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Product and by-product formation in laboratory studies on disinfection electrolysis of water using boron-doped diamond anodes

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Abstract

Boron-doped diamond (BDD) electrodes were studied with respect to the formation of inorganic by-products in water electrolysis. Experiments in non-divided cells were performed with systems containing sulphate, chloride, chlorite, chlorate and nitrate ions. Discontinuous experiments in thermostated cells with rotating disk diamond anodes and expanded mesh IrO_2 cathodes were carried out at 20 °C. Current density was varied between 50 and 300 A m^{-2}. Ion chromatography was mainly used for species detection.

It was not possible to demonstrate the decomposition of sulphate although a slight tendency seems to exist in some experiments. Hydrogen peroxide is one of the anodic and cathodic by-products. Active chlorine is detectable at higher chloride concentrations compared with the use of mixed oxide anodes (MIO). One reason for this is the reaction of formed chlorine with ozone or hydrogen peroxide. Chlorate can be formed electrolysing chloride, hypochlorite and chlorite solutions. Perchlorate formation was detected. Cathodic processes are responsible for the formation of nitrite ions and ammonia. If chlorine is present, the formation of monochloramine is one possible side reaction. Results show that the processes are very complex. Reaction spectra may vary from case to case. Perchlorate formation is a high risk in drinking water treatment.

Keywords: BDD electrodes; Disinfection; Water hygienisation; Drinking water electrolysis; Disinfection by-products

1. Introduction

The so-called boron-doped diamond electrodes are materials of outstanding properties. They are chemically stable and work with wide electrochemical windows [1]. In the anodic region of polarization, potentials can be adjusted which enable the electrode to produce strong oxidants such as $OH^{\bullet}$ radicals and ozone. If the surface is free of pores, its application as a cathode material is also possible. The production of oxidizing species can be used for the electrochemical decomposition of organic water components. Water disinfection processes by direct electrolysis are other subjects for BDD electrode application. Unfortunately, no information exists to assess the potentials of inorganic disinfection product and by-product formation. However, theoretical considerations let one assume that potential risks exist in electrolysing drinking water. The aim of this work was to study water systems in the range of low chloride concentrations. To avoid interference and more complex reactions mainly single component electrolysis was used. New or improved methods for better analysis were applied to identify reaction products.

2. Experimentals and methods

A cell with a rotating anode (rotation rate 300 rpm) 4 mm above a cathode was used in discontinuous experiments at 20 °C [2]. Current density was varied between 50 and 300 A m^{-2} using constant current mode and *Statron* rectifiers. The disk anode (diameter 35 mm) was made from BDD (*Metakem*/*Condias*). For comparison, a mixed oxide electrode of the same dimensions containing 50% IrO_2 and 50% RuO_2 (relative molar concentration) on Ti was used in selected experiments. IrO_2 on Ti (*Magneto Special Anodes*, expanded mesh, diameter 40 mm, surface factor 2) was used as cathode material. Deionised water for HPLC (*Millipore*, conductivity not higher than 0.1 μS cm^{-1}, residual chloride concentration 0.1 ppm) and chemicals with purity equal or higher than 99.9%

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(*Fisher Scientific and Chempur*, all as sodium salts) in mg l^{-1} (ppm) range of concentrations were used in the experiments. The volume of electrolyte was 100–160 ml. The concentration of ions was measured using ion chromatography. Perchlorate was analysed using a *Metrosep Dual 4* column (*Metrohm*). H_2O_2 was measured by applying *Macherey&Nagel Peroxide 2* test kits based on the peroxidase reaction. Active chlorine was measured by the DPD method (*Dr. Lange LCK 310* or *Macherey&Nagel chlorine/ozone 2* test kits) or by ion chromatography. Because chloride and hypochlorite have overlapping peaks ion chromatography analysis was carried out twice with and without hypochlorite elimination. The corresponding values were calculated by solving a mathematical system of equations. In selected experiments, active chlorine concentration was calculated from UV spectrum measurements making sure that the sample pH was adjusted to 11.5. Bonded chlorine was measured by the DPD method adding three drops of KI solution to the sample after determining active chlorine. Experiments were repeated at least once.

3. Results and discussion

3.1. Formation of reactive oxygen species

Electrochemical kinetics at diamond anodes is not yet completely understood. It is accepted that $OH^\bullet$ radicals are produced anodically at sufficient high anodic polarization [3]:

$$H_2O \rightarrow OH^\bullet + H^+ + e \quad (1)$$

The radicals form hydrogen peroxide [4]:

$$2OH^\bullet \rightarrow H_2O_2 \quad (2)$$

but the reaction of peroxide with existing ozone can be another source of radicals in bulk electrolyte according to reaction (3):

$$H_2O_2 + 2O_3 \rightarrow 2OH^\bullet + 3O_2 \quad (3)$$

Additionally, it must be assumed that other intermediates or by-products occur as known from photochemistry and chemistry of ozonation. Due to the high complexity of chemical and electrochemical reactions, highly oxidative species are often classified as so-called **r**eactive **o**xygen **s**pecies (ROS). Besides the $OH^\bullet$ radicals, the formation of species such as H_2O_2 or HO_2^-, O_3, $O_2^{\bullet-}$, $HO_2^\bullet$, $O_3^{\bullet-}$, etc., is possible in chemical and electrochemical reactions. There is no possibility at present to realize a precise and complex chemical analysis as an inline method. Interference effects must be additionally expected. Usually, ozone and hydrogen peroxide are analysed by several methods but the concentration of *dissolved* ozone seems to be negligible [5]. It has been shown [6] that H_2O_2 was formed cathodically from dissolved oxygen when mixed oxide electrodes were used. The anodic formation at diamond anodes is higher by one order of magnitude under comparable conditions [7] and measured using H_2O_2 analysis kits.

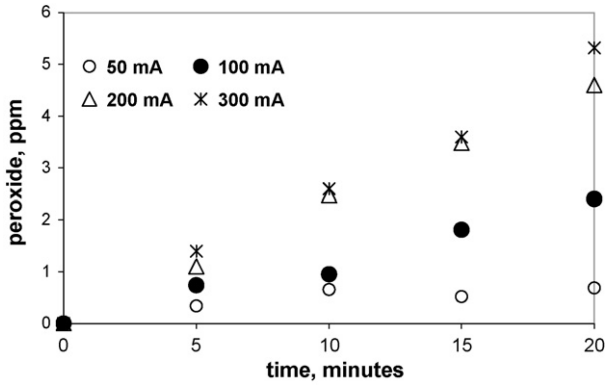

Fig. 1. Hydrogen peroxide formation in discontinuous electrolysis using rotating BDD anode and IrO_2 cathode (150 ml, water containing 240 ppm sulphate and 25 ppm carbonate as sodium salts, pH 10.1, 20 °C, and 300 rpm).

Fig. 1 shows the formation of H_2O_2 with varying cell current. Higher currents result in higher peroxide formation. At 50 mA (50 A m^{-2}) the formation and destruction rates seem to be balanced under the conditions chosen.

It must be mentioned that H_2O_2 can exist only in the absence of active chlorine. If active chlorine is present, the fast reaction (4) (written in a general form) decomposes both components:

$$H_2O_2 + Cl_2 \rightarrow 2HCl + O_2 \quad (4)$$

Other by-products such as ClO_2 may also react with peroxide:

$$2ClO_2 + H_2O_2 + 2OH^- \rightarrow 2ClO_2^- + O_2 + 2H_2O \quad (5)$$

Analogous conclusions can be made considering ozone and radical reactions leading to by-products of differing lifetimes and detection limits using conventional analysis methods. So, it cannot be totally excluded that under the described experimental conditions of Fig. 1, radicals such as $CO_3^{\bullet-}$ and $HCO_3^\bullet$ (or $^{\bullet-}H_2PO_4^\bullet$ and $HPO_4^{\bullet-}$ when phosphate buffers are used) exist temporarily. It was also reported that at higher salt concentrations percarbonates and peroxodicarbonates ($C_2O_6^{2-}$) and peroxodisulphate ($S_2O_8^{2-}$) are produced using diamond anodes [8,9]. The mechanisms have not yet been studied. The reaction shown in Eq. (6) assumes the formation of peroxodisulphate at BDD [10]:

$$2SO_4^{2-} + 2OH^\bullet \rightarrow S_2O_8^{2-} + 2OH^- \quad (6)$$

Indeed, an oxidant activity can be measured by the DPD method during electrolysis at mixed oxide anodes, for example in a 50-ppm carbonate solution at 200 A m^{-2}. However, both percarbonates and peroxodisulphate are not stable and can undergo hydrolysis reactions. This is probably the reason why a clear detection in drinking water electrolysis is difficult when, for example, the maximum sulphate concentration is not allowed to be higher than 240 ppm. Our ion chromatography studies statistically showed the decrease of sulphate concentration during sulphate electrolysis but could not definitely demonstrate sulphate depletion during the discontinuous experiments. However, choosing special experimental condi-

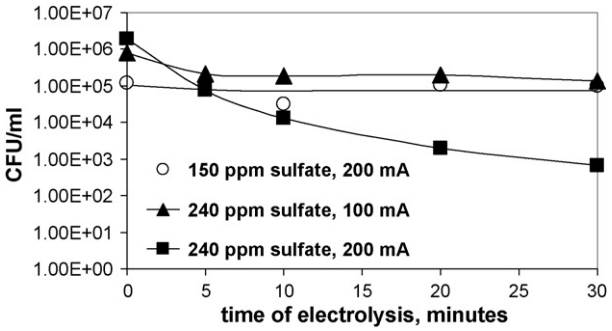

Fig. 2. Decrease of microorganism number (*Pseudomonas fluorescens*) after adding the same volume of sodium sulphate solution (1 ml) treated by electrolysis of varying sulphate concentrations and currents (rotating BDD anode, IrO_2 cathode, 160 ml, 20 °C, and 300 rpm [7]).

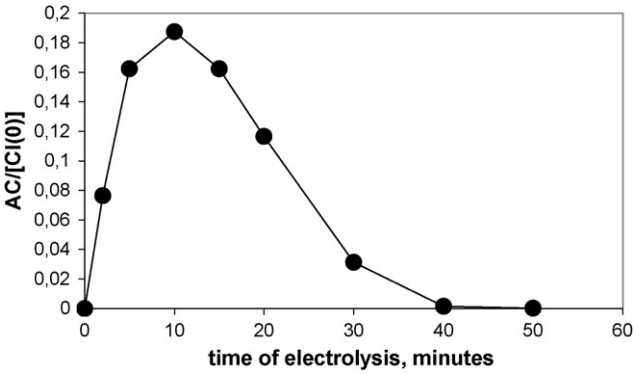

Fig. 3. Active chlorine concentration (AC) related to starting chloride concentration (Cl(0)) vs. time (rotating BDD anode, IrO_2 cathode, water containing 50 ppm [Cl^-] as sodium salt, 100 ml, 200 mA, 20 °C, 300 rpm, and DPD method of active chlorine analysis).

tions, higher disinfecting ability occurred when electrolysed sulphate solution was reacted with microorganisms [7]. To avoid the influence of very short-lived radicals the water treated by electrolysis was added to the suspension containing microorganisms. Fig. 2 shows the corresponding curves for different experiments. A clear killing effect was observed for a relatively higher current density and sulphate concentration and is not related to the action of hydrogen peroxide of a similar concentration as comparative experiments showed (not presented here). Thus, the formation of oxidizing species formed anodically from SO_4^{2-} must be concluded.

3.2. Electrolysis of chloride, chlorite and chlorate ions

The production of free or active chlorine components (free available chlorine, dissolved Cl_2, HOCl and OCl^-) is usually the aim of electrolysis due to the high disinfecting ability of these species. First studies of BDD were carried out by Ferro et al. [11]. They discussed a mechanism of forming Cl_2 from $2Cl^\bullet$. Dissolved chlorine quickly reacts with water and OH^- ions to form hypochlorous acid and hypochlorite ions. No kinetic studies exist in the literature for solutions with chloride concentration in the ppm range. Our studies on mixed oxide electrodes showed that a chlorine formation potential (measured with DPD) exists even at very low chloride concentrations of some ppm [2]. From these and other long-term electrochemical experiments with disappearing chloride ions, we assume that chlorine formation is possible at extremely low chloride concentrations but side reactions may lower the chlorine concentration again. One side reaction is obviously based on hydrogen peroxide that is formed anodically or cathodically. This means, for each system with defined temperature, electrode materials, distance between anode and cathode, current density, etc., one minimum chloride concentration value exists for clear measurement of produced active chlorine. For example, we found for one system containing only chloride and 50 ppm nitrate a minimum concentration of 10 ppm [Cl^-] is necessary for chlorine detection (DPD, detection limit 0.02 ppm) using a BDD anode. In general, active chlorine is an electrolysis product both at mixed oxide and doped diamond anodes. However, mechanism of formation, current efficiency and reaction behaviour differ significantly in the two cases. While the measured chlorine values in experiments using mixed oxide anodes usually increase continuously until reaching a limit, in experiments with diamond anodes a maximum of active chlorine is reached soon after starting the experiment (Fig. 3). In addition to the destruction of active chlorine by ROS to give chloride once more, the oxidation by $OH^\bullet$ radicals is also another option for discussion. In this case, chlorite and chlorate should be the products. Chlorite could not be measured by ion chromatography but, usually, chlorite is a short-lived component and may react with many other species or directly at the anode. A corresponding discussion was also made in [2]. The very good reactivity during electrolysis of sodium chlorite solutions is shown in Fig. 4. The formation of chlorine dioxide and chlorate was observed in this experiment indicating a stepwise mechanism of oxidation by $OH^\bullet$ radicals. It is interesting to

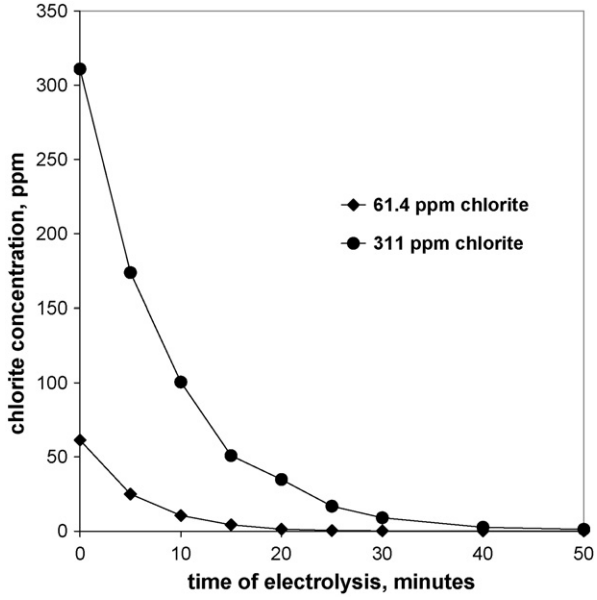

Fig. 4. Chlorite depletion in two discontinuous experiments varying starting concentration as indicated in the legend (rotating BDD anode, IrO_2 cathode, sodium salt, 100 ml, 200 mA, 20 °C, and 300 rpm).

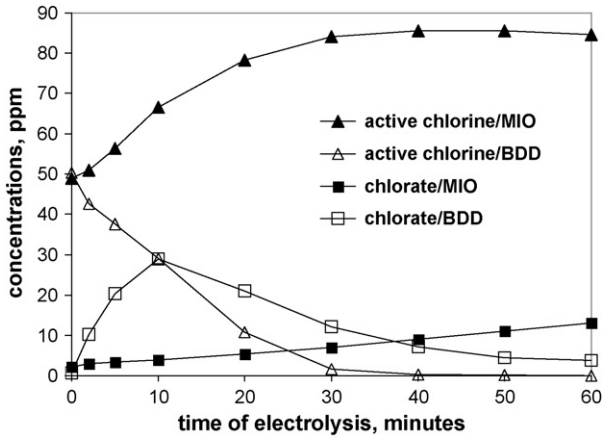

Fig. 5. Active chlorine and chlorate concentration vs. time of electrolysis in discontinuous experiments using rotating mixed oxide (MIO) or BDD anode (starting solution with 50 ppm hypochlorite as $Ca(OCl)_2$ + 50 ppm chloride as NaCl, IrO_2 cathode, 200 mA, 20 °C, and 300 rpm).

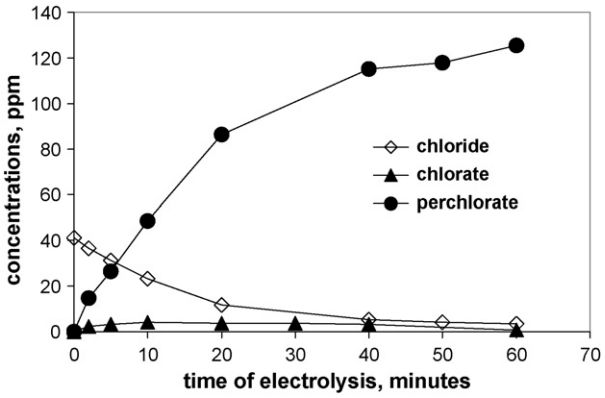

Fig. 7. Chloride, chlorate and perchlorate concentrations depending on time during discontinuous electrolysis of drinking water using rotating BDD anode (Koethen drinking water containing 41 ppm chloride, 162 ppm sulphate and 12.9 ppm nitrate, pH 7.9, IrO_2 cathode, 100 ml, 200 mA, 20 °C, and 300 rpm).

note that many assumptions for chlorate formation at other electrodes (Pt, IrO_2/RuO_2) also include chlorite as an intermediate of chlorate formation [12,13], but on electrocatalytically active surfaces and in contradistinction to the BDD anode that is not electrocatalytically active.

Chlorate formation is apparent from Fig. 5 showing results from experiments starting with water containing chloride and hypochlorite. In addition to the experiments using BDD anodes, results from experiments using mixed oxide anodes (MIO) are presented. As opposed to the MIO experiments, active chlorine concentration continuously decreases when the BDD is used. Chlorate is formed in both experiments but slowly in the MIO experiment and faster (going though a relatively high maximum) in the case of the BDD experiment. Chlorate is usually a stable product in disinfection processes based on chlorine or chlorine dioxide addition. The disappearance of chlorate in the BDD experiment indicates possible chemical or electrochemical reactions. The formation of perchlorate must be assumed because this process is known in the electrolysis of highly concentrated chlorate electrolytes [14]. To check this possibility selective perchlorate analysis was performed in addition to using a special IC column (*Metrohm*). Furthermore, chlorate and chlorite solutions were electrolysed separately. Fig. 6 presents the results. For all three electrolytes, perchlorate formation was observed. For the electrolytes containing hypochlorite and chlorite, chlorate was formed and reacted. Thus, it can be concluded that perchlorate is basically formed in an oxidation step starting from chlorate.

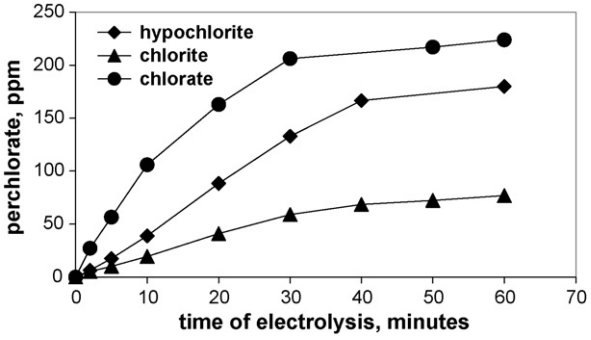

Fig. 6. Perchlorate formation during electrolysis using rotating BDD anode in electrolytes containing 102 ppm hypochlorite ($Ca(OCl)_2$) + 3 ppm chloride (NaCl), 111.2 ppm chlorite + 5.5 ppm chloride ($NaClO_2$ + NaCl) and 179.4 ppm chlorate ($NaClO_3$), respectively (IrO_2 cathode, 100 ml, 200 mA, 20 °C, and 300 rpm).

The occurrence of perchlorate in drinking water is a serious problem due to its carcinogenic potential [15]. After the contamination of large areas in the United States of America, two states set a limiting concentration of 2 and 6 ppb for perchlorate in drinking water. Even, if the conditions of our laboratory-scale experiments are not typical for all commercial applications, the probability of perchlorate formation in the ppb range is very high. Perchlorate was also found by electrolysing drinking water supplied by the regional waterworks (Fig. 7). No significant change should be expected if a BDD electrode was to replace the MIO cathode.

3.3. Electrolysis of nitrate ions

Nitrate is a drinking water component with a limiting concentration of 50 ppm according to the rules of many countries. Mostly, waterworks try to adjust to lower concentration values because nitrate is suspected to cause nitrosoamines in human body. It is also known from the literature that nitrate can be reduced at the cathode in acidic, neutral and alkaline media. Many cathode materials were tested. Doped diamond cathodes were studied in neutral media by several authors [16,17]. Nitrate could be reduced but reproducible results were obtained only in experiments using alkaline electrolytes. On the whole, the mechanisms of nitrate reduction are not yet clear and usually sum reactions are used to describe the processes of nitrite and ammonia formation (Eqs. (7)–(9)). Against the background of replacing the expensive diamond cathodes by mixed oxide cathodes and for better comparison, in our

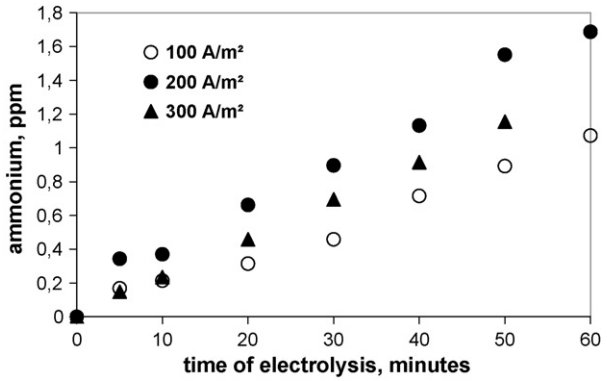

Fig. 8. Ammonium formation at varied currents in discontinuous electrolysis using rotating BDD anode (IrO_2 cathode, 100 ml, 47 ppm nitrate as sodium salt, 20 °C, and 300 rpm).

experiments BDD was used only as anode material:

$$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2OH^- \quad (7)$$

$$NO_3^- + 6H_2O + 8e \rightarrow NH_3 + 9OH^- \quad (8)$$

$$NO_2^- + 5H_2O + 6e \rightarrow NH_3 + 7OH^- \quad (9)$$

Ammonia may react to ammonium. In fact, nitrite and ammonium ions were clearly detected when performing nitrate electrolysis in the ppm concentration range. Fig. 8 shows results with respect to ammonium ions from corresponding experiments using varying cell currents. No significant differences occur. Probably, the electrocatalytic process of ammonia oxidation is not characteristic for the BDD anode and ammonium may accumulate.

If chloride oxidation provides chlorine species, still more complicated reaction schemes can be found. For example, chlorine reacts in the millisecond range with peroxide, but if chlorine exists in excess, reactions with ammonia are possible forming chloramines. Monochloramine was found in our experiments using a special spectrophotometric method (not presented here). The common method of analysing chloramines as so-called bonded chlorine is based on a DPD reaction

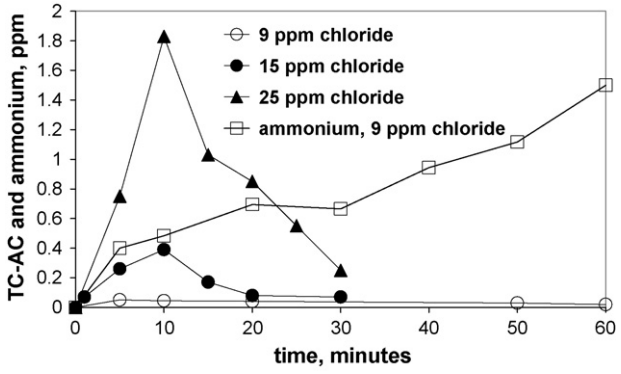

Fig. 9. Chloramine formation shown as difference between total chlorine TC and active chlorine AC and ammonium formation in discontinuous experiments using rotating BDD anode and IrO_2 cathode at varied chloride concentration in water containing nitrate (47 ppm nitrate, sodium salts, 160 ml and 100 ml (only experiment at 9 ppm chloride), 200 mA, 20 °C, and 300 rpm).

controlled by photospectroscopy. The results are presented in Fig. 9. Active chlorine rapidly reacts in the reaction with ammonia as is known from water chlorination chemistry and is dependant on pH [18]:

$$HClO + NH_3 \rightarrow NH_2Cl + H_2O \quad (10)$$

$$HClO + NH_2Cl \rightarrow NHCl_2 + H_2O \quad (11)$$

The higher the initial chloride concentration, the higher is the chloramine formation. It could be found that the observed maximum is mainly based on the disappearing active chlorine as depicted in Fig. 3 and the obvious reaction of chloramines to unknown by-products. Reactions between monochloramine and $OH^\bullet$ radicals were discussed recently [19]. The range of by-product concentration let one conclude that the nitrogen-based electrochemical reactions are not a significant problem in most of technical application; however, reactivity effects can be detected. The increase of ammonium concentration (measured by ion chromatography) in Fig. 9 differs from that in Fig. 8 due to the partial reaction with chlorine.

In the case of bonding chlorine with ammonia, the presence of nitrite ions is supported [6]. Under varied conditions, nitrite may be reoxidized anodically or by oxidants formed electrolytically.

4. Summary and conclusions

- Diamond anodes produce reactive oxygen species able to react with components of drinking water or other reaction products of electrolysis. Thus, a lowering of chlorine formation efficiency is possible.
- Electrolysis of water containing chloride, active chlorine or chlorite produces chlorate ions. The formation rate is much higher compared with the conventional disproportionation of hypochlorous acid to chlorate.
- The formation of perchlorate in drinking water electrolysis was demonstrated. Perchlorate is a disinfection by-product having a high health risk. Consequently, corresponding formation reactions must be suppressed or the application of BDD in drinking water electrolysis or other environmentally orientated purposes must be avoided.
- If nitrate is reduced, disinfection by-products such as nitrite, ammonium and chloramines can be found in the treated water. This is the case when the chlorine formation rate is low and comparable with the rate of nitrate reduction. More studies are necessary using BDD cathodes.
- Summarizing the present state of research, a more careful approach to BDD application in water electrolysis is recommended.

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