



Electrochemical water disinfection Part I: Hypochlorite production from very dilute chloride solutions

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Abstract

Electrolytic production of hypochlorite in very dilute chloride solutions is investigated using platinum and iridium oxide coated titanium expanded metal electrodes as anodes. The dependence of the hypochlorite production rate on temperature, chloride concentration and current density was determined. It was found that the hypochlorite production rate is consistently higher on iridium oxide coated titanium compared to platinum coated titanium electrodes.

1. Introduction

The electrolytic production of chlorine and hypochlorite from chloride is widely used in industry [1]. A large body of scientific literature has been published on this subject [2–11]; however, all investigations have been conducted using solutions with very high chloride ion concentrations (e.g., saturated solutions), or relatively high chloride concentrations. Even publications using the phrase ‘dilute chloride solutions’ in their title are concerned with a chloride concentration in the region of 15 g dm^{-3} [9].

In the literature, the term ‘hypochlorite’ is often used to denote the sum of hypochlorous acid and the hypochlorite anion. In technical literature, the term ‘active chlorine’ is used for the sum of chlorine, hypochlorous acid and hypochlorite. In the present study, the latter term is applied.

For water treatment, particularly for water disinfection purposes, a process called anodic oxidation [12], electrochemical disinfection [13], or electrochemical treatment [14] is frequently used. It is believed that the main disinfecting agent in this process is the hypochlorite ion or hypochlorous acid produced from the naturally occurring chloride ions in the processed water [13, 15]. The chloride content in naturally derived

water and drinking water can vary significantly between values as low as about 10 up to 250 mg dm^{-3} or more.

The process of electrochemical disinfection has several advantages over other more common processes of water disinfection. Compared with processes such as chlorination [16] by the use of gaseous chlorine or concentrated hypochlorite solution, no addition of chemicals is necessary. Additionally, the hazards in handling these chemicals are also avoided. Ozonization and especially ultraviolet irradiation can be very effective at the point of use but provide little or no residual disinfection capacity.

For an exact adaptation of electrochemical disinfection to the properties of the processed water, it is necessary to know the dependence of the electrolytic active chlorine production rate on the chloride concentration, temperature, current density and anode material. Despite the frequent use of electrochemical disinfection for water treatment, very little is known about its dependence on these factors. In this paper we compare the dependence on these factors for very dilute chloride solutions and solutions with higher chloride concentrations for the first time. The electrode materials investigated were iridium oxide ($\text{IrO}_2\text{--Ta}_2\text{O}_5$) and platinum coated titanium.

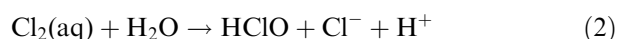
The main difficulty in obtaining reliable and reproducible results for the electrolytic active chlorine

production rate in these very dilute solutions is the fact that a substantial fraction of the chlorine produced rapidly reacts with oxidizable agents in the water and the apparatus. This process is known as chlorine decay or chlorine consumption [16, 17] and must be eliminated or minimized in each experiment in order to measure the exact hypochlorite production rate.

In electrolytic hypochlorite production there are two steps. First, the primary oxidation of chloride to chlorine at the anode surface:



this is followed by the secondary solution phase reaction:



Hypochlorous acid can dissociate to form hypochlorite and H^+ , the relative proportions of which depend on the pH of the water:



The goal of the present study was to provide as much information as possible on the practical use of electrochemical treatment for water disinfection.

2. Experimental details

The electrodes tested (Metakem GmbH, Germany) consisted of titanium expanded metal coated with either iridium oxide ($\text{IrO}_2\text{-Ta}_2\text{O}_5$ with 8 g Ir m^{-2} in a molar ratio of Ir to Ta: 70 to 30) or platinum (thickness $2 \mu\text{m}$). In all experiments, cathode and anode were of the same material and the polarity of the electrodes was not changed during the experiments. The electrodes had the following geometrical areas: platinum: $100 \text{ mm} \times 30 \text{ mm}$ (30 cm^2) and iridium oxide: $113 \text{ mm} \times 30 \text{ mm}$ (33.9 cm^2), the thickness of the titanium expanded metal was 1 mm. Current densities were calculated using a factor taking into account the area of the electrode meshes.

All experiments were carried out using divided electrode compartments to prevent the reduction of produced hypochlorite at the cathode. Anolyte and catholyte were divided by a Nafion[®] 450 cation exchange membrane. The electrode distance was 5 mm.

To minimize reactions of produced chlorine with the experimental apparatus, all walls were constructed with either PTFE-material or spray-coated with PTFE. The rubber seals in the ion exchange membrane were made from Viton[®] perfluorinated elastomer. The power

supply used was a Voltcraft[®] DIGI 40 and anolyte and catholyte were circulated at $300 \text{ cm}^3 \text{ min}^{-1}$ using ProMinent[®] gamma G4Ca pumps. Temperature was controlled by circulating water through a thermostat.

The solutions for the experiments with a defined chloride concentration were prepared using deionized water and a concentrated NaCl solution, which was also made with deionized water. No supporting electrolyte was added. Therefore the conductivity varied greatly between experiments with different chloride concentrations. The volumes of the anolyte and catholyte compartments were 1250 cm^3 and 280 cm^3 , respectively.

The overall concentration of dissolved chlorine in water chlorination is termed the 'active' chlorine and is the sum of the three possible species, Cl_2 , HClO and ClO^- . In the pH range 6–9, the active chlorine is almost entirely constituted by hypochlorous acid (HClO) and hypochlorite (ClO^-). In the present study the concentration was measured as active chlorine in mmol dm^{-3} or converted into mg dm^{-3} this conversion being based on the molecular weight of Cl (35.45 g mol^{-1}). The active chlorine production rate is given in mmol min^{-1} and mg h^{-1} or normalized with respect to the current in $\text{mmol min}^{-1} \text{ A}^{-1}$ and $\text{mg A}^{-1} \text{ h}^{-1}$. The active chlorine concentration was determined using iodometric titration [18]. The chlorate concentration was also determined using iodometric titration but was performed in a strongly acid solution ($\text{pH} < 1$).

To minimize chlorine consumption during electrolysis, 45 min of preelectrolysis was performed, which produced an active chlorine concentration of $0,15 \text{ mmol dm}^{-3}$. The chlorine produced during this process was sufficient to oxidize most of the chlorine consuming and oxidizable substances present and thus was effective in minimizing chlorine consumption during experiments. The duration of each experiment was 10 min. In this time the decrease in chloride concentration in the circulating anolyte was always less than 4% of its initial value. This lies within the degree of experimental error for the measurement of the chloride concentration. The anolyte pH was kept constant by adding small amounts of saturated NaOH solution.

In the experiments determining chlorine decay, using a volume of 250 cm^3 , pH 7 solution containing $0.83 \text{ mmol dm}^{-3}$ of active chlorine and 124 mg dm^{-3} of chloride was produced. The active chlorine concentration was measured in intervals of 30 min for 5 h and at five different temperatures.

In the experiments investigating the formation of calcareous deposits on the cathode, the electrode compartments were not divided by an ion exchange membrane. The composition of the tap water and the calcareous deposit was determined by GUT Analytik GmbH.

3. Results and discussion

3.1. Dependence of hypochlorite production rate on chloride concentration

The dependence of the active chlorine production rate on the chloride ion concentration for chloride concentrations up to 1500 mg dm^{-3} at 23°C and with a current density of 15 mA cm^{-2} is shown in Figure 1. It can be seen that the active chlorine production rate on IrO_2 is always higher than that on platinum. For both electrode types, the rate increases with increasing chloride concentration. At a chloride concentration of 60 mg dm^{-3} , iridium oxide produces 9.4 times as much active chlorine

as platinum. The current efficiency at this low chloride concentration is 4.6% for iridium oxide and 0.5% for platinum. With a rising chloride concentration, the absolute difference in the active chlorine production rate between IrO_2 and Pt rises, whereas the factor between the active chlorine production rate of both materials is reduced. Therefore, at a chloride concentration of 1500 mg dm^{-3} the factor is only 4.2. The current efficiencies for iridium oxide and platinum at this chloride concentration are 41.5% and 9.9%, respectively.

By further increasing the chloride concentration, even the absolute difference in the active chlorine production rate between the two materials can be lowered. Figure 2 displays the dependence of the active chlorine produc-

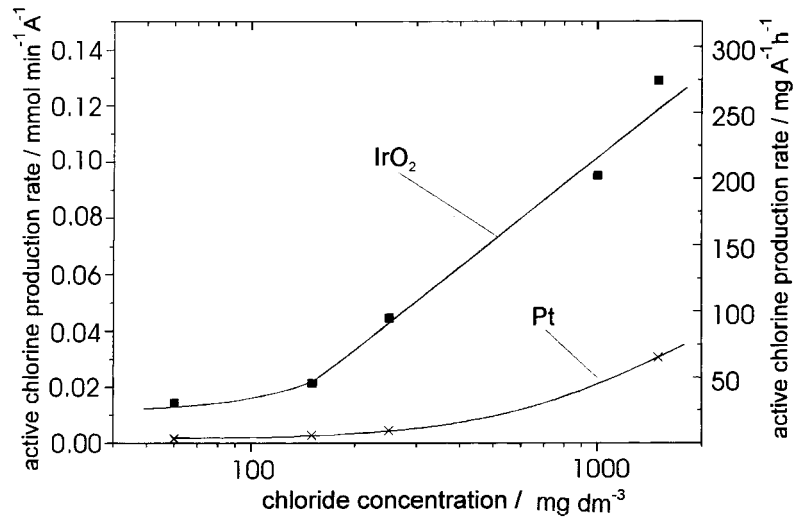


Fig. 1. Dependence of active chlorine production rate per A with iridium oxide and platinum coated titanium expanded metal electrodes on the chloride concentration in the range 0 and 1500 mg dm^{-3} (current density: 15 mA cm^{-2} , temperature 23°C).

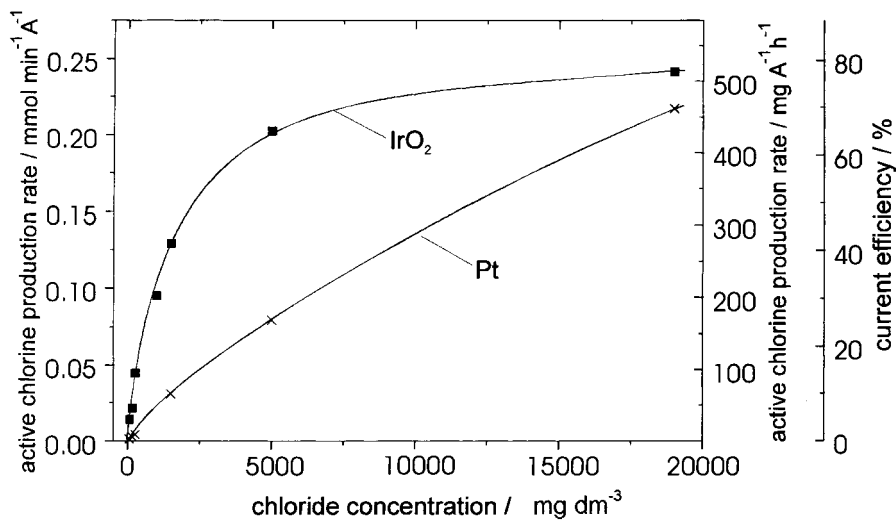


Fig. 2. Dependence of active chlorine production rate per A with iridium oxide and platinum coated titanium expanded metal electrodes on the chloride concentration (current density 15 mA cm^{-2} , temperature 23°C).

tion rate on the chloride concentration over a wider concentration range up to 19 g dm^{-3} (chloride concentration of seawater) at 23°C and a current density of 15 mA cm^{-2} . The current efficiency is also indicated in this Figure. The factor in the active chlorine production rate between iridium oxide and platinum at this high chloride ion concentration is only 1.1.

3.2. Dependence of the hypochlorite production rate on temperature

Figure 3 depicts the active chlorine production rate dependence on temperature (range $10\text{--}60^\circ\text{C}$) for iridium oxide and platinum. The chloride concentration used was 150 mg dm^{-3} at a current density 15 mA cm^{-2} . At all temperatures investigated, the active chlorine production rate on iridium oxide was substantially higher than on platinum. This was particularly true at temperatures less than 25°C .

On using the iridium oxide electrode, there was a remarkable reduction in the active chlorine production rate between 23 and 30°C . Over this small temperature range, the active chlorine production rate was lowered by a factor of 3.3. The experiments were repeated several times and consistently yielded the same result. Using the platinum electrode, no such strong decline of the active chlorine production rate could be detected. This strong reduction in the active chlorine production rate over a small temperature range was not observed at higher chloride concentrations. At the moment, we have no explanation for this strange, but highly reproducible, behavior of the IrO_2 electrode.

In Figure 4 the temperature dependence of the active chlorine production rate on iridium oxide is displayed for three different chloride concentrations at identical current densities of 15 mA cm^{-2} . The active chlorine production rate is lowered with increase in temperature; however, this strongly depends on the chloride concentration.

3.3. Dependence of hypochlorite production rate on current density

Figure 5 depicts the dependence of the active chlorine production rate on current and current density at 23°C with a chloride concentration of 150 mg dm^{-3} . There is a linear increase in the production rate with increasing current density. The slope (about $60 \text{ mg A}^{-1} \text{ h}^{-1}$), of the nearly linear increase in active chlorine production rate for IrO_2 , is much higher than the slope for Pt (about $10 \text{ mg A}^{-1} \text{ h}^{-1}$). In the practical use of electrochemical disinfection, this linear increase in the active chlorine production rate with current density could easily be used to adjust the active chlorine production rate in relation to changing water quality, that is, changing chlorine demand.

Figure 6 depicts the dependence of the active chlorine production rate normalized with respect to current on current density. At lower current densities, there is a slight increase in the active chlorine production rate. At higher current densities, between 40 and 70 mA cm^{-2} , the active chlorine production rate appears to be constant. The active chlorine production rate is always much higher using a IrO_2 electrode than a Pt. For

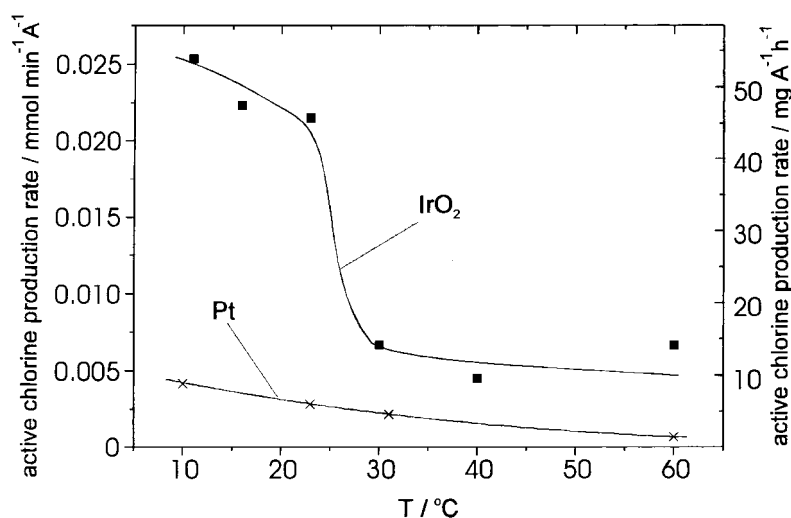


Fig. 3. Comparison of the temperature dependence of active chlorine production rate per A with iridium oxide and platinum coated titanium expanded metal electrodes (current density 15 mA cm^{-2} , chloride concentration 150 mg dm^{-3}).

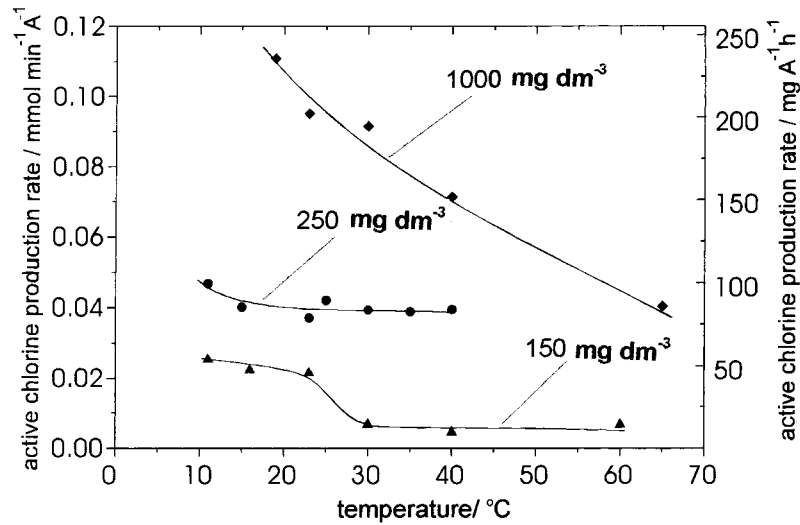


Fig. 4. Temperature dependence of active chlorine production rate per A with iridium oxide coated titanium expanded metal electrodes (current density 15 mA cm^{-2} , three different chloride concentrations: 150 , 250 and 1000 mg dm^{-3}).

instance, using the constant production rate rang, IrO_2 produces as 5.4 times as much active chlorine as Pt. The current efficiencies for iridium oxide and platinum over this range are 8.7% and 1.5%, respectively.

3.4. Chlorine decay

Chlorine decay is a major problem in accurately determining the exact amount of active chlorine produced. This phenomenon is well known in chlorination processes commonly used in water treatment. Each type

of water has a chlorine demand. The chlorine demand is the quantity of chlorine that will react with the inorganics and organic impurities contained within that water. Before active chlorine can be formed, the chlorine demand of the water must be satisfied. This process is usually termed breakpoint chlorination.

In the present study, preelectrolysis was performed. By using this process, in addition to pure chemicals and perfluorinated materials for the experimental equipment, it was possible to minimize the level of chlorine decay. Nevertheless, following this treatment, a further

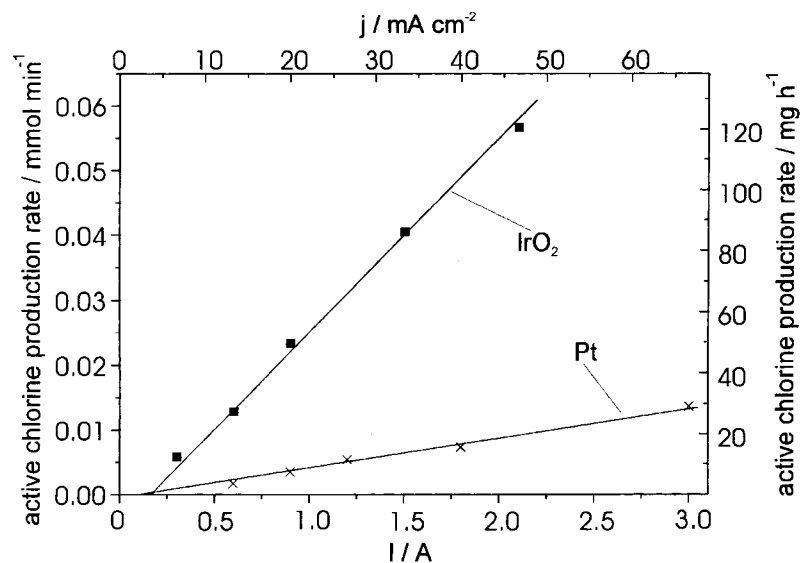


Fig. 5. Active chlorine production rate with iridium oxide and platinum coated titanium expanded metal electrodes, dependence on current and current density (chloride concentration 150 mg dm^{-3} , temperature $23 \text{ }^\circ\text{C}$).

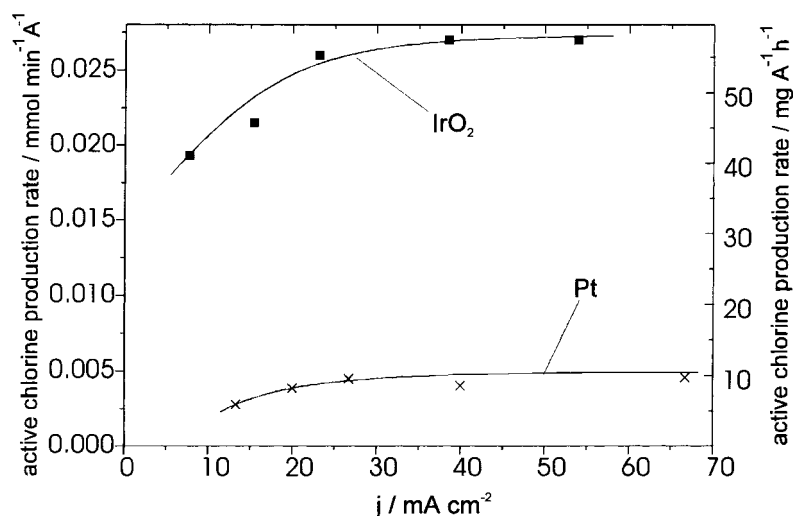


Fig. 6. Active chlorine production rate per A with iridium oxide and platinum coated titanium expanded metal electrodes, dependence on current density (chloride concentration 150 mg dm^{-3} , temperature $23 \text{ }^\circ\text{C}$).

slow, but constant, chlorine decay rate could still be measured. The chlorine decay rate strongly depends on the temperature and pH but does not appear to depend on the active chlorine concentration; this is true for the concentration ranges tested thus far. The measurements for the chlorine decay rate were repeated several times, the results of these experiments were shown to vary by up to one order of magnitude from one experiment to the next. In all experiments, there was an exponential increase in the reaction rate of chlorine decay with increasing temperature. An example for the temperature dependence at pH 7 is shown in Figure 7. The large differences in the chlorine decay rate between individual

experiments are probably due to differences in the small amounts of contaminating substances that catalyse chlorine decay.

Using platinum electrodes and increasing temperature, the measured rate of chlorine decay is of the same order of magnitude as the slight temperature decrease in the measured active chlorine production rate (see Figure 3). Therefore chlorine decay is probably the explanation for this decrease. However, the much steeper decrease seen using IrO_2 electrodes at a temperature of between 20 and $30 \text{ }^\circ\text{C}$ (Figure 3) and a chloride concentration of 1000 mg dm^{-3} (Figure 4), cannot be explained by this chlorine decay.

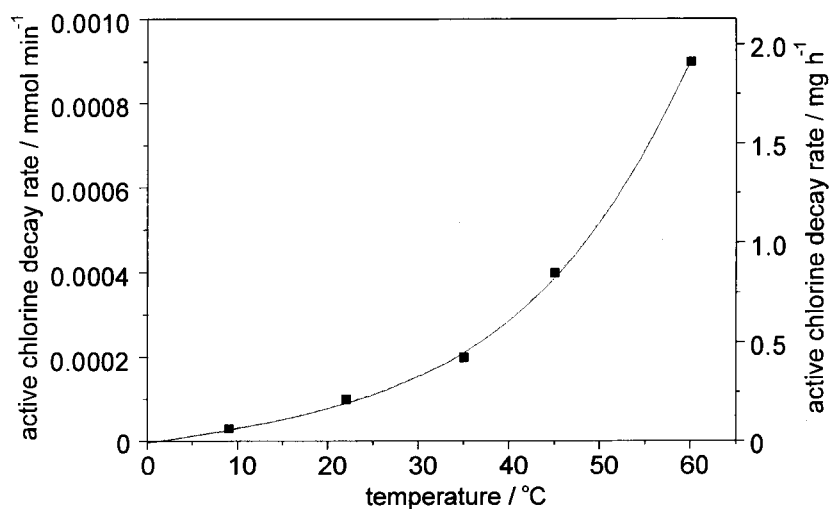


Fig. 7. Active chlorine decay rate dependence on temperature at pH 7 (initial active chlorine concentration: 29.5 mg dm^{-3} ; initial chloride concentration 124 mg dm^{-3} , electrolyte volume 250 cm^3).

3.5. Calcareous deposits on the cathode surface

A major problem in the practical use of electrochemical disinfection for water treatment is the formation of calcareous deposits on the cathode surface. It is generally assumed that the formation of these deposits is caused by the local pH change on the cathode surface. During electrolysis hydrogen from H^+ is produced at the cathode:



The resultant OH^- ions lead to an increase in pH.

To further investigate the scaling phenomenon on the cathode, electrolysis was always conducted over a period of 5 h at 40 °C, at a current density of 10 mA cm⁻² and using IrO₂ electrodes in four different waters with identical chloride ion concentrations (50 mg dm⁻³).

The first experiment was performed in tap water (Ca^{2+} concentration: 134 mg dm⁻³, Mg^{2+} concentration: 15 mg dm⁻³) to which a K_2HPO_4/KH_2PO_4 buffer solution was added. In this case, no calcareous deposit formed on the cathode surface during electrolysis. This demonstrates that the change in the pH is indeed responsible for the electrode scaling.

In the second experiment a calcium ion containing solution (Ca^{2+} concentration: 200 mg dm⁻³) was prepared by using deionized water (containing no HCO_3^-) and $CaCl_2$ and $Ca(NO_3)_2$ and then electrolysed. Again no scaling on the cathode surface occurred.

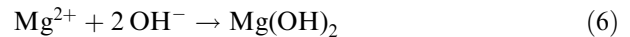
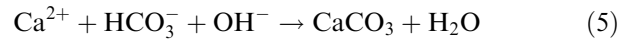
The third experiment was performed in tap water (in the absence of a K_2HPO_4/KH_2PO_4 buffer solution) and the usual calcareous deposit was obtained at the cathode. The concentration of the cationic components in the tap water and in the calcareous deposit are given in Table 1.

Table 1. Composition of calcareous deposit produced on the cathode surface during electrolysis in tap water

Element	Concentration in tap water /mg dm ⁻³	Composition of calcareous deposit /mass %
Ca	134	32
Mg	15	4.4
Mn	0.051	0.0022
Sn	<0.03	0.037
Zn	0.25	0.18
Pb	<0.03	0.0016
Cu	0.23	0.056
Fe	2.0	0.02
Na	24	0.032
K	4.5	0.074
Sum of cationic species in the calcareous deposit		36.8

In a fourth experiment, a solution containing magnesium ions (Mg^{2+} concentration: 200 mg dm⁻³) was also prepared using deionized water (containing no HCO_3^-) and $MgCl_2$ and $Mg(NO_3)_2$ for electrolysis. In this instance, a white precipitate formed. However, this precipitate was much less adherent to the cathode surface than the calcareous deposits produced in the third experiment.

The results of the last three experiments indicate that not only calcium ions, but also HCO_3^- ions are necessary (exp. 2) for the deposition of calcium containing deposits at higher pH values. If magnesium ions, but no HCO_3^- ions are present in the water (exp. 4), there is a deposition of magnesium hydroxide instead. With ordinary tap water, which contains calcium, magnesium, and HCO_3^- ions, a mixed precipitate is produced. Thus, the main reactions which are responsible for the formation of calcareous deposits at the cathode can be written as follows:

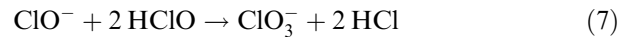


These findings are in agreement with previously published results on the formation of calcareous deposits on cathodically protected steel in seawater [20, 21].

In an undivided electrochemical reactor, the deposition of a thin calcareous film at the cathode leads to a lowering of the hypochlorite reduction [22]; this can be helpful in enhancing the overall current efficiency for hypochlorite production. However, it is usual that if a thin film of calcareous deposits has already been formed, the thickness of the film will steadily increase. This is particularly true at higher temperatures.

3.6. Chlorate formation

The kinetics of the formation of chlorate from hypochlorite and hypochlorous acid has been thoroughly investigated by de Valera [23] and follows the equation:



According to de Valera [23], the temperature dependence of the rate constant k for the formation of chlorate is given by Equation 8:

$$\frac{dc_{ClO_3^-}}{dt} = kc_{ClO^-}c_{HClO}^2 \quad (8)$$

$$k = 0.1733 e^{0.0889 T} \quad (9)$$

where T is in °C.

A simple calculation using these equations at 60 °C, taking the equilibrium concentrations of HOCl and OCl⁻ at the same temperature [3] at an overall active chlorine concentration of 10 mg dm⁻³ (2.82×10^{-3} mol dm⁻³) and a pH of 7.5, gives rise to a rate constant for chlorate formation of 35.92 (dm³)² mol⁻² s⁻¹ and a reaction rate dc_{chlorate}/dt of 7.25×10^{-11} mol dm⁻³ s⁻¹. If the active chlorine concentration is 1 mg dm⁻³ the formation rate is decreased to 7.25×10^{-14} mol dm⁻³ s⁻¹. This shows that the formation rate of chlorate from active chlorine is extremely low at the concentration is routinely used in drinking water disinfection. Several measurements of the chlorate concentration during the experiments in chloride solutions up to 250 mg dm⁻³ yielded the same result; i.e. no chlorate was detectable.

4. Conclusions

For the first time, hypochlorite production in very dilute chloride solutions has been investigated. The values for the hypochlorite production rate, which can be measured in natural occurring waters under the same conditions, will probably be lower than those measured in the present investigation. This is due to chlorine decay, which was minimized in the experiments conducted in this work. Of the electrode materials tested, iridium oxide electrodes consistently out-performed platinum electrodes for hypochlorite production. The observed linear increase in the active chlorine production rate with current density could be used to adjust the active chlorine production in line with changes in water quality, particularly in chlorine demand. In addition the production of chlorate was found to be negligible in this system. Thus, in principle, electrolytic hypochlorite production from very dilute chloride solutions can be applied for water disinfection purposes.

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