Development of an electrochemical module for combined water disinfection and softening

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Fundamentals and aims

Boron Doped Diamond (BDD) electrodes are an innovation with a high market potential. Their application for water disinfection by means of electrolytic ozone generation offers advantages compared to ozonisation by gas injection.
Operation of these electrodes in water with high Ca- und Mg-contents causes scaling of the BDD.
Aim of this project is to prevent impairment of the BDD electrodes and to implement a method for combined water disinfection and softening.

Fig.1:
Stack of 4 pairs of BDD electrodes with Nafion® membranes as Solid Polymer Electrolyte (SPE). Scaling can be observed between BDD and membrane.

Anode

$3\ H_2O \rightarrow O_3 + 6\ H^+ + 6\ e^-$ (a)

$H_2O \rightarrow HO\bullet + H^+ + e^-$ (b)

Ozone is generated at the BDD (a) via intermediation of hydroxyl radicals (b).

Cathode

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

$Ca^{2+} + HCO_3^- + OH^- \rightarrow H_2O + CaCO_3\downarrow$ (d)

Due to the local pH increase (c) at the cathode calcareous deposits are formed (d). The hydrogen carbonate and carbonate ions decrease the efficiency of the hydroxyl radicals (e), (f).

$HO\bullet + HCO_3^- \rightarrow OH^- + \bullet HCO_3$ (e)
$HO\bullet + CO_3^{2-} \rightarrow OH^- + \bullet CO_3^-$ (f)

Experiments and results

A technical loop for testing the BDD stacks has been constructed (Fig.2). Different polarisation routines have been tested to prevent scaling of the BDD and to develop a method for combined disinfection and softening.

Fig.2:
Technical loop for testing BDD stacks with different polarisation routines.

The ozone production is determined in dependence on different parameters as temperature, pressure or flow rate and reversion of polarity by performance tests at a current of 10A, 15A or 20A. Reversion of polarity should diminish the scaling of the BDD due to the dissolution of cathodically formed $CaCO_3$ (c), (d) by anodically formed H^+ (a), (b). Furthermore Fig.3 shows an increasing ozone production with decreasing interval of reversion of polarity at the BDD electrodes.

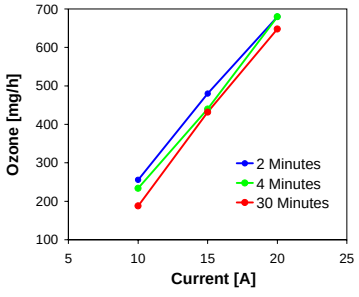

Fig.3:
Ozone production in dependence on the interval of reversion of polarity at a current of 10A, 15A or 20A. Stack of 2 pairs of BDD electrodes, drinking water, temperature: 15°C, flow rate: 2 $m^3\ h^{-1}$.

The long term test in Fig.4 shows decreasing Ca-concentration and conductivity, respectively softening of the test solution caused by scaling of the BDD stack.

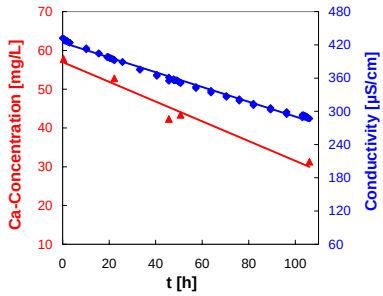

Fig.4:
Decreasing Conductivity and Ca-Concentration during a long term test in drinking water at 20 A. Stack of 4 pairs of BDD electrodes, temperature: 15°C, flow rate: 2 $m^3\ h^{-1}$, reversion of polarity: 4 minutes.

A

B

Fig.5:
Stack of 4 pairs of BDD electrodes with Nafion® membrane
(A) BDD and membrane are covered with Ca- and Mg-incrustations.
(B) Stack after cleaning with HCl.

Fig.5 (A) shows a scaled BDD stack which was employed to disinfect well water used in a brewery. This stack was cleaned in the technical loop by pumping 1M HCl at 50°C for 30 minutes through the housing with the scaled stack.
Fig.5 (B) shows dissolution of the incrustations.

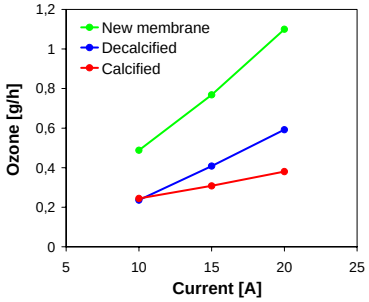

Fig.6:
Ozone performance before and after cleaning with HCl and after cleaning and installing a new Nafion® membrane. Current: 10A, 15A or 20A, stack of 4 pairs of BDD electrodes, temperature: 15°C, flow rate: 2 $m^3\ h^{-1}$.

Performance tests in Fig.6 reveal that an increase in ozone production can be achieved by cleaning with HCl and installing new membranes. Fig.7 shows a scanning electron microscope (SEM) picture of calcareous residues (calcite and brucite) remaining on the membranes despite cleaning with HCl.

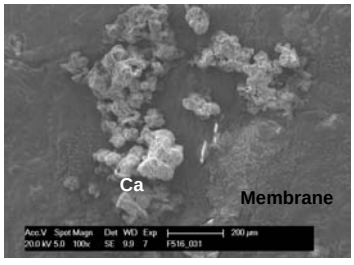

Fig.7:
SEM picture of calcareous residues which remain on a Nafion® membrane after cleaning with HCl.

Conclusions

Scaling of the BDD electrodes can be diminished but not prevented by reversion of polarity. Dissolution of incrustations can be achieved by cleaning with HCl but calcareous residues remain on the Nafion® membrane. Installation of new membranes in scaled and cleaned BDD stacks leads to a strong increase in ozone production.