JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) 99–104

Electrochemical waste water treatment using high overvoltage anodes
Part II: Anode performance and applications

S. STUCKI*, R. KÖTZ*, B. CARCER, W. SUTER

Asea Brown Boveri, Corporate Research CRB, CH-5405 Baden, Switzerland

Received 13 December 1989; revised 10 April 1990

The performance of highly doped SnO_2 anodes for the oxidative treatment of biologically refractory waste water was compared with PbO_2 and Pt. The oxidation of a wide range of organic compounds proceeds with an efficiency which is about 5 times higher than with platinum anodes. The oxidation efficiency was found to be independent of the pH of the water. In chloride containing media, SnO_2 anodes produce less chlorine gas than platinum anodes and hence show less potential to form hazardous chlorinated organic by-products. The design of a simple plate-and-frame reactor with undivided cells for waste water treatment using SnO_2 anodes was based on two experimental findings: (a) no interference of the cathode with the oxidation has been found: (b) the rate of oxidation is not limited by mass transfer, indicating the participation of homogeneous reactions in the overall oxidation. The new anode material reduces the specific energy requirement of electrochemical oxidation of organics in waste water to 30 to 50 kWh kg^{-1} of COD removed. This makes the process an interesting alternative to chemical oxidation using oxidants such as ozone and hydrogen peroxide, or wet oxidation using oxygen at elevated temperature and pressure.

1. Introduction

Biological treatment of waste water has become the most important process controlling the pollution of the aquatic environment by organic chemicals from municipal and industrial sources. The degradability of organic chemicals in a sewage plant depends strongly on the nature of the chemical compounds involved. Some of the chemicals that get into the waste water from industrial processes are degradable to such a small extent that they pass through the municipal sewage plants and accumulate in the environment. Legal practice in most countries has been to define a percentage of the chemical oxygen demand (COD) of a given waste stream which has to be removed by the biological treatment. In Germany for example, this ratio has been at 75%, in Switzerland 85%. It is most likely that the regulations will be tightened in the near future and that, as a consequence either industrial production will have to be changed and/or the treatment of industrial waste water will need additional processes in order to conform with the legal requirements.

Electrochemical oxidation as a pre-treatment of biologically refractory water contents before discharge to a biological/mechanical sewage plant has been proposed among other competing oxidation processes using highly reactive oxidants such as ozone, hydrogen peroxide etc. [1]. The poor current efficiency which is usually found with current electrode materials such as graphite or the dimensionally stable anodes such as noble metal (oxide) or PbO_2 coated titanium has been the major drawback of the process which otherwise would be convincingly simple and environmentally favourable. In the present study we report on the application of SnO_2 coated titanium as an anode with extremely high overvoltage for oxygen evolution which might turn electrochemical oxidation of biologically refractory waste water into an economical process.

2. Experimental details

The preparation and the analysis of the SnO_2 electrodes has been described in part I of this contribution.

Experiments on the performance of the anodes were run on two different scales. Those experiments on electrodes up to 10 cm^2 effective area were performed in a simple stirred beaker cell equipped with SCE reference and platinized titanium counter electrodes. A bench scale general purpose reactor from Electro-Cell AB was used for the evaluation of the relevant process engineering parameters. The cell was equipped with up to 5 anodes exposing 100 cm^2 of active area each. The cells could be operated with bipolar as well as monopolar electrode configuration. The bench scale reactor was equipped with a circulating electrolyte loop and controls for temperature, flux and

---

* Present address: Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland.

0021-891X/91 $03.00 + .12

pH. Materials in contact with the electrolyte solution were either PVDF, glass or titanium.

For oxidation experiments with model compounds, the substances were dissolved in a base electrolyte solution of 0.5 M Na_2SO_4 adjusted to the desired pH by addition of NaOH or H_2SO_4. Industrial waste waters of different origins were usually tested for oxidability in the electrochemical cells without pretreatment.

The progress of the oxidation reactions was monitored by measuring integral parameters such as TOC (total organic carbon) and COD (chemical oxygen demand) or by monitoring the disappearance of the pollutant molecule by u.v. absorption measurements. In some experiments in alkaline media the pH was maintained constant by an automatic dosage of NaOH solution to the electrolyte. The amount of NaOH dosage can be correlated with the amount of organics oxidized. Dosage curves have therefore been used to monitor the oxidation reaction. Attempts to identify the reaction intermediates and the end products of the oxidation reaction were made only to a limited extent with some of the model compounds by analysis of the multiple derivatives of the u.v. spectra.

For the evaluation of the EOI (electrochemical oxidation index) the evolved oxygen was measured volumetrically using a beaker type cell with a separated counter electrode compartment. The percentage of oxygen in the anode gas evolved from chloride containing electrolytes was analysed using a mass spectrometer.

3. Results and discussion

3.1. *Performance of SnO_2 electrodes with respect to different organic pollutants*

The oxidation power of the SnO_2-coated titanium electrode was compared with other electrode materials in the lab-scale beaker cell using different test molecules added to a base electrolyte of 0.5 N Na_2SO_4. Results for the oxidation of phenol at SnO_2 electrodes and standard electrodes like Pt or PbO_2 were described in part I. Significant differences in the oxidation efficiency were found and ascribed to a hole reaction mechanism proceeding on the SnO_2 anode.

A still much more drastic difference between SnO_2 on the one hand, and Pt- or PbO_2-coated titanium on the other can be seen in the oxidation of benzoic acid (Fig. 1a, b). For the three electrode materials SnO_2, Pt and PbO_2, Fig. 1a shows the disappearance of benzoic acid as a function of charge passed through the electrode and Fig. 1b shows the TOC reduction observed during the same set of experiments. The improved current efficiency of SnO_2 in this system is obvious.

In order to get a quantitative measure of the current efficiency, which could be used irrespective of the complexity of the mixture of dissolved organics in the water, the electrochemical oxidation index (EOI), as defined by Comninellis and Plattner [2], was used:

$$\mathrm{EOI} = \frac{1}{\tau}\int_0^\tau \frac{\dot{v} - \dot{v}_{\mathrm{org}}}{\dot{v}}\,\mathrm{d}t$$

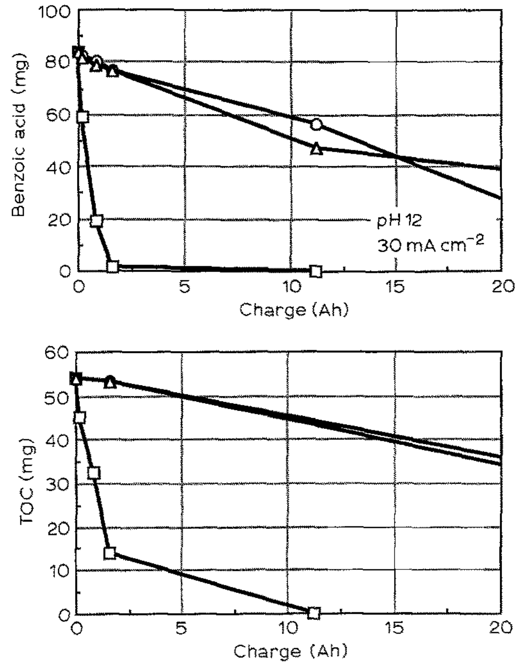

Fig. 1. Benzoic acid removal (a) and respective TOC removal (b) for three different electrode materials. Current density: 30 mA cm^{-2}, counter electrode Pt, pH 12, 150 ml electrolyte volume. Electrode materials: (□) SnO_2, (○) PbO_2 and (△) Pt.

The determination of the EOI involves the measurement of the evolved oxygen volume over the duration τ of an oxidation experiment in the presence ($\dot{v}_{\mathrm{org}}$) and absence ($\dot{v}$) of organics. For short durations τ, $\dot{v}_{\mathrm{org}}$ is

Table 1. Initial electrochemical oxidation efficiency determined for various test substances using Pt and SnO_2 anodes. (–) indicates not measured

Initial Electrochemical Oxidation Index (EOI)		
Organic species	*Platinum anode*	*ABB-Anode*
Ethanol	0.02	0.49
Aceton	0.02	0.21
Acetic acid	0.00	0.09
Formic acid	0.01	0.05
Tartaric acid	0.27	0.34
Oxalic acid	0.01	0.05
Malonic acid	0.01	0.21
Maleic acid	0.00	0.15
Benzoic acid	0.10	0.79
Naphtalene-2-sulphonic acid	0.04	0.51
Naphtalene-1-sulphonic acid	–	0.41
Phenol	0.15	0.60
Aniline	–	0.43
Aniline (#202, #202)	0.16	0.25
Aniline (MS)	0.10	0.50
Benzenesulphonic acid	–	0.28
5-Methyl-3-aminoisoxazole	–	0.25
Orange II	–	0.58
Antrachinon sulphonic acid	–	0.18
Nitrobenzene	–	0.80
Nitrobenzensulphonic acid	–	0.46
Triaminotriazin	–	0.02
EDTA	0.30	0.30
p-NDMA	0.30	0.37
4-Chlorphenol	–	0.35
	Ave. 0.05	Ave. 0.34

constant and the above equation reduces to:

$$\mathrm{EOI}_{\text{initial}} \simeq \frac{\dot{v} - \dot{v}_{\text{org}}}{\dot{v}}$$

For the oxidation of benzoic acid (Fig. 1) the initial EOI was found to be 0.79 for the SnO_2 anode and 0.10 for platinized titanium. The initial EOI of a variety of aromatic compounds and of simple aliphatic alcohols and carboxylic acids was determined for SnO_2 and (partially) for Pt/Ti and is listed in Table 1. It can be claimed that the efficiency in terms of EOI of the new anode material is about 5–7 times better than of platinized titanium. This superiority of the SnO_2 anode for oxidative treatment of dissolved organics in waste water was also proved using actual waste water from various industrial sources containing mainly biorefractory water soluble aromatic compounds.

3.2 *Influence of electrolyte parameters on oxidation efficiency*

3.2.1. Influence of pH. The efficiency of the oxidation of organics tends generally to be superior in alkaline media. This also holds for the anodic treatment using standard electrode materials. The waste water accessible to electrochemical oxidation treatment will, however, have any pH value, and pH adjustment before treatment to the more favourable values above 7 will in most cases be too expensive. The performance of the electrode was therefore tested in electrolyte solutions of various pH: the results from oxidation runs for benzoic acid at pH 1 and 12 are shown in Fig. 2a, b. The rate of oxidation is found to be, within experimental error, independent of pH. This result proves that the oxidation of benzoic acid is independent on the degree of dissociation (and hence charge) of the molecule and confirms the highly unselective reactivity of the electrode.

3.2.2. Chloride. One important issue in the application of electrochemical water treatment is the compatibility of the process with halides and in particular chlorides in the electrolyte, since electrochemical oxidation of halide containing solutions inevitably produces the respective halogens. Free halogens or adsorbed monoatomic halogens may react with the dissolved organics or their oxidation intermediates and form halogenated compounds which are generally more toxic than the original waste water contaminants and render the treatment contraproductive. It was found that with respect to halogen formation the SnO_2 electrode also shows superior performance if compared with platinized titanium. Figure 3 shows the concentration of oxygen in the anodically evolved gas from 0.5 M sulphuric acid solution with various additions of NaCl (no organics added). The anode gas was analysed for oxygen by mass spectroscopy and it is assumed that no gaseous reaction products other than oxygen and chlorine are evolved. The plot of Fig. 3 shows a linear relationship between the anode gas composition and the chloride concentration in the well stirred solution for both anode materials. The slope of the straight line for SnO_2 is much lower than for the platinum indicating that the formation of chlorine is much more catalyzed by platinum than by tin oxide. In practical terms this means that with SnO_2 anodes one might reasonably expect chlorination problems with chloride concentrations which are about 5 times higher than with platinum electrodes.

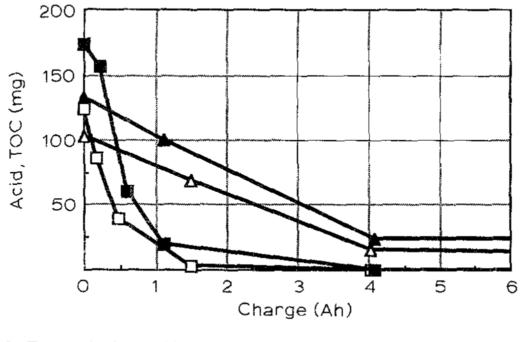

Fig. 2. Degradation of benzoic acid and respective TOC as a function of charge for pH 1 and pH 12 electrolyte (H_2SO_4 or NaOH). (□) Acid pH 1, (△) TOC pH 1, (■) acid pH 12 and (▲) TOC pH 12.

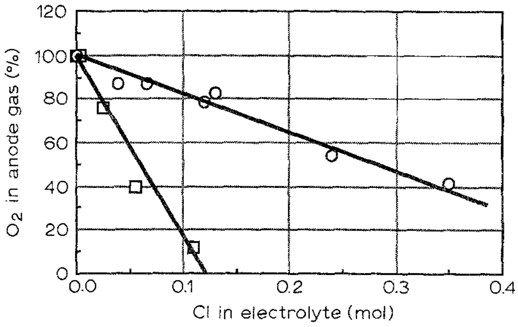

Fig. 3. Oxygen in the anode gas of a (□) Pt and a (○) SnO_2 anode during electrolysis of H_2SO_4 with increasing concentrations of NaCl (40 mA cm^{-2}). Gas was analysed using a mass spectrometer and a Teflon type membrane in front of the electrode.

3.2.3. Chlorinated compounds. It is obvious that from the above results the formation of halogenated organics by electrochemical treatment of halide containing waste water using SnO_2 anodes can still not be excluded. Since halogenated compounds are an important issue in waste water regulations it is probably mandatory to check the TOX (total organic halogens) of the water before and after the electrochemical treatment whenever halide containing water is to be processed. An example is given in Fig. 4: waste water from a pulp bleaching process with a chloride content of 1.0 g dm^{-3} and an AOX (adsorbable organic halogen, a characteristic sum parameter equivalent to TOX, describing the amount of organically bound halogen) of 110 mg dm^{-3} was processed using SnO_2 anodes. Figure 4 shows clearly that the process does not lead to the formation of AOX but rather that AOX is being destroyed.

3.3. *Electrochemical engineering aspects*

A large variety of electrochemical reactors for waste

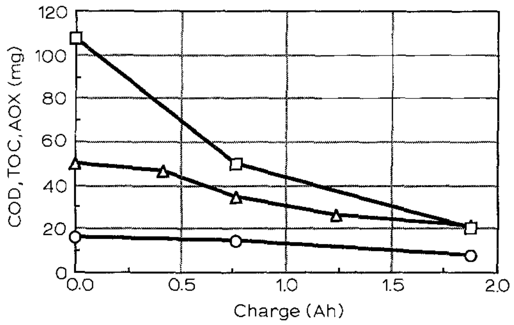

Fig. 4. Removal of (□) COD, (△) TOC, and (○) AOX by electrochemical oxidation using SnO_2 anodes. The waste water originates from the chlorine bleaching step of a pulp plant. Note that AOX is also reduced.

water treatment have been described in the literature, most of them dealing with cathodic deposition of heavy metals from waste streams and most of them using 3D electrodes for better recovery efficiency [3]. For anodic treatment the choice of the type of electrochemical reactor (bipolar or monopolar, divided or undivided cells, 3D or planar electrodes etc.) is not straightforward and depends on the electrochemistry of the organic reactions, the performance of the anode and the end concentration of the pollutants that needs to be achieved. The two most important questions that must be considered in designing an appropriate electrochemical reactor are: 'What is the influence of the reducing cathode on the process efficiency?' and 'How do current density and mass transfer influence the efficiency of the anode reaction?'.

The influence of the cathode on the oxidation process was studied in the stirred beaker cell in which the cathode could either be inserted into the bulk of the stirred solution to be oxidized, or in a counter electrode compartment separated from the stirred solution by a diaphragm. The characteristic decay curves obtained for the oxidation of model compounds was unaffected by the presence or absence of the cathode in the reaction medium as is reflected by the plot in Fig. 5. The high overpotential of the tin dioxide anode leads practically exclusively to irreversible oxidations with reaction products that cannot be reduced to any detectable degree by the cathode. Phenol oxidation on platinum, however, leads to the reversible quinone/hydroquinone redox system which gets reduced at the cathode while being re-oxidized at the anode and thus leading to parasitic current consumption in an undivided cell.

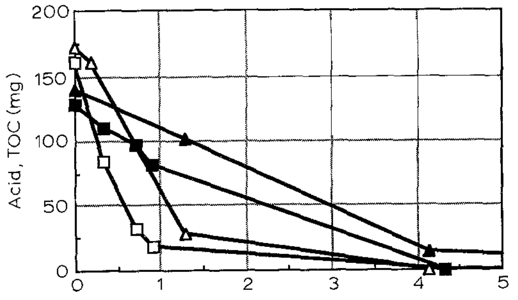

Fig. 5. Removal of benzoic acid and respective TOC as a function of charge for SnO_2 electrodes in a divided and undivided cell. Slopes, representing degradation rates, are almost unaffected. Key: (□) acid divided, (■) TOC divided, (△) acid undivided and (▲) TOC undivided.

Although the absence of the influence of the cathode on the oxidation of benzoic acid and phenol does not exclude that in any system of technical relevance such an influence might become important, it was decided that the reactor should be designed with undivided cells. Undivided cells enable much cheaper reactor designs (no separators and much simpler gasketing, manifolding and electrolyte circulation) and produce less ohmic losses than cells with diaphragms or membranes.

3.3.1. Mass transfer. In order to study the influence of mass transfer parameters on the efficiency of the process within the range of feasible current densities (up to $50\,mA\,cm^{-2}$) a parallel plate reactor with monopolar electrode arrangement and undivided cells was used. The reactor employed was the $1\,dm^2$ model by ElectroCell with PVDF frames and turbulence promoting spacers. The electrode distance was 5 mm.

In order to characterize the hydrodynamics of the reactor, the limiting currents of the employed electrode arrangement were measured using base electrolyte ($0.5\,M$ Na_2SO_4) with equivalent quantities of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ added as a reversible redox couple in a concentration range comparable to the concentrations encountered in typical waste water problems ($mM\,dm^{-3}$). The limiting currents were measured as a function of the concentration and of the flow velocity in the cell. The data is represented in Fig. 6.

The limiting current for a single electron transfer reaction is found to be in the order of $1\,mA\,cm^{-2}$ for the concentrations and flow velocities of interest. Since the reaction paths involved in the electrochemical oxidation even of model systems such as benzoic acid, and hence the average number of electrons transferred during the residence of the molecule at the surface of the electrode, are not known it is not possible to predict the limiting current densities for the anodic oxidation from the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$-data. However, the data allows estimation of the possible range of limiting current density and, hence, is useful

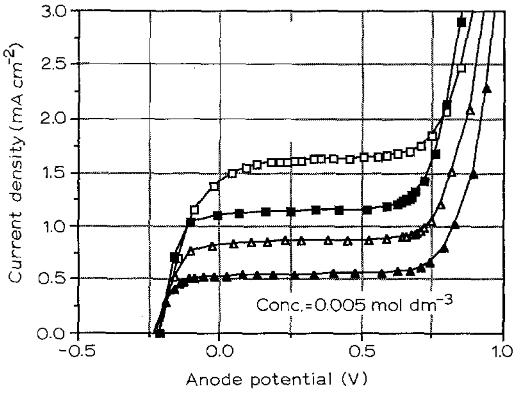

Fig. 6. Limiting currents for the $FeCN_6$ couple as a function of flow velocity in the ElectroCell reactor. Flow velocity, V*: (□) 11.4, (■) 7.6, (△) 4.5 and (▲) $2.7\,dm^3\,min^{-1}$.

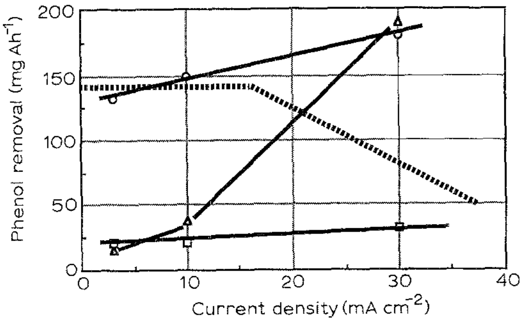

Fig. 7. Removal rate for phenol for the three different electrode materials as a function current density. The dashed line represents the expected rate assuming diffusion limitation and a 17-electron transfer reaction. Electrode materials: (□) Pt, (△) PbO_2 and (○) SnO_2.

in assessing the governing mechanisms of the oxidation reactions if compared with measurements of the oxidation rates as a function of current density and flow velocity.

The efficiency of phenol removal (expressed as mg phenol per Ah of charge passed through the electrode) is plotted as a function of current density at a constant flow velocity for PbO_2, SnO_2 and Pt (Fig. 7). The limiting current density for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple at the same molar concentration and the same flow conditions can be calculated from the data of Fig. 6 to be 1.0 mA cm^{-2}.

The maximum expected removal rate as calculated from the mass transfer measurements is plotted as a dotted line in Fig. 7 making the rather improbable assumption that every phenol molecule reaching the electrode surface would be oxidized by 17 electrons with a current efficiency of 100% (i.e. a limiting current density which would be 17 times that of the single electron transfer of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple). The number of 17 electrons for the oxidation reaction of phenol was determined from the experimentally observed phenol removal rate of 200 mg Ah^{-1} (see Fig. 9 in part I). Obviously no limiting current is observed up to a current density of 30 mA cm^{-2} or twice the expected current density for the 17 electron transfer reaction in the case of the oxidation reaction on SnO_2. The efficiency even seems to improve with increasing current density on both, PbO_2 and SnO_2.

An equivalent information is obtained from Fig. 8 which shows the rate of oxidation of benzoic acid and its intermediates (expressed as equivalents of NaOH necessary to keep the solution at a pH value of 12 for each Ah of charge passed through the electrode) as a function of flow velocity at a constant current density of 10 mA cm^{-2}. In the range of flow velocities accessible by the experimental flow system the rate of oxidation was found independent of the flow velocity.

The above findings suggest that the oxidation of organics on the electrode material investigated cannot be a pure electrochemical charge transfer reaction at the interface electrode/electrolyte since in that case a limiting current well below 17 mA cm^{-2} would have to be detected. Wabner *et al.* [4] who studied the oxidation of organics using PbO_2 anodes came to a similar conclusion. They concluded that the electrode produced the chemically very reactive hydroxyl radicals which perform a homogeneous oxidation reaction in the bulk of the electrolyte. Reaction rates of OH* radicals, including the annihilation reaction $OH^* + OH^* \longrightarrow H_2O_2$, are diffusion controlled, i.e. if generated from a planar source (the electrode surface) a mass transfer limitation of the reactor is also to be expected. It seems more likely that the electrochemical oxidation step generates organic radicals as intermediates which diffuse away from the electrode and react with oxygen and/or other organics within the bulk of the electrolyte. Similar reaction schemes have been proposed for the radical pathways of ozone oxidation reactions in aqueous media involving OH* [5]. More than plausible guesses can, however, not be inferred from the available data without identifying at least some of the intermediates generated at the anode by e.g. ESR, DEMS or another suitable technique.

The most important result from the above is, however, that for an application of the technique the current density and the flow velocity can essentially be optimized with respect to energy consumption (pumping energy and electrical losses at the electrodes and in the electrolyte) of the process and lifetime of the electrodes and not, as in the case of electrochemical trace metal recovery from waste water, with respect to mass transfer. The electrode lifetime has been found to be related to current density. Current densities not exceeding 30 mA cm^{-2} have been found to represent a viable compromise between lifetime, energy consumption and specific plant cost.

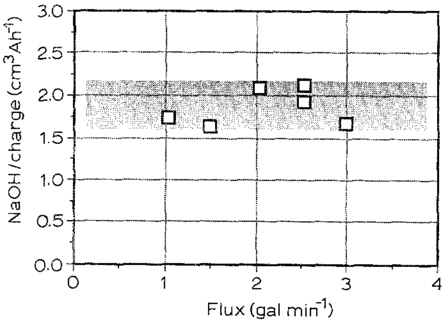

Fig. 8. NaOH (1 N) dosage, being equivalent with oxidation rate, for benzoic acid removal as a function of electrolyte flux rate. Reactor: ElectroCell.

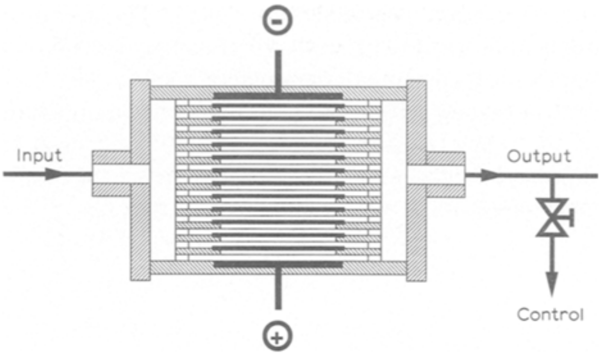

Fig. 9. Bipolar reactor for anodic waste water treatment (plate and frame type).

Figure 9 shows schematically the pilot scale plate-and-frame bipolar reactor which has been designed and built for electrochemical water treatment using SnO_2 coated titanium electrodes. These electrodes are platinized on the cathode side in order to catalyze hydrogen evolution and to prevent corrosion when operated in acidic media. Assuming an EOI of 40% as an average at an operating current density of $30\,mA\,cm^{-2}$ we obtain with this reactor a space-time yield of $6.4\,kg\,COD\,h^{-1}\,m^{-3}$. The bipolar electrode plates are mounted on PVC frames which are designed such that parasitic bypass currents can be kept small.

3.4. *Economic considerations and comparison with other processes*

A typical oxidation efficiency for the process using SnO_2 electrodes is between 30–40% (cf. Table 1) which leads to a power consumption of 40–50 kWh for removal of 1 kg COD assuming a typical cell voltage of 4.0 V. With s.Fr. 0.1 (Swiss franc) for 1 kWh this results in s.Fr. 4–5 for removal of 1 kg COD. The oxidation efficiency, however, has to be determined for each waste water composition separately and may deviate significantly from the average value. The lower limit of operation costs can be estimated assuming an oxidation efficiency of 100% and a cell voltage of 2.5 V, neglecting ohmic losses. Under these conditions power consumption will be $11\,kWh\,kg^{-1}$ COD or roughly s.Fr. $1\,kg^{-1}$ COD.

The oxidation efficiency not only determines to a large degree the energy cost of the process, but also the investment cost, which, in an electrochemical process with simple plate-and-frame cell design and minimum peripheral instrumentation is related to the total area of electrode surface. Figure 10 illustrates the dependence both of the energy consumption and the required electrode area for the removal of a quantity of COD per unit of time, as a function of the electrochemical oxidation index (EOI). From this it becomes clear that the observed improvement of the EOI when replacing platinum by SnO_2 has a decisive effect on the economy of the process. Estimates based on our experiments and a rough breakdown of cell manufacturing costs have shown that the process might become competitive for a number of waste water treatment problems encountered in the process industries with treatment processes such as wet oxidation, ozonation, oxidation with hydrogen peroxide and others. The technical applicability of the process will of course depend on a number of additional parameters such as the concentration and type of the pollutants, the composition of the water as an electrolyte, safety, the need of expensive control and surveillance, floor space requirements and, above all, lifetime of electrodes.

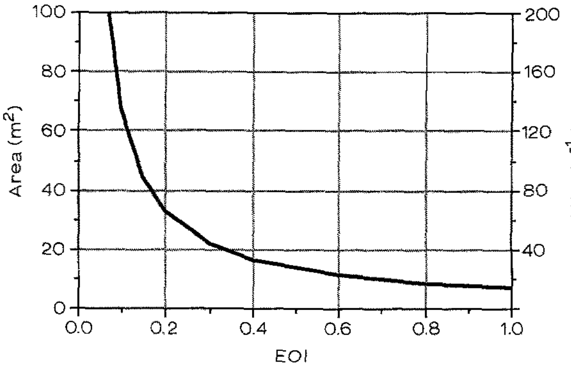

Fig. 10. Energy consumption and required electrode area as a function of electrochemical oxidation efficiency. Based on: removal of $1\,kg\,COD\,h^{-1}$ at $i = 500\,A\,m^{-2}$ with U cell = 4.0 V.

4. Conclusions

The application of the high overvoltage anode material SnO_2 with antimony doping (as described in part I) in waste water treatment has been shown to be superior to the state-of-the-art electrode materials PbO_2 and Pt. The oxidaton reactions on SnO_2 are very much unselective, which means that the electrode can be applied for a multitude of different waste water compositions with an acceptable current efficiency. The mechanism of the oxidation reactions involved is not known, mass transfer considerations, however, suggest that homogeneous reactions in the bulk of the solution must be taken into account. The mass transfer of the organic pollutants to the planar anodes has not been found to be limiting in the operation of the cells at current densities which are mainly given by the life time of the electrodes and the ohmic losses within the waste water acting as the electrolyte for the process.

The specific energy consumption of the process is in the order of $50\,kWh\,kg^{-1}$ COD. The COD concentrations between 500 and 15 000 p.p.m. are reasonably accessible to this treatment method. The process competes with wet oxidation or combustion for high COD concentrations and with physical processes like adsorption or precipitation on the low concentration end. The feasibility of the process for the treatment of a given waste water has to be assessed individually.

References

[1] E. Plattner and C. Comninellis, in 'Process Technologies for Water Treatment' (edited by S. Stucki). Plenum, New York (1988) p. 205.
[2] C. Comninellis and E. Plattner, *Chimia* **42** (1988) 250.
[3] G. Kreysa, in 'Process Technologies for Water Treatment' (edited by S. Stucki). Plenum, New York (1988) p. 65.
[4] D. Wabner and C. Grambow, *J. Electroanal. Chem.* **195** (1985) 95.
[5] J. Hoigne and H. Bader, *Water Res.* **17** (1983) 173.