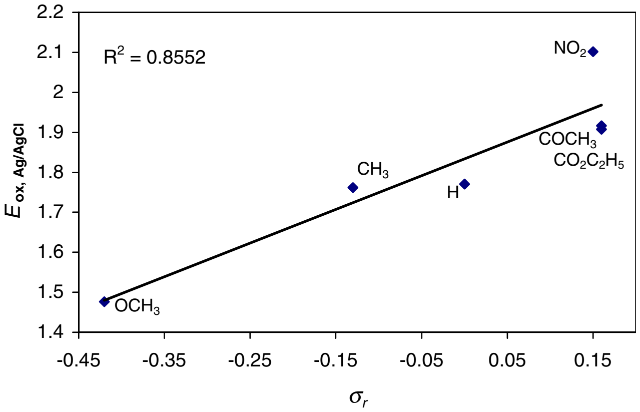

Fig. 8. Influence of rotation rate on active chlorine formation at several times of discontinuous experiment (water system B (Table 2), current 300 mA, temperature 20–22 °C, Ti cathode, $V = 0.150\ dm^3$).

quently their formation must be avoided. In a series of experiments nitrite formation was measured by two different spectroscopic methods. Performing repeat experiments of nitrate electrolysis in the range to 50 mg dm^{-3} (maximal nitrate depletion of 1.5 mg dm^{-3} was observed within 40 min) and analysing spectra in the UV range, a large oscillation of the absorbance signals occurs. This is because nitrate (decreasing concentration) and nitrite (increasing concentration) have close characteristic peaks at 202 and 206 nm, respectively. The absorbance sensitivity of both ions is also very high in the lower range of concentration. Negative differential spectra were also measured in discontinuous experiments, mainly when nitrate was present in the water (Figure 9). These spectra show a typical peak at 290 nm for hypochlorite. At lower wavelengths between 190 and 230 nm many water components interfere so that discussion is difficult. Nitrate reduction, indicated by shifting the absorbance to negative values in this wavelength region, was confirmed in many electrolysis experiments. When more chlorine products are formed the spectra again shift into the positive region.

Another discontinuous experiment was carried out starting with "chloride-free" water containing mainly sodium nitrate and sodium sulphate. The results are shown in Figure 10. There is only a small initial increase in the measured values, when the chlorine production is still relatively small. After the addition of a small amount of chloride, the newly produced active chlorine reacts with the excess ammonia so that the active chlorine concentration increases slowly and then drops despite the expected better active chlorine formation conditions. When, in the further course of the experiment, the active chlorine concentrations do not change significantly the total chlorine concentration increases remarkably, probably because chloramines are formed. Simultaneous measurement shows that nitrite concentration increases to 0.15 mg dm^{-3} until the addition and thereafter falls to 0.045 mg dm^{-3}, probably due to the relatively fast reaction [23]

$$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^- \qquad (14)$$

However, according to [23] a "combined (chloramines) chlorine residual will not react with nitrites". In this situation, nitrite concentration is measurable by analytical methods.

4. Conclusions

The application of RuO_2 containing anodes results in effective chlorine production. Activity could still be measured by the DPD method when the chloride ion concentration was lower than 10 mg dm^{-3}. Losses of

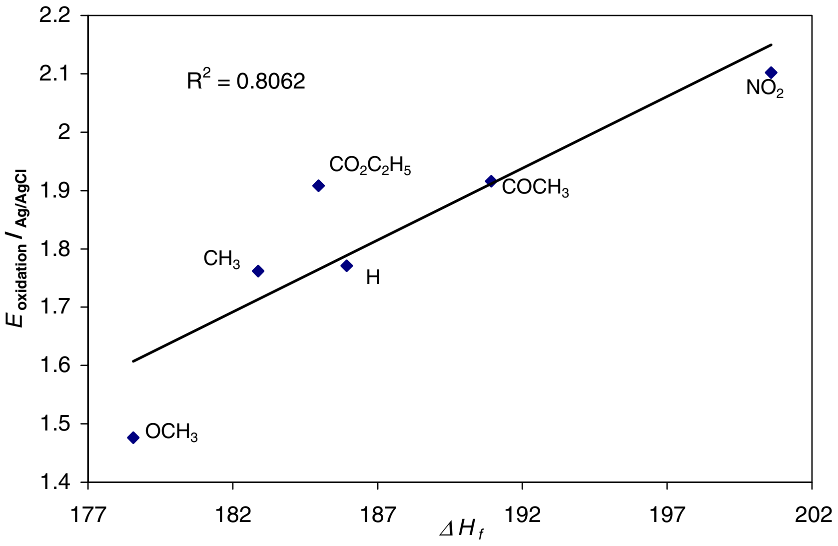

Fig. 9. Differential UV spectra for 10 min samples in discontinuous electrolysis experiments with waters of different composition as indicated in Table 2 (current 300 mA, rotation rate 300 rpm, stainless steel cathode, temperature 295 K, $V = 0.150\ dm^3$, indicated pH at the end of experiment after 20 min).

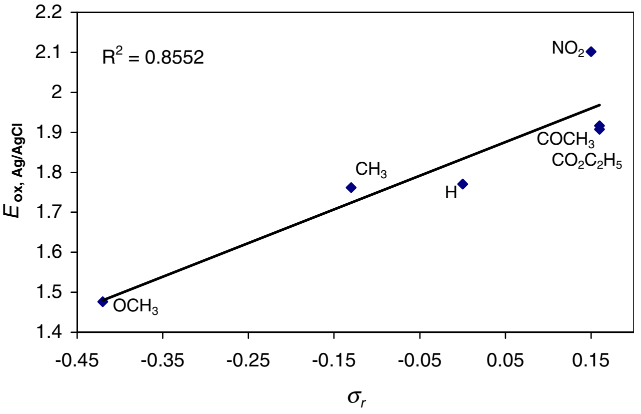

Fig. 10. Active and total chlorine concentration vs time in a discontinuous experiment with "chloride-free" water. Twenty-five minutes after the beginning, the current was increased from 100 to 300 mA and after 40 min reduced again to 100 mA. Thirty-five minutes after the beginning, chloride as NaCl was added to adjust a concentration of about 10 mg [Cl^-] dm^{-3} (rotation rate 300 rpm, temperature 20 °C, $V = 0.150\ dm^3$, IrO_2 cathode, sulphate −240 mg dm^{-3} and nitrate −50 mg dm^{-3}, as sodium salts).

chlorine by chlorine consuming reactions can reduce the chlorine yield in this case and considerably lower the disinfection ability of the generated species. Surprisingly, nitrite ions were detected in the analysis. These may react with chlorine. For electrolysis applications in the continuous mode and with low residence times in the reactor, lower by-product concentrations can be expected; however, the same reactions are possible. Treatment conditions with very low chlorine generation efficiencies should be avoided. The migration-controlled process can be accelerated by higher current densities but the probability of by-product formation increases. More studies are necessary to obtain better information about these health-relevant mechanisms. Furthermore, optimal current efficiencies exist, which must be determined by case studies for different water qualities. The cathode material has only a small influence on the chlorine production for the studied systems. However, fine analysis studies for waters with very low chloride concentration may show new aspects which have not yet been considered.

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