Electrochemical water disinfection Part III: Hypochlorite production from potable water with ultrasound assisted cathode cleaning

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Abstract

A new type of electrochemical reactor for use in electrochemical water disinfection was tested. To solve the problem of the formation of calcium carbonate scales on the cathode surface a cathode which simultaneously acts as a sonotrode was used. This sonotrode is an efficient means for *in situ* cleaning the cathode surface from calcareous deposits formed during hydrogen evolution from potable water. The production rate of active chlorine from potable water in the new reactor in dependence on current, ultrasound intensity, and flow-through velocity was measured. The production of active chlorine is not significantly changed by the effect of ultrasound.

1. Introduction

Electrochemical water disinfection is a rarely used but highly efficient method for water disinfection [1–4]. The disinfecting species, mainly hypochlorous acid and hypochlorite, are produced electrochemically from the naturally occurring chloride ions in the electrolysed water [3, 4]. For this purpose a stack of two or more electrodes onto which a d.c. voltage is applied is usually introduced to the water stream to be disinfected. The use of cylindrically shaped electrodes is also possible.

The widespread use of this method is mainly prevented by problems caused by the deposition of calcareous deposits on the cathode surface [4]. This is due to the increased pH on the cathode surface as a result of hydrogen evolution [3, 4]. Besides the well known use of acids and the polarity reversal method [3, 4], many other different techniques to clean the cathode surface from calcareous deposits have been described.

So, the use of spherical particles whose density is higher than that of water and which are fluidized by the water flowing through the reactor has been described [5]. These particles are prevented from leaving the electrochemical reactor by gratings which are arranged in front of the lower water inlet opening and the upper water outlet opening of the reactor. The movement of the fluidized bed of spherical particles leads to a mechanical cleaning of the electrode stack located in the reactor.

The use of a cathode which consists of an elastically deformable electrically conductive body was also proposed for use in a scaling free electrode arrangement [6]. The cathode undergoes elastic oscillations preferably by bending or torsion. In this way the formation of undesired deposits is prevented. In a similar approach a spiral or helical metal cathode equipped with a heater is used. The alternate expansion and contraction of the cathode which is obtained during alternate heating and cooling is reported to shed the scale [7].

The cathode surface can also be cleaned continuously by use of a rotating brush [8] or rotating vanes [9]. During rotating both devices move over the circular shaped cathode surface and remove freshly formed deposits. However, all the methods described above are known to be inefficient in long term use. Although they lead to a lowering of the scaling rate of the cathode they do not totally prevent electrode scaling. This eventually always leads to cathodes totally covered with thick calcareous deposits. With increasing thickness of the deposits on the cathode, the flow of electric current and also the flow of water through the cell become more and more inhibited. Thus, the most efficient methods which are used today for cleaning the cathode from calcium carbonate scaling are still the use of polarity reversal or acid washing [3, 4]. Unfortunately, these methods also have several drawbacks, for example, polarity reversal leads to a reduction in electrode lifetime and of the active chlorine production rate [4] whereas the use of acid backwashing leads to the need for generally unwanted storage and use of hazardous chemical substances. Consequently, new technologies for *in situ* cathode cleaning are needed.

Ultrasound is known to be an efficient tool for cleaning surfaces. Additionally, the use of ultrasound in electrochemistry is a well established technique, called

sonoelectrochemistry [10–12]. Thus, it should also be possible to clean cathode surfaces from calcareous deposits. This was investigated in the present study by using a sonotrode which acts as cathode.

It should be noted that there are also several reports on the use of ultrasound in connection with water disinfection and the removal of biofilms. So it is reported that it is possible to kill microorganisms by subjecting water to ultrasonic vibrations at frequencies of 20 kHz or higher. Ultrasonic treatment of water creates pressure waves in the water and consequently cavitation effects which lead to rupture of cell walls [13–15]. Mott et al. [16] used axially propagated ultrasound for the removal of biofilms from water-filled tubes. Thus, the combination of ultrasound and electrochemical production of disinfecting agents should, in principle, result in a much more efficient disinfecting process compared to electrochemical disinfection without ultrasound.

However, the aim of the present study was only to investigate the possibility of *in situ* cathode cleaning by ultrasound and the influence of ultrasound on the electrochemical production of disinfecting species measured as active chlorine.

2. Experimental details

Figure 1 shows the electrochemical reactor used. The reactor tube itself was made from transparent Plexiglas® whereas the end pieces are made of PVC. Inside the reactor pipe an inner titanium cathode cylinder and a outer cylindrical expanded mesh anode were arranged. The cathode also served as the ultrasonic horn and, thus, acted as a sonotrode.

The titanium sonotrode/cathode was 3 cm (dia.) × 16.2 cm (long). The electrolytic active length of the sonotrode/cathode was about 10 cm. Thus, the active cathode surface area was 94 cm^2. The standard current used in the experiments was 2 A. This gave a cathodic current density of 21 mA cm^{-2}.

The anode was made from a ruthenium oxide coated titanium expanded mesh (Hereaus Elektrochemie, Germany). The dimensions of the anode were 3.8 cm (inner diameter) × 21.5 cm (length). The electrode gap between the sonotrode/cathode and the anode was 4 mm. The electrochemically active area of the anode (active electrode length: 10 cm, factor for the active area of the expanded mesh: 0.75) was 89 cm^2. At the standard current of 2 A an anodic current density of 22 mA cm^{-2} resulted.

The ultrasonic horn transducer (Dr Hielscher GmbH, Teltow, Germany) produced ultrasound with a frequency of 24 kHz and an maximum intensity of 250 W. The intensity was adjustable between 20% and 100%.

All experiments were performed in the laboratory of Gerus mbH (Berlin, Germany) in 2-electrode-technique using a 30 V, 5 A voltcraft d.c. power supply (Conrad). The water used in the experiments was tap water with a
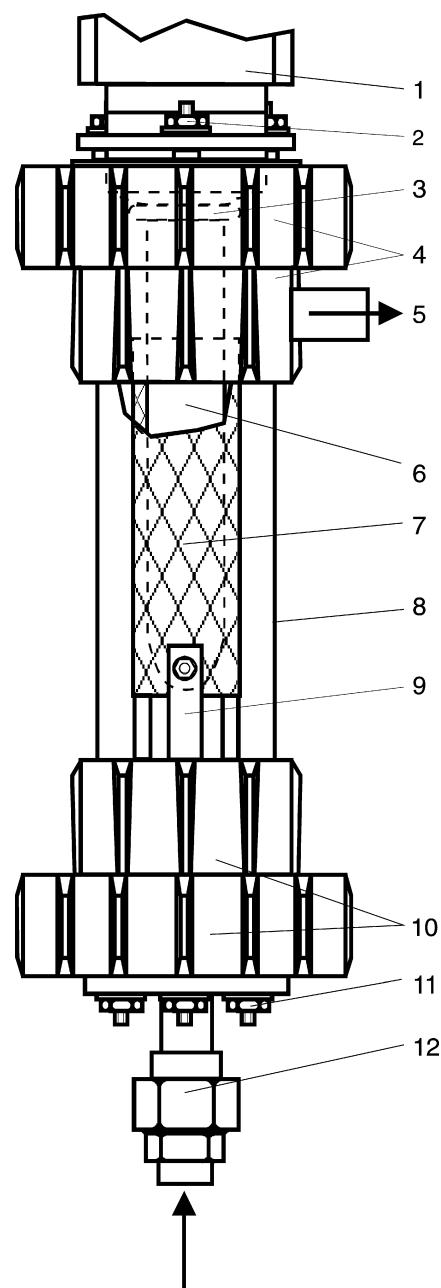

Fig. 1. Schematic drawing of the reactor used in the experiments: (1) ultrasound transducer, (2) mounting means for ultrasound device (screw means are also used as cathodic current connector), (3) O-ring sealing for sonotrode, (4) screw-thread, (5) water outlet, (6) sonotrode (cathode), (7) expanded metal tube (anode), (8) reactor pipe, (9) anodic current connector, (10) screw-thread, (11) screw means for securement of anode (also used as anodic current connector), and (12) water inlet.

conductivity of about 0.8 mS cm^{-1}. The concentration of some dissolved species is given in Table 1. It should be noted that these concentrations may slightly vary with time. This can be of any importance especially for the chlorine consumption of the water which can vary from experiment to experiment.

Water was only passed once through the reactor. The flow through velocity was adjusted by use of a membrane valve and measured with a rotameter. The active chlorine concentration in the electrolysed water was

Table 1. Concentration of some dissolved ions in the tap water (Berlin-Oberschöneweide) used in the present experiments (analysis on 24 July 1998 performed by GUT Analytik GmbH Berlin)

Substance	Concentration /mg dm^{-3}	Concentration /mmol dm^{-3}
Cl$^-$	55	1.55
SO$_4^{2-}$	220	2.29
HCO$_3^-$	61	3.93
Mn^{2+}	<0.003	–
Ca^{2+}	119	2.97
Mg^{2+}	15	0.62

Fig. 2. Dependence of the measured active chlorine production rate on the current and the anodic current density (flow rate 120 dm^3 h^{-1}; ultrasound intensity 100%; temperature about 20 °C); the theoretical real active chlorine production rate and the fast chlorine consumption are also displayed.

measured using the photometric DPD method (DPD $\cdots$ *N*,*N*-diethyl-1,4-phenylene diamine) [17] with a Nanocolor® 100D photometer (Macherey–Nagel, Germany). Active chlorine is the sum of the three different dissolved chlorine species (Cl$_2$, HClO and ClO$^-$) which are present in the water. The active chlorine concentration is usually given in mg dm^{-3} the conversion from mol dm^{-3} of hypochlorous acid, hypochlorite and chlorine is based on the molecular weight of chlorine (70.9 g mol^{-1}).

3. Results and discussion

3.1. *Influence of ultrasound on the deposition of calcareous deposits on the cathode*

The use of ultrasound does not prevent the formation of solid particles of CaCO$_3$ and Mg(OH)$_2$ due to the pH increase in the vicinity of the cathode surface. But the vibrations of the sonotrode/cathode lead to a constant release of small particles of scale from the surface of the sonotrode. This results in a cathode surface which is free, or almost free, from calcareous deposits on long time scale. Experiments were performed for about two months with constantly electrolysing water without the necessity of an additional cleaning of the cathode. For the purpose of cleaning, the ultrasound can be applied constantly or in short pulses onto the sonotrode/cathode. Both regimes give the same positive results.

However, problems can arise due to the ultrasound energy mainly emitted by the tip of the ultrasound horn in the direction of the lower part of the electrochemical reactor. But if the water pressure is not much more than 1 bar this energy can be absorbed without deleterious consequences. At higher water pressures deformations, and eventually, destruction of the reactor can result.

3.2. *Dependence of active chlorine production rate on current*

The dependence of the active chlorine production on the applied current was measured using an ultrasound intensity of 100%. The results of these measurements are displayed in Figure 2. A linear increase in the active chlorine production rate with the current can be seen.
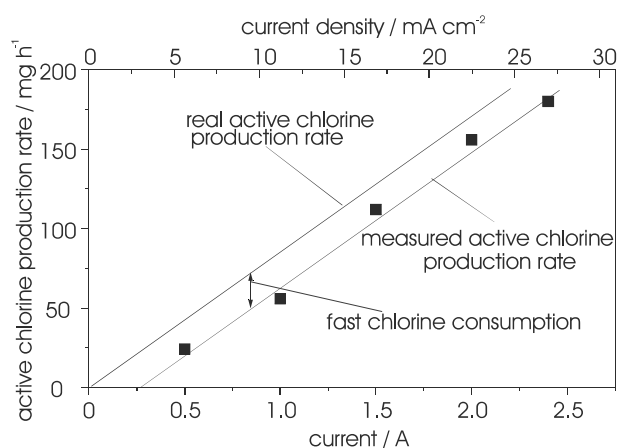
This is the same behavior as measured in recent experiments without the use of ultrasound [3, 4]. In these experiments it was found that the linear increase of active chlorine production with flowing current starts near 0 A in water with low or extremely low chlorine consumption [3]. A higher chlorine consumption leads to a parallel shift of this linear increase. The higher the chlorine consumption the higher is this shift. This was explained by the fact that the fast chlorine consumption leads to a measured active chlorine concentration which is lower than the produced one [4]. The difference between the produced and measured active chlorine concentration is due to chlorine consumption which is, of course, independent on the current.

Thus, it is possible to express the fast chlorine consumption of water in values of a (lost) active chlorine concentration. A value of about 25 mg h^{-1} results for the experiment displayed in Figure 2. At a flow rate of 120 dm^3 h^{-1} this gives an active chlorine consumption of 0.21 mg dm^{-3} in equivalents of active chlorine concentration.

The slope of the linear increase of the active chlorine production rate (mg h^{-1}) with increasing current shown in Figure 2 is about 85 mg A^{-1} h^{-1}. This value for a RuO$_2$ anode at a chloride ion concentration of 55 mg dm^{-3} is higher than the values measured in previous experiments [3, 4] on IrO$_2$ and Pt electrodes. For comparison the values for the active chlorine production rate (mg h^{-1} and mg A^{-1} h^{-1}) given in [3] have to be multiplied by a factor of 2 because the calculation in this work was based on the atomic weight of chlorine rather than on the molecular weight. Thus, at a chloride concentration of 150 mg dm^{-3} we measured a slope of 120 mg A^{-1} h^{-1} for IrO$_2$ and 20 mg A^{-1} h^{-1} for platinum electrodes, respectively [3]. At a chloride concentration of 60 mg dm^{-3} slopes of 30 mg A^{-1} h^{-1} for IrO$_2$ and 10 mg A^{-1} h^{-1} for Pt were measured [4].

We assume that the slope of the linear increase of chlorine production rate (mg h^{-1}) at very low chloride ion concentrations depends on both the chloride concentration and the choice of anode material used. More detailed experiments in this connection are in progress.

3.3. Dependence of active chlorine production rate on volumetric flow rate and ultrasound intensity

Figure 3 shows that the flow rate has little influence on the active chlorine production rate. Generally, an increase in the active chlorine production rate with an increased flow rate would be expected because of the improved mass transfer of chloride ions to the electrode surface. But at higher flow rates a greater number of substances which cause active chlorine consumption pass through the reactor. Therefore, by increasing the flow rate both the real active chlorine production and the fast chlorine consumption are increased. Depending on the numbers involved, this can also lead to a decreasing or a constant measured active chlorine production rate [4].

The ultrasound intensity has also no significant influence on the active chlorine production rate as can clearly be seen from Figure 4. This means, that the diffusion of chloride ions to the anode surface is not significantly enhanced by means of sonication. This is reasonable because the ultrasound energy is mainly emitted by the tip of the sonotrode in direction to the lower part of the reactor.

However, the use of ultrasound changes the electrochemical processes in the reactor. This is displayed Figure 5 which depicts the dependence of cell voltage on ultrasound intensity. The higher the ultrasound intensity the higher the cell voltage.

Another effect of ultrasound is the size of the gas bubbles released from the electrodes. Without the use of ultrasound many very small gas bubbles are produced, whereas with ultrasound fewer much bigger gas bubbles are produced. This allows a much faster degasification
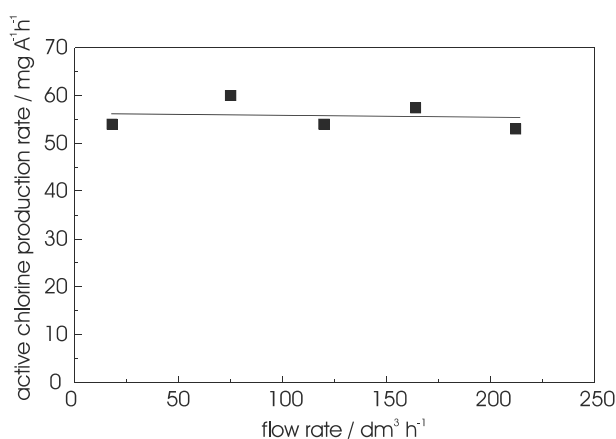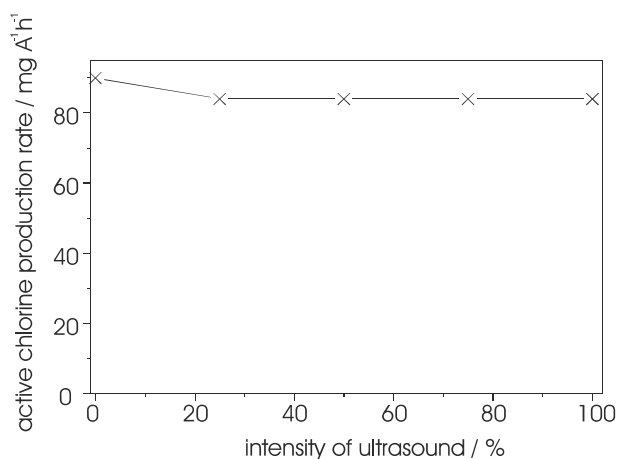
Fig. 4. Active chlorine production rate in dependence on ultrasound intensity (current 2 A; anodic current density 22 mA cm^{-2}; flow rate 120 dm^3 h^{-1}; temperature ~20 °C).
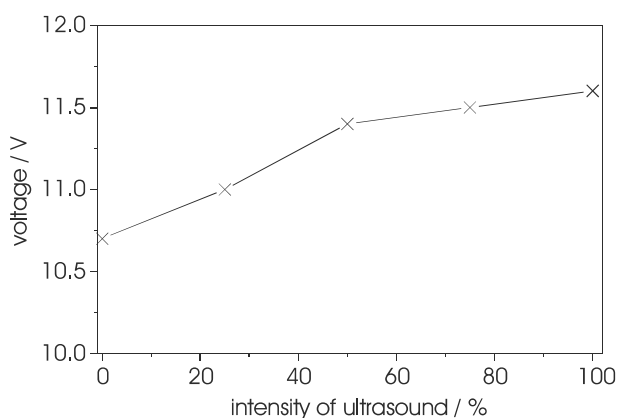
Fig. 5. Dependence of the cell voltage on the intensity of ultrasound (current 2 A; anodic current density 22 mA cm^{-2}; flow rate 120 dm^3 h^{-1}; temperature ~20 °C).

of water disinfected by the electrochemical method which should be especially helpful in applications in closed systems.

The largest part of the cell voltage is due to the ohmic voltage drop in the electrolyte. The increase of voltage with ultrasound can be explained by an increase of the ohmic drop in the electrolyte due to the formation of larger gas bubbles.

4. Conclusions

With the use of ultrasound produced at a sonotrode working as a cathode it is possible to efficiently remove calcium carbonate scales from the cathode surface. Thus, electrochemical water disinfection in potable water can be performed on a long-time scale without the necessity for cathode cleaning by use of acids or by the polarity reversal method. The active chlorine production rate on the anode is not significantly changed by the ultrasonic action.

Fig. 3. Measured active chlorine production rate against flow rate (current 2 A; anodic current density 22 mA cm^{-2}; ultrasound intensity 100%; temperature ~20 °C).

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