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Electrochemical water disinfection. Part II: Hypochlorite production from potable water, chlorine consumption and the problem of calcareous deposits

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Abstract

The electrolytic production of hypochlorite from tap water in a flow-through reactor system is investigated using stacked platinum or iridium oxide coated titanium sheet or expanded metal electrodes. The influence of fast chlorine consumption and polarity reversal on the hypochlorite production rate was determined along with the dependence of the hypochlorite production rate on temperature, flow through velocity and current density. It was found that in most cases, the hypochlorite production rate was higher on iridium oxide compared to platinum electrodes. An increase in the flow-through velocity leads to an increased hypochlorite production rate while the hypochlorite production rate falls with increasing temperature.

1. Introduction

Electrochemical disinfection is one possible method for water treatment [1–6]. In this process, oxidizing and bactericidal substances are not added to the water; they are produced from naturally occurring substances in the water by electrolysis without the requirement for additional chemicals. The oxidizing substances which are be produced are short-lived, free radical species such as O•, OH• and more stable substances such as HClO, ClO^-, H_2O_2, O_3, MnO_4^{2-}, $S_2O_8^{2-}$ amongst others [3]. However, the most important electrochemically produced components for the disinfection process are hypochlorous acid and hypochlorite [2]. In electrochemical disinfection, the main reaction is the electrolysis of water; hydrogen is produced at the cathode and oxygen at the anode; the anodic production of hypochlorite is a side reaction.

In Part I we reported on electrolytic hypochlorite production in very dilute chloride solutions [6]. These experiments were performed by minimizing the chlorine consumption by using deionized water, pure chemicals and PTFE materials for the experimental setup, and by performing a preelectrolysis process prior to each experiment. The present paper is also concerned with electrolytic hypochlorite production from very dilute solutions, but without the requirement to minimize chlorine consumption. The aim being to probe the practical use of electrochemical disinfection for drinking water. Comparing the results of the present paper with our previously published results [6] gives helpful hints for the exact adaptation of electrochemical disinfection to the amount of and the properties of the water that is to be disinfected.

2. Experimental details

Experiments were performed using a flow-through reactor in the water laboratory of AQUA Butzke–Werke AG (Ludwigsfelde near Berlin). The reactor (Gerus mbH) comprised of a polybutene pipe with an electrode stack (Figure 1), the reactor pipe having an inner diameter of 50 mm and a length of 230 mm. The electrode stack was made up of a number of equidistant monopolar plate electrodes. The following variations of the electrode stack were tested: (i) electrode substrates: titanium sheets or titanium expanded metal; (ii) elec-

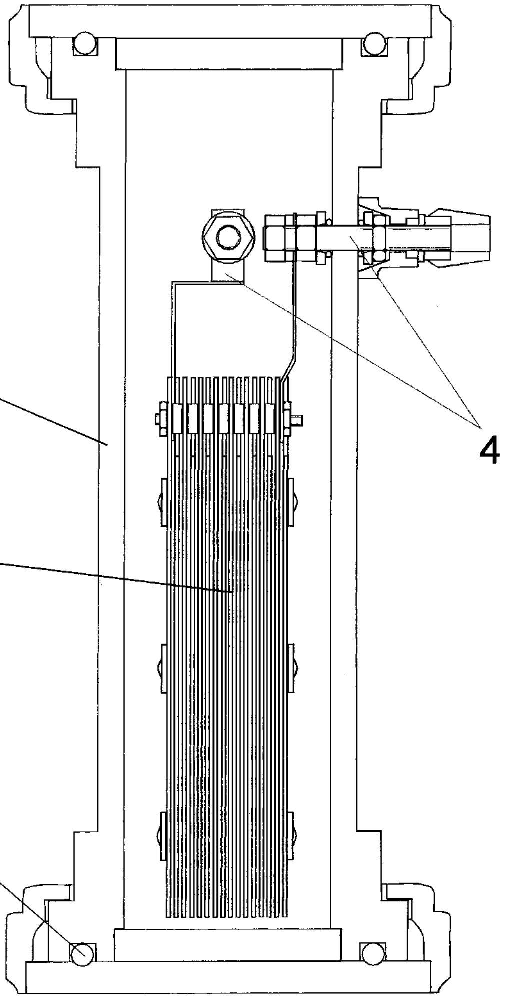

Fig. 1. Schematic view of the electrochemical reactor used in the present study. Key: (1) reactor pipe, (2) rubber O-ring sealing, (3) electrode stack and (4) current feeder.

trode coatings: platinum (thickness 2 μm) or iridium oxide (IrO_2–Ta_2O_5 with 8 g Ir m^{-2}; molar ratio of Ir to Ta: 70 to 30).

The geometrical area of a sheet electrode was 30 mm × 133 mm while the expanded metal electrode had a geometric area of 30 mm × 110 mm. A standard electrode stack consisted of 12 plates of sheet electrodes (electrode distance 2 mm) or 22 plates of expanded metal electrodes (electrode distance 1 mm). With an applied current of 10 A, this configuration gave an approximate current density of 20 mA cm^{-2} for both electrode stacks. For the calculation of the current density on the expanded metal electrodes, a factor of 0.75 for the area was used. All electrodes were produced by Metakem GmbH (Usingen, Germany).

The electrolytic water disinfection experiments were performed by the continuous pumping through the reactor of potable water from the Ludwigsfelde municipality at various flow velocities. Water was only passaged once through the reactor. The water temperature varied between 10 and 60 °C and in all experiments, the chloride concentration was $\sim$70 mg l^{-1} (1.97 mmol l^{-1}), conductivity was $\sim$0.9 mS cm^{-1}, pH was 7.3, and the Ca^{2+} and Mg^{2+} concentrations were 130 and 10 mg l^{-1}, respectively. The power source was a 20 V, 100 A rectifier (Munk).

The hypochlorite concentration was measured in a bypass situated directly after the electrolysis cell using an amperometric active chlorine sensor (Iotronic GmbH); this hypochlorite concentration was taken to be the so-called active chlorine level. Active chlorine is the sum of the three different dissolved chlorine species (Cl_2, HClO, and ClO^-) which are present in the water [6, 7].

3. Results and discussion

3.1. *Active chlorine consumption*

Figure 2 shows the dependence of the active chlorine production rate on current density at a flow-through velocity of 120 l h^{-1} at two different temperatures. Iridium oxide coated titanium sheets were used as electrodes. A comparison of the results in Figure 2 with the previously published results using minimized chlorine consumption (see Figure 5 in [6]) shows that in both cases, there is a linear increase in the active chlorine production rate with increasing current density. However, with minimized chlorine consumption this straight line begins near 0 mA cm^{-2} [6], whereas in the present study the linear increase starts at much higher current densities; that is, 11 mA cm^{-2} at 30 °C and at

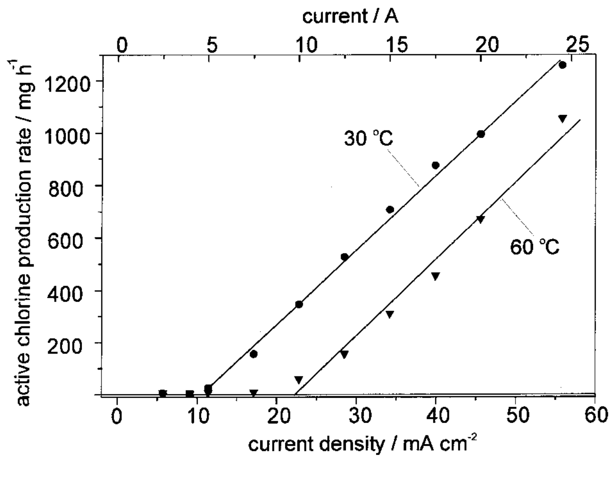

Fig. 2. Dependence of the active chlorine production rate on current density at 30 and 60 °C on IrO_2 sheet electrodes (flow rate 120 l h^{-1}).

23 mA cm^{-2} at 60 °C. This suggests that there is a parallel shift in the nearly linear increase of the active chlorine production rate with current density. The degree of shift increases with increasing temperature.

This parallel shift can be explained by the enhanced active chlorine consumption and, in particular, by the fast chlorine consumption. The active chlorine consumption is the result of reactions with components in the water and with the walls of the water distribution system. Briefly, two types of active chlorine consumption can be distinguished [8, 9]. First, there is a fast chlorine consumption due to fast reactions with certain substances in the water. Secondly, there is a kinetically slower chlorine consumption due to reactions with other dissolved substances, with suspended particles, and with the pipe walls of the plumbing system. The latter is a function of pipe diameter, flow through velocity, nature of the pipe material and of the amount and nature of the deposits on the pipe wall [9].

An example of fast chlorine consumption is the reaction with dissolved iron species. It was found in the present investigation, that the concentration of dissolved iron in electrolysed water was reduced from approximately 0.1 mg l^{-1} before entering the electrochemical reactor, to less than 0.006 mg l^{-1} directly on exit from the reactor. This is below the detection limit of the method used. After a few weeks of continuous electrolysis, a brown staining on the reactor walls in the area of the electrode stack and on the pipes behind the reactor was visible. This staining was probably unsoluble Fe(III) substances, and it can be assumed that dissolved Fe(II) was oxidized by active chlorine to Fe(III) which precipitated on the reactor walls.

This fast chlorine consumption is completed before the measurement of the active chlorine concentration. As a result, we were unable to measure the real produced active chlorine concentration but rather measured the difference between the produced active chlorine concentration and that which removed by the fast chlorine consumption. Therefore, the fast chlorine consumption can be expressed as an equivalent of (lost) active chlorine concentration. This connection is indicated in the equation:

$$c_{\text{active chlorine, produced}} = c_{\text{active chlorine, measured}} + c_{\text{active chlorine, fast consumption}} \quad (1)$$

The equivalent concentration of fast chlorine consumption depends on the substances dissolved in the water and on the water temperature. The higher the water temperature, the higher the fast chlorine consumption. This is because a temperature increase generally leads to an increase in reaction rate. In Figure 3, a schematic representation of the relationship between the active chlorine production, fast chlorine consumption and the measured active chlorine production is shown. If this theory is used to calculate the hypothetical fast chlorine consumption from the parallel shift of the two curves shown in Figure 2, values of about 2.5 mg l^{-1} for 30 °C and 6 mg l^{-1} for 60 °C are obtained.

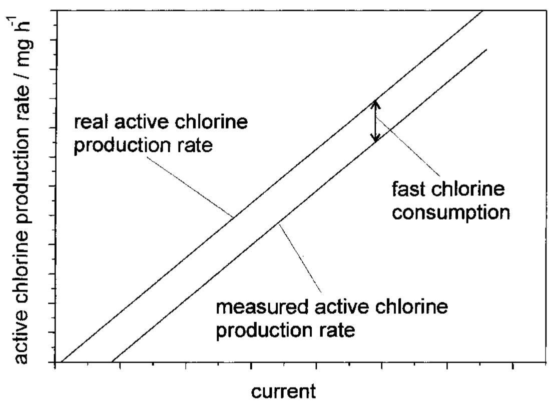

Fig. 3. Schematic representation of the connection between the real active chlorine production rate, fast chlorine consumption and measured active chlorine production rate.

If it is not carefully accounted for, chlorine consumption by the electrolysed water can lead to discrepancies in the dependence of the active chlorine production on temperature, current density and flow through velocity. For example, if the real active chlorine concentration is constant but the flow through velocity is increased, more substances which cause fast chlorine consumption are able to react with the active chlorine produced. Consequently, an apparently lower active chlorine production is measured.

Further comparison of the results of the present investigation with our recent results [6] shows that there are differences in the slope of the linear increase of chlorine production on $\mathrm{IrO_2}$ with current density. In the present study, using a chloride concentration of 60 mg l^{-1}, a slope of 30 mg A^{-1} h^{-1} was measured whereas the slope measured in [6] with a concentration of 150 mg l^{-1} chloride ions was 60 mg A^{-1} h^{-1}. A dependence of this slope on chloride concentration is possible but was not investigated in the present study as only the original tap water with a fixed chloride concentration was used for the experiments. This phenomenon will be investigated further.

All the values for active chlorine production presented in the current investigation are only measured values of the active chlorine production rate. The real active chlorine production rate can be calculated by adding the hypothetical fast chlorine consumption to these values. Due to variations in the water quality, drastic changes in the fast chlorine consumption and, consequently, in the measured active chlorine production rate, can occur. The measured active chlorine production rate can be relatively constant over extended periods of time but can also change on an hourly basis. This makes it difficult to apply a method of electrochemical disinfection to water treatment.

3.2. *Calcareous deposits and polarity reversal for their removal*

During water electrolysis, a thin film of calcareous deposits is formed at the cathode surface. This film mainly consists of $CaCO_3$ and $Mg(OH)_2$ [6, 10–12] being produced in the vicinity of the cathode surface as a result of a local pH increase [13] due to the evolution of hydrogen:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \qquad (2)$$

whereas the pH on the cathode surface is increased, the pH on the anode surface is decreased due to the evolution of oxygen:

$$2\,H_2O + 4\,e^- \rightarrow O_2 + 4\,H^+ \qquad (3)$$

This phenomenon can be used for the removal of cathode scaling; for this, a regular reversal of electrode polarity is necessary [14, 15].

Following polarity reversal, the former cathode with calcareous deposits acts as an anode and, with continued electrolysis, a local pH decrease at the anode surface occurs. This leads to dissolution of the scale on the anode surface according to the following equations:

$$CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \qquad (4)$$

$$Mg(OH)_2 + 2\,H^+ \rightarrow Mg^{2+} + 2\,H_2O \qquad (5)$$

The scale that is more distant from the anode surface is unable to adhere and is, therefore, flushed away by the water flow. By applying this method of polarity reversal, it is possible to clean calcareous deposits from the electrode. The time between two polarity reversals should be in the range of 10–60 min. A strong outgassing effect is visible for a few seconds following polarity reversal on the electrode that was formerly the cathode. This is probably due to the formation of CO_2 according to Equation 4.

When the polarity reversal method is used for electrode cleaning, it is necessary that all parts of the titanium electrode substrates are coated with electrochemically active films (e.g., IrO_2 or Pt as used in this study) otherwise polarity reversal does not work. This is due to the fact that titanium, as a valve metal, allows current flow only when used as a cathode. When used as an anode, the titanium surface is passive and little or no current flows through it. Therefore, the resultant pH decrease at the anode surface is not strong enough to dissolve the scale.

If cathodically formed scale deposits are not completely removed, they continue to grow. The remaining deposits act as nucleation centers for the growth of calcareous scale. The higher the water temperature, the greater the hardness of the water and the flow velocity, the greater the growth rate. The increase in flow velocity improves the mass transfer of Ca^{2+} and Mg^{2+} ions to the surface. Eventually, this leads to a total blockage of the electrode stack, as the gaps between the electrodes become filled with scale [15].

Polarity reversal has a strong side effect on the activity of electrode materials in active chlorine production. Figure 4 shows an example of the change in the active chlorine production rate for iridium oxide and platinum electrodes directly after a polarity reversal. On platinum electrodes, the active chlorine production rate rises sharply directly following polarity reversal. This can be attributed to a change in the platinum surface during the time the electrode was acting as a cathode. In this time, the thin oxide film of PtO_x (platinum oxide) which was formed when the electrode was the anode is reduced to Pt (platinum) metal. Platinum metal has a much higher activity for chlorine production (or rather a lower activity for oxygen evolution) than the PtO_x surface. Following polarity reversal, the electrode is working as anode and produces oxygen and chlorine. Again, the

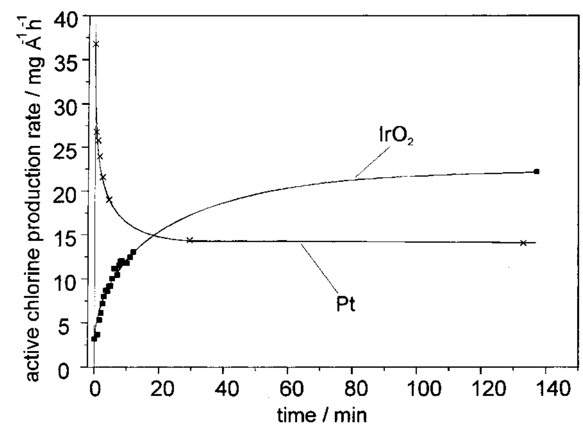

Fig. 4. Change in the active chlorine production rate with time (*t*) following polarity reversal (polarity reversal at $t = 0$ min) at 60 °C, 15 A (current density 34 mA cm^{-2}), flow rate of 120 l h^{-1} on IrO_2 and Pt coated titanium sheet electrodes.

surface becomes covered with a thin layer of oxide and consequently the chlorine production rate decreases. Most of the decrease in the active chlorine production rate occurs in the first 5 min. After 30 min, the active chlorine production rate steadies to a constant value of approximately 0.4× the value obtained directly following polarity reversal. Using platinum, the change in the active chlorine production rate after current reversal is reproducible.

With iridium oxide, the inverse effect compared to platinum is observed. Directly after polarity reversal the chlorine production rate is very low. The active chlorine production rate slowly increases during anodic oxygen and chlorine production but this increase is much slower than the decrease in the active chlorine production rate on platinum. In addition, even if an IrO_2 electrode has only been used once as cathode, the value obtained for the active chlorine production rate never matches that obtained using a new IrO_2 electrode, which has never been used as cathode. The amount of the decrease in the active chlorine production rate depends upon the time that the electrode was polarized as a cathode and on the current density during this time. The longer the electrode is used as cathode and the higher the cathodic current density, the lower the active chlorine production rate following polarity reversal. The increase in the active chlorine production rate during the anodic cycle also depends on the current density. The higher the current density, the faster the rise in the active chlorine production rate.

The lowering of the active chlorine production rate by iridium oxide after cathodic polarization of the electrode is probably due to the partial reduction of the mixed oxides that comprise the electrode coating. This leads to a composition that is less active for chlorine evolution than the composition of a newly prepared electrode. When polarized as an anode, the reduced mixed oxides are reoxidized and therefore the chlorine production rate increases. However, the initial composition of the iridium oxide electrode cannot be reproduced.

Another negative side effect in the use of polarity reversal is the diminution of the electrode lifetime. This problem mainly concerns iridium oxide coated titanium electrodes. For example, at a current density of 20 mA cm^{-2}, a temperature of 40 °C, and a regular polarity reversal cycle of 15 min, the electrode lifetime of iridium oxide coated electrodes is decreased to approximately three months. Again, this diminution is greater at higher than lower current densities. Under the same conditions, the lifetime of a platinum-coated electrode is more than twelve months (an experiment is still in progress).

3.3. *Dependence of hypochlorite production rate on IrO_2 and Pt on current density, flow through velocity and temperature*

All results presented in this section were produced by using electrodes to which a regular polarity reversal (30 min for each half cycle) was applied. To make the results more comparable all measurements were performed approximately 20 min after polarity reversal.

Previous results [6] with minimized chlorine consumption indicated that IrO_2 is generally much more effective than platinum in active chlorine production and that the active chlorine production rate is lowered by an increase in temperature. The chlorine production rate [mg h^{-1}] exhibits an almost linear increase with increasing current density, whereas the active chlorine production rate [mg A^{-1} h^{-1}] is only slightly increased by increasing the current density. The influence of the flow through velocity was not investigated in this study. However, it is generally assumed that by increasing the flow through velocity, the mass transfer to the electrode is enhanced; this would lead to an increase in the active chlorine production rate.

Figure 5 shows a comparison of the active chlorine production rate by iridium oxide and platinum sheet electrodes at 60 °C. Following the parallel shift due to the fast chlorine consumption, a linear increase in the active chlorine production rate was measured. The slopes for IrO_2 and Pt were 30 and 10 mg A^{-1} h^{-1}, respectively. Surprisingly, at lower current densities, a platinum electrode is able to produce more active chlorine than an iridium oxide electrode. Starting with a current density of 37 mA cm^{-2}, iridium oxide produces more chlorine than platinum. The differential between the two materials increases further with in-

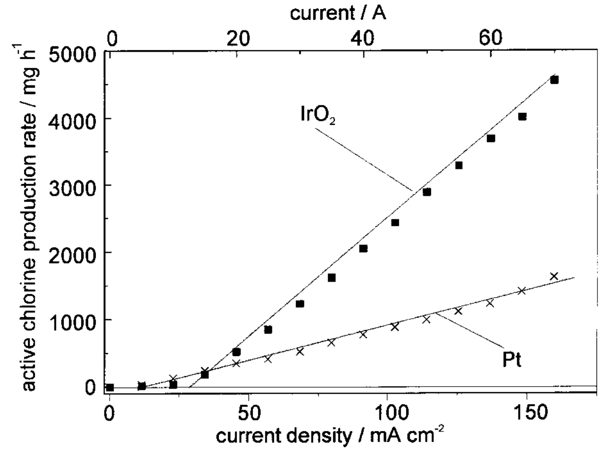

Fig. 5. Comparison of the active chlorine production rate on iridium oxide and platinum sheet electrodes (60 °C, 120 l h^{-1}).

creasing current density. This is due to the difference in the slopes for the active chlorine production rate as a function of current density. The slope of the increase in the active chlorine production rate on iridium oxide using 70 mg l^{-1} chloride and with polarity reversal is 30 mg A^{-1} h^{-1}. This value is about half that measured for iridium oxide using a chloride concentration of 150 mg l^{-1} with no polarity reversal (60 mg A^{-1} h^{-1}) [6]. The slope for Pt is almost constant at both chloride concentrations, with or without polarity reversal. Thus, the change in the slope of the increase in the active chlorine production rate by the iridium oxide electrode as a function of current density, can also be explained by the change in the activity of the iridium oxide electrode material for chlorine production due to polarity reversal.

Figure 6 shows the same values for the active chlorine production rate as seen in Figure 5, but the values are normalized for the current. Even at 60 °C, with a high chlorine consumption, the measured active chlorine production rate (mg A^{-1} h^{-1}) on Pt is higher when compared to the values obtained using minimized chlorine consumption at 23 °C, a low flow through velocity and the same current density (see Figure 6 in [6]). For example, in the present study a current density of 60 mA cm^{-2} yields a production rate of about 18 mg A^{-1} h^{-1}, whereas in our previous study [6] a production rate of only 10 mg A^{-1} h^{-1} was measured. This is due to the enhanced mass transfer as a result of the much higher flow-through velocity in the reactor used in the current study.

Despite an increased mass transfer rate, the measurement of the active chlorine production rate on IrO_2 at 60 °C with high chlorine consumption does not reach the values obtained using minimized chlorine consumption at 23 °C [6]. For example, at a current density of 60 mA cm^{-2}, as in the present investigation, a production rate of 35 mg A^{-1} h^{-1} was measured, whereas in our previous study the rate was 58 mg A^{-1} h^{-1}. This is due to the strong decrease in the active chlorine production rate on IrO_2 due to the effects of polarity reversal.

The temperature dependence of the active chlorine production rate on IrO_2 at two different current densities is shown in Figure 7. The active chlorine production rate is decreased with increasing temperature. This is explained by a lowering of the real active chlorine production rate and, more importantly, an increase in chlorine consumption with temperature [6]. The increase in fast chlorine consumption is the dominant factor when looking at the temperature dependence of the active chlorine production rate.

In Figure 8, the dependence of the active chlorine production rate on flow through velocity and current density is shown for IrO_2 sheet electrodes. The measured active chlorine production rate slightly increases with increased flow-through velocity. Generally, a much steeper increase in the production rate with an increased flow-through velocity would be expected. That only a slight increase is observed is due to the fact that increasing flow-through velocity also increases chlorine consumption. This is because at higher flow-through velocities a greater number of substances which cause active chlorine consumption pass through the reactor. Therefore, by increasing the flow-through velocity both the real active chlorine production and the fast chlorine consumption rate are increased. Depending on the numbers involved, this can also lead to a decrease in the measured active chlorine production rate (see Equation 1).

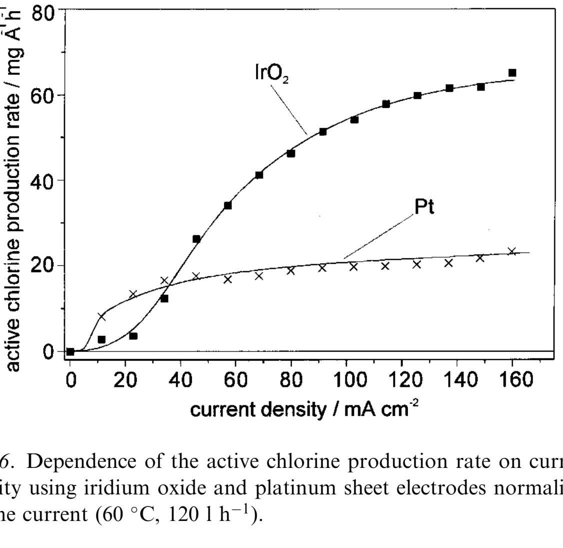

Fig. 6. Dependence of the active chlorine production rate on current density using iridium oxide and platinum sheet electrodes normalized on the current (60 °C, 120 l h^{-1}).

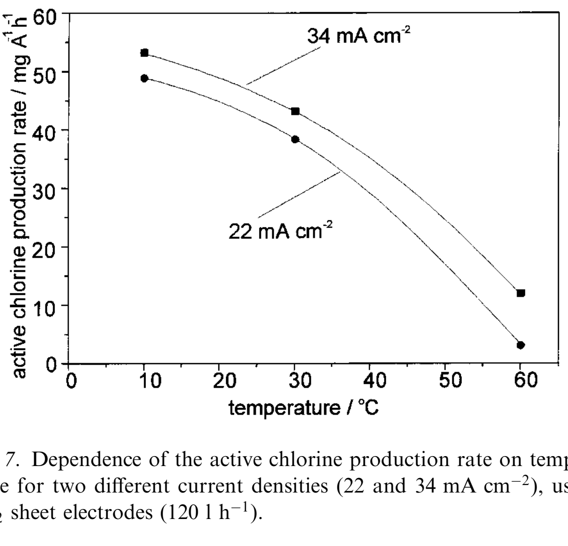

Fig. 7. Dependence of the active chlorine production rate on temperature for two different current densities (22 and 34 mA cm^{-2}), using IrO_2 sheet electrodes (120 l h^{-1}).

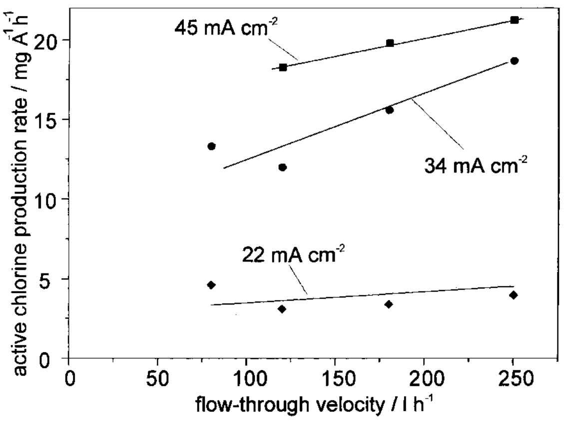

Fig. 8. Dependence of the active chlorine production rate on flow through velocity for three different current densities (22, 34 and 45 mA cm^{-2}), using IrO_2 sheet electrodes (60 °C).

Figure 9 compares the dependence of the active chlorine production rate by IrO_2 sheet and expanded metal electrodes on current density. In the lower current density range, the active chlorine production rate is higher with expanded metal electrodes than with sheet electrodes. This is explained by the improved mass transfer of chloride ions to the anode surface due to a more turbulent flow between the expanded metal electrodes as compared to sheet electrodes. At higher current densities, sheet electrodes produce more active chlorine than expanded metal electrodes. This may be due to the fact that at higher active chlorine concentrations, the reduction of the produced active chlorine on the cathode becomes more important. The more turbulent flow characteristics lead to higher reduction losses on the expanded mesh electrodes as compared to the sheet electrodes.

4. Conclusions

The use of electrochemical disinfection for water treatment has been investigated by measuring the active chlorine production rate in potable water at different temperatures, flow-through velocities, current densities, and by using different electrode materials.

Fast chlorine consumption has considerable influence on measured values of active chlorine production. To adapt the method of electrochemical disinfection to the amount, and quality, of the water that is to be disinfected, the fast chlorine consumption of this water must first to be determined and taken into account. The chloride content and chlorine consumption properties of the water to be processed can vary considerably. The size of the electrochemical reactor must be chosen in a way that allows it to respond to a reduction in the chloride concentration and to an increase in chlorine consumption.

A major problem is the formation of calcareous deposits on the cathode surface. These deposits can be removed by regular polarity reversal of the electrodes. Unfortunately, in the case of iridium oxide electrodes, which in general are more effective than platinum electrodes, this polarity reversal leads to a shortening of the electrode lifetime and a reduction in the active chlorine production rate. When electrodes to which polarity reversal has been applied are used, platinum is more effective in active chlorine production in the lower current

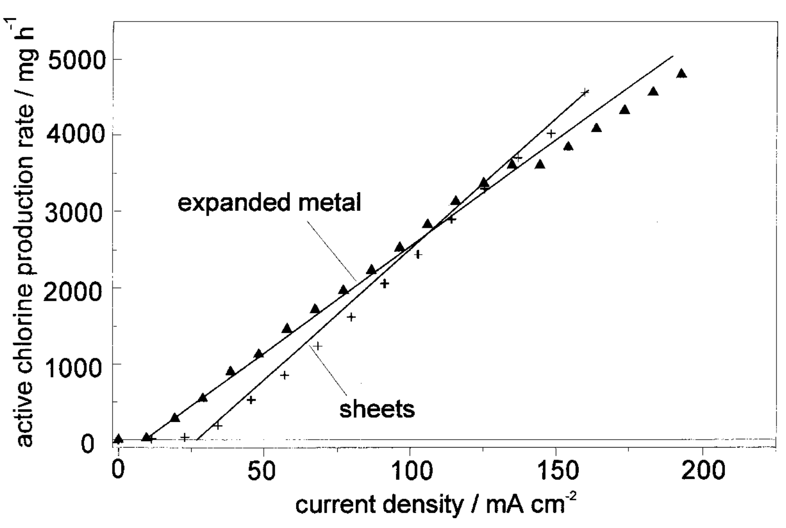

Fig. 9. Comparison of the active chlorine production rate on IrO_2 sheet and expanded metal electrodes, dependence on current density (120 l h^{-1}, 60 °C).

density range, whereas at higher current densities, iridium oxide is the more effective electrode material.

The improved mass transfer on expanded metal electrodes leads to an increase in the active chlorine production rate on the anode and in parallel, to an increase in the chlorine reduction rate on the cathode. The addition of these two processes produces the result that at lower current densities and active chlorine production rates, the measured active chlorine rate is higher on expanded metal than on sheet electrodes. However, at higher current densities and production rates the sheet electrode stacks deliver more active chlorine than expanded metal electrodes.

References

1. A. Reis, *GIT Fachz. Lab.* **20** (1976) 197–204 (in German).
2. G.E. Stoner, G.L. Cahen, Jr., M. Sachyani and E. Gileadi, *Bioelectrochem. Bioenerg.* **9** (1982) 229–243.
3. G. Patermarakis and E. Fountoukidis, *Water Res.* **24** (1990) 1491–1496.
4. M. Schöberl, Eur. Pat. *EP 0 515 628 B1.* (1991).
5. N. Kanekuni, N. Shono, M. Kiyohara, K. Tabata, S. Kono and M. Hayakawa, Eur. Pat. Appl. *EP 0 711 730 A1.* (1995).
6. A. Kraft, M. Stadelmann, M. Blaschke, D. Kreysig, B. Sandt, F. Schröder and J. Rennau, *J. Appl. Electrochem.* **29** (1999) 861–868.
7. A.R. Despic, M.M. Jaksic and B.Z. Nikolic, *J. Appl. Electrochem.* **2** (1972) 337–343.
8. B.M. Saunier and R.E. Sellek, *J.A.W.W.A.* **71** (1972) 297–332.
9. L. Kiene, W. Yu and Y. Levi, C.R. A.W.W.A., Annual Conference, San Antonio, (1993), pp. 503–511.
10. J.-F. Yan, T.V. Nguyen, R.E. White and R.B. Griffin, *J. Electrochem. Soc.* **140** (1993) 733–742.
11. J.-F. Yan, R.E. White and R.B. Griffin, *J. Electrochem. Soc.* **140** (1993) 1275–1280.
12. C. Gabrielli, M. Keddam, H. Perrot, A. Khalil, R. Rosset and M. Zidoune, *J. Appl. Electrochem.* **26** (1996) 1125–1132.
13. C.-Y. Chan, K.H. Khoo, T.K. Lim and A.T. Kuhn, *Surf. Technol.* **15** (1982) 383–394.
14. A.T. Kuhn and R.B. Lartey, *Chemie-Ing. Techn.* **47** (1975) 129–35.
15. G.H. Kelsall, *I. Chem. E. Symp. No.127*, ‘Electrochemical Engineering and the Environment’, (1992) pp. 71–83.